357. *The Heat of Adsorption of Gases on Zinc Oxide and* $ZnO–Cr_2O_3$ *at Low Pressures and Room Temperatures.*

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THE heats of adsorption of hydrogen and carbon monoxide on oxide catalysts at liquid-air temperatures are of the same order as those obtained when gases are adsorbed on mica or rock-salt (*viz.*, 0·5—2 kg.-cals./mol.); but at higher temperatures, whether directly measured or calculated from the adsorption isobars, they are 10—20 times larger. For instance, Taylor and Sickman (*J. Amer. Chem. Soc.*, 1932, **54**, 602) found for hydrogen on zinc oxide, at low temperatures, 1·1 kg.-cals., and at 450° K, 21 kg.-cals. per mol. As far as can be gathered from the experimental data, the adsorbed gases in both types can be recovered unchanged on evacuation. The two types are quite distinct, as is shown by their separation by minima on the adsorption isobars obtained by H. S. Taylor and his co-workers (see also Benton, *Trans. Faraday Soc.*, 1932, **28**, 209). Taylor has called the second type of adsorption " activated," because it takes place at rates which vary with temperature, and from these rates he calculates the energy of activation of the adsorption process. However, the adsorbents are porous, and time will be required for the passage of the gas through fine capillaries or for its solution in the crystalline lattice (Ward, *ibid.*, p. 399), and the activation energy measured could be that of the surface flow down the capillaries (Lennard-Jones, *ibid.*, p. 333). In experiments where slow adsorption processes have been investigated, such as those of hydrogen on copper (Ward, *Proc. Roy. Soc.*, 1931, **133**, *A*, 522), of hydrogen chloride on rock-salt (Bradley, *Trans. Faraday Soc.*, 1934, **30**, 587), and of sulphur dioxide on cellulose (Wheeler, unpublished), the data obtained are in good agreement with the theory that the rate-determining factor is that of capillary flow. There is but little evidence in favour of the view that the slow rate of the second type of adsorption is due to the *activation energy of the adsorption process.*

The use of the term " activated " for the second type of adsorption is open to criticism; for, first, there has been no proof that it possesses an activation energy, and secondly, it directs attention to an attribute which is not specific to this type of adsorption alone but is an essential feature of chemisorption. If its only distinctive feature is that it possesses an activation energy, then the older term, chemisorption, is to be preferred. If, on the other hand, there is a fundamental difference between it and chemisorption, then the term " activated " adsorption is still unsatisfactory since it does not indicate what is the essential difference between the two types.

In addition, there is a third type which is irreversible. One of us and Kingman (*Trans. Faraday Soc.*, 1931, **27**, 322) showed that when hydrogen or carbon monoxide is adsorbed on $ZnO–Cr_2O_3$ at room temperature (heat of adsorption, 20 kg.-cals.), the gas could be recovered unchanged on raising the temperature, whereas at 200° it was again adsorbed but this time irreversibly. The catalyst had not been specially reduced with hydrogen at high temperatures, and Taylor suggested (*Trans. Faraday Soc.*, 1932, **28**, 433) that the readsorption was due to the presence on the surface of oxygen, which entered into reaction with the hydrogen. Any oxygen present must have been there in chemical combination with the surface ($Q =$ 43 kg.-cals.), and it is therefore probable that the irreversible adsorption is due to a chemical change between the hydrogen or carbon monoxide and a higher oxide of chromium, the product of which is not decomposed below 300—400°. Kistiakowski and Flosdorf (*J. Physical Chem.*, 1930, **34**, 1907) observed that the freshly prepared mixed oxide gives a heat of adsorption of hydrogen of 60 kg.-cals., and noted that the hydrogen could not be recovered as such on evacuation but was evolved as water at high temperatures, whereas on the reduced catalyst the heat was much smaller and the hydrogen could be recovered unchanged. There is thus little doubt as to the existence of the third type of adsorption.

In the present investigation, measurements have been made of the heats of adsorption of a number of gases on zinc oxide and $ZnO–Cr_2O_3$, with a view to elucidate the nature of the adsorption processes occurring on these catalysts. The principal object has been to survey the whole field, and not to study any particular aspect in great detail.

EXPERIMENTAL.

The Adsorption of Hydrogen on ZnO–Cr$_2$O$_3$ *at Room Temperatures.*—Kistiakowski and Flosdorf's experiments, which showed that the oxidised and the reduced catalyst behave differently towards hydrogen, have been confirmed, although the heats of adsorption now found are lower than theirs.

The mixed oxide, prepared as described by Taylor and Sherman (*Trans. Faraday Soc.*, 1932, **28**, 249), was reduced at 400° until no more hydrogen was taken up. It was then activated at 460° for 3 hrs. in a high vacuum, this temperature being chosen because lower temperatures give a much less adsorptive product. The oxide was dark green, in marked contrast with that used in earlier work (*loc. cit.*), which was white or slightly purple. Hertel and Holt (*Z. physikal. Chem.*, 1935, *B*, **28**, 393) showed that basic zinc chromate on being heated above 400° is converted into an oxide which gives the X-ray diagrams of a spinel, ZnCr$_2$O$_4$, and zinc oxide, and that the last could be extracted with dilute hydrochloric acid. Analysis shows that the oxide used in our experiments (Found : ZnO, 47·5; Cr$_2$O$_3$, 48·9%) contained an excess of zinc oxide over that expected if ZnCr$_2$O$_4$ were the sole constituent.

The adsorption of hydrogen on the mixed oxide is slow but is nearly completed within an hour. The heats were measured in calorimeter 1e (see preceding paper) by adding successive quantities of hydrogen to the catalyst at 2-hour intervals without evacuation or baking-out

FIG. 1.
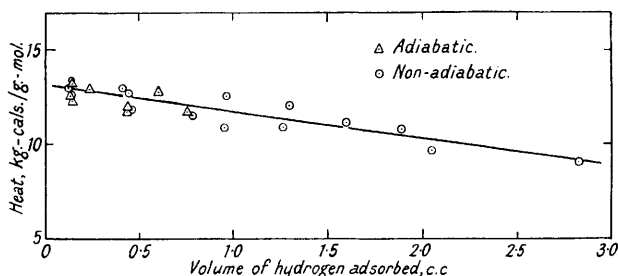
between the admissions of the gas. The results for any series always showed a slight downward drift as the surface became covered with hydrogen. A typical series is shown in Table I. Between Expts. 4 and 5, the oxide was left over-night.

TABLE I.

Weight of ZnO–Cr$_2$O$_3$, 14·8 g. Temp. of thermostat, 17°.

Expt. No.	Vol. of H$_2$, c.c. at *N.T.P.*		Press. at 5 mins. (cm. × 10^{-3}).	Total vol. adsorbed at 5 mins. (c.c. at *N.T.P.*).	Heat of adsorption (kg.-cals./mol.).
	admitted.	adsorbed after 5 mins.			
1	0·324	0·289	4·68	0·289	12·3
2	0·336	0·239	12·97	0·561	11·9
3	0·337	0·201	19·84	0·852	11·7
4	0·361	—	27·08	—	—
5	0·349	0·178	22·60	1·38	12·0
6	0·364	0·135	33·52	1·66	11·2
7	1·80	0·42	189·7	2·26	9·7

The experimental results for all the series are collected in Fig. 1, and the fluctuations observed are probably due to variation in the conditions of the baking-out, for a difference of 1° or 2° in the neighbourhood of 460° affects the activity of the catalyst appreciably. Adiabatic and non-adiabatic measurements gave the same heats within the experimental error. The pressures above the catalyst after 5 mins. exceed 5 × 10^{-3} cm., so that there can be only a negligible temperature gradient across the adsorbent, and hence the thermocouple records the average temperature of the adsorbent in all cases. The downward drift is therefore not due to a progressive decline of the inequalities of temperature. The cooling correction amounts to only 3—5%, so there is little chance of error on account of corrections for heat loss. Consequently, the downward drift in the values is probably real. The break in the drift between Expts. 3 and 4 is due to diffusion of the adsorbed gas into the grains over-night : this is a very common effect on porous adsorbents.

Part of the hydrogen adsorbed on the reduced oxide can be rapidly removed on evacuation at room temperature, but temperatures above 100° are required to remove most of it. When 0·26 c.c. is adsorbed, the total heat of desorption is only one-seventh of the heat of adsorption, and one-third when 1·2 c.c. are adsorbed. This indicates that the adsorption on the reduced surface is composite in character.

After the above series, the oxide was evacuated at 400° to remove adsorbed hydrogen, and then oxidised at the same temperature, 120 c.c. of oxygen being taken up. It was then activated at 460° for 3 hours; 0·28 c.c. of hydrogen was admitted, and the heat of adsorption measured. In four experiments, $Q = 49·7$, 46·7, 48·1, and 47·5 kg.-cals./mol. The adsorption was slow, and the amount of gas adsorbed after 5 minutes was small, $\sim 0·06$ c.c. The heat of desorption at room temperature is about one-eighth of the heat of adsorption, and the remainder cannot be desorbed below 200°. Therefore, the true heat of adsorption of the irreversible process may be very high, ~ 90 kg.-cals. The heats were independent of the time, and the gas pressures were high enough to maintain a uniform temperature across the adsorbent. A second admission gave 13 kg.-cals. after 0·16 c.c. had been adsorbed, indicating some reduction of the surface by the adsorbed gas. The two types of adsorption are obviously difficult to separate in the case of the adsorption of hydrogen on ZnO–Cr$_2$O$_3$.

The catalyst was now progressively reduced, and heats were measured at various stages during the reduction. Hydrogen was admitted in known amounts to the cold oxide, and the temperature gradually raised to 400°. This procedure ensured that the oxide was uniformly reduced. The oxide was activated as before in a vacuum for 2 hours at 460°, and in each experiment in the series, 0·27—0·28 c.c. of gas was admitted. Fig. 2 shows the heats of adsorption and the quantity of gas adsorbed after 5 mins. plotted against the amount of hydrogen used in the reduction of the catalyst. The adsorption at room temperatures was always very small compared with the quantities of hydrogen used in the reduction. The ratio of the area of adsorption to that of the reducible surface is 1 : 4000 for the oxidised surface, falling to about 1 : 100 for the reduced surface. From Fig. 2 it will be seen that the amount adsorbed decreases to a flat minimum before increasing,* and the heat of adsorption falls very slowly from 48 to 13 kg.-cals. The amount of gas adsorbed on the oxidised centres can be calculated from these curves. On the assumption that there are only two types of adsorption centres with heats of 48 and 13 kg.-cals. respectively, the following values are obtained :

FIG. 2.

| Vol. H$_2$ used in reduction (c.c.)	0	10	30	50	70	80	90	100	110	120	130	140
C.c. $\times$ 10^2 on oxidised centres	6·0	5·6	5·7	5·8	5·3	4·7	3·7	3·0	2·0	1·1	0·3	0·0

The oxidised centres are not appreciably diminished in number until one-half of the surface is reduced, indicating that these centres are situated at an interface between the oxidised and the reduced areas.

The Adsorption of Carbon Monoxide on ZnO–Cr$_2$O$_3$.—The adsorption of carbon monoxide was not studied in the same detail as that of hydrogen, only sufficient work being done to obtain a general idea of the behaviour of the gas. As with hydrogen, the oxide was reduced at 400° until no more hydrogen was used, and then activated at 460° for 3 hours. Calorimeter 1e was employed. Table II gives the heats for successive admissions, there being an interval of 2 hours between the experiments except between Expts. 5 and 6, where 24 hours elapsed.

When 0·74 c.c. was adsorbed, the heat of desorption was about 20% of the heat of adsorption, showing that here also the adsorption was composite in character.

The heats are of the same order as those obtained with hydrogen, and fall off with successive

* Very similar curves were found by Kingman (*Trans. Faraday Soc.,* 1931, **27**, 654).
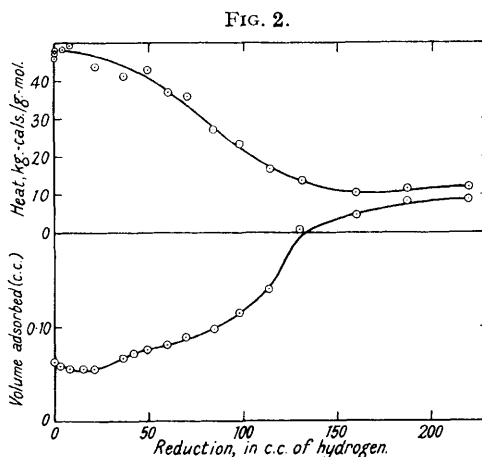
additions of gas in much the same way. They show but little drift during a single experiment, as is usually the case when the heat is but slightly dependent on the area covered.

TABLE II.

Adsorption of carbon monoxide on reduced $ZnO–Cr_2O_3$ at 18°.

Expt. No.	Vol. of CO, c.c. at *N.T.P.*		Press. at 5 mins. (cm. $\times$ 10^{-3}).	Total vol. adsorbed at 5 mins. (c.c. at *N.T.P.*).	Heat of adsorption (kg.-cals./mol.).
	admitted.	adsorbed after 5 mins.			
1	0·282	0·257	3·33	0·257	14·9
2	0·284	0·218	9·71	0·492	12·0
3	0·279	0·183	17·1	0·714	—
4	0·268	0·161	26·5	0·911	10·9
5	0·277	0·153	37·2	1·11	10·7
6	0·280	0·146	33·3	1·42	12·3

Carbon monoxide is very strongly adsorbed on the oxidised catalyst, and the rate of adsorption is more rapid than in the cases previously discussed. In consequence, the gas pressure in the first admission falls below that allowable for accurate working of the calorimeter and thus the first value in Table III may be somewhat high. The heat of adsorption falls off from 44 to 16 kg.-cals. as the surface becomes covered with carbon monoxide, and this is due to a reduction of the surface by the first quantities of adsorbed gas and a subsequent adsorption on reduced centres (see below). On account of this fall, the heats of adsorption increase with time (cols. 6 and 7), owing to the diffusion of the gas into the interior of the grains, which leaves the external surface in a more active state. This is borne out by the effect of leaving the surface over-night between Expts. 5 and 6 : it will be seen from col. 4 that the rate of adsorption in Expt. 6 is greater than in Expt. 5.

TABLE III.

Adsorption of carbon monoxide on oxidised $ZnO–Cr_2O_3$ at 18°.

Expt. No.	Vol. of CO, c.c. at *N.T.P.*		Press. at 5 mins. (cm. $\times$ 10^{-3}).	Total vol. adsorbed after 5 mins. (c.c. at *N.T.P.*).	Heat of adsorption (kg.-cals./mol.).	
	admitted.	adsorbed in 5 mins.			5 mins.	10 mins.
1	0·271	0·260	1·40	0·260	40·4	44·0
2	0·273	0·232	5·39	0·502	30·5	36·6
3	0·272	0·210	8·19	0·753	24·3	28·4
4	0·269	0·196	10·1	1·01	20·7	23·9
5	0·264	0·182	12·0	1·26	17·7	20·1
6	0·270	0·218	6·87	1·57	29·4	33·2
7	0·275	0·200	11·2	1·81	19·4	22·0
8	0·273	0·183	14·8	2·06	16·6	18·6
9	0·268	0·168	18·3	2·30	14·9	16·0

The heat of desorption when 1·42 c.c. had been adsorbed was 27% of the heat of adsorption, indicating that the heat of the irreversible adsorption is $\sim$ 40 kg.-cals., which is practically that of the first admission.

Adsorption of Oxygen on $ZnO–Cr_2O_3$.—Oxygen is not appreciably adsorbed on the surface oxidised at 400°. When 0·28 c.c. is admitted, only 4—7% of the gas is adsorbed, and the heat of adsorption is less than 2 kg.-cals., so the adsorption may be of the van der Waals type. On the reduced surface, large amounts of oxygen are adsorbed, and the adsorption is so rapid that a poor distribution of the gas on the catalyst is obtained. The differential heats cannot be measured in calorimeter 1e, and attempts made to measure these quantities are described in the preceding paper (p. 1436). The total heat obtained by adsorbing sufficient gas to saturate the oxide at room temperature, *viz.*, 8—9 c.c., was 42·9 and 42·8 kg.-cals./mol. in two experiments. This value is much too low for the heat of formation of zinc oxide, and much too high for that of chromium trioxide from the sesquioxide.

Since no appreciable amounts of oxygen were adsorbed on the oxidised catalyst, it was possible to use this gas to discover if the adsorption of carbon monoxide or hydrogen on this surface led to any reduction of the catalyst. The introduction of carbon monoxide and oxygen together in the ratio 1 : 1 led to the disappearance of the whole of the carbon monoxide and practically one-half of the oxygen, whilst a 2 : 1 mixture was completely adsorbed within a short time (see following table). The heats of adsorption increased with time, as with carbon mon-

oxide alone. The heats are given after the tenth minute and are comparable with those in Table III. They are expressed in terms of g.-mols. of carbon monoxide.

Adsorption of carbon monoxide and oxygen on oxidised ZnO–Cr$_2$O$_3$.

Expt. No.	CO : O by vol.	Total vol. of gas admitted (c.c. at *N.T.P.*).	O$_2$ taken up, %.	Heat after 10 mins. (kg.-cals./mol.).
1	1 : 1	0·264	48·5	62·4
2		0·264	48·2	57·3
3		0·266	47·5	53·1
4		0·388	45·6	54·5
5		0·530	46·0	—
1	2 : 1	0·268	100	66·3

The heat of adsorption of oxygen on the oxidised surface in the presence of carbon monoxide is of the order 40—50 kg.-cals., which is the same as that of oxygen on the reduced surface.

In the adsorption of hydrogen and oxygen on ZnO–Cr$_2$O$_3$, the results were not so definite. When 0·28 c.c. of hydrogen and oxygen in the ratio 2 : 1 was introduced to the oxidised catalyst, there was an additional adsorption of only 14—15%. This is, however, sufficient to show that hydrogen also reduces the surface of the oxidised catalyst. When 0·28 c.c. of ethylene and oxygen in the ratio 1 : 1 was admitted, there was an excess of 11% adsorbed on the oxidised catalyst, so the same effect occurs also with this mixture.

Adsorption of Carbon Dioxide on ZnO–Cr$_2$O$_3$.—In view of the joint action of carbon monoxide and oxygen on the oxidised surface, it was of interest to measure the heat of adsorption of carbon dioxide. This gas was strongly adsorbed, giving a constant heat in 4—5 mins., and in accord with this, the heat did not fall off very rapidly as the surface was covered. The first heat may be a little high.

Adsorption of carbon dioxide on oxidised ZnO–Cr$_2$O$_3$ *at* 18°.

Expt. No.	Vol. of CO$_2$, c.c. at *N.T.P.* admitted.	adsorbed after 5 mins.	Press. at 5 mins. (cm. × 10⁻³).	Total vol. adsorbed after 5 mins. (c.c. at *N.T.P.*).	Heat of adsorption (kg.-cals./mol.).
1	0·269	0·264	0·64	0·264	15·0
2	0·481	0·415	8·45	0·685	13·3

The heat of adsorption of carbon dioxide on the reduced was of the same order as on the oxidised catalyst. It was constant after the seventh minute. The heats of adsorption for successive admissions were 17·7, 16·1, 16·3, 15·5, 15·7 kg.-cals./mol. Since none of the gas can be desorbed at room temperature, the formation of a carbonate on a lower oxide is indicated.

Adsorption of Hydrocarbons on ZnO–Cr$_2$O$_3$.—The heats of adsorption of ethylene on both the oxidised and the reduced catalyst did not vary with time. On the former there was a rapid adsorption, and 0·24 c.c. was completely adsorbed in 8 mins., and $Q = 19·9$, 14·5, 13·4, and 12 for four successive admissions. For the reduced catalyst, the heat was lower : in successive admissions $Q = 11·3$, 9·6, 9·6 kg.-cals. When 0·63 c.c. is adsorbed, the heat of desorption is 50% of that of adsorption. Taylor and Howard (*J. Amer. Chem. Soc.*, 1934, **56**, 2259) have found that ethylene can be adsorbed by chromium oxide reversibly at room temperature.

Ethane is adsorbed on both surfaces ; on the reduced surface only slightly, 0·026 out of 0·275 c.c. giving 6·4 kg.-cals./mol., and on the oxidised surface there was a very slow adsorption : 0·0382, 0·0446, 0·0518, 0·0566, 0·0614 c.c. after 2, 5, 8, 11, and 14 mins. respectively, which gave 21·5 kg.-cals. at 5 mins. and 28·7 kg.-cals. at 10 mins. On the reduced surface the adsorption is completely reversible.

Methane was slightly adsorbed on the oxidised catalyst, 0·0056 c.c. instantaneously from 0·23 c.c. The heat was very small, and hence the adsorption was probably of the van der Waals type.

The Adsorption of Gases on Zinc Oxide.—*Hydrogen.* Experiments were made with zinc oxide, to determine if adsorption thereon was responsible for any of the phenomena encountered in the case of the mixed oxide. It was important to know whether (1) the oxidised and reduced surfaces of zinc oxide behaved similarly to those of the mixed oxide, and (2) if the oxidised surface could be reduced with carbon monoxide at room temperature.

The zinc oxide was that previously employed by Garner and Kingman (*loc. cit.*). It had not been subjected to a higher temperature than 460° ; and it did not adsorb appreciable quantities of hydrogen from the gas at 0·1 cm. pressure and room temperature, in agreement with earlier

work on the oxide (*loc. cit.*). At 400°, hydrogen disappeared at the rate of 3 c.c./hr., but the product after activation at 460° did not adsorb appreciable quantities of oxygen either at room temperature or at 400°. The product of reduction at 400° must have volatilised away at 460°. It was thus not possible to oxidise and reduce the catalyst in the manner previously adopted for $ZnO-Cr_2O_3$. Calorimeter 1f was employed in this series.

Carbon monoxide. The adsorption is practically instantaneous, with no appreciable creep of gas into the grains of oxide. It is thus mainly confined to the outer surface, and this causes the instrumental effects described in the preceding paper. The heats of adsorption decrease with time in an unusual manner, not becoming constant until the tenth minute, whereas the heats of desorption behave normally (see table). The desorption was carried out with the pumps full on, and after desorption at room temperature there was no gas liberated at higher temperatures. The experiments were repeated many times and were reproducible.

Adsorption of carbon monoxide on zinc oxide (oxidised).

Weight of ZnO, 5·98 g.

Admission.	Press. $\times 10^3$. (cm.).	Vol. adsorbed (c.c.).	Heat of adsorption (kg.-cals.) at (minutes).			
			2.	5.	8.	10.
1	20·3	0·126	20·0	18·8	18·3	18·2
2	75·8	0·230	13·8	13·0	12·7	12·3
Desorption			15·6	16·1	16·2	16·2
Reduced surface			25·8	22·1	20·6	

The heat of desorption calculated on the total adsorbed gas is a little higher than the total heat of adsorption (15·4 kg.-cals. at 10 mins.). In another experiment, the heats of adsorption and desorption were the same, *viz.*, 14·4 kg.-cals. The agreement between the two heats shows that the adsorption is reversible and that carbon monoxide is desorbed. It is suggested that the fall in the heat of adsorption with time is due to a poor grain conductivity due to the absence of gas in the capillaries.

The heat of adsorption on the reduced surface, *viz.*, 20·6 kg.-cals. after 8 mins., is a little higher than on the oxidised surface, in marked contrast with $ZnO-Cr_2O_3$. Oxygen is not appreciably adsorbed on the oxidised catalyst in the presence of carbon monoxide, for when 0·335 c.c. of a 2 : 1 mixture is admitted, only 0·006 c.c. of oxygen is adsorbed. This shows that the phenomena reported in the previous section are not due to the presence of zinc oxide in the catalyst.

Ethylene (on oxidised surface). The heat of adsorption in this case did not fall off with time, as with carbon monoxide, on account of an improvement of the grain conductivity due to a creep of the gas into the grains. The amounts of ethylene adsorbed were higher than for carbon monoxide, and when 0·275 c.c. was admitted, 0·258 c.c. was adsorbed in 2 mins. and 0·267 c.c. in 5 mins. The whole of the gas is not desorbed at room temperature, a portion requiring evacuation at a higher temperature. With 0·83 c.c. of ethylene adsorbed, the heat of desorption was 40% of that of adsorption.

Admission.	Press. $\times 10^3$ in 5 mins. (cm.).	Vol. adsorbed (c.c.).	Heat of adsorption (kg.-cals.) at 5 mins.
1	1·09	0·267	25·2
2	4·58	0·517	21·3
3	17·0	0·702	19·1

Oxygen is not adsorbed from a 2 : 1 mixture of ethylene and oxygen, and ethane is not appreciably adsorbed.

Carbon dioxide (on oxidised surface). Instantaneous adsorption occurred with no subsequent creep, and the heat of adsorption fell off with time. The heat is of the same order as that of the heat of formation of zinc carbonate, *viz.*, 12 kg.-cals.

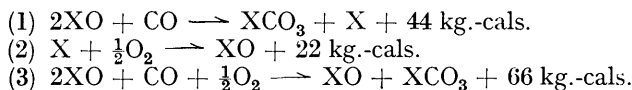| Admission.	Press. $\times 10^3$ (cm.).	Vol. adsorbed (c.c.).	Heat of adsorption (kg.-cals.) at (minutes).			
			2.	5.	8.	11.
1	23·5	0·055	15·5	13·4	13·1	12·7
2	80·8	0·135	10·9	9·7	9·4	9·4

The heat of desorption for Expt. 1 gave 13·0 kg.-cals., in agreement with the heat of adsorption, and in another experiment a heat of desorption of 12·7 kg.-cals. was obtained. The adsorption of carbon dioxide on zinc oxide is thus reversible, in strong contrast with the adsorption on $ZnO-Cr_2O_3$, where it is irreversible.

The agreement within 1 kg.-cal. between the heats of adsorption and desorption of carbon dioxide on zinc oxide confirms the view put forward in the first paper (p. 1436), *viz.*, that even with a hard vacuum inside the calorimeter, the error due to temperature gradients is not large provided the gas be well distributed throughout the oxide. On account of variations in the heat with surface covered, it is not worth while attempting a greater accuracy.

Some preliminary work with chromium sesquioxide has shown that this substance can be oxidised and reduced, and that carbon monoxide when adsorbed on it reduces the surface in the same way as was found with $ZnO-Cr_2O_3$.

CONCLUSIONS.

The experiments have established the fact that hydrogen and carbon monoxide are adsorbed by $ZnO-Cr_2O_3$ at room temperatures in two ways. On the oxidised surface, the gases are adsorbed irreversibly with heats of approximately 45 kg.-cals., whilst on the reduced surfaces they are adsorbed reversibly with heats 10—15 kg.-cals./g.-mol. The magnitude of the heats of adsorption on the oxidised catalyst is affected by the reduction of the surface during the adsorption process and by the subsequent adsorption of gas on the reduced areas. The reduction of the surface has been demonstrated by experiments on the adsorption of mixtures of oxygen with either hydrogen or carbon monoxide. The processes which occur in the adsorption of carbon monoxide on oxidised $ZnO-Cr_2O_3$ can be represented by the equations

(1) $2XO + CO \longrightarrow XCO_3 + X + 44$ kg.-cals.
(2) $X + \frac{1}{2}O_2 \longrightarrow XO + 22$ kg.-cals.
(3) $2XO + CO + \frac{1}{2}O_2 \longrightarrow XO + XCO_3 + 66$ kg.-cals.

All of these heats are experimental values, but the close agreement obtained is probably accidental. One consequence of this reduction of the surface is that the heats of adsorption on the oxidised surface fall off as the surface becomes covered. The fall of the differential heat from 45—50 kg.-cals. down to that for the reduced surface was well established in the case of hydrogen and carbon monoxide on $ZnO-Cr_2O_3$.

The fall in the differential heats as the surface becomes covered with gas is not, however, limited to the oxidised surfaces, but occurs also on the reduced surfaces, although in these cases the effect is not so marked. For hydrogen on metals (cf. Maxted and Lewis, *J.*, 1933, 502) the differential heat has been found to be independent of the surface covered, but Beebe and Wildner (*J. Amer. Chem. Soc.*, 1934, **56**, 642), using carbon monoxide on copper, obtained a very similar curve to that given in Fig. 1. In the case of the oxides, there is no doubt as to the variability of the activity of the adsorption centres.

In general, the gases diffuse into fine capillaries in the interior of the grains, and this is often a very slow process which continues for many hours before equilibrium is established between the external and internal surfaces. Consequently, for a given total adsorption, the degree of saturation of the external surface varies with the time. On this account, it may happen that the differential heats depend on the time interval between successive admissions of gas. Where the differential heat is only slightly dependent on the area covered, this effect is little in evidence (Tables I and II), but where the variation in the differential heats is large, the time interval plays an important part (Table III). Another consequence of the diffusion into the fine capillaries of the adsorbent is that the heat of adsorption may increase with the time, adsorption first occurring on less active centres on the exterior of the grains and then by surface flow passing to more active centres in the interior. These effects reduce the accuracy with which the heat measurements can be made, and limit the usefulness of this method of investigating heterogeneous catalysis.

Chemisorption undoubtedly occurs in the interaction of carbon monoxide and hydrogen with oxidised $ZnO-Cr_2O_3$, since the products of desorption are mainly water and carbon dioxide respectively. Also, it must be concluded that the adsorption of oxygen on reduced $ZnO-Cr_2O_3$ is chemisorption, but there are other more doubtful cases. At room temperatures, carbon dioxide is adsorbed on $ZnO-Cr_2O_3$ irreversibly and on zinc oxide reversibly. The heats of adsorption in both cases are practically the same, *viz.*, 12—15 kg.-cals., and it does not seem possible to distinguish between them merely on account of the difference in

reversibility. The adsorption of carbon dioxide on zinc oxide is very probably a case of reversible chemisorption. There is also a class which is of particular interest from the point of view of heterogeneous catalysis, *viz.*, the adsorption of the gases on the reduced catalysts, for which the heats range between 10 and 25 kg.-cals.

The fact that the heats for hydrogen, carbon monoxide, and ethylene are nearly the same for any one reduced surface and different for different surfaces may be of significance (Table IV). If the gases are held in capillaries or re-entrant angles between positively and negatively charged ions, the heats of adsorption would be much higher than on a plane surface and would depend on the diameters of the surface ions, the diameters of the molecules of absorbent, and on their polarisabilities. Since the diameters and the polarisabilities of the three molecules increase in the order hydrogen, carbon monoxide, ethylene, the effects on the heat of adsorption, due to these properties, will to some extent balance out, so that the equality of the heats of adsorption is not very surprising. It is, however, difficult to account for heats of the order of 20—25 kg.-cals. on this basis.

TABLE IV.

Heats of Adsorption (kg.-cals.).

	ZnO–Cr_2O_3.				ZnO–Cr_2O_3.		
Gas.	Oxidised.	Reduced.	ZnO.	Gas.	Oxidised.	Reduced.	ZnO.
H_2	48 ⇀ 13	13 ⇀ 10	(21) *	C_2H_6	22 ⇀ 29	6·4	—
CO	44 ⇀ 16	15 ⇀ 11	18 ⇀ 12	CO_2	15 ⇀ 13	18 ⇀ 16	13 ⇀ 9
C_2H_4	20 ⇀ 17	11 ⇀ 10	25 ⇀ 19	O_2	—	42·9	—

* H. S. Taylor (calculated from isobars).

Chemisorption is not ruled out as an explanation of the adsorption on reduced catalysts. The behaviour of carbon monoxide on the oxidised surface of ZnO–Cr_2O_3 gives a clue to a possible mechanism. In this case, the first stage in the adsorption can be represented by (*a*), where the carbon monoxide is held to oxygen atoms by subsidiary valencies, and (*b*) shows the final stage where a carbonate ion has been produced.
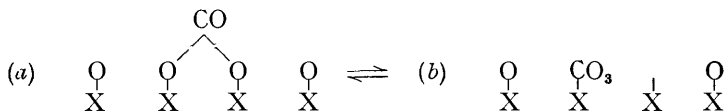
If an equilibrium is established between (*a*) and (*b*), then it is clear that either carbon monoxide or dioxide may be desorbed, depending on the magnitude of the activation energies for the two dissociation processes and on the rate of conversion of (*a*) into (*b*) and *vice versa*. The fact that gaseous equilibria between carbon monoxide and dioxide are established in contact with oxide surfaces lends support to the idea. In the case of the oxidised surfaces which we have studied, the conditions are favourable for the desorption of carbon dioxide, but it is possible that the same mechanism operating on the reduced surfaces might lead to the desorption of carbon monoxide. According to this view, the high heats of adsorption on the reduced catalysts are due to chemisorption.

The heats of adsorption on the oxidised catalysts are too high for it to be possible to desorb the gases at room temperature. The rate of desorption will be given by an equation of the general type $r = \nu e^{-(E + Q)/RT}$, where Q is the heat of adsorption, E the activation energy of the adsorption process, and ν the rate at which $Q + E$ can be supplied by the surface, which is unlikely to exceed 10^{13}. It can be calculated that the maximum value of $Q + E$ for which desorption should be complete within a few minutes at room temperature is of the order of 20 kg.-cals. Desorption is possible in the majority of the cases of the adsorption of gases on the reduced catalysts. For carbon monoxide on zinc oxide, $Q_{max.} = 18$ kg.-cals., and desorption is complete within a few minutes; E in this case must be very small. Ethylene on zinc oxide cannot be completely desorbed, in agreement with the high heat of adsorption ($Q = 25$—19 kg.-cals.). The heats on ZnO–Cr_2O_3 are lower than on zinc oxide, and it would be expected that the gases should be more easily desorbed from the former than from the latter. The reverse is actually true, so there is evidently some

factor present in the case of $ZnO-Cr_2O_3$ which is not operative for zinc oxide. This might be the existence of an activation energy for the adsorption process. It was observed, however, that in all cases where there is penetration of the capillaries of the absorbent, desorption could not be readily completed at room temperature, so the factor in question is that of the removal of gas from capillaries. A slow rate of desorption cannot be taken as proof that the adsorption processes possess activation energies.

SUMMARY.

Heats of adsorption have been measured for a number of gases on zinc oxide and $ZnO-Cr_2O_3$ in the oxidised and in the reduced state. The heats decrease as the surfaces become covered with gas, particularly in the case of the oxidised surfaces. The adsorption of carbon monoxide and hydrogen on oxidised $ZnO-Cr_2O_3$ involves irreversible processes which occur with the liberation of 45 kg.-cals./mol. The surface undergoes reduction simultaneously with the adsorption, and hydrogen or carbon monoxide is adsorbed on the reduced areas with heats of 10—15 kg.-cals. Oxygen is also adsorbed on the reduced centres so produced, and a 2 : 1 mixture of carbon monoxide and oxygen is completely adsorbed by oxidised $ZnO-Cr_2O_3$.

The adsorption of carbon monoxide, hydrogen, ethylene, and ethane on the reduced surfaces is reversible and occurs with heats of the order of 10—25 kg.-cals. Only in cases where there is no penetration of capillaries can the desorption be completed at room temperature within a reasonable time. From the behaviour on desorption, conclusions are drawn with respect to the activation energies of the adsorption process. A mechanism is suggested for the adsorption on the reduced catalysts.

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