191. *The Heat of Adsorption of Gases on Chromium Sesquioxide at Low Pressures and Room Temperatures.*

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Measurements of the heat of adsorption of carbon monoxide, carbon dioxide, hydrogen, and oxygen on chromium trioxide have been made at 18° for the oxide in an oxidised and in a reduced state. The absorbing surface was ten times larger for the reduced than for the oxidised substance. The heat measurements indicate that the adsorption on an oxide surface of carbon monoxide or hydrogen is a two-stage process, the first being the formation of carbonate or hydroxyl ions on the surface, together with some surface unsaturation, and the second the disappearance of the unsaturation. The unsaturation disappears very slowly after the adsorption of carbon monoxide unless hydrogen is present on the surface, and very quickly in the case of the adsorption of hydrogen. The heats of adsorption of oxygen depend on the degree of unsaturation of the surface. Attention is directed to the part which the mobility of the atoms of the adsorbent plays in the chemisorption of gases on chromic oxide.

The results for chromic oxide are compared with those previously obtained for ZnO,Cr_2O_3 and for zinc oxide, and conclusions drawn as to the changes in adsorptive capacity which occur on mixing two oxides.

In an earlier investigation by Veal and one of us (J., 1935, 1487), the heats of adsorption of a number of gases on zinc oxide and ZnO,Cr_2O_3 were measured. The heats for chromium sesquioxide have now been obtained and some conclusions can be drawn as to the nature of the change in adsorptive properties which occurs when zinc and chromic oxides are mixed. Howard and Taylor (*J. Amer. Chem. Soc.*, 1934, **56**, 2259) have discussed the effect of promoter action in the above case, in the light of measurements made of the rates of adsorption of gases on the two oxides and the spinel formed between them. Their work has special reference to the promotion of the hydrogenation of ethylene. They derive from the rates of adsorption of hydrogen that the activation energies at 194·5° K. are respectively 11, 19, and 1 kg.-cal. for ZnO, Cr_2O_3, and ZnO,Cr_2O_3, and conclude that the rate of activated adsorption is a very important factor in the determination of the activity of a promoter.

From the adsorption isotherms of hydrogen on chromic oxide the above authors calculate that the heat of adsorption between 83° and 194·5° K. is 1·8 kg.-cals. and at 611—648°, 27 kg.-cals. Beebe and Dowden (*ibid.*, 1938, **60**, 2912) have measured the heats of adsorption of hydrogen at 90° K. and find that the differential heats fall gradually with increasing surface densities from 5·11 to 3·16 kg.-cals. The discrepancy between the experimental and the calculated heats of adsorption at low temperatures is very marked and shows that the calculation of heats of adsorption from adsorption isotherms is subject to serious errors. The discrepancy is still greater at high temperatures, for the experimental value obtained in the present investigation is 72—74 kg.-cals. It would appear, therefore, that the processes occurring in the adsorption of gases by oxides of the type of chromium trioxide are too complex to permit of the use of adsorption isotherms in the calculation of heats of adsorption.

Beebe and Dowden (*loc. cit.*) record that the adsorption of carbon monoxide on chromic oxide at 90° K. occurs in two stages, the first being the van der Waals adsorption of carbon monoxide with a heat of 4 kg.-cals., followed by a rearrangement on the surface with the liberation of a further 8 kg.-cals., which these authors believe to be chemisorption. At 0°, the heat of adsorption of carbon monoxide was 15·2 → 9·9 kg.-cals., with no evidence of the occurrence of a slow process. In the present investigation, the heat of adsorption at room temperature was found to vary with surface density from 29 to 22 kg.-cals. The difference between the results at 0° and 18° indicates that there is a marked temperature coefficient of the heat of adsorption of carbon monoxide in the region of room temperature. It is shown in the present paper that there is considerable surface unsaturation produced by the adsorption of carbon monoxide, and this disappears with the liberation of heat if hydrogen atoms be present on the surface, the heat of adsorption in these circumstances being 60—62 kg.-cals. It is shown also that this unsaturation disappears on raising the temperature of the oxide. Thus, there are clearly distinguished three stages in the adsorption of carbon monoxide on chromium trioxide : (*a*) van der Waals adsorption, (*b*) chemisorption with the production of unsaturation, and (*c*) disappearance of the unsaturation.

EXPERIMENTAL.

Preparation of Chromium Oxide.—A 20% solution of sodium chromate, acidified with sulphuric acid, was reduced by sulphur dioxide. A slight excess of aqueous ammonia (*d* 0·880) was added, and the solution boiled. The precipitate was washed free from electrolyte, dried, and broken into grains.

Calorimeter.—This was of the type 1.f used by Garner and Veal (*loc. cit.*). A number of measurements of heats of adsorption on the oxide showed that it possessed a very poor heat conductivity. This was increased by mixing the oxide with pieces of thin gold wire which were so shaped as to prevent their being telescoped into a compact mass. The weights of the materials used in the calorimeter bulb were the following : Cr_2O_3, 16·125; Au, 16·232; Pt, 1·200; pyrex, 0·748 g., and the specific heats employed were 0·18, 0·035, 0·0314, 0·20 cal./deg. respectively. These gave a water equivalent of 3·658 cals./° C. The cooling coefficients for helium gas in the calorimeter containing the gold wire are given below in ° C. per mm. per 1° C. :

Hard vac.	0·001	$1{\cdot}8 \times 10^{-3}$	0·011	$1{\cdot}25 \times 10^{-1}$	0·014
4×10^{-4}	0·004	$1{\cdot}8 \times 10^{-2}$	0·011	$6{\cdot}5 \times 10^{-1}$	0·015

Helium was mixed with the gas used in the adsorption measurements in the ratio 1 : 1, and the gas pressures in the measurement of the heats of adsorption ranged between 10^{-3} and 10^{-2} cm. Before the gas was admitted to the calorimeter, care had to be taken that the latter had reached thermal equilibrium with its surroundings, and the attainment of equilibrium was accelerated by the addition of 10^{-3} to 10^{-2} cm. of helium before each experiment. The rise in temperature of the calorimeter was recorded photographically, as described in the previous paper, and the deflection obtained was 17—22 cm. per degree. The calorimeter and its Dewar vessel were enclosed in a heat-insulated box to prevent draughts on the calorimeter leads, and the leads were securely fixed in glass tubes to diminish vibration, but in other respects the apparatus was essentially similar to that used in the earlier investigation (*loc. cit.*).

Heats of Adsorption.—The employment of helium as a diluting gas was found to be essential, and even when this gas was used, difficulties were encountered when the oxide was very active as an adsorbent owing to the slow distribution of locally evolved heat. Typical series of measurements are given in Table I for the heats of adsorption of first admissions of carbon monoxide. These are calculated from the amounts of gas adsorbed and the galvanometer deflections, the cooling coefficients used being given on p. 894.

TABLE I.

Time, mins.		1.	2.	3.	4.	5.	6.	7.	8.	11.	14.	17.	20.
Expt. 1	kg.-cals./mol.	—	43	35·5	31·1	29·0	28·3	27·7	27·4	26·7	27·0	27·2	27·1
Expt. 2		78·1	40·7	32·3	28·7	26·6	26·7	26·1	26·2	26·2	26·8	27·0	27·3

The initial high values show the occurrence of local heating around the thermocouple, and the subsequent values the dispersion of this heat. Usually, constant values were obtained within 10 mins. During this 10 mins., the cooling correction amounts to one-tenth of the heat evolved, and hence the initial poor distribution of heat might lead to serious errors. To test if this was the case, comparable experiments were carried out with the calorimetric fluid at a constant temperature (Expt. 1, Table I) and with the calorimetric fluid raised in temperature, immediately after admitting the gas, to that expected in the calorimeter as a result of the adsorption (Expt. 2). The results in the above table show that, within the experimental error of $\pm$ 1 kg.-cal., there are no appreciable errors introduced by the local heating. The same held true for second and third admissions of gas. The agreement between the values obtained by the two methods shows that the cooling corrections used were sufficiently accurate for our purpose.

Difficulties were, however, experienced in the adsorption of small amounts of oxygen on the reduced catalyst owing to local distribution of heat, and these could not be overcome except by increasing the amount of gas to be adsorbed and decreasing the sensitivity of the galvanometer. In the limiting case, of great surface activity and immediate adsorption on collision of the gas molecules with the surface, accurate values could not be obtained for differential heats of adsorption on this oxide. Such cases were, however, few in number, and where they occur the heats obtained are given in parentheses in the following tables.

The period and temperature of degassing the oxide were strictly controlled, the calorimeter being baked out at 450° before each run of experiments.

The Reduced and Oxidised Surface of Chromium Oxide.—During the preparation of the oxide, it was reduced with hydrogen, and considerable difficulty was experienced in freeing the surface from hydrogen, even by evacuation at 450°. It was found that, on admitting small volumes of carbon monoxide to the oxidised surface, which had previously been treated with hydrogen, and desorbing at 450°, the gas evolved was mainly carbon dioxide but contained some water. Twelve such experiments were performed before the evolved water became too small to be measured.

The reduced and the oxidised state of chromium oxide were obtained by treatment with carbon monoxide and with oxygen respectively at 400—450° until no further reaction occurred. Before cooling to room temperature, the oxide was baked out at 450° for 3 hours to remove carbon dioxide, etc. These two surfaces were used in the majority of the experiments. The weight of oxide used was 16·125 g.

The adsorbing surface was about ten times larger for the reduced than for the oxidised substance, as the following figures for the amount of carbon monoxide and dioxide taken up at room temperature and at pressures of 10^{-2} cm. show :

	CO, c.c.	CO_2, c.c.	O_2, c.c.
Oxidised	3·13	3·21	0·050
Reduced	32·3	32·5	30

These values were obtained towards the end of the research, when the activity of the oxide had been somewhat reduced.

Veal has found (*loc. cit.*) that 14·8 g. of ZnO,Cr_2O_3, when reduced as far as possible, will take up 120 c.c. of oxygen at room temperature. This is about $\frac{1}{20}$ of that required to convert the Cr_2O_3 present into CrO_3. This volume is so large that it must be concluded that in the reduced state the spinel possesses a very porous structure. This porous material may consist of non-crystalline matter separating the crystal grains, or may be formed from crystals by the removal of oxygen without collapse of the lattice. The former hypothesis is probably the more correct, since Hüttig, Radler, and Kittel (*Z. Elektrochem.*, 1932, **38**, 442) have shown by *X*-ray measurements that the spinel structure is not developed throughout the lattice unless the oxide is heated above 500°, which is 50° higher than the maximum temperature to which the oxides were subjected in our experiments. It is probable, therefore, that the active surface is limited to non-crystalline matter. In the case of the sample of chromic oxide employed, the porosity as shown by the adsorption on the reduced surface is one-fifth of that of the spinel.

It is necessary to assume that there is a good deal of porosity in these oxides, to account for (*a*) the differences between the amounts of gas adsorbed on the reduced and the oxidised surfaces and for (*b*) the results obtained as the oxidised surface is progressively reduced. We shall have occasion to distinguish between adsorption on the external surfaces and on the internal surfaces of the solid.

The Adsorption of Oxygen.—(i) *On the oxidised surface.* The adsorption of oxygen on the oxidised surface, after baking out at 450°, as would be expected is very small, *viz.*, 0·05—0·08 c.c. That there is any adsorption at all is probably due to losses from the surface during the baking out. The heat of adsorption on the oxidised surface is 37 kg.-cals. Beebe and Dowden (*loc. cit.*), working with a more active catalyst, obtained values decreasing with surface density from 50 to 17·6 kg.-cals. at 0°.

(ii) *On the partly reduced surface.* The oxide was progressively reduced with carbon monoxide, and, before the heat measurements, this gas was removed as dioxide by baking out for 3 hours at 450°. The amounts of oxygen adsorbed and the heat measurements are given in Table II. The oxygen admitted in the heat measurements was approximately 0·6 c.c. except where denoted by an asterisk, where 6 c.c. of oxygen were admitted.

TABLE II.

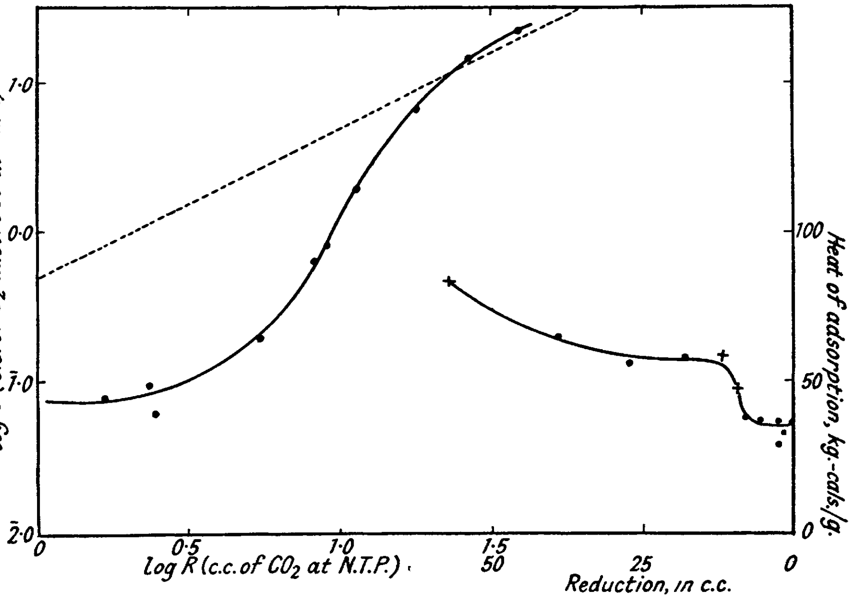
Expt. No.	CO_2 removed (S), c.c. at *N.T.P.*	Total O_2 adsorbed (R), c.c.	Heat of adsorption at 11th minute (kg.-cals./g.-mol.). Admission: 1.	2.	3.
1	2·38	0·095	36·9	—	—
2	5·43	0·199	36·7	—	—
3	9·01	0·823	(47·8)	41·0	33·0
4	11·32	1·974	(59·0)	(54·5)	—
5	1·69	0·079	33	—	—
6	2·46	0·063	29	—	—
7	8·08	0·660	38	—	—
8	17·83	6·519	58 *	—	—
9	26·93	14·895	56 *	30 *	—
10	39·3	22·61	65 *	56 *	53 *
11	57·1	—	(84)	(98)	—

The experimental procedure adopted for experiments 5—8 was different from the rest. Before each of these experiments, the oxide was oxidised and baked out at 450°, reduced with carbon monoxide at 400°, and baked out again at 450°. It was then ready for the measurement of the heats of adsorption, and the determination of the total oxygen adsorption. The other experiments consist of two series, *viz.*, 1—4 and 8—11, for which the above steps were carried out only at the beginning of the series. Between each experiment, however, the carbon dioxide was removed by baking out at 450°.

In Expts. 1, 2, 5, 6, and 7, where the amount of oxygen which would be adsorbed at saturation was small, the heats of adsorption reached a constant value within 11 mins. Where, however, small quantities of oxygen were admitted to a surface whose saturation value was considerably greater than the volume of oxygen admitted, then there was a downward drift of the values with time. This held for the first admission of Expts. 3, 4, and 11, when 0·6 c.c. of gas was admitted to the oxide. The heats in these cases, which have been enclosed in parentheses, are not very reliable. If, however, quantities of the order of 6 c.c. are admitted, as in the experiments denoted by an asterisk above, then the drift is eliminated, indicating that in these cases there is a good distribution of heat throughout the calorimeter and that reliable values are being obtained.

The values for log S (the carbon dioxide removed) are plotted against log R (the oxygen adsorbed) in the figure. They fall on a sigmoid curve, which is considerably below the stoicheiometric adsorption (broken line) in the early stages of the reduction process, but reach the theoretical values finally. The initial lag in the adsorption of oxygen can be accounted for as follows. The oxygen is adsorbed on vacant spaces on the external surface of the solid, and the above lag indicates that at first the reduction of the surface does not materially increase the number of vacant spaces on the external surface. This probably means that, as a result of the baking-out for 3 hrs. at 450°, there has been a migration of oxygen from the interior of the solid, filling up the vacant spaces caused by the removal of molecules of carbon dioxide. Thus the mobility of oxygen throughout the solid at 450° would account for the small magnitude of the oxygen adsorption in the early stages of the reduction. As the reduction proceeds, the solid becomes porous to gases, and adsorption occurs in the capillary passage. The oxygen adsorption and the heat of adsorption increase, and finally, when the oxide is very considerably reduced, the oxygen can penetrate to all of the vacant spaces produced in the solid. This entails a certain degree of mobility of oxygen atoms through the solid at room temperature, which would be possible if the activation energy for the diffusion of oxygen were < 20 kg.-cals. It is, however, doubtful if this diffusion could occur through the lattice at room temperatures; it would probably be restricted to the disorganised material. To explain the curve, it would also be necessary to assume two states of chemisorption of oxygen, one which dissociates readily, and the other with the oxygen atoms firmly bound, which assumption would be in accord with the heat measurements, which show two ranges of values for the heat of adsorption, *viz.*, 35 and 55 kg.-cals. (see figure). The binding with the higher heat would choke the capillaries and prevent further diffusion, but this would not be a serious matter when the oxide had been reduced to a considerable extent, since there would be alternative routes to any one adsorption space.

(iii) *On a surface containing adsorbed carbon monoxide.* It was found that when oxygen was admitted to a fully oxidised surface to which carbon monoxide had been added, the heats of adsorption were much larger than on a carbon monoxide-free surface. The oxidised surface was saturated with carbon monoxide, and the heats of adsorption of oxygen determined. All the values showed a tendency to rise with time, as the following example shows :



Time (mins.)	2	5	8	11	14	17	20
Heat (kg.-cals.)	111·2	110·1	112·3	116·0	118·2	119·3	120·0

This may be taken to mean either that the gas is diffusing to centres of higher activity or that there is some energy of reorganisation liberated, after the adsorption is complete. The values obtained for the 11th minute are :

Admission.	1.	2.	3.	4.
Heat (kg.-cals.)	103·6	109·1	—	—
	116·0	124·7	101·5	76·1

These experiments indicate that the surface containing adsorbed carbon monoxide is very considerably unsaturated.

Results were also obtained for the heat of adsorption of oxygen on the reduced surface on which had been adsorbed 8·7 c.c. of carbon monoxide. The distribution of gas was poor, and a constant heat was barely obtained at the 20th minute. The approximate values for successive admissions of 0·65 c.c. of oxygen are 88, 91, 89, 82 kg.-cals.

After admitting small volumes of carbon monoxide, 0·4 c.c., to the oxidised surface, it was found that it would take up a little more than half this quantity of oxygen, but that when larger quantities of carbon monoxide were used, much smaller quantities were taken up than correspond with the 2 : 1 ratio. Hence, it appears that carbon monoxide itself can occupy some of the places of unsaturation that it produces.

The Adsorption of Carbon Monoxide.—(i) *On an oxidised surface.* The heat of adsorption of carbon monoxide on the oxidised surface was determined by admitting 0·9 c.c. of gas. Nine successive admissions of this volume were made, and the following values obtained : 29·3, 23·3, 22·9, 22·2, 22·5, 21·6, 21·7, 22·4, 22·5 kg.-cals. Other series gave similar results. The adsorption was a slow process, and hence a good distribution of the gas was obtained throughout the oxide and constant values were obtained after 6—10 mins. After the extensive treatment of the surface with hydrogen, the heats of adsorption of carbon monoxide on the oxidised surface became much greater (see later).

(ii) *On a reduced surface.* The heats for successive admissions of 0·3, 0·6, 0·85, 4·7 and 4·9 c.c. were (28), 26·6, 23·5, 11·5, 12·5, indicating considerable heterogeneity in the adsorption process. Between experiments 4 and 5, 3·4 c.c. of carbon monoxide were admitted without measurements being made of the heat of adsorption. The distribution of the heat on the reduced surface was not so good as on the oxidised surface, constant heats not being obtained until the 17th minute. This is probably because of the rapid adsorption on a very unsaturated surface with the resulting local liberation of heat.

(iii) *On a surface which had previously been treated with hydrogen.* A surface treated with hydrogen and oxidised at 450° still contained sufficient hydrogen to affect the heat of adsorption on carbon monoxide on the oxidised surface, the heat becoming 60—62 kg.-cals., instead of 29 kg.-cals. obtained on the surface freed from hydrogen. This rise in the heat of adsorption of carbon monoxide is accompanied by a reduction of the heat of adsorption of oxygen on the carbon monoxide-covered surface, *viz.*, from 110 to 72 kg.-cals., as the following figures show :

Heat of Adsorption of Carbon Monoxide on the Hydrogen-treated Surface.

	Heat of adsorption (kg.-cals.) of :	
	CO on oxidised surface.	O_2 on the CO-treated surface.
I	62	72
II	60	77
Normal result	29	110

As the hydrogen was removed by successive oxygenation and baking out, etc., the heat of adsorption of carbon monoxide gradually returned to its normal value. By this time the oxidised surface would no longer adsorb appreciable quantities of hydrogen. It would appear that the processes whereby the hydrogen is removed from the surface destroy the possibility of hydrogen's being adsorbed on the oxidised surface.

The Adsorption of Hydrogen.—(i) *On an oxidised surface.* When first prepared, the oxidised surface adsorbed appreciable quantities of hydrogen, *viz.*, 1·5 c.c., but as the research proceeded, the adsorption decreased and finally became negligible. A series carried out immediately after the series with carbon monoxide mentioned previously (see above) gave the following heats for successive admissions of 0·20 c.c., *viz.*, 72·2, 71·4, 74·2, 73·1, 74·9, 72·1 kg.-cals. The heats were constant after 6—8 mins. A similar series was carried out without the use of helium as a diluent gas, and similar values were obtained. The hydrogen has obviously entered into chemical combination with the surface as hydroxide. The adsorbed hydrogen is very difficult to remove even on long treatment at 450°.

While the surface was active towards hydrogen, experiments were carried out to determine if oxygen could be adsorbed on the surface containing hydrogen. Thus, 1·56 c.c. of hydrogen were adsorbed on the oxidised surface and this was followed by 0·203 c.c. of oxygen. Only 0·06 c.c. of oxygen was adsorbed, which is the normal amount of oxygen adsorbed on the oxidised surface. The adsorption of hydrogen has not produced any permanent unsaturation of the surface, and this is what would have been expected in view of the high heat of adsorption of hydrogen. If, however, the oxygen and hydrogen were admitted together in the proportion of $2H_2 + O_2$, then oxygen disappeared from the gaseous phase with the hydrogen, with an average heat of 86 kg.-cals. It appears, therefore, that the surface is rendered unsaturated by the hydrogen, but that this unsaturation rapidly disappears, with the evolution of large quantities of heat.

(ii) *On a reduced surface.* Hydrogen is adsorbed on the reduced surface to the extent of about 6 c.c., and the heat of adsorption is lower than on the oxidised surface, *viz.*, 36 kg.-cals.

Adsorption of Carbon Dioxide.—(i) *On an oxidised surface.* Successive admissions of 0·6 c.c. gave the following values : 17·9, 17·9, 17·6, 17·0, 17·3 kg.-cals. These were constant after 11 mins.

Other series gave similar results. Very little of this gas could be desorbed at room temperature. For instance, of 0·6 c.c. admitted (5th admission), calculations made from the heat of desorption showed only 0·1 c.c. to be desorbed. This behaviour is quite different from that of carbon dioxide on zinc oxide and the spinel ZnO,Cr_2O_3, for in these cases the gas is desorbed quantitatively at room temperature. With a heat of adsorption of 17·3 kg.-cals., this points to the presence of an activation energy for the adsorption of carbon dioxide on chromium oxide.

(ii) *On a partly reduced surface* (reduction = 16·7 c.c. of carbon monoxide). The heats of adsorption were 21·4 and 21·0 kg.-cals. for two successive admissions.

(iii) *On a reduced surface.* The heats fell away rapidly with time, and approached a constant value only at the 20th minute. One series gave 30·9, 28·3, 28·4, 28·3, 24·0, 21·2 kg.-cals. for the 20th minute. There is thus an increase in the heat of adsorption on passing from the oxidised to the reduced surface.

No appreciable quantities of oxygen are adsorbed on the oxidised surface saturated with carbon dioxide, but 0·47 c.c. of carbon monoxide can be adsorbed on an oxidised surface saturated with carbon dioxide, showing that all of the centres on which carbon monoxide can be adsorbed are not occupied by the dioxide.

Desorption of Gas from Surface Treated with Carbon Monoxide and Carbon Dioxide.—It has been shown that the heats of adsorption of carbon monoxide and dioxide on a hydrogen-free, oxidised surface are of a similar magnitude, *viz.*, 29—22 and 18 kg.-cals., respectively. If carbonates were formed in each case, it would have been expected that the heat of adsorption of carbon monoxide would be considerably greater than that of carbon dioxide, as it is in fact on MnO and ZnO,Cr_2O_3. Attempts were therefore made by Mr. T. Ward to test if the adsorption complex were the same in the two cases: 3·82 g. of oxide were completely oxidised at 450°, either carbon monoxide or the dioxide being adsorbed on the surface at room temperature, and the quantity of carbon dioxide evolved during evacuation for an hour was measured for a range of temperatures. The temperature of the oxide was raised in stages to 70°, 120°, 170°, 220°, 270°, 320°, 370° and 420°. The results are in Table III.

TABLE III.

CO on the oxidised surface.

Temp.	70°	120°	170°	220°	270°	320°	370°	420°
C.c. evolved	0·212	0·110	0·016	0·008	0·004	0·007	0·013	0·047

CO_2 on the oxidised surface.

Temp.	70°	120°	170°	220°	270°	320°	370°	420°
C.c. evolved	0·292	0·111	0·071	0·016	0·027	0·039	0·047	0·142

CO on the reduced surface.

Temp.	20°	70°	120°	170°	220°	270°	320°	370°	420°
C.c. evolved	0·026	0·110	0·057	0·007	0·002	0·001	0·001	0·003	0·038

CO_2 on the reduced surface.

Temp.	20°	70°	120°	170°	220°	270°	320°	370°	420°
C.c. evolved	0·21	0·13	0·004	0·001	0·001	0·000	0·000	0·001	0·055

The bulk of the gas in the four experiments is evolved as carbon dioxide over the range 20—120°, and little over the range 120—370°. Gas is evolved at 420—450°, but in smaller quantities than over the lower temperature range. There is no marked difference between the rates of decomposition of the adsorption complexes formed from carbon monoxide and dioxide, and the conclusion to be drawn is that the product is the same in both cases.

DISCUSSION.

Adsorption on Chromic Oxide.—The chromic oxide used in this investigation underwent a progressive decrease of activity with time. This was shown by the decreased capacity for the adsorption of hydrogen and carbon monoxide on the oxidised surface. The decreased activity is very probably due to crystallisation of amorphous material at the temperature of the baking out, *viz.*, 450°. The work on the adsorption of oxygen on the partly reduced surface indicates also that there is present uncrystallised material in the solid. The solid probably consists of very small crystals, bound together by disorganised matter, and contains large and small capillary passages, the smallest of which are only opened up on reduction. The reduced surface is therefore considerably larger than the oxidised surface, which is in accord with the greater adsorption observed on the reduced surface.

Not only does the solid undergo a process of sintering at 450° but there is also evidence in favour of the view that there is considerable mobility of oxygen at this temperature. Thus the vacant spaces produced on reducing the surface with carbon monoxide disappear on baking out at 450°. This is most probably due to the diffusion of oxygen atoms out of the disorganised material to the surface of the grains.

Carbon monoxide is adsorbed on the oxidised surface with a relatively low heat, *viz.*, 29—22 kg.-cals., the bulk of the gas being adsorbed with the latter heat. There are at least two types of adsorption centres, for on desorption carbon dioxide is liberated over two ranges of temperature, *viz.*, 20—120° and 420—450°. The heat for the reduced surface covers a wider range, *viz.*, 28 $\rightarrow$ 12 kg.-cals. The heats for the adsorption of carbon monoxide are surprisingly low if we bear in mind the corresponding heats for the adsorption of carbon dioxide for the oxidised and the reduced surface, *viz.*, 18 and 30—21 kg.-cals., especially as the rates of desorption of the dioxide are very similar in the two cases. If carbon monoxide and dioxide each gave the same products on adsorption, we should expect that the heat of adsorption of the former would be considerably larger than that of the latter, whereas they are of the same order. The explanation is to be sought in the unsaturation of the surface produced by the carbon monoxide. This unsaturation persists for a sufficient length of time for it to be detected by the adsorption of oxygen afterwards. In the case of carbon monoxide, the process of adsorption can be depicted as follows:

There will be left vacant one unsaturated position on the surface for every carbonate ion produced. The heat of adsorption of oxygen on such positions is very high, *viz.*, 110 kg.-cals. There is sufficient energy available for the dissociation of the oxygen molecule, so that one oxygen atom can enter the vacant position and the other can diffuse until it finds another similar position. On removal of carbon dioxide from the monoxide-treated surface during the baking out, a portion of the unsaturation energy is lost by some reorganisation of the surface, probably due to the movement of the positions of unsaturation into adjacent positions and the formation of new valencies between the metal and oxygen atoms. The heat of reaction of oxygen with the reorganised surface is (on this account) much lower, *viz.*, 55 kg.-cals. (see Expts. 8, 9, and 10, p. 896), so that approximately 55 kg.-cals. are lost during reorganisation; and this process probably occurs at a relatively low temperature, *viz.*, 70—120°, since a surface covered with carbon monoxide behaves like one covered with dioxide at these temperatures. We can draw up the following balance sheet for reactions of oxygen and carbon monoxide and dioxide with the surface, the values taken being those for the oxidised surface where the heats have a precise meaning:

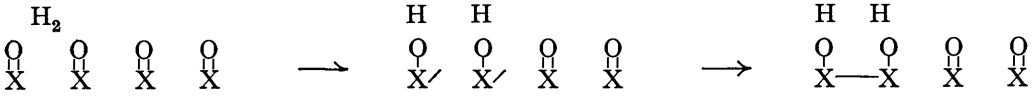
$$
\begin{array}{ll}
(1) & 2XO + CO \longrightarrow XCO_3 + X + 29 \text{ kg.-cals.} \\
(2) & 2XO + CO_2 \longrightarrow XCO_3 + XO + 18 \text{ kg.-cals.} \\
(3) & X + \tfrac{1}{2}O_2 \longrightarrow XO + 55 \text{ kg.-cals.} \\
(4) & CO + \tfrac{1}{2}O_2 \longrightarrow CO_2 + 68 \text{ kg.-cals.}
\end{array}
$$

The sum of the heats liberated in (1) and (3) should be the same as the sum for (2) and (4). They are so within the experimental error; hence the heat of formation of the surface carbonate is the same by the two methods.

Hydrogen is very strongly held by the oxidised material, giving heats of adsorption of 72 kg.-cals., and cannot be removed from the surface without some destruction of the activity of the catalyst. There must be formed a surface chromium hydroxide, and the haphazard splitting off of water molecules from this substance must leave some isolated hydroxyl groups on the surface. These can form water only if there is some mobility of the hydroxyl groups or hydrogen atoms over the surface to bring them together in pairs.

The high energy of adsorption of hydrogen probably leads to a high activation energy for movement over the surface, so that the removal of the last traces of water requires a high temperature. The action of carbon monoxide in ejecting water from the surface is probably due to the increased surface mobility brought about during the adsorption of this gas. The heat of adsorption on the reduced surface is considerably lower, *viz.*, 36 kg.-cals.

It is of interest to note that the adsorption of hydrogen does not leave the surface unsaturated, and this is readily understood since a hydrogen molecule will produce two adjacent hydroxyl groups on the surface, and probably at the same time two adjacent unsaturated positions. The latter will probably disappear with the liberation of heat, and this accounts for the high heat of adsorption of hydrogen. A possible mechanism for this process is given below :



If, however, oxygen is present at the time the hydrogen is being adsorbed, then some of the oxygen molecules can combine with the surface before the unsaturation can disappear. The spinel behaves in a very similar fashion.

The fact that the adsorption of carbon monoxide on a surface which has been thoroughly treated with hydrogen and then baked out is higher, *viz.*, 60 kg.-cals., than on a surface free from hydrogen, *viz.*, 22 kg.-cals., is also of some interest, since it shows that the presence of isolated hydroxyl groups on the surface facilitates the reorganisation of the surface energy.

The heats of adsorption of carbon monoxide, hydrogen, oxygen, and carbon dioxide on chromic oxide, zinc oxide, and the spinel are compared in the following table :

	Cr_2O_3.		ZnO,Cr_2O_3.		
	Oxidised.	Reduced.	Oxidised.	Reduced.	ZnO.
CO	29—22 *	28 ⇀ 12 *	44 ⇀ 16	15 ⇀ 11	18 ⇀ 12
H_2	72 *	36	48 ⇀ 13	13 ⇀ 10	(21)
O_2	37 *	55 *	—	42·9 *	—
CO_2	18 *	(30—21)	15 ⇀ 13	18 ⇀ 16	13 ⇀ 9
O_2 after CO	110		45		

* These are the values for the bulk of the gas adsorbed.

Promoter Action.—The main interest lies in the comparison of the results for spinel and chromium oxide. The heat of adsorption of hydrogen is much greater in the case of chromium oxide, and this means a tighter binding with the surface. The heat of adsorption of carbon monoxide is lower, but the reason for this lies in the very high unsaturation energy produced by the adsorption of carbon monoxide on chromium oxide. If this energy were set free, as it probably is at high temperatures, the heat of adsorption would be higher on the chromium oxide than on the spinel. This is borne out by the fact that there is little difference between the heats of adsorption of carbon dioxide on the two solids. The heat of adsorption of oxygen on the reduced surface is considerably greater for chromium oxide than for the spinel. The principal conclusions to be drawn are (*a*) that the strengths of the binding of hydrogen and oxygen on the surface are greater for chromium oxide than for the spinel, (*b*) that the surface unsaturation of chromium oxide is considerably less mobile than that of the spinel, and (*c*) that the skeleton of the structure of the spinel is more stable than that of chromium oxide.

Hüttig (*Tekn. Samfundets Hanglingar*, 1936, **5**, 125) concluded, from measurements of a number of physical and chemical properties of mixed oxides, that the formation of a compound occurs on heating in two stages. During the first stage, which is attained at relatively low temperatures of degassing, there is produced a surface compound between the two oxides, and in the second stage, occurring at higher temperatures, this compound is formed as a crystalline lattice. The maximum of catalytic activity and adsorptive capacity usually occurs during the first stage. In the case of ZnO,Cr_2O_3, Hüttig, Radler, and Kittel (*loc. cit.*) show that treatment at 500° is necessary before the characteristic

X-ray lines of the spinel appear, so that in the present investigation, where the temperatures do not exceed 450°, we are concerned mainly with the first stage during which compounds are formed in the non-crystalline material. It is thus the properties of the non-crystalline material that determine its catalytic activity.

In order that an oxide should be a good catalyst, the framework of the non-crystalline material must be reasonably stable, behaving similarly to a zeolite in that it does not collapse or crystallise under the chemical reactions occurring within it. In addition, there must be also considerable mobility of the adsorbed molecules and ions on and away from the surface, and this means, in general, low heats of chemisorption. It would appear that zinc oxide stabilises the skeleton of the active surface of chromium oxide and at the same time increases the general mobility of the atoms composing the complexes formed during chemisorption on the surface.

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