

3. The specific gravities of anhydrous lanthanum chloride and bromide at 25° are found by displacement of toluene to be 3.842 and 5.057, respectively.

4. The greater efficiency of calcium bromide as a drying agent at low temperatures is experimentally investigated.

CAMBRIDGE, MASSACHUSETTS

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[CONTRIBUTION FROM THE FRICK CHEMICAL LABORATORY OF PRINCETON UNIVERSITY]  
**ADSORPTION AND REACTIONS AT SURFACES OF ZINC OXIDE**

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The present investigations originated in an attempt to obtain additional experimental data on the decomposition of alcohols at oxide surfaces in order to test two alternative theories for the distribution of decomposition between dehydrogenation and dehydration reactions at such surfaces. The two theories may be described as the Adkins-Burk-Balandin theory of multiple attachment at surfaces having varied spacings which determine the mode of decomposition and the Taylor theory of dual surfaces according to which the mode of decomposition is determined by the ionic charge of the group to which the adsorbed alcohol molecule is attached. There is no necessity to set forth the evidence for and relative merits of the two points of view since this has recently been independently done in detail by Schwab<sup>1</sup> in his recent text on catalysis. It will suffice to summarize the experiments performed with respect to the alternative reactions at various surfaces of zinc compounds, to emphasize the limited nature of the conclusions which may, as yet, be safely drawn from such work, and finally to detail the results concerning the adsorption of water vapor and hydrogen at zinc oxide surfaces, indicating their paramount importance in this problem of alternative reactions at a given surface.

Prior to the adsorption experiments a very large number of experiments were made with the object of obtaining definitive data on the velocity, nature and temperature coefficients of the decomposition of isopropanol on various zinc compound surfaces. As the result of a mass of experimental data obtained over a period of one year with six different types of surface, we are forced to the conclusion that *much of what has previously been deduced as characteristic of such surfaces is based on an entirely too restricted range of experimental measurements*. Our multiplication of such measurements served to show definitely that for even *approximately* reproducible results the most stringent regulation of a variety of experimental details must be arranged. Similar apparently capricious results

<sup>1</sup> Schwab, "Katalyse vom Standpunkt der chemischen Kinetik," Julius Springer, Berlin, 1931, pp. 173, 184-186, 203.

were obtained by Smith and Hawks<sup>2</sup> in their studies of methanol decomposition at zinc and cadmium oxide surfaces.

In our experimental arrangement the most careful attention was given to precision of experimental details. The alcohol was passed at carefully controlled speeds over small (1-2 g.) samples of the compound under study which was heated in an automatically controlled fused salt-bath maintained at temperatures varying not more than  $\pm 0.1^\circ$  during an experiment. In addition, a thermocouple embedded within the solid gave us an indication of the temperature obtaining within the mass. It is significant that this latter was frequently  $50^\circ$  lower than the bath temperature so that the mass could, therefore, not be at a uniform temperature throughout. The alcohol was specially prepared by hydrogenation of acetone at a nickel surface, any acetone removed by shaking with sodium bisulfite, the product being dried carefully with lime. It was free of acetone and contained less than 0.1% of water. Six different types of zinc compound were prepared under carefully controlled conditions and utilized for these studies: zinc oxide I, *ex* oxalate, by ignition in a current of air at  $400^\circ$  of pure zinc oxalate (*ex* zinc nitrate and ammonium oxalate molar solutions); zinc oxide II, a commercial c. p. product; zinc oxide III, made by adding excess sodium hydroxide to a hot solution of c. p. zinc sulfate, washing until free of sulfates and drying at  $250^\circ$ ; zinc oxide IV, a second sample prepared as in the case of III except that all washing was omitted.<sup>3</sup> Normal zinc phosphate, V, was made from c. p. zinc oxide and U. S. P. phosphoric acid, following the directions of Eberly, Gross and Crowell.<sup>4</sup> Zinc pyrophosphate, VI, was made by heating zinc ammonium phosphate to  $400^\circ$  in a current of air.

In view of the capricious behavior exhibited in all of this work on reactions we have decided to abstain from the presentation of any experimental results and to content ourselves with formulating the only conclusions that may with certainty be drawn from the whole body of experimental data. These conclusions may thus be summarized.

(1) The decomposition of isopropanol at zinc oxide surfaces is not zero order at atmospheric pressure. Thus, on zinc oxide I at a temperature of  $341 \pm 3^\circ$  an increase in rate of alcohol passage from 25 to 80 cc. liquid alcohol per hour resulted in a corresponding steady increase in gas yield from 57.7 cc. per minute at the lower to 94 cc. per minute at the upper rate of alcohol flow.

<sup>2</sup> Smith and Hawks, *J. Phys. Chem.*, **32**, 415 (1928).

<sup>3</sup> The two preparations III and IV were prepared with the object of duplicating a preparation of Lazier and Adkins, *THIS JOURNAL*, **47**, 1719 (1925), which appeared to possess predominantly dehydrating characteristics. Our lack of success in producing such a zinc oxide is discussed later.

<sup>4</sup> Eberly, Gross and Crowell, *ibid.*, **42**, 1433 (1920).

(2) The dehydrogenation-dehydration ratio is not characteristic for particular methods of preparation so far as these can at present be defined nor does it vary with temperature in the same way for different preparations. Thus, on zinc oxide I the apparent activation energies of dehydrogenation and dehydration were, respectively, about 14 and 20 kg. cal. On zinc oxide II the activation energy of dehydrogenation was 30 kg. cal. On zinc oxide III, a more active surface than zinc oxide I, both the dehydrogenation and dehydration reactions have energies of activation of approximately 20 kg. cal.

(3) Zinc oxide, whatever the source, is predominantly dehydrogenating (> 90%). Large quantities of salts (as in zinc oxide IV) reduce the activity but do not destroy it. Zinc oxide IV gave 63.7 cc. of gas per minute at 372°, whereas zinc oxide III gave this rate at approximately 290° when the alcohol flow was 50 cc. per hour. The gas in each case was > 98% hydrogen. We are at a loss to explain the result of Lazier and Adkins<sup>3</sup> already cited unless their abnormal dehydration values are to be attributed to the presence of tertiary alcohols in their reaction material.

(4) Zinc ortho- and pyrophosphate are almost exclusively dehydrating catalysts. This observation points definitely to the importance of the 3- and 4-valent anions in determining dehydration.

(5) Water is a strong reversible poison for zinc oxide catalysts. The presence of 1% of water in the isopropanol decreased the rate of decomposition to one-half the value with anhydrous alcohol. Our experimental evidence indicated that water produced by the dehydration process was even more pronouncedly retarding than the added water. It was this observation which led to the following investigation of the adsorption of water by zinc oxide I in an effort to obtain independent evidence of the importance of adsorbed water in the decomposition process.

### I. The Adsorption of Water Vapor by Zinc Oxide I

**Apparatus and Method.**—The apparatus consisted of a bulb containing the catalyst connected to a constant volume manometer and through stopcocks to a mercury pump evacuation system and a 100-cc. bulb which was connected through a three-way stopcock to a mercury reservoir and a small bulb containing water. The catalyst tube was heated to a constant temperature by an electric furnace. This furnace consisted of a Pyrex Dewar flask wrapped on the outside with a heating coil of nichrome wire. A capillary tube connected the annular space between the walls of the Dewar flask with a U-tube provided with sealed-in platinum contacts and containing mercury. A relay connected through these mercury contacts regulated the current heating the Dewar flask, the expansion or contraction of the air in the annular space in the Dewar flask operating the relay. The bulb containing the catalyst was placed inside the Dewar flask. The temperature of the catalyst could be kept constant within 0.1°.

Pure zinc oxalate was placed in the catalyst bulb and gradually heated to 400° with the pumps running. When gas evolution had apparently ceased, the temperature was raised to 450° and the catalyst evacuated at this temperature for ten hours. The catalyst was cooled to room temperature, and water vapor added to the system by

opening the 100-cc. bulb to the small bulb of water, which was immersed in ice or water at a temperature below that of the room, closing off from the water after ten minutes, opening the 100-cc. bulb to the catalyst and finally filling the bulb with mercury to drive all the water vapor into the catalyst system. These operations were repeated until the desired amount of water had been admitted. The catalyst was then heated to the temperature at which the vapor pressure of the adsorbed water was to be measured, and maintained at that temperature until the pressure remained constant. It was then heated to a higher temperature, the pressure noted, etc. The results were checked by making a similar series of determinations at decreasing temperatures.

### Experimental Results

Preliminary measurements indicated a large adsorption even at high temperatures, much larger than was expected. The results of more precise measurements are given in Table I.

TABLE I  
 ADSORPTION OF WATER VAPOR ON 10 G. OF ZINC OXIDE I  
 Total water vapor in system, cc. N. T. P.

10.45			11.34			12.56		
T, °C.	P <sub>mm.</sub>	V <sub>ads.</sub> , cc.	T, °C.	P <sub>mm.</sub>	V <sub>ads.</sub> , cc.	T, °C.	P <sub>mm.</sub>	V <sub>ads.</sub> , cc.
313	1.4	10.38	298	1.3	11.27	298	2.5	12.43
318	1.9	10.35	315	2.3	11.22	315	4.4	12.34
330	2.8	10.31	333	4.5	11.12	333	7.7	12.17
340	3.8	10.26	352	8.2	10.92	352	13.5	11.88
352	5.9	10.15	372	15.6	10.57	372	24.1	11.36
372	10.3	9.93	386	22.9	10.34			
386	15.9	9.65						
401	21.4	9.39						

A plot of the logarithm of the pressure as a function of the reciprocal of the absolute temperature gave straight lines, from which adsorption isosteres were constructed. The heat of adsorption, given in Table II, was calculated by means of the Clapeyron equation.

TABLE II  
 HEAT OF ADSORPTION OF WATER ON ZINC OXIDE I

Amount adsorbed, cc. N. T. P. per gram	1.03	1.12
Heat of adsorption, calories	30,300	32,200

The catalyst adsorbed water vapor almost instantly at room temperatures. Attempts to detect the "activated" adsorption shown by Taylor<sup>5</sup> to occur on adsorption of hydrogen, oxygen and carbon monoxide by active catalysts were made. It was expected that if a catalyst which had adsorbed water vapor at room temperature, presumably in the unactivated form, as indicated by the rapid adsorption at this temperature, were rapidly heated, the water vapor would desorb and then return to the surface at a higher temperature. The expected rise and subsequent fall of pressure on heating was not observed in any of a number of experiments. However,

<sup>5</sup> H. S. Taylor, *THIS JOURNAL*, 53, 578 (1931).

evidence that there is a second type of adsorption of water requiring an activation energy was obtained by adding water vapor to the catalyst, not at room temperature, but at 250–270°. The first portions of water vapor admitted were again adsorbed very rapidly, but after considerable water had accumulated on the surface the adsorption became measurably slow. Lack of time prevented a thorough investigation, but the results obtained show conclusively that at high temperatures a slow adsorption appears. The data presented in Table III indicate the type of results obtained.

TABLE III

## RATE OF ADSORPTION OF WATER BY 10 G. OF ZINC OXIDE I

14.7 cc. N. T. P. H<sub>2</sub>O already on surface; 2.09 cc. N. T. P. H<sub>2</sub>O added. Total H<sub>2</sub>O in system, 16.8 cc. N. T. P.

Time after adding water, minutes	Pressure mm.	Temperature, °C.
10	5.5	248
22	3.5	249
30	2.9	249
55	2.0	250
Temperature raised to 270°	.2.4	270

A second addition of 2.09 cc. N. T. P. of water was made. Total H<sub>2</sub>O in system, 18.9 cc.

0	17.8	270
5	14.5	270
10	13.7	270
20	13.0	270
30	12.8	270
50	12.2	270
200	11.5	270
260	11.3	270

On lowering the temperature to 25°, the pressure became 0.0 mm.

## Discussion

With a fresh catalyst, desorption was very slow, ten hours or more being required to reach equilibrium at high temperatures. After water had been adsorbed and removed by evacuation at 450°, this slow attainment of equilibrium was much less apparent, and slightly higher vapor pressures were obtained. As the catalyst had already been heated to this temperature, and as evidence presented in the section on the adsorption of hydrogen proves that the catalyst does not progressively sinter at 450° in a high vacuum, it is likely that the last traces of water are not removed by the evacuation process, and the figures given for the amount adsorbed are probably somewhat too low.

The amount of water adsorbed is remarkable, and is much larger than that of hydrogen (see Part II), and the heat of adsorption is higher. In the absence of other data this would indicate that zinc oxide I should be

at least as good a dehydration catalyst as a dehydrogenation catalyst.<sup>6</sup> As the water formed by the dehydration process must, however, escape from the surface if the process is to continue, the energy necessary to remove the water from the surface must be considered.

That this may be the dominating factor in determining the rate of dehydration is rendered probable when we consider that, as pointed out by Taylor,<sup>5</sup> the activation energy of desorption is the sum of the heat of adsorption and the activation energy of the water adsorption. We have seen that the heat of adsorption is *ca.* 30,000 calories; the activation energy of the water adsorption is probably not less than 15,000–20,000 calories, considering the temperature (250–270°) at which slow adsorption is manifested, giving an activation energy of evaporation of the adsorbed water of at least 45,000 calories on a large part of the surface having dehydrating ability. This accounts for the marked poisoning of water on the dehydration process.

The desorption of the water will be aided by decreasing the partial pressure of water in the gas in the neighborhood of the catalyst surface. This was actually observed in the decomposition experiments, for a relative increase in the dehydration reaction was observed with increasing rates of alcohol flow.

## II. The Adsorption of Hydrogen by Zinc Oxide I

The adsorption of hydrogen on zinc oxide has been studied by Lazier and Adkins,<sup>7</sup> who found that at 22° and 740 mm. a 100-g. sample of zinc oxide *ex* hydroxide adsorbed 1.8 cc. at N. T. P. of hydrogen, and that 100 g. of zinc oxide *ex* isopropoxide adsorbed 23.4 cc. at N. T. P.; and by Taylor and Kistiakowsky,<sup>8</sup> who measured a number of isotherms on zinc oxide I. Garner and Kingman<sup>9</sup> have recently studied a zinc oxide preparation with a very minute adsorption for hydrogen.

Recent advances in the theory of activated adsorption<sup>10</sup> have made further study of zinc oxide desirable.

### Theoretical

The theory and importance of adsorption requiring activation energy is given in the last three papers quoted above.<sup>10</sup> As experimental material illustrating some of the points will be presented, it is desirable to indicate the simplest form of the theory of the now characteristic adsorption isobars of adsorption on active catalysts.

<sup>6</sup> Pease, *THIS JOURNAL*, **45**, 1196, 2235 (1923).

<sup>7</sup> Lazier and Adkins, *J. Phys. Chem.*, **30**, 353 (1926).

<sup>8</sup> Taylor and Kistiakowsky, *THIS JOURNAL*, **49**, 2468 (1927).

<sup>9</sup> Garner and Kingman, *Trans. Faraday Soc.*, **37**, 322 (1931).

<sup>10</sup> H. S. Taylor, *THIS JOURNAL*, **53**, 578 (1931); Taylor and Williamson, *ibid.*, **53**, 2168 (1931); H. S. Taylor, *Chem. Reviews*, **9**, 1–46 (1931).

Suppose adsorption taking place at constant pressure on a plane uniform surface with an activation energy  $E$  and a heat of adsorption  $\lambda$ , which are assumed constants independent of the amount adsorbed. The rate of condensation of gas molecules on the surface will be proportional to the number of molecules striking the surface per unit time with an energy greater than  $E$ , that is, roughly, the rate of condensation  $= k_1 e^{-E/RT}$ . The rate of evaporation will be proportional<sup>5</sup> to  $e^{-(E + \lambda)/RT}$ , and to the fraction of the surface covered or, roughly, the rate of evaporation  $= k_2 v e^{-(E + \lambda)/RT}$ , where  $v$  is the volume adsorbed after the time  $t$ . The total rate of adsorption will be

$$\frac{dv}{dt} = k_1 e^{-(E/RT)} - k_2 v e^{-(E + \lambda)/RT} \quad (1)$$

When equilibrium prevails,  $dv/dt = 0$ , and

$$v_0 = \frac{k_1}{k_2} e^{\lambda/RT} \quad (2)$$

where  $v_0$  is the quantity adsorbed at equilibrium at the given pressure.

Integrated, equation (1) gives, using the boundary condition that  $v = 0$  when  $t = 0$

$$v = \frac{k_1}{k_2} e^{\lambda/RT} (1 - e^{-k_2 t e^{-(E + \lambda)/RT}}) = v_0 (1 - e^{-k_2 t e^{-(E + \lambda)/RT}}) \quad (3)$$

Equation (3) may be put in the more convenient logarithmic form

$$\log_e (v_0 - v) = \log_e v_0 - k_2 t e^{-(E + \lambda)/RT} \quad (4)$$

Thus the graph of  $\log_e (v_0 - v)$  as a function of  $t$  is a straight line whose slope is  $-k_2 e^{-(E + \lambda)/RT}$ . This affords a convenient graphical method of determining  $v_0$  by assuming values for  $v_0$  and plotting  $\log_e (v_0 - v)$  as a function of  $t$  until a satisfactory straight line is obtained. If  $k_2$  is known<sup>5</sup>  $E + \lambda$  may be calculated, or conversely if  $E$  and  $\lambda$  are known,  $k_2$  may be calculated. By plotting the logarithm of the negative of the slope of equation (4) as a function of  $1/T$  a straight line should again be obtained whose slope obviously allows  $E + \lambda$  to be calculated independently of any assumption of the order of magnitude of  $k_2$ .

The isobaric adsorption given by equation (3) has one extremum whose position  $T_{\max}$  is obtained by solving  $dv/dT = 0$  for  $T$ . This extremum proves to be a maximum for even very improbable values of  $k_1$ ,  $k_2$ ,  $E$  and  $\lambda$ . Essentially, we are led to solve the equation

$$1 + \frac{k_2 t (E + \lambda)}{\lambda} e^{-(E + \lambda)/RT_{\max}} - e^{k_2 t e^{-(E + \lambda)/RT_{\max}}} = 0$$

or putting

$$k_2 t e^{-(E + \lambda)/RT} = z$$

the equation

$$1 + \frac{E + \lambda}{\lambda} z = e^z$$

This equation has a root different from 0, say  $z_0$ , best obtained graphi-

cally. The isobar will have a maximum if  $z_0 < k_2t$ , the corresponding temperature  $T_{\max}$  being

$$T_{\max} = \frac{E + \lambda}{R \log_e (k_2t/z_0)} \quad (5)$$

### Experimental

**Apparatus and Experimental Method.**—The apparatus and experimental method were those of Taylor and Williamson.<sup>10</sup> This apparatus consisted of a system of pumps, manometer, burets, etc., which allowed a quantity of pure dry hydrogen to be admitted to the evacuated catalyst, which was maintained at a constant temperature, and the rate of pressure change to be measured, from which the rate of adsorption could be calculated from the known volume of the system.

The catalysts were prepared from pure zinc oxalate as in Part I; 20.0-g. samples were used. The catalyst was pumped off in a high vacuum for three to four hours at 450° between runs.

**Experimental Results.**—The results of the velocity determinations are given graphically in Fig. 1 and one typical series of measurements, that for 184°, is given in Table IV.

TABLE IV  
RATE OF ADSORPTION OF HYDROGEN BY 20 GRAMS OF ZINC OXIDE I AT 184°

Time, mins.	Pressure, mm.	Amount adsorbed in cc., N. T. P.	Time, mins.	Pressure mm.	Amount adsorbed in cc., N. T. P.
0		0	75	423.5	8.10
2	539.5	2.25	90	417.5	8.40
5	505.5	3.95	105	412.0	8.70
10	486.0	4.90	120	407.5	8.95
15	474.0	5.60	135	402.5	9.20
20	467.0	5.90	160	396.0	9.50
25	459.5	6.30	180	392.0	9.70
30	454.0	6.55	210	387.0	9.95
35	449.0	6.80	230	384.0	10.10
40	444.5	7.05	360	363.0	11.15
45	440.5	7.25	420	355.5	11.50
50	437.5	7.40	510	345.5	12.05
55	434.5	7.55	1165	315.0	14.10
60	431.5	7.70			

The experiments were made in the order, 0, 110, 132, 184, 218 and 306°. The heats of activation calculated from these data are given in Table V, which shows the reliability limits of the velocity measurements.

After obtaining these rates an attempt was made to measure isotherms at 306 and 444°. Progressively diminishing values for the amount of adsorption in successive runs and darkening of the catalyst vitiated the results. Nevertheless, a heat of adsorption of *ca.* 16,000 calories was indicated on the now ruined catalyst. The total adsorption fell to about



TABLE V  
ACTIVATION ENERGY OF HYDROGEN ADSORPTION BY ZINC OXIDE I

Amount adsorbed cc. N. T. P.	Activation energy, Kg. calories			
	110-132°	132-184°	184-218°	218-306°
3.0	7.6	7.0	3.8	..
3.5	9.0	7.5	8.0	..
4.0	13.2	9.5	10.5	..
4.5	14.4	11.4	10.7	..
5.0	15.4	12.7	10.5	..
5.5	16.0	13.4	10.0	12.1
6.0	15.9	14.0	10.3	..
6.5	..	14.4	10.3	..
7.0	..	14.4	10.9	..
7.5	..	14.7	11.0	..
8.0	..	..	11.2	..
8.5	..	..	11.1	..
9.0	..	..	11.1	..

one-third of its initial value, certainly due to destruction of active areas by reduction.<sup>11</sup>

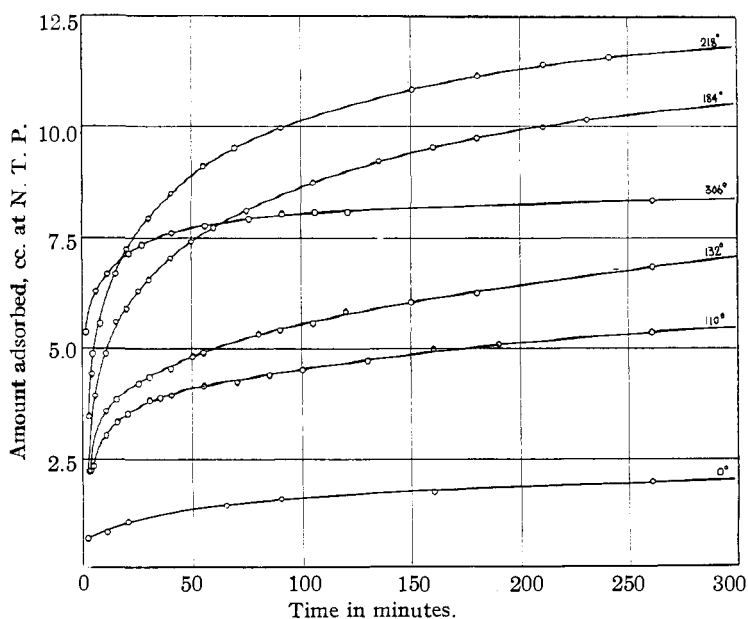


Fig. 1.—Rate of adsorption of hydrogen by 20.0 g. of zinc oxide I.

A velocity run at 184° with a fresh catalyst gave initially an abnormally high rate and adsorbed amount compared to the former catalyst. After this run, an attempt was made to recover the hydrogen by evacuation

<sup>11</sup> Taylor and Starkweather, THIS JOURNAL, 52, 2314 (1930).

with a Sprengel pump. At 184° the dead space was quickly pumped out, but desorption occurred very slowly. By gradually raising the temperature to 450° and pumping overnight, the volume of hydrogen admitted was recovered quantitatively, showing that no reduction of the catalyst had taken place. A repetition of the velocity determination at 184° now gave results so nearly the same as those given in Fig. 1 that the catalysts may be considered as identical.

Isotherms in liquid air and solid carbon dioxide were next made with the results shown in Fig. 2, which also gives the final amount adsorbed and final pressures of the velocity runs of Fig. 1. From these data the isobaric adsorption at 400 mm. shown in Fig. 3 was calculated.

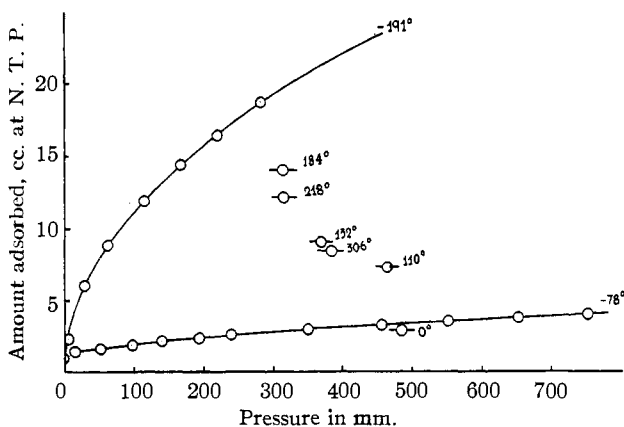


Fig. 2.—Adsorption isotherms of hydrogen on 20.0 g. of zinc oxide I.

### Discussion

The activation energy of the "activated" adsorption of hydrogen on zinc oxide I has already been given. The excellent internal agreement of these activation energies proves that the catalyst does not sinter progressively at 450° in high vacuum, and that three to four hours pumping at this temperature gave a reproducible surface. The latter part of the rate curves at 184 and 218° gave straight lines when fitted to equation (4) of the preceding theoretical discussion, which indicates that  $E + \lambda$  is constant over the latter portions of the surface covered by the hydrogen. From the equation so obtained values for  $v_0$  at 184 and 218° were calculated. From these and equation (2) a value of 20,800 calories was calculated for the heat of adsorption, a better value than the 16,000 calories obtained from the "isotherms" on the partially deactivated catalyst. Using a value of  $E = 14,000$  calories and  $\lambda = 21,000$  calories, a value of  $k_2 = 9.25 \times 10^{12}$  was calculated from equation (4).  $k_1/k_2$ , and, if desired,  $k_1$  can be calculated from the data already obtained and equation (2).

Thus  $z_0$  was found to be 0.947, and from equation (5) a value of  $T_{\max.} = 470^\circ\text{A.}$  was calculated for a time  $t = 1200$  minutes, approximately the time used in constructing Fig. 3, which shows the temperature of the maximum adsorption to be  $T_{\max.} = 450^\circ\text{A.}$ , a much better agreement than might be expected.

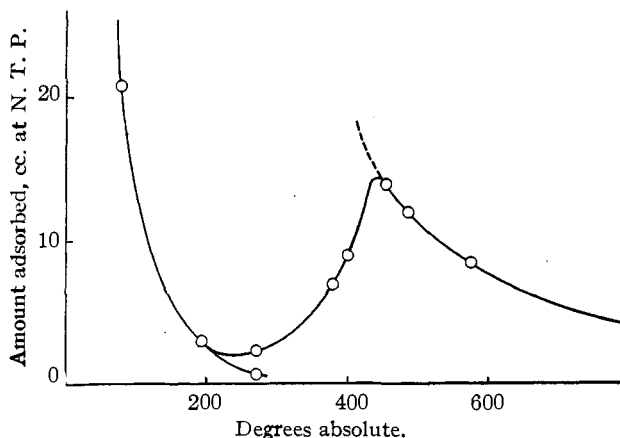


Fig. 3.—Adsorption isobar of hydrogen on 20.0 g. of zinc oxide I at 400 mm. pressure.

As on the manganese catalysts studied by Taylor and Williamson,<sup>10</sup> the activation energy for the first portions of gas adsorbed is much lower than the more or less constant value obtained for the less active spots. Attention should also be called to the fact that equilibrium was obtained in less than one minute at liquid air and solid carbon dioxide temperatures, indicating a negligible activation energy for the low temperature adsorption process.

From the low temperature isotherms given in Fig. 3 a heat of adsorption for the low temperature process of 1100 calories was calculated from the Clapeyron equation. This should be compared with the 21,000 calories of the activated adsorption.

Thus the two types of adsorption to be expected on active catalysts have again been demonstrated, one form occurring rapidly at low temperatures with a low heat of adsorption, the other occurring at much higher temperatures with a very much higher heat of adsorption and with a rate increasing exponentially with temperature. At intermediate temperatures these two forms may overlap.

### Summary

1. The difficulties attending measurements of the velocity of decomposition of alcohols on zinc oxide surfaces have been indicated.
2. The adsorption of water vapor by such surfaces is an important factor in the velocity of decomposition of alcohols.

3. The vapor pressure of water adsorbed on zinc oxide *ex* oxalate has been measured at 300–400°.

4. The heat of adsorption of water vapor, probably of the activated form, on zinc oxide *ex* oxalate is approximately 30,000 calories.

5. Evidence for the activated adsorption of water on zinc oxide *ex* oxalate has been obtained.

6. An explanation of the low dehydration–dehydrogenation ratio of zinc oxide has been given.

7. The velocity of the adsorption of hydrogen by zinc oxide *ex* oxalate has been measured in the temperature interval 0–306°, and isotherms have been obtained at –191 and –78.5°.

8. Two types of adsorption of hydrogen by zinc oxide *ex* oxalate have been distinguished, their heats of adsorption determined, and the activation energy for the activated type has been measured over a wide range.

9. The theory of activated adsorption has been developed mathematically, leading to expressions for the temperature of maximum adsorption, and methods of calculating the activation energy and heat of adsorption in difficult cases have been presented.

10. Except in the initial stages, the theoretical equations reproduce the course of the activated adsorption of hydrogen on zinc oxide with great fidelity.

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### FURTHER RESEARCH ON ELEMENT 87

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Detection of element 87 in pollucite and lepidolite was announced by Allison and Murphy.<sup>1</sup> They employed the magneto-optic method<sup>2</sup> which was developed in this Laboratory.

In continuing this research, a more extended study was made to determine whether the minima attributed to compounds of 87 might be due to some other substance and a search was made for other sources of 87.

In this work, water solutions of the substances studied were prepared. Soluble salts were simply dissolved; insoluble ones were extracted with acid or aqua regia. The desired anion was obtained by adding the appropriate acid or sodium hydroxide and the solution was then examined by the magneto-optic method. Every substance was examined both as

<sup>1</sup> Allison and Murphy, *Phys. Rev.*, **35**, 285 (1930).

<sup>2</sup> Allison, *ibid.*, **30**, 66 (1927); Allison and Murphy, *THIS JOURNAL*, **52**, 3796 (1930).