[CONTRIBUTION FROM THE MOORE LABORATORY OF CHEMISTRY, AMHERST COLLEGE]

Heats of Adsorption of Gases on Chromic Oxide at Low Temperatures*

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As a result of numerous researches on the adsorption of gases on catalytically active solid surfaces, van der Waals and activated adsorptions have become clearly recognized as separate and distinct types. In many instances it has been shown that a gas may be held in both states of adsorption upon the same solid surface. Frequently the two types occur in more or less well separated temperature ranges, the activated type being characteristic of the higher temperature. In certain cases, however, the critical increment of the activated adsorption is sufficiently low so that the temperature range of this process overlaps that of the low temperature van der Waals adsorption.

In the present investigation heats of adsorption, in the low temperature region, have been measured calorimetrically using the six gases, argon, hydrogen, deuterium, carbon monoxide, nitrogen, and oxygen on a reduced chromic oxide surface. The order of magnitude of the heats indicates that all these gases, with the single exception of argon, are in part held in a state of activated adsorption as well as in the van der Waals state even at the low temperature of −183°. Moreover, in the experiments with carbon monoxide, nitrogen, and oxygen, the complex form of the time–temperature curves on a partially covered surface has led us to the conclusion that the adsorbed gas changes over on the surface from an initial van der Waals state to a final state of activated adsorption.

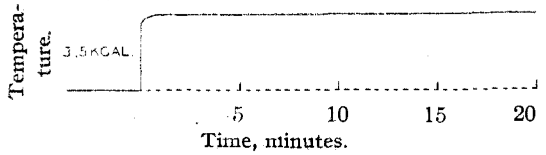

Fig. 1.—Time–temperature curve for argon at −183°.

The catalytic activity of chromic oxide at −183° for the reaction $H_2 + D_2 \rightleftarrows 2HD$[1] leads to the conclusion that the adsorption of hydrogen and of deuterium on that adsorbent is, in part at least, of the activated form. Special interest is therefore attached to the heats of adsorption of the hydrogen isotopes which give independent evidence for the activated adsorption of these gases at −183°. The present work confirms the results of a previous investigation by Beebe and Orfield[2] using hydrogen alone.

Experimental

Apparatus.—A detailed description of the vacuum jacketed calorimeter used in this work has been given in an earlier publication. The calorimeter, which had a total heat capacity of 4.839 cal. at −183° and contained 11.95 g. of chromic oxide, was used without any dismantling or alteration after the heat measurements with hydrogen previously described.[2] The thermocouple wires were led into the calorimeter by means of tungsten bridges sealed through the Pyrex glass. The whole calorimeter vessel including the tungsten bridges was immersed in a suitable bath for constant temperature. For the temperatures −183, −195, and 0°, respectively, baths of liquid oxygen, liquid nitrogen, and an ice–water mixture were used. In the experiments designated in Table II for hydrogen and deuterium, and in all the other work except the first carbon monoxide series, a small quantity (about 0.2 cc.) of helium was admitted to the inside of the calorimeter. This produced a residual pressure of approximately 0.1 mm., and served to improve the conditions for effective heat distribution.

Especially in the hydrogen and deuterium measurements, very careful attention was given to experimental details such as the temperature and duration of outgassing, and the protection of the external leads of the thermocouple from chance fluctuations in room temperature. As a result, it was possible to read the differential heats with greater precision than in the earlier work, and the results were remarkably reproducible in successive series of measurements for all corresponding increments of gas added to the surface.

In Fig. 1 is given a typical time–temperature curve for argon at −183°. The rapid rise to maximum temperature following the admission of the gas, and the almost negligible rate of cooling after the temperature rise, both indicate that the calorimetric conditions were very satisfactory, and the temperature recorded by the thermocouple was truly the average temperature of the whole metal calorimeter with negligible heat lag due to poor thermal distribution. This type of curve, which was obtained under all conditions in the measurements with argon as well as with the isotopes of hydrogen,[3] will be referred to as a *normal* time–temperature curve in comparison to curves of *abnormal* type resulting from the more complex nature of the adsorption processes in the cases of the other gases studied at −183°.

(*) Supported by a grant from the Penrose Fund of the American Philosophical Society.

(1) Gould, Bleakney and Taylor, *J. Chem. Phys.*, **2**, 362 (1934).

(2) Beebe and Orfield, THIS JOURNAL, **59**, 1627 (1937).

(3) Owing to a misunderstanding, the time–temperature curve in Fig. 2 of the paper by Beebe and Orfield was inverted when printed. The downward break in the curve as printed actually represents a rise in temperature.

Because of the much greater rate of heat loss from the metal calorimeter by radiation at the higher temperature, the rate of cooling after the liberation of the heat of adsorption was very much more rapid at 0° than at −183°. However, owing to the rapid rate of adsorption and consequent quick rise to maximum temperature, the heat at 0° could be determined from the time–temperature curves with a fair degree of accuracy. It is noteworthy, however, that this calorimetric method is more satisfactory at the lower temperature.

Materials.—The hydrogen was prepared from electrolytic tank hydrogen by first passing over hot copper and then through a trap filled with glass wool and immersed in liquid air.

Deuterium was produced by electrolysis of 99% deuterium oxide with careful provision for the exclusion of gaseous impurities during the electrolysis and the transfer of the gas.

The method of preparation of carbon monoxide has been described previously.[4] Analysis showed that it contained at least 98% of carbon monoxide and no oxygen.

Pure oxygen was obtained by heating potassium permanganate crystals *in vacuo*.

The nitrogen was obtained from tank nitrogen by mixing with 5% of electrolytic hydrogen, passing the mixed gases over a mixture of copper and copper oxide granules at 400°, and removing the water vapor by means of a calcium chloride tube and liquid air trap.

The argon gas purchased from the Air Reduction Sales Company was spectroscopically pure.

The chromic oxide was the same "unglowed" sample used in the earlier experiments.[2] Following each series of heat measurements, the surface was outgassed for three hours at 400°, except in the case of oxygen. For the removal of the latter gas, the final three-hour period of outgassing was preceded by a one-hour period of reduction in a hydrogen atmosphere. During this reduction the hydrogen was removed and replaced several times to eliminate the water vapor produced.

Results

The Adsorption Isotherms at −183°.—In Fig. 2 are plotted the isotherms from data obtained in the course of the heat measurements at −183°. Hydrogen, deuterium, and carbon monoxide were adsorbed instantaneously (in less than two minutes) with no residual pressure up to 20, 28, and 120 cc., respectively. Argon, nitrogen, and oxygen produced small residual pressures even for the initial increments of gas admitted. In no case was the amount of gas, unadsorbed after two minutes, more than 4% of the total increment admitted. In all cases in which there was residual unadsorbed gas the pressure underwent a slow decrease which was usually complete in twenty minutes. The pressures plotted in Fig. 2 were read twenty minutes after admission of the gas increments. The amount of gas adsorbed in the interval between two and twenty minutes after admission was never more than 2% of the total increment adsorbed, and in most cases much less than that. It was therefore disregarded and the amount of gas adsorbed after two minutes was used in the calculation of the differential heats.

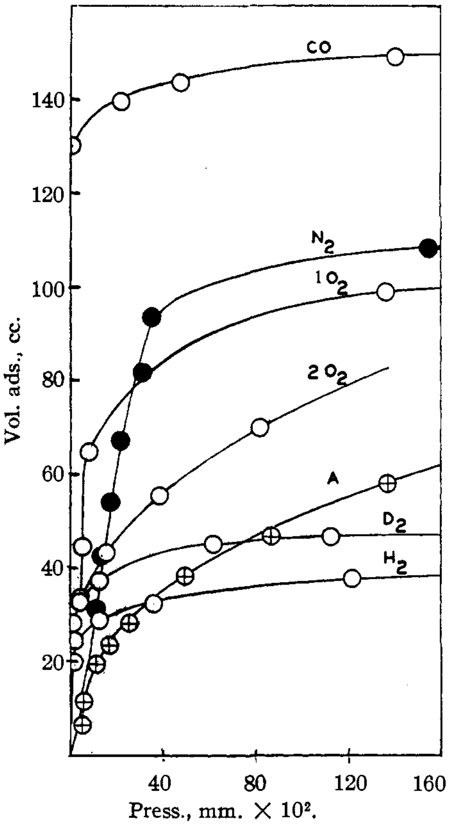

Fig. 2.—Adsorption isotherms on 11.95 g. of Cr_2O_3 at −183°.

With the exception of oxygen, the isotherms were remarkably reproducible. The curves shown in Fig. 2 for carbon monoxide and nitrogen are composites of four series with the former and two with the latter. Only one series was measured with argon. The isotherms for hydrogen and deuterium in Fig. 2 represent data from four series with deuterium and three with hydrogen. These measurements with the hydrogen isotopes were performed before any of the other gases were admitted to the chromic oxide surface. The order of experiments was D_2, D_2, H_2, D_2, H_2, H_2, D_2. For simplicity, only a few representative points have been plotted, but for the scale used, other points not plotted would fall on the isothermal lines without any apparent deviation. It is therefore definitely established that deu-

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[4] Beebe and Wildner, THIS JOURNAL, 56, 642 (1934).

terium is more firmly held than hydrogen on a chromic oxide surface at −183°.

Analysis showed that the adsorbed carbon monoxide could be removed unchanged by evacuation at 400°, the desorbed gas containing no carbon dioxide. No attempt was made to analyze the other gases after desorption but the reproducibility of the isotherms as well as the differential heat curves, for all the gases studied with the exception of oxygen, provide strong evidence that the three-hour evacuation at 400° was sufficient to remove the adsorbed gases completely without changing the state of the chromic oxide surface. The adsorbed film of oxygen could be removed only as water vapor after reduction in hydrogen. This treatment resulted in a change in the activity of the surface as shown by the failure of the isotherms and heat curves to coincide in the successive series of measurement for oxygen. No experiments with oxygen were attempted until all the other work had been completed. Hence only in the case of the first oxygen series was the surface the same as that employed for the other gases.

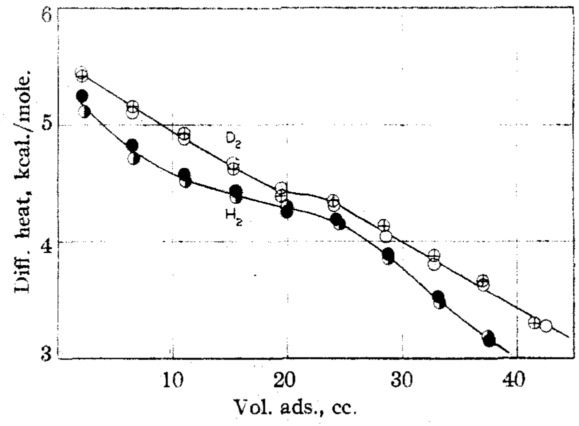

Fig. 3.—Series 1, H_2 ●; Series 2, H_2 ◑; Series 1, D_2 ⊕; Series 2, D_2 ○.

The Heats of Adsorption at −183°, Argon, Hydrogen, and Deuterium.—The results for the single series of differential heat measurements with argon are given in the lower curve in Fig. 8. Because of the magnitude of the differential heats which fall between 4.2 and 2.7 kcal./mole and because of the normal form of the time–temperature curves (Fig. 1) it is concluded that the process for argon at −183° is a simple van der Waals adsorption.

In all, four series of differential heat measurements were made with deuterium and three with hydrogen. The results of two series with each isotope are shown in Fig. 3. Details for typical series are also given in Table I. It is apparent that the heats are definitely higher with the heavier isotope for all corresponding portions of the chromic oxide surface.

TABLE I

Total vol. ads. cc.		Diff. heat kcal./mole		Resid. press., cm. Hg × 10^3	
H_2	D_2	H_2	D_2	H_2	D_2
2.20	2.14	5.11	5.43	....	...
6.55	6.51	4.82	5.14	....	...
11.00	10.93	4.57	4.91	....	...
15.52	15.25	4.44	4.62	....	...
19.91	19.59	4.31	4.39	0.32	...
24.31	24.00	4.18	4.33	1.67	...
28.74	28.40	3.89	4.14	11.30	0.45
33.16	32.78	3.53	3.87	32.61	2.55
37.57	37.14	3.16	3.64	115.50	9.43
	42.5		3.30		32.50

The integral heats, obtained by a process of summation of the differential heats for the increments comprising the first 37.2 cc. of each isotope adsorbed, are listed in Table II (Series 1–7). The integral heats evolved when 37.2 cc. of gas was admitted at one time were also measured in one experiment for each hydrogen isotope. The results are given in Table II (Series 8 and 9). It is interesting that the values obtained by direct admission of the whole 37.2 cc. are higher than those found by a summation of the differential heats. We believe that this difference is a real one and not due to experimental error. A similar discrepancy has been observed by Magnus and his co-workers[5] in the case of sulfur dioxide on charcoal, and these authors have suggested an explanation based on the assumption of slow establishment of equilibrium in the crevices of the adsorbent. It is probable that a similar

TABLE II

Series no.	Gas adsorbed	Integral heat, kcal./mole (37.2 cc. ads.)	
1	D_2		4.79
2	D_2		4.76
3[a]	H_2	4.27	
4[a]	D_2		4.77
5	H_2	4.45	
6	H_2	4.47	
7	D_2		4.81
	Av.	4.40	4.78
8	D_2		5.12
9	H_2	4.81	

[a] Helium present.

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(5) Magnus, Giebenhain and Velde, *Z. physik. Chem.*, **150A**, 285 (1930).

explanation is applicable in the present instance, In any case, it appears to be established that for the interval 0 to 37.2 cc. adsorbed, the integral heat of adsorption of deuterium exceeded that of hydrogen by approximately 0.35 kcal. per mole.

The Heats of Adsorption at −183°, Carbon Monoxide, Nitrogen, and Oxygen.—Unlike the gases already discussed, carbon monoxide, nitrogen, and oxygen failed to produce normal time–temperature curves under all conditions. This anomalous behavior is illustrated in the case of carbon monoxide by the curves in Fig. 4. Curves I, II, and III are the time–temperature curves obtained with approximately equal increments of about 4.5 cc. of the gas on a surface to which had been added already 0, 55, and 112 cc., respectively, *i. e.*, these curves were obtained from measurements on a bare surface, a partly covered surface, and a nearly saturated surface.

A normal type of curve was obtained when no carbon monoxide was previously adsorbed (Curve I); however, with successive increments of the gas the rise to maximum temperature became less and less sharp, and then began to divide into a rapid and a slow stage (Curve II) until finally the slow stage had assumed such a low rate that it could scarcely be detected in the twenty-minute period of observation (Curve III). Except when the experiments were interrupted overnight (see below), all the other time–temperature curves observed in the series of measurements fitted in form to their intermediate positions in the series. In all the carbon monoxide increments up to 120 cc. adsorbed, *all the gas disappeared from the gas phase within one minute after admission.*

From these observations we are forced to conclude that the adsorption of carbon monoxide on chromic oxide at −183° consists of two distinct and separate processes which we shall call Process A and Process B. Process A is rapid for all states of the surface and gives a heat of approximately 4 kcal.; Process B is rapid for a bare surface but becomes progressively slower for successive increments until it is too slow to observe. Process B yields an additional heat of about 8 kcal., bringing the total heat up to 12 kcal. For reasons given later under Discussion we believe Process A is a van der Waals adsorption, and that the final result of Process B is a state of activated adsorption. If this is true, the heat values 4 and 12 kcal. represent differential heats of van der Waals and of activated adsorption, respectively, and have therefore been so designated in Fig. 5. Furthermore, because of the slow evolution of heat long after all the gas had disappeared from the gas phase, it seems probable that the gas, initially adsorbed by van der Waals forces, subsequently underwent a change into the activated state without leaving the surface.

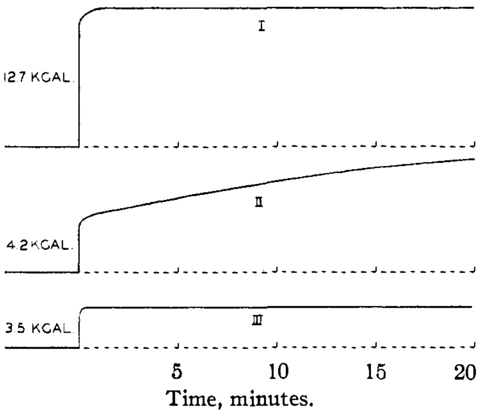

Fig. 4.—Time–temperature curves for CO at −183°.

The data listed in Fig. 5[6] indicate that there is a decrease in the differential heats of activated adsorption with increasing surface covered suggesting a variation in surface activity.[7] However, we do not feel certain that this has been demonstrated conclusively because of the difficulty in estimating the total heat rise, especially in the region 30–80 cc. adsorbed.

The heat experiments with nitrogen and oxygen produced the same division into Processes A and B. As in the case of carbon monoxide, the heat of Process A was about 4 kcal. for both these gases. The heats of activated adsorption were, however, about 8 kcal. for nitrogen and 20–27

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(6) From the experimental observations on a relatively bare surface, it is possible to estimate the differential heats of the activated adsorption only. On a nearly covered surface where Process A occurs exclusively, only van der Waals heats are measured. On partially covered surfaces (Curve II, Fig. 4), however, it is possible to determine both the heat of van der Waals absorption from the initial rapid heat evolution, and the heat of activated adsorption from the total heat evolved. For this reason heat data for both types of adsorption are given for the region 40–80 cc. adsorbed. The heat of activated adsorption could be determined with fair accuracy for the initial increments up to a total of 30 cc. Beyond that point it became increasingly difficult to estimate the total heat evolution because of the decreasing rate of Process B with each successive increment. Beginning at about 40 cc. adsorption, it was possible to estimate the initial sharp rise due to van der Waals adsorption. Beyond 55 cc. the results could be determined more accurately because Process A was more sharply differentiated for the later increments.

(7) It is possible that the activated adsorption of carbon monoxide, oxygen, and nitrogen is non-selective as it has been shown to be with hydrogen (see below). In that case, the true differential heats would decrease more rapidly with successive increments than in the experimental values given in Fig. 5.

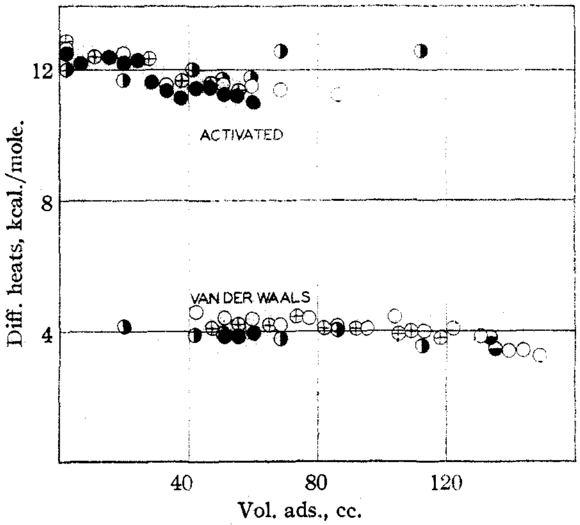

Fig. 5.—CO on Cr_2O_3: Series 1, 2, and 3 at −183° ⊕, ○, and ●; after outgassing at −183° ◒; Series 1 at −195° ◑.

kcal. for oxygen. Typical time–temperature curves are given in Figs. 6 and 7 for initial, intermediate, and final increments of each gas. The differential heats for both activated and van der Waals adsorption are shown in Figs. 8 and 9.

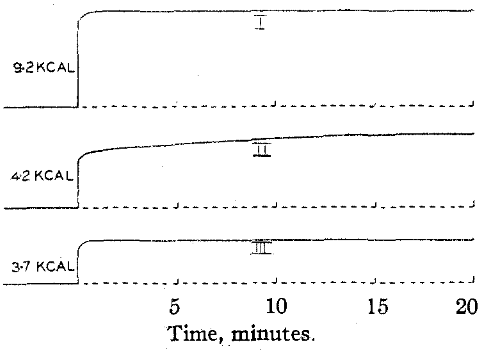

Fig. 6.—Time-temperature curves for nitrogen at −183°.

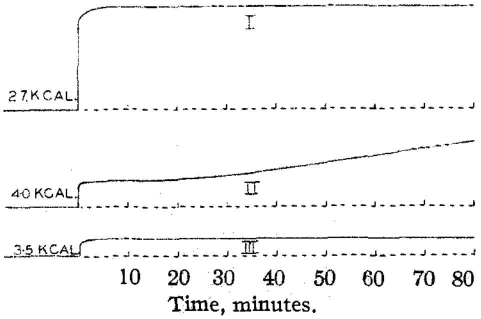

Fig. 7.—Time-temperature curves for oxygen at −183°.

Owing to the change in activity of the chromic oxide surface in the three oxygen experiments, the differential heat values were not reproducible. Series 1, 2, and 3 produced initial heats of 27, 21, and 25.5 kcal., respectively. It is noteworthy that the same order of activity for the three series is indicated by the adsorption isotherms from Series 1 and 2 in Fig. 2. Unfortunately, Series 3 was not carried far enough to determine the position of the isotherm.

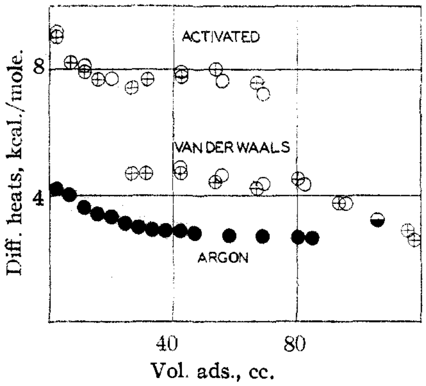

Fig. 8.—N_2 and argon at −183°: Series 1, N_2 ⊕; Series 2, N_2 ○; N_2 after outgassing at −183° ◒; argon ●.

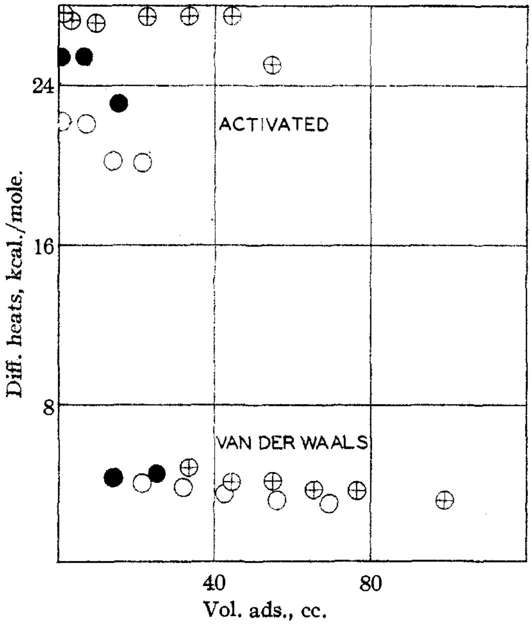

Fig. 9.—O_2 on Cr_2O_3 at −183°: Series 1 ⊕; Series 2 ○; Series 3 ●.

Following several of the series of heat measurements, the chromic oxide surface was outgassed for one hour at −183°. The differential heats were measured for increments subsequently added to the surface. As might have been expected, the form of the time–temperature curves and the magnitude of the heats both indicated van der Waals adsorption exclusively. The data for two such experiments with carbon monoxide and one with nitrogen are given in Figs. 5 and 8. A similar result was obtained in previous work in this Laboratory with carbon monoxide on copper at −183°.[8] These experiments demonstrate the reversibility of the van der Waals process at −183°, as well as the irreversible nature of the activated adsorption.

Carbon Monoxide on an Oxygen Covered Surface, and Oxygen on a Carbon Monoxide Covered Surface at −183°.—An investigation was made of the heat liberated by the addition of carbon monoxide to an oxygen covered surface at −183°.[9] Following oxygen Series 3 at −183°, the unadsorbed oxygen and presumably most of the van der Waals adsorbed oxygen were removed by evacuation for one hour at the same temperature. It is estimated that 25 cc. of activated adsorbed oxygen remained. The differential heats for carbon monoxide on this surface were then determined. The time–temperature curves for intermediate increments in the series had the abnormal form observed with carbon monoxide on an initially bare surface, indicating the presence of the rapid Process A, van der Waals adsorption, followed by a slow Process B, activated adsorption. The results of this experiment are given in Table III.

TABLE III

HEATS OF ADSORPTION AT −183°

Vol. of increment ads., cc.	Resid. press., mm. × 10^2	Diff. heat of ads., kcal./mole van der Waals	Diff. heat of ads., kcal./mole Activated	Total vol. ads., cc.
		CO on O_2 Covered Surface		
2.24	2.2	..	12.84	2.24
3.67	not meas.	..	12.38	5.87
3.39	7.1	..	11.41	9.29
3.75	12.9	..	11.41	17.51
4.34	32.0	4.50	9.67	30.65
4.36	74.3	4.21	...	44.11
4.42	102.5	4.31	...	48.54
4.38	117.9	3.98	...	66.64
		O_2 on CO Covered Surface		
1.84	..	..	12.73	1.84
2.26	..	..	11.59	4.10
4.32	77.0	3.20	...	8.42

Another series of heat measurements was conducted for oxygen on a carbon monoxide covered surface at −183°. In this experiment the surface was prepared by adding carbon monoxide at −183° until there was a residual pressure, and then outgassing for one hour at that temperature, leaving a surface film of approximately 100 cc. of carbon monoxide adsorbed in the activated state. The differential heats then obtained upon admission of successive increments of oxygen are given in Table III. The time–temperature curves were normal, giving no evidence for a slow process. The magnitude of the heats indicates an activated adsorption for the initial increments with a van der Waals adsorption of the final increment added.

A comparison of our data in Table III, with the results of the experiments with a single gas on an initially bare surface, reveals the following facts: (1) the presence of 25 cc. of adsorbed oxygen reduces the volume of carbon monoxide adsorbed in the activated state from 113 to 40 cc. (at 1 mm. residual pressure) but causes no great change in the heat of activated adsorption which is approximately 12 kcal. whether the surface was initially bare or oxygen-covered; (2) 100 cc. of adsorbed carbon monoxide brings about a very great decrease in the volume of oxygen adsorbed in the activated form from 25 to 4 cc.; moreover, the heat of the activated adsorption of oxygen is reduced from 25 kcal. on the initially bare surface to 13 kcal. on the carbon monoxide covered surface.

The complexity of the experimental conditions especially when two gases are present simultaneously on the chromic oxide surface which itself contains two different kinds of atoms makes an explanation of the above observations rather precarious. An explanation appears to be possible if we assume that: (1) the activated adsorption of oxygen occurs on the surface chromium atoms only; (2) the activated adsorption of the carbon monoxide occurs chiefly on the oxygen atoms of the chromic oxide but to some extent on the most active chromium atoms. However, we prefer not to present such an explanation until further experimental results are available.

Heat of Adsorption of Carbon Monoxide at −195°; the Energy of Activation of Process B.—In order to find the temperature coefficient of the rate of Process B, heat measurements were made in one series for carbon monoxide at −195°. The results were analogous to those at −183°

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[8] Beebe, Low and Goldwasser, THIS JOURNAL, 58, 2196 (1936).

[9] Because it was impossible to reproduce exactly the state of activity of the surface after oxygen was once admitted, it is important to know the order in which the experiments were conducted. After the oxygen measurements were begun, the order of experiments was, oxygen Series 1 and 2 at −183°, oxygen Series 3 and carbon monoxide on an oxygen covered surface at −183°, oxygen on a carbon monoxide covered surface at −183°, and oxygen on a plain surface at 0°.

except that Process B was slower for corresponding surface covered. As a result it was possible to differentiate Processes A and B earlier in the series (20 cc. adsorbed). Process B persisted further in the series making it possible to estimate the heats of activated adsorption up to 112 cc. adsorbed. The differential heats are given in Fig. 5. This persistence of Process B at −195° for larger amounts adsorbed than at −183° was possibly due to the higher total adsorptive capacity of the chromic oxide at the lower temperature. The adsorptive capacity beyond 112 cc. was not determined because the supply of liquid nitrogen ran out at that point.

From the rates of heat evolution at −195 and −183°, it was possible to estimate the rates of Process B at those two temperatures. From these data the energy of activation of the process was calculated. For surfaces on which the amounts already adsorbed before admission of the increment were 40, 50, 60, and 70 cc., respectively, the corresponding activation energies were 180, 300, 420, and 690 cal.

Heats of Adsorption at 0°.—The adsorption of argon and of the isotopes of hydrogen was negligibly small at 0° in the low pressure range studied, and the adsorptive capacity of the chromic oxide for carbon monoxide, oxygen, and nitrogen was much less at 0 than at −183°. The differential heats were determined for each of the latter three gases. The results for carbon monoxide and oxygen are given in Table IV. Only two increments of nitrogen of 1.88 cc. each were adsorbed. These had residual pressures of 1 and 1.7 mm., respectively, and each produced heats of 18.1 kcal.

At 0° the time-temperature curves were normal in type with all three gases giving no evidence for the two Processes A and B found at −183°. It is probable that van der Waals adsorption (Process A) was absent, and that the rate of the activated adsorption (Process B), which was slow after the initial increments at −183°, was too rapid to observe on any part of the surface at the higher temperature.

TABLE IV

HEATS OF ADSORPTION ON CHROMIC OXIDE AT 0°

Vol. of increment ads., cc.	Resid. press., mm. × 10^2	Diff. heat of ads., kcal./mole	Total vol. ads., cc.
Carbon Monoxide			
2.22	1.3	15.2	2.22
2.28	1.4	14.1	4.50
2.20	3.1	13.8	12.90
2.21	3.9	13.2	19.60
2.33	6.2	12.5	26.0
2.21	16.2	12.3	35.0
2.17	40.6	12.0	44.0
2.13	104.1	10.7	52.8
2.00	297.5	9.9	61.4
Oxygen			
1.59	..	50.0	1.59
1.01	..	49.6	2.60
1.05	..	50.1	3.63
0.98	..	46.9	4.65
1.11	..	48.4	5.89
1.02	..	44.2	6.83
1.09	..	43.3	14.47
0.83	23.0	17.6	27.42

Discussion

Hydrogen and Deuterium at −183°.—The most important conclusion to be drawn from the work on the hydrogen isotopes is that the heats are altogether too high to be accounted for by van der Waals forces alone, and the process must be in large part of the activated type. The significance of the heat measurements, in connection with the catalytic activity of chromic oxide at −183° observed by Gould, Bleakney, and Taylor,[1] has been discussed in detail by Beebe and Orfield.[2] The discussion given by them for hydrogen may be applied equally well to the present data with deuterium.

According to Urey and his co-workers,[10] the heats of vaporization of hydrogen and deuterium are, respectively, 183 and 276 cal. per mole. We find the higher heat of adsorption for the heavier isotope. It should not be inferred from this, however, that only van der Waals forces are in operation at −183°.

In a study of the dissociation pressures of potassium deuteride and hydride in the temperature range 270 to 360°, Sollers and Crenshaw[11] have found that potassium holds hydrogen more strongly than deuterium, but a detailed study of their data leads them to suggest that at low temperatures the hydride may have the higher dissociation pressure. This would be in accordance with the results of the present investigation on chromic oxide shown in Fig. 2, and exactly the reverse of the case of hydrogen and deuterium adsorption on copper previously studied in this Laboratory.[12]

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(10) Scott, Brickwedde, Urey and Wahl, *J. Chem. Phys.*, **2**, 454 (1934).

(11) Sollers and Crenshaw, THIS JOURNAL, **59**, 2015 (1937).

(12) Beebe, Low, Wildner and Goldwasser, *ibid.*, **57**, 2527 (1935).

The difference in the shapes of the two differential heat curves in Fig. 3 seemed at first perplexing, but can be explained, we believe, in the following manner. It has been demonstrated[13] that the adsorption of the initial increments of hydrogen on chromic oxide at −183° is non-selective,[14,15] occurring on those portions of the surface with which it first comes in contact.[2] If this non-selectivity of the process were complete the heat values would be constant for the whole region studied because they would really represent integral heats of adsorption for successive layers.[4] If, on the other hand, the adsorption were non-selective for a part of the surface but selective for the remainder, then a discontinuous curve like Curve A in Fig. 10 would be expected provided the true distribution of energies on the surface is represented by Curve C. It is easy to see that the experimentally determined curve for hydrogen is of the form of Curve B which lies between Curves A and C. It is further noteworthy that the region of non-selective adsorption cannot go much beyond 20 cc. adsorbed because from here on there is a residual gas pressure, as shown in Table I, indicating equilibrium conditions under which non-selective adsorption would be impossible.

The fact that the horizontal step in the heat curves, which is so definite for hydrogen, is almost absent in the deuterium data, suggests that the phenomenon of non-selective adsorption is much less marked for the heavier isotope. Now non-selective adsorption occurs when the rate of adsorption is great compared to the rate of diffusion of the gas; this causes the gas to be adsorbed on those successive layers of the adsorbent with which it first comes in contact. The slower rate of diffusion of deuterium should give more time for the non-selective process to occur. Since, however, it is the hydrogen adsorption which is the more non-selective of the two, it seems evident that the rate of adsorption of the lighter isotope must be the greater by a ratio considerably more than enough to compensate for the $\sqrt{2}$ diffusion factor. Of course the rates cannot be compared by direct measurement because the adsorption of either isotope is complete in less than one minute after admission to the adsorbent surface.

Pace and Taylor[16] found no difference for hydrogen and deuterium in the rates of the activated adsorption process on chromic oxide at 218° and one atmosphere pressure. It is not surprising that the present investigation, carried out at −183° and very low pressures, should yield results which differ from those of the above authors. Moreover, because of the very low value of T used in the exponential $e^{-E/RT}$, a small difference in the activation energies for the two isotopes would be sufficient to account for a relatively large difference in the rates of adsorption.

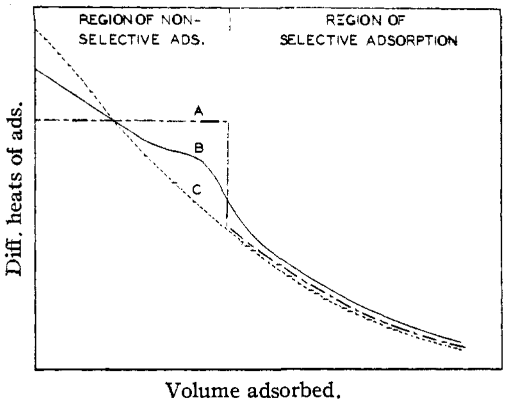

Fig. 10.

Carbon Monoxide, Nitrogen, and Oxygen at −183°.—Evidence has been presented under Results to show that on a partially covered surface at −183° the adsorption of carbon monoxide, nitrogen, and oxygen consists of two processes which have been called Process A and Process B. Analysis of the experimental data shows that Process A is rapid under all conditions and is non-specific in nature, yielding a heat of about 4 kcal. regardless of the nature of the gas adsorbed[17] or of the state of the adsorbing surface. We believe that these observations justify the assumption that Process A is a van der Waals adsorption exclusively. Process B differs from Process A in two important respects: (1) the heats of adsorption are much higher than in Process A and are specific to the gas used and to the condition of the chromic oxide surface; and (2) the rate of adsorption varies greatly as a function of the amount of gas already on the surface. The first of the above characteristics of Process B eliminates the possibility that it is a van der Waals process,[18] and

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(13) This was done with a calorimeter similar to that described by Beebe [*Trans. Faraday Soc.*, **28**, 761 (1932)]. Using this instrument at −183°, it was found that the form of the time–temperature curve obtained upon admission of hydrogen was greatly influenced by the position of the thermocouple. This was interpreted to indicate non-selective adsorption by the same reasoning as that used by Beebe in the case of carbon monoxide on copper at 0°.

(14) Russell and Ghering, This Journal, **57**, 2544 (1935).

(15) This phenomenon has been called "non-uniform" in previous publications from this Laboratory. We believe, however, that the term "non-selective" used by Russell and Ghering, describes the process more accurately; we shall therefore use it in the future.

(16) Pace and Taylor, *J. Chem. Phys.*, **2**, 578 (1934).

(17) The three gases carbon monoxide, nitrogen, and oxygen and in addition argon have boiling points which all fall within the twelve-degree range from −183 to −195° and as a consequence we should expect them to have approximately the same heats of vaporization. It is therefore not surprising that the heats of van der Waals adsorption which result from changes of a physical nature are found experimentally to be nearly the same for all four gases.

(18) Barrer, *Proc. Roy. Soc.* (London), **161A**, 476 (1937), has calculated from the isotherms at low temperatures the heats of adsorption of nitrogen, argon, and hydrogen on graphite and has suggested that the higher values obtained for the initial increments of gas adsorbed may be attributed to the van der Waals adsorption of the molecules in cracks sufficiently narrow to permit both walls to influence the adsorption. For crevices with plane and nearly parallel sides, the heat of adsorption would be approximately double the value for a plane surface. Moreover, the calculations of DeBoer and Custers, *Z. physik. Chem.*, **25B**, 225 (1934), showed, for adsorption in hemispherical pockets, tubes, and cells, maximum energies of four, six, and eight times, respectively, the energies on a plane surface. The high initial heats of 8 kcal. observed by us in the case of nitrogen conceivably might be explained on the basis of the calculations of DeBoer and Custers. However, the higher heats of 12 and 27 kcal. with carbon monoxide and oxygen could scarcely be

we must conclude that the final result of Process B is a state of activated adsorption.[19]

From the experimental evidence, however, it is difficult to decide with certainty whether the rate controlling factor in Process B is one of activated adsorption or of activated surface diffusion. As we shall see, the choice between these alternatives depends upon the accessibility of the adsorbing surfaces to the incoming gas. We shall use the case of carbon monoxide in this discussion, although it also applies to nitrogen and oxygen.

We have already assumed that the chromic oxide surface is capable of both van der Waals and activated adsorption. Let us make certain further assumptions:

1. The van der Waals adsorption requires zero activation energy, and it is easy for a van der Waals adsorbed molecule to be desorbed and begin a surface migration.

2. The activated adsorption requires a small finite activation energy which increases with successive increments from an initial negligibly small value to a relatively large value as the surface becomes more completely covered.[20] Desorption occurs with great difficulty for molecules held on the surface in the activated state.

3. All the surface, whether internal or external, is easily accessible either by direct gaseous diffusion or by a very rapid surface migration of the van der Waals adsorbed carbon monoxide to the internal part of the surface.

On the basis of these assumptions the time required for the activated adsorption would be the rate controlling factor. The adsorption of the first carbon monoxide increment admitted to a bare chromic oxide surface would be in part van der Waals and in part activated depending upon whether the chance collisions of the carbon monoxide molecules with the surface brought them first into contact with points of low or high surface energy. But the molecules held by van der Waals forces would soon move to adjacent active points, with the net effect that the gas would disappear immediately from the gas phase and the time–temperature curve would show a quick rise in temperature giving a heat of 12 kcal. (Curve I, Fig. 4). After the initial increments had been added, the most active surface points would become covered so that there would be none left capable of immediate activated adsorption. As a result, the next increment added would be first adsorbed by van der Waals forces but these adsorbed molecules would then migrate rapidly on the surface to points capable of activated adsorption but requiring a finite activation energy so that this activated process would be slower. The time–temperature curve (Curve II, Fig. 4) would then be divided, with a quick rise corresponding to a rapid van der Waals adsorption of 4 kcal. of heat and the slow rise due to Process B, the activated adsorption, producing a heat of about 12 kcal. This activated adsorption process would of course become progressively slower as the degree of activity of remaining uncovered surface points became less and less. Finally, when all points capable of activated adsorption were covered, the slow Process B would be eliminated and only van der Waals adsorption would occur on the remaining surface, resulting in the normal type of curve (Curve III, Fig. 4) with a heat of 4 kcal. On the basis of this theory the experimentally determined activation energies for Process B, which ranged from 180 to 690 cal. for the interval 40–70 cc., would be the energies of activation of the activated adsorption.

On the other hand, we may arrive at an alternative explanation of Process B by changing assumptions 2 and 3 above as follows:

2. The activated adsorption requires a negligibly small activation energy on all parts of the surface, adsorption occurring immediately once a gas molecule comes into contact with an active surface point.

3. Only the external part of the surface is readily accessible to the gas,[21] a finite time being

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accounted for in that way. In addition to this the large variation in the heats of Process B with the three gases makes it very probable that it is not a van der Waals process.

(19) The absence of any slow Process B at −183° in the curves for hydrogen and deuterium seems, at first, to be anomalous, especially when we consider that there is evidence that the adsorption of these gases is activated in part at least. If we assume, however, that the activated adsorption for the isotopes of hydrogen requires an even smaller energy of activation than does that for carbon monoxide, nitrogen, or oxygen, we may predict that, at an even lower temperature, the rate of Process B might be sufficiently slow to differentiate it from Process A.

(20) The decreasing differential heats with successive increments (Fig. 5) indicate variable surface activity. At −183°, even small differences in the activity of the surface points, and consequently in the activation energies required for adsorption, would suffice to account for relatively large differences in the rates of adsorption on different portions of the surface. This is true because of the small value of T used in the exponential $\epsilon^{-E/RT}$.

(21) During the preparation of the adsorbent, the removal of water molecules from the hydrated chromic oxide gel must have produced a relatively large percentage of internal surface on the walls of cracks or capillaries penetrating the granules. The point at issue is whether these cracks or capillaries are of sufficient width so that the carbon monoxide molecules can reach their walls with ease or whether a considerable length of time might be required. In other words, is the internal surface "internal" to a carbon monoxide molecule?

required for the surface migration of carbon monoxide molecules, initially adsorbed on the external surface, down the faces of the cracks or capillaries into the internal surface of the chromic oxide.

We may then explain the time–temperature curves for partially covered surfaces (Curve II, Fig. 4) as indicating an initial van der Waals adsorption on the easily accessible external surface followed by a slow surface migration to the points located in the internal surface which are capable of activated adsorption. The decreasing rate of Process B with successive increments of gas added to the surface would then be attributed to the increasing periods of time required for the surface diffusion of the adsorbed molecules into the more and more difficultly accessible areas of the internal surface. In other words, the rate controlling factor would be an activated diffusion, and the experimental values 180 to 690 cal. would be the activation energies for this diffusion process.[22]

It is of course possible that both activated adsorption and activated diffusion have some influence on the rate of the slow process observed. Regardless of the mechanism,[23] the important point, which must be emphasized, is that we have definite evidence that there are two distinct types of adsorption on the same partially covered chromic oxide surface at −183°, and that the gas initially held by van der Waals forces changed over, *on the surface*, into the activated state.

The Effect of Temperature on the Adsorption.—In comparing the results at −183° with those at 0° using carbon monoxide, nitrogen, and oxygen, respectively, on the chromic oxide, it is apparent that the amount of each of these gases adsorbed is considerably less at the higher temperature. This is not surprising in the case of the carbon monoxide and that of the nitrogen because the adsorption of these gases is a reversible process, a large fraction of the gas adsorbed at −183° being desorbed when the temperature is raised to 0°. This would mean simply that certain surface points capable of holding carbon monoxide or nitrogen at −183° are no longer able to do so at 0°. The adsorption of oxygen, on the other hand, is irreversible, and oxygen once adsorbed in the activated state is removable only by reduction in a hydrogen atmosphere at about 400°. It is not easy to see, therefore, why the volume adsorbed at 0° should not be at least as great as that adsorbed at −183°. We suggest the possibility that pairs of oxygen atoms may be held in an activated state on each chromium atom of the surface at −183° but that single atoms of the oxygen are held on each chromium atom at 0°. This postulated difference in the nature of the adsorption complexes at the two temperatures would also account for the observed change in the heat of adsorption from 25 kcal. at −183° to 50 kcal. at 0°.[24] The marked difference in the heats of adsorption of nitrogen at the two temperatures seems to indicate that, with this gas also, there must be a great difference in the nature of the binding forces in operation at the two temperatures. In contrast with the data for oxygen and nitrogen, the heats of activated adsorption of carbon monoxide are very nearly the same at −183 and 0°, indicating that there is little difference in the nature of the binding at the two temperatures.

Anomalous Effect Caused by Interruption of a Series of Heat Measurements.—In the measurements with carbon monoxide at −183° the successive increments usually were admitted at intervals of approximately one hour. When the series was interrupted overnight, say for a period of fifteen hours, with the surface partially covered, the first time–temperature curve recorded the next morning was always anomalous in two respects: (1) the slow Process B was almost completely absent; and (2) the heat of the rapid Process A was measurably higher (about 0.2 kcal.) than that for the preceding increment, or of the next increment following after a one-hour period. In other words, when the adsorption had been carried to the stage at which the next time–temperature curve would be like Curve II in Fig. 4 if the series were not interrupted, the curve actually obtained after an overnight interruption was more nearly of the form of Curve III, Fig. 4, and the heat of Process A was 4.4 instead of 4.2 kcal. The second time–temperature curve recorded in the morning was free from these anomalous characteristics, giving a heat of 4.2 kcal. for Process A and having the slow rise in temperature indicating the recurrence of Process B. This anomalous behavior was always observed whenever a carbon monoxide series in the intermediate stage was interrupted overnight.

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[22] Lennard-Jones [*Trans. Faraday Soc.*, **28**, 333 (1932)] has calculated an activation energy of this order of magnitude for the surface diffusion of argon on potassium chloride at −183°.

[23] In this discussion we have assumed that the van der Waals and activated adsorption occur exclusively on different surface points. It is possible, however, that the *same* points may be capable of both types of adsorption, and this possibility already has been suggested by Lennard-Jones.[22] On the latter assumption, Process B might represent the change of a molecule, held to a given point by van der Waals forces, over into the activated state on the *same* point. There is nothing in our observations to justify the elimination of this possibility which would, of course, be unfavorable to the theory of activated diffusion as the rate controlling factor in Process B.

[24] This high heat of reaction at 0° is of the same order of magnitude as the heat of the stoichiometric reaction between oxygen and chromic oxide to form chromium trioxide (36.2 kcal. per mole of oxygen). It seems probable, therefore, that the surface reaction is somewhat similar to the stoichiometric one in this case.

The same was always true for the oxygen and nitrogen adsorption experiments.

We believe this anomaly can be explained as follows. Suppose there are surface points on which the carbon monoxide molecules are held by forces of the van der Waals type, but with a binding energy slightly greater than the average van der Waals binding, and suppose that as a result of this greater binding force a considerable time is required for the desorption of molecules from these points, which we shall call X-points. These X-points would become covered in the early increments and owing to the greater difficulty of desorption they would then remain covered during the admission of later increments at the stage represented by Curve II, Fig. 4, so long as the series of measurements was continued without interruption. On the other hand, upon standing overnight, the X-points would be left vacant by the slow process of desorption, the desorbed molecules being subsequently adsorbed on points capable of activated adsorption. The first increment admitted in the morning would then be adsorbed on the X-points, with a heat of 4.4 kcal., which is 0.2 kcal. in excess of the normal 4.2 kcal. Moreover, because of the difficulty of desorption from the X-points, Process B, resulting from a shift over to the state of activated adsorption, would be practically eliminated. However, for the next increment following after the normal one-hour interval, with the X-points covered, the normal heat of 4.2 kcal. would be obtained and the normal rate of Process B would be observed.

Conclusion.—We wish to emphasize the novel application of the calorimetric method in the present investigation. Using charcoal at 20° as an adsorbent, Lendle[25] has measured the heat evolved during the slow activated adsorption on charcoal of oxygen *from the gas phase*, a process which could also be followed by observing the slow disappearance of unadsorbed gas. Barry and Barrett[26] have made a similar calorimetric study in the case of the adsorption of water vapor on gold. In the experiments with carbon monoxide on chromic oxide at −183°, there was no residual unadsorbed gas after the first minute, and the slow evolution of heat could be attributed only to a change *on the surface* from the van der Waals to the activated state.[27] Because all the gas disappeared almost instantaneously, the calorimetric method offered the only means of observing the presence of the slow process. It will be interesting to find out how general is this activated adsorption via an initial van der Waals process. Calorimetric work at −183° now in progress in this Laboratory shows that the adsorption of oxygen on iron synthetic ammonia catalyst follows the same complex mechanism, the time–temperature curves being of the same general form as Curve II, Fig. 7. The details of this work will be published at a later date.

Summary

1. The heats of adsorption of argon, hydrogen, deuterium, carbon monoxide, nitrogen, and oxygen, on reduced chromic oxide, have been determined calorimetrically in the low temperature region.

2. The magnitude of the heats indicates that all these gases except argon are adsorbed in part in the activated state even at −183°.

3. The form of the time–temperature curves on a partially covered surface at −183° indicates that with carbon monoxide, nitrogen, and oxygen the adsorption is complex, the gases initially adsorbed in the van der Waals state undergoing a slow change on the surface over into a state of activated adsorption.

4. From the heat measurements with carbon monoxide at −183 and −195° the activation energy of the above slow surface change has been estimated at 180 to 690 cal./mole. It is suggested that the rate controlling process in this slow change may be (1) a slow activated adsorption, or (2) a slow surface diffusion.

5. The effects of carbon monoxide on the heat of oxygen adsorption and of oxygen on the heat of carbon monoxide adsorption have been investigated experimentally.

6. The heats of adsorption of carbon monoxide, nitrogen, and oxygen have been measured at 0° as well as at −183°, and the results at the two temperatures have been compared.

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(25) Lendle, *Z. physik. Chem.*, **172A**, 77 (1935).

(26) Barry and Barrett, THIS JOURNAL, **55**, 3088 (1933).

(27) In accounting for certain anomalies observed in their study of the effect of pressure on the rate of adsorption of hydrogen on chromic oxide at about 200°, Burwell and Taylor [THIS JOURNAL, **58**, 697 (1936)] were led to postulate a similar mechanism, "the slow process being a reaction between surface atoms which receive the necessary activation energy and hydrogen molecules adsorbed by van der Waals forces."