

A probable cause is the change in temperature at the boundary produced by the heat of mixing of the two solutions.

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THE ACTIVATION ENERGY OF ADSORPTION PROCESSES

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The rapid development, during the last decade, of the experimental study of adsorption phenomena at solid surfaces having catalytic activity has served to emphasize those adsorption processes in which a high degree of specificity is manifest. This work has centered attention on the operation of valence forces in determining adsorption and has indicated the existence of adsorption processes not markedly different from chemical reactions. The accumulation of experimental material has yielded, however, a number of data which, from the standpoint of classical adsorption theory, are abnormal. There has been considerable discussion of types of adsorption and distinctions drawn between "primary" and "secondary" adsorption.¹ In other cases there has been a tendency to speak of "reversible" and "irreversible" adsorption and to recognize only the former as conforming to true adsorption, to ignore the latter in the theoretical treatment of the subject. This latter attitude² undoubtedly arose from the lack of a general theory applicable to all types of adsorption. At the same time, owing to the orientation of experimental work, the data in conflict with the simplified theoretical treatment have grown so rapidly that it may now be stated that the experimental literature of adsorption dealing with the abnormal cases is now as extensive as that conforming to the simple theory. There are now numerous data showing abnormal variations in the extent of adsorption with both temperature and pressure, abnormal variations of the heats of adsorption with temperature and pressure, large variations in the velocity of attainment of equilibrium in different adsorption systems and in the velocity of evaporation of adsorbed gases inconsistent with present adsorption theory. Since these several factors in part determine the velocity of chemical processes at surfaces, the lack of a general theory covering such phenomena has resulted in an inadequate, and, in some cases, an incorrect treatment of the theory of chemical reactions at surfaces. It is the object of the present communication to point out the inadequacy of the classical theory of adsorption and

¹ Benton, *THIS JOURNAL*, 45, 887, 900 (1923).

² Hückel, "Adsorption und Kapillarkondensation," *Akademische Verlagsgesellschaft*, 1928.

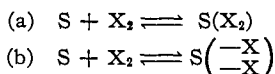
to indicate how it may very simply be modified to yield a general theory covering all types of adsorption.

It has been quite generally assumed on the basis of both theoretical considerations³ and practical experience that the velocity of adsorption is great. There has been a constant tendency to ascribe any variation from a rapid process to the operation of secondary factors not essentially connected with the adsorption process. As one example, we may cite the assumption of diffusion processes, either in solutions or through the minute cavities or fissures in porous solid adsorbents, as responsible for the failure to establish equilibrium conditions rapidly in adsorption processes. Whatever importance may, in individual cases, be assigned to the operation of such secondary factors, it is the object of the present paper to propose and to establish by experimental evidence that the adsorption process *per se* is not necessarily a rapid process, may indeed be a very slow process, too slow to be measurable, and that for each adsorption process there is a characteristic velocity which is determined by the same factors which govern the velocity of chemical reactions, and therefore by temperature, pressure, concentration and the nature of the adsorbing surface. Since, as is now usual in discussions of chemical kinetics, we speak of the activation energy of a given chemical process we may, in the same sense, speak of the activation energy of an adsorption process. We shall show that, paralleling the enormous variation in activation energy of chemical reactions, there is a similar large variation in the activation energies of adsorption processes. Furthermore, we shall demonstrate that it is to this variability in activation energy of the adsorption process that the abnormalities we have already discussed are to be ascribed.

General Theory of Activation Energy in Adsorption Processes

The consequences of the concept of activation energy in adsorption processes may best be examined by a general consideration of the adsorption of a gas at a plane surface composed of a definite number of elementary spaces. The conditions governing adsorption equilibrium at such surfaces have already been detailed by Langmuir.⁴

(1) **Equilibrium in Processes Involving Activation Energy.**—Extending this treatment of equilibrium to processes involving activation energy, we shall consider the adsorption of a diatomic gas (X_2) which may be adsorbed on the surface (S) in question in two forms (a) as molecules, (b) as individual atoms. We may represent the two processes by means of the equations



³ Lenard, *Sitzb. Akad. Heidelberg*, 5A, 16 (1914).

⁴ Langmuir, *THIS JOURNAL*, 38, 2221 (1916).

We shall assume that, in a particular case, the heats of adsorption for the two processes (a) and (b) are respectively Q_a and Q_b and that Q_b is greater than Q_a . We shall further assume that the activation energies are different and that the activation energy of process (a), E_a , is small, but that the activation energy of (b), E_b , is markedly higher. Under these conditions the activation energies of the reverse processes of vaporization are, respectively, $E_a + Q_a$ and $E_b + Q_b$.

It is a consequence of the Langmuir concept of adsorption as due to the time lag between condensation and evaporation that the average time which molecules occupy the surface depends upon the ratio of the rates of adsorption and desorption and, therefore, accepting the above assumptions, on the ratio $A_a e^{-E_a/RT}/B_a e^{-(Q_a + E_a)/RT} = (A_a/B_a) e^{+Q_a/RT}$ in the one case and on $(A_b/B_b) e^{+Q_b/RT}$ in the other case. Since the variations

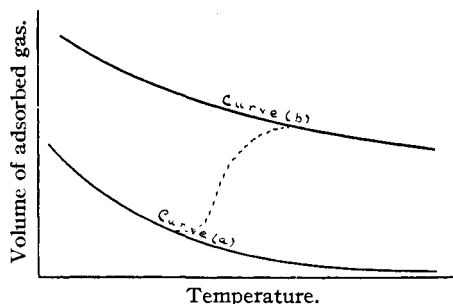


Fig. 1.—Schematic representation of adsorption isobars with two activation energies for the adsorption processes.

in A_a and A_b , B_a and B_b are minor⁵ as compared with the variation of the exponential for different values of Q_a and Q_b , it follows that the relative magnitudes of Q_a and Q_b largely determine the positions of the adsorption-temperature isobars for the two processes. For the case assumed, $Q_b > Q_a$, the isobar for (b) will lie above that for process (a) (Fig. 1). If the heats of adsorption for the two processes

were equal the two curves would more nearly coincide. The differences would depend only on differences in A_a , A_b , B_a and B_b . Were Q_b less than Q_a the curve for the isobar would lie below that of Q_a . There is no experimental evidence as yet of such a case.

(2) **Extent of Adsorption and Temperature.**—It may happen, by reason of the respective magnitudes of E_a and E_b , that, over a given range of low temperatures, the velocity of process (b) will be negligibly slow compared with that of (a). Under such circumstances the experimental results obtained will follow curve (a). As the temperature is raised there will be the normal decrease in adsorption of X_2 with temperature, but, simultaneously, there will be an increase in the velocity of process (b) so that, at sufficiently high temperatures, the experimental values obtained

⁵ In the simple Langmuir theory A_a and A_b are the rates at which molecules strike unit surface inelastically and are identical. The B factors in the evaporation process are similar to the factor C in the equation for a unimolecular reaction $dx/dt = C e^{-E/RT}$. Polanyi and Wigner [*Z. physik. Chem.*, 139, 439 (1928)] have shown that, in this latter case, the variation of the C values in the available experimental data is very small.

will be due practically exclusively to the adsorption process (b). Between the two extremes of temperature there will be a region in which the results obtained will be intermediate between (a) and (b) and determined by the relative magnitudes of Q_a , Q_b , E_a and E_b . This intermediate stage may reveal itself by rising values of the adsorption at a given pressure with increasing temperature. This condition is indicated by the dotted line in Fig. 1. The location of the two adsorption curves with respect one to another will determine the magnitude of the increase in adsorption (if any) due to such causes.

(3) Adsorption Equilibrium and Nature of the Activation Process.—

The conclusions thus reached with respect to the two adsorption processes involving, respectively, molecular and atomic adsorption are not limited to such processes but are applicable to any two processes of adsorption of a given molecular species producing any two forms of adsorbed product, the two processes differing in their activation energies. Dissociation of the molecule to yield atoms on the surface represents only one particular case of the general principle. It is apparent that adsorption may involve a plurality of types of change, in which case there will be a corresponding number of possible curves in Fig. 1 and a corresponding complexity in the observed adsorption-temperature relations. Thus, if a third type of adsorption occurred involving a higher activation energy E_c and a higher heat of adsorption Q_c , the isobar would lie above that of curve (b) and, in a given temperature range, there would be again a transition region of metastable adsorptions rising with increase of temperature. It should also be pointed out that if a case were found where Q_b was less than Q_a it is theoretically possible that the adsorption isobars experimentally realized would consist of two sections of decreasing adsorption with increasing temperature with an intermediate metastable region in which the decrease with temperature would be very much more pronounced. For simplicity, in the succeeding theoretical treatment only two types of adsorption will be discussed. It will be convenient to designate as type (a) the adsorption that occurs with low or negligible activation energies and as type (b) the adsorptions involving high activation energies. This in no sense, however, imposes on us the restriction that the adsorptions are of any particular type, for example, molecular and atomic. Any two adsorption processes of the same gaseous species may be involved.

(4) Activation Energy and Attainment of Equilibrium.—One further consequence of the present concept of activation energy on the results of experimental measurement may now be indicated. It is evident that because of the large activation energy, E_b , the portion of the curve (b) to the left of the dotted ascending curve cannot be experimentally realized by measurements conducted wholly at the lower temperatures involved. It is, however, also evident that values much higher than those correspond-

ing to curve (a) at the temperatures in question will be obtained if adsorption equilibrium is first established at higher temperatures, where both processes are occurring, and then the system be brought to the lower temperature. One can conclude from the theory that desorption of gas as far as curve (a) will not occur on cooling, that values considerably higher than those of curve (a) will be obtained and that these values will *approximate* to but will, in general, be somewhat lower than those for true equilibrium in the process (b) at the temperature in question.

(5) **Effect of Varying Adsorbent.**—Variation in the nature of the adsorbent with a given adsorbate will yield variations in the adsorption dependent on the values of Q_a , Q_b , E_a and E_b for the system in question. The discussion may be simplified if we assume that with every adsorbent the value of E_a is negligibly small. A variation in the value of E_b from case to case will involve a variation in the temperature at which the transition from adsorption along curve (a) to that along curve (b) occurs. For low values of E_b the transition will occur at low temperatures and may even result in the absence of all evidence of a transition. If E_b attains high values the transition will take place only at elevated temperatures. With a wide range of adsorbents these extremes of transition may be expected in practice.

(6) **Effect of Concentration of Adsorbate.**—The effect of increasing concentration of adsorbable gas may be indicated by again assuming that E_a is small and that the adsorption complex $S(X_2)$ is an intermediate stage in the formation of the second type of adsorption. The rate of the second stage will, therefore, be determined by the concentration of $S(X_2)$ and the activation energy E_b . The gas striking the surface will form initially complexes of type (a). Without the necessary activation energy, the molecules will re-evaporate. With increasing gas pressure the number of molecules striking the surface increases and, therefore, the probability of a collision with the necessary activation energy present at the place of collision will increase. The adsorption complex formed will become increasingly of the type (b). While this behavior will not be exhibited by the form of the adsorption isotherm it may be deduced from the values for the heat of adsorption (see below) at various equilibrium pressures.

(7) **Effect of Non-Uniform Surface.**—In actual practice adsorption studies are not made with uniform surfaces but with surfaces of varied activity. This reveals itself in the case of a single process of adsorption by a steadily falling value for the heat of adsorption. The adsorptions involving high heats of adsorption occur first and are succeeded by processes with lower and lower heat of adsorption. This factor introduces a constantly varying Q into the equations determining the evaporation process. Were the E factor constant, the effect of this falling Q would be to increase the rate of evaporation by increase in the term $e^{-(Q + E)/RT}$. There is

reason to believe, however, from analogy with the activation energy of chemical reactions at surfaces,⁶ that the activation energy of adsorption processes should become larger and larger the less active the surface area. This increase in E with surface covered would tend, therefore, to offset to some extent the effect of diminishing Q .

In the case discussed in the preceding section where the extent of adsorption according to type (b) increases with increasing partial pressure of the gas, it is evident that the heat of adsorption-pressure (or amount of adsorbed gas) curve might show two descending sections corresponding mainly to types (a) and (b) with an intermediate section of transition values between. Such a possibility is shown diagrammatically in Fig. 2. It is also evident that, with suitable values for the activation energies and heats of adsorption, the preliminary fall in the first portion of the curve might be eliminated, leaving a curve showing a maximum. With low values for both E_a and E_b or, alternatively, at high temperatures, the curve would be entirely of the (b) type and show continuously falling values.

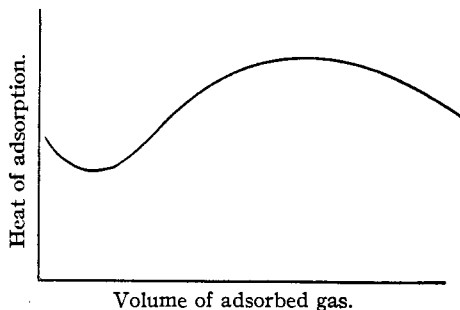


Fig. 2.—Variation of heat of adsorption with amount adsorbed for two adsorption processes having different activation energies.

(8) **Heat of Adsorption and Temperature.**—When, owing to a high value of E_b or the low temperature of operation, the adsorption is purely of type (a), the heats of adsorption measured will be characteristic of the adsorption process (a) and the extent of the surface covered. At high temperatures, where process (b) predominates, the heats of adsorption would in the same way be characteristic of that process. For this reason one can deduce a change in heats of adsorption with temperature. Since adsorption of the type (a) is the low temperature, non-specific, non-activated type, we can in general expect low heats of adsorption Q_a . For the specific adsorption involving activation and activation energy of adsorption, with the operation of valence forces at the surface, we should in general expect somewhat higher values for Q_b , of the order of magnitude familiar in chemical processes. It must be remembered, however, that since, for example, the activation process may involve in the case of a diatomic molecule a dissociation of the molecule into atoms, there is always the possibility of Q_b becoming a small magnitude.⁷ At intermediate tempera-

⁶ Taylor, *Z. Elektrochem.*, 35, 542 (1929); "Treatise on Physical Chemistry," Vol. II, D. Van Nostrand Co., New York, 1931, 2d ed., Chap. XV, pp. 1081-1086.

⁷ Compare, for example, the chemical reaction $N_2 + O_2 = 2NO$; the net heat of

tures where both adsorptions are involved, values intermediate to Q_a and Q_b would be obtained. It is also to be remembered in this connection, as already emphasized in the preceding section, that the Q value obtained under a given set of conditions is also a function of the nature of the surface covered, highest with the most active areas, whether the adsorption is of the (a) or (b) type.

(9) **Extent of Saturation of a Non-Uniform Surface.**—From the preceding discussion it will be evident that, on a non-uniform surface, it can readily follow that the combined operation of the Q and E values may result in a set of conditions such that only on a fraction of the surface may the activating adsorption (b) occur. If the temperature be such that adsorption of the type (a) is negligibly small, it would follow that the adsorption isotherms obtained would show all the characteristics of saturation with, however, only a small fraction of the surface covered with adsorbed gas. Such a condition would be of first importance in those chemical reactions at surfaces where activation was a condition precedent to reaction.

(10) **The Temperature Coefficient of Surface Reactions and the Concept of Activation Energy of Adsorption.**—It is well known that, in surface reactions, the observed activation energy of the chemical reaction is identical with the true activation energy only in exceptional circumstances (actually, in the so-called zero order reactions). For other reactions the observed and true activation energies are related to one another by equations which involve also the heats of adsorption of the reactants and products. Thus, as has been indicated⁸ by Polanyi⁹ and Hinshelwood,¹⁰ for a unimolecular process involving decomposition of a substance A, the true energy of activation of the reaction (E_t) is related to the observed value E_o by the equation

$$E_o = E_t - Q_A \quad (1)$$

where Q_A is the heat of adsorption of the substance A. For a similar process involving retardation by a reaction product B the relation is

$$E_o = E_t - Q_A + Q_B \quad (2)$$

where Q_B is the heat of adsorption of the reaction product B.

As pointed out by Hinshelwood, these equations presuppose that the establishment of adsorption equilibrium is rapid in comparison with any disturbance of it due to the removal of the molecule in chemical change. When, however, owing to the operation of an activation energy term, E , the rate of adsorption leading to activation is very materially decreased, this reaction is -43 kg. calories, as it involves the heat of dissociation of nitrogen and oxygen molecules, respectively, 200 and 120 kg. calories.

⁸ For a general treatment of this subject see Taylor, "Treatise on Physical Chemistry," 2d ed., D. Van Nostrand Co., New York, 1931, Vol. II, Chap. XV, p. 1081.

⁹ Polanyi, *Z. Elektrochem.*, 27, 143 (1921).

¹⁰ Hinshelwood, "Kinetics of Chemical Change," 2d ed., Oxford University Press, Oxford, 1929, Chap. VIII, p. 232.

condition may no longer hold and the equations derived will be inapplicable. This consideration applies to both Equations 1 and 2 above.

(11) **Velocity of Evaporation and Adsorption of Molecules.**—It has been customary hitherto in treating the velocity of evaporation of adsorbed molecules to assume its proportionality to $e^{-Q/RT}$ where Q was the heat of adsorption. This is only true so long as the activation energy of the adsorption process is negligibly small. The correct expression for the evaporation process involves $e^{-(E+Q)/RT}$; it is evident that cases might arise in which great differences in the velocity of evaporation of two adsorbed gases were obtained, even though the Q 's were identical, because the E 's were markedly different. It is also not impossible that, owing to marked differences in the values of E in two cases, the velocity of evaporation in the process with a higher Q value should be more rapid than the velocity of evaporation with the lower Q . In the reverse process of adsorption the same principles apply.

With this review of the general principles involved in the application of the concept of activation energy to adsorption processes accomplished, we may now pass to an examination of experimental data in order to ascertain how far the general conclusions reached in the preceding may find experimental verification. We shall examine data with reference to adsorption processes for such gases as hydrogen, oxygen, carbon monoxide, nitrogen, sulfur dioxide and water vapor on a variety of surfaces. We shall find our theoretical conclusions abundantly verified by practical experience.

Experimental Data and the Concept of Activation Energy of Adsorption

It will be convenient to classify the experimental data with reference to the gas adsorbed, discussing in each case the various adsorbents studied.

Adsorption of Hydrogen.—There are pertinent data for hydrogen adsorption on the catalytically active metals, nickel, copper, platinum, palladium, as well as on charcoal and a few oxide surfaces.

NICKEL.—The most abundant data are available in this case on nickel surfaces. The recent research of Benton and White,¹¹ extending the earlier studies of Gauger and Taylor,¹² provide data for adsorption equilibria over the temperature range -209 to 305° . Benton and White's results show that the activation energies involved are low since the transition (Section (2) of General Theory) from a region of low adsorption to one of high adsorption occurs in the temperature range of -190 to -100° . Above this latter temperature, the activation process is rapid. Benton and White observed different amounts of adsorption at low temperatures according as one operated exclusively at low temperatures or saturated at high temperatures and then cooled down. This checks with the conclu-

¹¹ Benton and White, *THIS JOURNAL*, **52**, 2325 (1930).

¹² Gauger and Taylor, *ibid.*, **45**, 920 (1923).

sions of Section (4) in the General Theory. The increased adsorption obtained by cooling to -191° over that observed at 0° will be in part due to increased adsorption of the activated adsorbate in passing through the metastable region plus any additional hydrogen adsorbed with the low activation energy.

Benton and White's data on the velocity with which equilibrium is attained also conform to the requirements of the present theory. At the temperatures of -183 and -191° , "the pressure became constant almost immediately after admitting the gas;" at these temperatures we have type (a) adsorption with low values of E_a . In the higher¹³ temperature range equilibrium was fairly rapidly established at very low pressures, slowly at moderate pressures and somewhat less slowly at higher pressures. These are consistent with an adsorption involving an activation energy as set forth earlier in Sections (6) and (11). Gauger and Taylor had earlier noted that an interval of ten minutes was insufficient at room temperatures and upward to establish equilibrium and that isotherms thus obtained were different from those obtained by de-sorbing gas from the surface. The work of Gauger and Taylor also showed the effect discussed in Section (9) of the varying extent of surface covered, with apparent saturation, at different temperatures.

An increase in the heat of adsorption with increase of surface covered has been shown in Section (8) to be a possible consequence of adsorption processes involving activation energy. Such an increase was demonstrated by Fryling¹⁴ in the case of active nickel catalysts. In other cases with less active adsorbents this phenomenon was absent in the measurements at 0° . In all cases at this temperature the heats of adsorption were high (ca. 15,000 cal.) as compared with those involving only van der Waals forces.

One can summarize, therefore, the case of nickel-hydrogen by observing that it conforms closely to the conditions imposed by the general theory. In the system metal-hydrogen this constitutes the best investigated case. With other metals the data are scantier and, to economize space, they will only be recorded in bare outline.

PLATINUM.—Platinum shows the phenomenon of *diminishing* adsorption with decreasing temperature as noted with nickel above.¹⁵ Apparently, the decreased absorption sets in at a higher temperature than in the case of nickel since de Hemptinne records diminished adsorption at -78° , whereas the decrease with nickel occurred below -110° . G. B. Taylor, Kistiakowsky and Perry¹⁶ record high heats of adsorption at 0° of the order of 10,-

¹³ We cannot explain why the equilibrium below -191° was slowly established unless it was due to the experimental difficulty of maintaining constant temperature.

¹⁴ Fryling, *J. Phys. Chem.*, **29**, 1235 (1925).

¹⁵ De Hemptinne, *Z. physik. Chem.*, **27**, 429 (1898).

¹⁶ G. B. Taylor, Kistiakowsky and Perry, *J. Phys. Chem.*, **34**, 799 (1930).

000-30,000 calories. A determination of the heat of adsorption in the low temperature range would be revealing. On the present thesis it should be much lower than the values at 0° .

PALLADIUM.—De Hemptinne records a higher absorption of hydrogen by palladium at -78° than at 0° . On the other hand, there is excellent experimental evidence by Firth¹⁷ that massive palladium foil will not take up hydrogen at liquid-air temperatures. Palladium saturated with hydrogen at ordinary temperatures did not evolve this gas on cooling to liquid-air temperatures. In a later communication, Firth¹⁸ compares the absorption of palladium black samples which have been either (a) saturated at 110° with hydrogen and then cooled in hydrogen to the temperature of measurement or (b) have been saturated with hydrogen only at the temperature in question. In both cases there is a decrease in absorption with increase of temperature from liquid-air temperatures upward. Prior saturation at 110° always gave the higher values. The curve (b) shows a pronounced *minimum* around 20° , which indicates that an activation sets in around this temperature, leading to the increased adsorption represented by the difference in values of curves (a) and (b). A similar minimum sorption has also been found by Gutbier, Gebhardt and Ottenstein.¹⁹ In the case of palladium conditions are complicated by the high solubility of the gas in the metal. This point will be treated subsequently in a special paragraph. There appear to be no data on heats of adsorption.

COPPER.—There is no evidence in the published data of adsorptions on copper similar to that cited in the preceding cases. Through the courtesy of Dr. R. N. Pease, however, some unpublished data by C. A. Harris may be quoted to the same effect.²⁰ On a particular sample of active copper, Harris found a pronounced maximum in the adsorption of hydrogen on copper between 0 and 100° . At 56.5° and 760 mm. pressure the adsorption was 35% greater than at 0° . At 100 and 155° the adsorption was slightly greater than at 0° but less again at 193° . There is also good evidence in this work that by saturating at higher temperatures and then returning to 0° the adsorptions recorded could be increased many-fold (cf. Section (4)). These latter results should be accepted with reserve since the adsorbed hydrogen was not recovered from the surface after the experiment. There is, however, every reason to believe that such results are quite sound and in accord with those already recorded. That such is the case is emphasized by the knowledge that Taylor and Kistiakowsky²¹ found a pronounced

¹⁷ Firth, *J. Chem. Soc.*, 117, 171 (1920).

¹⁸ Firth, *ibid.*, 119, 1120 (1921).

¹⁹ Gutbier, Gebhardt and Ottenstein, *Ber.*, 46, 1453 (1913).

²⁰ Master's Thesis, University of Virginia, 1924.

²¹ Taylor and Kistiakowsky, *Z. physik. Chem.*, 125, 341 (1927).

maximum in the curve for the heat of adsorption of hydrogen on an active copper catalyst. Some unpublished data by Washburn also indicate an activation energy for the hydrogen adsorption. Although the heat of adsorption is only 10,000 calories as compared with 15,000 calories for ethylene, it is a familiar experimental fact that it is easier to remove this adsorbed ethylene from the surface than it is to remove hydrogen (cf. the discussion of carbon monoxide on platinum later).

The evidence cited in this case would indicate that the activation energy necessary in the case of the copper-hydrogen system is markedly higher than with nickel, platinum and palladium.

CARBON.—There is indirect evidence that, with carbon, activation occurs at even lower temperatures than with nickel and palladium. At -78° and at liquid air temperatures²² the adsorption of hydrogen on charcoal is very much greater than at 0° , and greatest at the lowest temperature. Above -200° , therefore, there is no evidence of diminishing adsorption. There is, however, indirect evidence that even at liquid hydrogen temperatures adsorbed hydrogen is at any rate in part activated. Bonhoeffer and Harteck²³ showed that charcoal is an excellent catalyst for the conversion of ortho- to para-hydrogen at these low temperatures. There is good reason to believe that this interconversion of the two forms must occur through the atomic state, which, therefore, must be present at the surface.²⁴ If so, the activation energy of the adsorption process must indeed be small. It is pertinent to point out that the data presented above for nickel, platinum and palladium provide the reason for the inefficiency of these metals in the para-hydrogen conversion at liquid-air temperatures and lower, whereas they are good catalysts for the reconversion process at room temperatures. This peculiar behavior puzzled both Bonhoeffer and Harteck, who believed, however, that it might be due to some "triviale Ursache." Measurements of the heats of adsorption over a range of temperatures and pressures would be instructive in respect to the matters here raised.

OXIDE CATALYSTS.—It is known that series of oxides are efficient agents for hydrogenation-dehydrogenation processes and that these operate normally in a higher temperature range than the metal hydrogenation catalysts. On this basis one might anticipate that the phenomena discussed concerning adsorption by the metals in the low temperature range might be repeated with the oxide catalysts in a higher temperature range. Evidence is accumulating that this is true.

²² Dewar, *Proc. Roy. Inst.*, **18**, 437 (1906).

²³ Bonhoeffer and Harteck, *Z. physik. Chem.*, **4B**, 113 (1929).

²⁴ The conversion of ortho- to para-hydrogen involves a change of the nuclear spin of one hydrogen atom. According to present accepted ideas this can only occur by a definite exchange of atoms. Cf. Farkas, *Z. Elektrochem.*, **36**, 782 (1930).

Garner and Kingman have recently reported²⁵ that hydrogen (or carbon monoxide) adsorbed at low pressures and room temperature on ZnO-Cr₂O₃ catalysts was given off at 100–120°, but after twenty to thirty minutes was re-adsorbed on the surface of the catalysts. This is precisely what is expected from a high temperature adsorption with high activation energy. Indeed, this concept of activation energy requires the evaporation and re-absorption as two independent processes, a phenomenon which appeared to Garner and Kingman as "curious." It is in accord with the experience of Taylor and Kistiakowsky²⁶ with zinc oxide and with zinc-chromium oxide catalysts which showed that desorption only occurs rapidly by evacuation above 300°. Further, on zinc-chromium oxides, Kistiakowsky and Flosdorf²⁷ have recently shown the presence of a maximum in the heat of adsorption-pressure curve as with hydrogen on nickel and copper. Garner and Kingman state that the phenomenon they observed with zinc oxide is given by copper oxide.

With hydrogen on manganous oxide some measurements by Williamson at present in progress in this Laboratory have shown a pronounced increase of hydrogen adsorption with temperature. At 0 and 100° negligible amounts of hydrogen are adsorbed. At 184° adsorption can just be demonstrated while at 305° as much as 10 cc. of gas has been adsorbed by the sample in question. Our work shows also that on saturating at the higher temperature and cooling to lower temperatures, complete desorption does not occur. These experiments, therefore, extend the region of transition from one type of adsorption to another, from temperatures below -110° in the case of metals to above 200° in the case of oxides.

Dr. H. N. Alyea has directed my attention to the experiments of Bone and Wheeler²⁸ with quartz at 650° in which it was found that considerable quantities of hydrogen were taken up at this temperature. In view of the preceding examples a renewed investigation with glass and quartz in this region is desirable and is being undertaken by Dr. Alyea. One might observe that it seems doubtful that under the circumstances given the adsorption should be of atomic hydrogen since Langmuir has shown that glass surfaces loaded with atomic hydrogen at liquid-air temperatures readily yield this hydrogen in the molecular form on raising the temperature. The possibility of occlusion or solution of the gas in the preceding cases will receive separate discussion at a later stage.

Adsorption of Oxygen.—The data on oxygen adsorption which are of interest in respect to activation energy concern such varied surfaces as carbon, silver, gold, nickel, tungsten and platinum.

²⁵ Garner and Kingman, *Nature*, 126, 352 (1930).

²⁶ Taylor and Kistiakowsky, *THIS JOURNAL*, 49, 2468 (1927).

²⁷ Kistiakowsky and Flosdorf, *J. Phys. Chem.*, 34, 1907 (1930).

²⁸ Bone and Wheeler, *Phil. Trans. Roy. Soc.*, 206A, 1 (1906).

CARBON.—It has long been recognized that the adsorption of oxygen on carbon did not obey the simple general theory of adsorption at solid surfaces but no satisfactory treatment of the subject has hitherto been available. It may now be shown that the adsorption consists of more than one type and that activation energy is involved. There does not appear to be any evidence of an increase of adsorption with increase of temperature. There is definite evidence, however, of two types of adsorption similar to those discussed in the general theoretical portion of this paper. Dewar²⁹ showed that the oxygen adsorbed by charcoal at -185° was given off on heating to room temperature. Lowry and Hulett showed³⁰ with a given char that of the oxygen which saturated the sample at room temperatures, not more than 50% was recoverable as oxygen on evacuation. The residue could only be recovered as carbon oxides. The extent of oxygen fixation was a function of the char. Rhead and Wheeler showed that the oxygen retained by charcoal³¹ at temperatures of 200° and upward could not be recovered as oxygen at all, only as carbon oxides. The influence of temperature on the fixation or activation process is evident not only from these several researches but also from the experimental data of Rhead and Wheeler in the temperature range of $300-600^{\circ}$.

The data for heats of adsorption on charcoal are also illuminating. At -185° Dewar obtained a value of 3744 calories per mole. At higher temperatures the principal data have been obtained by Garner and his co-workers³² and by Keyes and Marshall.³³ The data of the latter showed a heat of adsorption at 0° of 72,000 calories per mole. More recently Marshall and Bramston-Cook show values falling from 89,600 calories at nearly zero concentration to 70,000 calories, at which value it flattens prior to the normal fall. The data of Garner and his colleagues all agree in indicating very low values on the earlier portions of the curve with values rising subsequently to a maximum and then a falling curve, as in the experiments with hydrogen on nickel, copper and zinc-chromium oxides. Whatever the ultimate explanation of these experimental discrepancies may be,³⁴ is immaterial to the present discussion. It is sufficient to

²⁹ Dewar, *Proc. Roy. Soc. (London)*, **74**, 126 (1904); *Proc. Roy. Inst.*, **18**, 184 (1905).

³⁰ Lowry and Hulett, *THIS JOURNAL*, **42**, 1408 (1920).

³¹ Rhead and Wheeler, *J. Chem. Soc.*, 101, 831 (1912); 103, 461 (1913).

³² Blench and Garner, *J. Chem. Soc.*, **125**, 1288 (1924); Garner and McKie, *ibid.*, 2451 (1927); McKie, *ibid.*, 2870 (1928); Cameron, *Trans. Faraday Soc.*, **26**, 239 (1930).

³³ Keyes and Marshall, *THIS JOURNAL*, **49**, 156 (1927); Marshall and Bramston-Cook, *ibid.*, **51**, 2019 (1929).

³⁴ See Bull and Garner, *Nature*, **124**, 409 (1929). The simplest explanation would seem to be that the divergencies were due to the difference in methods employed. The ice calorimeter permits longer time intervals for the measurement during which time the activation process may have occurred, the high heat value being thereby obtained. The Garner method operates on shorter time intervals and so adsorption without activation is probably the major process whose heat effect was measured.

record the existence of rising heats of adsorption in yet another case of abnormal adsorption of a gas at a solid surface. On extending their measurements to high temperatures, Blench and Garner obtained heats of adsorption as high as 227,000 calories. The extraordinary increase in the heat data from liquid-air temperatures to high temperatures is striking evidence of a plurality of processes in the fixation of oxygen by charcoal.

SILVER.—Adsorption experiments by Benton and Elgin, with oxygen on silver,³⁵ are in excellent agreement with the concept of activation energy. Their measurements indicate an increasing adsorption in the region 26–110° and a great slowness in attaining equilibrium. At 110° a period of twenty-four hours was required before a constant value of 14.84 cc. adsorption was attained. The adsorption was rapid in the first stages but after the addition of each successive quantity a gradual and long-continued pressure decrease occurred. Furthermore, only a very small fraction of the total amount adsorbed could be recovered by evacuation. It would be interesting to extend such measurements to very low temperatures to see how low in temperature this irreversibility extends. A measurement of heats of adsorption over the same temperature range should also be instructive. In this same investigation the authors record an immeasurably small adsorption of hydrogen at 26 and 110°. Measurements with this gas above and below this temperature range would be instructive, especially since silver is known to possess a certain small activity as a hydrogenation–dehydrogenation catalyst.

GOLD.—Experiments by the same authors, with oxygen on gold,³⁶ are compelling evidence in support of adsorption with an activation energy. The authors find that “at about 650 mm. pressure the gold took up 3.57 cc. at 98°, 4.78 cc. at 130° and 5.73 cc. at 157°.” Measurements were continued at a temperature of 130° for forty-eight hours after apparent equilibrium had been reached without altering the above value. Without removing the oxygen the temperature was raised to 157° and the system allowed to come to equilibrium, which also was the same as before. The temperature was then lowered to 130°. Although this temperature was maintained for eighty hours, no decrease occurred in the amount of gas adsorbed. This is convincing proof that it is the activation energy of the process which is determining the extent of adsorption at any temperature. Benton and Elgin observe that at 130° approximately twenty-four hours are required for attainment of apparent equilibrium, one hundred eight hours at 98°.³⁷ At 25° an adsorption of only 0.1 cc. had occurred in seven

³⁵ Benton and Elgin, *THIS JOURNAL*, **43**, 3027 (1926). This and the example next discussed were called to my attention by my colleague, Dr. J. C. Elgin.

³⁶ Benton and Elgin, *ibid.*, **49**, 2426 (1927).

³⁷ If one uses these times as a rough measure of reaction velocity at the two temperatures one obtains by insertion in the equation $d \ln k/dt = E/RT^2$ the value of $E =$

hours of contact. They further demonstrate that the rate of adsorption is nearly independent of the gas pressure, which indicates that the activation energy is supplied to adsorbed gas and hence by the surface. The rates of adsorption with gold were pronouncedly slower than with silver. The oxygen adsorbed at 130° was not recoverable by evacuation. Experiments at very low and at higher temperatures would be of great interest both with respect to adsorption, reversibility and heat of adsorption. On the gold sample, a scarcely measurable adsorption of hydrogen occurred at 130° . The study of higher temperatures should be of interest.

NICKEL.—A similar condition apparently holds with an active nickel surface but at somewhat lower temperatures. Russell³⁸ has recently found that oxygen is strongly, irreversibly and rapidly adsorbed by nickel in an ice-bath. The heat evolution is of the order of 100,000 calories per mole adsorbed.

Experiments with oxygen and nickel at liquid air temperatures are to be undertaken by Dr. Russell at the writer's request.

TUNGSTEN.—The retention of oxygen by clean tungsten filaments was demonstrated by Langmuir, who also showed that the stability of the oxide film was so great that no interaction with hydrogen occurred up to 1500°K . The film may be formed at room temperatures but its properties are somewhat different from that produced by heating the filament in oxygen at low partial pressures at about 1900°K . for a few seconds.³⁹ From its behavior toward cesium under these conditions there is reason to believe that the oxygen taken up at 1900°K . is then probably held as negative oxygen ions. The heat of adsorption of this oxygen has been estimated by Langmuir to be 160,000 calories per gram atom.⁴⁰ Dr. S. Dushman has kindly consented to ascertain whether this strong affinity between tungsten and oxygen manifests itself at liquid-air temperatures. Langmuir believes that oxygen may be adsorbed on tungsten surfaces in at least three different forms.

PLATINUM.—Langmuir similarly showed that oxygen was held tenaciously by platinum and could be removed by reaction with hydrogen. Recent experiments⁴¹ have shown that the heat of adsorption may be as high as 163,000 calories per mole of oxygen adsorbed and that values in the neighborhood of 100,000 are usual. The adsorption process is fairly rapid 13,830 calories. To this value must be added the activation energy of the molecular absorption process since this influences the concentration of molecules at the surface at the two temperatures. The data, therefore, suggest in this case an activation energy of around 15,000 calories.

³⁸ Personal communication by Dr. W. W. Russell of Brown University, Providence, Rhode Island.

³⁹ Langmuir and Kingdon, *Phys. Rev.*, **24**, 570 (1924).

⁴⁰ Langmuir, Lecture at Princeton University, September, 1929.

⁴¹ G. B. Taylor, Kistiakowsky and Perry, *J. Phys. Chem.*, **34**, 799 (1930).

at 0° but detailed experiments at lower temperatures have not yet been performed. Langmuir states⁴² that in some earlier work he observed that platinum at liquid-air temperatures took up a certain amount of oxygen. On warming the system some oxygen was evolved, but at higher temperatures this same oxygen was once more reabsorbed. This experimental fact indicates a change in the state of oxygen absorption between liquid air and room temperatures.

Adsorption of Carbon Monoxide.—Experimental evidence in support of the concept of activation energy of adsorption processes is available also in the adsorption of carbon monoxide by nickel, copper, platinum and palladium.

NICKEL.—Carbon monoxide in contact with nickel shows strikingly the function of temperature in the adsorption process. At ordinary temperatures, as is well known, carbon monoxide and nickel react to form nickel carbonyl. At 180° this reaction is suppressed and a truly reversible adsorption of carbon monoxide occurs.⁴³ At about 270° the carbon monoxide begins to be irreversibly adsorbed and a portion remains in contact with the surface on evacuation. It is this carbon monoxide which reacts with hydrogen to yield methane and water, or with other carbon monoxide gas to yield carbon dioxide and carbon. We might suggest that at this temperature the atoms of carbon monoxide are now attached to the nickel surface directly as Ni₃C and NiO. Indeed experimental evidence indicates the presence of nickel carbide as an intermediate stage in methane synthesis.⁴⁴ It is this last process, whatever its nature, that involves the high activation energy. Further, it can be demonstrated that this process of activation only occurs at 270° on the most active portions of the nickel surface since relatively small amounts of sulfur compounds poison the surface for the methane reaction. In this case, therefore, we have an experimental example of the case discussed in Section (9) of the general theory in which only a small fraction of the total surface is capable of effecting the activation in question.

COPPER.—On copper surfaces carbon monoxide showed a curve for heat of adsorption as a function of surface covered which first fell, then rose to a maximum and then once more showed falling values.²¹ This is the case discussed in Section (7) of the general theory and illustrated in Fig. 2. It constitutes good evidence of a dual nature of the adsorption process on copper. The heats of adsorption measured were of the order of 10,000–20,000 calories. No evidence as to rising adsorptions over a temperature range has been located in the literature but a study of the region below 0° would be of interest. It is known that no such activation of the carbon

⁴² Personal communication.

⁴³ Taylor and Burns, *THIS JOURNAL*, 43, 1283 (1921).

⁴⁴ Bahr and Bahr, *Ber.*, 61B, 2177, 2465 (1928).

monoxide molecule occurs on copper as takes place on nickel at 300°. Even up to higher temperatures no decomposition of carbon monoxide to carbon dioxide and carbon occurs on copper nor can methane be produced under ordinary conditions with copper. One may thus conclude that the activation energy of this latter adsorption on copper is very high indeed.

PLATINUM.—De Hemptinne records a less adsorption of carbon monoxide on platinum at -78° than at $+15^{\circ}$. Taylor and Burns found smaller values at 25° than at 110° . It is well known that the reversibility of carbon monoxide adsorption on platinum is slight.⁴⁶ G. B. Taylor, Kistiakowsky and Perry obtained measured values of the heat of adsorption with as much as 21.7 cc. of adsorbed gas with heats of adsorption greater than 20,000 calories per mole. Of this only 0.7 cc. was removed by degassing at 350° . The significance of this is apparent when we find that on the same catalyst 5 cc. of hydrogen with heats of adsorption greater than 20,000 calories can be removed by degassing at 250° for four hours. Such results obviously suggested to the authors that "the true rate of evaporation from the surface must be influenced by other factors besides the heat of adsorption to a very considerable degree." The authors showed that differences in the rates of diffusion are too small to account for the observed phenomena, this being the reverse of the observation by Benton and Elgin cited above concerning oxygen on gold, namely, that the gas pressure was without influence on the rate of adsorption. It follows that in the case of carbon monoxide adsorption on platinum the activation energy of the adsorption process must be higher than that of hydrogen.

PALLADIUM.—De Hemptinne found an increase in carbon monoxide adsorption between -78 and $+15^{\circ}$. Taylor and Burns found no change between 25 and 110° .

OXIDE CATALYSTS.—We have already referred to the observation of Garner and Kingman that carbon monoxide adsorbed on $ZnO-Cr_2O_3$ surfaces at room temperature was first evolved on heating to 110° and then reabsorbed after twenty to thirty minutes. This is direct evidence of adsorption having an activation energy. The same conclusion is abundantly evident from the comprehensive paper by Benton¹ on the adsorption of gases by oxide catalysts. His data on the extent of "primary" and "secondary" adsorptions of carbon monoxide, their variation with temperature and pressure are all excellent material for a demonstration that the so-called "primary" adsorption is a process involving a high activation energy compared with that of the "secondary" adsorption. Indeed one might inquire how, without this concept of activation energy, one is to account for the fact that "secondary" adsorption, involving the weaker forces of adsorption, occurs at -78° in preference to "primary" adsorption which only becomes important at higher temperatures but in which the

⁴⁶ Langmuir, *THIS JOURNAL*, 40, 1361 (1918).

forces of adsorption are stronger. It is evident that secondary and primary adsorptions are in reality processes with low and with larger activation energies. None of Benton's data show an intermediate temperature range of increasing adsorption, a factor which is evidently to be attributed to the relative positions of curves (a) and (b) of Fig. 1 in these cases. Benton observes, however, that the carbon monoxide could be much more easily removed after a measurement at -79° than at 0° .

Adsorption of Nitrogen.—Adsorption of nitrogen with activation is of obvious importance in ammonia synthesis. The recent work of Frankenburg and Mayrhofer on iron surfaces laid down by condensation of iron vapor⁴⁶ along with ice or sodium chloride molecules on glass was successful in demonstrating a stoichiometric ratio Fe:H₂ of 1:1 for hydrogen adsorption. No similar adsorption of nitrogen could be detected although there were slight indications of a nitrogen adsorption if hydrogen was also present. This suggested to the authors that thermal activation of the nitrogen is also necessary. That such activation leads to nitrogen fixation on the iron surface at least in the presence of hydrogen is evident from the fact that in the dissociation of ammonia streaming over heated iron relatively large amounts of nitrogen are continuously present on the surface. It follows then, from the principle of "microscopic reversibility" or "entire equilibrium," that a nitrogen-hydrogen mixture passed over iron will lead to a fixation of nitrogen on the surface. In this case also, therefore, we are led to postulate activation energy of the adsorption process.

Adsorption of Water Vapor.—From what has preceded it is evident that we may expect dual processes of adsorption of water vapor on such surfaces as are active in hydration and dehydration processes, and hence on such surfaces as alumina, thoria and the like. This does not seem to have been directly tested. There is, however, one very instructive if indefinite piece of evidence that such dual activation occurs. Dohse and Kälberer⁴⁷ found that the decomposition of isopropyl alcohol on bauxite was a unimolecular reaction, inhibited by the product water and having an apparent activation energy of 39,000 calories. The true activation energy of the process, obtained from a study of the zero order reaction by constant removal of the water vapor or by investigation at low surface concentrations, gave a value of 26,000 calories. For a unimolecular process inhibited by a product, water, we saw in Section (10) of the general theory that the Polanyi-Hinshelwood equation gives

$$E_{\text{obs.}} = E_{\text{true}} - \lambda_{\text{C}_3\text{H}_7\text{OH}} + \lambda_{\text{H}_2\text{O}}$$

For low surface concentrations Dohse and Kälberer actually measured the heats of adsorption, finding $\lambda_{\text{C}_3\text{H}_7\text{OH}}$ to be 21,000 calories and $\lambda_{\text{H}_2\text{O}} = 13,000$ calories. From the equation, then, we have

⁴⁶ Frankenburg and Mayrhofer, *Z. Elektrochem.*, **35**, 590 (1929).

⁴⁷ Dohse and Kälberer, *Z. physik. Chem.*, **5B**, 131 (1929).

$$E_{\text{true}} = 39,000 + 21,000 - 13,000 = 47,000 \text{ calories}$$

in obvious disagreement with the value of 26,000 calories found for the uninhibited zero order reaction. This discrepancy is even more conspicuous when we note that water vapor with a measured heat of adsorption of 13,000 calories is inhibiting the decomposition of isopropyl alcohol with a measured adsorption heat of 21,000 calories. This shows that the heat of adsorption is no simple measure of the rate of evaporation, an additional example, therefore, of the point raised in Section (11) of the general theory and in the case of platinum-carbon monoxide adsorption. To account satisfactorily for inhibition by water in the present case we are forced to assume an activation energy of the order of at least 22,000 calories greater than that of isopropyl alcohol. Such a divergence would bring both types of experimental result into agreement.⁴⁸

Adsorption of Sulfur Dioxide.—**PLATINUM.**—The data already cited with respect to reversibility in the adsorption of hydrogen and carbon monoxide on platinum may be supplemented by the case of sulfur dioxide. G. B. Taylor, Kistiakowsky and Perry showed that of 6.5 cc. of gas held with heats larger than 20,000 calories only 3.5 cc. is removed by degassing at 350°, whereas more than 5 cc. of hydrogen with heats greater than 20,000 calories could be removed at 250°. On another sample of platinum, sulfur dioxide with heats smaller than 20,000 calories could not be removed at 250° whereas, with hydrogen of higher heats of adsorption, removal was readily accomplished. It is thus necessary to postulate a high heat of activation for the adsorption of sulfur dioxide on platinum.

General Conclusions

It has been suggested that the slow process, requiring an activation energy, might be a solution process in the material and that the slowness of diffusion to the interior of the adsorbent was the rate-determining factor. The presence of palladium, in the list of examples cited, at once suggests this possibility. It ought to be emphasized, however, that this cannot be the general explanation. In many of the cases here dealt with the quantities of gas involved are of several orders higher magnitude than the known solubility of the gas in the substance concerned. The surface factor, too, is paramount in the cases we have been considering, whereas this factor is not of such importance where solubility is concerned. The variation of adsorption with pressure is not that to be expected on the basis of solubility.

It is obvious that the concept of activation energy for adsorption processes here developed is of great importance in the general problem of reactivity at surfaces. It is evident at once that adsorption *per se* need

⁴⁸ There is the additional possibility that, at the reaction temperature, the heat of adsorption of water is markedly greater than that recorded above. This would require a smaller spread between the activation energies.

not be related to catalytic activity. There should be, however, a closer concordance between reactivity and the adsorption processes occurring with marked activation energy. Limitations of space prevent such a discussion in this place but opportunity to treat this problem separately will be taken at a later date.

Summary

A general theory of adsorption involving several forms of adsorption at surfaces has been shown to lead to a number of conclusions capable of experimental verification. It has been shown, from abundant data in the literature, that these conclusions are already experimentally verified. It seems necessary, therefore, to abandon entirely the assumption implicit in older theories that the processes of adsorption are rapid. The assumption that all processes of adsorption possess their own characteristic activation energies permits a single general treatment of adsorption inclusive of processes which hitherto have been considered separate and unrelated. It has been shown that the only essential distinction between "secondary" and "primary" adsorptions or between "reversible" and "irreversible" adsorptions is that "secondary" or reversible adsorption processes are adsorptions normally with small heats of adsorption and small activation energies and that in the so-called "primary" or "irreversible" adsorptions, moderate or large energies of activation are involved, frequently with high heats of adsorption. The velocities of these latter processes may indeed be extremely slow. In general, it is the adsorptions with the higher energies of activation which are important in catalytic change.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF COLUMBIA UNIVERSITY
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THE QUINHYDRONE ELECTRODE. II

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. Introduction

While there have been a number of papers which included work more or less directly related to the effect of oxygen on the potential and to the use of nitrogen in the preparation of the quinhydrone half cell, we are not aware of any study having been made of the reproducibility of the electrode possible under conditions of preparation and use which excluded oxygen in acid solution. It is the object of this paper, then, to present the results of such a study made in 0.1 *N* hydrochloric acid and to compare the reproducibility of the quinhydrone electrodes prepared with nitrogen with those obtained with air and upon which we have previously reported.¹

¹ Morgan, Lammert and Campbell, *THIS JOURNAL*, 53, 454 (1931).