[CONTRIBUTION FROM THE FRICK CHEMICAL LABORATORY, PRINCETON UNIVERSITY]

The Interaction of Hydrogen and Deuterium on Zinc Oxide

BY ELGENE A. SMITH AND HUGH S. TAYLOR

In developing the concept of activated adsorption, Taylor[1] discussed as a particular case an adsorbent possessing two types of activated adsorption. If the activation energies and heats of adsorption are sufficiently different, the adsorption isobar should show two maxima with a region of non-equilibrium points between them. This prediction was realized experimentally by Taylor and Strother[2] in the adsorption of hydrogen on zinc oxide. Emmett and Harkness[3] have discovered another example of this phenomenon in the adsorption of hydrogen on promoted iron catalysts. The existence of these two forms of activated adsorption should lead to anomalies in those reactions involving hydrogen which take place on zinc oxide in the temperature range of these maxima. However, the study of such a reaction is complicated by two important difficulties. In the first place it is very difficult to obtain reproducible rates of reaction on zinc oxide, as shown by Taylor and Sickman.[4] In the second place, while hydrogen shows two types of activated adsorption, the behavior of the other reactant might not be known in any such detail. It is very likely that the effect of the second reactant might mask the effect of the hydrogen adsorption. Thus, the difficulty of obtaining precise velocity measurements combined with the unknown effect of the second reactant make the utility of studying such a reaction very doubtful, at least for the purpose of obtaining detailed information concerning the type of surface and the adsorption and desorption processes operative.

The situation was changed, however, when pure deuterium became available, since it is an ideal reactant to use with hydrogen. Deuterium will have very similar adsorption characteristics, although the temperatures of the isobar maxima may be shifted slightly. However, the possibility that measurement of the rate of the reaction $H_2 + D_2 \longrightarrow 2HD$ would yield definite information concerning the processes of adsorption and desorption on zinc oxide was very good. Some indication of the uniformity of the catalyzing surface might reasonably be expected. There are no complicating side reactions, and, although the difficulty of reproducibility still remains, it is at a minimum for this reaction. All in all, this reaction is an ideal one for the study of catalyst characteristics. Hence the present work of obtaining a detailed knowledge of the above reaction over a wide range of temperatures was undertaken.

Preparation of Materials

Hydrogen.—The hydrogen used was prepared electrolytically from a 15% caustic soda solution. After passing over platinized asbestos and calcium chloride it was dried thoroughly by allowing it to leak slowly through a liquid air trap.

Deuterium.—The deuterium used throughout these experiments was obtained from one of the portable laboratory generators. Oxygen was removed by passage over a hot platinum wire. Like the hydrogen it was dried by slow passage through a liquid air trap. The deuterium gas was 99% D.

Para-Hydrogen.—Forty-five per cent. para-hydrogen was prepared by the method of Farkas,[5] over charcoal at liquid air temperature.

Mixtures of H_2 and D_2.—Throughout these experiments, mixtures of a D/H ratio of unity were used. This was to obtain as large an analytical spread as possible between the mechanical mixture and the equilibrated gas. These mixtures were made up manometrically from the pure H_2 and D_2 gases. Complete mixing was obtained by allowing to stand overnight or by heating one side of the storage flask a few times.

Zinc Oxide Catalyst.—The zinc oxide was prepared *ex* oxalate according to the usual procedure of this Laboratory as recommended by Taylor and Sickman.[6] The zinc oxide remaining after the decomposition of the oxalate was broken up into small pieces of 1–2 mm. in diameter. These pieces, while crumbling to a powder rather easily, had enough rigidity to allow their disposition in the catalyst tube without crushing. This made possible a smooth flow of gas through the catalyst tube without the use of a support of any kind.

Apparatus and Calibration

Dynamic Apparatus.—The dynamic runs were made with pressures over the catalyst of between 30 and 80 mm. A constant pressure was maintained over the catalyst by means of the calibrated leak Lk and the needle valve V, combined with a constant pressure source St and a Hyvac pump (see Fig. 1). The gas in the storage bulb was maintained at a constant pressure by the pressure exerted by the gas liberated in W when the electrical circuit was completed

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[1] Taylor, THIS JOURNAL, **53**, 578 (1931).

[2] Taylor and Strother, *ibid.*, **56**, 586 (1934).

[3] Emmett and Harkness, *ibid.*, **57**, 1631 (1935).

[4] Taylor and Sickman, *ibid.*, **54**, 692 (1932).

[5] Farkas, "Light and Heavy Hydrogen," Cambridge University Press, 1935, p. 30.

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

at the tungsten tip in the manometer M_3. A potential of 30 v. was used in the electrical circuit. Proper adjustment of the resistance R permitted the attainment of a workable balance between arcing at the tip and a sufficient speed of gas evolution. This arrangement kept the pressure in St constant to less than one mm. Four separate tips at different heights allowed four working pressures to be used. In the apparatus these pressures were 634, 471, 350, and 168 mm. For all of these pressures in St, a standard pressure of about 50 mm. was maintained over the catalyst K by adjusting the opening of the needle valve V which was connected directly to the Hyvac pump.

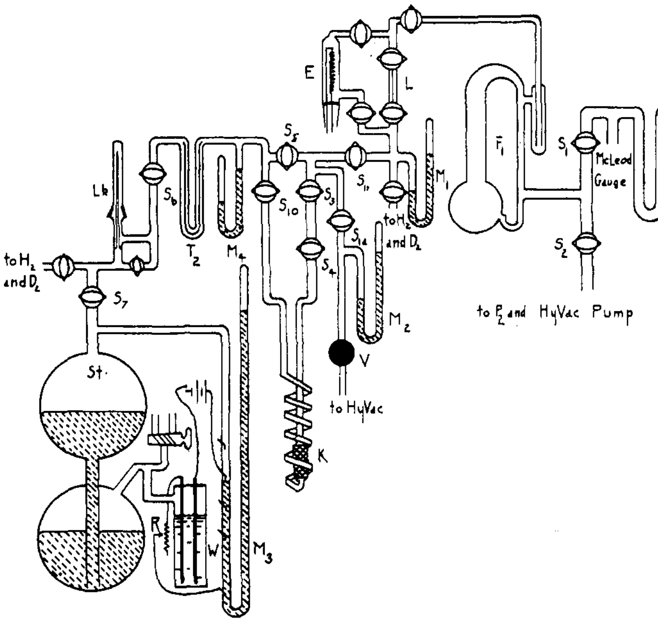

Fig. 1.

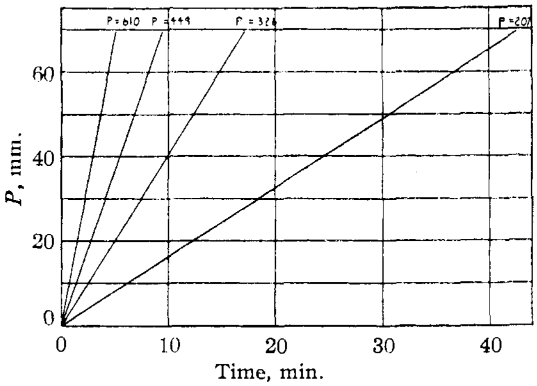

Fig. 2.

The pressure on the catalyst was read on the manometer M_2. Manometer M_4 was used in conjunction with M_2 to show the pressure difference across the catalyst tube. This difference amounted to about 3 mm. M_2 was used as the standard manometer. T_2 was cooled in liquid air to freeze out the mercury vapor which was found to poison the zinc oxide catalyst.

Calibration of Leak.—The calibration of the leak Lk was carried out as follows. A liter bulb was attached between S_5 and S_6. The bulb and leak were evacuated as far as S_7. S_7 was then opened and the rate of pressure increase with time was followed on M_4. During the course of the calibration the source was kept at constant pressure P by means described above. From the slopes of the curves obtained in this manner the relative rates of egress of gas were accurately determined. Fairly good measurements of the absolute rates of flow were obtained by simple gas law calculations. However, as the exact volume of the flask and connecting tubing was not measured, the number of moles leaking through per minute may be in error by some constant factor. For the calculations of the contact times, however, the absolute values of the flow were used, as this procedure will give contact times of the right order of magnitude and will not affect the relative accuracy. It must be borne in mind that the contact times so calculated will not be comparable with those used in the static experiments, not only because of the condition discussed above but also because the exact reaction volume in dynamic experiments is always somewhat in doubt especially when it is partially filled with catalyst. The contact times will be discussed at greater length below.

The results of these calibrations are plotted in Fig. 2 in which the pressure P is shown as a function of time. As may be seen from the curves, it is a linear function. This linearity was somewhat surprising but further experiments on similar leaks with air confirmed the result and further showed that the linearity held until the pressure in the flask was about one-third of that in the source. Since this is so, and as long as one stays below this limit, it may be seen that the number of moles coming through the leak per minute is independent of the exact pressure over the

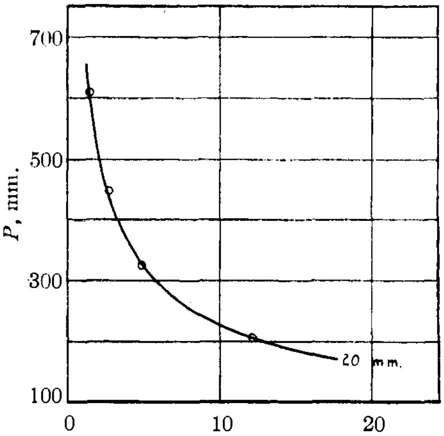

Fig. 3.

catalyst. This fact has been very useful when runs have been made at different pressures. The actual calibration of the leak was conducted at 610, 449, 326, and 207 mm. as shown in Fig. 2. These curves are represented in another manner in Fig. 3. Here the source pressures are plotted as ordinates and the times necessary to build up twenty mm. pressure in the evacuated flask are plotted as abscissas. These curves show the very marked effect of the source pressures on the rate of flow. Some of the experimental work was done at these pressures but during the greater part of the work another manometer M_9 was used with contacts at 634, 471, 350, and 168 mm. The rates of flow at these pressures were obtained from Fig. 3 by interpolation and extrapolation.

Calculation of Flow Rates and Contact Times.—The rates of flow were calculated in the following manner. Under the conditions obtaining in the flask we may differentiate the gas law equation $PV = nRT$ with respect to time and obtain

$$dn/dt = (V/RT)\ dP/dt$$

V and T being known and dP/dt measured we may calculate dn/dt. From these values were calculated the number of cubic centimeters of gas (N.T.P.) flowing through the leak per minute. Table I shows these values.

TABLE I

Source pressure	d cc./dt
610	18.76
449	10.55
326	5.783
207	2.355

For working contact times we have assumed for simplicity that the entire cross section of the tube is available for flow. The times thus obtained are admittedly too large but as comparative times only are important they should be satisfactory. Furthermore, we have assumed that by the time the gas has reached the catalyst tube it has attained the temperature of the bath used and has expanded or contracted to this temperature. The long pre-heating coil and the slow flows justify this assumption. One catalyst tube used (No. 2) was 16.5 mm. in diameter and a length of 85 mm. was occupied by catalyst. Hence the catalyst volume is $(0.825)^2$ 3.14 × 8.5 cc. The volume of gas streaming over the catalyst per minute is, say, 18.76 cc. (N. T. P.). If b is the working pressure over the catalyst, and T is the catalyst temperature, the volume of gas passing per minute is $18.76 \times (760/p)(T/273)$. The contact time is obtained by dividing the catalyst volume by the volume of gas passing per minute. Thus

$$\text{c.t.}_{\text{min.}} = (0.825)^2 \times 3.14 \times 8.5 \times 273\ p/760T18.76$$

or in general

$$\text{c.t.}_{\text{sec.}} = 391.72\ \frac{p}{T\ (\text{cc./min.})}$$

A similar procedure has been used to calculate all of the dynamic contact times.

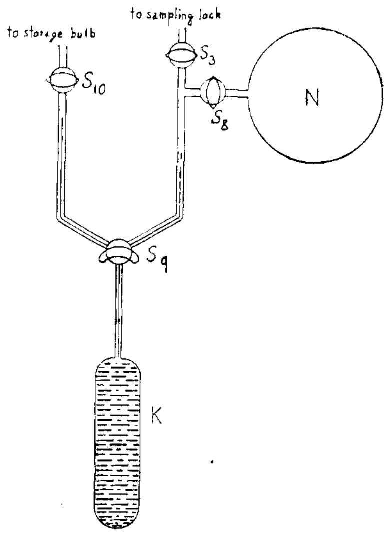

Fig. 4.—Static apparatus.

Static Experimental Arrangement.—For the static experiments the arrangement shown in Fig. 4 was employed. The same general arrangement as in Fig. 1 was used with the section shown in Fig. 4 replacing that section of Fig. 1 between stopcocks S_3 and S_{10} as shown. N was a quarter liter bulb which was used to remove by expansion the gas phase for analysis from the catalyst tube K. In some of the experiments small samples were taken from time to time. These were collected by expansion in the tubing between stopcocks S_2, S_8, and S_9. Capillary tubing was used between S_9 and K to cut down the dead volume as much as possible.

Analytical Procedure

Method of Analysis.—The analysis of the samples throughout these experiments was carried out by the Farkas micro-thermal conductivity method.[7] As the theory of the method has been discussed fully by Farkas, it will not be developed here. It will suffice to say that by means of the different specific heats of H_2, HD, and D_2, at liquid air temperatures one is able to determine the concentrations of the three species of molecules in a gas sample containing only these molecules. An empirical calibration and a knowledge of the equilibrium constant for the reaction $H_2 + D_2 = 2HD$ are also necessary. The equilibrium constant was calculated by Urey and Rittenberg[8] and later experimentally confirmed by Rittenberg, Bleakney, and Urey[9] and by Gould, Bleakney, and Taylor.[10]

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(7) A. Farkas and L. Farkas, *Proc. Roy. Soc.* (London), **A144**, 467 (1934); A. Farkas, "Light and Heavy Hydrogen," p. 134.

(8) Urey and Rittenberg, *J. Chem. Phys.*, **1**, 137 (1933).

(9) Rittenberg, Bleakney and Urey, *ibid.*, **2**, 48 (1934).

(10) Gould, Bleakney and Taylor, *ibid.*, **2**, 362 (1934).

The varying success of the Farkas method for the analysis of hydrogen–deuterium mixtures and the different operating conditions advocated for it by the various laboratories make it seem worth while to discuss in some detail the method of operation which we have found most suitable for our purposes. The following treatment assumes a working knowledge of the method.

The measuring cell is composed of a two-inch (5-cm.) length of 0.4 mil bare platinum wire mounted axially in a 16-mm. tube. The wire is held taut by a small tungsten spring. The lead wires are enclosed in a glass tube which is evacuated to cut down lead and convection losses. The electrical circuit is a simple Wheatstone bridge circuit with a bridge ratio of 300:1.

As one of the difficulties of this method is the construction of the conductivity cell, we will discuss here a method of construction which has proved entirely satisfactory. The only serious problem encountered is that of mounting the fine wire taut and in such a manner as to avoid vibration of the wire. As Pyrex glass was used exclusively the wire must be spot welded for even silver solder will melt during the subsequent glass blowing. As the wire is fine and breaks in two easily, the electrodes of the welder cannot be placed directly in contact with the wire. To overcome this difficulty the practice was adopted of welding a small piece of platinum foil onto the tungsten lead. This foil was then folded over with the fine wire between the folds. The two parts of the foil were then welded together catching the wire between them. Although metal electrodes tend to stick to and tear the foil, carbon electrodes are admirably suited for such work. Two 8-mm. carbon electrodes heated by the 110 v. circuit with a variable resistance in series proved a very convenient form of spot welder.

The main problem is that of making the final weld while the spring is under tension and of letting the spring draw the wire taut without snapping the wire. The device illustrated in Fig. 5 was made to accomplish this. The distance between the jaws E and F may be changed gradually by turning the knurled head D. The spring was clamped at rest between jaws E and F when at their minimum distance apart, while the other lead was clamped in G. The two platinum foils were then welded on at A and B. The wire, both ends protruding over the edge of a suitable support, was brought into position and the weld made at A. The other end was then welded at B with as little slack in the wire as possible. The jaw F was opened and the wire tightened by carefully moving the jaw E until the spring S had stretched a suitable amount. The final weld was made at C, the jaws E and G opened, and the glass jacket sealed on. The tendency toward a lateral vibration of the wire was controlled by slipping the end of the spring between S and B through a little glass sleeve which was fastened to the rigid tungsten lead at H. This proved a very satisfactory method of mounting fine wires. We wish here to express our appreciation for the invaluable coöperation of Dr. N. R. Trenner in the development of this method.

The question of preliminary heat treatment of the wire requires a little discussion. In our experience, the heating of a wire to 500° renders it practically useless for quite a period of time. The calibration curves are entirely changed and the stability of the surface is very bad. When the gas layer is driven off the surface of the wire by heating, the accommodation coefficient takes on a very small value as evidenced by the much higher temperature of the wire. Thus the resistance values one obtains after this treatment are considerably higher than before, and, indeed, the $\Delta\Omega$ one obtains between H_2 and D_2 is appreciably larger than the usual value. However, the wire tends, rapidly at first, and then more or less slowly, to return to its original condition, presumably by the reformation of a surface gas layer. This return to normal, if left to itself, may take days or weeks, and until it is nearly back its condition is very unstable and duplication of readings is well nigh impossible. However, our experience has shown that the speed of formation of this surface layer may be increased greatly by the simple procedure of admitting a few cc. pressure of air to the cell and gently torching out the entire cell for ten minutes. After pumping the cell out overnight it is, at least, in a condition to carry out a recalibration. Heating the wire electrically either in air or in hydrogen has proven ineffectual. It has been evident, however, that a wire which has been overheated is always more prone to change than one which has never had this treatment.

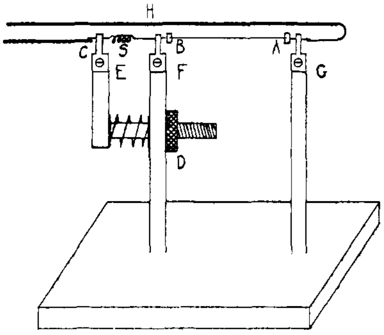

Fig. 5.

The error, inherent in the Farkas arrangement, due to a separation of the isotopes during the adjustment of the pressure was eliminated in much the same manner as that used by Wirtz.[11] A sample is admitted to a section of tubing containing a small manometer M_1 (see Fig. 6). The actual sample analyzed is then taken into lock L, whence it is pumped by F_1 to the measuring cell C. After a few trials one can tell from the manometer reading the number of shots from lock L which are necessary to fill the cell. The final adjustment of pressure is made by means of raising or lowering the mercury level in the side tube of the McLeod gage G, the large volume of the gage being closed from the rest of the system by the mercury level.

The calibration should be carried out with respect to the temperature of the liquid air of the bath as well as with respect to the composition of the gas. The effect of the liquid air temperature is shown clearly by Fig. 7 in which the resistances as read on the bridge and corresponding to temperatures T_2 and T_2' are plotted against the temperature of the liquid air. These curves were obtained over a period of weeks and show that one may duplicate the same actual resistance of the wire as well as the difference $\Delta\Omega$.

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(11) Wirtz, *Z. physik. Chem.*, **B32**, 334 (1936).

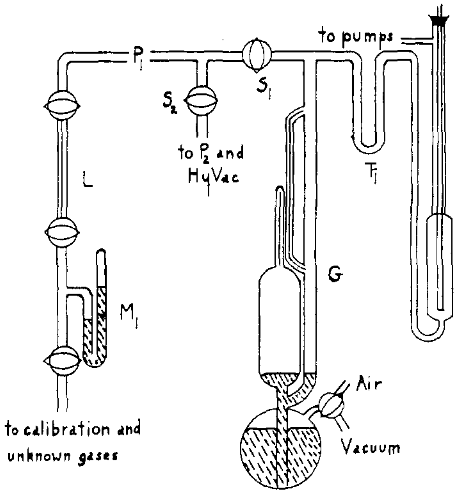

Fig. 6.

As long as these absolute values remain the same, experience has shown that the entire calibration curve remains constant. Occasionally these resistances will change for no apparent reason. However, these changes are entirely discontinuous and a single reading suffices to detect such a change. The values may go either up or down usually from 20 to 40 ohms on the bridge box. Such a change in the surface of the wire merely results in shifting all the curves of Fig. 7 up or down by the same amount and one gets another family of curves entirely similar to that shown.

We have observed two types of calibration curves. These types are listed as 4(a) and 4(c) by Wirtz.[11] The linear relationship between the composition and $\Delta\Omega$ for the unequilibrated gas held with the first gage used, while the latter type has held for the later ones. Both types have never been observed on the same gage and never has a lower resistance value been obtained for the equilibrated gas than for the unequilibrated mixture.

A slight modification of the actual measurement technique which we have found considerably improved the reproducibility on successive samples, is the slight overheating of the wire on each sample. After the introduction of the sample into the cell and the approximate adjustment of the pressure, the wire is raised to a temperature about 20° higher than the final T_2. It is left at this temperature for a minute, after which it is again brought to T_1 and the final pressure adjustment made. T_2 is then determined in the usual manner.

In connection with this procedure, the wires have shown themselves to be perfectly stable beneath a rather definite but unknown temperature. The wire may be overheated up to this temperature and on lowering the current will renew again the starting temperature. If, however, the wire is heated above this temperature the resistance takes a sudden jump and on again lowering the current the wire comes to equilibrium at a considerably higher temperature than before. The considerably changed resistance values obtained after such a treatment indicate a different condition of the wire surface and so different accommodation coefficients.

The deleterious effect of traces of air and oxygen on the conductivity wire has been widely reported. Whether these reports are based on actual experiments or are merely reiterations of the original statement is a matter of doubt. Accordingly a few experiments testing this point were performed. Hydrogen containing 0.5% of oxygen gave a reading which could not be distinguished from that of pure hydrogen, while a 1% oxygen mixture had a small but not disastrous effect. Mixtures containing more than about 1% of oxygen gave distinctly wrong values but the wire was unaffected by these mixtures in subsequent readings in pure hydrogen.

The operating wire temperatures used were those recommended by Farkas. As stated by Wirtz, no improvement of results is obtained by the use of other temperatures. As for the pressure in the cell, we used 0.07 mm. of mercury. While this pressure does not give quite as big a spread as a lower pressure, the reproducibility here is just sufficiently better to recommend its use.

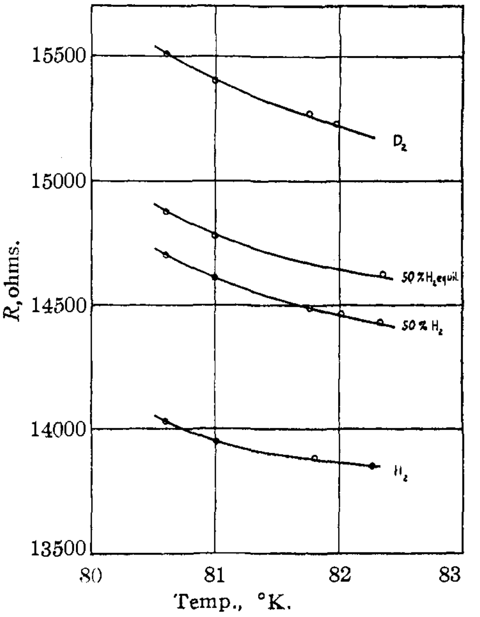

Fig. 7.

Experimental Procedure

In the dynamic experiments analyses were made on the adit gas, untreated and after equilibration in the vessel E on a platinum wire brought to a red heat electrically. The exit gas was measured immediately afterward for greater accuracy in the resistance values and to minimize corrections due to changes in the liquid air temperature of the gage. This was followed by an equilibration of the exit gas and the final measurement of conductance. Special attention was paid to purging the catalyst system. In two sets of experiments pressures of 60 and 53 mm. over the catalyst were used and the temperatures of the catalyst controlled by vapor baths.

In the static runs two different procedures were used. In the first case (Procedure 1) gas was admitted to the catalyst and shut off by means of S_9 (Fig. 4). After an appropriate time interval the gas was allowed to expand into the flask N. This flask was large in comparison to the catalyst tube in order to collect practically the entire gas sample. The gas in this flask was then analyzed as in the dynamic case except that here the exit gas itself was brought to equilibrium to obtain the complete reaction value. This was necessary because of the shift in the H to D ratio in the catalyst tube. This shift will be discussed in detail later. By taking samples in this way we get only one point on the rate curve from each experiment. The times of contact used in this method varied from one minute to three hours.

Procedure 2 consisted of taking small samples from time to time from the reaction vessel. These small samples were taken by expansion in the tubing between stopcocks 3, 8, and 9. This volume had to be large compared to the capillary tubing between S_9 and K but small compared to the size of the entire catalyst tube. In fact it was about one-fifth of the entire catalyst tube size. By taking samples in this manner the entire course of the reaction in a single experiment could be obtained. This procedure was used for two other reasons than that of time saving. In the first place, we wished to investigate the time necessary for the H to D ratio shift mentioned above to take place and, in the second place, this procedure assured that the catalyst surface remained the same for the entire rate curve. Thus the comparison of a rate curve obtained in this manner with one obtained by Procedure 1 will tell whether the surface has been reproducible. The effect of the decrease in pressure caused by the removal of these samples will be discussed later. Procedure 2 could be used only when the rate of the reaction was fairly slow, for approximately fifteen minutes were necessary to complete the analysis of one sample before the next could be taken. Usually about six such samples were taken at fifteen-minute intervals. In general, the pressures used in the static experiments were about 155 mm.

For temperature control the usual baths were used at 0, −78, and −190°. An ice–salt mixture was used at −18°. A temperature of −45° was obtained by cooling acetone with solid carbon dioxide, with subsequent dropping in of small amounts of dry ice from time to time. A pentane thermometer in the bath gave the temperature. Temperatures between −78 and −190° were obtained by cooling petroleum ether with liquid air. The liquid air was blown through a lead coil immersed in the ether. The temperature was kept constant by judicious applications of liquid air.

In the static experiments as in the dynamic, the catalyst was evacuated for at least an hour at 400°.

Experimental Results

Static Measurements.—Measurements by the static method covering the temperature range 143 to 273°K. are summarized in Tables II and III. They were made on Catalyst No. 3, which consisted of 14.2 g. of the same preparation of zinc oxide as was used in Catalyst No. 2 of the dynamic runs. Table II summarizes the results of runs 57–86 made by Procedure 1, while Table III summarizes results of runs S1–S25 by Procedure 2. Of the data in Table II only those at 195 and 228° lend themselves to calculation of activation energy. They yield a value of 7800 cal. Above 228°K. the rate is so rapid that the effect of the back reaction is too great.

TABLE II

RESULTS BY PROCEDURE 1 ON ZINC OXIDE NO. 3 (14.2 g.)

Run	Contact time	Catalyst temp., °K.	Mole % HD
57	30 sec.	273	36.0
58	70 sec.	273	43.6
67	20 min.	195	10.8
75	20 min.	195	10.4
66	31 min.	195	15.0
70	40 min.	195	17.8
76	42 min.	195	19.6
73	60 min.	195	23.0
74	60 min.	195	24.3
77	60 min.	195	24.0
65	81 min.	195	32.6
69	81 min.	195	32.3
78	103 min.	195	36.2
79	4 min.	228	21.8
80	8 min.	228	28.4
81	15 min.	228	35.8
83	40 sec.	255	21.9
86	60 sec.	255	25.0
84	80 sec.	255	30.1
85	120 sec.	255	31.4

TABLE III

SUMMARY OF RESULTS BY STATIC PROCEDURE 2 ON ZINC OXIDE NO. 3

Runs	Temp., °K.	u	E, cal.
S7, 8, 9, 13, 19, 21, 22	195	0.938	4900
S10, 15	178	.280	600
S14, 18	143	.180	

The data summarized in Table III using Procedure 2 were from runs in which the actual data were corrected for variations in the temperature of the liquid air gage bath during the seventy-five minutes of a run in which six samples of exit gas were analyzed. They were corrected by a tested procedure[12] to a gage bath temperature of 80.92°K., variations in the temperature being sometimes as much as 0.20°.

In these experiments the percentage reaction per minute, u, was independent of the pressure over a range of 340–40 mm. pressure, that is, the actual number of moles reacted is proportional to the pressure. Thus, in the low temperature range at least, the reaction is first order, as might be expected at low pressures where the adsorption is proportional to the pressure.

Adsorption Ratio of H_2 and D_2 at Low Temperatures.—At temperatures of 255°K. and below, a shift in the hydrogen–deuterium ratio was

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[12] See Elgene A. Smith, Thesis, Princeton, 1937.

observed. The shift was of the order of 1–2%. The shifts were somewhat erratic but always in the direction of increasing hydrogen content of the gas phase. The cause was slight preferential adsorption of deuterium on the catalyst since the last gas to be desorbed from the surface was always deuterium rich. The average shifts at the several temperatures amounted to 0.65% at 255, 1.25% at 228°, 1.4% at 195° and to 2.9% at 80°K. At the latter temperature the differential adsorption process is complete in two minutes but required longer intervals of time at 195°K. The ready reversibility of the adsorption indicates that it is adsorption of the van der Waals type which is involved, the deuterium being more largely adsorbed due to its greater ease of condensation. The linear variation of shift with temperature indicates that the shift becomes zero at 300°K. where this type of adsorption probably approaches zero.

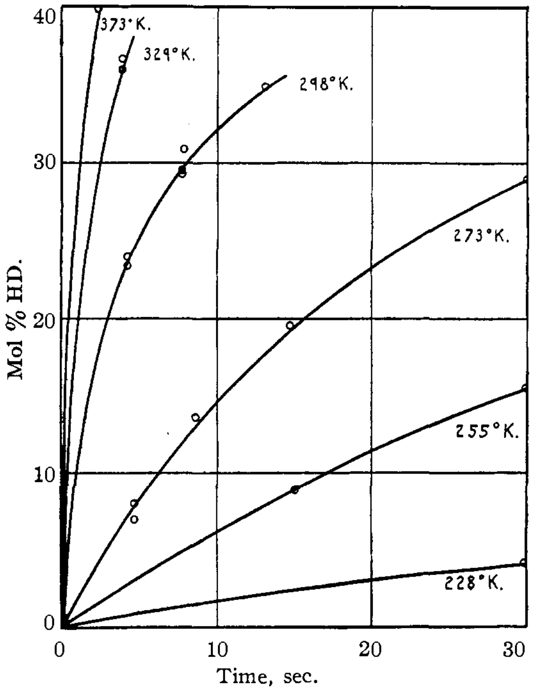

Fig. 8.

Para-Hydrogen Conversion at Low Temperatures.—At about 140°K. the reaction $H_2 + D_2 \longrightarrow 2HD$ on this catalyst becomes immeasurably slow. Measurements at 80, 100 and 118°K. showed that changes in thermal conductivity of the gas mixture over the catalyst were due to the occurrence of the reaction $o\text{-}H_2 \longrightarrow p\text{-}H_2$. When a mixture of one part of the equilibrium mixture of 47% para – 53% ortho H_2 with one part of deuterium was prepared and placed on the catalyst at liquid air temperature no change in thermal conductance of the gas occurred during one and one-half hours. The results also indicate that the conversion was taking place by the low temperature magnetic mechanism[5] (pp. 92–96). This reaction does not interfere at 143°K. and upward since, already at 143°K., the change in thermal conductivity due to ortho-para equilibration was within the error of experiment.

Dynamic Measurements.—Experiments 20–55 were made on Catalyst 2 which consisted of 16.5 g. of unsupported zinc oxide in the form of small lumps. The contact times on this catalyst varied from three to sixty seconds. These times are suitable for rate measurements from 228 to 373°K. although at 329 and 373°K. the rates are very rapid and the only values obtained were close to equilibrium.

Experiments 96–143 were made on Catalyst 4 which consisted of 0.1 g. of zinc oxide in a short length of 5-mm. Pyrex tubing. The contact times on this catalyst varied from 0.015 to 0.40 second. These times suit the rate of measurements from 329 to 491°K.

Due to an accident in which chlorobenzene vapor was introduced into the apparatus (Expt. 144) a series of experiments, 147–174, with a new catalyst (No. 5) was vitiated by gradual decrease in catalytic activity. With Catalyst 6, (0.14 g.) in Expts. 175–191, there is a slow decline of activity but a strict alternation of runs made possible the evaluation of the data in the temperature interval 383–457°K.

The data on Catalyst 2 are shown graphically in Fig. 8. Table IV gives the apparent activation energies calculated from the slopes of the straight lines from the origin to the shortest contact times at each temperature, u being the mole % HD divided by the contact time. The small values between 298 and 373°K. are caused by the back reaction being no longer negligible.

TABLE IV

ACTIVATION ENERGIES FROM DYNAMIC MEASUREMENTS ON CATALYST 2

Run	Catalyst pressure, mm.	Contact time, sec.	Mole % HD	u	Temp., °K.	E cal.
46	41	2.2	34.8	15.8	373	2900
41, 43, 44	62	3.8	35.7	9.4	329	3300
26, 27	62	4.2	23.7	5.65	298.5	7400
28, 30	62	4.6	8.1	1.77	273	8800
50	63	15.2	8.9	0.584	255	7400
40	63	67.5	6.6	.098	228	

The corresponding data on Catalyst 4 are given in Fig. 9 and Table V. The low value between 383 and 457° is of major interest as it occurred in the range where Strother noted inflections in the adsorption of hydrogen. This range was therefore studied in more detail at the intermediate temperatures 405 and 430°K., on Catalysts 5 and 6.

TABLE V

Run	Catalyst pressure, mm.	Contact time, sec.	Mole % HD	*u*	Temp., °K.	*E*, kcal.
97, 98	55	0.0142	7.4	521	491	13
102	54	.0481	9.6	200	457	2.7
115, 116	54	.0334	3.7	111	383	12.5
122	54	.0590	4.2	71.2	373	6
119	55	.0644	2.9	45.0	353	9
123	54	.2741	4.4	16	329	

The data on Catalyst 5 confirmed (semi-quantitatively for the reason given above) the data presented in Table VI for Catalyst 6.

TABLE VI

Run	Contact time, sec.	Catalyst temp., °K.	Mole % HD	*E*, kcal.
175	0.066	457	31.8	7.4
176	.071	430	23.8	
177	.075	405	20.0	
178	.071	430	22.0	
179	.079	383	10.7	11.7
180	.075	405	18.2	
181	.065	457	27.6	
182	.079	383	10.1	6.6
183	.037	457	13.0	
184	.039	430	9.0	0
185	.042	405	9.1	
186	.040	430	8.9	12.0
187	.044	383	4.5	
188	.044	383	3.8	10.6
189	.042	405	8.1	0
190	.040	430	8.1	5.8
191	.037	457	10.3	

General Summary of Activation Energies.—As collected in Table VII the apparent activation energies at low temperatures have very low values but quickly reach a value of 7–8 kcal. This value holds until a temperature of 373°K. is reached when the value rises to 11 kcal. Between 405 and 430°K. the rise in reaction velocity with temperature halts to increase once more between 457 and 491°K. where the apparent energy of activation has reached as much as 13 kcal.

TABLE VII

GENERAL TABLE OF ACTIVATION ENERGIES

Temp., °K.	*E* kcal.	Temp., °K.	*E* kcal.	Temp., °K.	*E* kcal.
491	13	373	6	255.5	7
457	7	353	9	227	7.8
430	0	329		195	4.4
405	11	298	7	178	0.6
383	12	273	8.8	143	
373		255.5		82	*p*-H_2 conversion

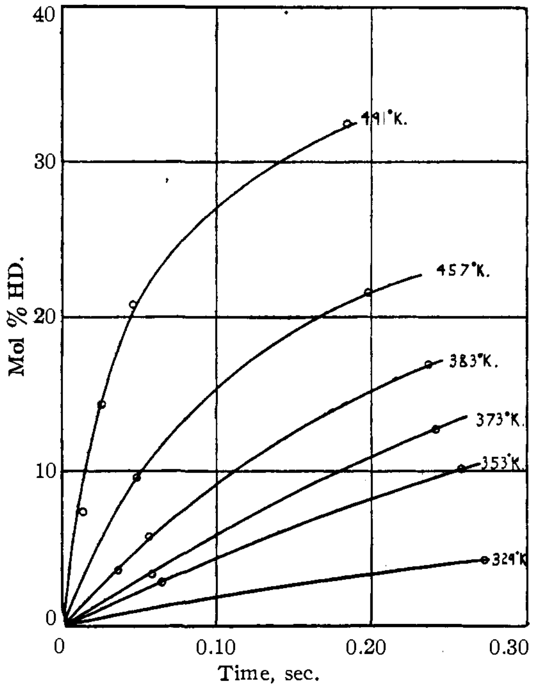

Fig. 9.

Discussion of Results

The reaction is so simple that the only mechanism by which the equilibrium is established involves only the activated or dissociative adsorption of the reactants, H_2 and D_2, and the evaporation of the resultant molecules, 2HD. No arrangement of the adsorbed particles other than contiguity is required and the rate-determining step must be the desorption process.

The data of Table VII reveal that this rate-determining desorption involves progressively increasing energies of activation with increase in the temperature of reaction, falling into the three groups already noted, 0.6 and 4.9 kcal. below 195°, 7–8 kcal. from 195 to 373°K. and 11–13 kcal. above this temperature with an interval 405–430°K. where the apparent activation is zero for reasons to be discussed below. The extension of the measurements of velocity of reaction over a range of 250° has revealed decisively the non-uniformity of the surface and the existence of energetically different areas of the surface on which the reaction can occur. Ordinarily, reaction kinetic studies at surfaces yield a straight line relationship when log k is plotted against $1/T$. In such cases, we assume, with Schwab,[13] that there is one kind of center so overwhelmingly active that it is possible to describe the results by means of a uniform surface. This is true of our data between 195 and 373°K. Outside these temperature limits this is not true. Below 195°K. areas of surface are involved in which the desorption process occurs with even less than 1 kcal. of activation energy. On such areas the activated adsorption must involve negligibly low activation energies and *also* negligible heats of adsorption. Such areas are, therefore, energetically quite distinct from those involved in previous adsorption studies[2,4] where activation energies of adsorption from 5–12 kcal. were found in the temperature range 0–300°.

An additional striking feature of the results in the higher temperature ranges emerges from calculations which indicate that the exchange reaction per gram of zinc oxide takes place from 50–800 times as fast as the net rate of adsorption as measured by Strother[2] at atmospheric pressure, using his data for the five-minute isobar. This means that, since HD is desorbed gas, the desorption process plays an important part in the net rate of adsorption occurring in the first few minutes. Also, this observation serves to identify the adsorption process effective in the exchange reaction with the fast initial adsorption of gas observed by Strother and also in the case of chromium oxide by Burwell and Taylor.[14]

It is now apparent why the change of reaction rate with temperature is abnormal between 383 and 457°K. It is in this range that the fraction of the surface covered by the rapid adsorption process is decreasing with rise of temperature. Strother's data show that between 350 and 450°K. the volume of gas adsorbed in five minutes decreases from 5 to 2.5 cc. As the desorption rate is diminished through a diminution of the surface covered, it is to be expected that the rate of reaction will not increase in the usual manner with increase of temperature. Actually, between 405 and 430°K. the effect of decreasing covered surface effectually cancels the accelerating effect of temperature on the exponential term $\exp -(E_{\text{Des.}}/RT)$. From Strother's data it is seen that, above 450°K., the surface covered in unit time again begins to increase. Our data in the same range show a corresponding influence on reaction rate with an apparent activation energy of 13 kcal. This value indicates a surface energetically different also from that in the intermediate temperature range (E = 7–8 kcal.).

The surface active in the range 143–178° with a desorption energy of 0.6 kcal. must be bare and therefore inactive at temperatures of 450°K. and upward. Conversely the areas active at the high temperature are inactive at the low temperatures because the activation energy of desorption and possibly of adsorption are too high for such areas to function at the low temperatures. The concept of centers of varying activity is thus once more compellingly required and this time by actual kinetic measurements.

Summary

1. The rate of the reaction $H_2 + D_2 \longrightarrow 2HD$ on zinc oxide has been studied from 140 to 491°K., and the reaction shown to be first order.

2. From the temperature coefficient of the reaction, apparent activation energies have been calculated. These values are low at low temperatures but quickly reach a steady value of about 7–8 kcal. in the temperature range from 195 to 329°K. From 353 to 491° the activation energies obtained were about 12 kcal.

3. It was shown that activated adsorption which only reaches equilibrium in periods of time measured in hours is incapable of causing this reaction to proceed at the measured velocity.

4. An activated adsorption characterized by a very small value for E was shown to be responsible for the reaction. The existence of such an adsorption on zinc oxide was deduced from the adsorption data of Strother.

5. In the temperature range from 383 to 457°K. the reaction was shown to have an abnormal temperature coefficient. It was further shown that most of this abnormality was concentrated in the range from 405 to 430° at which temperatures the rates were identical.

6. This abnormality was explained on the basis of a decrease in the active surface covered with an increase in temperature. This explanation was justified on the basis of Strother's five-minute isobar for the adsorption of hydrogen on zinc oxide.

7. Strother's observation of two types of activated adsorption of hydrogen on zinc oxide was confirmed.

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[13] G. M. Schwab, "Catalysis from the Standpoint of Chemical Kinetics," translated by H. S. Taylor and R. Spence, D. Van Nostrand Company, New York, 1937, p. 284.

[14] Burwell and Taylor, THIS JOURNAL, **58**, 697 (1936).

8. A preferential adsorption of D_2 was observed at low temperatures and was explained on the basis of van der Waals adsorption.

9. Ortho–para hydrogen conversion was noted below 140°K.

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[CONTRIBUTION FROM THE BAKER LABORATORY OF CHEMISTRY AT CORNELL UNIVERSITY]

The Chlorinates. II. Temperature–Concentration Equilibria in the System Alpha-Carbon Tetrachloride–Chlorine. The Carbon Perchlorides[1]

BY J. ALLEN WHEAT, II, AND A. W. BROWNE

Since chloroform has been found to form four solvates, the hemi-, mono-, di-, and trichlorinates, at low temperatures in liquid chlorine solution,[1] it is to be expected that carbon tetrachloride should form five solvates of this type.

The system carbon tetrachloride–chlorine already has been studied by Biltz and Meinecke[2] who found, at −48°, a sharp break in the otherwise smooth melting point curve. This point was construed as an inversion point at which, on cooling, α-carbon tetrachloride undergoes transformation into β-carbon tetrachloride. The polymorphism of carbon tetrachloride had already been established.[3] No conclusive evidence of the formation of solvates was obtained, although some indication that β-carbon tetrachloride may form a very unstable compound with chlorine was noted.[4]

In the present investigation of the temperature-concentration equilibria in the system carbon tetrachloride–chlorine the experimental procedure was substantially identical with that described in the preceding article.[1] The results obtained are presented in Table I and are plotted in Fig. 1.

TABLE I

TEMPERATURE–CONCENTRATION OR SOLUBILITY DATA OF THE SYSTEM CCl_4–Cl_2

Temperatures designated with an *asterisk* represent the congruent melting points of the respective solvates. If enclosed in parentheses they have been determined by graphic interpolation.

Temp., °C.	Concn., mole % Cl_2	Curve (Fig. 1)
− 22.5	0.0	A. (Solid CCl_4, liq., vapor)
− 26.0	2.5	
− 33.5	6.8	
− 35.5	9.3	
− 42.0	12.1	
− 48.5	17.3	AB. (Solid CCl_4, satd. soln., vapor)
− 57.5	20.6	
− 61.5	23.0	
− 72.0	25.8	
− 75.0	27.0	
(− 81.0)	28.3	B. (Eutectic: solid CCl_4, solid $(CCl_4)_2{\cdot}Cl_2$, satd. soln., vapor)
− 77.5	29.4	
− 72.0	30.8	
− 68.5	32.3	
(− 67.0)*	33.3	
− 67.5	33.9	
− 71.0	35.3	BCD. (Solid $(CCl_4)_2{\cdot}Cl_2$, satd. soln., vapor)
− 76.0	37.7	
− 79.5	38.8	
− 84.0	40.6	
− 88.5	42.5	
− 94.0	44.5	
(− 98.0)	45.6	D. (Eutectic: solid $(CCl_4)_2{\cdot}Cl_2$, solid $CCl_4{\cdot}Cl_2$, satd. soln., vapor)
− 97.0	46.2	
− 93.0	48.1	
− 90.5*	50.0	
− 92.0	52.0	
− 94.0	54.5	DEF. (Solid $CCl_4{\cdot}Cl_2$, satd. soln., vapor)
− 97.5	57.0	
102.0	59.9	
−106.5	61.5	
−108.5	62.6	
−116.5	63.6	
(−122.0)	64.4	F. (Eutectic: solid $CCl_4{\cdot}Cl_2$, solid $CCl_4{\cdot}2Cl_2$, satd. soln., vapor)
−119.0	64.7	
−115.0	65.9	
(−112.5)*	66.7	
−113.0	67.0	FGH. (Solid $CCl_4{\cdot}2Cl_2$, satd. soln., vapor)
−114.0	68.3	
−115.5	69.4	
−117.5	70.7	
−122.0	71.9	
(−124.0)	72.5	H. (Eutectic: solid $CCl_4{\cdot}2Cl$, solid $CCl_4{\cdot}3Cl_2$, satd. soln., vapor)
−122.0	73.2	
−117.5	74.0	

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(1) For the first article of this series see THIS JOURNAL, **58**, 2410 (1936).

(2) Biltz and Meinecke, *Z. anorg. allgem. Chem.*, **131**, 1 (1923).

(3) Tammann, *Wied. Ann.*, **66**, 490 (1898); "Kristallisieren und Schmelzen," Barth, Leipzig, 1903, p. 222.

(4) Since the system at the inversion point contains carbon tetrachloride and chlorine in the molecular ratio of approximately 6:1, it is apparent that any solvate formed at this point (or to the left of it on the diagram) would contain *at least* 6 moles of carbon tetrachloride to one of chlorine.