[CONTRIBUTION FROM THE ALUMINUM RESEARCH LABORATORIES, ALUMINUM COMPANY OF AMERICA]

Sorption of Hydrogen on Alumina

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Only one series of experimental data on the hydrogen sorption of alumina is available in the literature. H. S. Taylor[1] reported the sorption at 650 mm. and 445 and 525° to be of the order of 0.2 ml. STP/g. for an alumina formed by heating the precipitate from treating aluminum nitrate with ammonia. The heat of sorption was about 27,500 cal. per mole, sorption was reversible, and no water was formed during sorption and desorption. Th. Schoon and H. Klette[2] did not give quantitative data but reported verification of the "stair-like form of the adsorption isotherm" for hydrogen on a number of materials including alumina.

The present work presents values of hydrogen sorption on various forms of alumina in the temperature range 400 to 900°, and in the pressure range 9 to 620 mm. The scope of this investigation was limited, but since these values may be of interest, they are presented here.

Experimental

Materials.—The hydrogen was the oil pumped product of Linde Air Products Company which contained a nominal 0.2% methane and less than 0.1% of other impurities. It was passed over copper turnings at 500° and through phosphorus pentoxide or activated alumina. Linde oxygen was dried by passage over activated alumina. The aluminas, samples 1 to 6, were prepared from commercial products of the Aluminum Ore Company. Sample 7, "pure" alumina, was prepared by amalgamation of high purity aluminum foil with mercuric nitrate, oxidation in a water solution containing 2% oxalic acid, filtering, washing with distilled water, drying and calcining. Sample 8, aluminum dross, was skimmed from molten aluminum and was separated from the unoxidized aluminum. Samples 7 and 8 were tabletted with a stearic acid binder and calcined and then were crushed, as were samples 1 to 6, to 20–48 mesh. Chemical analyses of the samples are shown in Table I.

TABLE I

CHEMICAL ANALYSES OF SAMPLES, %

Sample	L. O. I.	Na_2O	CaO	SiO_2	Fe_2O_3	TiO_2	Cl	SO_4
1	3.81	0.36	..	0.016	0.008	0.003	0.056	..
2–4	3.96	.19	..	.026	.017	.006	.035	..
6	19.55	.03	0.40	4.05	.01–0.1	$<$ .01	$<$ .01	0.33
7	...	$<$ .01	$<$ .01	0.01–0.1	.01–0.1	$<$ .01	...	..
8	...	$<$ .01	$<$ .01	.01–0.1	.1–1.0	$<$ .01	...	..

Apparatus.—The sorption bulb was a 6-cm. tube of 17 mm. transparent Vycor glass. This was fused to a 15 cm. tube of 5 mm. quartz which was sealed by deKhotinsky cement to the sorption system. The bulb was heated by a closely fitted, well-insulated furnace. Aluminum baffles were placed above the furnace to prevent heat from softening the cement. A chromel–alumel thermocouple was wired to the outside of the bulb at its mid-point. The sorption system consisted of water-jacketed buret, manometer, hydrogen supply, mercury diffusion and Hyvac pumps, suitable capillary tubing and Cello-Grease lubricated stopcocks. The buret and manometer were connected to reservoirs of mercury to which pressure or vacuum could be applied to control the mercury height.

A separate system for the preliminary heating of the alumina samples included a porcelain boat to hold the sample, a chromel–alumel thermocouple wired to the inside of the boat, a 1-inch quartz combustion tube surrounded by a tube furnace, and a supply of hydrogen to flow 2 cu. ft./hr. through the combustion tube. An adapter was provided into which the porcelain boat could be pulled and from which the alumina could be poured into the sorption bulb while maintained in flowing hydrogen. When this was employed, the bulb and sorption system were filled with hydrogen, the deKhotinsky joint completed rapidly without admission of air and the system immediately evacuated.

Procedure.—The free space of the empty sorption bulb was measured with hydrogen, from volumes read within two minutes after its admission, for the temperatures and pressures of interest. The effective diffusion of hydrogen (outward diffusion of hydrogen minus the smaller inward diffusion of air) was observed for the sorption bulb as a function of time, temperature and hydrogen pressure. A 5-g. sample was put in the sorption bulb, the effective free space calculated for the bulb containing sample on the assumption of an alumina density of 3.8 g./ml., the hydrogen uptake measured as a function of time, and the sorption calculated as the excess hydrogen uptake beyond that of the free space and diffusion.

The temperature of the sorption bulb was maintained within 3° throughout the run by a thermoregulator. Room temperatures were not held constant, but the gas volumes in the system were calculated to constant temperature. The volume of mercury in the buret was adjusted manually from time to time to keep the pressure constant, and corrections were made for any small variations in pressure, usually within 1%.

The treatment of the samples before sorption and their surface areas, as measured by the BET method[3] employing n-butane at 0°, are shown in Table II. The n-butane area was assumed to be 32.1 sq. Å. per molecule for the area calculation.

Preliminary Observations.—The empty Vycor glass sorption bulb resisted deformation in vacuum for sixteen hours at 985°. However, with alumina in the bulb, after less than one hour at 1050°, the bulb broke at the quartz–Vycor glass seal on subsequent cooling to room temperature. The Vycor glass lost its transparency during the runs with alumina; the temperature at which this occurred was not established.

The influence of absolute temperature K on the

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(1) H. S. Taylor, *Z. physik. Chem.*, Bodenstein-Festband, 475–480 (1931).

(2) Th. Schoon and H. Klette, *Naturwissenschaften*, **29**, 653–654 (1941).

(3) Brunauer, Emmett and Teller, THIS JOURNAL, **60**, 309 (1938).

TABLE II

DESCRIPTION OF SAMPLES

Sample	Type	2-Hour heating Temp., °C.	2-Hour heating Atmosphere	Surface area[a] Initial	Surface area[a] Final
1	F[b]	...	....	97	75
2	F	...	....	97	..
3	F	950	Hydrogen	38	34
4	F	750	Hydrogen	56	..
5	F	925	Hydrogen	38	..
6	H[b]	950	Hydrogen	162	..
7	Pure	750	Air	193	..
8	Dross	750	Air	...	8

[a] Square meters/gram, BET method, *n*-butane 0°, *n*-butane 32.1 sq. Å. [b] Product of the Aluminum Ore Company, East St. Louis, Ill.

free space of the bulb and its connecting tubing was given by an equation of the form

$$\text{Free space} = (A/K) + B$$

where A and B are constants. The free space at a given temperature was independent of pressure within the range of the observations, 10 to 700 mm.

The precision of readings was usually volume 0.02 ml., pressure 0.2 mm., sorption bulb temperature 2°, room temperature 0.3°. For the runs at 9 mm. pressure, the pressure was measured with a measuring microscope for which the precision was 0.02 mm. The lack of reproducibility of the measurements was manyfold that of the known errors in measuring gas quantities. The weight of sample was that of the evacuated sample at the conclusion of a sorption run.

Diffusion of Hydrogen through the Sorption Bulb.—The sorption bulb showed diffusion of hydrogen of 0.020 and 0.033 ml. STP/hour at 800 and 900°, respectively, at a pressure of 620 mm. Figure 1 is a plot of the log permeability constant as a function of the reciprocal of absolute temperature. Values lie within the range of published data[4] for the diffusion of hydrogen through pure quartz if the thickness of the Vycor glass bulb is taken as 1 mm. and the area as 35 cm. sq. There was a rapid apparent sorption of 0.10 ml. STP in four hours during the first diffusion run, akin to solubility of hydrogen in the Vycor glass, as reported by Williamson with Pyrex glass and silica.[5] Diffusion rates after the initial anomalous take up of hydrogen were essentially constants of the sorption bulb and did not change appreciably with aging of the bulb. The diffusion rate of hydrogen at 900° increased linearly with pressure, but it extrapolated at zero pressure to a negative value which was probably caused by the inward diffusion of air. A direct measurement of the outward diffusion of oxygen at 900° and 620 mm. indicated a rate one-twelfth that of hydrogen.

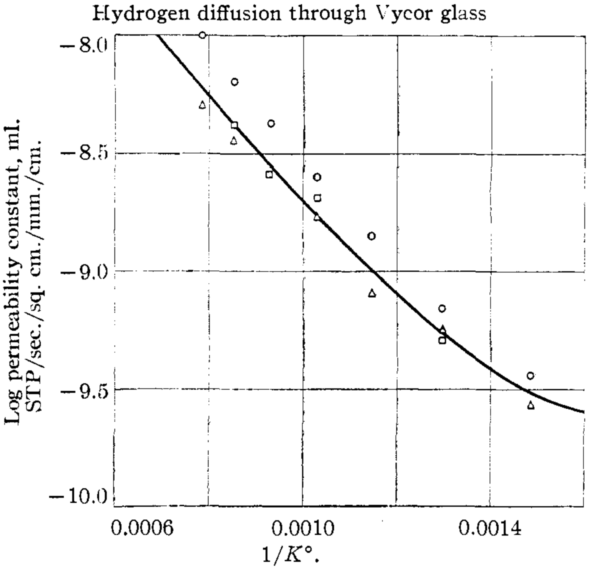

Fig. 1.—Hydrogen diffusion through Vycor glass: O, △, quartz (reference (4)); □, Vycor.

Hydrogen Sorption on Alumina

The results are summarized in Table III and a typical run is plotted in Fig. 2. The effect of temperature on hydrogen sorption is displayed in Fig. 3.

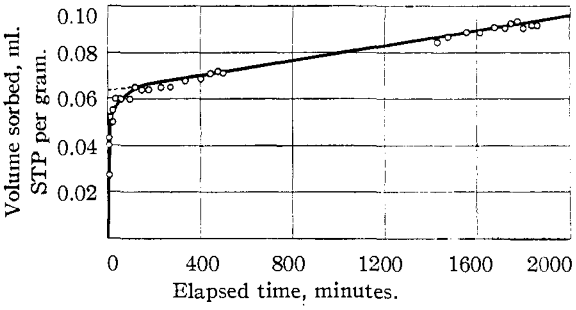

Fig. 2.—Typical hydrogen sorption rate activated alumina F, sample 3, 900°, 98 mm.

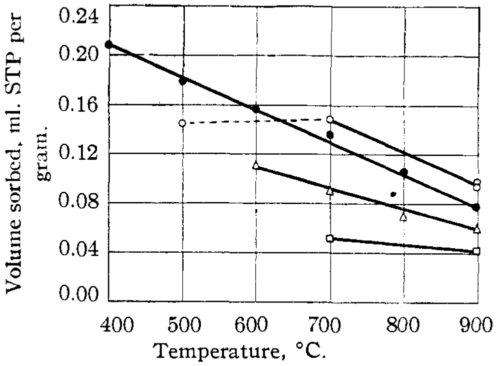

Fig. 3.—Effect of temperature on hydrogen sorption, activated alumina F: O, sample 3, 620 mm.; ●, sample 3, 98 mm.; △, sample 2, 98 mm.; □, sample 4, 98 mm.

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[4] Barrer, "Diffusion in and through Solids," Cambridge University Press, Cambridge, England, 1941, p. 135.

[5] Williamson, THIS JOURNAL, 55, 1437 (1933).

TABLE III

HYDROGEN SORPTION ON ALUMINA

Sample	Evacuation		Hydrogen sorption				
	Time, hr.	Temp., °C.	Temp., °C.	Pressure, mm.	Duration, hr.	Equilibrium, hr.	Ml. STP/g.
1	48	800	800	620	70	3	0.88
	168	800	800	620	70	3	.17
2	16	985	900	620	25	1	06
	...	...	800	620	5	..	.07
	...	...	700	620	18	..	.09
	...	...	600	620	48	..	.11
3	24	900	900	620	6	2	.094
	16	900	900	620	1	..	.098
	2	900	900	620	21	1	.066
	98	900	700	620	2	...	.1
	16	900	700	620	33	15	.148
	21	900	700	620	72	15	.148
	16	900	500	620	53	30	.145
	16	900	500	620	22	..	.14
	72	900	900	620	24	..	.05[a]
	4	900	900	620	3	3	.124
	88	900	900	620	8	2	.105
	16	900	900	98	31	3	.064
	51	900	900	9.2	3	..	.04
	21	900	900	9.6	6	2	.04
	16	900	900	620	7	2	.140
	16	900	900	620	7	3	.134
	18	900	900	0	25	..	.00
	45	900	900	620	25	3	.138
	...	...	900	98	26	5	.078
	...	...	800	98	23	3	.106
	...	...	700	98	96	6	.136
	...	...	600	98	48	10	.157
	...	...	500	98	70	23	.179
	...	...	400	98	74	40	.208
	...	...	900	98	24	2	.093
4	16	700	700	98	6	..	.03
	64	700	700	98	72	15	.028
	18	900	900	98	27	15	.110
	115	900	900	98	6	3	.077
	17	900	700	98	31	20	.052
	...	...	900	98	..	1	.042
	17	900	700	98	6	..	.05
5	16	900	900	98	26	4	.257
	16	900	900	98	26	4	.170
	16[b]	900	900	98	8	3	.090
	16	900	900	98	72	3	.063
	...	...	700	98	7	1	.080
6	5	900	900	98	3	1	.085
	16	900	900	98	27	3	.049
	40[b]	900	900	98	30	3	.211
	...	...	700	98	97	1	.246
7	239	750	700	99	51	50(?)	.51
	160	700	700	99	56	50(?)	.18
	329	700	700	99	3	..	.10
8	47	750	700	98	28	15	.14
	89	700	700	98	52	15	.14

[a] Oxygen sorption. [b] After air exposure at 900°.

Activated Alumina F.—Sample 1 had a very high apparent hydrogen sorption in its initial run and maintained a portion of the increase on a rerun after prolonged evacuation. Sample 2, which was evacuated at a higher temperature, had sorption at 900° and 620 mm. of 0.06 ml. STP/g. After the 900° run, the sample was cooled without evacuation whereby sorption increased to 0.11 ml. STP/g. at 600°.

Activated Alumina F Heated in Hydrogen at 950°.—Sample 3, heated in hydrogen, transferred without air exposure, and evacuated, showed sorption at 900° and 620 mm. of 0.098 ml. STP/g. The sorption for the following run was less, probably because the sample was evacuated only two hours at 900° beforehand. Evacuation for at least sixteen hours at 900° was adopted as standard for the subsequent runs. At 700° sorption increased to 0.148 ml. STP/g. The 500° sorption value is inconsistent in that it is not greater than the value at 700°. With oxygen rather than with hydrogen the sorption was one-third that shown by comparable hydrogen runs. Hydrogen sorption measured after the oxygen sorption was greater than it was in previous hydrogen sorption runs. A portion of this increase was maintained in a check hydrogen run. Sorption decreased but slowly on decrease of pressure from 620 to 9 mm. at 900° and was approximately proportional to the fourth root of pressure. Some further change in the sample occurred during or after the low pressure runs whereby the sorption of hydrogen at 900° and 620 mm. increased. After eighteen hours' evacuation at 900°, no further desorption was apparent at 900° and zero mm. In subsequent runs, the temperature of sorption was varied without evacuation of the sample after each run. Sorption increased with decrease in temperature at 98 mm. from 0.078 ml. STP/g. at 900° to 0.208 ml. STP/g. at 400°. At 900° after the preceding lower temperature determinations, sorption was 0.093 ml. STP/g.

Activated Alumina F Heated in Hydrogen at 750°.—Sample 4, heated in hydrogen at 750°, transferred without air exposure, and evacuated had hydrogen sorption at 700° and 98 mm. of only 0.03 ml. STP/g. This value is less than half of that found for sample 3, which was calcined in hydrogen at 950°, in spite of the 50% larger surface area of sample 4. Sample 4, after evacuation at 900°, had its hydrogen sorption increased to 0.11 ml. STP/g. at 900° and 98 mm. Prolonged heating at 900° caused a decrease in the hydrogen sorption of sample 4.

Washed Activated Alumina F.—Sample 3 was washed with distilled water (Sample 5). Conductivity measurements of the wash water showed that 0.07% sodium oxide was removed. After heating in hydrogen and evacuating without air exposure, hydrogen sorption at 900° and 98 mm. was initially 0.257 ml. STP/g. and decreased in a subsequent run. This sample was exposed to air for thirty minutes at 900°, following which hydrogen sorption decreased and, on cooling to 700°, sorption increased. The final value of sorption was less than for the unwashed sample.

Activated Alumina H.—Sample 6, calcined in hydrogen and evacuated without air exposure, had sorption of 0.085 ml. STP/g. at 900° and 98 mm. The value decreased on a subsequent run to the order of magnitude of values for the F alumina. After air exposure at 900°, hydrogen sorption increased and on cooling to 700°, sorption increased further.

High Purity Alumina.—Sample 7 of pure alumina was heated in air at 750° and evacuated at 750°. The initial value at 700° and 99 mm. was high and diminished in two successive runs to 0.10 ml. STP/g. The last of these values is in the range for Activated Aluminas F and H.

Alumina from Aluminum Dross.—Sample 8 of alumina from aluminum dross was heated at 750° in air, and evacuated at 750°. Sorption in two successive runs was like that for Activated Aluminas F and H.

Discussion

These results on the hydrogen sorption of alumina from 400 to 900°, while not completely consistent, show three generalizations: (1) sorption increases with decreasing temperature; (2) sorption changes but slowly with hydrogen pressure from 9 to 620 mm.; (3) sorption is slow.

There does not appear to be a good correlation of hydrogen sorption with the surface area of the aluminas or with their known amounts of chemical impurities. The apparent sorption of hydrogen is increased temporarily by exposure of the alumina to air or oxygen before measurement, by washing with water or by heating from 750 to 900° in vacuum. Prolonged evacuation of the alumina at high temperature is necessary to remove previously sorbed hydrogen from it. The sorption values indicate that less than one per cent. of the available alumina area is covered with hydrogen at equilibrium.

Summary

The sorption of hydrogen on various samples of alumina has been measured from 400 to 900° and from 9 to 620 mm. Sorption is in the range 0.05 to 0.2 ml. STP/g., increases with decreasing temperature, and increases proportional to the fourth root of pressure. The results reported in this paper are roughly consistent with those of Taylor.[1] Sorption equilibrium is slow and difficult to reproduce and there is evidence of an irreversible hydrogen reaction on alumina. The samples tested have sorption in the same range in spite of large differences in their surface areas and impurity contents.

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Generalized Form of the Reaction-Rate Law for Homogeneous Reactions[1a]

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The classical equations of reaction kinetics, relating the rate of reaction to the concentrations of the reacting substances, are correctly applied to static systems maintained at constant volume and to flowing systems in which no volume change occurs during the reaction. A large number of reactions have been studied in flowing systems, in which the pressure is essentially constant but in which the volume changes. There does not appear to be substantial agreement as to the proper form of rate law applying to such systems. Benton[1c] has considered several special cases, and Hulburt[2] has recently presented a discussion of reaction kinetics in flow systems based upon the hydrodynamic equations for reaction mixtures which includes a treatment of first and second order reactions. It is not, however, obvious from the discussion that the proper form of rate law has been employed. In the present communication, the appropriate rate equation for a flowing system is derived, it being assumed that the reaction is homogeneous.

The general hydrodynamic equations for reacting fluids have been given by Bateman[3] and Eckart.[4] The present discussion is based upon the equation for the transport of each kind of substance, which may be written in the form

$$\rho \frac{\mathrm{d}m_k}{\mathrm{d}t} = \rho\Gamma_k + \nabla\cdot D_k\nabla\rho m_k \qquad (1)$$

where ρ is the mean density of the mixture, m_k the concentration of the k-th constitutent of the mixture in moles per unit weight of mixture, t the time, Γ_k the rate of production of the k-th constituent in moles per unit weight of mixture, and D_k the diffusivity of the k-th constituent in the mixture. The Euler total time derivative $\mathrm{d}/\mathrm{d}t$ follows the fluid and refers to changes in an elementary volume which moves with the fluid and always contains the same molecules (either in reacted or unreacted form). The Euler total time derivative is related to Euler and Lagrange partial derivatives by

$$\frac{\mathrm{d}}{\mathrm{d}t} = \left(\frac{\partial}{\partial t}\right)_{\mathbf{R}} + \mathbf{u}\cdot\nabla = \left(\frac{\partial}{\partial t}\right)_{\mathbf{R}_0} \qquad (2)$$

where $\mathbf{R} = \mathbf{R}\ (\mathbf{R}_0, t)$ is the position vector at time t of the elementary volume which was at $\mathbf{R}_0$ at a reference time t_0, and $\mathbf{u}$ is the (vector) velocity of the fluid.[5] If the reactor is isothermal, the form of the function $\mathbf{R}\ (\mathbf{R}_0, t)$ is obtained from a consideration of the fundamental hydrodynamic equations for transport of total mass and momentum, and it is always possible, at least in principle, to find this solution of the purely hydrodynamic aspect of the problem. It follows from equation (2) that equation (1) can be integrated in a manner exactly analogous to that for the static case, after the form of the source function Γ_k is explicitly given, provided only that the integration be performed along a path of constant Lagrange coördinate $\mathbf{R}_0$. The limits of integration for the time will be the time t_1 at which a selected element of volume enters the reactor and the time t_2 at which the

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(1a) Published by permission of the Direction, Bureau of Mines, U. S. Department of the Interior. Article not copyrighted.

(1b) Physical Chemist, Central Experiment Station, Bureau of Mines, Pittsburgh, Pennsylvania.

(1c) Benton, THIS JOURNAL, **53**, 2984 (1931).

(2) Hulburt, *Ind. Eng. Chem.*, **36**, 1012 (1944).

(3) Bateman, *Proc. Natl. Acad. Sci.*, **25**, 388 (1939).

(4) Eckart, *Phys. Rev.*, **58**, 269 (1940).

(5) $\mathbf{R}_0$, the Euler coördinate of the element of volume at the reference time t_0, is the Lagrange coördinate of the element of volume. Specification of its value can be considered to provide the element with a label which it carries throughout its subsequent history, and a restriction to constant Lagrange coördinate provides a notation indicating that differentiation or integration subject to this restriction is to be performed following the fluid in the same sense with which the Euler total time derivative follows the fluid.