[CONTRIBUTION FROM THE FRICK CHEMICAL LABORATORY OF PRINCETON UNIVERSITY]

A Contribution to the Study of the Hydrogen–Oxygen Reaction. The Adsorption of Hydrogen on Pyrex and Quartz

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In a paper[1] which considered the relation of the walls to the initiation of reaction chains in mixtures of hydrogen and oxygen a theory was advanced to explain the upper explosion limit obtaining in such systems. The chief postulate was that the partial pressure of hydrogen in the gas phase was just sufficient to saturate the walls with hydrogen at the critical explosion pressure, and that if the latter were lowered ever so slightly partial desorption would occur. This would be followed by a "flank attack" of the oxygen through the freshly exposed surface, and the sweeping off of the whole surface film as the first step of the explosion.

The purpose of the investigation to be described below was to test this theory by the experimental determination of rates of adsorption and equilibrium measurements for the systems quartz–hydrogen and Pyrex–hydrogen in the temperature range where explosions occur. Earlier workers found that large quantities of hydrogen were taken up by the porcelain[2] and Pyrex[1] above 400°, but the determination of the pressure required to saturate the surface at various temperatures, and of the rates with which the two phases approach equilibrium at constant pressure, remained incomplete. More recently it was shown[3] that hydrogen was adsorbed on silica at 550°, but the figures obtained were sufficient to give only a qualitative idea of the rate of saturation of the surface. However, the same paper contains an analysis of the surface reaction of hydrogen and oxygen which leads the authors to take issue with Alyea's explanation of the upper limit.

The molecular adsorption of hydrogen on quartz[4] is known to be barely measurable at liquid-air temperatures. Diffusion takes place through quartz walls above 300°,[5] and increases exponentially with temperature.[6] Pyrex, in spite of its great adsorbing power, is impermeable[6] to hydrogen, although slight surface reduction takes place.

Apparatus

Cylindrical bulbs of Pyrex and quartz filled with about 90 g. of pulverized Pyrex and quartz, respectively, were cleaned with dilute nitric acid, washed thoroughly with distilled water, and dried by heating and pumping off. They were placed in the brass core of a well-lagged resistance furnace, and sealed onto the system with capillary tubing.

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[1] Alyea, THIS JOURNAL, **53**, 1324 (1931).

[2] Bone and Wheeler, *Phil. Trans.*, **A206**, 1 (1906).

[3] Garstang and Hinshelwood, *Proc. Roy. Soc.* (London), **A134**, 1 (1931).

[4] Paranjpe, *Proc. Asiatic Soc. Bengal*, **15**, 136 (1919).

[5] Johnson and Burt, *J. Opt. Soc. Am.*, **6**, 734 (1922).

[6] Williams and Ferguson, THIS JOURNAL, **44**, 2160 (1922).

The rest of the system consisted of a compensated gas buret, a closed arm mercury manometer, an electrolytic hydrogen generator with purifying train, and the various pumps. The furnace was held at the required temperature by a Leeds and Northrup thermoregulator actuated by a platinum resistance thermometer. The temperature of the packed bulb was read by means of a calibrated chromel–alumel thermocouple which was sunk in an insulated well in the brass core of the furnace and connected to a Type K Leeds and Northrup potentiometer.

Procedure.—The general method of carrying out adsorption measurements has been described frequently.[7] In this particular case the "dead spaces" were determined with helium below 300°, the gas laws being used for extrapolation into the higher temperature range. When the bulbs were first sealed on they were given a pretreatment with hydrogen at 500° for several hours to remove any easily reducible matter. Subsequently, all determinations were preceded by at least twenty-four hours of evacuation, quartz being heated to 600° and Pyrex to 550° during this process.

All values given below have been reduced to standard conditions.

Results with Quartz.—An attempt was made to obtain an isotherm at 565° by admitting successive portions of hydrogen and waiting for the pressure to reach equilibrium. Unfortunately, the rate of diffusion of hydrogen through quartz parallels the rate of adsorption to such an extent that loss of gas by the former process becomes appreciable when the temperature is raised to a point at which adsorption is reasonably rapid. For this reason the isotherm had to be abandoned after two weeks' contact time. Of a total of 19.9 cc. introduced into the bulb only 14.4 cc. could be recovered by evacuation at 600°.

RATE OF ADSORPTION OF HYDROGEN ON QUARTZ

TABLE I

P, 760 Mm.	Temp., 400°
Time, min.	$V_{\text{ads.}}$, cc.
0	0.00
2	.15
15	.35
35	.45
80	.50
400	.55
1200	.60
1560	.65
2640	.85

TABLE II

P, 760 Mm.	Temp., 446°
Time, min.	$V_{\text{ads.}}$, cc.
0	0.0
1	.2
15	.6
30	.8
45	.9
60	1.1
90	1.3
120	1.4
255	1.5
585	1.7
1515	1.9

TABLE III

P, 760 Mm.	Temp., 476°
Time, min.	$V_{\text{ads.}}$, cc.
0	0.0
2	0.4
15	1.1
30	1.3
45	1.5
60	1.7
120	2.0
180	2.1
240	2.2
660	2.6
1320	3.0

RATE OF ADSORPTION OF HYDROGEN ON PYREX

TABLE IV

P, 760 Mm.	Temp., 526°		
Time, min.	$V_{\text{ads.}}$, cc.	Time, min	$V_{\text{ads.}}$, cc.
0	0.0	30	1.7
5	.4	38	2.2
10	.7	51	2.8
16	1.0	60	3.3
20	1.1	75	3.8
25	1.4		

TABLE V

P, 760 Mm.	Temp., 542°		
Time, min.	$V_{\text{ads.}}$, cc.	Time, min.	$V_{\text{ads.}}$, cc.
0	0.0	26	3.0
3	0.4	32	3.4
6	0.9	38	4.0
10	1.5	47	4.2
15	2.0	52	4.6
20	2.5	59	4.9

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(7) Pease, THIS JOURNAL, **45**, 1197 (1923); Taylor and Williamson, *ibid.*, **53**, 2168 (1931).

Rate measurements were next carried out under conditions which permitted introduction of the gas at constant pressure, the chosen value being 760 mm.

These rate determinations are shown graphically in Fig. 1. Because of the relatively low temperatures and the short time of contact the gas was almost completely recoverable on evacuation at 600°.

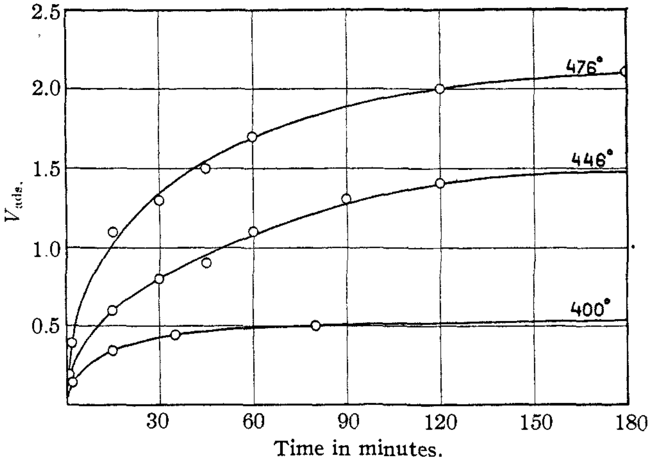

Fig. 1.—Rates of adsorption of hydrogen on quartz.

Results with Pyrex.—The impermeability to hydrogen and the relatively high power of adsorption shown by this glass led to results which were quite conclusive. The rate of adsorption was first determined with the results given in Tables IV and V.

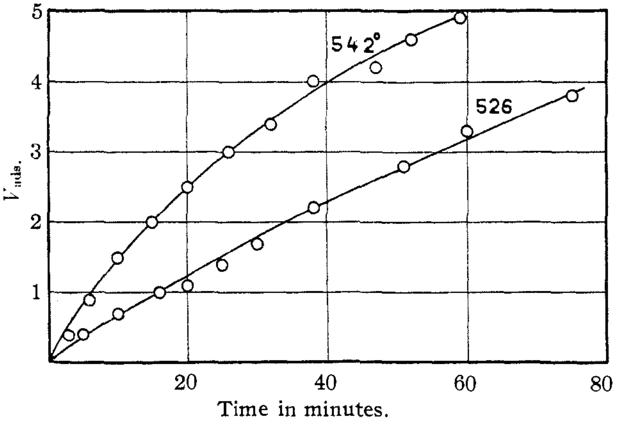

Fig. 2.—Rates of adsorption of hydrogen on Pyrex.

The measurements are plotted in Fig. 2. The gas was almost completely recoverable at 550°, evacuation being continued for thirty-six hours.

Finally, equilibrium values were successfully obtained at 542°, making it possible to construct an isotherm. The values follow.

TABLE VI

ISOTHERMAL ADSORPTION OF HYDROGEN ON PYREX

Temp., 542°

$V_{ads.}$	P	$P/V_{ads.}$	
0.0	0	..	
18.3	181	9.89	Gas admitted = 22.5 cc.
16.9	48	2.84	Gas recovered = 21.3 cc.
16.2	40	2.47	

The total time of contact was sixty-two hours, and when this is considered with the recovery efficiency of approximately 95%, it becomes evident that loss of hydrogen by reduction of the Pyrex or by diffusion occurs at a rate which is negligible compared with the velocity of adsorption.

Conclusions.—The rate measurements obtained with quartz show marked acceleration with temperature. In no case, however, is there any evidence of the break which would be expected if fairly rapid adsorption were followed by slow diffusion processes. We may therefore conclude that the formation of a saturated surface layer will only be realized after a relatively long time in this temperature region, and that such a layer when formed will not respond instantly to changes in pressure of the hydrogen in the neighboring gas phase.

Definite corroboration of this view is obtainable with Pyrex. True adsorption will satisfy the Langmuir isotherm

$$\sigma = \frac{bP}{1 + bP} \text{ or } V_{ads.} = \frac{aP}{1 + bP}$$

where σ is the fraction of the available surface which is covered, a and b are constants, P and $V_{ads.}$ being already defined in this article. The equation may be rearranged to give

$$\frac{P}{V} = \frac{b}{a}P + \frac{1}{a}$$

If we plot the function P/V against P, points on a true adsorption isotherm should therefore give a straight line whose slope is b/a and whose intercept on the ordinate is $1/a$. This procedure has been adopted for the values from Table VI.

The non-horizontal straight line so obtained shows clearly that the preponderating process is true adsorption and not some form of solution. If the latter were the case the results would obey Henry's law and the slope of the curve would be zero. Having obtained a linear relation for the experimental points extrapolation is made easy, and we can link the adsorption measurements with values obtained in kinetic studies.

Unpublished results of Frost in Princeton have shown that the upper explosion limit of a $2H_2O:O_2$ mixture in contact with Pyrex at 542° is approximately 120 mm. total, which means a hydrogen partial pressure of 80 mm. Inspection of the curve drawn from Table VI shows that this corresponds to a P/V value of 4.55 which in turn yields 17.6 cc. as the quantity adsorbed at equilibrium. If now we turn to Table V, it will be found that exposure of the system to hydrogen at a pressure of one atmosphere for an hour will result in the adsorption of only 5 cc. The attainment of the equilibrium value would require an exposure of several hours at one atmosphere, and would require a somewhat longer time if the pressure were markedly lower. Furthermore, the rate of adsorption has been shown to decrease rapidly as the temperature is lowered, the decrement shown in Fig. 2 being roughly 50% for a sixteen degree drop. This means that surface saturation in the neighborhood of 450° will be a process requiring several days.

On the other hand, several investigators have found that the upper explosion limit is a reproducible quantity which can be obtained within a few seconds of the introduction of the gas mixture, in spite of the fact that only a tiny fraction of the surface can be covered in this time. Explosions can still be obtained at 450°, and it has been shown that there is a tremendous adsorption lag at this temperature.

These experimental results suggest that some modification of Alyea's explanation of the upper explosion limit may be necessary in order to remove the difficulties now existing. Further experimental work may indicate the reason for these difficulties and thereby give positive support to a completely harmonious theory.

It may be observed that a mechanism which depends on conditions in the gas phase rather than at the walls has been put forward by Semenov.[8] It later received the support of Hinshelwood and his school.[3]

Summary

1. The rate of adsorption of hydrogen on quartz and Pyrex has been measured between 400 and 550° at a pressure of 760 mm.

2. Equilibrium values have been obtained on Pyrex, and have been shown to correspond to true adsorption.

3. By combining 1 and 2 it has been shown that the attainment of equilibrium requires several hours' contact of gas and surface.

4. Lack of agreement between these results and a theory advanced by Alyea to explain the upper explosion limit of the hydrogen–oxygen reaction has been indicated.

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(8) Kopp, Kovalshii, Sagulin and Semenov, *Z. physik. Chem.*, **B6**, 307 (1930).