157. *Reversible and Irreversible Adsorption of Vapours by Solid Oxides and Hydrated Oxides.**

By J. J. Kipling and D. B. Peakall.

Criteria are put forward for distinguishing between physical and chemical adsorption at room temperature on oxides and hydrated oxides. On a number of such adsorbents most simple organic vapours are adsorbed physically. On alumina, silica gel, and titania gel, water vapour and the vapours of the lower aliphatic alcohols are held by chemisorption if oxide ions are present at the surface. Physical adsorption can occur on the chemisorbed layer. Factors influencing desorption in such systems are discussed.

Although it is possible to define physical adsorption and chemisorption of a vapour by a solid as distinct phenomena, an increasing number of cases is being reported in which it is not immediately obvious which type of adsorption is being observed (see, *e.g.*, Trapnell [1]). Moreover, there appears to be no single experimental measurement which can provide a criterion applicable to all cases. Many authors would like to use the heat of adsorption for this purpose, heats of physical adsorption being usually lower than heats of chemisorption. There are, however, enough exceptions to this general rule for de Boer [2] to suggest that another criterion is desirable. The results for two systems with which this paper is concerned show the limitations of this criterion.

From the data of Rossini *et al.*[3] it can be calculated that the heat of reaction of water vapour with Al_2O_3,H_2O (crystalline form not stated) to give gibbsite is 13·6 kcal./mole of water at 25°, and is 10·9 kcal./mole if the product is amorphous $Al(OH)_3$. As the latent heat is 10·5 kcal./mole, and the expected maximum for the heat of physical adsorption is 14·0 kcal./mole,[1] the observed heat of adsorption of water vapour on activated alumina, 10·7 kcal./mole,[4] does not enable a definite conclusion to be drawn as to whether adsorption is physical or chemical. Similar data are not available for every silica gel which might be used, but an experimental figure of 11·0 kcal./mole of water vapour [4] may be compared with the calculated heat of conversion of quartz into H_4SiO_4 of 9·8 kcal./mole of water.

Superimposed on this is the probability that if a monolayer were chemisorbed, further vapour would, at room temperature, be physically adsorbed. The integral heat of adsorption may therefore be an average of the values for chemisorption and physical adsorption. Differential heats of adsorption would be more informative. Very few are

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* Some aspects of this work were discussed at the Chemical Society Symposium on " Chemisorption " held at the University College of North Staffordshire, Keele, in July, 1956.

[1] Trapnell, " Chemisorption," Butterworths, London, 1955.

[2] de Boer, *Adv. Colloid Sci.*, 1950, **3**, 1.

[3] Rossini, Wagman, Evans, Levine, and Jaffe, National Bureau of Standards, Circular 500, Washington, 1952.

[4] Gregg and Jacobs, *Trans. Faraday Soc.*, 1948, **44**, 574.

recorded in the literature, but it is notable that the isosteric heat of adsorption of water vapour on γ-Al_2O_3 is 105 kcal./mole of water at 1·075% adsorption, though it falls rapidly to 14 kcal./mole at 2·0%. Such very high values are thought to indicate that the water is chemisorbed by a " solid with high energy surface strain condition." [5]

The difficulty of using the heat of adsorption as a criterion for these systems has led us to seek alternatives, and we have found that the following enable a reasonable distinction to be made between the two types of adsorption; they may also have a wider applicability.

1. The desorption process should be thoroughly examined, especially the rate of desorption as a function of time. A physically adsorbed vapour can usually be desorbed readily and completely at the temperature at which it was originally adsorbed. Recently a number of systems has become prominent in which adsorption is mainly physical, but difficulty in removing a small fraction of the adsorbate has led authors to refer to irreversible adsorption and sometimes specifically to chemisorption. Examples include an irreversible hysteresis involving chemisorption in the adsorption of methyl alcohol by silica gel,[6] a slow surface reaction at 100° between *n*-propyl alcohol and ferric oxides,[7] and frequent references to irreversible hysteresis or permanent adsorption at room temperature of water on silica gel [8,9,10] and on alumina.[10] The criterion which we suggest to meet such cases is valuable when it can be applied precisely, as will be considered in the Discussion.

2. The effect of temperature on desorption may be informative. A *small* rise in temperature may leave unaltered the amount of vapour chemisorbed. It will always increase the rate of desorption of physically held vapour.

3. Chemisorption implies that a specific chemical reaction takes place. It may be possible to define this and seek evidence that it occurs as postulated. Thus we have calculated for two solids the amounts of several vapours which could be chemisorbed on them and have obtained values close to those determined experimentally. This is a quantitative advance on the work of Pierce and Rice who examined the specificity of irreversible adsorption of water and of ethyl alcohol on a series of oxides.[11]

We have been concerned mainly with adsorption on different types of alumina and on silica gel, but have also re-examined experimentally some of the cases of adsorption on magnesium oxide and zinc oxide reported by Schreiner and Kemball,[12] though using a different method. Their technique was to determine the adsorption isotherm and then to evacuate the solid with the adsorbed vapour for 15 hr. The volume of vapour which was then needed to complete the monolayer was determined, from which could be calculated the quantity of adsorbed material which remained on the surface after evacuation and which they regarded as " irreversibly adsorbed." In our experimental method, a weighed quantity of adsorbent was saturated with adsorbate and was weighed at intervals during subsequent desorption. This gave a gravimetric record of the extent of desorption and an indication of the rate of desorption at intervals.

DISCUSSION

The Criteria of Irreversibility and of Temperature Effect.—Schreiner and Kemball took as an arbitrary definition of irreversibility failure to clean the adsorbing surface by evacuation at 25° for 15 hr. We have suggested that this criterion is not entirely satisfactory,[13] particularly as they did not indicate whether desorption continued after

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[5] Cornelis, Milliken, Mills, and Oblad, *J. Phys. Chem.*, 1955, **59**, 809.
[6] Avgul, Dzhigit, Kiselev, and Shcherbakova, *Zhur. fiz. Khim.*, 1952, **26**, 977.
[7] Basford, Harkins, and Twiss, *J. Phys. Chem.*, 1954, **58**, 307.
[8] Barratt, Birnie, and Cohen, *J. Amer. Chem. Soc.*, 1940, **62**, 2839.
[9] Sing and Madeley, *J. Appl. Chem.*, 1954, **4**, 365.
[10] Papee, *Compt. rend.*, 1952, **234**, 952, 2536; *Bull. Soc. chim. France*, 1955, 14.
[11] Pearce and Rice, *J. Phys. Chem.*, 1929, **33**, 692.
[12] Schreiner and Kemball, *Trans. Faraday Soc.*, 1953, **49**, 292.
[13] Kipling and Peakall, *Research*, 1955, **8**, S 31.

15 hours' evacuation. Desorption of organic vapours may be much slower than this at room temperature if the adsorbent is appreciably porous, a good example being found in the case of desorption of carbon tetrachloride from charcoal,[14] where only physical adsorption could be involved. [In the original work, desorption was carried out by passing a dry air-stream through a short column of charcoal. We have compared this method with desorption by continuous evacuation of a small sample contained in a flask connected to a high-vacuum pump, and have found that the times required for desorption were essentially the same for this system.] The carbon tetrachloride was not completely removed after 15 hr., and indeed was still being desorbed after 180 hr. (Table 1). It thus seems important in considering irreversibility as a criterion of chemisorption to record the rate of desorption at the time of concluding the experiment.

TABLE 1. *Desorption of carbon tetrachloride from charcoal and carbon black, at* 20°.

Time of desorption (hr.)	Rate of desorption (mg./g./hr.)	Surface still covered (%)
Charcoal * (method *A*)		
5		46·5
	2·7	
24		35·0
	0·8	
48		30·8
	0·6	
96		24·3
	0·4	
120		22·3
	0·4	
180		17·3

Time of desorption (hr.)	Rate of desorption (mg./g./hr.)	Surface still covered (%)
Charcoal (method *B*)		
5		43·9
	1·9	
24		36·0
	0·9	
48		31·2
	0·5	
96		25·5
	0·4	
120		23·4
Spheron 6 (method *A*)		
2		5
	—	
6		3
	—	
24		0

* Complete desorption from the same sample was recorded by method *A* within 24 hours at 60°

In the remaining systems studied, either of the two methods described above has been used, according to convenience. Table 2 shows that with the oxides which we have investigated the results can be divided into three groups : (1) those in which desorption was complete within the time stated, usually 100 hr., (2) those in which desorption was still taking place after that time, and (3) those in which the rate of desorption had fallen below a measurable rate while leaving a substantial quantity of adsorbate still on the surface.

The first group clearly represents reversible physical adsorption only. It will be noted that it includes four systems which appeared to Schreiner and Kemball, on the basis of desorption for a shorter period, to be showing irreversible adsorption (carbon tetrachloride on zinc oxide; acetone, chlorobenzene, and *n*-propylamine on magnesium oxide).

In the second group, desorption was still continuing at the end of the specified period, and the amount of vapour remaining on the surface was small. It seems reasonable to suppose, therefore, that desorption could be completed in a longer time. This was confirmed in most cases by continuing the desorption at 60°, when the remainder of the vapour was quickly removed. This is the behaviour of a system showing physical adsorption, and suggests that the systems in the second group, although exhibiting stronger adsorption than those in the first group, nevertheless are still showing reversible physical adsorption. The treatment at 60° is not comparable to Schreiner and Kemball's evacuation at 410° of the zinc oxide on which carbon tetrachloride had been adsorbed. At such a temperature, pyrolysis of the carbon tetrachloride, either adsorbed or in the gas phase, might well be expected to occur, with possible reaction between the decomposition products and the surface.

In the third group, the quantity of adsorbed material retained (in all cases either an

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[14] Barrow, Danby, Davoud, Hinshelwood, and Staveley, *J.*, 1947, 401.

TABLE 2.

Group 1. (Figures in parentheses give time of contact in days before desorption was started.)

Desorption complete within:	100 hr. (method *A* *)		24 hr. (method *A*)
Adsorbent	Adsorbates	Adsorbent	Adsorbates
Boehmite	C_6H_6(5), *cyclo*-C_6H_{12}(5), $C_2H_4Cl_2$(1)	MgO	CCl_4(1), Me_2CO(1), PhCl(1) Pr^nNH_2(1)
γ-Al_2O_3	C_6H_6(4)		
SiO_2 gel I	C_6H_6(5), *cyclo*-C_6H_{12}(5), $C_2H_4Cl_2$(1)	ZnO	CCl_4(1)
TiO_2 gel	C_6H_6(5), *cyclo*-C_6H_{12}(5), $C_2H_4Cl_2$(5)	Spheron 6	CCl_4(1)

Group 2.

Solid	Vapour	Time of contact (days)	Method of desorpn.* (Time, hr.)	Residual amount adsd. (mmoles/g.)	Final rate of desorpn. (mg./g./hr.)
Boehmite	MeOAc	5 †	*A* (100)	0·37	0·38
,,	,,	5	*B* (100)	0·36	0·23
,,	,,	5	*C* (100)	0·28	0·18
" Gibbsite "-type adsorbent	EtOH	1 †	*A* (100)	0·41	0·4
SiO_2 gel I	MeOAc	5 †	*A* (100)	0·37	0·12
MgO	EtOH	1	*A* (24)	0·031	0·0
,,	,,	7 ‡	*A* (24)	0·031	0·0
ZnO	MeOAc	1 †	*A* (24)	0·003	0·0
,,	Me_2CO	1	*A* (24)	0·007	0·0
,,	EtOH	1 ‡	*A* (24)	0·004	0·0
		Group 3.			
γ-Al_2O_3	MeOH	7	*B* (100)	1·47	0·1
,,	EtOH	7	*B* (100)	0·88	0·1
,,	Bu^nOH	7	*B* (100)	0·71	0·0
,,	H_2O	7	*B* (100)	3·42	0·0
Boehmite	MeOH	1	*B* (100)	1·57	0·1
,,	,,	7	*B* (100)	1·89	0·0
,,	EtOH	1	*B* (100)	0·80	0·1
,,	,,	15	*B* (100)	1·01	0·1
,,	,,	30	*B* (100)	0·98	0·1
,,	,,	1	*C* (100)	0·84	0·1
,,	,,	7	*C* (100)	1·02	0·1
,,	Pr^nOH	7	*B* (100)	0·89	0·1
,,	Bu^nOH	7	*B* (100)	0·87	0·07
,,	H_2O	21	*A* (100)	4·17	0·0
,,	,,	1	*B* (100)	3·36	0·0
,,	,,	7	*B* (100)	4·08	0·0
,,	,,	1	*C* (100)	3·45	0·0
,,	,,	3	*C* (100)	3·75	0·0
SiO_2 gel I	MeOH	1	*B* (100)	0·76	0·1
,,	,,	7	*B* (100)	1·12	0·1
,,	EtOH	1	*B* (100)	0·76	0·1
,,	,,	7	*B* (100)	1·19	0·07
,,	Bu^nOH	7	*B* (100)	1·05	0·06
,,	H_2O	1	*B* (100)	0·78	0·0
,,	,,	7	*B* (100)	1·03	0·0
TiO_2 gel	EtOH	1	*B* (100)	0·65	0·0
,,	,,	7	*B* (100)	0·68	0·0
,,	Bu^nOH	7	*B* (100)	0·69	0·0
,,	H_2O	7	*B* (70)	0·75	0·0
SiO_2 gel II	MeOH	14	*B* (100)	1·70	0·0
,,	EtOH	14	*B* (100)	1·41	0·05
,,	Bu^nOH	14	*B* (100)	1·24	0·03
,,	H_2O	14	*B* (100)	1·83	0·0
MgO	H_2O	7	*A* (100)	10·13	0·0
ZnO	H_2O	7	*A* (50)	0·055	0·0

* See Experimental section for details. † Further desorption (method *A*) occurs at 60°.
‡ No further desorption occurs at 60°.

alcohol or water) was considerable in relation to the surface area of the solid. Moreover, raising the temperature to 60° did not effect further measurable desorption. It is also important to notice that the amount of vapour retained by the surface depended on the time of contact allowed before the commencement of desorption. This suggests that a slow chemical reaction took place when the adsorbate and adsorbent were in contact; it appeared to be completed within 7—14 days. The total adsorbate includes the material chemisorbed, together with further vapour physically adsorbed by the new surface so formed. The physically adsorbed material is, of course, readily desorbed.

The Criterion of Specificity.—(i) *Alumina.* We have previous commented on the significance of alumina in this work, in that substances of composition Al_2O_3, AlO·OH, and $Al(OH)_3$ can be recognised as crystallographically distinct phases, presenting surfaces containing oxide, oxide and hydroxide, and hydroxide ions respectively.[15] The results show that the type of adsorption obtained with these adsorbents is sometimes specifically determined by the nature of the surface.

Chemisorption of a water molecule by an oxide ion would result in formation of two hydroxide ions. We can calculate the extent to which this should occur. The unit cell of γ-Al_2O_3 can be represented as a cube of side 7·84 Å, presenting eight oxide ions at each face.[16] * For a sample of surface area 156 m.²/g. (see Experimental Section), 3·37 mmoles of water can be taken up by the oxide ions in 1 g. of solid. This agrees well with the observed value of 3·43 mmoles/g. Water in excess of this amount is physically adsorbed, which accords with our supposition that the surface is equivalent to that of gibbsite.

de Boer and Houben [18] have found the same adsorption of water for unit surface area of γ-Al_2O_3, using a sample of different total surface area (85 m.²/g.). They have, however, interpreted their results in terms of the conversion of the two outermost layers into AlO,OH, and suggest that water can be physically adsorbed on its surface. This does not agree with our finding that both water and alcohols can be chemisorbed by boehmite, but not by a gibbsite-like surface. The formation of a " surface layer of gibbsite " by reaction of water with corundum (α-Al_2O_3), exactly analogous to the reaction we propose for γ-Al_2O_3, has recently been postulated.[19]

The corresponding calculation for boehmite (γ-AlO,OH) is rather less precise because the AlO·OH " molecule " presents different areas in the three planes of the crystal: 11·2, 10·5, and 17·4 Å² in the *a* (100), *b* (010), and *c* (001) planes respectively [20] (Plate). If we assume that the molecule is equally likely to present each of these faces at the surface of the sample, then three molecules of water are required for every 39·1 Å² of surface, or 3·2 mmoles/g. for a material of surface area 250 m.²/g. The maximum adsorption would occur if the entire surface presented the *b* plane, giving a value of 4·0 mmoles/g.; the minimum (for presentation entirely in the *c* plane) would be 2·4 mmoles/g.

In fact, the commercial material contains rather less " combined water " (actually 16·6% referred to Al_2O_3) than the ideal formula requires (17·5%). This deficiency implies that the material has been slightly over-calcined, giving an excess of oxide ions over the stoicheiometric proportion, which could take up a further 0·5 mmoles of water per g. of solid. The oxide ions, which are likely to have been formed in highest concentration at the surface, may have been replaced, in part, by hydroxide ions migrating from the interior of the granules, but as the manufacturing process presumably terminated a short period after the composition AlO·OH was reached, a substantial proportion of the oxide ions may remain at the surface.

The calculated maximum figure now becomes 4·5 (allowing the maximum surface effect for over-calcining) and the minimum 2·4 mmoles/g. (allowing no surface effect for over-calcining). The experimental value of 4·1 mmoles/g. could represent adsorption to the extent of a monolayer, but could not represent conversion of two layers of oxide into

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* Calculations based on a different unit cell [17] give essentially the same result.

[15] Kipling and Peakall, *J.*, 1956, 4828.

[16] Hagg and Soderholm, *Z. phys. Chem.*, 1935, **29**, *B*, 881; Kordes, *Z. Krist.*, 1935, **91**, 193.

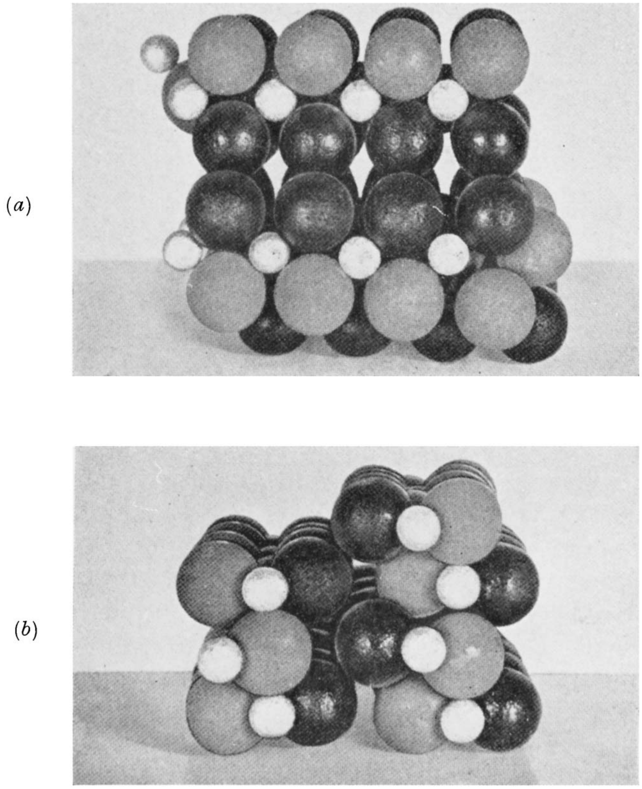
[17] Jellinek and Fankuchen, *Ind. Eng. Chem.*, 1945, **37**, 158.

[18] de Boer and Houben, Proc. International Symposium on the Reactivity of Solids, Gothenburg, 1952.

[19] O'Connor, Johansen, and Buchanan, *Trans. Faraday Soc.*, 1956, **52**, 229.

[20] Reichertz and Yost, *J. Chem. Phys.*, 1946, **14**, 495.

PLATE. *Models of* γ-$\mathrm{AlO{\cdot}OH}$ *crystal showing* (a) *the a plane,* (*b*) *the c plane.*



Black balls, hydroxyl ions; grey balls, oxygen ions; white balls, aluminium ions. (From Technical Paper No. 10 of the Aluminum Company of America, by courtesy of Dr. A. S. Russell.)

[*To face p.* 839.

hydroxide ions. Work on similar oxides [21] suggests that migration from the surface to the interior of the solid is not likely to occur at room temperature at a measurable rate. The most reasonable conclusion, therefore, is that water is chemisorbed at the surface only and that it saturates there all the available oxide ions, giving a surface equivalent to that of gibbsite, γ-Al(OH)$_3$. This accords with the *X*-ray findings of Imelik.[22] The behaviour of boehmite in this respect should be contrasted with that of magnesium oxide which, at room temperature, suffers bulk conversion into the hydroxide.[23]

Our conclusion explains the unexpectedly high adsorption of water by titania coated with alumina which was reported by Harkins and Jura,[24] and their observation that an excessively long time was required for equilibrium to be established. Similarly, the exchange of oxygen-18 between water and both γ-Al_2O_3 and γ-Al_2O_3,H_2O at 100° and below [21] is indicative of the type of chemisorption we have postulated.

The specific adsorption of the alcohols is equally important. In this case the chemisorption might occur at either the oxide or the hydroxide sites. Experimentally it is found with anhydrous alumina and with boehmite, but not with the gibbsite-like surface. We therefore conclude that there is no reaction with the hydroxide groups, the oxide ions only being involved. The reaction with boehmite can then be represented by the equation $\mathrm{AlOH(:O) + EtOH = Al(OEt)(OH)_2}$.

After 100 hr., there is still a slow desorption of ethyl alcohol, though not of water, adsorbed on anhydrous γ-alumina and on boehmite. While it is possible that this represents further desorption of physically adsorbed alcohol, it is much more likely to be due to the decomposition of the chemisorbed alcohol to give ethylene. This reaction has been shown to occur on boehmite at room temperature at a rate which would explain our residual desorption.[25]

Alcohols are chemisorbed on both anhydrous alumina and boehmite to a much smaller extent than is water. This can be understood by considering the size of the alkyl groups relative to the spacings in the surface. Thus a methyl group (of radius 2 Å) adsorbed on one oxygen ion (of radius 1·3 Å [26]) in the γ-Al_2O_3 surface blocks access to the neighbouring oxygen atoms, so that reaction can only occur at every other oxygen atom. For the larger alkyl groups (cross-section 18·4 Å^2 [27]) only one oxygen atom in three is available (Fig. 1). The calculated chemisorption is then as shown in Table 3. The experimental values are lower than those calculated; this could be attributed to the exclusion of the longer-chain molecules from the narrowest pores, or to inefficient packing caused by random adsorption in such a system.[1, 28]

TABLE 3. *Chemisorption by* γ-Al_2O_3 (*mmoles/g.*).

	Water	Methyl alcohol	Ethyl alcohol	*n*-Butyl alcohol
Calculated	3·37	1·68	1·12	1·12
Observed	3·42	1·47	0·88	0·71

The corresponding calculation for boehmite again requires consideration of the three faces individually. By reference to diagrams of the structure [20] or to photographs of models (see Plate),[29] it is possible to estimate semi-quantitatively the number of oxide ions which can take part in chemisorption of each of the four alcohol molecules which we have examined. Thus alkyl groups perpendicular to the surface could, as a maximum, be adsorbed on 1 in every 3 oxide ions in the *a* plane (1 in every 2 for methyl) and on 1 in every 2 in the *c*

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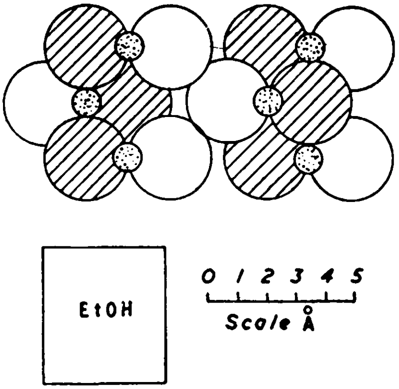
[21] Whalley and Winter, *J.*, 1950, 1175; Mills and Hindin, *J. Amer. Chem. Soc.*, 1950, **72**, 5549.
[22] Imelik, *Compt. rend.*, 1951, **223**, 1284.
[23] Razouk and Mikhail, *J. Phys. Chem.*, 1955, **59**, 636.
[24] Harkins and Jura, *J. Amer. Chem. Soc.*, 1944, **66**, 1366.
[25] Heinemann, Wert, and McCarter, *Ind. Eng. Chem.*, 1949, **41**, 2928.
[26] Pauling, " The Nature of the Chemical Bond," Cornell Univ. Press, New York, 1948.
[27] Kipling, *J. Colloid Sci.*, 1955, **10**, 156.
[28] Langmuir, *J.*, 1940, 511.
[29] Russell, Technical Paper No. 10 of the Aluminum Company of America, Pittsburgh, 1953.

plane. In the *b* plane, the oxide ions are recessed below the level of the hydroxide groups and are inaccessible to the alcohol molecules (Fig. 2), unless considerable distortion takes place. On the assumptions made for adsorption of water this gives a maximum chemisorption of 1·03 mmoles/g. in the general case, and 1·24 mmoles/g. for the smaller methyl alcohol. The experimental figures are again somewhat lower than this, except in the case of methyl alcohol (Table 4).

FIG. 1. *Size of ethyl radical in relation to the ions in the a plane of the* γ-AlO·OH *crystal.*



Open circles, OH$^-$; shaded circles, O^{2-}; dotted circles, Al.

FIG. 2. (*a*) *Face of b plane in* γ-AlO·OH *crystal.* (*b*) *Cross-section through* AB.

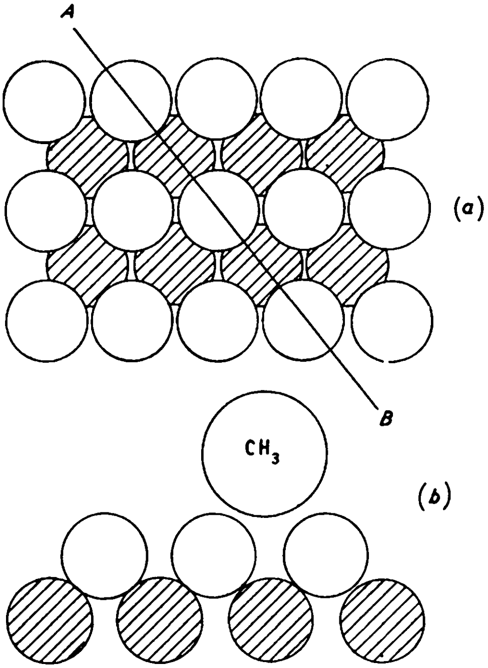


TABLE 4. *Chemisorption on* γ-AlO·OH (*mmoles/g.*).

	Water	Methyl alcohol	Ethyl alcohol	*n*-Butyl alcohol
Calculated	3·70	1·24, 1·85	1·03	1·03
Observed	4·08	1·89	0·98	0·87

It has been suggested that the methyl group in methyl alcohol (but not in any other alcohol) can form hydrogen bonds with oxygen atoms in silicate minerals.[30] The same phenomenon with boehmite might allow adsorption on alternate atoms in the *b* plane, giving a maximum chemisorption of 1·85 mmoles/g., close to the observed value. For the other alcohols the differences between the observed and calculated values are similar to those found for anhydrous alumina and can be explained in the same way. They would, of course, be somewhat larger if the calculated values were based on a model for the surface which would give agreement between the calculated and observed values for water. The precision of these calculations is limited, however, by our inability to allow for such distortions of the crystal lattice as may occur at the surface.

(ii) *Silica gel.* Chemisorption of water by silica gel would also involve conversion of oxide into hydroxide groups. As silica gels have no uniform composition, the number of oxide groups in a given area is uncertain, and thus any calculation of a theoretical adsorption value comparable to that made above is precluded. Nevertheless, our value for chemisorbed water is about the same (*ca.* 2%) as that for the " irreversibly adsorbed "

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[30] MacEwen, *Trans. Faraday Soc.*, 1948, **44**, 349; cf. Bradley, *J. Amer. Chem. Soc.*, 1945, **67**, 975

water observed by Rao,[31] Sing and Madeley,[9] and Papee,[10] and for the water which Kurosaki showed, from changes in the apparent dielectric constant of the gel, to be " firmly bound " to the surface.[32]

These comparisons should not be pressed too far without further data about the various gels used and the times allowed for adsorption. It does seem, however, that in each case chemisorption of the type we suggest explains the observed results and confirms earlier views on the " hydration " of silica gel.[33,34] It also confirms the view [35] that there are limitations in the use of water vapour adsorption isotherms for determining the surface areas of silica gels.[36]

By contrast with boehmite, silica gel can chemisorb as many mols. of ethyl alcohol as of water. Shapiro and Weiss and others [37,38] have shown that most of the " constitutional " water in silica gels is present as hydroxide groups in the surface. The oxide groups are probably present in smaller numbers and may thus be well spaced as compared with those in boehmite. If this is so, the chemisorption of an alcohol molecule by one oxide group should not interfere with chemisorption by any other oxide group, and the numbers of alcohol and of water molecules adsorbed should be equal. This conclusion was tested by heating the original gel to 425° for a time which reduced the " constitutional " water from 4% to 2·5%. The second sample would thus have a higher ratio of oxide to hydroxide groups in the surface, though the specific surface area (as shown by the adsorption of benzene vapour) was unchanged. The second sample chemisorbed fewer millimoles of any alcohol per gram than of water, and again there was a considerable difference in the amounts of methyl and of ethyl alcohols adsorbed. This result confirms the general explanation given in the section on alumina.

(iii) *Titania gel.* Our general results run parallel to those for silica gel. The amount of water chemisorbed is again about the same as that which Rao found to be irreversibly adsorbed.[39]

(iv) *Magnesium oxide and zinc oxide.* While this work was in progress a paper was published showing that water vapour reacts with more of the magnesium oxide crystal than the surface layer, the extent of the reaction depending on the temperature at which the sample is prepared.[23] Our results agree with this. The reaction with ethyl alcohol, however, is a surface reaction which does not go to completion.

The experiments with zinc oxide are more difficult to interpret with certainty because the surface area is so small. It seems probable, however, that both water and ethyl alcohol are chemisorbed to the extent of less than a monolayer.

General. The criteria we have suggested, when applied to our experimental work, lead to the conclusion that organic vapours are not, in general, chemisorbed by alumina or by silica gel at room temperature. The exceptions are the lower aliphatic alcohols which are specifically held by oxide ions, as is also water vapour. The evidence presented under the three criteria suggested seem to justify the use of the term " chemisorption " where authors have previously referred to " irreversible hysteresis " or " permanent adsorption." [8,9,10]

A final comment may be made on the rates of desorption. These depend to some extent on the strength of binding of the vapour to the surface. Another factor, however, may be of equal or even greater importance. The desorption of carbon tetrachloride from the charcoal used in this work is very much slower than its desorption from the carbon black. There is not sufficient difference in the chemical nature of the surface to account for this, nor does the difference (about 5-fold) in the specific surface areas seem to be

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[31] Rao, *J. Phys. Chem.*, 1941, **45**, 513.
[32] Kurosaki, *J. Phys. Chem.*, 1954, **58**, 320.
[33] Carman, *Trans. Faraday Soc.*, 1940, **36**, 964.
[34] Zhdanov, *Doklady Akad. Nauk S.S.S.R.*, 1949, **68**, 99.
[35] Shapiro and Kolthoff, *J. Amer. Chem. Soc.*, 1950, **72**, 776.
[36] Gans, Brooks, and Boyd, *Ind. Eng. Chem. Anal.*, 1942, **14**, 396.
[37] Shapiro and Weiss, *J. Phys. Chem.*, 1953, **57**, 219.
[38] Iler, " The Colloid Chemistry of Silica and Silicates," Cornell Univ. Press, New York, 1955.
[39] Rao, *J. Phys. Chem.*, 1941, **45**, 500.

directly relevant. On the other hand, the charcoal is a highly porous material containing very fine pores, whereas the carbon black is effectively non-porous. The transfer of vapours through fine capillaries is so slow as to retard very considerably, for charcoals, the desorption of even weakly held adsorbates, as can be seen from examples given by de Boer.[40] [It is presumably because this is the rate-determining stage of desorption that our two methods of desorption require equal times.] Clearly any criteria of reversibility of adsorption based on times required for desorption must recognise the importance of porosity of the adsorbent.

EXPERIMENTAL

Adsorbents.—The activated alumina (boehmite) was Messrs. Peter Spence's " Type A " activated alumina, stated by the manufacturers to be essentially sub-crystalline γ-Al$_2$O$_3$,H$_2$O, with a surface area of 250 m.^{2}/g. When heated to 1100°, it lost 14·2% of its weight, or 16·6% referred to the residual α-Al$_2$O$_3$.

γ-Al$_2$O$_3$ (anhydrous alumina) was made by heating the boehmite to 700° for 24 hr.; this is sample 2 of our earlier paper.[15] Comparison of the monolayer value for benzene on γ-Al$_2$O$_3$ with those on boehmite gives a surface area for γ-Al$_2$O$_3$ of 156 m.^{2}/g. Gregg and Sing's results [41] suggest that alumina prepared at 700° may retain up to 1% of combined water. In view of the difficulty of removing this water, we think it unlikely that the surface layer contains a sufficient proportion of it to alter significantly the conclusions drawn above.

Boehmite with the gibbsite-type (hydroxylic) surface was prepared by allowing boehmite to stand under water for 4 weeks at room temperature and then drying it at about 80°. This procedure was followed because gibbsite cannot be made in bulk with a large specific surface area.

The silica gel was Messrs. Joseph Crosfield's non-activated " Sorbsil." On dehydration in a furnace it lost approximately 4% of its weight. A second sample was made by heating this gel for 24 hr. at 425°. On ignition, the second sample lost 2·5% of water.

The titania gel was made by precipitation with ammonium hydroxide from an aqueous solution of titanium tetrachloride. The precipitate was washed by decantation and dried slowly at temperatures not exceeding 100°. Further washing with water in a Soxhlet apparatus was needed to remove final traces of chloride.

The zinc and magnesium oxides were " AnalaR " samples.

The charcoal was that used by Blackburn and Kipling,[42] and the carbon black was Spheron Grade 6, supplied by Godfrey L. Cabot, Inc.

Adsorbates.—Purification of most of the adsorbates has been described previously.[15, 42, 43] Carbon tetrachloride was dried (Na$_2$SO$_4$) and fractionated. The fraction used had n_D^{20} 1·4602—1·4603 in agreement with the value given by Timmermans.[44]

Procedure.—The solids were saturated at room temperature with the substance to be investigated, and the time between saturation and the start of desorption was noted. Desorption was carried out by one of the following methods: (*A*) The adsorbent was packed into a short column (2·3 cm. long, 1·8 cm. diam.), through which an air-stream, free from moisture and carbon dioxide, could be passed at $\frac{1}{2}$—1 litre per min. The column could be kept in a thermostat at either 20° or 60°. It was weighed at intervals to follow the extent of desorption. (*B*) A similar quantity of adsorbent was placed in a small flask connected to a high-vacuum pump. The flask was weighed at intervals. The residual pressure did not exceed 10^{-2} mm. mercury. (*C*) In a few cases, the residual pressure, after evacuation with a mercury pump, was about 10^{-5} mm. Hg.

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