[CONTRIBUTION FROM THE FRICK CHEMICAL LABORATORY OF PRINCETON UNIVERSITY]

Adsorption of Hydrogen by Zinc Oxide, Zinc Chromite, and Zinc Oxide–Molybdenum Oxide

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The object of the present research, continuing previous investigations in this Laboratory, was to examine more penetratingly the association of hydrogen with various oxide surfaces, using more accurate control of temperature and pressure variation in order more fully to explore the various energetic factors operative in the association of molecules with surfaces.

To this end a means of automatically maintaining constant pressure in slow adsorption processes has been utilized. The study of the adsorption of hydrogen by zinc oxide has been undertaken in more detail than in the previous studies of Taylor and Sickman.[1] Employing the new technique, we have found evidence of what appears to be two types of adsorption with characteristic activation energies besides the usual van der Waals adsorption.

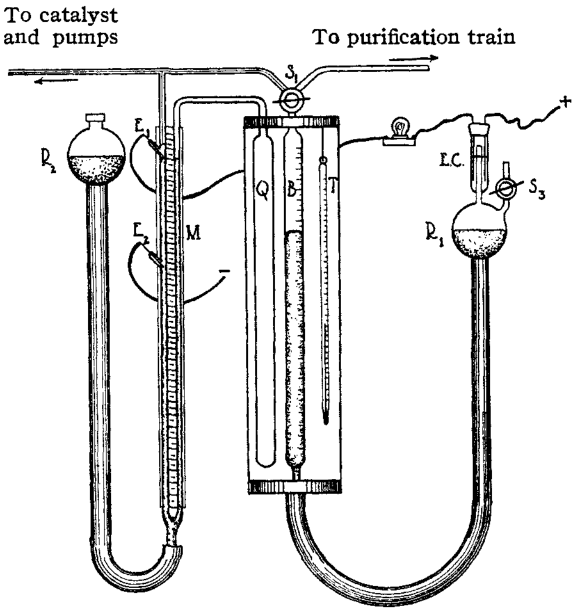

Fig. 1.—Constant pressure control system.

The adsorption of hydrogen by zinc oxide catalysts promoted with chromium oxide and with molybdenum oxide also has been subjected to more intensive study. The former catalyst was discovered to be very much more active than the unpromoted catalyst, whereas the activity of the latter was greatly below that of zinc oxide.

Experimental Details

Apparatus.—The apparatus used in these experiments was similar to that of Taylor and Williamson[2] modified to maintain constant pressure.

The catalyst was contained in a 25-mm. Pyrex tube. This was joined to the manometer M and the buret B (see Fig. 1) by 2-mm. Pyrex capillary tubing, and to the evacuation system composed of a Langmuir diffusion pump and a Wegner-Deka-Micro oil pump through a stopcock.

Pressure Control.—The pressure was kept constant by so arranging the mercury reservoir R_2 that the contact between the mercury meniscus of the manometer and the tungsten electrode E_1 was just broken.

As the hydrogen was adsorbed the pressure decreased, permitting the mercury meniscus to make contact with the electrode E_1. A current of six volts was thereby sent through the electrolytic cell E. C. containing an alkaline solution. The gas generated increased the pressure on the surface of the mercury reservoir, forcing the mercury into the buret and consequently building the pressure up sufficiently to break the contact. A small electric bulb connected in series with the cell aided in the adjustment of the apparatus at the beginning of a run. The stopcock S_3 was closed while the apparatus was in use and opened at the conclusion of the experiment to release the pressure developed.

The above device for maintaining constant pressure was found to be exceedingly satisfactory. No lag was observable. Micro-leveling-bulb adjusters were used to support the mercury reservoirs to facilitate their adjustment at the start of a run.

Temperature Control.—The temperature of the catalyst was constantly checked with a thermocouple, oxygen thermometer, or pentane thermometer as required by the temperature range. Quite accurate temperature control between 0 and 444° was secured through the use of numerous vapor baths.

Gases Employed.—Electrolytic hydrogen from an alkali cell was used. The hydrogen was freed from oxygen by passage over copper maintained at 450–500° and subsequently over calcium chloride, ascarite, and phosphorus pentoxide.

The tank helium, used for the determination of the dead space, was purified in the same manner with the addition of a liquid air trap containing activated charcoal to eliminate any hydrocarbon impurity.

Preparation of Catalysts.—The zinc oxide catalyst from the oxalate was prepared in the same manner as that of Taylor and Sickman.[1]

Zinc ammonium chromate[3] was precipitated by mixing zinc nitrate and neutral ammonium chromate in equimolecular proportion. After heating at 400°, it was

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[1] Taylor and Sickman, THIS JOURNAL, 54, 602 (1932).

[2] Taylor and Williamson, *ibid.*, 53, 2168 (1931).

[3] Taylor and Kistiakowsky, *ibid.*, 49, 2468 (1927).

reduced *in situ* with hydrogen at 450° for five hours. At the end of this time a phosphorus pentoxide tube did not gain in weight when the off-gas was passed through it. The catalyst was now a light green. The catalyst prepared in this fashion was zinc chromite.[4]

Zinc paramolybdate[5] was prepared from zinc nitrate and ammonium molybdate, and was heated at 500° for five and a half hours. The catalyst was reduced for three and a half days with hydrogen at 475° before a phosphorus pentoxide tube failed to gain in weight when treated with the off-gas. The high temperature of reduction doubtless decreased its activity. However, because of the data obtained by Ogden[6] concerning this catalyst, it seemed desirable to run experiments at 444°.

Experimental Procedure

The volume of the dead space of the apparatus was measured by the method described in detail by Williamson[7] substituting helium for nitrogen. The volumes were determined at the several temperatures to be investigated, thereby eliminating errors of calculation. The rates of adsorption of hydrogen at constant pressure by the various catalysts were determined at pressures which were dictated by the rates of adsorption at various temperatures. The adsorption isotherms were determined in the usual manner, by introducing a known amount of gas to the evacuated catalyst and measuring the equilibrium pressure.

Experimental Results

Experiments with Zinc Oxide.—According to Taylor and Sickman activated adsorption of hydrogen occurs in the temperature range between 0 and 302°. Their investigation was conducted with an approximate constant volume technique only. We find, in the temperature range from 110 to 302°, results analogous to those of the authors cited. However, when runs were made between 0 and 110° (a region not previously utilized), surprising anomalous data were consistently obtained. The rates of adsorption and the amounts adsorbed at 56 and 80° were discovered to be greater than at 110°; *e. g.*, this feature is exhibited by the rate curve of the adsorption process at 56° crossing that at 110°.

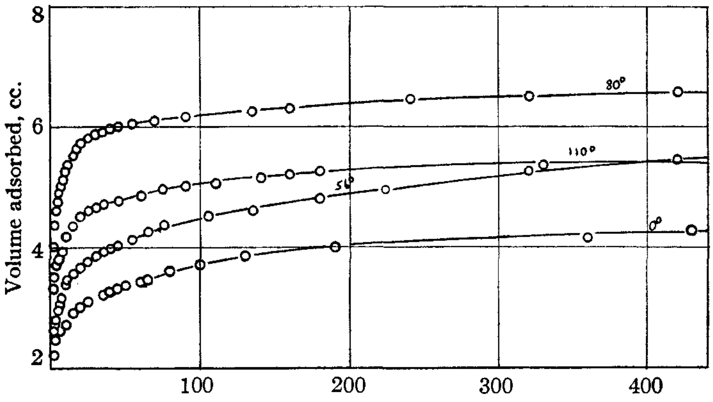

Fig. 2.—Velocity of adsorption of hydrogen by zinc oxide at 1 atm. pressure.

In order to check this perplexing observation the rate curves at the two temperatures were repeated. A run was made at the lower temperature, then at the higher temperature, followed by another experiment at the lower temperature. This stepwise procedure was designed to eliminate the possible progressive alteration of the catalytic surface. In this fashion twenty-four experiments were performed at the two temperatures in question. The maximum deviation was approximately 5%. The abnormality of the rate of adsorption at the lower temperature appeared to be vindicated. There was a possibility, however, that the surface of the catalyst was poisoned in some manner, so another sample of the catalyst was taken for experimentation.

The weight of the zinc oxide catalyst used in this second instance was 26.38 g. The same results were again obtained. The evacuation temperature for these experiments was 400° and had been found suitable to afford reproducible results. The question arose whether or not a partial reduction of the catalyst might account for the discrepancy. Judging from the literature[8] it is impossible to reduce zinc oxide with hydrogen under the conditions of the experiments. Nevertheless, hydrogen was passed over the catalyst for twelve hours at 450°; no water vapor was detected by using a phosphorus pentoxide tube. The rate of adsorption of hydrogen was determined at several temperatures. The results of these experiments are given in Figs. 2 and 3. Figure 4 represents the isobar from values of the velocity curves after five minutes and a thousand minutes. It demonstrates clearly the existence of two maxima in the activated-adsorption region. The first maximum occurs approximately at 80° and the second at about the same temperature as that found by Taylor and Sickman,[1] namely, 218°.

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(4) Lazier, U. S. Patent, 1,746,783, Feb. 11, 1930; Natta, *Giorn. chim. ind. e. appl.*, **12**, 13 (1930).

(5) Mellor, Vol. XI, pp. 562, 586.

(6) Ogden, Master's Thesis, Manchester, England. 1932.

(7) Williamson, Doctor's Thesis, Princeton, 1931.

(8) Deville, *Ann. chim. phys.*, [3] **43**, 477 (1855); G. B. Taylor and Starkweather, THIS JOURNAL, **52**, 2323 (1930).

After prolonged heating of the catalyst at 450° its activity was greatly decreased. Doubtless there was considerable sintering of the catalyst. But the surprising phenomenon of the two maxima was still observable.

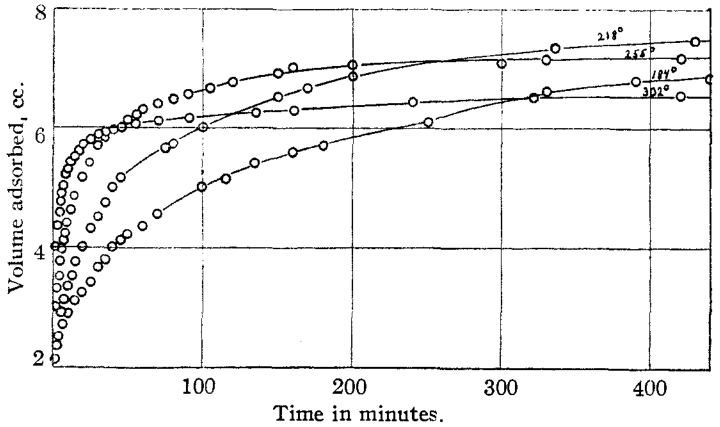

Fig. 3.—Velocity of adsorption of hydrogen by zinc oxide at 1 atm. pressure.

In order to check further the results so far obtained another sample of zinc oxide was prepared as before, and experiments at one temperature were bounded by runs at widely divergent temperatures. In this fashion the influence of progressively cleaning the surface was also minimized. Consequently the objections on this score raised by Burrage[9] cease to have weight.

The presence of the two maxima in the isobar of this catalyst was even more marked than in the case of the former sample. Thus it would appear that the existence of more than one maximum is real and reproducible. Taylor,[10] in an early article on activated adsorption, pointed out the possibility of two types of activated adsorption occurring on the same surface. The foregoing data appear to supply evidence for this prediction.

For both these catalysts adsorption isotherms at −78° and liquid air temperatures were studied. From the isotherms of the second sample the total adsorptions at low temperatures appearing on the isobar of Fig. 4 were obtained.

Experiments with Zinc Chromite.—Taylor and Kistiakowsky[3] and also Garner and Kingman[11] have published data indicating that zinc chromite has a much greater capacity for the adsorption than zinc oxide alone. This is true also of our sample which was reduced *in situ* and weighed 12.5 g. The rates of adsorption at one atmosphere were measured. The form of the curves changes normally with the temperature increment. There is evidence of only one slow adsorption process beginning at −78°. The isobar climbs slowly to a maximum at about 200° and then decreases.

The fact that activated adsorption occurred at −78° was indicative of a remarkably low activation energy for the more active spots on the surface of the catalyst. Because of the very slight activation energy of the first few cubic centimeters of the hydrogen adsorbed, their velocity of adsorption could not be measured at one atmosphere pressure.

In order to measure the velocity of this extremely rapid process, rate measurements were made at one-half an atmosphere and one-quarter of an atmosphere. The data obtained were reproducible to 0.1 cc. in 15 cc. adsorbed. From these experiments the activation energies given in Tables IV, V and VI were calculated.

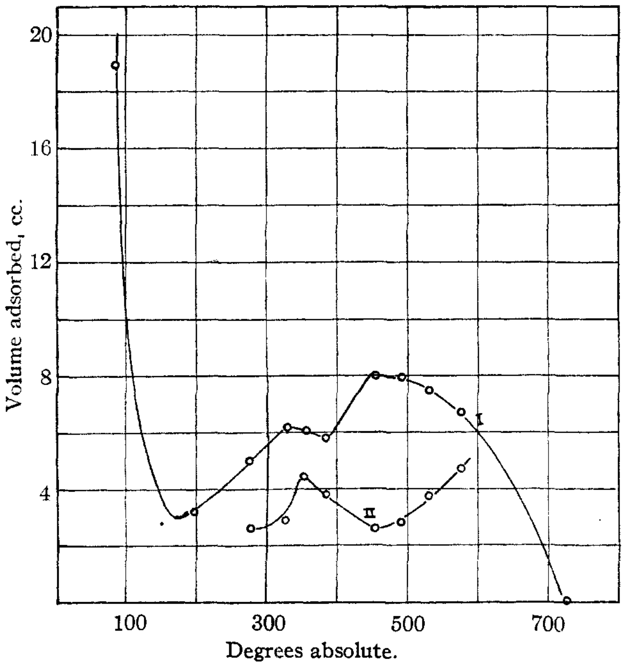

Fig. 4.—Adsorption isobar (760 mm.) of hydrogen on zinc oxide.

At 255 and 302° adsorption isotherms were measured. These temperatures being well over the maximum point of adsorption, equilibrium was rapidly attained at the various pressures re-

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(9) Burrage, Faraday Soc. Symposium, 1932; *Trans. Faraday Soc.*, **29**, 677 (1933).

(10) Taylor, This Journal, **53**, 578 (1931).

(11) Garner and Kingman, *Trans. Faraday Soc.*, **27**, 322 (1931).

TABLE I

ADSORPTION ISOBAR OF HYDROGEN ON ZINC CHROMITE

Time in min. before reading	Cc. of hydrogen adsorbed N. T. P. at °A.									
	82	190	273	330	353	383	457	491	527	575
1000	28.2	8.0	14.0	15.6	16.5	17.1	20.1	19.7	17.6	16.3
5	..	..	11.2	11.9	12.4	13.0	13.6	14.3	15.0	14.5

quired by the experiment. The heat of adsorption was estimated from these isotherms to be about 23 kilocalories.

Experiments on Zinc Oxide–Molybdenum Oxide.—According to the work of Ogden[6] on the adsorption of hydrogen by zinc oxide promoted by molybdenum, the activity of the catalyst was below that of zinc oxide alone. Activated adsorption set in only at (approximately) 200°. Due to the initial temperature of reduction of his catalyst, Ogden was unable to secure velocity measurements above the temperature of maximum adsorption. Profiting by his experience, the catalyst used in these experiments was reduced at a higher temperature. The temperature of the maximum value of adsorption was in the neighborhood of 375° (*cf.* Table II).

TABLE II

ADSORPTION ISOBAR OF HYDROGEN ON ZINC OXIDE PROMOTED WITH MOLYBDENUM OXIDE

Weight of sample 38.09 g.

Time in min. before reading	Cc. of hydrogen adsorbed, N. T. P. at °A.								
	82	190	273	383	491	527	575	613	717
1000	6.8	0.0	0.0	0.0	1.2	2.3	4.0	5.1	4.4
5		0.0	0.0	0.0	0.05	0.2	0.5	1.6	3.1

This temperature range is quite different from that of the studies on zinc oxide and zinc chromite. Furthermore, since the velocity of the adsorption was sufficiently low, it was possible to record the rate of adsorption of the first gas adsorbed, so that the activation energy required might be calculated. This had been impossible in the case of the two former catalysts. Confirming Ogden, we found that the surface of the catalyst was very stable and that the results were easily reproduced.

Discussion and Calculations

The activation energy characteristic of a slow adsorption process may be calculated from rate curves of adsorption at two different temperatures. The slope of the tangent at any point gives the velocity of adsorption at that time.

Since the activity of the active spots on the surface of the catalyst varies, the first few cubic centimeters adsorbed should have the least activation energy with a progressively increasing activation energy as the surface approaches saturation at any temperature. For a single type of activated adsorption there should be activation energies of a characteristic range of magnitudes. Further, for a specified amount adsorbed, there should be a definite value for the activation energy. The values listed in Table III were calculated from the experiments of Figs. 2 and 3.

TABLE III

ACTIVATION ENERGIES OF ADSORPTION IN KILOCALORIES OF HYDROGEN ON ZINC OXIDE

H_2 ads. N. T. P., cc.	2.3	2.7	3.1	3.35	3.75	4.00	4.50	6.00
E, 0–56°	..	3.3	4.8	5.2	6.0	6.4	..	..
E, 184–218°	7.7	9.7	10.2	10.1	10.7	11.0	12.0	15.3

The values for the activation energies of adsorption processes in the higher temperature range are two to three times as great as those of the lower temperature range, 0–110°.

The activation energies given in the third column of the table are very similar to the values found by Taylor and Sickman in the same temperature range. Since the above figures were calculated from experiments conducted at constant pressure (760 mm.), it is not surprising that there is a greater difference between the two extremes than in Taylor and Sickman's data. They worked at constant volume, the pressure decreasing slightly during the course of the run.

Examining these conclusions more critically, we find that the heat of the van der Waals adsorption from the isotherms at liquid air temperature and −78° was about 1000 cal. According to this figure there should be no measurable amount of van der Waals adsorption at room temperature and above. It is, therefore, impossible to ascribe the second maximum of the isobar to the overlapping of the van der Waals adsorption region and the zone of activated adsorption.

In addition, an inspection of the graphs will show that it is not merely a question of the quantity of the gas adsorbed at the various temperatures that gives evidence of the two types of activated adsorption, but also the relative velocities at the different temperatures must be considered. The velocity of adsorption increases with rise in temperature, then falls off; with further elevation of the temperature it begins to rise again. This state of affairs would not exist unless there were two mechanisms requiring different activation energies.

For zinc chromite only one adsorption process requiring an activation energy was evident. The activation energies calculated for these experiments are collected in Tables IV, V and VI. The agreement between the data thus compiled is good and testifies somewhat to the correctness of the assumptions and procedure on which they are based.

TABLE IV

ACTIVATION ENERGIES IN KCAL. CALCULATED FROM EXPERIMENTS AT ONE-QUARTER ATMOSPHERE ON ZINC CHROMITE

H_2 ads. N. T. P., cc.	6.50	6.75	7.05	7.40	7.95
E, 80–218°	1.4	1.6	1.8	2.5	2.6

TABLE V

ACTIVATION ENERGIES IN KCAL. CALCULATED FROM EXPERIMENTS AT ONE-HALF ATMOSPHERE ON ZINC CHROMITE

H_2 ads. N. T. P., cc.	7.55	7.90	8.30	8.70	9.00	9.50
E, 80–110°	3.6	3.0	3.3	3.6	3.7	4.2
E, 110–184°	3.2	3.3	3.2	3.4	4.3	4.6

By a comparison of the activation energies necessary for the adsorption of hydrogen on zinc oxide and on zinc chromite, the relative activities of the two catalysts may be roughly estimated. The presence of the promoter greatly decreases the energy necessary for the adsorption of the hydrogen to occur.

TABLE VI

ACTIVATION ENERGIES IN KCAL. CALCULATED FROM EXPERIMENTS AT ONE ATMOSPHERE ON ZINC CHROMITE

H_2 ads. N. T. P., cc.	12.60	13.10	13.50	14.50	14.95	15.25	15.50
E, 80–110°	6.0	8.0	11.0	12.1	13.5	..	..
E, 110–184°	..	9.1	9.7	10.5	11.0	11.5	11.8

Table VII lists the activation energies for the adsorption of hydrogen at one atmosphere pressure on the zinc oxide–molybdenum oxide catalyst. The total adsorptive capacity of the catalyst was decreased and the activation energy was markedly increased by the molybdenum.

TABLE VII

ACTIVATION ENERGIES IN KCAL. FOR THE ADSORPTION OF HYDROGEN ON ZINC OXIDE–MOLYBDENUM OXIDE AT ONE ATMOSPHERE PRESSURE

H_2 ads. N. T. P., cc.	0.15	0.40	0.50	0.70	0.95	1.15
E, 254–302°	17.2	22.4	24.6	26.5	27.4	27.3
E, 302–337°	..	..	..	24.9	26.0	27.0
H_2 ads. N. T. P., cc.	1.40	1.80	2.00	2.40	2.95	3.20
E, 254–302°	27.6	28.2	..	..	..	..
E, 302–337°	27.2	27.8	28.5	32.0	32.8	33.9

Summary

Hydrogen was adsorbed by zinc oxide in what appeared to be three different types of adsorption: (1) van der Waals adsorption between liquid air temperature and −78°; (2) a slow adsorption process extended from 0° to about 100°, requiring an activation energy of the order of 5 kcal.; and (3) another slow adsorption process commencing in the neighborhood of 100° and still measurable at 302°, having an activation energy of the order of 12 kcal. These results were found to be reproducible on three different samples of the catalyst.

Using chromium oxide as a promoter for zinc oxide produced a catalyst which was considerably more active than the unpromoted oxide. The quantity of hydrogen adsorbed, due to van der Waals forces, was very much greater in the case of this adsorbent. Only one form of activated adsorption was evident. It began at −78°. Such a low temperature of adsorption was indicative of an extremely low activation energy. The highest adsorption was obtained at 218°.

Zinc oxide promoted with molybdenum oxide was less active. Van der Waals adsorption of hydrogen occurred at the temperature of liquid air. No adsorption took place between −78 and 200°. Above this temperature hydrogen was adsorbed slowly. The activation energy for the first portion of the gas taken up was 17 kcal. The maximum adsorption took place at 400°.

In all of the velocity measurements the pressure was maintained constant.

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