KINETICS OF CHEMISORPTION OF GASES ON SOLIDS

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CONTENTS

I. INTRODUCTION

The chemisorption of gases on solids proceeding at a measurable rate has been the subject of numerous investigations. The influence of varying experimental conditions on adsorption kinetics has been studied by various means, but the individual investigations are mainly incomplete, at times fragmentary, and are scattered through the literature of four decades. Comparison of data is further hindered by lack of unity in representation of rate data. Attempts to represent the experimental data by algebraic mass-action functions involving integral or fractional powers of concentration, or by partial pressure of gas and a constant rate parameter of definite order, have not been successful. Simi-

larly, various empirical formulations for chemisorption kinetics were often unconvincing and limited to the particular adsorbate–adsorbent system under consideration. The Elovich equation, however, has general application to chemisorption kinetics (298). That equation is satisfactorily applicable to most chemisorption data and will cover a large range of the course of the slow adsorption, failing mostly only towards the end of the reaction where the process becomes excessively slow. In view of this versatility it was thought desirable to collect, contrast, and compare the data on chemisorption kinetics on the basis of the Elovich equation.

The use of that equation is not free from criticism. Thus Laidler (170) "takes a rather dim view" of it, while Gray (114) believes that it is an approximation to the more detailed kinetics claimed to be obtained by semiconductivity methods. Similarly, Parravano and Boudart (242) suggest that the logarithmic rate law seems to represent a number of different processes such as bulk or surface diffusion, activation or deactivation of catalytic surfaces, and chemisorption, and that it appears futile to explain the relation in terms of an unique mechanism. This may be so.

However, it has been repeatedly demonstrated that the Elovich equation has unquestionably widespread utility and is precise in reproducing kinetic data. Also, several different approaches to the mechanism of chemisorption have resulted in the logarithmic rate law, so that the latter can no longer be regarded as a purely empirical formulation. Consequently, the Elovich equation has been adopted for present use in order to express, compare, and contrast with precision the otherwise chaotic data of chemisorption kinetics.

The name "Elovich" has been retained in order to be consistent with earlier literature, and not from a desire to indulge in fruitless polemics. Synonyms that have been used include "Roginsky–Zeldovich," "Becker–Zeldovich," "Zeldovich–Roginsky," "Elovitz," and "Tamman." Significant, perhaps, is the statement of S. J. Elovitch [sic] that "this equation was first applied by Tamman and Koster" (84, 295).

The literature cited in *Chemical Abstracts* to September, 1959, and the contents of Volumes I and II of the excellent *Bibliography of Solid Adsorbents* (65, 66) were surveyed for kinetic data. Since such data are frequently presented within a paper dealing mainly with a different topic, omissions are expected. Only primary direct data on chemisorption kinetics were considered, and reduction of such data to a unified set of rate parameters has frequently, where possible and feasible, entailed replotting and recalculation. Statements that "faster" or "slower" adsorption occurred under certain conditions, or secondary information on kinetics consisting of deductions or inferences from reaction kinetics, have been mostly disregarded. Also, for the sake of brevity, only fairly complete investigations on any one

topic are described in detail, reports of isolated rate experiments being discarded unless unique. Mainly adsorptions on bulk adsorbents are considered (see Section III). Because the subject is even empirically quite complex, emphasis is placed primarily on experiment rather than theory, prediction, or hindsight. Classification of effects is based on experimental variables.

II. CHARACTERISTICS OF THE ELOVICH EQUATION

Application of the Elovich equation,

$$\frac{dq}{dt} = ae^{-\alpha q} \qquad (1)$$

where q is the amount adsorbed at time t, and a and α are constant during any one experiment, is best made using an integrated form of the equation. Mathematically, from equation 1, a plot of the logarithms of the momentary rates at various times as a function of q should be linear. Calculation of rate parameters by this latter procedure, however, involves a graphical differentiation or a calculation of rates averaged over short time intervals, is fraught with difficulty, and because it can lead to error (197, 297), is to be avoided.

Assuming that $q = 0$ at $t = 0$, equation 1 becomes

$$q = \frac{2.3}{\alpha} \log (1 + a\alpha t) \qquad (2)$$

or

$$q = \frac{2.3}{\alpha} \log (t + t_0) - \frac{2.3}{\alpha} \log t_0 \qquad (3)$$

where $t_0 = 1/a\alpha$. If a volume of gas, q_0, is adsorbed instantaneously and before equation 1 begins to apply, the integrated form of the equation becomes

$$q = \frac{2.3}{\alpha} \log (t + k) - \frac{2.3}{\alpha} \log t_0 \qquad (4)$$

where $k = t_0 \exp \alpha q_0$. If k is negligible in comparison with t, then equation 4 reduces to

$$q = \frac{2.3}{\alpha} \log t - \frac{2.3}{\alpha} \log t_0 \qquad (5)$$

or

$$q = \frac{2.3}{\alpha} \log a\alpha t \qquad (6)$$

Equation 6 results directly from equation 2 if $a\alpha t >> 1$. For k values practically larger than zero, plots of log t are not linear but are convex toward the log t axis and may be linearized by provision of a constant k of suitable magnitude, so that a plot of q versus log $(t + k)$ results. If k values are experimentally indistinguishable from zero, linear q–log t plots are obtained, i.e., equation 6 applies. Procedures for testing equation 1 and for evaluating the parameters a, α, and k by numerical

and graphical methods are given elsewhere (46, 64, 85, 172, 182, 221, 247, 270, 298).

The plot of q versus log $(t + k)$ has a slope equal to $2.3/\alpha$. From any of the equations the rate of adsorption, $dq/dt = 2.3/\alpha t$, the constant α being inversely proportional to the ambient rate of adsorption when $a\alpha$ is large or k or t_0 is very small. It is thus possible to describe the adsorption over its entire course by means of one constant, α. Comparison of rates at some time t is similarly possible through comparison of α values, and this simple and easy procedure is followed throughout.

Identity of α values for a number of plots of q versus log $(t + k)$ means that the plots are parallel and that rates of adsorption at some arbitrary times t are equal. This does not imply identity of q_t, the amounts adsorbed at such times t, because the occurrence of a rapid initial adsorption or of another kinetic stage may displace the plots. It is stressed that emphasis throughout is placed on rates and not on amounts of adsorption.

III. Slow and Fast Chemisorption

Chemisorption rate data can be crudely separated into two groups. The criterion for this is the relative rate of gas uptake. If the rate is measurable by the usual experimental techniques, it is "slow"; if it occurs too quickly to be measurable and appears to be instantaneous, even at low temperatures, it is "fast." Significantly, such grouping also differentiates the adsorbents, leading to the frequently made generalization that slow processes are found with bulk adsorbents, but that fast processes occur with rigorously clean filaments and films. There are significant exceptions.

The slow process was the first to be detected and described. Historically this came about with the differentiation of gas uptake by solids into physical adsorption and chemisorption. The adsorbents used were bulk solids, and detected rates of chemisorption were mainly slow and showed temperature dependence. These characteristics suggested the necessity of an energy of activation for adsorption, and the term "activated adsorption" was frequently used. Refinement of techniques yielded data which cast doubt on the generalization implied by this terminology. The preparation of rigorously clean tungsten ribbon by Roberts (258) permitted adsorption to be studied under better conditions. Similar work with evaporated metal films followed and yielded fast chemisorptions that were found to be essentially nonactivated. This brought about the generality that the previously used bulk adsorbents were not rigorously degassed, that they were "dirty," and that slow chemisorptions were caused by surface contamination; and, conversely, that nonactivated fast adsorptions occurred with film and filament adsorbents prepared and treated under rigorously "clean" conditions.

There is some evidence to support such distinction of adsorbents. It has been shown that bulk metal adsorbents having characteristics approaching those of extremely pure wires and films could be prepared if the metals were reduced with highly purified hydrogen and kept free of contamination. The results of kinetic measurements of the chemisorption of hydrogen on nickel sheet are shown in figure 1 (324). Each of the successive runs numbered 1 to 6 was made after reduction with hydrogen at 300°C. for 24 hr., followed by degassing. The rate of a secondary slow process is seen to decrease, while that of a fast process increases. Finally, for runs 5 and 6, equilibrium is reached in a time shorter than 30 sec.

Some Japanese work on this topic is described by Kwan (166). The difficulty of preparing clean films of iron was stressed by Eggleton and Tompkins (74), and the implication that oxide contamination is present on
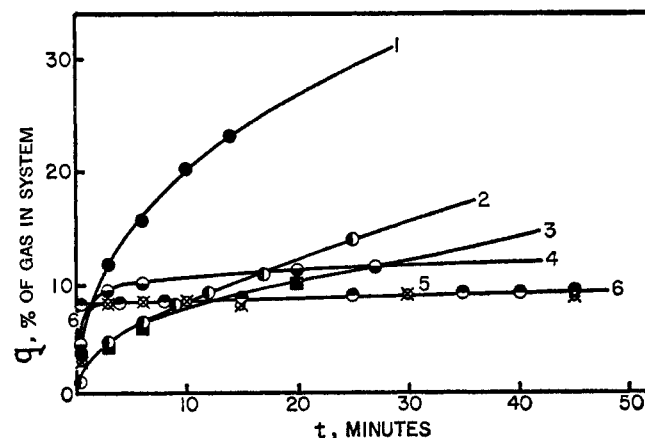
Fig. 1. Adsorption of hydrogen on nickel sheet at 300°C. (data of Van Itterbeek, Mariens, and Verpoorten (324)).

many so-called reduced catalysts was emphasized by Tompkins (308). With silica-supported nickel catalysts, Schuit and de Boer (277, 278) found activated adsorption of hydrogen to occur on a partially oxidized but not on a thoroughly reduced nickel surface. On successively more rigorous reduction of the catalyst the extent of a fast adsorption was increased at the expense of a slow process that followed the initial fast process. Heating the reduced catalyst in an inert atmosphere or in vacuo tended to diminish the fast adsorption, and it was suggested that a reoxidation of the surface occurred by diffusion of oxygen from the interior to the surface and by liberation of water by the silicon dioxide carrier. In similar studies, Roberts and Sykes (259, 260) studied the adsorption properties of nickel powder under various conditions of reduction. A bulk adsorbent with properties approaching those of evaporated nickel films was obtained as a result of gradual improvement of surface purity. This was attributed to reduction of surface oxide and removal of nonvolatile impurities by aggregation into separate phases or diffusion into the lattice.

The interpretation of these and similar experiments is that slow adsorption really occurs "on top of" contaminants if the solid is not rigorously cleaned and kept free from impurities. This view may be invoked to explain some of the discrepancies between the properties of bulk and film adsorbents. For example, ruthenium film, according to Trapnell's classification (310, 311), does not chemisorb nitrogen, yet Low and Taylor (193) report a slow adsorption of nitrogen on alumina-supported ruthenium but point out that their adsorbent possibly contained traces of unremoved hydrogen, which could permit the adsorption of nitrogen. Similarly, nickel film does not adsorb nitrogen (310, 311). However, Kokes and Emmett (159) report that both pure nickel catalysts and those promoted with small amounts of silica will chemisorb nitrogen to a slight extent at about 250–300°C., but point out that their catalysts may have contained some chemisorbed hydrogen. Also, increased magnetization of nickel by chemisorption of nitrogen (279) was shown (45) to be absent unless the metal surface was partially covered with hydrogen. Similarly, "clean" copper powder adsorbs hydrogen (27, 164, 300), while thoroughly reduced copper powder (33) and evaporated copper films (30, 155, 310) do not.

However, it has been shown that clean surfaces do show slow adsorption at relatively high coverages, although most of the adsorption is fast. Thus, Rideal and Trapnell (257) report a slow adsorption of oxygen on tungsten film after the occurrence of an instantaneous process. On iron and nickel films the kinetics of uptake of hydrogen and carbon monoxide were shown to be Elovichian (123, 247, 248, 308). Similar slow chemisorptions were reported for hydrogen on nickel wire (203), carbon monoxide on nickel film (234), and nitrogen on metal films (116). For example, with the adsorption of hydrogen on palladium films, Matsuda and Nakata (204) found fast and slow processes. Doses of hydrogen admitted to the films were taken up within 0.5 sec. in early runs, a small but sharply constant residual pressure being left that increased with successive runs. After a few runs a slow Elovichian adsorption appeared which continued for a few minutes. The amount of fast adsorption approached a saturation value with increasing pressure.

An intermediate situation seems to exist in that some supposedly "dirty" bulk solids show partially the fast adsorption characteristic of films. The fast process was described (298) as a massive initial adsorption preceding measurable slow chemisorption. Examples of this are the adsorptions of hydrogen on $2MnO \cdot Cr_2O_3$ (336), zinc oxide (283), Cr_2O_3 (51), and $ZnO \cdot MoO_3$ (237, 238, 272). Stone (288) made the interesting comment that, for such cases where there is an initial rapid gas uptake followed by a slow Elovichian chemisorption, "there are indications that the constants a and α are relatively insensitive to variations in gas pressure. If this can be established, the slow process must arise exclusively from a continuous change being affected in the solid by the recently chemisorbed gas. Such changes are likely to be electronic in nature." However, not enough data are available to pursue these relations.

In view of experiments with films, contamination cannot be considered to be the sole cause of slow adsorption. Some recent work with films on changes of resistance (236, 267, 268, 293), work function (82, 83, 267), sticking coefficients (21, 77, 235), and similar effects (22, 41, 113, 218, 266, 275, 327, 328) shows that even with clean adsorbents the adsorption process is not homogeneous but consists of more than one effect. Particularly pertinent seems the work of Ehrlich (76, 77, 78, 79, 136) who, using flashed tungsten filaments and field emission techniques, has shown the occurrence of weakly chemisorbed surface structures that are the precursors of strongly bonded structures on tungsten.

The difference between bulk and film adsorbents is presently unresolved, unless one assumes that only those systems showing solely fast adsorption are clean. This is unwarranted and would be as extreme as a suggestion that work with bulk adsorbents is not useful because such adsorbents are not suitable for rigorous cleaning techniques, such as flashing at high temperatures. Without doubt some of the early work was done, because of contemporary ignorance, under conditions unfavorable for the production of clean surfaces and should be repeated. Summary refutation of all work with bulk adsorbents, however, evades the issue: namely, that clean bulk adsorbents do chemisorb and that this is of interest *per se*.

Much of the rate work with films and filaments is still of exploratory nature and, with the exception of pressure, change of experimental variables is qualitative. Consequently, most of the work described in later sections deals with bulk adsorbents. Some characteristics of adsorption on clean adsorbents have been reviewed elsewhere (20, 21, 28, 219, 258, 292, 311).

IV. GENERAL KINETIC CHARACTERISTICS

A. "NORMAL" ISOTHERMAL BEHAVIOR

The general characteristics of slow chemisorption are shown by the q–t plot of figure 2. At the beginning the adsorption is rapid but decelerating. The deceleration continues throughout the whole reaction. The adsorption usually becomes imperceptibly slow or ceases entirely in the presence of unadsorbed gas. The length of time necessary to reach this terminal stage is dependent on the chemical composition of the gas-solid system, on the temperature, and on the pressure. On a plot of q versus $\log (t + k)$, or an Elovich plot, such data frequently present a line that is straight over
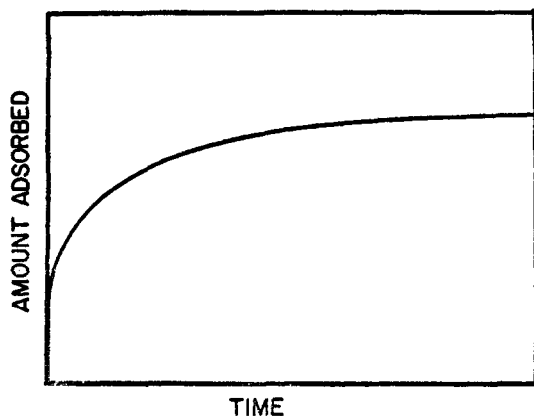
FIG. 2. Slow chemisorption; typical rate behavior.

most of the course of the adsorption, failing only at points corresponding to long times of adsorption where experimental precision is often illusory. A plot of such "normal" character is shown in figure 3. The systems hydrogen-2MnO·Cr_2O_3 (336), oxygen-cobalt(II) oxide (100), hydrogen-nickel-kieselguhr (180), hydrogen-Cr_2O_3 (51), and carbon monoxide-manganese(IV) oxide (85, 261, 262, 341) yield further examples of linear plots of q versus log $(t + k)$.

B. ISOTHERMAL ANOMALIES

Taylor and Thon (298) found discontinuities in certain q-log $(t + k)$ plots of the data of Sickman and Taylor (283) on the adsorption of hydrogen on zinc oxide. Some time after the start of the adsorption, linear Elovich plots abruptly changed in slope. The occurrence of such discontinuities, or breaks, was not very frequent; consequently the breaks were considered to be anomalous. It was suggested that if α was characteristic of the nature of the sites involved in the adsorption, then the break indicated a changeover from one kind of site to another at a certain stage of the
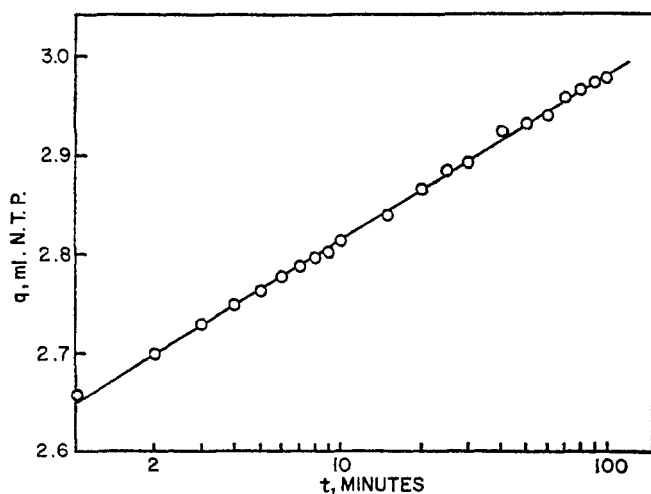

FIG. 3. Adsorption of hydrogen on ruthenium (data of Low and Taylor (193)). P_s = 61.1 cm. of dibutyl phthalate; 257°C.; 15.82 g. of catalyst.

adsorption. The mechanism for the occurrence of breaks was thus similar to that proposed by Taylor and Liang (301) (see Section VI,B) and suggested that Elovich plots seemed to reveal isothermally the same two-site phenomenon which the Taylor-Liang curves revealed under isobaric conditions.

Such breaks are not artifacts of kinetic treatments. Consider plot A of figure 4. A smooth curve is drawn through the experimental points (187). The resulting plot looks like a typical adsorption plot: a little scatter of points is apparent, but the overall result seems to be satisfactory. For plot B of figure 4, the points of those data have been displaced by 10 min. for clarity, and a line was drawn to connect them. An obvious discontinuity appears. A similar discontinuity is shown by the Elovich plot C of the same data. With the hydrogen-zinc oxide system such discontinuities in q-t plots
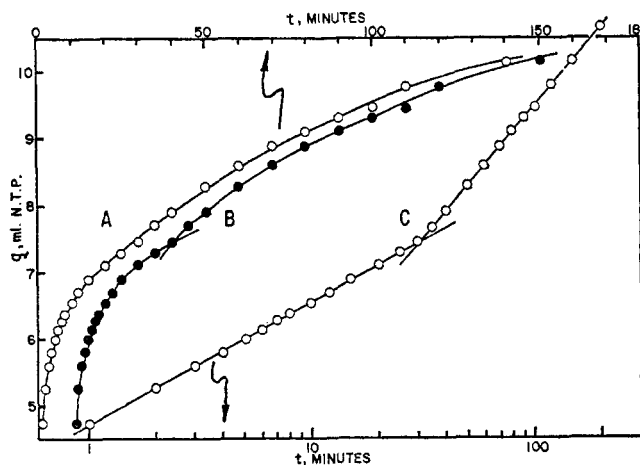
FIG. 4. Isothermal anomalies in the system hydrogen-zinc oxide (data of Low (187)).

become more distinct at temperatures over about 150°C. At lower temperatures the q-t line becomes smoother, and plots of data taken at 0°C. appear on visual examination to be quite undisturbed. However, Elovich plots indicate two kinetic stages at all temperatures from 0° to 257°C. Similar discontinuities, even in q-t plots, occur in the data of Sickman and Taylor (283) and Taylor and Strother (305) on the hydrogen-zinc oxide system. The Elovich plot is thus more sensitive and reveals irregularities ordinarily overlooked. Parenthetically, Maxted and Evans (206) obtained curves "of the flexed linear type" on plotting their data for the adsorption of hydrogen on clean platinum and on platinum poisoned with hydrogen sulfide as log [log $(m/m - q)$] versus log t, using the integrated form of Bangham and Sever's equation (10). Elovich plots of the same data similarly reveal breaks.

C. MULTIPLE KINETIC STAGES

Taylor and Thon (298) noted the occurrence of anomalies involving changes to both a relatively faster

and a relatively slower rate of adsorption, and an occasional inability to obtain linear plots, with high-temperature data of systems such as hydrogen–zinc oxide (283, 305) or hydrogen–platinum (208). It was then suspected that such serious anomalies were connected with an irreversible chemical reaction, and the electron diffraction evidence of Yang (339), showing irreversible reduction of zinc oxide by hydrogen above 300°C., was cited as an example. Later work, however, showed the anomalies to be less serious and of more consistent nature.

A study of the effects of temperature and pressure on the adsorption of hydrogen on iridium (194) showed, with the exception of one run, that the slopes of q–log t plots increased after the time of occurrence of the break, t_b. In a few cases, notably at low pressures, this region of increased slope was followed by one of
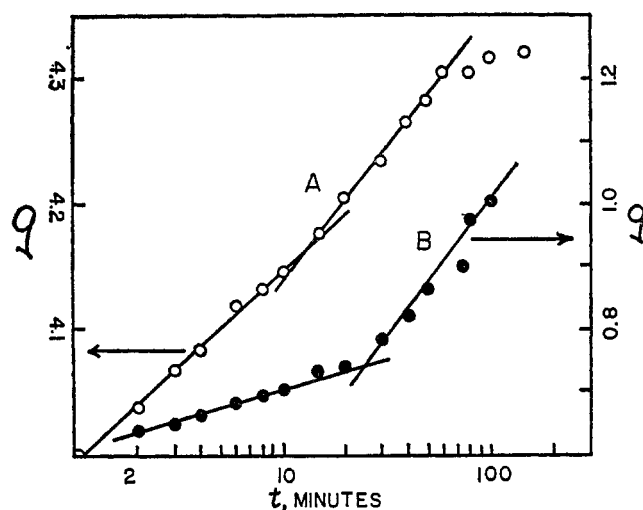

Fig. 5. Typical adsorption plots (data of Low (189)). A: hydrogen–rhodium, 100°C., 51.3 cm. of dibutyl phthalate. B: hydrogen–palladium, 100°C., 51.7 cm. of dibutyl phthalate.

decreased slope. Each portion of the q–log t plot could thus be described by the Elovich equation, using appropriate a and α values for each line segment. With the adsorption of hydrogen on ZnO·Cr₂O₃ Elovich plots consisted of two linear segments (192). At 147° and 200°C. the ratio of the values $(\alpha_1/\alpha_2) > 1$, where the subscripts 1 and 2 refer here to the α value for the segments appearing first and last, respectively. Such behavior is similar to that found by Decrue and Susz (64) in part for the same system, but even more so for the system hydrogen–tungsten(IV) sulfide (64) and also for water–zinc oxide (196).

Further work with the systems hydrogen–palladium and hydrogen–rhodium (189) showed that the occurrence of values of α_1/α_2 larger and smaller than unity within the same system was not inconsistent. The type of data obtained is shown by the plots of figures 5 and 6. In comparing rate curves of experiments performed
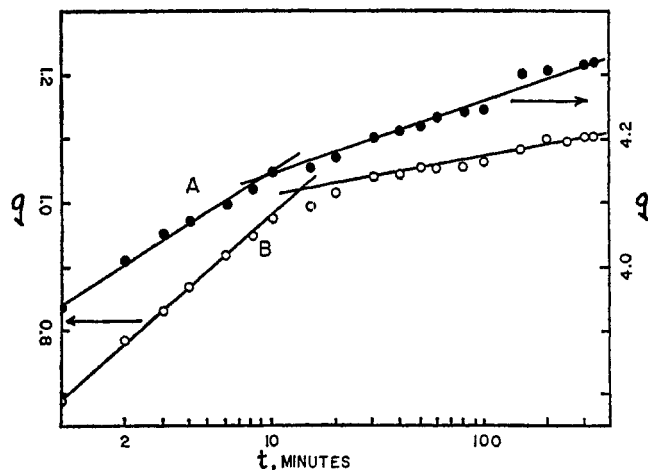
Fig. 6. Typical adsorption plots (data of Low (189)). A: hydrogen–rhodium, 56°C., 50.5 cm. of dibutyl phthalate. B: hydrogen–palladium, 200°C., 44.2 cm. of dibutyl phthalate.

at different initial gas pressures and different temperatures, it became apparent that comparison of kinetic stages on the basis of their order of appearance resulted in misleading interpretation. If stages were compared on the basis of the relative magnitude of the constant α of the following kinetic stage, on the basis of the scheme depicted in figure 7, the correlation of rate parameters of individual stages with temperature and pressure became possible.

With these systems it is probable that all stages are present in any one run, but, because of limitations imposed by technique and by the experimental variables of temperature and pressure, not all stages necessarily appear, i.e., are detected, during the course of a single experiment. For the adsorption of hydrogen on palladium and rhodium it seems that at initial pressures, P_s, in the vicinity of 20 mm. of mercury, stages III and IV appear, so that an Elovich plot would have the appearance of the region A enclosed by the dotted lines of figure 7. The previous stages are assumed to
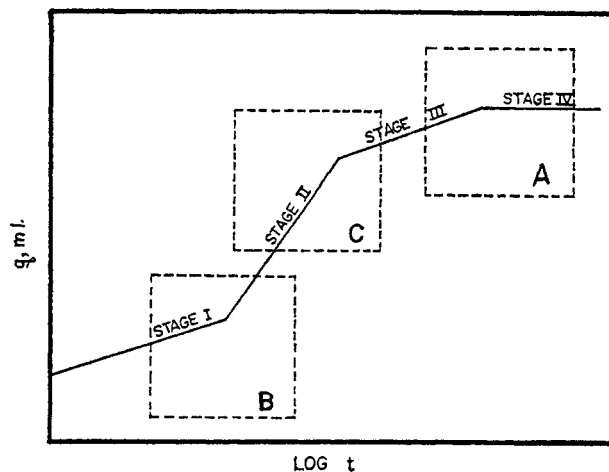
Fig. 7. Composite of kinetic stages.

have appeared before the time of the first measurement. At higher values of P_s, stages I and II appear, so that a q–log t plot would have the appearance of region B of figure 7. In this case, stages III and IV would appear if the adsorption could be followed for a sufficiently long period of time. In practice this is often not possible because the rate of adsorption at long times becomes so slow that precision of measurements is poor and continuation of the experiment is useless. At intermediate P_s values stages II and III appear, so that a q–log t plot would have the appearance of region C of figure 7. In the systems hydrogen–palladium and hydrogen–rhodium several plots of data of experiments at intermediate pressures consisted of the combination of stages I, II, and III, i.e., a combination of regions A, B, and C. This is illustrated by the plots of figure 8. The composite structure of figure 7 thus seems consistent.
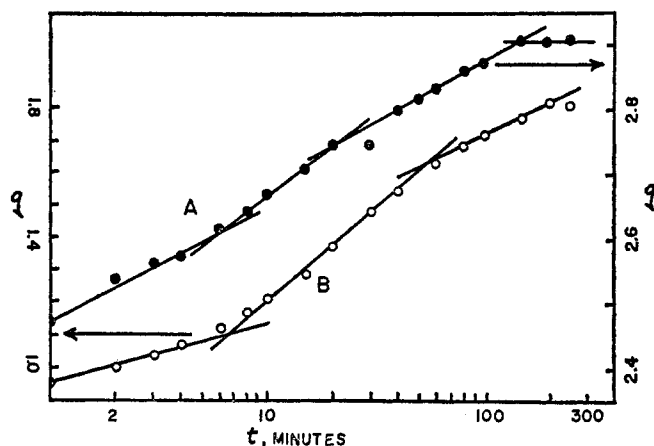

Fig. 8. Multiple kinetic stages (data of Low (189)). A: hydrogen–rhodium, 257°C., 51.7 cm. of dibutyl phthalate. B: hydrogen–palladium, 56°C., 50.88 cm. of dibutyl phthalate.

The time of appearance and temporal range of existence of the individual kinetic stages are affected by P_s and by temperature. For the hydrogen–rhodium system, for example, at 100°C. stage I appears only at relatively high P_s, while at all temperatures from 0° to 400°C. the appearance of stage III occurs only at relatively low P_s. In general, low initial gas pressures and high temperature favor the early appearance of any one stage.

D. CHARACTERISTICS AND MECHANISMS

Thus in certain systems more than one kinetic stage is observed, evidenced by one or two breaks. Sometimes the break occurs a few minutes after the start of the experiment, and the rest of the adsorption occurs uneventfully; this behavior is found with hydrogen–iridium (194). Plots of data of that system frequently reveal breaks after 2 to 10 min., the adsorption continuing after the break for a further 200 to 500 min.

At other times, a break is observed after a comparatively long time (30 to 90 min.), such as in the system hydrogen–zinc oxide (187).

Two possibilities present themselves. First, both cases of single-stage and of multiple-stage kinetics may exist, the multiplicity being determined by the chemical composition of the gas and/or of the solid, by contamination, or by some other factor. Second, multiple stages may be universal, but frequently undetected. It is conceivable that adsorption with a particular system occurs very rapidly via one, or two, kinetic stages. If this reaction occurs in the time period after the original exposure of the solid to the gas and before the first measurements, only a single kinetic stage may be detected over the whole observable course of the adsorption. It is perhaps significant that with the systems hydrogen–palladium and hydrogen–rhodium (189), the rate plots of which usually show two or three linear segments, several Elovich plots were obtained which were linear over the entire course of the experiment. These infrequently occurring plots were obtained under experimental conditions at an intermediate region of temperature and P_s in which either stages I and II or stages II and III could be expected to appear. The values of the Elovich parameters of such solitary stages corresponded to those of stage II values interpolated from known stage II values. Consequently these single-stage plots were assigned stage II connotation. It thus seems possible that the Elovich plots of a hypothetical gas–solid system be linear throughout, but only within certain perhaps quite wide ranges of temperature and P_s. However, it would be premature to suggest universal kinetic multiplicity. In the absence of adequate and precise kinetic information at relatively short and long adsorption times the matter is unresolved.

A complete physical explanation for the observed multiple stages is not at hand. Serious interaction between gas and adsorbent, resulting in complete destruction of the adsorbent, seems unlikely except for certain systems under extremes of temperature. The changes in chemisorption kinetics are reminiscent of, but definitely not mechanistically comparable to, similar changes in kinetics sometimes encountered in the oxidation of metals. Several possible mechanisms present themselves, these not being mutually exclusive.

It is possible that multiple stages result from surface contamination. This is supported by such observations as that originally (193) linear q–log t plots were found with the system hydrogen–ruthenium, while in a later study using the same adsorbent (191) breaks occurred; or that, with the adsorption of carbon monoxide on clean ruthenium (191) the rate declined monotonically, whereas it was discontinuous when hydrogen was preadsorbed by the solid; or, that for the hydrogen–nickel–silica system (277) on vigorous reduction a fast adsorption was increased in magnitude at the expense

of a slow adsorption; or, that under conditions of preadsorption of carbon monoxide on ruthenium, two kinetic processes of hydrogen adsorption exist (191), the region of discontinuity of rates being approximately linearly dependent on the amount of carbon monoxide. Further evidence as to the effect of contamination by preadsorption of relatively large amounts of gas is given in Section VII. However, rigorous reduction conditions, the apparent stability of adsorbent surfaces, and particularly the dependence of kinetic stages on temperature and pressure suggest that a simple contamination phenomenon is unlikely to account for kinetic multiplicity. With a model consisting of a surface partially covered with contaminant, so that adsorption would proceed wholly or mainly over one part of the surface until it was covered and then would continue on the residual surface, breaks should occur at identical stages of coverage and be independent of temperature and pressure. This is not so.

It is possible that more than one surface–adsorbate structure influences kinetics. For example, Eischens, Francis, and Pliskin (80) reported evidence for two structures of carbon monoxide chemisorbed on palladium. At low coverage an infrared spectrum attributed to a carbon monoxide molecule bonded from the carbon atom to two palladium atoms was obtained. At higher coverage a second structure, Pd—C≡O, was formed. It is plausible that during the course of an adsorption such a change in predominance of formation or of existence of one surface complex is responsible for a change in adsorption kinetics.

A mechanism of similar nature but which need only involve one surface species is the probability of anisotropic adsorptions. If one crystal face adsorbs faster than another, or if adsorption occurs predominantly on a particular crystal face until a certain degree of coverage is achieved, when adsorption continues on a different type of face, then a sequence of adsorption stages will result. However, in the event of sequential or preferential adsorption, the overall effect detected by relatively gross volume–time measurements would probably represent a summation of effects.

For somewhat less concrete mechanisms, "surface heterogeneity" may be postulated. The heterogeneity implies that different parts of the surface have different adsorptive properties, and that these parts are randomly distributed and may be of atomic magnitude ("adsorption sites") or may be multiatomic surface patches, homogeneous within the patch but differing from other patches. Again, heterogeneity may imply sites either having a small number of discrete energy levels or a complete spectral distribution of energies. Heterogeneity is further discussed by de Boer (43) and by Taylor (299).

Since most bulk solids that have been used as adsorbents are polycrystalline, are frequently ill-defined

chemically, are of dubious structure, and are of unknown electronic properties, it is not inappropriate to attempt to explain effects in terms of the catchall, surface heterogeneity. However, a more definite mechanism is required, capable of describing not only the existence of discontinuous adsorption rates but also the pressure and temperature dependence of such discontinuities. Some model of a surface which changes its character drastically by the very act of adsorption seems to be required. Further experimental work is necessary.

V. The Effects of Pressure

The effects of pressure on chemisorption kinetics appear to be quite involved and controversial. More than one pressure effect exists, and the data fall roughly into several categories differentiated by emphasis on initial pressure, P_s, or on ambient pressure, P_a. Further complication is introduced by claims for first or for fractional order dependence on P_a.

A part of the difficulty is introduced by the use of two experimental methods. In an adsorption system of constant volume, i.e., one consisting of a vessel of known and constant volume, in which the progress of adsorption is followed by measuring the decline in pressure, the latter is continually falling as long as gas uptake occurs. Occasionally large diminutions in pressure occur, and to correct for these, adsorption rates are sometimes reported as $-dP/Pdt$. At other times, partly because the Elovich equation will satisfactorily describe the course of adsorption during which such pressure drops are found, the pressure drop is disregarded. In such a system the initial pressure, P_s, is that pressure calculated to exist on introducing the adsorbate, assuming that there is no adsorption. In a constant-volume system P_s is usually much larger than P_a, the latter being the pressure measured at some time during the course of the adsorption. In constant-pressure systems P_s equals P_a. The adsorption is then followed by reducing the volume of the adsorption system by amounts equal to the amounts of gas adsorbed and thus restoring P_a, or by keeping P_a constant by some similar technique and determining the adsorbed gas gravimetrically or by other means.

It is emphasized that constant-volume as well as constant-pressure data can be equally well expressed by the Elovich equation. The validity of the latter for slow chemisorptions determined in constant-volume systems in which P_a is diminished considerably during the course of the adsorption caused the suggestion (298) that P_s had a greater influence on rates than P_a and the possibility of assigning different roles to P_s and to P_a. Some recent work on bulk adsorbents is differentiated in this manner.

During the reëvaluation of various data used for comparison purposes in later sections, P_a effects (if any)

on rates were neglected. Comparisons subsequent to this section were thus made on the basis of P_s, this being sometimes the only pressure criterion. Errors, if any, may be expected to be negligible.

A. INDEPENDENCE OF AMBIENT PRESSURE

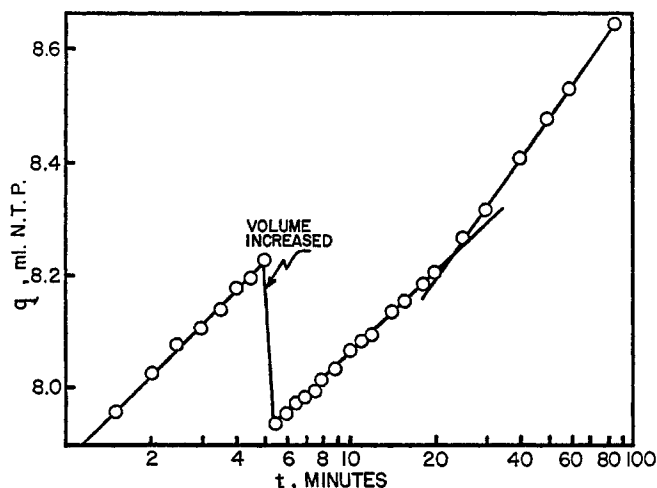The earliest indication of the relative unimportance of P_a to adsorption rates with bulk solids comes from

FIG. 9. Adsorption of hydrogen on nickel–kieselguhr (data of Leibowitz, Low, and Taylor (180)). 270°C.; P_s = 73.9 cm. of dibutyl phthalate. Accompanying the volume increase the pressure fell from 31.63 to 22.70 cm. of dibutyl phthalate and after 85 min. was 20.13 cm. of dibutyl phthalate.

the data of Ogden and Taylor (237, 238). In order to be able to measure the uptake of hydrogen on manganese-(IV) oxide in a constant-volume system over long periods of time, the gas was replenished whenever the pressure in the system became too low for precise measurement. No changes of rate are detectable in q–t or in Elovich plots at points of gas addition. Further evidence along similar lines comes from a study of the influence of pressure on the kinetics of the adsorption of hydrogen on nickel–kieselguhr (180). Various experiments, described in detail elsewhere (180), were made in which P_a of a constant-volume system was caused to change abruptly during the course of adsorption. No appreciable changes in adsorption rates were found. Figure 9 shows the data for such an experiment. At t = 5 min. P_a was reduced from 31.63 to 22.70 cm. of dibutyl phthalate by increasing the volume of the system abruptly. The adsorption appears to continue at the same relative rate (α values before and after the pressure drop are equal). The break at about 25 min. occurs also in an undisturbed run under comparable P_s and temperature conditions.

A small rapid desorption is apparent in figure 9, and desorptions or adsorptions of similar magnitude, equivalent to roughly 3 per cent of the gas adsorbed, were detected with other experiments when pressure drops or rises were caused to occur. These were not calibration

errors, because no such effects were found using helium under equivalent conditions. The causes of the phenomena are uncertain.

In other experiments the adsorption system was modified by the addition of a series of bulbs of known volume, so that the volume of the system could be changed at will. Various experiments were made at −78°C., using systems of varying size, V_s, P_s remaining constant at 53 cm. of dibutyl phthalate. With V_s ranging from 242 to 5600 ml., no great changes in adsorption rate were found. Table 1 shows that the volume of the system was changed by a factor of 20. The value of a seems to vary by as much as a factor of 100, but, being an extrapolated initial rate of a very rapid process, this is not unexpected. The absence of trend in the a values with variation in V_s suggests that they are effectively constant. The constancy of α is more obvious. The apparent decrease at large V_s simply reflects the very slow pressure change occurring. Within experimental error α also is constant. This constancy is achieved despite the fact that the pressure after 100 min., shown in the table as P_{final} when the adsorption rate was very slow, changed by over 100 per cent. For the system of largest volume the pressure change is small, so that effectively the system is also at constant pressure. It appears therefore that the Elovich analysis of adsorption rates for a given P_s will yield the same parameters whether runs are made at constant volume or at constant pressure.

It is important to note, however, that this independence of the prevailing conditions of constancy of volume or of pressure does not mean that the same absolute amounts will be adsorbed under the two conditions (180). The Elovich equation deals with the rate of adsorption. There is a definite increase from 6.9 to 9.6 ml.

TABLE 1

The effect of pressure on adsorption

Data of Leibowitz, Low, and Taylor (180)

Temperature = −78°C.; P_s = 53 cm. of dibutyl phthalate

V_s	a	α	$q_t = 1$	$P_t = 1$	P_{final}
ml.				cm.	cm.
242	7×10^6	2.5	6.9	31	22
290	7×10^7	2.4	7.6	32	24
340	3×10^7	2.5	7.6	35	28
884	2×10^6	2.2	7.6	46	45
3980	6×10^6	2	7.9	50	48
5600	2×10^8	2	9.6	52	50

in $q_{t=1}$ as V_s increases. This increase was explained in terms of the Taylor–Thon mechanism (298). It was suggested (180, 298) that q_{t_0}, here approximated as $q_{t=1}$, represents the initial adsorption occurring during the site-creation processes prior to the onset of the "slow" measurable adsorption. During this short time interval a stationary state is set up between site crea-

tion, site occupancy, and site decay. In a constant-volume system the larger the volume, the less will be the pressure change accompanying site creation and occupancy. Therefore, the higher will be the momentary pressure, thus favoring a large occupancy. With an increased initial adsorption in systems of larger volume, the total adsorption at all succeeding stages must also be larger even though a, which is the initial rate of adsorption, and α, which is the relative rate of site decay, are constant.

Such independence of P_a and dependence on P_s is predicted by the theories of Taylor and Thon (298) and of Landsberg (172) and seems to be substantiated by the above experiments and by the relations of rate to P_s. The small rapid adsorptions and desorptions encountered in the hydrogen–nickel work, however, suggest further work on this topic in order to define the differentiation of P_a and P_s effects more precisely. It is possible that the small and apparently reversible adsorptions detected upon changes in pressure are themselves pressure-sensitive.

B. DEPENDENCE ON INITIAL PRESSURE

For some recent constant-volume work with bulk catalysts rate parameters were correlated with P_s, changes in P_a being considered inconsequential. The general overall effect of increasing pressure is to increase both rates and extents of adsorption. Recent work, however, suggests that P_s-rate relations are not simple. Linear variations of parameter values with changing P_s are obtained, but frequently these are discontinuous. Constant-volume experiments on the adsorption of hydrogen on nickel–kieselguhr (180), zinc oxide (198), platinum (198), ruthenium (193), iridium (194), rhodium and palladium (189), iron (198), and $ZnO \cdot Cr_2O_3$ (192) led to the following observations for these systems:

(a) The parameters a and α are pressure-sensitive, a increasing and α decreasing with increasing P_s. Linear relations of the type

$$\alpha = A + BP_s$$

and

$$\ln a = C + DP_s$$

where A, B, C, and D are constants, exist over subatmospheric P_s regions.

(b) The effect of changing P_s on parameter values is greater in relatively low P_s regions than in high P_s regions. This leads to discontinuous α–P_s and $\ln a$–P_s plots, an example of which is shown in figure 10. The low-pressure regions are in general poorly defined because of the large variations of parameter values with small changes of P_s. The discontinuities observed suggest the necessity for more plentiful data spaced at closer P_s intervals than was obtained in earlier investigations.

For the constant-pressure data of Burwell and Taylor (51) for the system hydrogen–Cr_2O_3 there is (298) a hint of an increase in α with increasing P_s, a is approximately proportional to $P_s^{0.8}$, and q_t is directly proportional to P_s. Comparisons were made (298) on the basis of points at 0.25, 0.5, and 1 atm. If the detected discontinuities are real—and close scrutiny of experimental techniques indicates this—then not enough data are available for the hydrogen–Cr_2O_3 system to define P_s relations closely.

The general phenomenon of decreasing α and increasing a with increasing P_s is found with the systems oxygen–nickel(II) oxide (89), nitrogen–iron (140, 276), hydrogen–copper (164, 329), oxygen–silver (284), and
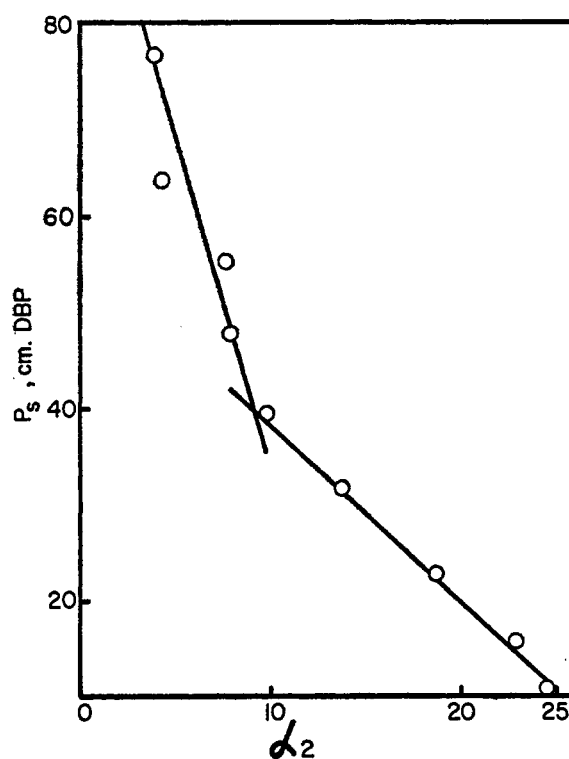
FIG. 10. Adsorption of hydrogen on platinum at 200°C. (data of Low and Taylor (198)).

hydrogen–tungsten(IV) sulfide (64). There is irregularity with oxygen–glass (264, 282); adsorption rates at 0.5 atm. are sometimes greater than at 0.75 atm.

The suggestions as to the ineffectiveness of P_a and dependence on P_s are particularly interesting because, if only P_s is effective, then the end-point of the adsorption is related to P_s and not to P_a. The concept of the adsorption equilibrium then becomes uncertain and attention is focussed on the termination of the chemisorption rate process. Although equilibrium seems to be verified by experiments whereby the end-point of an adsorption is approached from high and from low pressures (35, 98, 163), sufficient facts on pressure effects, desorption, and kinetics exist to permit criticism of the general acceptance and applicability of a terminal equi-

librium of the type invoked for physical adsorption. Desorption of chemisorbed gas is known frequently to require a drastic change of conditions from those of adsorption (24, 161, 312); sometimes the gas is not recoverable in the form in which it was adsorbed (107, 196, 281) and the presence of a gas phase aids desorption (150, 180, 330). Also, the generally applicable Elovich equation has the form of an expression representing the course of a reaction going to completion with negligible reverse reaction. Or, desorption, if present at all, is negligible. Indeed, with kinetic expressions formally based on a Langmuir equilibrium that are formulated as the sum of adsorption and desorption terms, the desorption component is often neglected. Since the Elovich equation frequently represents adsorption to conditions of high degrees of surface coverage, this also implies that desorption effects are of secondary importance. Also, the rate parameters seem to be, and have been interpreted to be, mainly a function of P_s and not of P_a.

Such experimental evidence suggests that the concept of the termination of a chemisorption process in a simple Langmuir adsorption–desorption equilibrium is not entirely satisfactory. If chemisorption proceeds through precursors of a physically adsorbed layer, as suggested by Becker (19) or by Ehrlich (75), such an equilibrium would be even more involved. This topic is discussed, more appropriately, in detail elsewhere (188, 296, 297, 307).

C. DEPENDENCE ON AMBIENT PRESSURE

There seems to be some consistency among claims as to dependence on P_a. With bulk adsorbents it would appear that the rate is directly proportional to P_a. Formulations to that effect were used to indicate P_a effects for systems such as hydrogen–promoted cobalt (110, 111), hydrogen–iron (167), hydrogen–, deuterium–, methane–, or methane-d_4–charcoal (16), oxygen–copper(I) oxide (149), and nitrogen–iron (276).

With evaporated films however, a square-root dependence has frequently been used. Thus Oda (233) showed that the relation

$$-\,dP_a/dt \;=\; k_1 P_a{}^{1/2}$$

gave good agreement with oxygen–nickel film data except at very early stages. Also, Matsuda (203) expressed the rate of chemisorption of hydrogen by nickel wire by a modified Elovich equation,

$$dq/dt \;=\; k_1 P_a{}^{1/2}\,\exp(-k_2 q/RT)$$

where k_1 and k_2 are constants. Similar square-root or near square-root dependence was reported for oxygen–metal films (176), hydrogen–iron film (123, 247, 308), oxygen–tungsten film (257), and for nitrogen–iron, nitrogen–chromium, and nitrogen–tantalum (116).

The reason for the discrepancy between the P_a dependencies on bulk and film adsorbents is uncertain, seems unrelated to dissociative versus undissociative adsorption effects which, classically, could give rise to such discrepancy, but may be connected with contamination which may influence the kinetics by changing the character of the surface. Recently the kinetics of the adsorption of nitrogen on ammonia-synthesis catalyst were redetermined by Scholten and Zwietering (276), using precise gravimetric techniques under "clean" conditions. First-order relations of rate to P_a were found, in direct contradiction to the proportionality to $P_a{}^{1/2}$ reported by Greenhalgh, Slack, and Trapnell (116) for nitrogen–iron film. Scholten and Zwietering tentatively assume that the strong chemisorption on iron films is preceded by a weak dual site adsorption of the type suggested by Dowden (70), and that the transition from weak to strong chemisorption is the rate-determining step. Dowden postulated chemisorption states which are intermediate in energy between physical adsorption and strong chemisorption (69) and which are the precursors of strong chemisorption. Indications of such weak chemisorption at $-196°C$. of nitrogen and iron film was reported by Beeck (29) and later confirmed by Porter and Tompkins (241) and by Greenhalgh, Slack, and Trapnell (116). No evidence for such weak chemisorption was found with the bulk ammonia-synthesis catalyst, and this may account for the discrepancy.

The controversial nature of the pressure effects seems surprising. A superficial skimming of all available literature, however, creates the impression that experimentally the effects of pressure on kinetics have been purposely neglected, preference being given to equilibrium studies, and that this was done because effects of pressure on rates were obvious. This was wishful thinking and was probably brought about by too close mechanistic analogy to physical adsorption. In view of the importance of pressure effects to theory, much more work on this topic is justified.

VI. THE EFFECTS OF TEMPERATURE

A. ISOTHERMAL EFFECTS

Many reports exist on comparison of kinetics at different temperatures, each experiment being performed under isothermal conditions. Frequently only two temperatures were used, and all too frequently temperature effects were reported only in the form of an Arrhenius activation energy. These, when not accompanied by kinetic data, have been disregarded. Only relatively extensive investigations were considered. A table of activation energies is given by Hunsman (142).

The effects of temperature on the kinetics of slow chemisorption are more complex than was originally believed (298). Enough data are at hand to permit some generalization as to adsorption on bulk catalysts.

(a) The parameters a and α vary in linear fashion with temperature, viz.

$$\alpha = A + B/T$$

$$\ln a = C + D/T$$

where A, B, C, and D are constants.

Relations of this sort were found for the adsorption of hydrogen on nickel–kieselguhr (180), ruthenium (193), iridium (194), palladium and rhodium (189), zinc oxide for short temperature regions (187), $ZnO \cdot Cr_2O_3$ (63, 64, 192), Cr_2O_3 (51), and tungsten(IV) sulfide (64).

(b) When there is more than one kinetic stage, the changes in rate with temperature for all stages seem to be in the same direction, but the effects are not of the same magnitude for each stage (187, 189). The latter effect is illustrated by changes in α with temperature for the hydrogen–zinc oxide system (187). The ratios α_1/α_2 of the rates of the second to the first kinetic stage were not constant but increased with increasing temperature over increasing regions of the isobar.

(c) Increasing temperature favors the early appearance of any given kinetic stage (189). This is indicated by the systems hydrogen–palladium and hydrogen–rhodium (189) and to some extent by the hydrogen–iridium (194), the hydrogen–$ZnO \cdot Cr_2O_3$ (192), and other systems. For a system showing breaks in Elovich plots, the coördinates of intersection of two linear portions decrease in roughly linear fashion as the temperature increases.

(d) Allowing for uncertainties of extrapolation, the initial massive adsorption, q_0, if present, increases only slightly, if at all (298), with increasing temperature.

(e) The linear relations between rate parameters and temperature are valid only over limited regions of temperature not in the vicinity of a maximum or a minimum of the adsorption isobar. A reversal of temperature coefficients frequently occurs at such positions of the isobar. Such reversal seems to be general and is illustrated by the plots of figure 11. Most studies of temperature effects on kinetics were made over temperature regions of the isobar corresponding to regions of increasing or decreasing adsorption. Relatively few data were obtained at temperature regions including an adsorption maximum or minimum. Systems which show reversal of temperature coefficients at such isobar regions include hydrogen–zinc oxide (187), carbon monoxide–palladium (302), oxygen–glass (264, 282), hydrogen–$ZnO \cdot Cr_2O_3$ (291, 305), and hydrogen–$ZnO \cdot Mo_2O_5$ (291, 305), probably hydrogen–nickel–kieselguhr (269), and oxygen–silver (284, 324). The data for the last two systems are fragmentary.

(f) The temperature coefficients of a and α may be positive or negative, depending on the gas–solid system and on the temperature range. There seems to be some connection between the region of the isobar concerned and the temperature coefficients, so that several com-

binations of effects are possible. For purposes of comparison it is assumed that the reversal of temperature coefficients at isobar maxima is general. It is thus possible to reduce the number of effects to three by comparing all data on the basis of the sign of the temperature coefficients corresponding to the declining region of the isobar. For this purpose, temperature coefficients obtained for systems in temperature regions corresponding to an ascending region of the isobar have been reversed in sign; e.g., for oxygen–$CuO \cdot CrO_3$ (100) in the range 125–200°C. the total adsorption at $t = 300$ min. increases with increasing temperature while α values decline and a values increase, but for comparison pur-
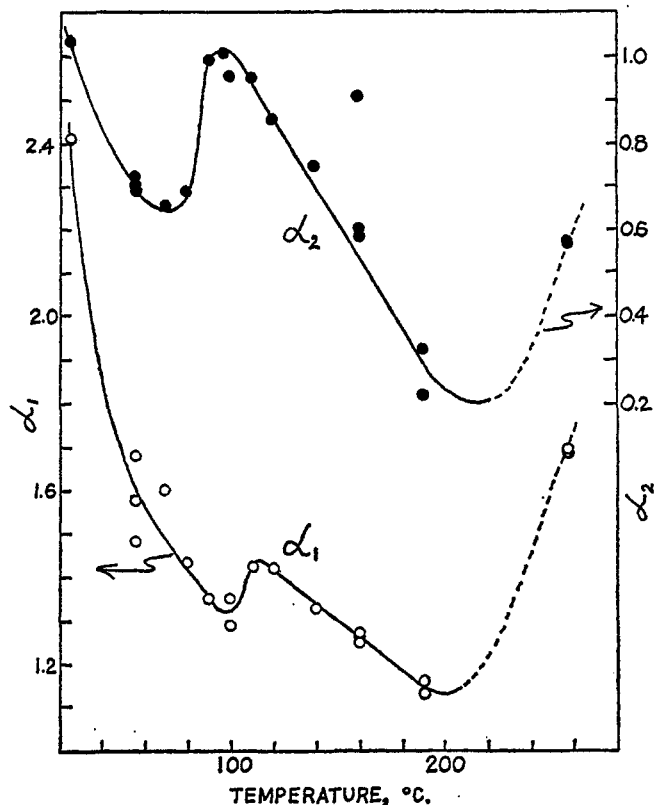
FIG. 11. Adsorption of hydrogen on zinc oxide (data of Low (187)).

poses the changes are indicated as increases for α and decreases for a. A compilation of such data is given in table 2. Positive signs refer to increases, negative signs to decreases, of the parameter values with increasing temperature. Note that the signs in conjunction with I and T refer to ascending or descending isobar regions, I, and temperature regions of the actual experiments. A temperature in parentheses indicates the rough position of the maximum of the isobar. Interrogation points indicate uncertainty caused by insufficient, inconclusive, or poor data.

There is an irregularity in the change of rate parameters with temperature for hydrogen–$ZnO \cdot MoO_3$. The data of Ogden and Taylor (237, 238) show that α values

TABLE 2

Temperature effects

System	I	T	a	α	References
		°C.			
Hydrogen–ruthenium	−	(0) 100–257	+	+	(193)
Oxygen–silver	+−	180 (200) 260	+?	+	(284)
Hydrogen–tungsten(IV) sulfide	+	0–184	+?	+	(64)
Carbon monoxide–palladium	+−	−78 (0) 280	+?	+	(302)
Oxygen–copper(I) oxide	+	−35–60	+	+	(149)
Hydrogen–ZnO·Cr₂O₃	+−	110 (190) 254	+	+	(291)
	+	80–132	+	+	(64)
Hydrogen–iridium	−	0–257	−	−	(194)
Hydrogen–rhodium	−	0–400	−	−	(189)
Hydrogen–platinum	−	0–257	−	−	(198)
Oxygen–silver	−	160–325	−	−	(324)
Hydrogen–nickel	−	0 (200) 500	−	−	(180)
Hydrogen–ZnO·MoO₃	+	110–254	−?	−	(237, 303)
	+	186–350	−	−	(272)
Carbon monoxide–ZnO·MoO₃	+	214 (320) 351	−	−	(303)
Hydrogen–palladium	−	0–400	−	+	(189)
Carbon monoxide–cobalt	+	78–255	−	+	(3)
Hydrogen–cobalt	+	89–257	−	+	(3)
Oxygen–glass	+−	0 (155) 300	−	+	(264, 282)
Hydrogen–zinc oxide	+−+−	0–257	−	+	(187)
Hydrogen–ZnO·Mo₂O₅	+−	218 (380) 444	−	+	(291)
Sulfur dioxide–Ag₃VO₄	+	210–368	−	+	(2)
Oxygen–Ag₃VO₄	+	216–368	−	+	(2)
Oxygen–CuO·Cr₂O₃	+	125–200	−	+	(99)
Carbon monoxide–CuO·Cr₂O₃	−	125–200	−?	+	(99)
Hydrogen–Cr₂O₃	+	−78–218	−	+	(51)
Carbon monoxide–Cr₂O₃	+	224–351	−	+	(141, 303)
Hydrogen–manganese(II) oxide	+	184–218 (300)	−	+	(306)
Hydrogen–copper	−	300–400	−	+	(164)
Hydrogen–copper(II) oxide	−	518–808	−	+	(128)
Hydrogen–MnO·Cr₂O₃	+	100–132 (300)	−	+	(306)
Hydrogen–iron	+−	50 (100) 400	−	+	(222)
	−+−	−78 (100) 450	−?	+?	(88)
Hydrogen–silicon–molybdenum	−	350–400	−?	+?	(118)
Oxygen–platinum	+	0–100	−	+	(207)

decline in the region 110–154°C., then jump to a value almost ten times as great at 218°C., and decline thereafter. The data are shown in table 3. The data of Sastri and Ramanathan (272) on the same system similarly show such a drop between 184° and 250°C., followed by a recovery at higher temperatures. The temperature region of about 100°C. to about 350°C. corresponds to an ascending region of the isobar. The reason for the anomaly is unknown, although Taylor and Thon suggest it to be indicative of a change in the nature of adsorption sites (298). However, the anomaly occurs in the region of the second maximum (about 200°C.) of the hydrogen–zinc oxide isobar (187) and could be brought about by a change in adsorption of hydrogen on discrete particles of zinc oxide within the coprecipitated oxide adsorbent.

The data for the various systems fall into these groups: $(\alpha+, a+)$, $(\alpha+, a-)$, and $(\alpha-, a-)$. Complete correlation of chemical properties with adsorption characteristics for such a variety of diverse systems seems hopeless, since in many cases the experimental conditions and the adsorbents are ill defined. For the adsorption of hydrogen on the cubic platinum metals rhodium, palladium, iridium, and platinum, there seems

TABLE 3

Adsorption of hydrogen on ZnO·Cr₂O₃
Data of Ogden and Taylor (237, 238)

T	α	$a \times 10^2$	$q_{t_0} \times 10^2$
°C.			
110	7.8	0.053	0.2
132	4.1	0.16	0.5
154	1.5	0.60	0.3
218	12	0.15	0.3
254	12	0.50	0.6

to be some order. Palladium, having a filled d band, behaves differently from the other metals with unfilled d bands. Ruthenium is excluded because of its hexagonal structure. Similarly copper, with ten $3d$ electrons, behaves like palladium of the $(\alpha+, a-)$ group, while nickel, with eight $3d$ electrons, belongs to the $(\alpha-, a-)$ group. However, such relations cannot be pushed too far, because classification and correlation are hindered by many points of contention regarding the nature of the adsorbents (see Section III). For example, bulk copper is known to adsorb hydrogen (27, 164, 300, 329), but clean copper films do not (30, 155).

Rigorously reduced bulk copper also does not chemisorb hydrogen (33). Similarly, one of the two maxima of the hydrogen–iron isobar described by Emmett and Harkness (88) is not found if reduction of the solid is not rigorous (87). This suggests that the experiments of Raal (253) on the chemisorption of hydrogen, carbon monoxide, and carbon dioxide on iron Fischer–Tropsch catalyst were made with an incompletely reduced catalyst, because Raal's hydrogen–iron isobars show only one maximum.

The cause of the discrepancy in table 2 between two sets of data for oxygen–silver is unknown but could be contamination or incomplete reduction of the silver. Hirota and Kobayashi (139) deduce from the different catalytic behavior of reduced silver that the silver surface retains a special kind of residual oxygen even at temperatures above those at which silver oxide is unstable (34). Some oxygen apparently remains on the surface even after reduction with hydrogen. Again, recent work on nickel suggests the presence of some residual oxygen even on rigorously reduced nickel catalysts (260, 277, 278). In view of these and similar points, rigorous correlation without eristics seems implausible at present.

B. ABRUPT TEMPERATURE CHANGES

Scattered through the literature are remarks to the effect that, when a solid that is partially or wholly covered with adsorbate is quickly raised in temperature, a desorption followed by a readsorption occurs. The effect was systematically examined by Taylor and Liang (301) and Sadek and Taylor (269) and reviewed by Taylor (299). With some systems, e.g., hydrogen–zinc oxide, when subjected to an abrupt temperature decrease, increased adsorption was found. The effect is explained in terms of a mechanism (301) involving two adsorption sites A and B with corresponding activation energies E_A and E_B and heats of adsorption H_A and H_B, respectively. The values of these are such that at a low temperature, $T_1 < T_2$, sites A become covered while sites B remain sensibly bare. On changing to temperature T_2, gas is desorbed from sites A while sites B become progressively covered. If the rate of desorption at T_2 from A is initially faster than that of adsorption on B, the net observed effect on changing from T_1 to T_2 will be an immediate desorption followed by an adsorption.

Sastri and Ramanathan (272) derived an equation for estimating the point of minimum adsorption following a temperature increase, attaining good agreement with data for hydrogen–ZnO·Mo_2O_5. Sastri and Srinivasan (273) presented evidence that the effects found with the adsorption of hydrogen on cobalt Fischer–Tropsch catalysts arise predominantly from surface phenomena and reflect surface heterogeneity.

Inspection of such data, available in graphed form,

suggests in general that the rates of adsorption following an abrupt temperature rise equal or surpass those at the lower temperature. Since the rate data are inadequate and no data from "undisturbed" isothermal experiments on the identical systems are available for comparison of rates, further work is indicated.

C. CONTINUOUS TEMPERATURE CHANGE

On increasing (187) the temperature from 33°C. to 314°C. at 4° per minute during the adsorption of hydrogen on clean zinc oxide at 40 cm. of mercury the rate of adsorption declined only slightly during the first 20 min. At about 180°C., however, adsorption ceased to increase, and desorption commenced at about 200°C. After 90 min. the temperature rise was decreased to 0.2°C. per minute and adsorption proceeded. Figure 12 shows the data.

In a different experiment the temperature was allowed to drop from 323°C. at $t = 0$ to 69°C. at $t = 180$,
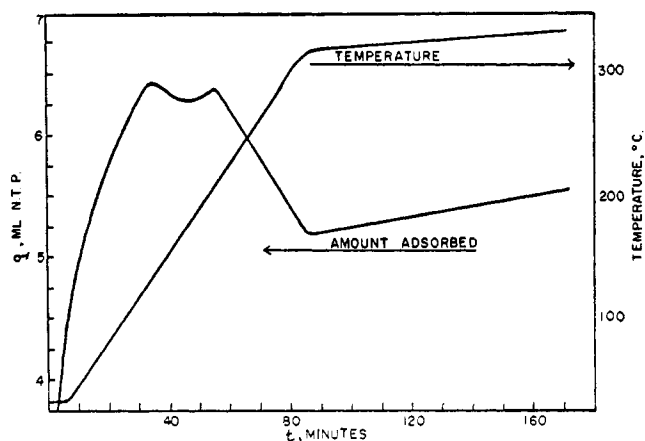
FIG. 12. Effects of increasing temperature on the adsorption of hydrogen on zinc oxide (data of Low (187)).

and was kept constant thereafter. A slow decline in adsorption rate with declining temperature was observed. The rate remained roughly constant in the constant-temperature region from 90 to 180 min. The results of the two experiments are thus comparable to those of the experiments in which temperature is changed abruptly (301). Apparently quite drastic departures from the techniques of Taylor and Liang (301) will not bring about significantly different results in the case of the hydrogen–zinc oxide system.

D. ADIABATIC ADSORPTION

Some chemisorption rate data obtained under adiabatic conditions are given by Magnus and Sartori (201), who measured adsorption kinetics simultaneously with the temperature rise produced by the adsorption of hydrogen on nickel contained in a calorimeter. The temperature rise, ΔT, with time was stated to follow the expression

$$d\Delta T/dt = k_1 \exp(-k_2 t)$$

where k_1 and k_2 are constants. Substitution of q for ΔT in that expression did not satisfactorily account for the adsorption kinetics, and a correction was applied. Assuming, when $q = N$, that equilibrium is reached (saturation), then at some time t, when only q is taken up, there remains $(N - q)$ to be taken up. This removal
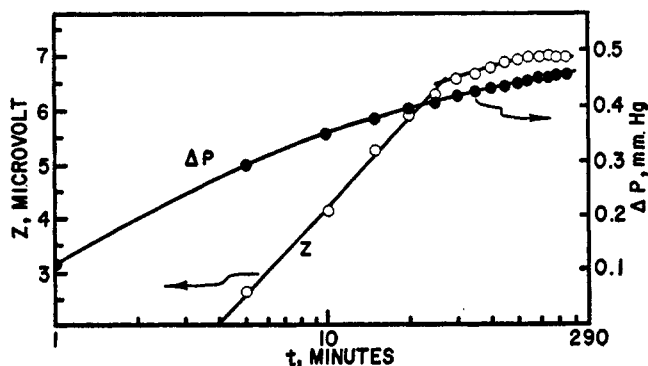

FIG. 13. Adiabatic adsorption of hydrogen on nickel (data of Magnus and Sartori (201)). 25°C.; 50 g. of nickel; $P_s = 0.516$ mm. of mercury.

from the equilibrium point acts on the adsorption velocity and is added to $k_1 \exp(k_2 t)$, so that

$$dq/dt = k_1 \exp(-k_2 t) + k_3(N - q)$$

Values of the four constants may be estimated from the data. Figure 13 shows Elovich plots of the pressure change, ΔP, and of Z (thermocouple potential, proportional to ΔT) for an adiabatic experiment. The linearity of the Z–log t plots seems to support Taylor and Thon's suggestion (298) that the heat of adsorption changes in exponential fashion, $H \propto \exp(-\alpha q)$. The nonlinearity of the ΔP–log t plot suggests that the Elovich equation is not applicable, the plot showing concavity to the log t axis. This behavior is reminiscent of that shown, in part, by Elovich plots for the systems hydrogen–iron (195), hydrogen–Cr_2O_3 (51, 270), and nitrogen–iron (195, 342). Particularly, for the hydrogen–iron system, the q–log $(t + k)$ relations were such that no unique value of k was applicable over the whole course of an experiment. This is illustrated by the plots of figure 14. A value of k chosen to linearize the first region of the run had no linearizing effect on later regions, while a larger k value showed the presence of an isothermal discontinuity but caused curvature of the first region. Intermediate k values were altogether unsatisfactory, leading to sigmoid curves. Numerical procedures (270) showed the Elovich equation to be applicable over the major portion of the runs, but the k values so determined led to plots such as that marked D in figure 14. The concavity of that plot, as well as that of the ΔP–log t plot of figure 13, can be removed and the line straightened by applying a negative k value but, whereas this is empirically feasible, it is undesirable. Low and Taylor showed that the Elovich equation cannot be

applicable to adiabatic kinetics (195) and suggest that the peculiarities shown by the isothermal kinetics are due to poor thermal conduction of the adsorbent. This may well be the case with a finely powdered adsorbent which increases in temperature because of the exothermal adsorption. The latter may thus occur under pseudoadiabatic conditions during the early regions of the experiment.

VII. The Effects of Preadsorbed Gas

Experiments on this topic consist, essentially, of permitting the solid to preadsorb a known amount of gas A; the adsorption of gas B "on top of" the preadsorbed gas A is then studied, and a comparison is made of the kinetics and extents of adsorption of gas B on the clean surface and on the purposely contaminated surface. Early studies were mainly concerned with the effects of preadsorption on isotherms and isobars; consequently few kinetic data are available.

All data on the effect can be subject to some criticism because of possible "nonselective" (265) adsorption of the preadsorbate. It is possible that, when the preadsorbate is admitted to the evacuated chamber containing the adsorbent, the gas is adsorbed on those areas of the solid with which it first comes into contact. Such a case of stratification was described by Burwell and Taylor (52) in their study with powdered zinc oxide contained in a vertical cylindrical chamber. Hydrogen saturated with water vapor was introduced at the top of the chamber. A fraction of the material near the point of introduction of the gas selectively adsorbed the water from the gas mixture.

Similarly, in studying the evolution of heat on ad-

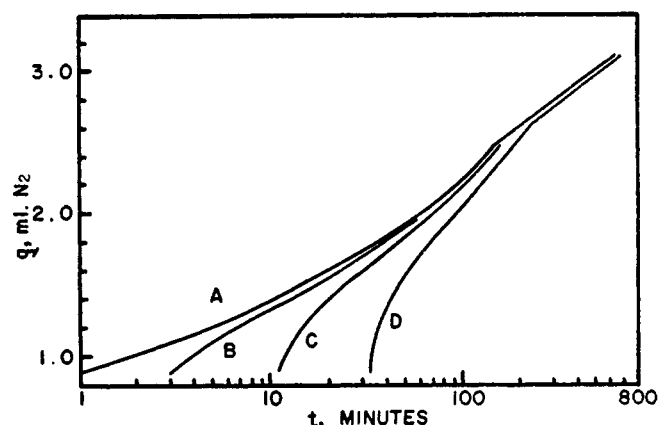FIG. 14. Isothermal adsorption of nitrogen on iron (data of Zwietering and Roukens (342)).

sorbing carbon monoxide on copper in a calorimeter, Beebe (25) found nonselective adsorption. The form of the time–temperature curve obtained for that system for the first small increment of gas admitted to the catalyst was dependent on the position of the thermocouple in the adsorbent bed. The nonselective adsorption,

found in the anomalies of time–temperature curves, disappeared when there was a residual gas pressure. The calorimetric work of Bull, Hall, and Garner (49) with the adsorption of oxygen on charcoal and the experiments of Russell and Ghering (265) on the adsorption of oxygen on copper afford further examples of the effect.
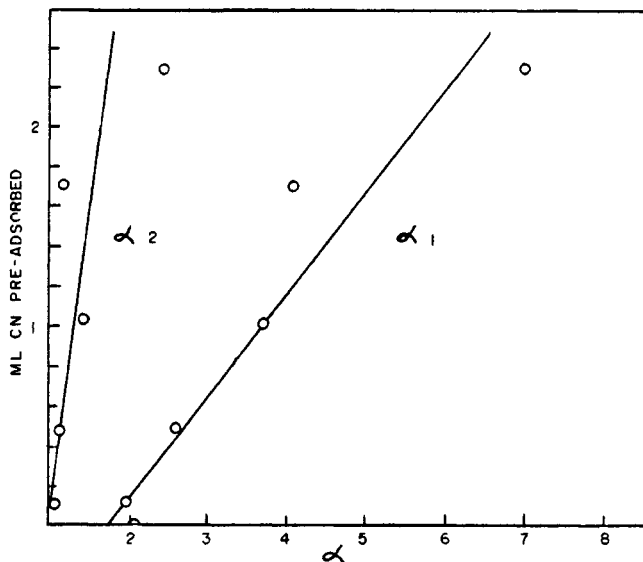

Fig. 15. Adsorption of hydrogen on cyanogen-poisoned nickel at −78°C. (calculated from data of Iijima (145)). 8.27 g. of nickel; 23.5 cm. of mercury.

In spite of the possibility of nonselective adsorption, interesting results have been obtained. Several types of "poisoning" appear to be possible.

A. TYPES OF POISONING

Each of the parameters a or α of the Elovich equation may be affected by preadsorption, so that (191) empirically four general effects are possible. (I) If, on preadsorption, α decreases and a increases, then both rates and extents of adsorption are increased, and the effect is an enhancement; (II) if α increases and a decreases, the effect is a true poisoning, since both rates and extents of adsorption are diminished; (III) if α decreases and a decreases, or (IV) if α increases and a increases, two further cases of "poisoning" are apparent in which the rate may increase but the extent of adsorption decrease, or the rate may decrease but the total amount adsorbed increase. Examples of each type of effect exist, although the data are meager.

1. Type I: enhancement

On adsorbing hydrogen on top of 0.78 ml. of oxygen on Ru·Al₂O₃ (191) the parameter a was changed from 10^6 (on the clean surface) to 10^{12}, while α declined from about 3 to 2.3 and the total amount adsorbed increased. The overall effect is thus one of "promotion" or "enhancement." This type of enhancement may be operative in "autocatalytic" adsorption (see Section IX).

2. Type II: poisoning

Increases in α concurrent with decreases in a with increasing amounts of preadsorbate are apparent in Iijima's data on the adsorption of hydrogen on nickel. The effect occurred when unmeasured amounts of mercury were preadsorbed (143) and also with the preadsorption of cyanogen (145). Elovichian rate parameters obtained by recalculating data for the latter study are given graphically in figures 15 and 16. The measurements were made in a system of constant volume at −122°C., using 8.27 g. of nickel prepared from nickel-(II) oxide. The pressure 1 min. after introduction of hydrogen was about 23.5 cm. of mercury. The Elovich plot for each experiment is discontinuous. Also, the effect of increasing amounts of preadsorbed cyanogen, q_{CN}, is to decrease q_b from 4.25 ml. at $q_{CN} = 0$ to 1.1 ml. at $q_{CN} = 2.29$ ml., while t_b increases from 14.5 to 18 min. under these conditions, in roughly linear relation to q_{CN}.

Burwell and Taylor (52) found that preadsorbed water greatly inhibited the adsorption of carbon monoxide and of hydrogen on zinc oxide. In each case a decreased and α increased. For example, for the adsorption of hydrogen at 218°C. and 1 atm. on 22.7 g. of zinc oxide, $\alpha = 1.6$ and $a = 22.6$; on the surface saturated with 14.8 ml. of water vapor, $\alpha = 15$ and $a = 6.5$. Low and Taylor (196) found similar effects with the same system and reported that the rates and extents of adsorption of water by zinc oxide were greatly decreased by preadsorbed hydrogen.
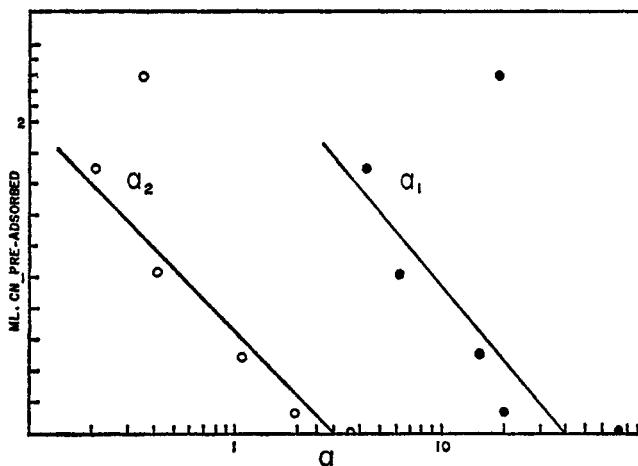
Fig. 16. Adsorption of hydrogen on cyanogen-poisoned nickel at −78°C. (calculated from data of Iijima (145)). 8.27 g. of nickel; 23.5 cm. of mercury.

3. Type III: pseudoenhancement

For hydrogen adsorbed on top of carbon monoxide on Ru·Al₂O₃ (191), the initial rate decreased with increasing amount of preadsorbed carbon monoxide, q_{CO}, a falling from about 10^6 on the clean surface to about 10^1 on a surface with $q_{CO} = 6.5$ ml. Simultaneously the
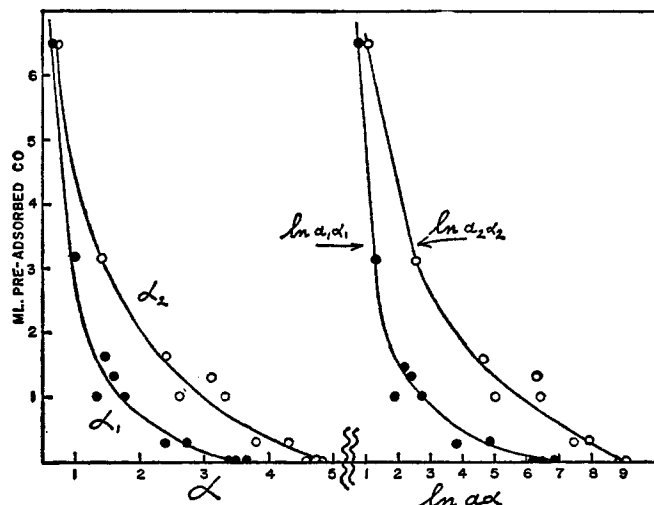
Fig. 17. Adsorption of hydrogen on carbon monoxide-poisoned ruthenium at 100°C. (data of Low and Taylor (191)). 28 g. of catalyst of 0.5 per cent ruthenium on Al_2O_3; $P_s = 70$ cm. of dibutyl phthalate.

total amounts adsorbed after 100 min. increased and the parameters α decreased with increasing q_{CO}. The overall effect is one of increased ambient rates and extent of adsorption, i.e., a promotion, the increase in ambient rates overshadowing the decrease in initial rates. The data are shown graphically by figure 17. A similar effect is reported for the adsorption of hydrogen on cobalt (3). Pretreatment of the catalyst with carbon monoxide causes an increase in ambient rates of adsorption of hydrogen at low temperatures, but the total amounts of hydrogen taken up after an arbitrary time are smaller than those on the untreated catalyst.

The adsorption of hydrogen on platinum pretreated with hydrogen sulfide affords a further example of decrease in both rate parameters (209). Amounts adsorbed

Fig. 18. Adsorption of hydrogen on hydrogen sulfide-poisoned platinum at 18°C. and 1 atm. (calculated from data of Maxted and Moon (209)).
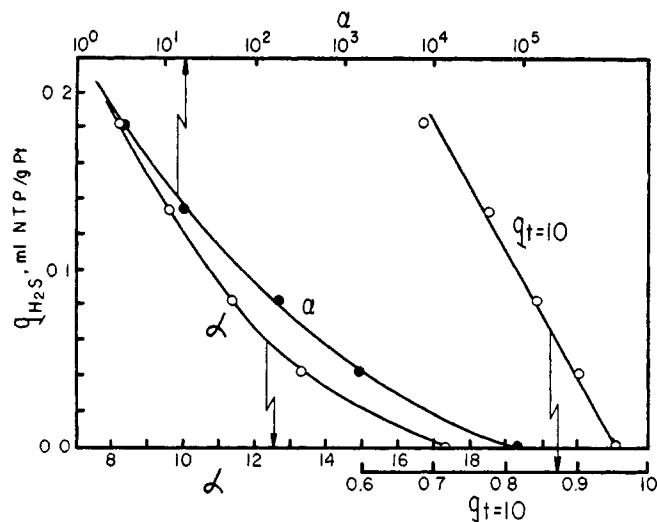
per gram of platinum after 1, 5, and 10 min. are reported (210), yielding roughly linear q–log t plots. Calculation of a and α values from the data at 1 and 10 min., for experiments at 1 atm. on top of varying amounts of hydrogen sulfide, yields the plots of figure 18. The increase in α is overshadowed by the decrease in a, resulting in an overall decline in q, shown by the $q_{t=10}$–q_{H_2S} plot of figure 18. Curiously, a second set (211) of similar data over the range 2–10 min. at pressures between 0.05 and 0.06 mm. of mercury shows no apparent effect on the adsorption of hydrogen on varying q_{H_2S} from zero to 0.18 ml. per gram of platinum. Other sets of data on experiments of short duration (from $t = 0.3$ to $t = 2$ min.) and also of long duration (up to 1600 min.) are summarized (206) in terms of the constants n and k of the logarithmic form of Bangham and Sever's equation (10), viz.:

$$\phi = \log [\log (m/m - q)] = \log k + n \log t$$
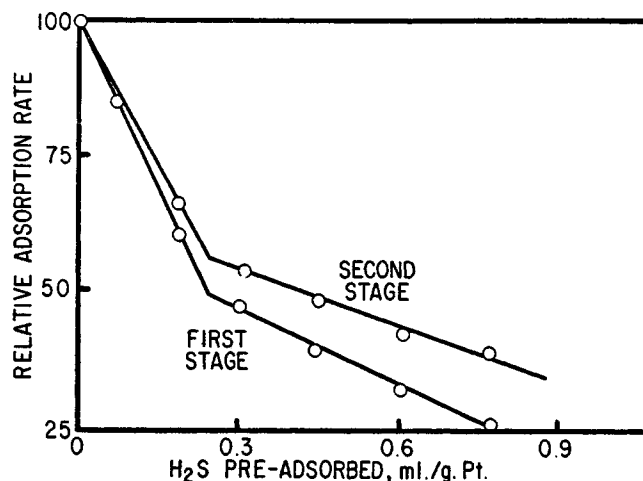
Fig. 19. Relative rates of adsorption of hydrogen on hydrogen sulfide-poisoned nickel at 0°C. and 1 atm. The comparison is on the basis of rate constants n and k of Maxted and Evans (206).

Values of the constant m, the saturation volume, are not given. An Elovich plot of the only set of q–t data given over an extensive time period is discontinuous, the break occurring at $t = 3$ min. The corresponding ϕ–log t plots are similarly discontinuous, resulting in distinct values of n and k for each linear section. Further, the change in those constants with changing q_{H_2S} is itself discontinuous. Figure 19 shows plots of relative adsorption rates as function of amount of preadsorbate for each linear segment of ϕ–log t plots.

4. Type IV: pseudopoisoning

Preadsorption (143) of carbon monoxide on nickel decreases the total amount of adsorption of hydrogen. Figure 20 shows Elovich plots constructed from the original data for experiments with varying amounts of preadsorbate. The effect of preadsorption is more pronounced on the first kinetic stage than on the second.

For the first stage, there is a definite increase in α_1 and a_1 with increasing amounts of preadsorbate. The data are not sufficiently precise to permit a conclusion as to the behavior of α_2 or a_2. Roughly linear changes in the coördinates q_b and t_b of the break with changing q_{CO} exist. The overall effect with increasing q_{CO} is one of decreased amounts of adsorption, of decreased ambient adsorption rates, but of increased initial adsorption rates.

Similar effects result (91) when hydrogen is adsorbed on top of hydrogen on nickel. Preadsorbed undefined amounts of hydrogen decreased the total subsequent adsorption of hydrogen on nickel but increased the initial rate and decreased the ambient rate of adsorption.

FIG. 20. Amounts of hydrogen adsorbed on carbon monoxide-poisoned nickel (data from Iijima's Figure 6 (143)). For these experiments with 10 g. of nickel at 20°C. at a pressure of 20.9 cm. of mercury the plot number and milliliters of preadsorbed carbon monoxide are, respectively: 0, 0; 1, 0.07; 2, 0.32; 3, 0.79; 4, 1.77; 5, 3.45; 6, 6.97; 7, 13.13.
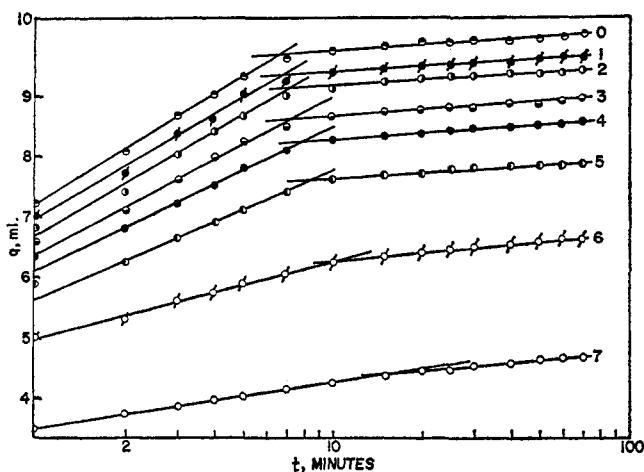
B. MECHANISM

Catalytic "poisoning" phenomena are reviewed elsewhere (148, 205, 232). Preadsorption phenomena, being directly connected with catalytic poisoning, have not received individual attention but are included in mechanism discussions of those reviews. The preadsorption effects described, with other experiments on the influence of adsorbed gas on the properties of solids (1), suggest that the mechanism involved is more complicated than one based on geometric considerations and that primarily changes in the electronic character of the surface are involved. Certainly, classical mechanisms whereby the preadsorbate merely blocks the surface and prevents subsequent adsorption may be rejected except for those cases involving extreme coverage. Also, the formation of complexes on the surface, whereby one gas is literally adsorbed on top of another, is uncertain. For example, Sastri and Viswanathan (274) found enhanced adsorption of hydrogen on a Fischer–Tropsch

catalyst containing preadsorbed carbon monoxide. The enhancement so caused was relatively larger the smaller the volume of gas preadsorbed. The formation of H—C—O surface complexes was suggested, these being also postulated as intermediates in the Fischer–Tropsch synthesis (290). However, Eischens and Pliskin (81) studied the effects of hydrogen on carbon monoxide chemisorbed on iron and platinum by infrared techniques and found no evidence of hydrogenated carbon monoxide complexes. Formation of appreciable quantities of complex is excluded under the specific conditions of the experiments. Commenting on the effects of other gases on the spectra of chemisorbed carbon monoxide, Eischens and Pliskin suggest that it is likely that shifts in band positions observed during such experiments are due to the effect of the added gas on the electronic nature of the metal rather than to a change in the structure of chemisorbed carbon monoxide.

Commenting on the regularities observed, Low and Taylor (191) suggested that the preadsorption effects were due to either one, or a combination of two, general surface effects. In extension of previous theories (298), preadsorption may affect (A) a site-creation process occurring at the initial contact between gas and surface, and/or (B) the bimolecular process whereby such surface sites disappear. Thus "poisons" may permit easier disappearance of sites, while "promotors" may hinder that process and thus permit a longer "site-life." Several combinations of A and B are possible and, manifested as changes in the parameters a and α, may be applied to effects of types I to IV.

In general, although there is a wealth of inferences on catalytic poisoning scattered through the literature, the data on the simpler preadsorption effect are meager. Further work is required. Also, since determination of adsorption rates is more fruitful than the usual static isotherm or isobar measurements, kinetic measurements are preferable and necessary to define chemisorption poisoning more precisely.

VIII. SIMULTANEOUS ADSORPTION

Although the literature on catalysis contains many inferences as to the simultaneous adsorption of reactants, few direct experiments exist in which the rates of adsorption of both constituents of an adsorbing binary gas mixture have been measured. Burwell and Taylor (52) measured the rate of adsorption of a hydrogen–water mixture on zinc oxide but, because of preferential adsorption of water (see Section VII), the observations were rejected by them.

Ghosh, Sastri, and Kini (111) observed continuously the progress of adsorption of each gas of a hydrogen–carbon monoxide mixture by means of a built-in thermal conductivity meter. The 7.55 g. of catalyst consisted of Co:Cu:ThO$_2$:CaO:Cr$_2$O$_3$:kieselguhr in the proportions 100:12:7:0.7:14:159. P_s was probably 700 mm. of
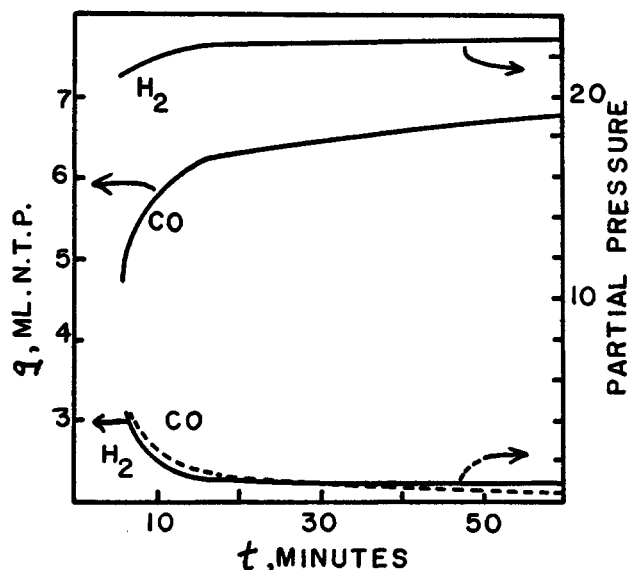
Fig. 21. Adsorption of a hydrogen–carbon monoxide mixture by a cobalt catalyst (data of Ghosh, Sastri, and Kini (111)).

mercury. The data are reproduced in figure 21. "The curve for H_2 indicates that at the beginning H_2 is adsorbed more quickly than CO. This is followed by a decrease in the H_2 adsorption while the adsorption of CO continues to increase in proportion, until eventually a state of saturation is reached with respect to either gas. This suggests that a partial replacement of initially adsorbed H_2 by CO takes place during the formation of CO:H complexes on the catalyst surface. At higher temperatures the transient drop in H_2 adsorption becomes less apparent, presumably due to a quickening of the substitution process."

The rates of adsorption on cobalt of hydrogen, and of hydrogen containing 4 per cent carbon monoxide, were determined by Agliardi and Marelli (3). Total amounts of gas adsorbed at different times were measured. No periodic gas analyses were made. Similarly measured were rates of the adsorption of hydrogen on cobalt containing preadsorbed carbon monoxide, and also rates of the adsorption of carbon monoxide on "clean" cobalt. The authors stated that on the catalyst pretreated with carbon monoxide, the amount of hydrogen adsorbed is less, but the rate of that adsorption is faster, than the adsorption of hydrogen on the untreated catalyst. Also, that the hydrogen–carbon monoxide mixture is adsorbed at first faster than pure hydrogen.

On replotting of the data the situation is seen to be much more complex. Figure 22 shows two pairs of comparable runs. Adsorption of hydrogen is compared to that of the hydrogen–4 per cent carbon monoxide mixture. For clarity, the upper two plots of runs 5 and 14 are displaced by $+1$ ml. Elovich plots of the data show breaks. For the lower two plots of experiments at about 89°C. the slopes and hence rates of adsorption are

roughly equal for both linear segments. Similarly, for the upper two plots of experiments at about 257°C., the slopes of the first segment of each plot are identical. Completely different rates of adsorption exist for the second segments. However, in view of the multiple kinetic stages detected with hydrogen–palladium and hydrogen–rhodium and which probably exist in other systems, such direct comparison seems improper. Rather, attention should be focussed on comparable kinetic stages. For the upper plots only the segments marked II according to the scheme of figure 7 should be compared in order to permit consistent speculation on mechanism. Four pairs of runs at about 89°, 169°, 212°, and 257°C. were given. Those at the first two temperatures show identical characteristics, as do those at the last two temperatures. Apparently, at some intermediate temperature a change in adsorption characteristics occurs. These data justify no further comments.

The paucity of data on this topic is surprising in view of the possible application to heterogeneous catalysis. Although analysis of such data is likely to prove difficult, because of the intricacies hinted at by the data on cobalt, further work is desirable.

IX. Autocatalytic Adsorption

Additions of gas in incremental fashion to an adsorbent have sometimes resulted in a peculiar adsorption effect. The rate of adsorption increased with increasing amounts of gas adsorbed on the surface. For example, Beebe, Low, Wildner, and Goldwasser (26) admitted 0.387 ml. of hydrogen to 58 g. of copper at $-78°C$. After 4 min. 0.298 ml., or 77 per cent, had been

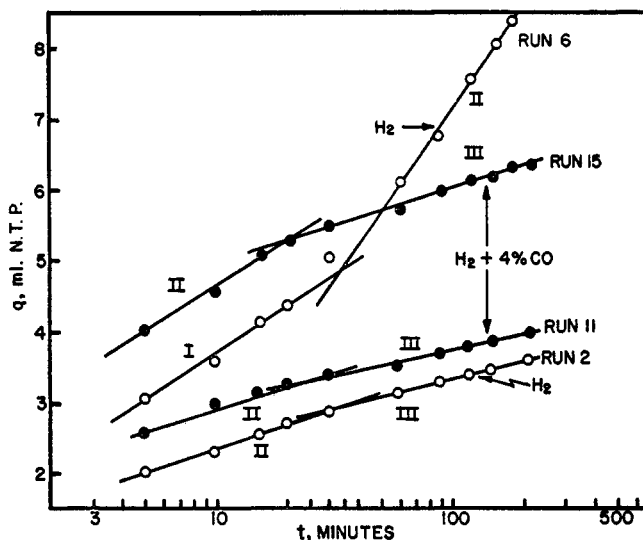Fig. 22. Adsorption of hydrogen and of hydrogen–carbon monoxide on cobalt (data of Agliardi and Marelli (6)). Constant pressure = 286 mm. of mercury. Run 2: hydrogen, 89°C. Run 11: hydrogen–carbon monoxide, 85°C. Run 6: hydrogen, 257°C. Run 15: hydrogen–carbon monoxide, 256°C. The hydrogen–carbon monoxide mixture contained 4 per cent carbon monoxide. Adsorbent, 3.13 g. of cobalt from the formate.

adsorbed and after 30 min. the whole 0.387 ml. was adsorbed. Then increment 2 of 0.369 ml. was added. After 4 min. 97 per cent of it was adsorbed. Addition of increment 3 of 0.383 ml. followed and was 97.6 per cent adsorbed after 4 min. and 100 per cent adsorbed after 30 min. Similar data are given for deuterium, e.g., increments of 0.387, 0.394, and 0.366 ml. of deuterium were taken up to extents of 53.5, 95.0, and 96.0 per cent, respectively, 4 min. after addition of gas. Because of the increase in rate with amount adsorbed, the effect was stated to be autocatalytic.

A similar effect was reported by Benton and White (36) for the adsorption of hydrogen on iron. At 0°C. at $P_s = 120.5$ mm. of mercury there was a rapid initial adsorption of 0.2 ml. of hydrogen on 54.6 g. of iron. The rate then declined almost to zero within 2 or 3 hr., remained roughly constant for a further 50 hr., then increased for a further 50 hr., and then declined. A total of 1.47 ml. was adsorbed. An Elovich treatment of the same data yields a plot convex to the log t axis up to about 60 hr. and roughly linear thereafter. At 110°C. the adsorption was much faster but gave some slight evidence of the same effect. Because there was an induction period lasting some 8 or 10 hr. during which there was relatively little further adsorption, the process was concluded to be autocatalytic.

The autocatalytic connotation is somewhat vague. Several mechanisms seem to be possible. (A) If there is some connection between coverage and the appearance of one of a sequence of given kinetic stages, such as that shown by figure 7, adsorption of the first increment may be occurring via stage I, while several succeeding increments may be adsorbed via stage II, and subsequent increments may be adsorbed via stage III. Since the stage II adsorption is faster than that of stage I, the process appears to be autocatalytic. (B) The preadsorption of one gas may increase the subsequent rate of adsorption of another gas. It is not inconceivable that preadsorption of a gas will cause an enhanced rate of adsorption of the same gas. (C) A relative or actual increase in rate during an uninterrupted experiment, such as shown by the hydrogen–iron example, may simply be due to some change in the adsorption mechanism, such as the changeover from one kind of site to another postulated for isothermal anomalies. In the case of hydrogen–iron the peculiarity in the q–t curve is roughly represented by a transition from one (presumably linear) stage to a second linear stage.

X. The Isotope Effect

The relative rates and amounts of adsorption of hydrogen and of deuterium on solids have been measured, compared, and reported during the past two decades with curiously inconsistent results. Inspection of the literature reveals that comparisons were made on the basis of rate equations of different nature, or simply

consist of statements that the velocity of adsorption of one gas is different from that of another. The data are strongly differentiated into two groups, apparently dependent on the nature of the adsorbent. The first group, dealing with experiments on metals, shows the presence of isotope effects but is afflicted with some confusion. The second group, comprising experiments on oxides, reflects identity of adsorption rates for hydrogen and deuterium. Reëvaluation showed all rates to be adequately represented by the Elovich equation, and the data for metals to be in qualitative concordance with the predictions of Wheeler (335) and of Bigeleisen (37).

Using a statistical-mechanical treatment, Wheeler predicted hydrogen and deuterium molecules to be equally adsorbed at equilibrium. For adsorption as atoms, hydrogen would be more strongly adsorbed, but at a certain temperature an inversion would occur, with deuterium being adsorbed in greater amounts at equilibrium. Bigeleisen, by a treatment based on absolute reaction rate and kinetic theories, predicted that when different isotopic atoms are chemically bound as molecules in the reactant species, the lighter molecules will have a greater rate constant than the heavy molecules, and that, if the isotopic atoms are free atoms in the initial state, the rate constant for the heavy atoms may be greater than that for the light atoms, so that the order of rate constants for reactions involving hydrogen isotopes would be $k_T > k_D > k_H$.

A. METAL ADSORBENTS

Great differences in the adsorption of hydrogen and deuterium on nickel in the range 0–100°C. were reported qualitatively (153). The amount of rapid initial adsorption of deuterium was greater than that of hydrogen. The velocity of the following slow adsorption increased for hydrogen until 55°C. and for deuterium until 70°C. Up to 55°C. the adsorption of hydrogen was faster than that of deuterium. Above these temperatures both adsorption rates decreased until 100°C., the rates becoming equal at that temperature. Above 100°C. the rates of adsorption increased, and at 200°C. deuterium was adsorbed faster than hydrogen.

Iijima (144) determined the rates of adsorption of hydrogen and deuterium on nickel at −45°C. to −122°C. and stated that "the velocity constant of adsorption of deuterium is smaller than that of hydrogen." Recalculation of his q–t data shows q–log t plots to be linear at −45°C., but at −122°C. and −78°C. to consist of two intersecting straight lines. The values of the constants a and α are given in table 4, the subscripts 1 and 2 referring to the appropriate constants of the first and second linear portions. The extent and the initial rate, reflected by the magnitude of the constant a, of the adsorption of hydrogen is greater than that of deuterium at the three temperatures; but at −78°C. the

ambient rates of adsorption, reflected by the constant a_1, hint at an inversion.

Similarly (201), at 0°C. and 25°C., more hydrogen than deuterium was adsorbed on nickel, but the rate of adsorption of hydrogen was slower than that of deuterium.

TABLE 4

Adsorption of hydrogen on nickel

Data of Iijima (144)

Gas	T	a_1	α_1	a_2	a_2
	°C.				
Hydrogen	−112	2.7	40	1.2	1.7
Deuterium	−112	3.4	19	1.6	1.2
Hydrogen	−78	1.0	24	2.9	1.3×10^5
Deuterium	−78	0.9	10	3.1	0.4×10^5
Hydrogen	−45	1.6	900	—	—
Deuterium	−45	1.8	600	—	—

Low-temperature experiments are not in accord with Wheeler's prediction. At −255° to −253°C. the physical adsorption (322) of deuterium on nickel was about 15 per cent greater than that of hydrogen. At −213° to −204°C. the difference was about 10 per cent, while at room temperature the adsorption of hydrogen was greater than that of deuterium. Similarly, isobars at pressures of 0.05 to 0.4 cm. of mercury showed higher adsorption of hydrogen than of deuterium on nickel over the temperature range 250–469°C. (323).

In comparing rates of adsorption of hydrogen and of a 70 per cent deuterium–30 per cent hydrogen mixture on copper, Melville and Rideal (256) point to two sets of data, "the first at 96° showing that, throughout, the amount of deuterium adsorbed is almost exactly equal to that of the hydrogen, and the second at 170° where the rate of sorption of the heavier isotope is somewhat smaller." Reëvaluation of those data shows that the *rate* of adsorption of deuterium is *faster* than that of hydrogen at both temperatures. However, the *extent* of hydrogen adsorption is greater than that of deuterium. For example, for the first linear portion of the data at 96°C., $\alpha_H/\alpha_D = 10.1/7.7$ and $a_H/a_D = 19.6/5.8$; or, the initial rate of hydrogen adsorption is greater than that of deuterium, while the ambient rate of adsorption of deuterium is faster than that of hydrogen.

At −78°C. hydrogen and deuterium were adsorbed on copper in equal amounts at equilibrium (26). Plots of data taken 16 min. after admission of gas, however, show more hydrogen than deuterium to be adsorbed, suggesting that the rate of deuterium adsorption at −78°C. is faster than that of hydrogen. In the region 0–100°C. the ratio [H_2/D_2 adsorbed] undergoes an inversion, more hydrogen than deuterium being adsorbed at the lower temperatures and less at the higher temperatures. The rate of adsorption of deuterium is faster than that of hydrogen at 100°C., but at 0°C. the plots

of the original data indicate a faster adsorption for hydrogen over the range 5–35 min. On the published graph the range 3–17 min. of the deuterium experiment is represented by only one point at about 8 min. That point serves to depress the q–t curve sufficiently to indicate a slower adsorption for deuterium. Rejection of that point and the use of five points over the range 17–35 min. to locate the q–t line results in a faster rate of adsorption of deuterium than of hydrogen.

Further work (286) on copper showed that more hydrogen than deuterium is adsorbed at 0°C. after about 300 min., while the opposite is found at 125°C. At 125°C. the rate of adsorption of deuterium is slightly greater than that of hydrogen; at 0°C. the rate of adsorption of hydrogen is appreciably faster than that of deuterium up to about 90 min. However, replotting the data on a q–log t plot reveals the existence of two kinetic stages. If comparison is made of comparable kinetic stages (189), then the adsorption of deuterium is found to be faster than that of hydrogen after about 90 min.

The relative rates of adsorption of hydrogen and deuterium on platinum were expressed (208) by the equation

$$\frac{dq}{dt} = nk(m - q)t^{n-1}$$

where m is the saturation capacity. The velocity of adsorption of deuterium in terms of the rate constant (nk) was termed slower than that of hydrogen. Using values of n and k (m values were not given) at −79°, 18°, and 50°C., values of (q/m) suitable for comparison were obtained over the time interval 0.1 to 10 min. The (q/m)–log $(t + t_0)$ plots thus obtained were linear. Values of relative rate constants are given in table 5, where $t_0 = 1/a\alpha$. More hydrogen than deuterium is adsorbed at all temperatures. The rates of adsorption become roughly equal or, if the difference between the

TABLE 5

Adsorption of hydrogen and deuterium on platinum

Data of Maxted and Moon (208)

Gas	T	t_0	α'	a'
	°C.			
Deuterium	−79	0.3	52	0.0064
Hydrogen	−79	0.2	43	0.0116
Deuterium	18	0.25	9.0	0.44
Hydrogen	18	0.14	8.2	0.87
Deuterium	50	0.15	8.1	0.82
Hydrogen	50	0.04	8.2	2.44

α values of 8.1 and 8.2 at 50°C. is judged significant, undergo an inversion above 18°C.

The ratio of the adsorption rates on charcoal (16) of hydrogen to that of deuterium decreased from 2.37 at 227°C. to 1.44 at 617°C. A similar decline from 1.66 at 565°C. to 1.44 at 577°C. was reported for the ratios

of the rates of adsorption of methane and methane-d_4 on charcoal.

B. OXIDE ADSORBENTS

The original experiments on the isotope effect are those of Pace and Taylor (239), using adsorbents of $ZnO \cdot Cr_2O_3$, Cr_2O_3, and nickel–kieselguhr. Identity of adsorption rates of hydrogen and of deuterium is claimed, within experimental error, at temperatures of 110°, 132°, and 184°C. The results were confirmed by Kohlschütter's experiments (158) on Cr_2O_3 between 150°C. and 210°C. The gas pressure was 760 mm. of mercury. All data can be represented by the Elovich equation.

For the hydrogen–Cr_2O_3 system (158) on averaging the data of six runs with deuterium, or of five runs with hydrogen, made under identical conditions, it is found that the q values at each time t scatter with an average deviation of about 0.1 q. For these average values, q_D exceeds q_H by about 2 per cent; but, because of the scatter of points and of declining activity of the adsorbent in successive runs, such data are not conclusive. Similar scatter is found in the data for hydrogen–nickel–kieselguhr (239). The experimental errors are of the order of magnitude of the isotope effects found with metals (see tables 4 and 5); consequently, the identity of isotopic adsorption rates on oxides based on these data does not seem well founded. The work on oxides was made at 76 cm. of mercury, whereas low pressures were used in the experiments on metals. As pointed out by Beebe, Low, Wildner, and Goldwasser (26), work at low pressures on oxides may uncover isotope effects which are masked at high pressures.

Parravano, Friedrick, and Boudart (243) provide further information by reporting the identity of rates of adsorption of hydrogen and of deuterium on zinc oxide. A sensitive differential adsorption technique was used: equal amounts of zinc oxide were placed in two identical adsorption systems. The systems were connected to opposing arms of a dibutyl phthalate-filled differential manometer. One system was filled with hydrogen, the other with deuterium, and the adsorption allowed to proceed simultaneously under identical conditions for each system. No differences of adsorption rates—manifested by meniscus variations in the manometer—were detected for adsorptions on pure zinc oxide at 75°, 200°, and 300°C. and on lithia- or gallia-doped zinc oxide at 200°C. The pressure was constant at 730 mm. of mercury.

C. THE PACE–TAYLOR HYPOTHESIS

Because the kinetic expression for collisions gives a factor of $\sqrt{2}$ when hydrogen and deuterium are involved, observed adsorption rates for the isotopes were expected to differ. The absence of the expected isotope effect with oxide adsorbents led Pace and Taylor (239) to

suggest that the activation energy of the adsorption process is required by the solid adsorbent. This interesting suggestion and the nature of the slow step in chemisorption were further discussed by Boudart and Taylor (44), who also derive an expression for adsorption rate based on the idea that the number of adsorption sites, and hence the adsorption rate, are controlled by the thermal production of sites during adsorption. The discussion as to the nature of the slow step in chemisorption is continued by Parravano, Friedrick, and Boudart (243) on the basis of their more sensitive measurements with hydrogen–deuterium–zinc oxide. The absence of an isotope effect eliminates application of the chemical bombardment-dissociation mechanisms and also of diffusion mechanisms (surface hopping or bulk diffusion) to the zinc oxide case. ". . . the only alternative left open is a slow step which does not involve hydrogen, as a molecule or as adsorbed fragments. In other words, the slow step involves the generation of an active site. Adsorption can proceed only on active sites." (243)

XI. RAPID SORPTION BY POROUS SOLIDS

Winfield (337) determined rates of gas uptake by porous solids in a constant-volume system by measuring the pressure decrease with a capacitance-type glass-diaphragm manometer. The manometer signal was shown on an oscillograph and photographed continuously for the duration of the uptake of about 0.1 sec. The systems isopropyl alcohol–$Al_2O_3 \cdot H_2O$, ethanol–thorium(IV) oxide, water–thorium(IV) oxide, water–$Al_2O_3 \cdot H_2O$, water–γ-Al_2O_3, and methylvinylcarbinol–thorium(IV) oxide were studied at various initial pressures, P_s, of 1.5–4 mm. of mercury. Over the range 110–200°C. negative temperature coefficients were found. For the ethanol–thorium(IV) oxide system at 180°C. the sorption rate was first order with respect to P_s. In other less reliable experiments the rate of water uptake by thorium(IV) oxide appeared to be proportional to $(P_s)^{1.2}$. There was no simple relation between rates and different adsorbates. For the water–thorium(IV) oxide system the rates were independent of adsorbent bed geometry: beds compact and uniform in depth, as produced by evaporation of an alcoholic suspension, gave similar effects to beds lightly packed and irregular in contour with approximately ten times as much freely available surface. For the uptake of isopropyl alcohol on $Al_2O_3 \cdot H_2O$, and of ethanol and of water on thorium(IV) oxide, the rate was proportional to the power two or higher of the mass of adsorbent (or, surface area S). For the uptake of water vapor by shallow beds of $Al_2O_3 \cdot H_2O$, the rates were proportional to S. The rates were independent of S when water was adsorbed on deep beds of γ-Al_2O_3; when the amount of adsorbent was varied between 0.1 and 0.3 g. and the packing density and bed diameter were held constant, the measured sorption rates remained identical.

Sutherland and Winfield (294) developed a diffusion equation to describe these experiments. Processes considered are (A) Knudsen flow within the bed or within the granules of which the bed is composed together with simultaneous adsorption that is too fast to be a limiting factor, (B) chemisorption controlled by the rate of Knudsen flow, and (C) unrestricted chemisorption. Comparison of experimental and theoretical rates, using data for the pore structure of the adsorbents and Henry's law constants, showed that sorption by $Al_2O_3 \cdot H_2O$ could be accounted for by Knudsen flow accompanied by rapid adsorption on pore walls. The equations could not account for the dependence of the rate on S^2, and it was suggested that poisoning of the adsorbent might be responsible. The rate–S relation is stated to be a useful criterion for determining the limiting step in sorption. The power of S on which the rate depends and the probable slow step are: 0, gas flow through the depth of the bed; <1, probable surface migration; −1, gas flow into particle composites; >1, chemisorption.

The application of the diffusion equations and the Elovich equation to Winfield's and other data was considered by Freund (102), who rearranged the integrated Elovich equation as

$$P/P_s = 1 - (RT)/\alpha P_s V \ln (t/t_0 + 1)$$

and used Sutherland and Winfield's equation in the form

$$P/P_s = e^{bt}[1 - \mathrm{erf}(bt)^{1/2}]$$

P is the pressure at time t, P_s the initial pressure, R the gas constant, V the system volume, $b = CT^{1.5}e^{E/RT}$, E is the heat of sorption, and T is the absolute temperature. C is a constant involving pore radius, average pore length, the molecular weight of the gas, and the volume of the system. The graphical procedure (298) used for determining the Elovich parameters α and t_0 was applied to the diffusion equation, using the coördinates P/P_s and $\ln bt$. Agreement within about 5 per cent for α and 40 per cent for t_0 was found with values predicted by the diffusion equation and those experimentally determined, using the Elovich equation for six gas–solid systems. Better agreement cannot be expected because of several approximations made in the derivation of the diffusion equation and of experimental difficulties. For nonporous solids the diffusion mechanism and equations obviously are irrelevant.

XII. ANISOTROPIC ADSORPTION

Relatively few data on the influence of crystal face on adsorption exist, anisotropic reactions involving almost exclusively formation of films thicker than a monolayer. Such results, however, may be analogous and useful to an understanding of chemisorption processes. For catalytic reactions, geometric and electronic effects have been postulated, described, and reviewed

(117, 124, 309). Recent studies for which anisotropic rate effects were reported include catalytic reactions (124, 160); the decomposition of formic acid (60); the oxidation of germanium (178), stainless steel (31), copper (32, 199), iron (12, 32), and silver (216); the halogenation of copper (263). However, oxidation rate anisotropy is probably complicated by surface effects such as surface recrystallization (119, 124, 127), the effects of gases on solid lattices shown by the work of Forestier (92, 93, 94, 95), and low-temperature migration of surface atoms (244). Similar effects may complicate chemisorption studies. Chemisorption on clean single crystals has been reviewed by Becker (20) and Gomer (112) and, more recently, again by Becker (21). Anisotropy effects on the adsorption of acetylene, ethylene, and ethane on tungsten were found by Becker and Brandes (23).

XIII. THE ACTION OF EXTRANEOUS ENERGY

The effects of energy applied to gas–solid systems by some technique other than heating are complicated, involved, and far from clear. The results of such applied energy may be that (A) the gas–solid system is unchanged, (B) the reaction between the gas and solid is initiated and/or caused to proceed, (C) an existing gas–solid reaction is enhanced, or (D) an existing gas–solid reaction is inhibited or reversed. Examples of such types of effect exist, but the type of system, the conditions of energizing, the probable simultaneous occurrence of several processes, and the general variation of experimental techniques make analysis of the effects difficult. Further, most instances of adsorption of activated gases appear to involve penetration of gas into the solid, incorporation of gas into the lattice, or multilayer formation. These investigations originate with the earliest observations of gas uptake in discharge tubes, and such effects of activation have been critically reviewed by Pietsch (246) and by Dushman (73) up to 1947. Pertinent later literature, some nonkinetic, is reviewed here, the material being crudely grouped according to the nature of the activation.

A. HIGH-FREQUENCY VIBRATIONS

The tarnishing rate by iodine or hydrogen sulfide of a copper rod at 21°C. is increased by coupling the rod to a piezoelectrically vibrating quartz crystal (134). The enhancement may be due to increased material transport to the reaction zone and exposure of fresh surface through cracking of the surface film caused by vibration of the solid (134). Further work (133) with the copper–iodine and copper–hydrogen sulfide systems showed the uptakes to follow the equation $q^2 = kt$. For copper–iodine, the constant k was increased from 0.29 to 0.63 by the high-frequency vibration. The film formation in the system iron–oxygen followed the Elovich equation (162), the rate being increased by vibration. Similar

results were obtained for the nitriding of iron by ammonia (202, 217) by piezoelectrically or magnetically induced vibration.

B. "ACTIVATED" GASES

Artificial graphite, as cathode, was subjected to an electrical discharge in hydrogen (11). About 0.3–0.4 ml. of gas per gram was taken up in 2 hr. On standing the gas was not desorbed. No hydrogen was taken up in the absence of discharge. This "activated" graphite showed enhanced activity as a sorbent for oxygen.

Newman (231) deposited lead, thallium, arsenic, mercury, cadmium, antimony, bismuth, magnesium, calcium, zinc, tin, phosphorus, sulfur, or iodine on the cathode of an electric discharge tube. Under conditions of discharge, nitrogen was taken up by all these elements except lead, thallium, and arsenic, and in comparatively large amounts by phosphorus, sulfur, and iodine. Hydrogen was taken up only by phosphorus, sulfur, and iodine. The uptake was attributed almost entirely to chemical action brought about by active modifications of nitrogen and hydrogen produced by the discharge.

Tyapkina and Dankov (317) oxidized a silver film deposited on the inner wall of a glass tube having an internal diameter of 16 mm., an inner axial silver wire serving as cathode. At 18°C. saturation was not reached (determined by pressure decrease). The oxidation with time followed a parabolic curve and was much faster and deeper than in the absence of an electric discharge. Dankov and Ignatov (61) subjected aluminum surfaces at 0.5–0.8 mm. of mercury to oxygen activated by a silent discharge. On massive foil, subjected to prolonged discharge at either anode or cathode, a visible film formed. Thin, translucent, blue films became more translucent and less intensely colored after 10 min. exposure at the anode.

Nazarova (230) studied the oxidation kinetics and oxide structure of copper, aluminum, iron, zinc, and magnesium as anodes and cathodes in a glow discharge in oxygen. The metals behaved differently when used as anodes than as cathodes, apparently depending on the properties of the oxides formed. Under discharge conditions intensive oxidation occurred, exceeding by tens of times that occurring in air. The kinetics of the oxidation of copper obeyed the cubic law, whereas that of the other metals obeyed the logarithmic law. With aluminum, iron, zinc, and magnesium as anodes, the oxidation ceased after about 30 min., but when the discharge current was increased 1.5- to 2-fold, the process continued. With a copper anode no cessation was observed even 9 hr. after the start of the experiment. When the metals were used as cathodes, no renovation of the oxidation process was observed on doubling the discharge current at the end of the original

oxidation. On the aluminum anode an amorphous oxide film formed, whereas crystals of Al_2O_3 formed on the aluminum cathode. Copper(I) oxide formed on the copper anode, while copper(II) oxide formed on the copper cathode. The character of the oxidation process when the metal is the cathode is almost the same for the five metals. This is explained by assuming that the factor mainly responsible for the enhancement of oxidation is the local heating of the cathode due to impact of oxygen ions on the cathode surface, this explanation being substantiated by the similarity of the structure of oxides formed on cathodes and those formed by high-temperature oxidation of the metal in air. The effect is similar to that (17) found with the growth of Al_2O_3 crystals grown in oxygen on aluminum foil inserted in a 600-e.k.v. electron beam.

Engell and Hauffe (90) found that an electrodeless discharge in their adsorption system within the tubing leading to the catalyst caused enhanced uptake of oxygen by nickel(II) oxide. The discharge was 15 cm. from the catalyst chamber. At the end of the chamber, between discharge and catalyst, was a plug of glass wool. The adsorption, which had almost ceased after 150 min., increased from 0.4 to 0.67 ml. in 30 min. on application of the discharge. The effect is explained in terms of the "Randschichttheorie" (89, 90) by assuming that the electron transfer from the nickel(II) oxide surface to an activated oxygen particle is easier than to a normal oxygen molecule.

Similar results were obtained by Low and Taylor (190). An electrodeless discharge (caused by a Tesla coil) barely visible in a darkened room increased the rates and extents of adsorption of hydrogen on palladium, hydrogen on nickel–kieselguhr, carbon monoxide on zinc oxide, and hydrogen on zinc oxide. In each case, a plug of glass wool was in the system, 20 cm. from the point of discharge and between the latter and the adsorbent. Rates of adsorption increased markedly on starting the discharge and reverted to roughly the same values when the discharge ceased. The effect occurred on saturated and unsaturated surfaces. Figure 23 shows the effect on 18.76 g. of zinc oxide. The effect is interpreted in terms of a site-creation process (185, 186, 297, 298). It was suggested that creation of adsorption sites can occur on the adsorbent surface by a branching chain mechanism initiated by the reaction of an active particle, G, with a surface atom, S, causing a "dissociation" of the atom into two adsorption sites, V. The overall reaction for the branched chain is written $G + nS \rightarrow GV + (2n - 1)V$. The remaining $(2n - 1)$ sites can be active for adsorption or, alternately, suffer bimolecular recombination and decay. During the discharge a new site-creation process is induced and sites are produced to an extent which is enormous in comparison with the number of excited particles able to reach the surface. Chemisorption of

normal molecules then proceeds on the newly created sites, resulting in an enhanced rate of adsorption.

In certain cases the effects of the discharge have been found to persist after the discharge had been shut off. Thus, there is an indication in the q-t curve of oxygen on nickel(II) oxide of Engell and Hauffe that the en-
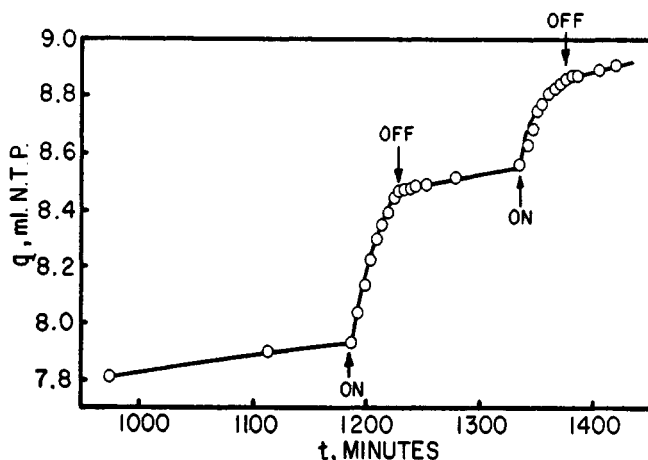

Fig. 23. Adsorption of hydrogen on zinc oxide (data of Low and Taylor (190)).

hanced adsorption persists for about 2 min. after cessation of the discharge. Other similar effects are reported (186, 190), and such an effect is illustrated by figure 24, which shows the effects of a radiofrequency-induced discharge on the adsorption of oxygen on nickel(II) oxide film measured by Gray and Darby (115) by a conductance method. The rate of change of the conductance λ, the latter being otherwise a measure of the amount adsorbed, was greatly influenced by activation of the gas. The normal increase in conductivity with time was suddenly accelerated when a discharge was applied, as shown in figure 24. No reading of λ could be taken while the discharge was on, but λ was measured and began to fall after the discharge was stopped. Gray and Darby suggested that the effects may be due to oxygen atoms being built into the lattice. The effect was shown due predominantly to atoms by removing ions using an electric field and magnetic deflection. Similarly, the uptake of oxygen by silica gel and quartz powder under irradiation of light of 2500 A. continued for several minutes after the illumination was stopped (287).

The oxidation of copper in activated oxygen has been studied by Dravnieks (71) in the pressure range 0.5–2.0 mm. of mercury and at temperatures ranging from 500° to 690°C. Enhancements of oxygen uptake were found to occur at 0.5, 1.0, and 2.0 mm. of mercury at 500°C. and at 0.5 mm. at 600° and 690°C. At higher pressures at the last two temperatures, however, the enhancement disappeared, and at 2.0 mm. and 600°C. a retardation in oxygen uptake was found. At 500°C. the oxidation curves, plotted according to the parabolic rate law,

appeared as two straight lines with an intermediate region of rapidly changing slope. The first parabolic rate was identified with oxidation to copper(I) oxide, the region of rapidly changing slope with beginning of precipitation of copper(II) oxide on the surface of the copper(I) oxide, and the second parabolic region with oxidation occurring in the presence of both oxides. At higher temperatures the oxidation curves could not be resolved into two distinct parabolas. The observations that activation may accelerate or retard the oxidation and may change the composition of the oxide scale were explained in terms of lower permeability of copper-(II) oxide than copper(I) oxide to reactants, and of rate of precipitation of copper(II) oxide. No effect was found with tantalum and nickel. With molybdenum at 690°C. a retardation of oxidation was indicated. The action of various hot ionized gases on zirconium and copper resulted in retardations or enhancements (72). Low (186) found that a Tesla coil discharge caused enhancement of rates of oxygen adsorption on clean bulk copper, molybdenum, magnesium, and aluminum and on degassed iron which had been previously exposed to oxygen. Similarly, nitrogen may be made to adsorb on a silica-supported nickel catalyst by passing a discharge through the gas (120), and apparently nitrogen atoms enter face-centered cubic nickel on bombardment with ions (315).

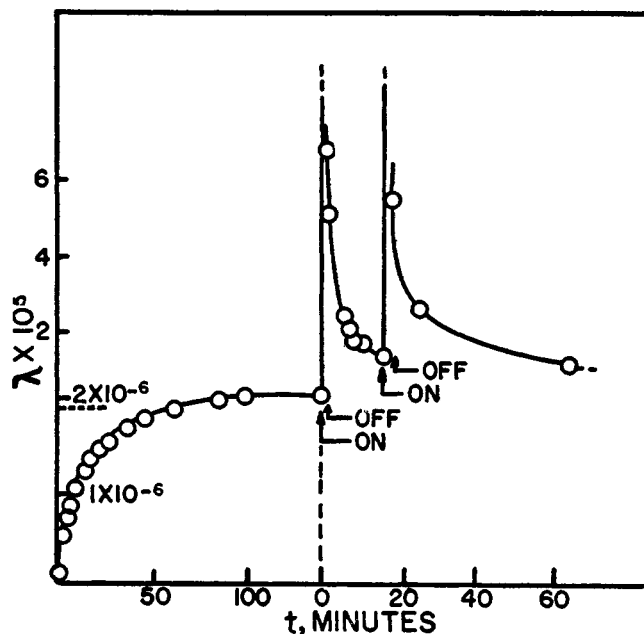Fig. 24. Adsorption of oxygen on nickel(II) oxide (data of Gray and Darby (115)).

Retardations were also observed. Figure 25 shows the effect (186) of a discharge on the adsorption of oxygen on copper. On starting the discharge ("On") the pressure in the system rose until the discharge was stopped ("Off"). The adsorption on copper occurred under conditions favoring (318) the formation of a film of

copper(II) oxide on the copper surface, and the evolution of gas during activation was suggested to be due to the enhanced transition, $2CuO \rightarrow Cu_2O + 1/2O_2$. In Dravnieks' study, retardations occurred with films predominantly copper(II) oxide, and accelerations on films predominantly copper(I) oxide, and were consequently explained in terms of such enhanced transitions. A decrease in the rate of adsorption of oxygen on clean iron was explained (186) by means of an enhanced transition of a surface film (96) of γ-Fe_2O_3 to cubic Fe_3O_4 with attendant release of oxygen. Because the observed effects were large in comparison to the magnitude of the stimulus, it was postulated that a chain disturbance was initiated on the surface, causing unstable copper(II) oxide, or Fe_2O_3, to give up oxygen. The observations of Dravnieks and of Low are thus consistent, at least for copper. In general, it appears that the effect of activating the gas may be twofold: (A) If more than one oxide can exist and a change in
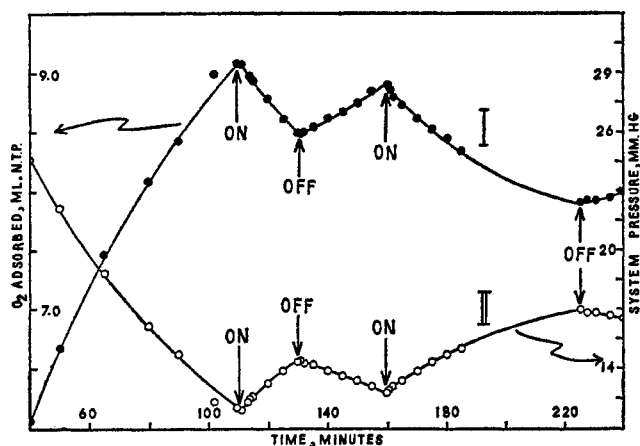

FIG. 25. Adsorption of oxygen on copper (data of Low (186)).

oxidation state can occur, that change may be enhanced by the activation. The effect appears as an actual gas evolution—as in Low's results on copper—or as a retardation of gas uptake—as in Dravnieks' results or in Low's data on iron. (B) If no change in oxidation state is possible, or if such a change has already occurred, then an enhancement of oxygen adsorption is possible.

During measurements of the atom concentration in activated oxygen with a platinum resistance thermometer, Fryburg (103) observed enhanced oxidation of platinum. The equation,

$$w = (k_1 + k_2 n_0)t$$

expresses the reaction at 1000°C. and 0.5 mm. of mercury; w is the weight of platinum oxidized per square centimeter, n_0 is the number of oxygen atoms striking unit area per second, and k_1 and k_2 are constants. The oxygen atoms were approximately 400

times more effective than oxygen molecules in causing oxidation of platinum.

Concentrations of hydrogen dissolved in nickel under hydrogen-ion bombardment were measured (226) using a nickel diffusion tube as cathode in a glow discharge. No increase above the normal diffusion rate was observed when clean nickel was bombarded. Increases of several orders of magnitude were obtained near 200°C. when the nickel was coated with nickel(II) oxide or barium oxide. It was suggested that energetic ions easily penetrate the outer surface of these materials and are then trapped in the interior by surface barriers.

Lander (171) bombarded zinc oxide single crystals with H_1^+, H_2^+, or H_3^+ produced by a mass spectrometer and determined steady-state concentrations of hydrogen atoms in the zinc oxide as function of temperature, ion current, and ion energy by measurement of conductivity. The bombardment-induced concentrations were extremely high relative to the solubility of normal hydrogen, e.g., higher by five orders of magnitude at 200°C. The ratios of saturation conductivities produced by H_1^+, H_2^+, and H_3^+ were 0.52:1.00:1.42, or nearly 1:2:3. The bombardment-induced conductivity is, to a good approximation, independent of the ion used if current is expressed as atom current. At relatively high currents some "surface damage" was produced, manifested as abrupt changes in the slope of conductivity-bombarding voltage plots. Bombardment in the presence of oxygen, or heating the crystals in low pressures of oxygen instead of in vacuo before bombardment, reduced the conductivity. A hot tungsten filament operating in hydrogen increased the conductivity slightly, the effect being believed to be due to atomic hydrogen. The behavior of zinc oxide under bombardment is ascribed to (1) ions of sufficient velocity to penetrate efficiently the surface barrier to normal reaction and (2) the fact that the barrier to escape of hydrogen atoms through the surface is high and is partly chemical and partly electrical in nature.

Leck (179) bombarded nickel, tungsten, aluminum, and molybdenum with positive ions of helium, neon, argon, krypton, hydrogen, nitrogen, oxygen, and carbon dioxide of energies up to 5 k.e.v. and measured the gas uptake. On subsequent heating, gas was evolved from the target at 973–1173°C. In similar experiments Bills (38) observed that relatively large positive-ion currents can be thermally desorbed from tungsten, tantalum, and molybdenum surfaces even several days after bombardment with low-energy nitrogen ions or with electrons. Emission–time and emission–temperature curves similar to thermoluminescence curves were obtained, suggesting that ions or possibly excited neutral particles are captured in traps of several different depths on the metal surface and that, as the surface temperature is increased, the traps of least depth are emptied first.

Law (177) noted an increased gas uptake during the

adsorption of hydrogen on silicon in the presence of an operating ion gauge. The increased uptake is ascribed to adsorption of atomic hydrogen produced by the gauge.

Young (340) observed the electrical clean-up of different gases in a Bayard–Alpert ionization gauge and found that the ion current striking the gauge wall was five to ten times that reaching the ion collector. An equation was derived for pressure, p, as function of time, t, during which adsorption has been taking place. By assuming that there are a certain number of sites, N, on the surface where an ion can stick and that there is a probability, F, of sticking at an unfilled site, and neglecting desorption at low coverage,

$$p = \frac{p_0 b}{e^{bt}(b + cp_0) - cp_0}$$

where p_0 is the pressure at $t = 0$ and the constants b and c involved N, F, the pumping speed, and the volume of the system. The equation agrees well with the data for low coverages. Young did not consider the possibility of reflection of activated particles at the surface or of their reflection combined with deactivations. Bills and Carleton (39) show that these are important effects and cannot be neglected in a complete theory. From the latter the equation for pumping rate S,

$$S = S_0/(1 + \eta q)/(q_m - q)$$

is derived, where S_0 is the rate at q equal to zero, q_m is the maximum amount of gas adsorbed, and η is a constant. The expression fits data on the adsorption of activated nitrogen and oxygen obtained by experiments with a Bayard–Alpert gauge in which constant pressure is maintained by admitting gas to it from a reservoir through a controlled leak while the adsorption is occurring. Good agreement between theory and experiment was obtained over a range of q sufficient to saturate the surface almost completely.

Blodgett (40) extended Langmuir's early work (173) on the clean-up of atomic hydrogen. When hydrogen is dissociated by an incandescent tungsten filament in a glass tube, some of it is cleaned up if the tube is cooled in liquid air. That amount is greatly increased by coating the inner tube wall with mercury or copper. In one experiment the amount taken up was equivalent to fourteen monolayers of atomic hydrogen. The clean-up proceeded at a diminished rate until the pressure fell to the value at which hydrogen left the mercury as fast as it entered. All cleaned-up gas was recovered when the tube was warmed to room temperature. After clean-up with copper there was little recovery until the temperature was above −83°C.

c. "LIGHT"

Extending theories of Mott (227), Cabrera (53) suggested that light of frequency ν should increase the rate of growth of oxide layers on metals when $h\nu >$ work function. Such an effect was found by Cabrera, Terrien, and Hamon (54), who caused an increase in the thickness of an oxide film formed on aluminum after 5 days from about 20 A. to 40 A. by irradiation with a mercury arc, such that $h\nu \sim 4$ e.v. Cabrera (53) extended Mott's theories (227, 228, 229) to this effect, obtaining agreement with experimental results, and suggested that the influence of light will be observable only for frequencies such that $h\nu > 2$ e.v.

Vol'kenshtein and Kogan (326) discuss the action of light on semiconductors and give criteria for the occurrence of photoadsorption and photodesorption in terms of the number of valences at the adsorbent surface.

Hydrogen activated (200) by mercury resonance radiation is taken up by thorium(IV) oxide at ordinary temperature. There is an initial pressure of a few millimeters of mercury above which there is no photoactivation.

Kennedy, Ritchie, and Mackenzie (151) found an irreversible uptake of oxygen when films of titanium-(IV) oxide powders were illuminated at 25°C. with light of ∼3650 A. The amount and rate of uptake were dependent on sample structure, preparation, and pretreatment. The rate of uptake was dependent on pressure and was proportional to light intensity. Parabolic as well as exponential rates were observed. For varying wavelengths, relative rates per unit light intensity were approximately in the ratio 12:5:1 for 3650, 4050, 4360 A. light. At temperatures of 5.9°, 23.5°, and 41°C. relative rates for otherwise similar conditions were 0.59, 1.00, 1.70, respectively, yielding a temperature coefficient of 5.4 kcal./mole. With nitric oxide a small pressure decline was observed in the dark, and on illumination a rapid pressure decrease occurred at a rate comparable to oxygen uptake. The reaction was generally similar to that of oxygen. Preliminary or intermediate phototreatment of titanium(IV) oxide in nitric oxide caused a decrease in the subsequent rate of oxygen uptake, and preliminary or intermediate phototreatment in oxygen caused a decrease in the subsequent rate of nitric oxide photoreaction. A mechanism of initial reversible chemisorption, followed by migration and irreversible adsorption induced by the action of light, is proposed. Silica gel and a quartz powder (287) took up oxygen when irradiated with light of 2500 A. or shorter wavelength. The uptake continued for several minutes after the illumination stopped and was eliminated by water or acetone vapor. No photosorption of hydrogen, nitrogen, or carbon monoxide occurred. A photostimulated, temperature-dependent, reversible sorption of oxygen on cadmium sulfide crystals is described by Bube (48). Similarly (156), a photoenhanced adsorption of oxygen on zinc sulfide is reported. Fujita and Kwan (106) illuminated oxidized and degassed zinc oxide with light of wavelengths near the fundamental adsorption of the

solid. Photodesorption occurred with the degassed sample in a reversible manner, whereas an irreversible photoadsorption was found with the oxidized sample, suggesting the presence of weakly chemisorbed oxygen molecules having a kind of electronic interaction with the zinc oxide surface, and that photodesorption or photoadsorption may occur by combination of an intermediate such as O_2^- with positive poles or electrons created by illumination. Pratt and Kolm (249) found that long-time changes in work functions of gold, germanium, and selenium are induced by electrostatic fields or by illumination. Light-induced adsorptions and work-function effects are discussed. It is suggested that chemisorbed gas on the surface acts as a semipermanent trap and that slow changes in this trap occupation are responsible for long-time processes. Photoconductance and photodesorption effects on zinc oxide, intimately related to photoadsorption, are discussed in several articles (2, 57, 135, 212, 215, 224, 240, 249).

XIV. The Effect of Electric and Magnetic Fields

Van Dingenen (321) subjected nickel powder to magnetic fields of 20,000 gauss or to electric fields of 10,000 v./cm. during the adsorption of hydrogen at 20°C. In the constant-volume system the pressure fell from about 1.423×10^{-3} mm. of mercury at 12 min. to about 1.412×10^{-3} mm. at 60 min. No change in adsorption rate due to the applied fields was detected in pressure-time curves. Isobars over the region 325–375°C., passing the region of the nickel Curie point, similarly showed no effect. Blüh (42) reported that the adsorption of carbon dioxide and sulfur dioxide on aluminum is induced by fields of 30 kv./cm. It is possible that much more intense local fields produced through surface irregularities caused activation of the gas.

XV. Carbon Adsorbents

Adsorption on carbons merits individual attention, if only because of the disparity between the vast volume of published work (65, 66, 129) and the actual knowledge of the properties of carbon adsorbents. Few data on chemisorption kinetics are extant, and their meaning is obscured by lack of knowledge (338) of the physical and chemical properties of the adsorbent and by the frequent occurrence of surface interactions other than simple chemisorption. Some recent work indicates that charcoals contain significant amounts of hydrogen, that the surface is acid (126, 251), and that it contains free radicals (8, 67, 147) and surface complexes (5, 6, 251, 252, 285, 334). An electron resonance study (147) suggests the existence of two types of oxygen interactions with the surface. The structure and properties of coals are similarly unknown (7), and there is some indication that with some uptakes of organic vapors under conditions of physical adsorption there are irreversible

changes in the adsorbent structure (104). Some recent literature on sorption by coals is reviewed elsewhere (105, 245). Oxidation phenomena are not pertinent.

Lendle (181) expressed oxygen adsorption on sugar charcoal in the range 0–350°C. by the empirical formula:

$$q = k_1 - k_1 \exp(-k_2 t)$$

Data are given in a small graph, and a table gives q values at times of 10, 30, 50, 70, and 90 min. The nature of the q–t curves (the latter being given as continuous curves without experimental points) reflects a rapid adsorption in the first 10–20 min., followed by a relatively slow uptake for the remainder of the experiment. Elovich plots of the meager data, as well as the shapes of the q–t plots, suggest the presence of two kinetic stages, II and III. However, the data are too sparse to permit precise curve fitting and can be used only qualitatively.

Kingman (154) measured the kinetics of hydrogen adsorption on a Norit G.R. charcoal, degassing at 950°C. between runs. The rate at 420–530°C. was proportional to the pressure P and to the extent of available surface, i.e.,

$$-dP/dt = k_1 P(C - q)$$

where k_1 and C are constants. Some change in k_1 was noted and attributed to a change in the surface due to the high-temperature degassing. Kingman noted that in the first few minutes the rate was always greater than that calculated and suggested the presence of a few very active carbon atoms with which reaction occurs with great rapidity. Elovich plots of the data of the two sample runs given show no such deviation in the early stages of the reaction; e.g., in one case the ΔP–log t plot was linear from 0.1 to 2 hr. and curved sharply towards the t-axis over the next 4 hr., thus showing the general characteristics of a reaction which was describable by the Elovich equation over about 90 per cent of its course and which then decelerated markedly as an end-point was approached. These characteristics are those which may be predicted from the experimental method, which was to introduce a volume of gas much smaller than that required to saturate the surface.

Barrer (13) studied the interaction of hydrogen with charcoal over a large temperature range. The kinetics were expressed by

$$-dP/dt = K(P - P_e)$$

where P_e is the pressure "at equilibrium." No q–t data were given. The temperature dependence of the kinetics was complex, shown by the plots of the rate constant K versus T (°C.) of figure 26. Between 300° and 600°C. K is exponentially dependent on T, while above 600°C. there is proportionality with $T^{1/2}$. Such latter dependence is characteristic of diffusion and was taken to indi-

cate penetration of gas into the interior of the adsorbent. The kinetics of chemisorption of methane and methane-d_4 were expressed by the same rate equation as for hydrogen (16).

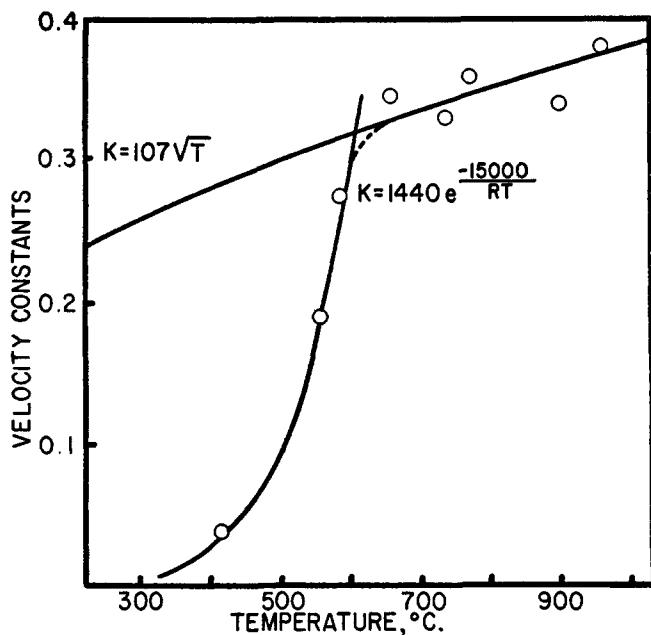Barrer (14) found a small but strong chemisorption of hydrogen on diamond. That adsorption, and that of

FIG. 26. Adsorption of hydrogen on charcoal (data of Barrer (13)). In the equations T is in °A.

hydrogen on graphite, were characterized by an initially rapid adsorption rate which was followed by a steady decrease in speed. When log $(P - P_e)$ was plotted as a function of t, the graphs showed curvature, and for not too great degrees of surface coverage, θ, the equation

$$d \log (P - P_e)/dt = k(1 - \theta) \exp(-E/RT)$$

could be used. No q-t values were given. Plots of the apparent activation energy E versus θ for graphite, two charcoals, and diamond reflect a difference in behavior of the adsorbents. The diamond curve is concave to the q-axis, not convex as for the other carbons, and it does not commence with a small E value at small q as do the plots for the other carbons. Barrer attributed these differences to variations in the carbon-carbon distances of the adsorbents.

For the adsorption of oxygen on diamond, there were four effects (15). (A) At −78°C. predominantly physical adsorption occurred. There was a slight chemisorption. (B) From 0° to 199°C. physical adsorption was slight in comparison with chemisorption. On successive additions of oxygen, adsorption proceeded more and more slowly. The residual gas atmosphere was pure oxygen. (C) From 244° to 370°C. a burst of carbon dioxide occurred at each admission of oxygen until, when all the oxygen was consumed, nearly pure carbon dioxide remained. The amount of the carbon dioxide was very

much smaller than the amount of oxygen originally taken up. (D) At higher temperatures the oxide surface film itself decomposed, the supernatant gas consisting of carbon monoxide and carbon dioxide. The rate of sorption was given as

$$-dP/dt = k(1 - \theta)P$$

but was of limited applicability because k was a function of coverage. No q-t data were given. Some idea of the peculiarity of the kinetics is shown by the d log P/dt-q plots of figure 27. The reversal of the direction curvature of the plots with increasing temperature is strongly reminiscent of an analogous change in adsorption for q-log t plots showing different adsorption stages, i.e., a change from plots consisting of stages II and III to those of stages I and II.

An analysis of kinetic data of the adsorption of oxygen, hydrogen, and carbon monoxide on charcoal was made by Keyer and Roginsky (152), who constructed the curves of figure 28 from the oxygen–carbon data of Rhead and Wheeler (254, 255). Four kinetic expressions are compared, the linear log q-log t plot being preferred, this bilogarithmic law being related to the statistical theory of a nonhomogeneous surface having an exponential distribution of site energies. Plots of log q versus log t for the three runs of Rhead and Wheeler are roughly linear, but there is considerable scatter of points, as there is also for Elovich plots of the same data. Those plots, however, indicate a discontinuity at

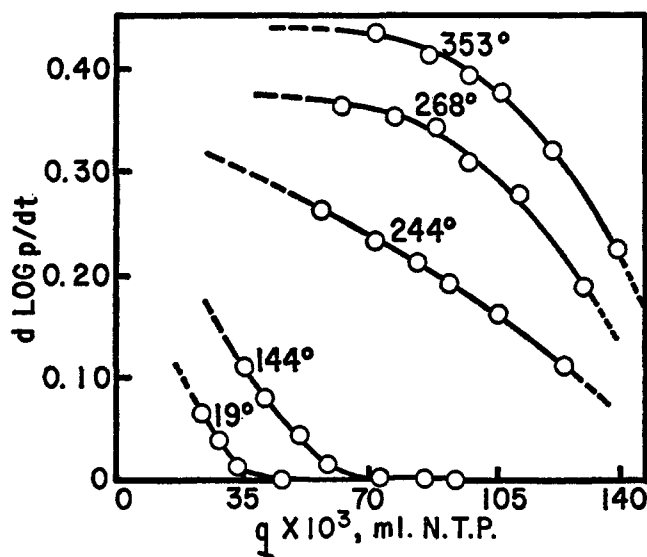FIG. 27. Sorption of oxygen by diamond (data of Barrer (15)).

about 8 min. If the line for curve 2 of figure 28 is redrawn, such a break appears. The q-log t plots of Keyer and Roginsky's data on the adsorption of oxygen on charcoals containing potassium carbonate or copper(II) acetate, given in a small graph, are S-shaped and show some scatter of points. The authors preferred log q-log t

plots, which are linear but also show scatter. The data are inadequate for precise curve fitting. Again, the Elovich plots have the characteristics of plots showing more than one kinetic stage. For Burstein's data on the adsorption of hydrogen on platinized charcoal (50), Keyer and Roginsky similarly prefer linear log q–log t plots to slightly curved q–log t plots. Again, there is considerable scatter of data. The q–log t plots could be discontinuous or could be linearized by replotting as log $(t + k)$, but the number of points is not abundant. Similar remarks apply to the treatment of Burstein's data for the adsorption of carbon monoxide on charcoal.
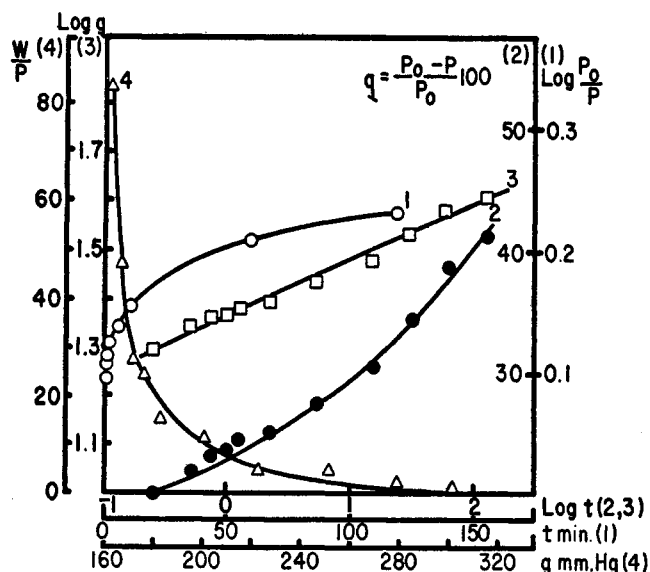

FIG. 28. Adsorption of oxygen on charcoal (data of Rhead and Wheeler (254, 255) plotted according to different equations). $T = 300°C.; P_0 = 734$ mm. of mercury.

Curve 1: $\ln \dfrac{P_0}{P_0 - q} = kt$

Curve 2: $q = A \ln (t + t_0)$

Curve 3: $q = A_1 t^{1/n}$

Curve 4: $dq/dt = k(P_0 - q)(S_0 - q)$, q being expressed in per cent of initial amount of gas S_0.

In résumé, several kinetic expressions have been more or less satisfactorily applied to gas–carbon kinetic data. Careful scrutiny suggests, however, that any claim for acceptance of a particular equation is definitely unwarranted. The state of knowledge of adsorption kinetics on carbons can be summarized as follows: (A) There are very few rate experiments. (B) For those few experiments, not enough detailed q–t data exist. (C) Experimental precision is poor. There is too much scatter and too few points to permit precise curve fitting. (D) For the adsorption of oxygen, at least, there is evidence for more than one gas–solid interaction. Probably all adsorption measurements should be accompanied by analysis of supernatant gas. (E) There are

some crude and qualitative indications that more than one kinetic process is involved. (F) The lack of adequate data suggests that not only are adsorptions on carbon surfaces complex, but that their kinetics are unknown.

XVI. THE ACTIVATION ENERGY

The effects of temperature on homogeneous and heterogeneous reactions are generally described in terms of the Arrhenius equation

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

where k is the specific rate constant, R the gas constant, and E the energy of activation. For homogeneous reactions E is taken as the energy with which molecules must be supplied, by collision or otherwise, before they can react. In general, E is related to the magnitude of the energy barrier which must be surmounted by the reactants. A similar significance is frequently assigned to E for the case of chemisorption, E being taken as a measure of the excess energy required by the gas to permit the formation of a chemical bond between gas and surface. The integrated Arrhenius equation

$$\ln k = -\frac{E}{RT} + \text{constant}$$

is used and, by graphical procedures or suitable algebraic manipulation, a value of E results from kinetic data obtained at two or more temperatures. However, in view of certain as yet unresolved complexities, the significance of E for adsorption cannot be analogous to that for homogeneous reactions.

Taylor and Liang (301) have considered the meaning of measured activation energies in the light of their temperature variation experiments (see Section VI,B). Surface heterogeneity is postulated, so that at temperature T_1 a rate measured would refer to adsorption on a part of the surface A, while at temperature T_2 a rate would reflect gas uptake by another part B. They say:

The two velocities thus found have, in reality, *no relation one to another*. They should not be used to determine activation energies in the manner first employed by using the equation log $(v_2/v_1) = (E/R)(1/T_1 - 1/T_2)$ where v_2/v_1 is the ratio of the velocities at the two temperatures or alternately is the inverse ratio of the times required for the adsorption of a given volume. Because the processes at each temperature are occurring on different areas, they have no connection one with another. They cannot be employed to determine an activation energy characteristic of a process. Insofar as activation energy is concerned they are two entirely different processes as different as they would be if A and B had entirely different chemical composition. The activation energy can only be properly derived in those cases where the given volume of gas is adsorbed *on the same area* at the two temperatures.

The above quotation referred, at the time, specifically to the hydrogen–zinc oxide system. However, the Taylor–Liang type of heterogeneity was shown to exist

in other systems, so that these comments are now more widely applicable.

Taylor and Liang (301) also considered activation energies obtained by comparing the times, t, for adsorption of stated volumes of hydrogen by zinc oxide at 0°, 111°, 154°, and 184°C. Reference to the double-humped adsorption isobar of hydrogen–zinc oxide shows these temperatures to lie in different regions of the isobar. The "fantastically irregular" (301) E values obtained upon substitution of appropriate t values in the usual equation

$$\log (t_1/t_2) = (E/RT_1T_2)(T_2 - T_1)$$

are subject to remarks similar to those quoted above.

The situation is sometimes further complicated by the appearance of multiple kinetic stages. For the hydrogen–zinc oxide system, at least two successive kinetic stages were detected (187) and different effects of temperature were found for each stage. This is shown by figure 29. The value of (α_1/α_2), the ratio of rates of the second to the first kinetic stage, is seen to undergo undulatory changes with temperature like those of the isobar. Further, the time of appearance of multiple kinetic stages detected during the adsorption of hydrogen on palladium and on rhodium is temperature-sensitive (189). It is thus conceivable that with such systems q or t values may be chosen from rate curves at different temperatures, in such fashion that these values actually relate to different kinetic stages. Further, there
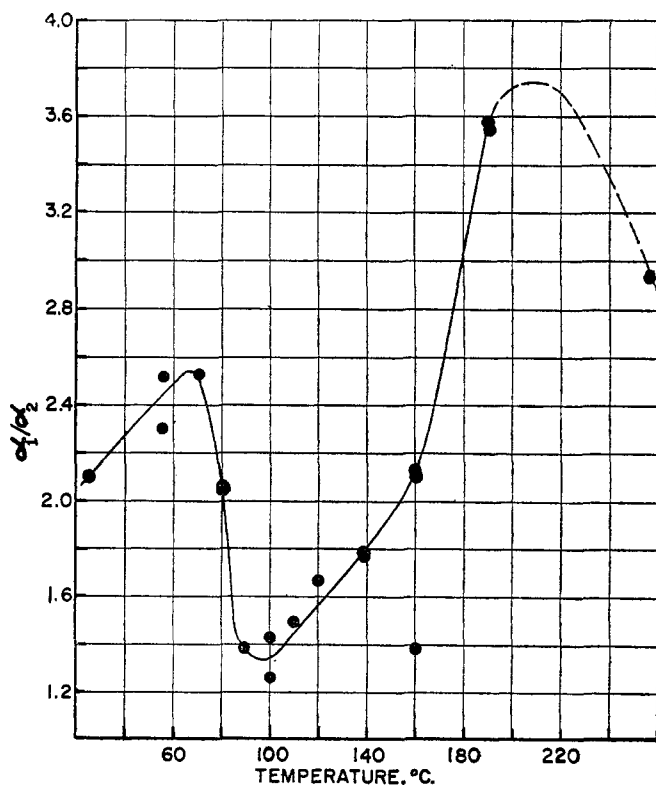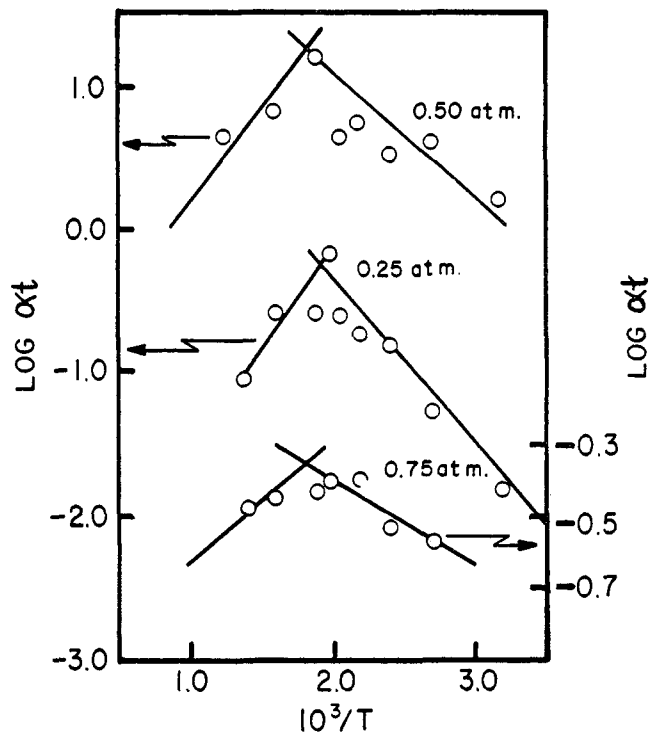
Fig. 30. Adsorption of oxygen on glass (data of Shereshefsky and Russell (282)).

seems to be a general inversion of temperature coefficients of rate parameters at regions of minima or maxima in adsorption isobars. Such an inversion is illustrated by the work of Shereshefsky and Russell (232), who found rates of chemisorption of oxygen on glass to be Elovichian and calculated Arrhenian activation energies, as follows: The slope of the q–log t plot is $2.3/\alpha$, permitting calculation of the rate r at time t; $r = dq/dt = 2.3/\alpha t$. The r thus determined is combined with the Arrhenius equation, so that

$$2.3/\alpha t = Ae^{-E/RT}$$

Figure 30 shows plots of log αt vs. $1/T$. Straight lines of slopes $E/2.3R$ are obtained, which permit evaluation of E. The data show that r increases with increasing temperature up to about 155°C., after which r declines. The authors note this fact and comment further that for a given pressure and surface coverage there are two values of E, one for the temperature range 0° to 155°C. and one for 155° to 300°C. They further note that in each temperature range E progressively increases with increasing degree of surface coverage, and that the E "in the higher temperature range is greater than in the lower." Values of E of the order of 5 kcal./mole and 9 kcal./mole are given for the low- and high-temperature regions. However, even cursory inspection of figure 30 shows that the values of E for the high-temperature region are *negative* instead of positive. Further, E becomes progressively more negative with increasing coverage. Also, Shereshefsky and Russell explain that the

Fig. 29. Adsorption of hydrogen on zinc oxide (data of Low (187)).

maximum in r at about 155°C. is indicative of two distinct adsorption processes, one increasing and the other decreasing with temperature. If such dual mechanism is suggested and accepted, then E—be it positive or negative—is without mechanistic significance. Under all such conditions of complication the ratio q_2/q_1 or t_1/t_2 or the use of r must lead to absurd results.
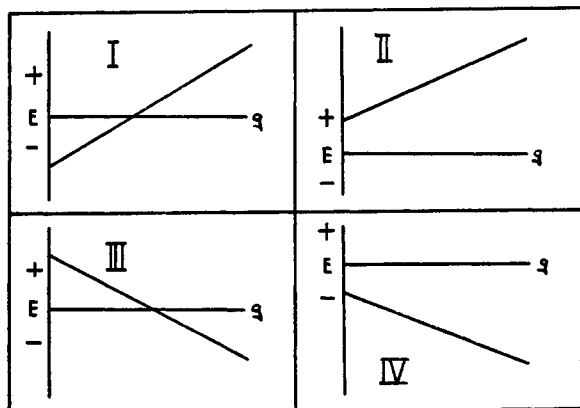

FIG. 31. Change in E with coverage.

Leibowitz, Low, and Taylor (180) calculated E using the Arrhenius equation in the form

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

where v is the velocity of adsorption at comparable stages of adsorption at various temperatures. The necessity of this form stems from the impossibility, as yet, of calculating a specific rate constant of adsorption. In accord with frequent usage, it has been assumed that comparable stages of adsorption are achieved by using for the velocities the times required for activated adsorption of equal volumes of gas. This is tantamount to writing

$$d \ln t/dT = -E/RT^2$$

Using the empirical temperature dependencies of α and $\ln a\alpha$, $\alpha = U + V/T$, and $\log a\alpha = X + Y/T$, it is easily shown that

$$E = RVq \left(\frac{e^{\alpha q}}{e^{\alpha q} - 1}\right) - RY$$

indicating that E must increase as q increases. If $e^{\alpha q} >> 1$, the expression reduces to $E = R (Vq - Y)$, indicating linear change in E with coverage. Since the parameters a and α may increase or decrease with temperature, four general cases of variation of E with coverage exist, shown in figure 31.

Case I with V and Y both positive was found for the hydrogen–nickel–kieselguhr (180) system, where E is given by $4.14q - 83.8$ kcal., q being in milliliters. The interesting feature is that E has a negative value for q values less than about 20 ml., which q value is larger

than any detected in that study. If the Arrhenius equation is used in the form:

$$d \ln (dq/dt)/dT = E/RT^2$$

it is easily shown that the E value is increased by an additional term whose value is only about 2 kcal. and therefore negligible with respect to the negativity of E.

Case III, with V and Y both negative, was found with hydrogen–ruthenium (193). An alternate treatment for E is possible. From the previous relation for E it is obvious that $(-YR)$ is a measure of E at $q = 0$. It is essentially an extrapolated value for E at the beginning of the slow adsorption. Such $E_{q=0}$ values are plotted as a function of initial pressure, P_s, in figure 32, where are also plotted values of J derived by expressing the temperature dependence of initial rates, a, by the relation $\ln a = I + J/T$. If the initial rate of the slow adsorption, a, is Arrhenian, its energy of activation, E_a, should be given by $E_a = -JR$. The similarity of the plots of figure 32, showing the change in slope at the same pressure, with apparent independence of the pressure above the break, becomes quantitative in the high-pressure range. From figure 31 the high-pressure value of $E_{q=0}$ is 17.7 kcal./mole. From figure 32 the high-pressure value of J is -8800, yielding $E_a = 17.6$ kcal./mole. The agreement of these values of E is, of course, necessary, and only indicates consistency in the alternative treatments. The independence of initial pressure on the part of $E_{q=0}$ above 25 cm. of dibutyl
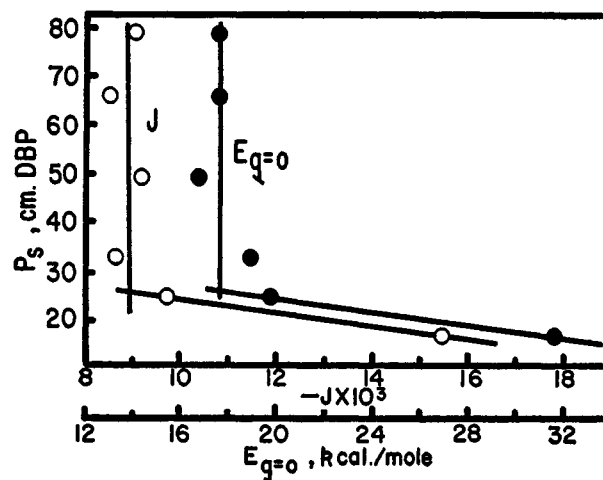
FIG. 32. Adsorption of hydrogen on ruthenium (data of Low and Taylor (193)). A: pressure dependence of $E_{q=0}$. B: pressure dependence of J.

phthalate contrasts with the marked dependence below 25 cm. This is in itself indicative that two different adsorption processes are involved.

Case IV, with V negative and Y positive, was found with hydrogen–iridium (194). From V and Y values it is found that at $P_s = 60$ cm. of dibutyl phthalate, $E = -12.36q - 2.97$, and that, at $P_s = 40$ cm. of

dibutyl phthalate, $E = 22.88q - 3.48$. Over the whole range of adsorption values of q, E is negative.

Case II is approximated by the data of Burwell and Taylor (51) for the adsorption of hydrogen on Cr_2O_3. Taking their data for 0.5 atm. it is found that $\alpha = (23700/T) - 45.5$, and $\log a\alpha = (1000/T) - 6$, whence $E = 47q - 2$ kcal. Although V and Y are both positive, the low value of Y leaves E positive except for very small values of q.

From the classical point of view it might be suggested that negative values of E, such as in Case I, result from a more rapid increase in desorption than increase in adsorption with increasing temperature. For such a case this cannot be true, since the negativity of E decreases as q increases while desorption, if it occurs spontaneously and appreciably at all, should increase and thus become more important as q increases.

Since a negative E value is without physical significance, and since sometimes absurd or fantastically irregular E values are obtained, it must be concluded that *the criteria chosen to determine E do not correspond to comparable stages in the adsorption process*. It seems improper to substitute v_2/v_1 or t_1/t_2 ratios for the specific rate constant k. Further, since k is proportional to the product of the concentrations of the chemical species involved in the adsorption, it is certainly incorrect to use a measured rate dq/dt in place of k. Such substitution completely disregards the state of one of the reactants—the surface. For an analogous case, were such substitution to be made for a homogeneous reaction where the rate is continually changing, then a continually changing E would be obtained.

The Taylor–Liang comments have been given. To those must be added those of Leibowitz, Low, and Taylor (180).

> The Elovich equation shows adsorption to be a decelerating process, to an extent dependent on the value of α, which is itself temperature dependent. To apply the Arrhenius equation to rates at a constant amount adsorbed disregards whatever is responsible for the parameter α. In the Taylor–Thon view the deceleration is the result of spontaneous site decay. Hence, for the adsorption of a constant amount of gas, a different proportion of the surface sites has decayed at different temperatures. The density of the remaining sites, one of the reactants, is different at different temperatures even though the amounts adsorbed are the same. The stages of reaction are thus not comparable.

Again the conventional choice of equal volumes of gas adsorbed at various temperatures, or of the slopes of volume–time plots for a constant amount adsorbed at various temperatures, is rejected. Unlike the Taylor–Liang statement, the rejection is general and not restricted to certain gas–solid systems. Similar comments, leading to such rejection, seem pertinent to the Pace–Taylor mechanism, the Vol'kenshtein thermal site-generation mechanism, or the Landsberg continuous site-creation mechanism. Thus, because of the complexi-

ties outlined, the popular interpretation of the measured Arrhenius E is beclouded. In view of the uncertainty of choice of comparable stages of adsorption, the significance of E must be debased from an energy of activation to a mere temperature coefficient. If knowledge of such a temperature coefficient is desirable, simpler and less ambiguous expressions than E, such as

$$(\alpha_1/\alpha_2)/(T_2 - T_1) \quad \text{or} \quad 100[(\alpha_2 - \alpha_1)/\alpha_1]/(T_2 - T_1)$$

are preferable.

The recognition of a number as an energy of activation implies that the entities taking part in the reaction are completely defined and that only one reaction path is permissible. In practice, absolute definition of these criteria is frequently not possible, and assumptions are made that are considered reasonable in view of known facts. However, for chemisorption it appears that in many and perhaps all cases the commonly made and usually unstated assumptions are not reasonable in view of the known complexities of the chemisorption process. The off-hand quotation of E values is thus abstruse and useless.

XVII. Mechanisms and Equations

A. SURFACE COVERAGE

A degree of surface coverage implies the existence of a definite adsorbing surface of known dimensions which can be covered by adsorbate. The concept is based on the analogous situation in physical adsorption, where direct fractional surface coverage can be estimated from a measurement of the total surface of the adsorbent. With chemisorption, however, the maximum amount of gas adsorbed is sometimes equivalent only to a fraction of the total geometric surface. By analogy to physical adsorption, the amount of gas taken up by this "active" portion of the surface is frequently expressed in terms of fractional coverage, which term is conventionally designated by θ. If θ is expressed as the ratio of amount adsorbed, q_t, at some time, t, to the total amount adsorbed after a great length of time, $q_{t\infty}$, i.e., $q_t/q_{t\infty}$, under closely defined experimental conditions, then θ may be a useful quantity for the expression of experimental results.

However, θ is frequently used with the implication that $\theta = N/N_0$. This is based on the concept that the surface has originally a fixed number of adsorption sites, N_0, and that these are used up as gas is adsorbed.

Taylor and Thon (298) point out that the observed $e^{-\alpha q}$ kinetics, which call for a relation,

$$-dN/dq = \alpha N$$

are inconsistent with the classical concept of an adsorbent surface containing a fixed number of sites. As pointed out by Landsberg (172), a logarithmic rate law

contradicts at least one of the more usual ideas of adsorption. The relations

$$N = N_0 - q \qquad (7)$$

$$dq/dt = kN \qquad (8)$$

are considered, where equation 7 reflects the classical concept of the constancy of the number of occupied sites plus the number of vacant sites, and equation 8 stipulates an adsorption rate proportional to the number of available sites. If a logarithmic law is supposed to be valid and equation 7 is supposed to hold, then

$$N_0 - N = (1/\alpha) \ln (1 + t/t_0)$$

$$dq/dt = [(bt_0)(1 + t/t_0)]^{-1} = k_1 \exp(\alpha N)$$

where k_1 is independent of time. Hence equation 8 fails. Conversely, if both the logarithmic law and equation 8 hold, then

$$\alpha(N + q) = k_2(t + t_0)^{-1} + \ln (1 + t/t_0)$$

so that equation 7 is violated. Because the semilogarithmic law appears to hold and because equations based on equation 7 have severely limited applicability, equation 8 is considered to be valid. This implies the nonexistence of a constant active portion of the surface and vitiates characterization of numbers of adsorption sites in terms of the classical θ. Whereas the geometric surface is constant, the "active area" may vary with experimental conditions, i.e., there are different numbers of sites. Under such conditions N/N_0 is a function of the state of the surface and not related to θ. The active area is not constant, in contrast to the classical picture of an unchanging geometrical area.

Consequently, θ and q are not indiscriminately interchangeable without definition. Trapnell labels the ordinate of graphs with q, but refers to the plots using θ, and similarly derives an equation for $d\theta/dt$, intimating equality to dq/dt (314). Cook and Oblad (58) refer to the equation

$$d\theta/dt = a \exp(-\alpha\theta)$$

termed Elovich, and Higuchi, Ree, and Eyring (137) commit a similar error. Similarly, Ely (86) and Porter and Tompkins (247) use the equation involving q, but resort to θ in their derivations and assume that q is proportional to θ. Such proportionality does not appear to be a valid assumption. θ and q require differentiation and θ requires more careful definition.

B. RATE EQUATIONS

Most of the rate equations for chemisorption that have been used originate from the concepts of Langmuir's mechanism (174, 175). The observed rate of adsorption is considered as the difference between the rate of adsorption proper and the rate of desorption.

$$dq/dt = k_a P (1 - \theta) - k_d \theta$$

where θ is the fraction of the surface that is covered, and k_a and k_d are the rate constants for adsorption and desorption, respectively. Approximations are necessary to apply this relation. At conditions far removed from the steady-state condition, $(1 - \theta) \approx 1$, and desorption can be neglected. An expression for "driving force" in terms of distance from equilibrium coverage or pressure may be added.

Thus Kobukowa (157) considered the expression

$$dq/dt = k_a(P - P_e)$$

where P_e is the equilibrium pressure. Integrating with $dq/dt \approx - dP/dt$, yields

$$\ln (P - P_e)/(P_i - P_e) = kt$$

where P_i is the initial pressure.

For adsorption of methane on nickel at about 10^{-2} cm. of mercury Kobukawa obtained straight lines on plotting log $(P - P_e)$ versus t. However, only five or six points were obtained for experiments of 60 min. duration. Barrer (14, 15) similarly expressed the adsorption of hydrogen on graphite and diamond. For hydrogen–charcoal Kingman (154) assumed that $k_d = 0$ and that $\theta \approx q \approx (P_i - P)$, obtaining

$$dq/dt = k_1 P (k_2 + P)$$

Equations are elaborated by Troesch (316) for constant-volume and constant-pressure systems. Classical equations are given elsewhere (169, 170) in detail for cases such as adsorption of more than one gas, or dissociation.

Ward (329) considered gas uptake to be partly a solution process with diffusion of gas from the surface to the interior as the rate-controlling step. The equation

$$q = 2SA (Dt/\pi)^{1/2}$$

was proposed, where S is the surface area, A the surface concentration of gas, and D the diffusion coefficient. Plots of q versus $t^{1/2}$ for the hydrogen–copper system were linear at low coverages, but deviation from linearity occurred and increased with increasing coverage. This equation was also used by Morozov (222) for the adsorption of hydrogen on iron. To correct for deviations Ward assumed that the copper adsorbent was in the form of spheres of radius R and that A was constant. The corrected general equation

$$q = A \left[\frac{4}{3}\pi R^3 - \frac{8R^3}{\pi} \sum_{1}^{\infty} \frac{1}{n^2} \exp(-Kn^2\pi^2 t/R^2) \right]$$

resulted, where k and n are constants. The fit of the last equation to the hydrogen–copper data extends to higher coverages than that of the first, but seems still inadequate. Ward's mechanism of solution is obsolete.

Burwell and Taylor (51) observed that data for different experiments on the chemisorption of hydrogen on Cr_2O_3 gel would approximate a common curve when

q was plotted against bt. b is a constant whose value is characteristic of temperature and pressure. Putting

$$b = P^n A \exp(-E/RT)$$

improved the approximation which, however, still remained inadequate. These data were examined by Clarke, Kassel, and Storch (56), who note that, when a smooth curve is drawn through the points of one experiment on a q–t plot, extrapolation to the starting time would indicate an appreciable amount of adsorption coincident with the beginning of the experiment. This amount is $0.2 + 1.1P$ ml. (and is equivalent to the amounts q_0 mentioned by Taylor and Thon (298)) and was subtracted from q values to give corrected values, q_c, which were applied to a derived equation. The latter was obtained from a simple model involving a primary adsorption process followed by diffusion to secondary adsorption sites. The equation

$$tP = (k_1 + k_2 P)q_c + (k_3 + k_4 P)q_c^2$$

gave reasonable results, plots of tP/q_c versus q_c being linear except at initial conditions.

Howard and Taylor (141) used the equation

$$dq/dt = k_1 q^{k_2}$$

to express the rate of adsorption of hydrogen and ethylene on Cr_2O_3 gel. The constants k_1 and k_2 are stated to be independent of q over wide intervals and are characteristic of the surface and the gas. The integrated equation is

$$\log q = k_3 + k_4 \log t$$

On plotting the data of $\log q$ as a function of $\log t$, lines showing a slight curvature are obtained.

A general equation of the form

$$q = k_1 t^{k_2}$$

was used by Bangham and Burt (9, 10) to describe the adsorption of carbon dioxide and ammonia by glass. This was later used in different corrected form. Thus Maxted and Moon (208, 209) used an equation

$$dq/dt = nk(q_e - q)t^{n-1}$$

which on integration becomes

$$\ln (q_e/q_e - q) = kt^n$$

where q_e is the amount adsorbed at the end of the process and k and n are constants. Data for the adsorption of hydrogen and deuterium on platinum, plotted as $\log \log (q_e/q_e - q)$ versus $\log t$, yield straight lines up to about $0.4q$. Maxted and Hassid (207) expressed data for the adsorption of oxygen on platinum in similar fashion.

Iijima used a similar equation,

$$\log (P/P - P_e) = k_1 + k_2 t$$

to express the adsorption of hydrogen, deuterium, and ethylene on nickel (143, 144, 145, 146).

Kwan (165) has deduced a power rate law, expressed as

$$-dP/dt = k_1 P\theta^{-k_2} - k_3\theta^{k_4}$$

where θ is fractional coverage. The constants are obtained by evaluating $-dP/dt$ graphically from the P–t curve. Log $[(-dP/Pdt)/(1 - \mathbf{P}/P)]$ is then plotted against $\log \theta$. Here $\mathbf{P}$ is the pressure of gas which would be in equilibrium with the amount of gas chemisorbed at time t and may be estimated from the isotherm. If the reverse rate is negligible it is sufficient to plot $(-dP/Pdt)$ versus $\log \theta$, i.e., the $k_3\theta^{k_4}$ term is neglected. The simpler equation was proposed earlier by Ghosh, Sastri, and Kini (110, 111, 271).

According to a table of Kwan (168) the power rate law is applicable to the adsorption of hydrogen on nickel (143), carbon (154), zinc oxide (304), and Cr_2O_3 (51); of oxygen on $CuO \cdot Cr_2O_3$ (100); of nitrogen on promoted iron (47) and tungsten (62, 98); and of hydrogen and carbon monoxide on Fischer–Tropsch catalyst (110, 111).

The common characteristics of such empirical or derived equations is that they frequently fail to represent rate data over considerable portions of an experiment. Even when "straight lines" are obtained for some part of a rate plot the representation of data is imprecise and at times improper and incompatible with the equation tested because of simplification or of approximations of values of q_e or P_e or $\mathbf{P}$. Also, scatter of data over "linear" portions sometimes is not random. For example, for Howard and Taylor's (144) data on the adsorption of hydrogen on Cr_2O_3 at 383°C., q changes from 4.0 ml. at $t = 2$ min. to $q = 28.1$ ml. at $t = 120$ min. A $\log q$–$\log t$ plot of the data (according to Howard and Taylor's equation) appears linear, with a least-squares correlation coefficient of 0.9974. This shows that the regression of $\log q$ on $\log t$ is very strong. Close inspection of the plot, however, shows a slight curvature, the data being distributed in nonrandom manner about the least-squares line. An Elovichian representation of the same data by the equation

$$q = k_1 + k_2 \log (t + 10)$$

yields a linear plot with apparently random distribution of points having a correlation coefficient of 0.9996.

In view of such uncertainty in representing rate data, these equations are almost useless from the mechanistic point of view.

C. THE PERTINENCE OF THE ELOVICH EQUATION

It is emphasized that chemisorption rate data are represented better by the Elovich equation than by other equations. This statement, however, requires qualification and amplifications.

The representation of a slow chemisorption by a monotonic q–log t plot is precise, as has been shown. The frequent occurrence of breaks in such plots, however, shows that the adsorption process is not simple: two or three sets of parameter values are sometimes required to represent the data over the entire measurable course of the experiment. Such complexity causes some doubt as to the general usefulness of the Elovich treatment. It must be pointed out, however, that other rate equations —if applicable at all over a reasonable portion of an experiment—in reality are frequently applied, accompanied by statements qualifying their applicability, to only the first, the middle, or the last stages of adsorption. Representation of data in such partial fashion is quite incomplete and, if strict adherence is held to a particular adsorption mechanism even though only a fraction of the experiment is represented by the appropriate rate equation, then a change in mechanism is implied for regions where the particular equation is not obeyed.

On using an Elovich treatment, even though breaks are found, the reaction is usually represented over its entire measurable course and no drastic change in mechanism is required. Rather than a change from one mechanism to another, a change in degree rather than in kind can be involved for an Elovichian rate representation. The situation found with the kinetics of metal oxidation is analogous: five different rate laws exist, each corresponding to a discrete oxidation mechanism. Occasionally, during the course of an experiment, the rate changes from one law to another, implying a change in mechanism. With logarithmic oxidation (Elovichian), breaks in q–log t plots are also observed (184, 319). For this case, no complete change in mechanism may be necessary. As recently shown by Uhlig (320) for the initial oxidation of nickel, the change in slope of the q–log t plot can be correlated with change in work function of the surface, while the material transport mechanism remains essentially unchanged. This change is thus one of degree rather than of kind. Similar changes of degree seem plausible for chemisorption, suggesting that a complete Elovichian representation is preferable to a fragmentary and inaccurate description of data by other means.

Conversely, the wide applicability of the Elovich equation has itself caused less optimistic comment. Parravano and Boudart (242) find that a number of different processes, such as bulk or surface diffusion and activation or deactivation of catalyst surfaces, as well as chemisorption may be represented by semilogarithmic formulation, and comment that it appears futile to explain this formulation in terms of a unique mechanism.

The treatment of breaks to date is largely empirical. None of the chemisorption mechanisms adequately account for "anomalies." This, however, appears to be a fault of theory rather than of kinetic treatment, and it seems plausible that a general theory incorporating the various complexities will be developed.

D. MECHANISMS INVOLVING THE ELOVICH EQUATION

Interpretation of rates of slow chemisorption has led to several divergent adsorption mechanisms. Each is concerned only with the simplest case of adsorption where the q–log $(t + k)$ plot is monotonic. Only the salient features of these mechanisms are outlined here.

Taylor and Thon (298) suggest that the validity of the Elovich equation, particularly in systems where the pressure of adsorbable gas varies considerably during the course of the adsorption, indicates that of the two reactants—gas and solid—it is only the mass action of the latter that determines the rate at each moment. The mass action of the gas determines the initial rate a. The subsequent kinetics are such that it appears as if beyond the initial stage the surface sites are always in relatively much shorter supply than the comparatively abundant supply of gas, except in final stages where depletion of gas can be important. The implication is that the rate of slow chemisorption is governed by the availability of sites and, further, that chemisorption eliminates sites over and beyond actual occupancy. To be compatible with the observed kinetics the number of sites n must be

$$n = n_0 \exp(-\alpha q)$$

where n_0 is the number of sites at $q \approx 0$, so that

$$-dn/dq = \alpha n$$

This rate of site incapacitation becomes, by substitution,

$$-dn/dt = \alpha n (dq/dt) = (\alpha a/n_0)n^2$$

or, if $a = k_0 n_0$,

$$-dn/dt = k_0 \alpha n^2$$

The last equation reflects a bimolecular site-site interaction at the stage of slow adsorption. Sites thus disappear in numbers exceeding occupancy.

Vol'kenshtein's theory (325) of generation of surface sites by the very act of adsorption is used. It is assumed that the rate of production of sites is $k(N - n)P$ under the action of a chemisorbable gas at pressure P. N is the maximum possible number of sites; hence $(N - n)$ is the distance from maximum, i.e., the driving force. If the rate of the accompanying spontaneous decay of sites is $k'n$, then the condition of stationarity is

$$k(N - n)P = k'n$$

and hence the steady-state site concentration is

$$n_0 = kNP/(kP + k')$$

which is numerically tantamount to a fractional order $P^{1/m}$ ($m > 1$). The initial rate is proportional to n_0, and

hence is of the same fractional order $1/m$. The establishment of the steady state in this fashion is rapid and definitely completed at some near-initial state. At the stage where sites are produced and multiply, their elimination by adsorptive occupation must be lagging behind their multiplication. This is definitely a thing of the past at the time t_0, which marks the beginning of pure second-order decay of the sites explosively produced in the near-initial creation period. Analogies from observations of luminescence and photoconductivity are used to support the mechanism of bimolecular decay of sites. In chemisorption the mechanism thus consists of a quasiexplosive production of active sites upon contact with the adsorbate. This is offset by a first-order spontaneous decay of sites, resulting in an "initial" steady-state site concentration, and is marked at that stage by an amount of gas that is "instantaneously" adsorbed. From that point on slow adsorption occurs, with bimolecular disappearance of sites and the corresponding exponential decline in the rate of adsorption.

The theory incorporating site generation and decay was extended by Taylor (296, 297), using a suggestion of Semenov (280). The latter assumes the existence of a certain number of free valences, V, on the surface which can radicalize an inert species striking from the gas phase. Conversely, if a free radical strikes an active point, S, on the surface, it can give rise to a surface "dissociation": $S \rightarrow V + V$. One V will saturate the radical, and the second will remain available for reaction with an inert species. A site for chemisorption thus behaves as does a radical in a homogeneous system. Taylor has considered these processes for the reaction of hydrogen with a surface. The reaction (a) may occur:

$$V + H \rightarrow HV + H \qquad (a)$$
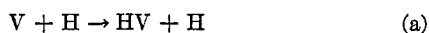
The hydrogen atom is produced in the surface layer near a normal surface atom S, and reaction equivalent to a "dissociation," $S \rightarrow V + V$, may be induced: $H + S \rightarrow HV + V$. This reaction, together with reaction (a), constitutes a chain reaction that regenerates V. The perturbation of one surface atom may be expected to influence neighboring atoms, so that a branched process (reaction b) results,

$$H + nS \rightarrow HV + (2n - 1)V \qquad (b)$$
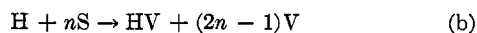
Two chain-ending reactions are considered,

$$H + V \rightarrow HV \qquad (c)$$
$$V + V \rightarrow S \qquad (d)$$

Also, since surface dissociation is induced by the adsorbate, the reverse association must also depend on adsorbate, by the principle of reversibility. Therefore, the specific rate of reaction (d), k_d, depends not solely on the surface but also on the adsorbate, and reactions (d) and (b) represent overall processes.

Applying steady-state conditions to H and V in reactions (a) to (d) yields

$$[V] = \frac{nk_a k_b[H_2][S]^n}{k_b k_d[S]^n + k_c k_d[V]} - \frac{k_a}{k_d}[H_2]$$

[V] is approximately dependent on [H$_2$]. Replacing [V] in the denominator of the first term by a proportionality to [H$_2$], it is seen that [V] will increase as [H$_2$] increases, but less rapidly than in direct proportionality to [H$_2$]. This is approximated by

$$[V] = K[H_2]^{1/m} \qquad (m > 1)$$

Owing to the chain branching, the establishment of the stationary state is very rapid and results in a large portion of the surface being "activated." This means that the available atoms S are used up and reaction (b) ceases. Reactions (a) and (c) constitute the adsorption of hydrogen accompanying (d), the site decay. Since experiment is considered to show this latter to be rate-controlling, the momentary site concentration [V] can be well approximated by

$$-d[V]/dt = k_d[V]^2$$

or

$$[V] = [V]_0/(1 + k_d t[V]_0)$$

where $[V]_0$ is the "initial" site density for the slow chemisorption, i.e., subsequent to the surface activation, and is thus the value given previously as approximately proportional to $[H_2]^{1/m}$. This [V] value is an approximation, since the loss of V's by reaction (c) was neglected. This approximation amounts to $k_d \gg 2k_a$.

The rate of chemisorption by reactions (a) and (c), where hydrogen gas is in large excess relative to sites V, is

$$dq/dt = k[V]$$

Substituting for [V] and integrating yields:

$$q = (k/k_a) \ln (1 + k_d t[V]_0)$$
$$dq/dt = k[V]_0 \exp(-k_d q/k)$$

Since $k[V]_0$ is the initial rate a, and putting $k_d/k = \alpha$, this yields the Elovich equation.

A number of relations follow from this derivation. (1) Since $a = k[V]_0$ and $[V]_0 \propto [H_2]^{1/m}$, then $a \propto [H_2]^{1/m}$. (2) Since k is a true velocity constant, a must increase with temperature corresponding to an energy of activation E. (3) If $k_d \gg 2k_a$, then for the corresponding activation energies $E_d < E_a$, and α should decrease as the temperature increases. (4) If t_0 is the time required to establish $[V]_0$, the amount of gas adsorbed in this time, q_{t_0}, is that involved in reaction (a) and either (b) or (c): namely, $2k_a[V][H_2]$, where this [V] is the number of biographical defects and therefore constant for a given surface. Hence q_{t_0} should be proportional to [H$_2$]. (5) From the logarithmic plots of data, $t_0 = 1/(a\alpha)$,

whence $1/t_0 \propto [\text{H}_2]^{1/m}$ and $t_0[\text{H}_2]^{1/m}$ should be constant. (6) The adsorption isotherm should be given by $q \propto [\text{H}]^{1/m}$, which is of the Freundlich type. (7) The heat of adsorption will be complex and composed of the heat of chemisorption proper and of the heat evolved in the interaction of sites. This latter should be proportional to [V] and hence decrease as q increases. (8) The so-called observed energy of activation of adsorption increases with coverage. (9) The dependence of k on the adsorbed species requires that the sites on a surface in the presence of two adsorbable species must decay at least as rapidly as in the presence of that species which when alone causes the faster decay. This inhibits adsorption of the other species, an inhibition caused by destruction of sites and not by occupation of sites.

Landsberg (172) has also considered a site-generating mechanism. Consider a surface having s_0 adsorption sites per unit area at $t = 0$ and s sites at some arbitrary time t. Let there be N impacts by gas molecules with the surface on unit area per unit time. Let x be the effective contact area between a molecule and the surface upon collision so that xs is the fraction of impacts that could be effective in trapping a molecule. The probability that a molecule sticks on impact is proportional to xs, $p = Cxs$, where C is a constant. The number of molecules sticking per unit area per unit time is

$$dq/dt = CxsN$$

Let b be the effective area over which sites become invalidated by the adsorption of a single molecule, b being not necessarily of the same order as x. The number of sites invalidated per unit area per unit time is therefore

$$-ds/dt = CNxs \cdot bs$$

Integration for s yields

$$s_0/s = 1 + CNxbs_0t$$

which, on insertion into the equation for q, yields

$$q = (1/b) \ln (1 + t/t_0) \qquad t_0 = 1/(CNxbs_0)$$

The actual area b_1 over which sites become invalidated is presumably larger than or of the same order as x. However, b_1 must be reduced by an area b_2 to yield b. The correction by b_2 originates in site creation; the adsorbed molecule may sometimes be expected to generate new sites (though not as many as it has invalidated) by one of a variety of mechanisms.

The mechanism thus requires a site inactivation other than that conventionally used whereby one adsorbed particle invalidates exactly one site:

$$s + q = s_0$$

Landsberg shows that the one-per-one site invalidation is violated at almost all times even in the absence of site generation if a logarithmic adsorption law holds. An

efficiency, $\eta = (s_0 - s)/q$, is defined which measures the number of sites invalidated per adsorbed particle. η is proportional to bs_0. In the absence of generation of sites, η can reach unity only in exceptional cases and can never decrease below this value, since each adsorbed particle uses up at least one site. However, according to conventional ideas, η is always unity, since each adsorbed particle invalidates exactly one site. Since $\eta < 1$ if $bs_0 < 1$, such cases have no physical meaning in the absence of site generation. This is so because the relation $bs_0 < 1$ implies that an area of inhibition is smaller than the average area surrounding one site. If $bs_0 > 1$, there is one single time t_1 in addition to the time $t = 0$ at which $\eta = 1$. In the absence of site generation the length of time for which a logarithmic rate law holds must be smaller than t_1, because

$$s + q < s_0 \text{ for } t < t_1 \text{ and } s + q > s_0 \text{ for } t > t_1$$

In the absence of site generation the second case is impossible. Landsberg shows that $t_1 > t_2$ if, and only if, $bs_0 > 1.386$. The $s + q = s_0$ relation is thus violated at almost all times. "Site generation" of some sort is thus plausible.

Meller (213) assumes that chemisorption occurs in two steps, and that the velocity of step I is independent of the concentration of adsorbate, so that this step is of zero order. The second step, II, is dependent on the number of available active sites. These sites are changed during the course of the adsorption; the change is a function of time and, in the simplest case, the rate of change of their physical structure is taken as inversely proportional to the first power of time, t. If neither step is slow enough to be rate-controlling, then the time necessary to reach a certain stage of reaction equals the sum of the times which would be necessary if the steps I and II were to occur independently of each other. This assumption is expressed as

$$1/(dq/dt) = 1/(dq/dt)_\text{I} + 1/(dq/dt)_\text{II}$$

where dq/dt is the measured velocity and the subscripts I and II, respectively, refer to the velocities of the first and second stages. This relation is valid only when all q values are equal. Then, according to the assumption first made,

$$1/(dq/dt) = 1/k_0 + 1/(k/t)$$

or

$$dq/dt = k_0/(1 + k_0t/k)$$

which becomes, after integration,

$$q = k \ln (1 + k_0t/k)$$

Comparison with the integrated form of the Elovich equation,

$$q = (1/\alpha) \ln (1 + t/t_0)$$

shows that $k = (1/\alpha)$ and $k_0/k = a\alpha = 1/t_0$.

The initial rate a thus equals the specific rate constant of the zero[th] reaction, while α is the reciprocal value of the rate constant of step II. Meller points out that the adsorption process is more complicated than that depicted by the simple model and stresses that deviations are to be expected at low and high surface coverage.

An interesting model of chemisorption and catalysis (58, 59, 220) is described by Cook and Oblad (58) as follows: A surface layer for various reasons is strained and, therefore, reacts readily chemically with many substances, the adsorbate in effect creating the adsorption sites and thus reducing the strain on the surface. The release of the strain involves crystallographic changes in the catalyst surface atoms or ions. Desorption involves a reverse of this process, the catalyst reverting to its former state of strain.

Cook and Oblad derive an Elovich-type equation using these concepts and absolute reaction-rate theory, such that

$$\frac{d\theta}{dt} = \frac{kT}{h} e^{-\Delta F_0^{\ddagger}/RT} e^{-\alpha'\theta/RT} f(R)$$

which leads to $d\theta/dt = a \exp(-\alpha\theta)$ when

$$a = \frac{kT}{h} e^{-\Delta F_0^{\ddagger}/RT} f(R)$$

and

$$\alpha = \alpha'/RT$$

$F_0^{\ddagger}$ is the activation energy for chemisorption on a homogeneous surface, θ is fractional coverage, k is the Boltzmann constant, α' is a constant, and h is Planck's constant. $f(R)$ is some function of the activity of the reactant (adsorbate) in the gas phase. f might be a function of θ, particularly as θ approaches unity. The experimental relations found, $\alpha \propto 1/T$ and $\ln a \propto 1/T$, seem to agree with the definition of the parameters a and α.

Eley (86) considered physical and chemical changes occurring at a reasonable rate that may be determined by the movement, or reaction, of a single molecule in a condensed phase. In many cases such processes follow a time course that is rather more extended than the ordinary first-order law. Eley derived the general relation,

$$-dx/dt = k_1 x \exp(k_2 x/kT)$$

which, when applied to chemisorption, becomes

$$dq/dt = k_3(q_e - q) \exp(-k_2 q/kT)$$

q_e is the amount adsorbed at the end of the process. k_1, k_2, and k_3 are constants. The equation approximates the Elovich equation when changes in the exponential term are dominant.

Stone (288) shows preference for an interpretation that assumes activated adsorption on a nonuniform sur-

face and is basically the treatment of Halsey (125). Sites of varying adsorption potential χ are assumed, and the activation energy E to reach these sites varies linearly with χ, $E = k_1\chi$, where $k_1 < 1$. On sites of any one χ value, the rate of chemisorption is

$$d\theta_\chi/dt = Pk_2(1 - \theta_\chi) \exp(-k_1\chi/kT)$$

θ_χ is the fraction of χ-valued sites, k_1 and k_2 are constants, k is the Boltzmann constant, and P is the pressure. If χ is so great that desorption is negligible, integration yields

$$\theta_\chi = 1 - \exp(-At)$$

where $A = Pk_2 \exp(-k_1\chi/kT)$. There is one such equation for each set of χ-sites. The total chemisorption is obtained by summing over all values of χ which are present from χ_a to χ_b. If the distribution is continuous,

$$\theta = \int_{\chi_a}^{\chi_b} N_\chi \theta_\chi d\chi$$

where N_χ is the distribution function. To evaluate the integral two approximations are made.

It is assumed that a given set of χ-sites fills abruptly to its equilibrium coverage at $t = t'$ and that this occurs at $\theta = (1 - 1/e)$, so that $t' = 1/A$. This happens to each set of χ-sites. The overall process is then reduced to a series of stepwise uptakes, the time at which each step occurs being related to the χ value of the sites involved by

$$1/t = Pk_2 \exp(-k_1\chi/kT)$$

so that

$$\chi_t = (kT/k_1) \ln Pk_2 t$$

The second assumption is that the total number of sites with a given value of χ is the same for all values of χ; i.e., N_χ is a constant, say, N_0. Then

$$\theta_t = \int_{\chi_a}^{\chi_b} N_0\theta_e \, d\chi = N_0\theta_e(\chi_t - \chi_a)$$

where $(\chi_t < \chi_b)$, and

$$\theta_t = N_0\theta_e[(kT/k_1) \ln (Pk_2t) - \chi_a]$$

θ is taken as directly proportional to q, so that the last equation is of the form

$$q = (\text{constant}) \ln t + (\text{constant})$$

Porter and Tompkins (247, 248) also use Halsey's treatment, which is valid for any model in which sites become occupied as a result of adsorbing particles having to overcome a potential barrier whose height increases with coverage. For the simplest case, Porter and Tompkins consider a surface composed of two parts. Area A has sites of high χ (high heat of adsorption) and the act of adsorption on A sites requires an activation

energy E_A. Area B has sites of low χ (low heat of adsorption H_B) and for B sites the activation energy E_B is zero or very small. The activation energy E_M^A for mobility on A is assumed to be less than E_A but greater than E_B. Also E_M^B is very small, so that there is free mobility of adsorbed particles, or adatoms, on B. When gas is admitted, B quickly adsorbs gas until the equilibrium value corresponding to the prevailing temperature and pressure is attained. This will be less than complete coverage because H_B is comparatively low. Area A, however, remains substantially bare initially, because E_A is required. During the rate process, A sites will be covered predominantly by mobile adatoms from B and to a much lesser extent directly from the gas phase. The rate-determining process is then the activated surface migration of adatoms and the measured activation energy is E_M^A, because sites on B rendered bare by migration are rapidly filled up from the gas phase.

A series of experiments on thermal cycling could be explained using this model. For such experiments an α value was obtained for the adsorption of hydrogen at some temperature T_1 on a clean metal film. Then, without evacuation and degassing, the temperature was raised to T_2, and then lowered to T_1. A further dose of hydrogen was admitted. The α value then obtained was markedly higher than that on the clean film. Repetition of the temperature cycle increased α still further. According to the diffusion model, warming and cooling without evacuation caused further surface migration of adatoms from sites of low χ and a greater filling-up of sites of high χ. The high α values then obtained with a new dose of hydrogen were due to E_M^B rising more sharply with increasing coverage. The thermal cycling thus caused a redistribution of sites.

More extensive thermal cycling experiments with and without evacuation (121, 122, 123) led to modification of the model. Gundry and Tompkins (123) introduced an intermediate chemisorbed state of the type postulated by Dowden (68, 70) as a necessary precursor to the final chemisorbed state of lowest potential energy. Instead of requiring the migration of a chemisorbed atom to a new site of higher adsorption potential, the new model involves the transition of the adatom at the original site to a different chemisorbed state. The concept of the nonuniform surface is thus not essential.

Several models have been suggested that involve electron transfer from gas to the surface. As a result of surface charge, a barrier hindering transfer is set up. The effect of surface barriers on adsorption on semiconductors has been discussed by several authors (4, 132, 223, 225, 331, 332).

If there is a barrier at the surface of a semiconductor, and if electrons must cross this barrier for chemisorption to occur, then the rate of chemisorption may be limited by the rate at which electrons can cross this barrier.

This rate is proportional to the number of electrons of energies greater than the barrier height, E, or

$$\text{Rate} \propto \exp(-E + \mu)/kT$$

where μ is the electrochemical potential of the electrons. For the case of a clean N-type semiconductor surface adsorbing an electronegative gas, for example, there is no surface barrier initially. As gas adsorbs the barrier is set up. Initially, the adsorption is very fast because E is small. As adsorption proceeds, E will increase, slow the adsorption, and will continue to increase to such an extent that eventually the rate at which electrons can cross the barrier is essentially zero and the adsorption ceases. Such a simple model was used by Morrison (223, 225) to explain surface effects on zinc oxide.

As pointed out by Weisz (331, 332, 333), for a barrier layer model a chemisorption rate law with the amount adsorbed in the exponential is a necessary consequence. Similarly, Melnick (214, 215) has shown that

$$dq/dt = B \exp(-E/kT)$$

where B varies slowly in comparison to $\exp(-E/kT)$ during chemisorption. E is the barrier height and is a function of q. The assumption that for small changes of q, using $q = q_0 + \Delta q$, E may be expanded in a Taylor series in Δq, results in

$$d\Delta q/dt = k_1 \exp(-k\Delta q)$$

If Δq is small in comparison to q, the adsorption follows the Elovich equation. The latter is thus an approximation not valid at small q where the adsorption rate is fast, but is valid only when q is large.

A similar electron-transfer model is used by Germain (108, 109), who arrives at the equation

$$dq/dt = a \exp(-\alpha q^2)$$

and considers this to approximate the Elovich equation.

Similar but more elaborate models were used for the barrier layer theory developed by Hauffe (130). This theory was applied to chemisorption, oxidation, and catalysis, and has been reviewed in detail by Hauffe (130). A detailed treatment of chemisorption on semiconductors results in the Elovich equation.

Absolute reaction-rate theory was applied to the system of alkali atoms on tungsten (137, 138). For desorption, Higuchi, Ree, and Eyring (137) derive the equation

$$-d\theta/dt = a\theta \exp(\alpha\theta) \tag{9}$$

where θ is the fraction of the surface covered with adsorbate. The physical meaning of a and of α was given: a is the frequency with which an adion on a bare surface transforms to an adatom, while α indicates the ratio of the decrease of the activation free energy for desorption at $\theta = 1$ to the mean kinetic energy of the adion.

Equation 9 was used by Becker (18) to describe rates of desorption of cesium atoms and ions from a tungsten surface. Higuchi, Ree, and Eyring term equation 9 as well as equation 10

$$d\theta/dt = a(1 - \theta) \exp(-\alpha\theta) \tag{10}$$

"Becker–Zeldovich," explaining that equation 10 was used by Zeldovich (341) and by Roginski and Zeldovich (261, 262) to express the rate of adsorption of carbon monoxide on manganese(II) oxide. The subsequent text and a footnote ascertain that equation 10 is considered to be the exact equivalent of the Elovich equation:

$$dq/dt = a \exp(- \alpha q) \tag{11}$$

As Higuchi, Ree, and Eyring point out, equations 9 and 10 have essentially the same form except for the positive and negative signs in the exponent which are, according to their theory, due to the fact that adsorption is a reverse process of desorption and vice versa. However, equations 10 and 11 are not identical.

The implied identity of equations 10 and 11 is unfortunate. Equation 10 has the same form as equation 11 only at low coverage when the term $(1 - \theta)$ tends to unity. Also, even at vanishing θ values, the constants a or α for the equations are not identical. The Elovich equation (equation 11) is not used with a "driving-force" term such as $(1 - \theta)$, although in the early Russian literature the equation

$$dq/dt = a(q_0 - q) \exp(-\alpha q) \tag{12}$$

is mentioned. Charachorin and Elovitz (55), for example, use equation 12, where q is the number of molecules adsorbed and q_0 is *the number of molecules originally present in the gas phase*. The term $(q_0 - q)$ is a correction for varying pressure within the adsorption systems.

As pointed out by Stone (149, 288) the mere linearity of q–log t plots cannot be used as a criterion for the choice of a mechanism. A knowledge of the effects of change of experimental variables on the kinetics may permit such choice and so is necessary. A comparison of effects is desirable in view of the different mechanisms employed in interpreting the semilogarithmic adsorption law.

The complexity of experimental results and their occasional contradictory nature preclude such comparison which at present would be premature, polemical, and of dubious value mainly because of the incompleteness of data. It suffices for present purposes to state that none of the models appears to be satisfactory.

The more general models, such as those of Taylor and Thon or of Landsberg, suffer because their flexibility seems to preclude quantitativity. Conversely, the more quantitative approaches seem at present to be imbued with too much rigor and cannot account for the complex behavior found experimentally. As a consequence

of this, the use of a particular chemisorption mechanism is almost a matter of personal preference until much more experimental and theoretical work has been done and an adequate model emerges.

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