

### 235. Heat of Adsorption of Gases on Manganous-Chromic Oxide at Room Temperature.

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Measurements have been made of the heats of adsorption of carbon monoxide, carbon dioxide, and oxygen. Carbon monoxide is irreversibly adsorbed, giving carbon dioxide on rise of temperature. The surface, after the addition of carbon monoxide, is unsaturated with respect to oxygen. The evolution of carbon dioxide is facilitated after the unsaturation has been removed, and carbon dioxide can be desorbed with a heat of desorption equal to the heat of adsorption of carbon dioxide. The adsorption of carbon dioxide is not "activated".

THIS investigation is a continuation of a series of experiments on the heats of adsorption of carbon monoxide, carbon dioxide, oxygen, and hydrogen on the metallic oxides, ZnO, MnO<sub>1.5</sub>, and Cr<sub>2</sub>O<sub>3</sub>, and the changes in adsorptive properties that occur on mixing two of the oxides (Garner and Veal, *J.*, 1935, 1436, 1487; Garner and Kingman, *Trans. Faraday Soc.*, 1931, 27, 322; Dowden and Garner, *J.*, 1939, 894; Garner and Ward, *ibid.*, p. 858). In the present work, a study has been made of the heats of adsorption of the above gases on the fully oxidised, reduced, and partly reduced surfaces of manganous-chromic oxide. Particular attention has been paid to the formation of carbonates from carbon monoxide and oxygen, and from carbon dioxide.

Although the properties of Cr<sub>2</sub>O<sub>3</sub> and MnO<sub>2</sub> as promoters are well known, little attention appears to have been paid to the study of adsorption on the mixed oxides. Taylor and Williamson (*J. Amer. Chem. Soc.*, 1931, 53, 2168) have shown that over the range -78.5° to 144° there are two forms of adsorption of hydrogen and carbon monoxide. At -78.5° hydrogen was adsorbed molecularly with a heat of 1.9 k.-cals./mol., as calculated from adsorption isotherms. At 300-400°, the heat of adsorption of hydrogen was ~20 k.-cals. Only qualitative results were obtained with carbon monoxide.

#### EXPERIMENTAL.

*Preparation of the Oxide.*—Manganous ammonium chromate was prepared by the method of Taylor and Williamson (*loc. cit.*) by the interaction of manganous nitrate and ammonium chromate, the solution being titrated until just neutral with ammonia and then filtered. The precipitate was washed thoroughly with ammonium nitrate solution, then with distilled water, and finally dried. It was now oxidised at 400° in a stream of oxygen for 48 hrs., a black amorphous powder being formed. The powder was unsuitable for use in the type of calorimeter employed; hence, it was pressed into small tablets by means of a pastel press, these tablets being then cut into squares 0.1 mm. in size. It was finally treated *in situ* with oxygen at 400°. No information concerning the X-ray structure of the spinel could be obtained.

*Specific Heat of the Oxide.*—This was determined by the method employed by Garner and Randall (*J.*, 1924, 125, 881). The average value for the determination was 0.166 cal./deg.

*Calorimeter.*—This was of the type 1f (Garner and Veal, *loc. cit.*), but with the slight alterations mentioned by Garner and Ward (*loc. cit.*), where the details of the method of measurement are given. The weights of the materials used were, platinum 1.6506 g., Pyrex 2.4023 g., oxide 19.680 g., and the specific heats 0.0314, 0.20, and 0.166 cal./deg. respectively. These values gave a water equivalent of the calorimeter of 3.800 cal./deg.

The calibration of the calorimeter was carried out by noting the change in temperature by a standardised Beckmann thermometer when the temperature of the calorimeter fluid was altered by the addition of either ice or hot water, and at the same time recording photographically the e.m.f. of the thermocouple on a Z.c. Kipp and Zonen galvanometer. The sensitivity was 15 cm. per degree.

A preliminary series of experiments showed that the heat conductance of the catalyst was good; the admission of helium as a diluting gas and the mixing of the oxide with gold wire (Garner and Dowden, *loc. cit.*) were therefore unnecessary. The cooling correction was determined after saturating the oxide with oxygen, carbon dioxide, etc., at pressures of  $10^{-4}$ — $10^{-2}$  cm., allowing the system to come to equilibrium, and then reducing the temperature of the calorimeter by  $1^\circ$  or  $2^\circ$ . The change in e.m.f. of the thermocouple was recorded, and the loss of temperature per minute for a difference of temperature of  $1^\circ$  between the calorimetric fluid and the thermocouple was obtained for every minute up to the 20th. The values obtained were, 1—6 mins.,  $0.020^\circ$ ; 6—10 mins.,  $0.018^\circ$ ; 10—15 mins.,  $0.016^\circ$ ; 15—20 mins.,  $0.015^\circ$ . These values were independent of the gas used, and held over a range of pressures from hard vacuum to  $10^{-2}$  cm. In the following experiments the pressure was not allowed to rise above  $10^{-2}$  cm.

There was no drift with time in the values of the heats of adsorption, except in a few experiments where slow reactions occurred, showing that a uniform distribution of gas was attained throughout the calorimeter.

For most of the work the oxide was reduced by carbon monoxide at  $400^\circ$ . Hydrogen was not employed in the reduction until the end of the experiments, in order to avoid contamination of the solid with hydrogen in the initial experiments.

**Adsorption of Oxygen.**—28 C.c. of carbon monoxide were required to reduce the surface, and beyond this point the reduction was so slow as to be noticeable only after several days. The extent of the reduction was determined by freezing out and measuring the volume of the carbon dioxide formed. The results for the heats of adsorption on the oxidised, reduced, and partly reduced surface are given below. The last value was obtained on a surface reduced with hydrogen. The partly reduced surface gave lower values for the heat of adsorption than either the fully oxidised or the fully reduced surface.

Reduction of surface (c.c. of CO).	Oxygen adsorbed (c.c.).	Heat of adsorption (k.-cals.).	Reduction of surface (c.c. of CO).	Oxygen adsorbed (c.c.).	Heat of adsorption (k.-cals.).
0	0.2	22 *	18	0.03	- 4.6 †
4	0.045	- 6.6 †	28	0.09	+ 19.1
8	0.10	- 6.0 †	30 (H <sub>2</sub> )	0.08	+ 52

\* After oxidation at  $400^\circ$ .

† The adsorption on the partially reduced surface was abnormal. The galvanometer showed an immediate absorption of heat, recorded above, followed by a slow positive evolution. The negative values were not due to the presence of temperature gradients in the oxide, since the addition of helium before the experiments gave no change in temperature.

**Adsorption of Carbon Dioxide.**—The oxidised surface adsorbed 1.8 c.c. of carbon dioxide at a pressure of  $10^{-2}$  cm. For the measurements of heats of adsorption, the gas was admitted 0.6 c.c. at a time and a heat of 20 k.-cals. was obtained for the first admission and 14 k.-cals. for the second. All of the gas could be desorbed on evacuation at room temperature, and the heat of desorption after the first admission gave 19 k.-cals. The rate of desorption was measured, and the Polanyi-Wigner equation,  $\text{rate} = N\nu e^{-Q/RT}$ , applied, the symbols are as defined in the preceding paper. If  $Q$  is calculated from the rate, a value of 22 k.-cals. is obtained for the heat of desorption. On the fully reduced surface the heat of adsorption of carbon dioxide was lower: 0.5 c.c. gave 14 k.-cals. The heat of desorption of this gas was 13 k.-cals. These results show that very little activation energy is needed for the adsorption of carbon dioxide, in agreement with the majority of the results in previous papers.

**Adsorption of Hydrogen.**—No hydrogen could be adsorbed on the oxidised or reduced surfaces at room temperature, although at  $400^\circ$  the catalyst could be readily reduced. Neither was there any appreciable adsorption of hydrogen when the gas was mixed with oxygen. This is in agreement with the experiments of Taylor and Williamson (*loc. cit.*), who did not obtain appreciable "activated" adsorption of hydrogen below  $100^\circ$ .

**Adsorption of Carbon Monoxide, followed by Oxygen.**—The carbon monoxide was adsorbed on the oxidised surface, and oxygen admitted subsequently to the same surface. The quantity of oxygen adsorbed was always less than the stoichiometric proportion given by the ratio  $\text{CO} : \frac{1}{2}\text{O}_2$ . Three series were carried out:

Gas.	C.c. adsorbed.	Heat of adsorption (k.-cals.).	Total (k.-cals.).	Gas.	C.c. adsorbed.	Heat of adsorption (k.-cals.).	Total (k.-cals.).
CO	0.602	46 }	85	CO	0.682	48 }	80
O <sub>2</sub>	0.132	78 }		O <sub>2</sub>	0.168	64 }	
CO	0.546	45 }	83				
O <sub>2</sub>	0.113	76 }					

Carbon monoxide could not be desorbed from the oxide at room temperature until the oxygen had been adsorbed, whereupon it could be completely desorbed as carbon dioxide with a heat of 22 k.-cals. This is the same as the heat of adsorption of carbon dioxide on the oxide surface, so that it is clear that the same adsorption state has been reached from carbon monoxide and oxygen as was obtained with carbon dioxide.

If the surface was saturated previously with 1.81 c.c. of carbon monoxide, only about 0.19 c.c. of oxygen was adsorbed, with a heat of 76 k.-cals., which was the same as that given in the above table, but in this case the heat was liberated slowly and was not completely evolved until 20 mins. had elapsed. This indicates that adsorbed oxygen is undergoing a slow reaction with the surface. On desorption, the carbon dioxide was evolved at room temperature with a heat of 20 k.-cals.

A mixture of  $\text{CO} + \frac{1}{2}\text{O}_2$  was admitted to the oxidised surface (0.4 and 0.8 c.c. respectively) and completely adsorbed. A heat of 85 k.-cals. was liberated, which is in agreement with the total heat

in the above table. The heat of desorption of carbon dioxide in this case was 18 k.-cals., which is within a few calories the same as the heat of adsorption of carbon dioxide.

On the surface reduced with 28 c.c. of carbon monoxide, carbon monoxide was adsorbed with a heat of 33 k.-cals. (0.7 c.c. adsorbed).

#### DISCUSSION.

The measurements of the heats of adsorption on the mixed oxide,  $\text{MnO}_{1.5}\text{Cr}_2\text{O}_3$ , and the two oxides separately do not bring to light any phenomena which might be said to characterise promoter action. The research has only been concerned with measurements at one temperature. For the study of promoter action, measurements need to be made over a range of temperatures, in order to cover adequately the range at which chemisorption occurs. At room temperature, the slight adsorption of hydrogen on the separate oxides, and negligible adsorption on the mixed oxides, make it impossible to obtain much information about promoter action in so far as the adsorption of hydrogen is concerned.

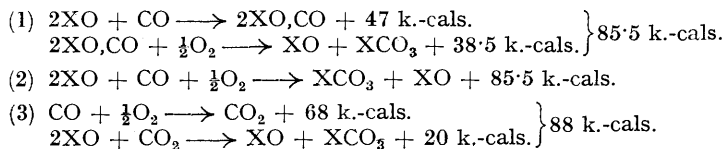
It has become evident as the work proceeded that measurements were giving information on the reduction of oxides by hydrogen and carbon monoxide. This aspect of the results will be dealt with in a separate communication. This discussion will be limited to aspects more specifically derived from the results in the present paper.

It is a striking fact that, for both manganous oxide and manganous-chromic oxide, the reduction of the surface at  $400^\circ$  does not materially increase the quantities of oxygen which can be taken up at room temperature. This is in marked contrast with the behaviour of  $\text{ZnO}$ ,  $\text{Cr}_2\text{O}_3$  and  $\text{Cr}_2\text{O}_3$ , where there is an increase on reduction of the quantities of oxygen adsorbed. These differences in behaviour are very probably due to differences in the mobility of the constituents of the lattice at the temperature at which the reduction is carried out. Too little is known about these movements in the case of these oxides to warrant an attempt at a very precise interpretation. The oxides belong to the semi-conductor class for which there is an appreciable electrical conductivity due to lattice defects. A possible interpretation of the results with manganous oxide and manganous-chromic oxide is that the oxygen ions are mobile at the temperature of reduction and that the effects of reduction of these oxides are made good by the diffusion of oxygen from the lattice to the surface at which reduction occurs.

When an oxide is reduced with hydrogen, it is difficult to remove the last traces of water. These materially affect the heats of adsorption, as was pointed out previously in the paper on  $\text{Cr}_2\text{O}_3$ . A hydrogen-reduced surface of manganous-chromic oxide gives a greater heat of adsorption of oxygen than a carbon monoxide-reduced surface. The heat obtained approaches that given when oxygen is adsorbed on a surface containing carbon monoxide. The high heat may thus be due to lattice defects caused by the presence of hydroxyl ions in the lattice.

The results obtained with carbon monoxide and carbon dioxide are perhaps of the greatest interest, since they can be interpreted unequivocally. Carbon dioxide is adsorbed on manganous oxide, manganous-chromic oxide, and chromic oxide to give carbonates without the necessity for activation energy. The heat of desorption is the same as the heat of adsorption, and the rate of desorption can be calculated from the Polanyi-Wigner equation.

When carbon monoxide is adsorbed on the oxidised surface, the product formed cannot be dissociated at room temperature, and carbon dioxide is evolved only after the temperature is raised. The surface is, however, unsaturated after the adsorption of carbon monoxide, and can take up oxygen. When the unsaturation has been removed, carbon dioxide can be desorbed by evacuation at room temperature. The same final state is produced, whether starting from carbon dioxide or from carbon monoxide, provided in the latter case that oxygen be added at the same time. This is made clear by the following data derived from the heats of adsorption :



The agreement between the heats for the three processes shows that a carbonate is produced in the reaction of carbon monoxide and oxygen with the oxide.

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