Summary

1. The thermal decomposition of methyl azide has been studied at temperatures from 200.0 to 240.0°, and from pressures of 0.08 to 46.6 cm.

2. The reaction has been found to be homogeneous. It is first order at high pressures but the rate constants decrease with decreasing pressure below 10 cm. initial pressure. The high pressure rate constant is given by the expression $k_\infty = 3.02 \times 10^{15} e^{43,500/RT}$.

3. To best fit the data to the theoretical expression relating rate constant and pressure a molecular diameter of 5×10^{-8} cm. and 13 classical oscillators are required.

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The Adsorption of Hydrogen by Silica Gel at Elevated Temperatures

BY L. H. REYERSON

In a recent paper Alyea[1] has suggested interesting mechanisms for the explosive and non-explosive reactions occurring between hydrogen and oxygen at elevated temperatures. Experimental evidence is given for a large adsorption of hydrogen by Pyrex glass surfaces at temperatures above 500°. Alyea concludes that this marked adsorption of hydrogen is due to activated adsorption. In discussing the mechanisms of the slow and explosive reactions Alyea postulates that this hydrogen is attached to the surface of the glass in an activated form, which it is not at room temperatures. Suggestions are made as to the possible attachment of the hydrogen to the surface as well as to the mechanism by which the chain reaction is initiated. As a result of this work it was felt that marked adsorption of hydrogen by silica gel should be obtained at temperatures above 500°. Previous work in this Laboratory had given inconclusive evidence that hydrogen was somewhat better adsorbed by silica gel in the neighborhood of 400° than it was below 300°. The adsorption of hydrogen by silica gel was therefore studied in the temperature range of 400 to 600°.

Experimental Procedure

A sample of high-grade silica gel prepared by the method of Patrick was purified by digestion with concentrated nitric acid. This treatment was followed by prolonged dialysis. The gel was then dried in a current of air at about 300°. Finally the gel was electrodialyzed for about two weeks in an electrodialysis cell using cellophane membranes to separate the middle section, containing the gel, from the two electrode sections. The dialysis was continued until the resistance across the cell reached a constant maximum value. The gel was then dried slowly and finally heated to about 300°. The

(1) Alyea, THIS JOURNAL, **53**, 1324–1336 (1931).

product of this treatment was a white glassy gel which was almost as transparent as glass. Twenty grams of this gel was placed in a long clear quartz bulb of two centimeters internal diameter. This was sealed to a high vacuum line through a quartz to Pyrex seal. A side tube above this seal provided means for admitting hydrogen after the gel had been thoroughly outgassed. An electric resistance furnace was built to accommodate the quartz bulb. This furnace was capable of maintaining temperatures above 600° for long periods of time. The gel was outgassed for several hours at a temperature above 500° before the hydrogen was added. Electrolytic hydrogen, from which oxygen had been removed, was washed and then thoroughly dried, before it was admitted to the quartz bulb. The temperature of the furnace was adjusted to the desired value and held constant for some time so that the silica gel had reached a uniform temperature when the hydrogen was added. When the silica gel had been sufficiently outgassed, the hydrogen was admitted and the pressure of the system immediately read on an open-end mercury manometer. Furnace temperatures were measured by a calibrated chromel-alumel thermocouple. The temperature of the furnace was held as nearly constant as possible for a number of hours, during which time readings on the manometer were taken at intervals. The temperature was then changed and readings continued for a number of hours at the new temperature. The charge of hydrogen was allowed to remain in contact with the silica gel for from forty to one hundred and eighty hours. The following results show that at no time during the experiments was there any evidence of appreciable adsorption of hydrogen at these elevated temperatures.

Results

The following condensed results taken from typical experiments show the actual pressure in the system as calculated from the manometer readings. The time is recorded in hours and minutes from the beginning of a run.

	Time elapsed, hrs. min.	Temp., °C.	Actual pressure of system, mm.
Run II	0:0	423	483.5
	3:30	429	481
	35:30	398	480
	50:00	399	478.5
Run III	0:0	543	187
	22:00	545	191
	46:00	548	198
	70:00	495	192
	74:00	495	192
	94:00	495	192
	166:30	498	187
Run IV	0:00	412	215
	2:30	414	214
	23:15	418	214.5
	46:30	425	215.5
Run VI	0:00	500	188
	1:00	500	188
	2:15	500	188
	6:30	565	198.5
	18:15	555	210.5
	90:15	525	205
	114:15	520	205
	167:45	520	201
Run VIII	0:00	512	660
	1:00	511	660
	1:48	512	660
	2:04	512	660
	16:40	511	655
	41:00	512	640

Discussion

These results indicate that, in the temperature range of 400 to 565°, silica gel does not in a quartz system appreciably adsorb hydrogen in the

manner suggested by Alyea. In a few isolated cases the temperature of the gel was carried up to 600° with no more adsorption occurring than at the temperatures recorded here. After an exposure to hydrogen at these elevated temperatures for more than a thousand hours there appeared to be no change in the physical structure or appearance of the silica gel. On the other hand, Pyrex glass subjected to similar treatment assumes a dark brown color. Mr. S. Yuster, working in the author's laboratory, repeated the Alyea experiments on Pyrex and was able to check qualitatively Alyea's results. Quantitative checks were not to be expected because of differences in surface exposed to hydrogen in the two cases. It thus becomes evident that Pyrex will adsorb large quantities of hydrogen at elevated temperatures while silica gel, under similar conditions, does not appreciably adsorb hydrogen.

According to Alyea, 500 cc. of coarsely powdered Pyrex tubing was used in making the adsorption studies. If the Pyrex particles averaged 1 mm. on an edge there was exposed to hydrogen adsorption about 3×10^5 sq. cm. of surface. If the Pyrex consisted of cubes having 0.1 mm. edge, then there was about 3×10^6 sq. cm. of surface exposed to the hydrogen. This certainly must be considered as the upper limit for the Pyrex surface that maintained in Alyea's experiments. In the case of the silica gel Patrick and Grimm[2] indicate that silica gel may have as much as 6×10^6 sq. cm. of surface per g. of gel. Assuming a value of one-sixth of that amount the 20 g. of gel used in these experiments would have 20×10^6 sq. cm. of surface for hydrogen adsorption. On this basis there was a minimum of from six to sixty times as much surface exposed by the silica gel than was the case in Alyea's experiments. In no case was a steady drop in pressure observed yet if activated adsorption were taking place it should occur more rapidly on this larger surface than it did on the Pyrex. At 530° in a period of ten hours Alyea reported that the hydrogen pressure had fallen from 700 mm. to 47 mm. In Run III at from 543 to 548° there was no measurable pressure change after forty-six hours. It is true that variations of pressure are recorded in these results but this is partly attributed to the fact that about two-thirds of the system containing the hydrogen was outside of the furnace and was therefore subject to temperature variations in the room. As noted in the experimental procedure the temperature would be held constant for a considerable period of time, usually ten to twenty hours, and then purposely changed in an attempt to find some region in which marked adsorption would be found. This accounts for the recorded changes in temperature and these are given for the close of a period of as nearly constant temperature as it was possible to maintain. Run VIII was held constant for the whole period of forty-one hours and this gives the only evidence of a possible adsorption. Temperature variations outside of the

(2) Patrick and Grimm, THIS JOURNAL, **43**, 2144 (1921).

furnace could account for some of this change or a possible loss of hydrogen by diffusion through the quartz wall.

In spite of the much greater surface exposed by the silica gel it does not adsorb hydrogen at elevated temperatures in the same way that Pyrex does. The suggestion of Alyea that the silica part of the Pyrex adsorbs considerable hydrogen in an activated state does not seem probable. It may well be that activated adsorption occurs on the Pyrex surface that is not silica. However, the blackening of the Pyrex indicates a chemical reaction and it is likely that a part at least of the hydrogen is used up in reducing that section of the Pyrex surface that is not silica. If the oxides of boron in the Pyrex are reduced under these conditions, then the hydrogen pumped off from the system should be tested for the presence of water vapor. The present set-up did not permit this to be done. The reduced boron might well adsorb additional hydrogen in an active condition just as some of the metals do. The mechanism of the adsorption of hydrogen by Pyrex appears to be more complicated than the original suggestions indicated. If any appreciable adsorption of hydrogen takes place on the silica gel surface between 400 and 600°, it must occur immediately on the admission of hydrogen to the system.

After submitting this note the writer has read the paper just published by A. T. Williamson, THIS JOURNAL, **55**, 1437 (1933). It is difficult to reconcile the adsorption on powdered quartz with results on silica gel. It is possible that the silica gel surface is different from the quartz. It is barely possible that the silica gel adsorbs all of the hydrogen that it will adsorb during the process of admitting the hydrogen. It is to be regretted that A. T. W. did not specify the source and purity of the quartz used because it is known that impurities in silica gel make it possible for the gel to adsorb additional small quantities of gas.

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Summary

Silica gel does not adsorb any appreciable amount of hydrogen on long standing at temperatures from 400 to 600°.

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