

gold being negative to the alloys and plate. This difference, however, disappears almost entirely if the solution is stirred with nitrogen.

Further work in other solutions and on the effect of oxidizing agents is in progress.

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[CONTRIBUTION FROM THE FRICK CHEMICAL LABORATORY OF PRINCETON UNIVERSITY]

MOLECULAR AND ACTIVATED ADSORPTION OF HYDROGEN ON MANGANOUS OXIDE SURFACES

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In a recent communication,¹ the rapidly accumulating data relative to the variation of adsorption and heats of adsorption of gases on numerous surfaces with variation in temperature and pressure as well as data on the velocities with which adsorption and desorption equilibria are attained have been collected and analyzed. The data have been shown to be a necessary consequence of a modified theory of adsorption which differs from the classical theory in the introduction of the concept of activation energy into adsorption processes. On classical theory, the activation energy of adsorption is zero and that for desorption is λ , which is identical in magnitude with the usual heat of adsorption. The modification proposed is to require an activation energy, E , for adsorption and, consequently, an activation energy, $E + \lambda$, for desorption processes. This introduction of the activation energy concept does not change the theoretical equilibrium value for adsorption in its dependence on λ . On the other hand, the individual rates of adsorption and desorption will decrease exponentially as E increases, so the rate of attainment of equilibrium may vary within wide limits which will be dependent upon the magnitude of E .

It was shown in the earlier paper that this method of treatment could be applied to a gas whose adsorption on a given surface was of two types, one involving a low heat of adsorption and a low activation energy, the other a high heat of adsorption and a high heat of activation. It was shown that this led to two theoretical adsorption isobars, that with the high heat of adsorption involving greater amounts of adsorbed gas at a given temperature and pressure. Dependent on the magnitude of the two activation energies it was shown that, at sufficiently low temperatures, the lower adsorption would be the only type occurring, at higher temperatures the higher adsorption, while, in an intermediate temperature range, dependent on the respective magnitudes of the two activation energies, a transition region of pseudo-equilibrium adsorption values would be

¹ Taylor, THIS JOURNAL, 53, 578 (1931).

obtained, showing increasing amounts of gas adsorbed with increase in temperature, the velocity of adsorption at a given temperature being determined by the activation energy of the high temperature adsorption. An examination of data for hydrogen adsorption on various surfaces abundantly confirmed the general conclusions thus reached. There were, however, no data of a quantitative nature relative to the *velocity* of adsorption. It was primarily to ascertain if such could be secured that the present work on manganous oxide surfaces was performed. This surface was chosen because of its known efficiency in hydrogenation reactions, involving activated hydrogen, and also because of its known resistance to reduction by hydrogen in the temperature range to be studied. It was anticipated and actually found that the transition from one type of adsorption to another would occur in a temperature range above room temperature. This permits a more easily operable experimental technique than is possible with such surfaces as nickel where, as Benton and White have already shown,² the transition interval from one to the other type of adsorption occurs below -110° . Our choice was a fortunate one in that, on a manganous oxide surface and on a surface of manganous oxide promoted with chromic oxide, we have been able to segregate the two types of hydrogen adsorption and separately examine their heats of adsorption and activation energies of adsorption. We also have made excellent measurements of the velocity of activated adsorption and from them deduced the activation energy of the process as a function of the extent of surface covered.

Experimental Details

Apparatus.—The adsorptions were measured in an apparatus of the type frequently used³ in our work with catalytic surfaces. The adsorbent was contained in a 25-mm. Pyrex tube attached through capillary tubing and suitable stopcocks to a gas buret graduated in 0.10 cc., a mercury manometer of 10 mm. bore, an evacuation system and a gas supply and purification train.

For evacuating the system when collection of the gas was not necessary, a two-stage mercury diffusion pump was used in series with a Hyvac oil pump. To recover the adsorbed gas on evacuation, use was made of an automatic Sprengel pump built according to the plans given by Dunoyer.⁴ With this, the system could be exhausted to very low pressures in a relatively short time, the pump pulling steadily as fresh gas was released from the surface of the adsorbent. Even the last small stubbornly held portion of the adsorbate could be removed completely by holding the adsorbent at 450° overnight with the Sprengel pump operating.

The adsorbent was heated by a close-fitting cylindrical electric furnace whenever the contact material was to be freed of adsorbate. When isotherms and isothermal rates were being studied, much closer temperature control was required. At the lower temperatures this was obtained by immersing the tube in a Dewar flask filled with solid

² Benton and White, *THIS JOURNAL*, **52**, 2325 (1930).

³ See, for example, Pease, *ibid.*, **45**, 1197 (1923).

⁴ Dunoyer-Smith, "Vacuum Practice," G. Bell and Sons, London, 1926.

carbon dioxide-ether, water-ice or pure water as the regulating media. At higher temperatures excellent isothermal baths could be obtained by refluxing pure materials at their boiling points. The boiler was a Pyrex "test-tube," 50 mm. in diameter, which was equipped with an asbestos jacket and a reflux tube sealed into its shoulder. It was closed at the top by a plug formed of asbestos tape. An electric heater, moulded to fit snugly, could be regulated to give steady ebullition which would fill the whole tube with saturated vapor, this vapor being completely condensed after moving a few centimeters up the reflux tube.

Materials.—Manganous oxide was prepared by ignition of manganous oxalate, made⁶ by the interaction of concentrated solutions of potassium permanganate and oxalic acid in presence of acetic acid. On ignition above 300° the oxalate decomposes yielding the gray-green monoxide. In the air this material, when active, takes up oxygen, changing to a darker color. Sabatier⁶ found that it was stable in the presence of hydrogen at a red heat, while Meyer⁷ found no evidence of reduction by hydrogen below 1200°. The samples used were submitted to a final reduction *in situ* with hydrogen at 350°.

Manganous-chromic oxide was prepared by ignition of manganous ammonium chromate formed as a dark precipitate by mixing solutions of manganous nitrate and ammonium chromate, ammonia being then added until the supernatant solution gave a neutral reaction to litmus.⁸ The filtered precipitate was washed with ammonium nitrate solution to prevent the formation of suspensoids, dried and then decomposed at about 400°. The product contains approximately two moles of MnO to one of Cr₂O₃. Prior to use it was given a final reduction *in situ*, yielding a grayish-brown powder. When exposed to air it oxidized to a velvety black higher oxide of manganese.

Manganous pyrophosphate was prepared by ignition of manganese ammonium phosphate at 650°.

Electrolytic hydrogen, carbon monoxide from formic acid, cylinder nitrogen and ethylene were subjected to careful purification and drying before use.

Procedure.—The adsorptions were in all cases measured by comparison of the quantities of adsorbable gas required to produce a given pressure at a stated temperature with those required for a non-adsorbed gas (nitrogen). The pressures and volumes recorded have all been reduced to standard conditions. It was found necessary to evacuate the surfaces prior to a measurement for many hours at 450° in order to ensure reproducibility of experimental results.

In the determination of adsorption isotherms measurements were made in some cases with ascending pressures and in other cases by removal of measured amounts of gas from the surface saturated with a known volume of gas at moderate pressures. The chosen procedure is indicated in the tabulated results by ascending or descending values of the pressure.

The velocities of adsorption were generally determined by introducing a known volume of gas, measuring the pressures produced by such gas over certain time intervals. The pressure at zero time was calculated from the data obtained under the given conditions with nitrogen.

Experimental Results

The data presented below are a summarized form of the detailed experimental results by one of us (A. T. W.) elsewhere.⁹

⁵ Kessler, *Z. anal. Chem.*, 11, 270 (1872).

⁶ Sabatier, *Ann. chim. phys.*, [8] 20, 289 (1910).

⁷ Meyer, *Chem. Abstracts*, 22, 936 (1928).

⁸ Lazier, U. S. Patent 1,746,783, Feb. 11, 1930; *Chem. Abstracts*, 24, 1649 (1930).

⁹ Williamson, "Thesis," Princeton, 1931.

A. Manganous Oxide. I.—Mass of sample, 22.8 grams: no measurable quantity of hydrogen was adsorbed by this surface at 0° , even over a period of several hours. At 184° no observable adsorptions were recorded at 101 mm. and 296 mm. pressure after fifteen minutes' time of contact but at 393 and 615 mm. adsorptions of 0.8 and 1.0 cc., respectively, were recorded after the system had stood for two or three hours under the given conditions. It was evident that slow activated adsorption was making its appearance so that an experiment, using a large volume of hydrogen (V), was made, pressures being recorded at stated intervals. The data obtained together with similar data at 305° are presented in Table I.

TABLE I

VELOCITY OF ADSORPTION OF HYDROGEN ON MANGANOUS OXIDE I AT 184° AND 305°
 $T, 184^\circ; V, 35.8$ cc. $T, 305^\circ; V, 37.7$ cc.

Time, hours	$P_{\text{mm.}}$	$V_{\text{ads.}}$ cc.	Time, hours	$P_{\text{mm.}}$	$V_{\text{ads.}}$ cc.
0	595	0.0	0	760	0.0
5	559	2.2	<1	668	4.5
8	543	3.1	2	618	7.0
22	525	4.2	3	613	7.3
26	523	4.3	8	581	8.9
35	516	4.8	10	577	9.1
46	508	5.2	16	566	9.6
51	506	5.4	22	562	9.8

It is evident from these data that the rate of adsorption at 305° is much greater than at 184° . In addition, a higher pseudo-equilibrium adsorption is approached. The velocity of adsorption at 305° suggested the possibility of obtaining an adsorption isotherm by removal of successive measured amounts of gas, allowing between each a period of from two to three hours for the reestablishment of equilibrium. The data thus obtained are presented in Table II. It will be realized that the amounts adsorbed represent upper limits for the isotherm at each pressure owing to the operation of the high activation energy of desorption as discussed in the introduction. The data do show, however, a normal adsorption and also illustrate the reversibility of the process.

TABLE II

ADSORPTION ISOTHERM OF HYDROGEN ON MANGANOUS OXIDE I AT 305°

$V, \text{cc.}$	$V_{\text{ads.}}$	P	$V, \text{cc.}$	$V_{\text{ads.}}$	P
37.7	9.5	567	14.0	4.8	186
32.2	8.6	476	10.8	4.1	134
28.5	8.1	412	7.4	3.6	77
25.1	7.5	355	5.3	3.1	44
20.6	6.5	284	3.4	2.7	14
17.2	5.9	228	2.0	2.0	0

The last two cc., which were held with an equilibrium pressure of less than 1 mm., were recovered by evacuation at 400° . There was no evidence

TABLE IV

ACTIVATION ENERGIES OF ADSORPTION OF HYDROGEN ON MANGANOUS OXIDE III

Adsorbed amount, cc.	Time required, hours		<i>E</i> , cal. per mole, adsorbed
	218°	184°	
First two	1.8	4.6	12,400
Third	2.7	11.7	19,400
Fourth	4.7	21.7	20,800

tion energy, which is a minimum for the first areas covered and rises to higher values for less active areas of the surface.

Adsorption is still marked at 444°. A single charge of hydrogen was left in the system at this temperature for seven hours, at the end of which time the rate of adsorption had become negligible. The adsorption amounted to 7.3 cc. at a pressure of 706 mm. On removing a sample of gas a new equilibrium at the end of twelve hours showed an adsorption of 6.8 cc. at a pressure of 495 mm.

Experiments at -78.5° showed no measurable adsorption of hydrogen even after five hours' contact time at a pressure of 330 mm.

The data obtained with this sample and manganous oxide I have been utilized to construct an adsorption isobar of hydrogen on manganous oxide in the temperature range -78-444° at a pressure of 506 mm. The data are collected in Table V.

TABLE V

ADSORPTION ISOBAR OF HYDROGEN ON MANGANOUS OXIDE AT *p* = 506 MM.

Temperature, ° Abs.....	194.5	273	457	578	717
<i>V</i> _{ads.} , cc./g.....	0.000	0.000	0.024	0.039	0.020

Since the value at 578° Abs. is on manganous oxide I, the sample of greater activity (see page 2171), the table has only semi-quantitative significance. It serves well to indicate however the increase of pseudo-equilibrium adsorption with increase of temperature. A more quantitative exemplification will now be presented for the case of hydrogen adsorption on a manganous-chromic oxide surface.

B. Manganous-Chromic Oxide.—Weight of sample, 46.5 g.: with this material a striking experimental demonstration of slow adsorption increasing in velocity with rise of temperature has been performed. Hydrogen was introduced into the adsorption vessel at room temperature until a pressure of approximately 500 mm. was obtained. The vessel was then heated very gradually by the electric furnace and the accompanying pressure change was noted. Up to about 100° the gas pressure increased normally. Shortly after this temperature was passed the expansion ceased and, with the temperature still rising, a contraction took place. This contraction accelerated and, between 200 and 300°, the gas was adsorbed with great rapidity. A minimum pressure of 10 mm. was reached between 350 and 400°. Above 400° the pressure slowly increased again

although to only a slight degree and at 430° it had built up to approximately 20 mm. This experiment constitutes startling evidence of activated adsorption. It also indicates the necessity of high temperature evacuation for complete removal of adsorbed gas. In preparing the surface for the experiments now to be presented, evacuation was effected at 450–470°.

An adsorption measurement at 184° revealed the tremendous adsorptive capacity of the sample. In all a volume of 179 cc. of hydrogen was admitted to produce a pseudo-equilibrium pressure of 209 mm. after five days of adsorption. The adsorption was very rapid in the first stages, subsequent quantities of hydrogen being taken up at progressively decreasing rates. Desorption of successive samples gave the following pseudo-equilibrium data which show the tenacity with which hydrogen is held.

TABLE VI
ADSORPTION ISOTHERM OF HYDROGEN ON MANGANOUS-CHROMIC OXIDE AT 184°

<i>V</i> , cc.	<i>V</i> _{ads.} , cc.	<i>P</i> _{mm.}
178.9	166.3	209
173.6	166.3	121
169.6	166.2	57
166.1	165.6	8

On cooling the system to 0° and holding at that temperature for twenty hours, no desorption occurred, although, as will later be shown, only minor amounts of the gas can be adsorbed in reasonable time intervals at this lower temperature.

High Temperature Isotherms.—Adsorption isotherms at 305 and 444° were next obtained by saturating at a given pressure and then removing the gas adsorbed in measured amounts by means of the Sprengel pump. Suitable time intervals were allowed between each successive removal to permit the approximate establishment of equilibrium. The data are presented in Table VII.

TABLE VII
ADSORPTION ISOTHERMS OF HYDROGEN ON MANGANOUS-CHROMIC OXIDE AT 305 AND 444°

<i>T</i> , 305°			<i>T</i> , 444°		
<i>V</i> , cc.	<i>V</i> _{ads.} , cc.	<i>P</i> _{mm.}	<i>V</i> , cc.	<i>V</i> _{ads.} , cc.	<i>P</i> _{mm.}
184.7	171.6	269	107.8	100.9	165
182.3	171.1	230	101.3	98.1	77
176.8	169.6	151	97.0	95.0	48
172.9	167.0	121	84.2	83.3	22
166.7	163.6	63	57.2	57.1	3
163.3	160.8	51			
159.0	156.9	44			

Velocity of Adsorption.—For measurement of the velocity of adsorption on the mixed oxide the temperatures chosen were 100 and 132°. The pressure range was again kept approximately the same in the two cases in

order to limit the variables to temperature and surface. The data are presented in Table VIII.

TABLE VIII
VELOCITY OF ADSORPTION OF HYDROGEN ON MANGANOUS-CHROMIC OXIDE AT 100
AND 132°

T, 100°; V, 43.8 cc.			T, 132°; V, 41.4 cc.		
Time, min.	P _{mm.}	V _{ads.} , cc.	Time, min.	P _{mm.}	V _{ads.} , cc.
0	612	0.0	0	624	0.0
4	485	9.1	2.5	486	9.1
9	455	11.2	3.8	464	10.5
13	438	12.4	5.5	441	12.1
22.5	410	14.4	8	417	13.7
29	396	15.4	13	382	16.0
36	382	16.4	20	347	18.3
49.5	361	17.9	24.5	330	19.5
67	341	19.4	43	280	22.8
98	313	21.4	49	269	23.5
127	293	22.8	51	265	23.8
153	278	23.9	61	249	24.8
185.5	263	25.0	71	235	25.8

These velocity data yield, by the same type of calculation used in the case of manganous oxide III, the following results for the activation energies of adsorption on successive areas of the surface.

TABLE IX
ACTIVATION ENERGIES OF ADSORPTION OF HYDROGEN ON MANGANOUS-CHROMIC OXIDE

Adsorbed amount	Time required, min.		E, cal. per mole adsorbed
	132°	100°	
First 10 cc.	3.2	6.0	5,920
10th-15th	7.3	20.0	9,500
15th-20th	15.9	48.0	10,400
20th-25th	37.2	111.5	10,400

As with manganous oxide, the activation energy is lowest for the first portions of gas adsorbed, which signifies that the velocity of adsorption is most rapid on the most active areas of the surface. With increased covering of the surface, E rises to a value which is constant for a considerable region of covered surface. Undoubtedly, with additional areas covered, the value of E would rise still further. The absolute values of the numerical results for E differ widely in the two cases and the same is true for the quantities adsorbed. With the single oxide, the activation energy ranges over the first four cc. adsorbed from 12,000 to 20,000 calories per mole. With the mixed oxide surface the range is from 6000-10,000 for the first twenty-five cc. adsorbed. The effect of this divergence on the velocity of adsorption at, for example, 177° = 450° Abs., on the areas having $E = 6000$ and 12,000 cal., respectively, is best exhibited by reference to the relation

$$v_{\text{MnO-Cr}_2\text{O}_3} : v_{\text{MnO}} = e^{-6000/2 \times 450} : e^{-12000/2 \times 450} = e^{6000/900} = e^{6.6} = 750$$

where v is the velocity of adsorption and is proportional to the expression $e^{-E/RT}$. This enormous effect of the admixture of chromic oxide with manganese oxide on both the velocity and extent of adsorption is undoubtedly of fundamental importance in the phenomenon of promoter action in the field of heterogeneous catalysis.

Low Temperature Adsorption.—The magnitude of the activation energy on the manganese–chromic oxide, $E = 6000$, indicates that this type of adsorption will be very slow indeed at -78.5° , actually e^{-15} or 3×10^{-7} of that at 132° . It might therefore be possible to measure the molecular adsorption of hydrogen at such temperatures. An isotherm was, therefore, measured. An immediate rapid adsorption, complete in a few minutes, occurred. In addition there appeared a very slow adsorption which continued for many hours and which is probably adsorption of the activated type on areas of the surface on which the activation energy is even less than 6000 calories. The following Table X which records results obtained both with increasing and decreasing pressure indicates the existence of the secondary type by reason of the divergence between the two sets of data, ascending and descending. That even the activated adsorption involved low activation energies is evident from the fact that the residual 3.2 cc. of gas indicated in the table was almost completely recovered by Sprengel evacuation at 0° .

TABLE X

ADSORPTION ISOTHERM OF HYDROGEN ON MANGANOUS–CHROMIC OXIDE AT -78.5°

V , cc.	$V_{\text{ads.}}$, cc.	P	V , cc.	$V_{\text{ads.}}$, cc.	P
4.1	2.6	12	22.1	10.4	91
15.7	7.6	63	17.1	9.9	56
33.4	10.2	181	10.1	6.5	28
38.7	11.2	215	8.0	5.8	17
35.0	11.3	185	4.8	4.4	3
27.7	10.9	131	3.2	3.2	0

The change in adsorption with time at -78.5° and the rapid desorption of gas on heating to 0° is indicated in Table XI, which also shows that at 0° the desorption of gas is followed by its slow re-adsorption in the activated form.

TABLE XI

EFFECT OF TEMPERATURE CHANGE ON HYDROGEN ADSORPTION AT -78.5° AND 0°

$V = 35.4$ cc.

-78.5°			0°		
Time, hours	$P_{\text{mm.}}$	$V_{\text{ads.}}$, cc.	Time, hours	$P_{\text{mm.}}$	$V_{\text{ads.}}$, cc.
0.0	276	0.0	1.0	Temperature raised to 0°	
.05	196	10.3	1.82	270	9.9
.26	184	11.9	5.3	256	11.3
.45	183	12.0	29.5	237	13.0
.82	182	12.1			

Heat of Low Temperature Adsorption.—On a clean surface of the mixed oxide, hydrogen was rapidly adsorbed at 0° to the extent of 7 cc. at a pressure of 165 mm. From the previous data at -78.5° we find that the same quantity of gas is adsorbed at a pressure of approximately 40 mm. Substituting these values in the Clapeyron-Clausius equation

$$\frac{d \ln P}{dt} = \frac{\lambda_{L.T.}}{RT^2}$$

we obtain as an approximate value for the heat of low temperature adsorption the value, $\lambda_{L.T.} = 1900$ calories per mole.

Heat of High Temperature Adsorption.—A similar calculation is possible for the high temperature data already presented in the isotherms at 305 and 444°. For 100 cc. of adsorbed gas the pressures at 578 and 717° Abs. are < 5 mm. and 140 mm., respectively. Substitution of these data in the above equation gives $\lambda_{H.T.} \sim 20,000$ calories per mole. The ten-fold variation between the two magnitudes $\lambda_{L.T.}$ and $\lambda_{H.T.}$ is the best evidence of the fundamental distinction between the two types of adsorption.

The Adsorption Isobar.—The data in the several regions of temperature may be utilized to construct adsorption isobars. The data of Table XII present the values obtained at a pressure of 165 mm. A graph of these data is given in Fig. 1.

TABLE XII

ADSORPTION ISOBAR OF HYDROGEN ON MANGANOUS-CHROMIC OXIDE AT $P = 165$ mm.

Temp., °Abs.	Amount adsorbed, cc.	Nature of adsorbed gas
194.5	10.6	Molecular
273	7.0	Molecular
273	14.0 ^a	Molecular + activated
457	166 ^a	Mainly activated
578	170	Mainly activated
717	101	Mainly activated

^a These values represent only pseudo-equilibria.

The data and diagram give a clear picture of the temperature range where molecular, mixed and activated adsorptions occur. The transition from one form to another is shown to cover a range of several hundred degrees.

Adsorption of Carbon Monoxide.—With carbon monoxide, an orientation experiment similar to that performed initially with hydrogen on manganous-chromic oxide also showed that two types of adsorption occur. Adsorption at -78.5° took place almost instantaneously and produced a low equilibrium pressure in a few minutes. On heating from -78.5 to 100°, the adsorbed quantity decreased normally, a normal pressure increase also occurring. Above 100° activated adsorption appeared, as evidenced by the increase in adsorption and decrease in pressure with rise of temperature. At 225° the transition seemed to be complete and at

450° desorption of the activated form was occurring. We can, therefore, conclude that carbon monoxide shows adsorption phenomena paralleling, qualitatively, those of hydrogen on manganous-chromic oxide. A quantitative study is being undertaken.

Adsorption of Ethylene.—With ethylene vigorous adsorption occurred at -78.5° . On warming the catalyst as far as 300° nothing but steady desorption was observed. Above 300° there was a slight decrease in pressure. This may have been due, however, to incipient polymerization.

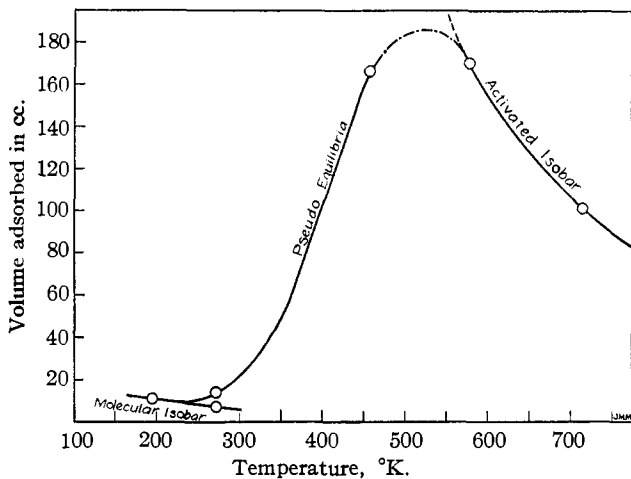


Fig. 1.—Adsorption isobar of hydrogen on manganous-chromic oxide at $P = 165$ mm.

C. Manganous Pyrophosphate.—Weight of sample, 34.7 g.: with this material a slow adsorption of hydrogen occurred at 305 and 444°. In magnitude and velocity it was far less than that obtained even with the single manganous oxide. The adsorption would appear to be activated since no hydrogen was adsorbed at 0° . The low magnitude and velocity of adsorption are consistent with the absence of dehydrogenation activity found for this material in other work to be reported elsewhere.

General Conclusions

The present investigations on manganous oxide and manganous-chromic oxide surfaces decisively demonstrate the adsorption of hydrogen on such surfaces in two different forms which are sharply differentiated. At low temperatures on manganous-chromic oxide the hydrogen is adsorbed rapidly with a negligible activation energy and with a heat of adsorption of approximately 1900 calories per mole. Adsorption of hydrogen in this form is readily reversible, for the gas can be completely recovered by evacuation at low temperatures. We describe such adsorption as “molecular” adsorption.

The second type of adsorption predominates at higher temperatures. On manganous-chromic oxide surfaces it makes its appearance at 0° as a slow drift in pressure after the initial rapid adsorption of the molecular form. The adsorption occurs with a definite velocity determined by the magnitude of an activation energy and the temperature. In its turn, the activation energy is a function of the surface area being covered. The first portions covered, with the mixed oxide, have a mean activation energy of 6000 calories; successive portions are associated with values rising gradually to higher magnitudes, for example, 10,400 calories. Over a range of several hundred degrees this activated adsorption apparently increases in magnitude with the temperature, a phenomenon to be ascribed to the influence of the activation energy on the velocity of adsorption.¹ Above 300° with manganous-chromic oxide the isobar begins to show a normal decrease with increase in temperature, and from isotherms in this temperature range heats of adsorption of the activated form of the order of 20,000 calories have been deduced. These high heats of adsorption coupled with the activation energy of adsorption adequately account for the observation that desorption of the activated adsorbate requires an evacuation lasting for several hours at temperatures above 450° .

With manganous oxide the results are similar in character but differ greatly in magnitude. There is no measurable adsorption of the molecular form at -78.5° . The activated form makes its appearance first in the neighborhood of 100° . The initial velocity of adsorption is some 750 times slower at 450° Abs. than on the mixed oxide since the initial activation energy is 12,000 calories, rising to 20,000 calories on successive areas covered. The quantities of adsorbed hydrogen on the single oxide are much smaller than those taken up by the mixed oxide at corresponding temperatures.

These experiments represent the first decisive measurements of the velocity of gaseous adsorption at surfaces and have yielded the first unequivocal calculations of the activation energies of adsorption processes. They yield abundant experimental proof of the theory of activation energy of adsorption recently put forward by one of us (H. S. T.). They introduce into the problem of gaseous reaction velocities at surfaces the velocity of activated adsorption, a factor of fundamental importance, hitherto ignored, of especial significance in the so-called problem of promoter action and in the specificity of reactions at such surfaces.¹⁰

Since the phenomena observed with hydrogen are also shown, qualitatively at least, by carbon monoxide, it is evident that the type of investigation here initiated with hydrogen can be extended to other gases activated at surfaces. Such studies are in progress.

¹⁰ See Taylor, *Chem. Reviews*, August, 1931.

Summary

1. The adsorptions and velocities of adsorption of hydrogen on manganous oxide and manganous-chromic oxide have been measured in the temperature range -78.5 to 444° .

2. Two forms of hydrogen adsorption have been demonstrated and differentiated, each with characteristic heats of adsorption and activation energies of adsorption on a given surface.

3. The activation energy of adsorption is a function of the composition of the surface and of the physical state of the surface; the velocity of adsorption is small on sintered surfaces and decreases rapidly with increased surface area covered.

4. Activated adsorption of the type here studied is not necessarily a rapid process but may, at certain temperatures, occur at rates so slow as to be immeasurable over periods even of years.

5. Similar observations have been made, qualitatively, with carbon monoxide. This type of investigation can, therefore, probably be generalized for various gases and surfaces,

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NOTES

A Micro Hydrogen Electrode.—The electrode described in this paper was designed to be used where small amounts of liquid were available for the determination. The electrode was made from an ordinary platinum hypodermic needle. The tip was cut off and the needle was threaded for about 5 mm. on the outside. A small shield made of platinum was made to screw on the needle over the tip. A short length of copper wire was soldered to the side of the nub of the needle, leaving enough room at the end to attach a rubber tube for the hydrogen. The entire electrode and cap were insulated by covering with bakelite paint. The electrode was then platinized on the inside. The potassium chloride can be brought into the vessel by means of a capillary or a piece of cotton string soaked in the potassium chloride.

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DEPARTMENT OF PHYSIOLOGICAL CHEMISTRY
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FELIX SAUNDERS

A Lampbank Rheostat.—A system of lamps in parallel makes a serviceable laboratory rheostat for use with magnetic stirrers, electric furnaces, motors, etc. The figure illustrates an easily and cheaply constructed lampbank that has proved to be very convenient. It avoids the use of the switches, sockets and wiring that the ordinary form of lamp board