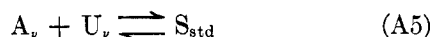


where  $C$  denotes the total concentration of  $A_\nu$  and also of  $U_\nu$  in the solution in which the  $(A + U)_\nu$  molecule is considered to be present. Had the reaction



been the only one to occur, the fraction  $\Theta_{\text{std}}$  of  $A_\nu$  or  $U_\nu$  strands in the form of  $S_{\text{std}}$  would obey the relation

$$-RT \ln [\Theta_{\text{std}}/(1 - \Theta_{\text{std}})^2] = \mu^0(S_{\text{std}}) - \mu^0(A_\nu) - \mu^0(U_\nu) - RT \ln C \quad (\text{A6})$$

Let the standard state  $S_{\text{std}}$  be chosen as that microscopic state where the first  $\nu_0$  ( $1 \leq \nu_0 \ll \nu$ ) nucleotide pairs are bonded and all the rest non-bonded.<sup>32</sup> For given values of  $\nu_0$  and  $C$ ,  $\Theta_{\text{std}}$  is expected to have some finite value, almost independent of  $\nu$ . (A rough estimate of the values of  $\Theta_{\text{std}}$  corresponding to different

values of  $\nu_0$  and  $C$  should be obtainable from experiments with  $A_{\nu_0}$  and  $U_{\nu_0}$  oligomers.) Hence, for sufficiently large values of  $\nu$ , the right-hand side of eq A4 becomes negligibly small, and in the limit of  $\nu \rightarrow \infty$

$$\Delta\mu^{(\infty)} = -RT \lim_{\nu \rightarrow \infty} \nu^{-1} \ln Z^{(\nu)} \quad (\text{A7})$$

This limiting value [or rather  $\exp(-\Delta\mu^{(\infty)}/RT)$ ] is evaluated by the statistical thermodynamic treatments for a *model* molecule where only a certain type of microscopic states is assumed to exist and where simplifying, though plausible assumptions are made about the mathematical structure of the statistical weights.<sup>25</sup>

(32) With this choice, the degree of ionization of the standard state will be practically equal to the sum of degrees of ionization of the separated strands.

## Hydrogen Sorption by Alumina at Low Pressures

by M. J. D. Low and E. S. Argano

*School of Chemistry, Rutgers, The State University, New Brunswick, New Jersey (Received March 8, 1966)*

The sorption of hydrogen by  $\gamma$ -alumina powder was measured from  $-193$  to  $663^\circ$  at pressures from about  $10^{-4}$  to  $10^{-8}$  torr. A flow system was used. Hydrogen sorption increased with increasing degassing temperature until, after a  $950^\circ$  pumping, the reproducibility was about 5%. Some dissociative chemisorption occurs over the entire temperature range studied. Physical adsorption predominates below  $200^\circ$ . The maximum chemisorption occurs near  $300^\circ$ . The mechanism is discussed.

The high surface area forms of alumina have found extensive use of heterogeneous catalysis, and a voluminous literature on alumina and alumina-containing catalysts has developed. To this have been added, in recent years, the results of many investigations designed to clarify the catalytic process by studying the structure and properties of pure alumina surfaces by a variety of instrumental techniques. Yet, one of the simplest reactions, the sorption of hydrogen by alumina surfaces, seems to have been neglected. The hydrogen-deuterium exchange catalyzed by alumina has been

studied,<sup>1-6</sup> as have the reaction of surface hydroxyls on alumina with gaseous deuterium<sup>7,8</sup> and the ortho-

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(7) M. J. D. Low, J. Courtois, and N. Ramasubramanian, unpublished results.

parahydrogen conversion.<sup>6</sup> Some indirect knowledge of the hydrogen-alumina interaction is thus available. However, direct studies of hydrogen adsorption by alumina appear to be few in number and limited in extent.<sup>9-13</sup> As such information should aid our understanding of alumina surfaces, we have measured the hydrogen sorption on  $\gamma$ -alumina from  $-193$  to  $663^\circ$ . Highly degassed surfaces were used and, as previous work had been done at pressures above about 1 torr, hydrogen sorption was measured at pressures ranging from about  $10^{-4}$  to about  $10^{-8}$  torr, using a flow system.

### Experimental Section

The dynamic flow method and apparatus of Wagener,<sup>14</sup> as modified for work on W and Ba films,<sup>15-17</sup> was used. The adsorption system was constructed of Pyrex glass with the exception of the sample chamber, which was of Vycor. The sorption system itself was enclosed in a movable oven, shown in Figure 1 by the area enclosed by dotted lines. The Vycor sample chamber could be heated with an auxiliary furnace. The sorption system consisted of a pair of inverted Bayard-Alpert ionization gauges used to monitor pressures, a capillary with a fixed conductance of  $22.4 \text{ cm}^3 \text{ sec}^{-1}$ , the Vycor sample chamber, and a Granville-Phillips ultrahigh vacuum valve, P. Hydrogen from a storage bulb (or, deuterium) was purified by diffusion through the walls of a palladium thimble and entered the system through an adjustable needle valve E (Edwards High Vacuum Ltd.), passing through two liquid nitrogen-cooled traps. The pressure was reduced by means of a three-stage oil diffusion pump using Corning 704 fluid, backed by a high-volume mechanical vacuum pump. The ionization gauges had iridium filaments and, in order to avoid spurious pumping effects, the low filament temperature of  $950^\circ$  was used, below the temperature of about  $1200^\circ$  at which the dissociation of hydrogen molecules to atoms proceeds. The ionization current used was kept low at 1 ma. The adsorbent used was 0.2 g of Alon-C  $\gamma$ -alumina<sup>18</sup> having an initial nitrogen BET surface area of  $102 \text{ m}^2/\text{g}$ .

The measuring procedure was as follows. After baking the system at  $450^\circ$  and outgassing the ionization gauges, using normal ultrahigh vacuum procedures, pressures below  $10^{-9}$  torr were reached when liquid nitrogen was added to the upper trap. After closing valve P, hydrogen was introduced through valve E until the desired pressure  $P_s$  on the sample was reached. The speed of uptake  $V$  was then calculated from the pressure drop using the relation

$$V = (P_m - P_s)F$$

where  $V$  is in units of  $\text{cm}^3 \text{ torr sec}^{-1}$  ( $1 \text{ cm}^3 \text{ torr} = 0.00132 \text{ ml STP}$ ),  $P_m$  is the pressure in the manifold in torr,  $P_s$  is the pressure in the sample space in torr, and  $F$  is the capillary conductance in  $\text{cm}^3 \text{ sec}^{-1}$ . After recording the initial speed of adsorption, the pressure  $P_s$  in the sample vessel was maintained constant by decreasing the hydrogen flow through the valve E so that  $P_m$  decreased until, at the end of the experiment,  $P_m = P_s$ . The amount of hydrogen taken up was calculated by the graphical integration of velocity-time plots. As the hydrogen sorption was estimated to be seven orders of magnitude larger than hydrogen diffusion through the walls of the Vycor sample chamber, errors due to this diffusion were negligible. When measurements were done at different temperatures, the  $P_s$  value was corrected in order to keep collision frequency at the adsorbent surface constant, by using the relation  $(P_1/P_2) = (T_2/T_1)^{1/2}$ , derived from the kinetic theory of gases.

### Experiments and Results

Some difficulty was initially experienced in obtaining reproducible results. As it is impossible to free an alumina surface of residual OH groups completely even at  $1000^\circ$ ,<sup>19</sup> this was not unexpected. Some results of the effects of degassing temperature on the hydrogen sorption are shown in Figure 2. The amount of hydrogen taken up by the alumina at room temperature at  $7 \times 10^{-7}$  torr increased with increasing outgassing temperatures. The higher the temperature, however, the relatively smaller the effect became. The results became more reproducible with increasing outgassing temperature, shown, for example, by the results of Figure 3. Hydrogen sorption was measured at  $27^\circ$  at a pressure  $P_s$  of  $7.2 \times 10^{-7}$  torr for each experiment. Prior to each experiment the system was outgassed for 21 hr at  $450^\circ$  and the adsorbent for 18 hr at  $850^\circ$  and for 3 hr at  $950^\circ$  to a residual pressure below  $1 \times$

(8) J. L. Carter, P. J. Lucchesi, P. Corneil, D. J. C. Yates, and J. H. Sinfelt, *J. Phys. Chem.*, **69**, 3070 (1965).

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(15) A. G. Nasini, F. Ricca, and G. Saini, *Vacuum*, **10**, 68 (1960).

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(18) G. Cabot Corp., Boston, Mass.

(19) J. B. Peri, *J. Phys. Chem.*, **69**, 711 (1965).

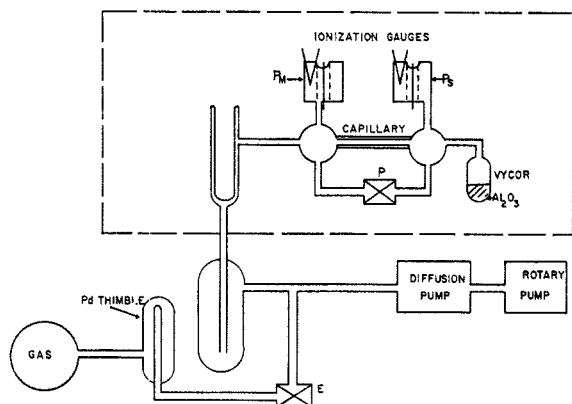


Figure 1. Ultrahigh vacuum system.

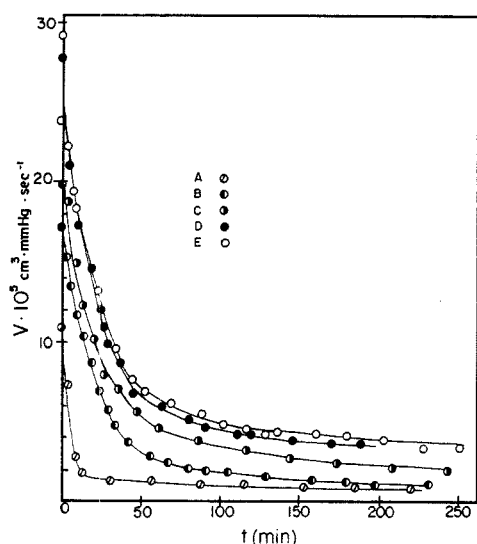


Figure 2. Effect of outgassing temperature (hydrogen sorption at 27° at constant pressure of  $7.2 \times 10^{-7}$  torr): (A) 650° for 20 hr, residual pressure  $6 \times 10^{-7}$  torr with system hot,  $1 \times 10^{-9}$  torr after cooling; (B) 750° for 18 hr, residual pressure  $4 \times 10^{-8}$  torr with system hot,  $1 \times 10^{-9}$  torr after cooling; (C) 850° for 18 hr, residual pressure  $2 \times 10^{-7}$  torr with system hot,  $1 \times 10^{-9}$  torr after cooling; (D) 850° for 50 hr, residual pressure  $1.5 \times 10^{-7}$  torr with system hot,  $1 \times 10^{-9}$  torr after cooling; (E) 850° for 18 hr and 950° for 3 hr, residual pressure  $<10^{-7}$  torr with system hot,  $<10^{-9}$  torr after cooling.

$10^{-7}$  torr with the system hot. The pressure fell to below  $1 \times 10^{-9}$  torr when the system was cooled. The data agree within about 5% for the first three consecutive experiments and within about 10% for all five experiments shown. A small change in the activity of the alumina surface occurred. This may be connected with the sintering of the alumina to some extent. At the end of the experiments the surface area of the alumina had decreased by 25%. This sintering, although causing a not negligible diminution

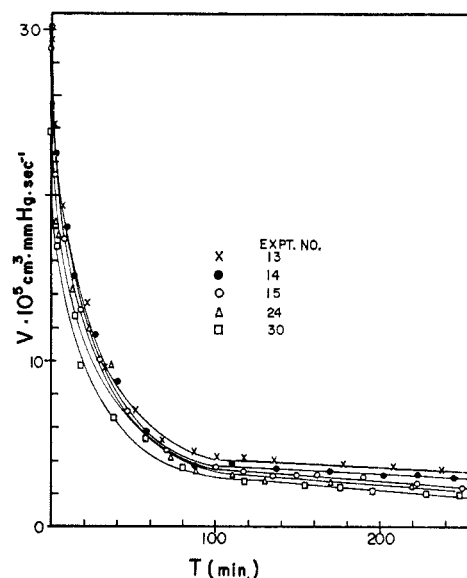


Figure 3. Sorption reproducibility (hydrogen sorption at 27°,  $P_s = 7.2 \times 10^{-7}$  torr): outgassing, 18 hr at 850° plus 3 hr at 950°; residual pressure of  $<10^{-9}$  torr in the cool system.

of the surface, appears to be of minor importance to the hydrogen sorption because only small changes in rates and amounts of hydrogen taken up were observed. The degassing of the adsorbent for 18 hr at 850° plus 3 hr at 950° was used prior to all other experiments.

The results of a series of experiments performed at 27° but at different pressures are shown in Figure 4. A slope of  $0.54 \approx 0.5$  was found for a plot of the logarithm of the initial hydrogen adsorption rate  $V_0$  vs. the logarithm of  $P_s$  for the range  $1.8 \times 10^{-8}$  to  $7.5 \times 10^{-5}$  torr. The initial part of the uptake thus obeys the relation

$$V_0 = kP^{1/2}$$

The total amount of hydrogen adsorbed,  $q_T$ , at pressures from  $3 \times 10^{-7}$  to  $5 \times 10^{-5}$  torr at 27° is shown in Figure 5. The Freundlich relation

$$q_T = AP^k$$

holds with the parameter  $k$  having the value 0.09. Russell and Stokes<sup>11</sup> found the value  $k = 0.25$  at much higher pressures.

The results of various experiments at different temperatures at  $P_s = 7 \times 10^{-7}$  torr are shown in Figures 6–8. Figure 6 shows the change in the sorption velocity  $V$  with the total amount sorbed,  $q$ , at different temperatures. The decrease in  $q$  with increasing temperature is similar to the effect reported by others working at higher pressures.<sup>11,12</sup> The curves at the

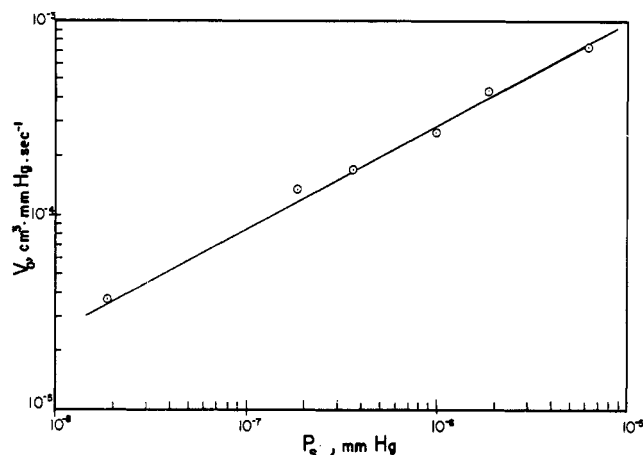


Figure 4. Pressure effect: pressure dependence of the initial rate of hydrogen sorption,  $V_0$ , at 27°.

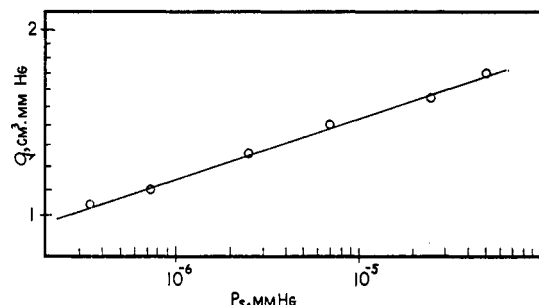


Figure 5. Pressure effect: pressure dependence of the total amount of hydrogen adsorbed,  $q_T$ , at 27°.

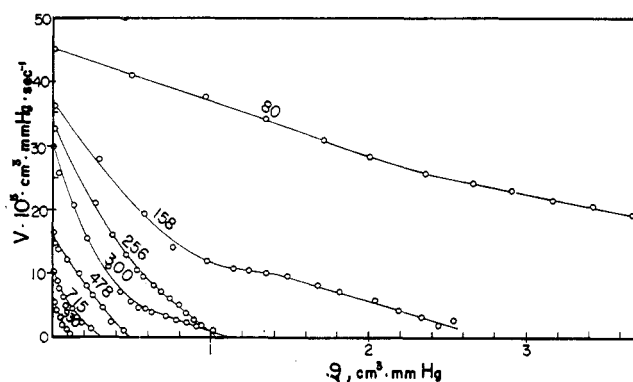


Figure 6. Effect of temperature ( $P_s = 7 \times 10^{-7}$  torr). The number next to each plot is the temperature in °K.

higher temperatures show a rapid decline in velocity with increasing amounts of sorption. At the lowest temperature the velocity decrease is nearly constant during the sorption. Some of these results are replotted in Figure 7. The plot of the total amounts sorbed, shown as open circles, *vs.* the temperature

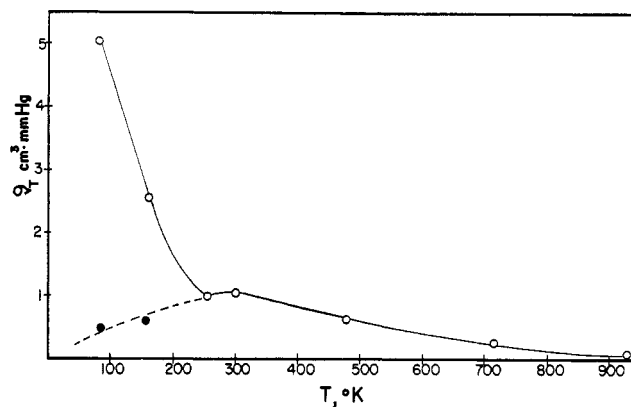


Figure 7. Sorption isobar.

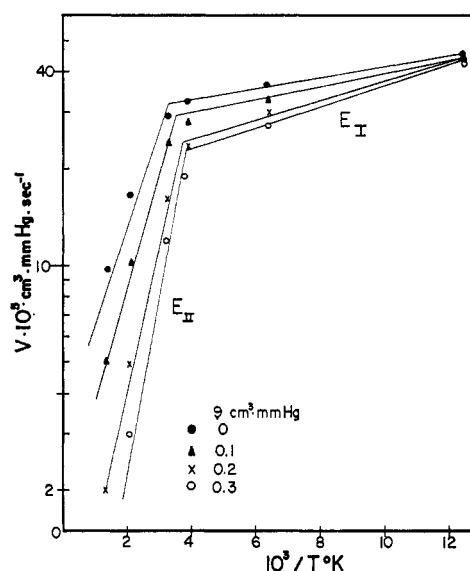


Figure 8. Activation energy.

constitutes an isobar. It indicates that two over-all processes are involved in the hydrogen sorption over the temperature range investigated. The voluminous sorption below about  $-70^\circ$  is attributed predominantly to the physical adsorption of molecular hydrogen.

At the end of the sorption of each of the two experiments at the lowest temperatures, the valve P of Figure 1 was opened so that the system could be pumped out readily and valve E was closed. The sample was then degassed for 4 hr at the temperature at which the sorption occurred. The sample was then warmed to  $27^\circ$ , and the amount of hydrogen that was desorbed was measured. Those amounts are shown as filled circles in Figure 7. As physically adsorbed hydrogen is weakly bound, it can reasonably be assumed that all or, at least, most of the physically adsorbed hydrogen was removed by the low-temperature pumping. The

residual gas desorbed at 27° was more tightly bound to the surface, and can be ascribed to chemisorption. The region in Figure 7 indicated by the broken line thus can be ascribed to chemisorption. This indicates that chemisorption occurs over the entire temperature range. The existence of one maximum in the vicinity of 27° indicates that only one type of chemisorption is involved.

From the absolute reaction rate theory, the sorption speed can be expressed by

$$N = Qf(\Theta) \exp[E(\Theta)/RT]$$

where  $N$  is the number of molecules taken up per unit time,  $Q$  is a frequency factor,  $f(\Theta)$  is a fraction of the number of sites available for sorption, and  $\exp[E(\Theta)/RT]$  is a temperature factor. That expression can be approximated by the relation

$$V = K \exp[E(\Theta)/RT]$$

where  $V$  is the speed of sorption in  $\text{cm}^3 \text{ mm sec}^{-1}$ , and  $K$  is a constant. The values of  $E$  calculated for various  $q$  values using the plots of Figure 8 are given in Table I. The existence of two processes in two separate temperature regions is indicated. The low-temperature process with negligible  $E$  is again ascribed to the physical adsorption of molecular hydrogen. The high-temperature process with an  $E$  value varying from 1.25 to 4.27 kcal/mole is ascribed to chemisorption. As there is a chemisorption contribution to the low-temperature sorption at temperatures below the maximum near 27° shown in Figure 7, this may contribute to the small variation of  $E$  of the over-all low-temperature sorption.

Table I:  $E$  as a Function of Coverage<sup>a</sup>

$q, \text{cm}^3 \text{ mm}$	0	0.1	0.2	0.3
$E_I, \text{cal mole}^{-1}$	80	118	150	200
$E_{II}, \text{cal mole}^{-1}$	1250	1850	2540	4270

<sup>a</sup> The segments  $E_I$  or  $E_{II}$  of the plots of Figure 8 were used to derive values of the energies  $E_I$  or  $E_{II}$ .

The kinetics of the sorption process was unusual in that the widely used Elovich equation<sup>20</sup> was not applicable. It was not possible to fit the kinetic data to an expression of the type

$$q = k_1 \log(t + t_0) + k_2$$

by choosing a suitable value of  $t_0$  in order to linearize the plot, sigmoidal curves being obtained. This suggests that it is not likely that any of the mecha-

nisms proposed to account for Elovichian kinetics would make a significant contribution to the sorption mechanism. It was, however, possible to express the data by an equation

$$q_t = q_T[1 - \exp(-ct^n)]$$

where  $q_t$  and  $q_T$  are the amounts adsorbed at time  $t$  and at the end of the adsorption. Figure 9 shows that, for data in the temperature region where chemisorption occurs, the fit according to this last equation is good. The fit is poor for the data at the lowest two temperatures, where physical adsorption predominates. The values for the parameters  $n$  and  $c$  are given in Table II. For chemisorption, the  $n$  values can be taken to be constant with an average value of 0.80, differing by about 3%. The  $c$  values for chemisorption are taken constant at 0.44. Different values can be calculated for the linear portions of the two low-temperature plots.

Table II: Hydrogen Sorption Kinetics

Temp, °K	$n$	$c$
80	1.01	0.43
158	0.96	0.43
256	0.81	0.440
277	0.827	0.438
478	0.77	0.443
715	0.787	0.442

Information on the rate-determining step in a process may frequently be obtained by experiments involving the use of different isotopes. Consequently, some sorption experiments were made with deuterium at -193, 207, and 442° under conditions identical with those made with hydrogen. It was found that the differences between sorption speeds and amounts sorbed for corresponding hydrogen and deuterium experiments fell within the limits of the error encountered with reproducibility, *i.e.*, there was some scatter between corresponding hydrogen and deuterium values, without any specific pattern. Or, the sorptions of hydrogen and deuterium were identical within experimental error, so that either the isotope effect is entirely absent, or it is smaller than about 5%. The complete absence of an isotope effect cannot be claimed, but the effect, if present, is at least an order of magnitude smaller than the predicted value of  $2^{1/2}$ .

Values of the sticking probability (St.P.), the ratio

(20) M. J. D. Low, *Chem. Rev.*, **60**, 262 (1960).

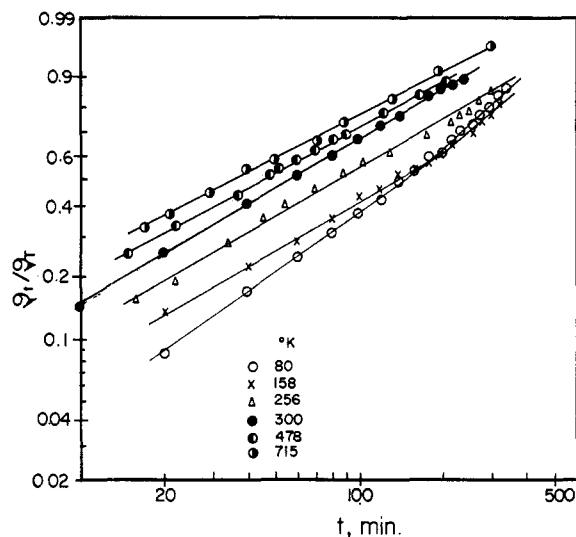


Figure 9. Lateral spreading kinetics. Rate data used to obtain the curves of Figure 6 were recalculated using the lateral spreading equation and are shown as Weibull probability plots.<sup>46</sup>

between the number of molecules taken up and the number striking the surface, can be calculated from<sup>17</sup>

$$\text{St.P.} = \frac{V(MT)^{1/2}(3.74 \times 10^{16})}{P_A(3.51 \times 10^{22})S}$$

where  $V$  is the sorption velocity in  $\text{cm}^3 \text{ torr sec}^{-1}$ ,  $M$  is the mass of the hydrogen molecule,  $P_A$  is the pressure on the surface,  $T$  is in  $^\circ\text{K}$ , and  $S$  is the surface area in  $\text{cm}^2$ . The calculated sticking probabilities for  $V_0$  vary from  $2 \times 10^{-12}$  to  $7 \times 10^{-12}$  over the temperature range from 427 to  $-193^\circ$ . These values are considerably smaller than those found with metals; *e.g.*, for nitrogen sorption on tungsten the sticking probabilities varied from 0.55 to 0.1.<sup>21,22</sup> Such low values indicate that collisions with the surface are extremely inefficient in causing sorption, and that most of the surface is inactive for sorption. This is also shown by estimates of the extent to which the surface is covered by adsorbed hydrogen. For 0.2 g of  $\text{Al}_2\text{O}_3$  having a surface area of  $77 \text{ m}^2/\text{g}$ , using the values of the total amount adsorbed at the various temperatures, the summary shown in Table III results. The number of sites occupied per  $1000 \text{ \AA}^2$  and the fraction of the total surface covered,  $\Theta$ , were computed on the basis of close packing of one hydrogen atom bound to each available surface  $\text{O}^{2-}$  ion. A value of  $8 \text{ \AA}^2$  was taken for the area of such an adsorption site.<sup>19</sup> The extent to which the surface is covered is quite small.

### Discussion

During the course of this work the kinetic data were obtained after very low residual pressures had been

Table III: Surface Coverage

Temp, $^\circ\text{K}$	$q_T$ ( $27^\circ$ ), $\text{cm}^3$ mm	No. of occupied sites/ $1000 \text{ \AA}^2$	$10^3\Theta$
80	5.04	0.85	1.69
158	2.28	0.38	3.6
256	1	0.17	0.32
300	1.1	0.185	0.37
478	0.5	0.0845	0.14
715	0.244	0.0412	0.11
936	0.11	0.0185	0.05

reached. This was done in order to obtain "clean" and stable surfaces and also to reduce as much as possible any uncertainty caused by the adsorption of  $\text{H}_2\text{O}$  and  $\text{CO}_2$  always present in any low-pressure system as residual gases. In the case of oxides, however, the problem of surface cleaning is not as simple as that found with metals, where rigorously clean surface conditions can be established by the generation of a clean surface by evaporation, the flashing of a ribbon, and the like. In the case of alumina, where a complex and heterogeneous surface exists, problems arise in terms of high-temperature stability, sintering, and particularly of residual surface hydroxyl groups. The latter are probably involved in an equilibrium,  $\text{H}_2\text{O} + \text{O}^{2-} \rightleftharpoons 2\text{OH}^-$ , with residual gaseous  $\text{H}_2\text{O}$ , this accounting predominantly for the temperature dependence of the residual pressures observed during outgassing experiments such as those of Figure 2. The amount of residual gases taken up by the surface on cooling to room temperature after high-temperature degassing was small, being of the order of 0.1% of the total amount of hydrogen sorbed at  $-193^\circ$ . Variations in gettering of this type may be responsible for some of the scatter observed, as in Figure 3, if the reproducibility depends on the establishment of identical equilibrium pressures. The extent of poisoning effects by this means cannot be assessed. The hydrogen sorption became more voluminous with increasing severity of degassing conditions, but the enhancing effect became smaller the higher the degassing temperature. In similar fashion, the dehydroxylation of alumina becomes more complete, but at a declining rate, with increasing severity of degassing.<sup>19</sup> This indicates that the removal of surface hydroxyl groups makes sites available for hydrogen chemisorption. It was found,<sup>7</sup> during a study of the surface of Alon-C aluminum by infrared spectroscopic techniques, that small increases

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(22) J. Eisinger, *ibid.*, **28**, 169 (1957); **30**, 412 (1957).

in the intensities of hydroxyl and deuterioxyl bands occurred on exposure of the alumina to hydrogen and deuterium. Evidence for a net formation of deuterioxyl groups over and above that due to exchange was also reported in a similar study of the exchange of deuterium with the hydroxyl groups of a different alumina.<sup>8</sup> Dissociative chemisorption is thus tied to the formation of surface hydroxyls, at least to some extent. However, the sticking probabilities were decreased and  $E$  values increased by very small amounts of adsorbate, so that the chemisorption was "self-poisoning." Also, the degree of surface coverage was low, the number of sites occupied being much smaller than the number of available surface oxide ions, assuming that every adsorbed hydrogen atom formed one hydroxyl group. Random reaction of hydrogen with surface oxide groups to form hydroxyls, replacing those destroyed during degassing, can then be ruled out, and sites of a special nature become necessary.

Dehydrated alumina surfaces have been considered to be strained,<sup>23,24</sup> active sites being identified with strained oxide linkages,<sup>25,26</sup> cation vacancies,<sup>27,28</sup> anion vacancies and exposed aluminum ions,<sup>29</sup> cation vacancies that have captured protons,<sup>30</sup> and anion-cation vacancy pairs.<sup>31</sup> The very complicated nature of the surface has been discussed in detail by Peri.<sup>19,32,33</sup> Pines and Ravoire<sup>4</sup> proposed the heterolytic dissociation of hydrogen or deuterium for the exchange reaction, so that hydride or deuteride adsorbed on an incompletely coordinated aluminum ion while protons and deuterons adsorbed preferentially on surface oxide ions. Acres, Eley, and Trillo<sup>6</sup> similarly suggested that groups of at least two adjacent free valencies are necessary for chemical dissociation of the hydrogen molecule, and Peri suggested paired sites for ammonia adsorption.<sup>33</sup> A variety of mechanisms is thus available. However, it is pertinent to note that the similarity of hydrogen and deuterium chemisorptions indicates that the rate-determining step in the chemisorption is not affected by the mass of the adsorbate.

Previously, the absence of the expected isotope effect with  $\text{ZnO} \cdot \text{Cr}_2\text{O}_3$ , Ni-kieselguhr, and  $\text{Cr}_2\text{O}_3$  led Pace and Taylor to suggest that the activation energy of the adsorption process is required by the solid adsorbent.<sup>34</sup> This idea was further developed by Boudart and Taylor<sup>35</sup> and, on the basis of more sensitive measurements with ZnO, by Parravano, Friedrich, and Boudart;<sup>36</sup> the absence of an isotope effect eliminates chemical bombardment-dissociation and also surface diffusion mechanisms for the ZnO case, the slow step being one not involving hydrogen as a molecule or adsorbed fragment but the generation of an active site. Alternately, Kesavulu and Taylor<sup>37</sup> pointed out

that these and other effects with ZnO could be explained in terms of a surface step involving an electron transfer and hence not requiring an isotope effect. A similar electronic step may be invoked for the case of alumina. The mechanism, however, is complicated by the nature of the chemisorption kinetics.

A double-logarithmic representation of chemisorption kinetics seems to have been first used by Maxted and Moon<sup>38</sup> to describe the adsorption of hydrogen and of deuterium by platinum, but has been generally neglected. The equation used above has been proposed for the lateral spreading of oxide films on metals,<sup>39-42</sup> the mechanism involving the diffusion of adsorbate away from surface adsorption sites. This model leads to a value of 2 for  $n$  for a surface having a fixed number of sites, and to a value of 3 for  $n$  for the case of site creation during adsorption.<sup>41,42</sup> Experimental values of  $n$  are smaller than unity, as shown in Table III and elsewhere,<sup>38,43-46</sup> indicating that the model is either entirely wrong or that modifications are needed.

In either case, the nature of the adsorption site is speculative. If the lateral spreading mechanism is rejected, then an electronic step is required. A possible

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mechanism involves the heterolytic dissociation on a dual site consisting of an incompletely coordinated aluminum ion and another component such as a surface oxide ion, this involving what is essentially a partial reduction of the aluminum ion. The subsequent oxidation of that ion could then be the rate-determining step. This is not necessary if a modified spreading mechanism is accepted, but then the surface diffusion of an entity other than a hydrogen atom or ion is re-

quired. This could involve OH and OD species, the mass difference then not giving rise to an appreciable isotope effect. The low-temperature surface migration of hydroxyls appears unlikely, but cannot be ruled out.

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## Ion Association of Magnesium Sulfate in Water at 25°

by Gordon Atkinson and Sergio Petrucci

*Department of Chemistry, University of Maryland, College Park, Maryland (Received March 15, 1966)*

The ultrasonic absorption of aqueous  $\text{MgSO}_4$  solutions has been measured at 25° over the frequency range 5–255 Mc. Two relaxations are found in this range. These together with the lower relaxation previously measured by others allow a complete analysis of the relaxation data in terms of the Eigen three-step association mechanism. The rate constants and equilibrium constant for the first and fastest step are consistent with a diffusion-controlled process of the two hydrated ions. The slower steps presumably depend on the rate of exchange of solvent molecules on the anion and cation of the ion pair.

The problem of ion association, formulated in the classical theories of Bjerrum<sup>1</sup> and Fuoss,<sup>2</sup> has attracted chemists for many years. Experimental studies of ion association by many different techniques appear regularly in the scientific literature. Two recent monographs<sup>3,4</sup> have summarized the present status of the theory and the experimental progress so far achieved. The constant interest in ion association derives both from its fundamental importance in solution theory and from its practical importance in such widely different fields as live polymer growth<sup>5</sup> and biochemistry.<sup>6</sup>

Fuoss in his monograph on conductance<sup>7</sup> proposes a mechanism for ion association based on the sphere-in-a-continuum model of the Debye-Hückel-Onsager theory. In his theory the ions are assumed to be spheres of radius  $a = R$  where  $R$  is the hydrodynamic radius. These spheres are hydrodynamically rigid

and conform to the Stokes model<sup>8</sup> but upon ion pairing undergo loss of solvent until the ionic center-to-center distance equals  $a$ . It was clear in the picture that the solvent shell around the unassociated ions had a thickness equal to  $a/2$ . This seems in conflict<sup>9</sup> with the

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