182. *The Heats of Adsorption of Gases on the Oxides of Manganese at Low Pressures and Room Temperature.*

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The heats of formation of carbon monoxide, carbon dioxide, oxygen, and hydrogen on an oxide of manganese in various stages of reduction have been measured in a thermocouple calorimeter. It is shown that the heats of adsorption obtained are dependent on the degree of unsaturation of the surface.

This investigation forms a part of a series which was planned to gain a knowledge of the changes in adsorptive properties which occur on mixing two oxides, and, in particular, to study those cases where compounds were formed between the oxides. Veal and one of us (J., 1935, 1487) have investigated the adsorption of gases on zinc oxide and ZnO,Cr_2O_3, and the present work deals with the oxides of manganese. Other investigations in hand include the measurements of the heats of adsorption of gases on Cr_2O_3 and Mn_2O_3,Cr_2O_3, and when these studies are completed it is hoped to be able to throw some light on the changes in surface activity which arise on admixture of two oxides. Attention has been directed mainly to the adsorption of hydrogen, oxygen, carbon monoxide, and carbon dioxide on these surfaces, and the heats of adsorption of these gases have been measured by means of the thermocouple calorimeter described by Veal and one of us (J., 1935, 1436), the adsorption processes being followed by pressure measurements.

The *X*-ray structures of the oxides of manganese prepared from oxalate and carbonate at various temperatures and subjected to varying amounts of oxygen have been determined by Blanc and Wehner (*Z. physikal. Chem.*, 1933, *A*, **168**, 59). When prepared at 350° from the oxalate, an active MnO could be obtained which would take up oxygen up to $MnO_{1\cdot58}$. It was shown that the MnO lattice was unchanged by taking up oxygen up to $MnO_{1\cdot13}$, above which ratio Mn_3O_4 appeared. The latter could take up oxygen up to

$MnO_{1\cdot42}$, whereat a hitherto unknown modification of Mn_2O_3 made its appearance. Also, starting from MnO_2, oxygen was removed and the ordinary Mn_2O_3 lattice obtained immediately, there being no evidence of solid solutions between these oxides. These experiments show that there is some solubility of oxygen in the lattices of MnO, Mn_3O_4, and Mn_2O_3, but that complete series of solid solutions are not formed from these oxides.

In the present work, it was decided to subject the oxide to the same treatment as was followed in the research on zinc oxide and ZnO,Cr_2O_3. This involved oxidation and reduction at 400° and freeing from adsorbed gases at 450°. The process of oxidation gave an oxide which contained a little less oxygen than corresponds with the formula Mn_2O_3. On reduction, this gave mixtures with compositions between Mn_3O_4 and Mn_2O_3, so that in the present research we are concerned with adsorption on surfaces being within this range.

The heat of adsorption of carbon monoxide on manganese oxides has been calculated by Charachorin and Elowitz (*Acta Physicochim. U.S.S.R.*, 1936, **5**, 323) from adsorption isotherms at —78·5° to 11·5°, and the average value found was 2·3 kg.-cals./mol. over the range 6—25 × 10^{18} mols. per g. of oxide. This is in agreement with the results of earlier papers by Roginsky and Zeldowitch (*ibid.*, 1934, **1**, 554, 595). The adsorption is evidently of the van der Waals type, but above —15° there was evidence of the commencement of chemisorption, and the activation energies determined from rate of change of pressure were found to vary from 5400 to 13,000 kg.-cals. with increasing surface density over the range —20° to 24·5°. It has been shown in the present work that the adsorption at room temperature is very complex, the adsorption being followed by a slow heat evolution of which no hint would be given on pressure–time curves The heats obtained vary from 67 to 22 kg.-cals., decreasing with increasing surface density. The above variations in the activation energies are therefore readily understandable. The above authors find the adsorption of carbon dioxide to be very complex, with evidence of chemisorption above 25°, and record no values for the heats of adsorption. Taylor and Williamson (*J. Amer. Chem. Soc.*, 1931, **53**, 2168) have studied the adsorption of hydrogen on manganous oxide and their results indicate that chemisorption occurs between 184° and 218° K. with activation energies increasing with surface density from 12·4 to 20·8 kg.-cals.

There are a number of investigations on the dissociation of manganese carbonate, of which that of Krustinsons (*Z. Elektrochem.*, 1932, **38**, 780) may be quoted. He finds that the natural crystalline carbonate has the dissociation pressure of 1 atm. at 408°, and that $Q = 25\cdot39$ kg.-cals. Synthetic manganese carbonate is found to dissociate at much lower temperatures, giving 1 atm. at 200—330°. There is no doubt that evacuation at 450° for several hours should suffice to decompose manganese carbonates completely. The heat of adsorption of carbon dioxide on the oxide used in the present research was 23⟶18 kg.-cals., which is somewhat lower than the above heat of dissociation.

EXPERIMENTAL.

Preparation of Oxide.—An aqueous solution of manganous sulphate was treated with potassium hydroxide solution, and the precipitate washed until there was no trace of potassium in the washings. The precipitate was broken up into small pieces, and oxidised at 400° in oxygen for several days. Analysis of the oxide, after baking out at 450°, showed that its empirical formula was $MnO_{1\cdot48}$.

Preparation of Surface of Oxide.—The oxide was employed in the fully oxidised, and in the fully and the partly reduced state. Reduction was brought about with either carbon monoxide or hydrogen at 400°, the latter substance being the more effective in reducing the oxygen content of the oxide. It was found that 64 c.c. of carbon monoxide could be oxidised in the process of reduction, giving a final composition of $MnO_{1\cdot46}$ for the oxide, but that 243 c.c. of hydrogen would react with the oxide surface giving a final composition of $MnO_{1\cdot40}$. The oxide was not reduced with hydrogen until a series of heats of adsorption had been made with carbon monoxide, dioxide, and oxygen. Before use in the measurement of heats of adsorption, the oxide was baked out at 450° for 3 hours under high vacuum.

Calorimeter.—This was of the type 1, f described by Garner and Veal (*loc. cit.*), and the weights of the components in the container were : platinum, 1·8972 g. ; pyrex, 4·7740 g. ; oxide, 11·1632 g. In calculating the water equivalent, the specific heats used were respectively 0·0314, 0·020, 0·164 cals./g. Experiments were carried out at 17° approx. The platinum–platinum-rhodium thermocouple was employed in conjunction with the Z.c. Kipp and Zonen galvanometer at a sensitivity of about 10 cm. per degree, the necessary calibrations being made against a standard Beckmann thermometer. The temperature of the calorimeter fluid was changed by the addition of either ice or hot water.

There were only two minor changes in the experimental arrangement. The thermocouple leads were brought out of the calorimeter in twin tubing with the object of minimising temperature differences along the leads, and the calorimeter and leads were enclosed in a wooden case with a window for observation of thermometers.

Cooling Correction.—It was found in a preliminary series of experiments that the cooling correction—loss of temperature per min. for a difference of temperature of 1° between the calorimetric fluid and the thermocouple—was independent of the gas pressures in the calorimeter up to 10^{-2} cm., and also that the thermal conductivity of the catalyst was sufficiently good to make it unnecessary to use helium as a diluting gas. It therefore became possible to employ a new method for determining the cooling corrections. This consisted in saturating the catalyst with gas, *e.g.*, carbon monoxide or dioxide up to pressures of 10^{-4}, 10^{-3}, 10^{-2} cm., etc., and then decreasing the temperature of the calorimeter by a fraction of a degree by adding ice-water, which change does not appreciably affect the equilibrium established between the gas and the surface. The cooling correction varied with time as follows: After 5—7½ mins., 0·0148°; 7½—10 mins., 0·0164°; 10—15 mins., 0·0186°; and 20—30 mins., 0·020° per min. for 1° difference of temperature. These values were found to be independent of the pressure in the calorimeter over the range from a hard vacuum to 10^{-2} cm., and independent of the nature of the gas. It was therefore decided to keep the gas pressure in the adsorption experiments below 10^{-2} cm., and to use the above cooling corrections in calculating heats of adsorption.

Preliminary Experiments on the Reduction with Carbon Monoxide.—The oxide, without having been previously in contact with hydrogen gas, was fully oxidised, and after being evacuated at 450°, was treated with small quantities of carbon monoxide at room temperature. After each treatment, the temperature was raised to 450° for 6 hrs. under a high vacuum, and any carbon dioxide evolved was collected in a liquid-air trap. The amounts of carbon monoxide adsorbed, and evolved as carbon dioxide are given below for a series in which the surface was progressively reduced. The range of gas pressures at equilibrium varied from 2 to 5 × 10^{-3} cm. The amount of carbon monoxide adsorbed on the surface at room temperature was ~ 2 c.c. at all stages in the reduction process, so the adsorption area of the oxide towards carbon monoxide is not appreciably modified by the reduction. The fluctuations in the values for carbon monoxide adsorbed are probably due to irregularities in the baking out. In the early stages of the reduction, the adsorbed carbon monoxide was evolved mainly as carbon dioxide, but in the later stages the efficiency of the reducing agent decreases. After 64 c.c. of carbon monoxide had been oxidised, the reduction became very slow.

Reduction, c.c. of CO ...	0	1·4	2·8	4·1	5·2	6·6	10·7	25·9	35·9	53·2
C.c. of CO admitted ...	1·87	2·34	2·23	1·81	1·95	2·09	2·43	3·90	3·92	3·93
C.c. of CO adsorbed ...	1·57	1·67	1·42	1·32	1·56	1·50	1·84	2·16	2·16	2·33
C.c. of CO_2 evolved	1·37	1·41	1·27	1·19	1·34	1·23	1·55	1·57	1·58	

Heats of Adsorption.—The heats of adsorption of carbon monoxide, carbon dioxide, oxygen, and hydrogen have been measured on the fully oxidised, fully reduced, and various intermediate surfaces. In the early experiments, helium was mixed with the gas, but it was found subsequently that the thermal conductivity of the oxide was sufficiently high to make the employment of helium unnecessary. Except for carbon monoxide, steady values were obtained after about 10 minutes, and these values are given in the following tables. For carbon monoxide there was a slow evolution of heat after the adsorption had taken place, and this was nearly complete in about 20 minutes.

Carbon Monoxide.—One complete series for the adsorption of carbon monoxide on the oxidised surface is given in Table I. The heats of adsorption are given in kg.-cals./mol. adsorbed up to various times during a run. Experiments 1—7 were performed on one day and the remainder on the following day. The gap between 7 and 9 is due to an attempt to desorb some of the adsorbed gas, which was unsuccessful. In spite of the interruption, the heats fall steadily throughout the series. Another series gave practically identical results.

In the early admissions of carbon monoxide, the adsorption was practically complete after 8 mins., and the subsequent evolution of heat must be due to some rearrangement either of the adsorbed gas on the surface or of the surface itself. Attempts were made to separate the two processes which occur, but they overlap to such an extent that quantitative separation was not found to be possible. Beebe and Dowden (*J. Amer. Chem. Soc.*, 1938, **60**, 2912), in studying the adsorption of carbon monoxide on Cr_2O_3 at liquid-air temperatures have shown the existence of two stages in the adsorption process which are clearly separable. The heats obtained for the two processes are, however, 4 and 12 kg.-cals. respectively, and they regard the first as van der Waals and the second as activated adsorption. In the case of the adsorption on Mn_2O_3 at room temperature, the first process is considered to be chemisorption, and the second to be in large part due to a reorganisation of the atoms forming the surface of the crystal lattice (see p. 862).

TABLE I.

Kg.-cals./mol.

Admission :	1.	2.	3.	4.	5.	6.	7.	9.	10.	11.
2 mins.	39·4	—	21·2	18·0	21·2	19·0	19·8	20·4	19·5	17·0
5	52·3	36·6	27·8	28·3	28·4	25·6	24·6	24·8	23·0	19·4
8	57·2	44·7	34·2	35·2	33·5	29·3	28·0	27·4	25·7	20·4
11	59·8	51·5	38·6	38·6	38·0	32·2	30·4	29·4	28·0	21·3
14	62·5	55·5	43·5	41·0	42·5	34·3	34·0	31·8	30·2	22·0
17	63·6	58·1	45·6	43·2	44·9	36·3	34·0	34·0	31·6	22·4
20	64·4	60·1	—	45·6	48·2	38·0	33·0	35·8	32·2	22·4
C.c. adm.	0·132	0·111	0·059	0·122	0·215	0·310	0·656	0·206	0·586	0·548
C.c. ads.	0·131	0·110	0·062	0·119	0·205	0·286	0·574	0·182	0·388	0·250

The heats of adsorption for the first admission of 0·2—0·4 c.c. of carbon monoxide to the surface in various stages of reduction are given in Table II. Each figure is the mean of several determinations except that an asterisk indicates that only one measurement was made. The heats of adsorption which are given for this gas are those obtained after the 20th minute, in spite of the fact that there may have been a slow adsorption of heat after this time. This has been done since the radiation correction becomes so large after 20 mins. that appreciable errors may be introduced into the heat measurements. There has, however, been very little heat lost, as is shown by the balance sheet on p. 863.

Carbon Dioxide.—The amount of carbon dioxide adsorbed at a pressure of 5×10^{-3} cm. was $\sim$ 1·5 c.c., and this remained practically constant throughout the reduction process. It will be noted that the quantities adsorbed are very similar to those found for carbon monoxide, indicating that these two gases may be adsorbed on the same centres. The heats of adsorption on the oxidised surface were measured on the admission of 0·3—0·5 c.c. of gas. The first admissions gave an average value of 23·3 kg.-cals., and the adsorbed gas was desorbed extremely slowly on applying a hard vacuum. The second admission gave 20·3 kg.-cals. and this gas could be desorbed and the heat of desorption measured. In the calculation of the heats of desorption, it was assumed that the whole of the adsorbed gas was desorbed within 20 mins. The figures obtained are shown below.

Admission :	1.	2.	3.	4.	5.	6.	7.	8.
Heat of adsorption (kg.-cals./mol.)	23·3	20·3	19	19·3	19·2	20·7	18·9	17·5
Heat of desorption (kg.-cals./mol.)	—	17·2	17·8	19·2	18·4	18·8	17·5	16·3
Initial rate of desorption (mols./sec. × 10^{-16})	—	—	1·5	0·9	1·2	1·0	1·3	1·3

The agreement between the heats of adsorption and desorption, except for admission 2, is sufficiently close to warrant the assumption that the activation energy for the adsorption of carbon dioxide on Mn_2O_3 is very small. This is in agreement with the conclusions of Zawadski and Bretsznajder (*Z. Elektrochem.*, 1935, **41**, 215), *viz.*, that the adsorption of carbon dioxide on oxides to give carbonates is a process requiring little or no activation energy. From the initial rates of desorption, the heat of desorption may be calculated from the Polanyi–Wigner theory, *e.g.*, rate $= N\nu e^{-Q/RT}$, where N is the number of molecules adsorbed, $\nu = 10^{13}$, and Q is the heat of desorption. The calculated values for the above series range from 21·0 to 21·5 kg.-cals./mol. These are 2—3 kg.-cals. higher than the experimental values, which is to be expected in view of the fact that we are dealing with diffusion processes in a porous material.

The heats of adsorption on the partly reduced surfaces were higher than on the fully oxidised or fully reduced surfaces, but after three admissions of 0·5 c.c., these heats fell to those obtained on the oxidised surface, *viz.*, 18—20 kg.-cals. The values for the first admissions of 0·3—0·5 c.c. are given in Table II.

Adsorption of Hydrogen.—The oxide adsorbed only small quantities of hydrogen at room

Reduction of surface, c.c. of H_2	0	24	79	234
Amount adsorbed at saturation	0·14	0·03	0·15	0·17

temperatures, and hence the heats were difficult to determine accurately. The amounts of gas adsorbed at a pressure of 5×10^{-3} cm. are given on p. 860 for various stages of reduction, and the heats are given in Table II.

Adsorption of Oxygen.—This gas was only slightly adsorbed at room temperature, greater amounts being adsorbed on the partly reduced surfaces than on the oxidised or fully reduced surfaces. The results for the amount of gas adsorbed at saturation are summarised below.

		CO.			H_2.
Reduction of surface, c.c.	0	9·2	18·6	64	234
Amount adsorbed at saturation	0·2	0·3	0·6	0·4	0·2

A number of second admissions were made. Thus, for the oxidised surface, the first 0·15 c.c. gave 24 and the next 0·05 c.c. gave 10—16 kg.-cals., according to the amounts adsorbed. The rate of adsorption of this oxygen was rapid, and yet there was no appreciable desorption at room temperature of the gas adsorbed with the low heats on applying the pumps. The adsorption of oxygen is therefore possibly activated, but no definite decision can be reached on this point since the Polanyi–Wigner equation might not apply to the desorption of chemisorbed oxygen as molecular oxygen.

TABLE II.

Summary of Heats of Adsorption on MnO_2.

			CO.			H_2.		
Reduction of surface, c.c.		0.	9·2.	18·6.	64.	24.	79.	243.
Heats of adsorption, kg.-cals./mol.	CO	67	78	74 *	62	—	61 *	45 *
	CO_2	23	36	34 *	36 *	—	—	17·4*
	H_2	48	—	—	—	44	58	30*
	O_2	24	29	36 *	31	—	—	22*

From the above results, it is clear (1) that the adsorption area for carbon monoxide, carbon dioxide, hydrogen, and oxygen is practically constant throughout the reduction process, and (2) that the heat of adsorption is greater on the partly reduced than on the fully oxidised and fully reduced surfaces, no marked differences being observed in the behaviour of the surface reduced in the two ways.

Adsorption of Oxygen on a Surface containing Adsorbed Carbon Monoxide.—It has been shown by Garner and Veal (*loc. cit.*) that for ZnO,Cr_2O_3, treatment of the surface with carbon monoxide increases its ability to absorb oxygen. The additional oxygen taken up in the case of the spinel was one-half of the carbon monoxide adsorbed. Similar experiments with the manganese oxide have now shown that additional oxygen is taken up after saturation of the surface with carbon monoxide. Experiments were carried out on (*a*) the oxidised surface after baking out for 3 hrs. at 450° and on (*b*) the same surface after the additional treatment with oxygen at room temperature. The results are given below :

	Gas adsorbed.	(*a*).	(*b*).
I	(i) O_2	—	0·15
	(ii) CO	1·44	1·85
	(iii) O_2	0·50	0·63

	Gas adsorbed.	(*a*).	(*b*).
II	(i) O_2	—	0·15
	(ii) CO_2	1·54	1·10
	(iii) O_2	0·11	0·09

	Gas adsorbed.	(*a*).	(*b*).
III	(i) CO	1·53	—
	(ii) CO_2	0·81	—

The additional oxygen taken up after the carbon monoxide treatment was about one-quarter of the carbon monoxide adsorbed, whereas there is no additional oxygen adsorbed after carbon dioxide treatment. It is clear that the adsorption of carbon monoxide activates the surface for the adsorption of oxygen. Expt. III is of interest since it is possible that the carbon dioxide is adsorbed on the activated portions of the surface, but this point was not investigated further.

A number of heat measurements were made for the adsorption of oxygen on a fully oxidised surface treated with small amounts of carbon monoxide, and these were distinctly higher than any obtained before on the gas-free surfaces. It was also found that the heat on the second admission was higher than for the first :

Admission of CO.	1.	2.
CO adsorbed, c.c.	0·178	0·69
Heat of adsorption, kg.-cals./mol. of O_2	47·5	54

Three series of experiments were also made on the fully oxidised surface with the mixture $2CO + O_2$ and the total heat obtained in each series was the same although there were variations between the single results (see Table III). There was no drift in the values for the heats given in the above two tables, constant heats being obtained after the 11th minute.

TABLE III.

	I.		II.		
	Gas adsorbed, c.c.	Heat, kg.-cals./mol.	Gas adsorbed, c.c.	Heat, kg.-cals./mol.	Average heat, kg.-cals./mol.
(i)	0·56	77·5	0·40	85	82
(ii)	0·59	89·0	0·42	71	80
(iii)	0·50	81·0	0·45	89	85

DISCUSSION.

In the adsorption of gases on surfaces, it is necessary to take into account, not only changes occurring in the adsorbed molecules themselves, but also those occurring in the surface and the lattice of the solid. Where van der Waals adsorption occurs and the molecules are held to the surface by physical forces, there will be but slight alterations occurring in the surface, but where the adsorption is of the nature of a chemical process, there may be far-reaching modifications of the surface of the adsorbent. In the present research some information has been gained as to the nature of the changes in the surface during chemisorption.

It has been shown that the area of the surface of the manganese oxide which is available for adsorption after baking out at 450° is not appreciably enlarged by reduction with either carbon monoxide or hydrogen over the range $Mn_2O_3 \rightarrow Mn_3O_4$. This is true for the adsorption of all of the following gases: carbon monoxide, carbon dioxide, hydrogen, and oxygen. It is noteworthy that the reduced surface adsorbs no more oxygen than the fully oxidised surface, although during reduction one-fourteenth of the total oxygen has been removed. This is in marked contrast with the behaviour of the reduced surfaces of ZnO,Cr_2O_3 and Cr_2O_3, which can adsorb very large quantities of oxygen at room temperature. In the process of reduction and subsequent baking out of the manganese oxide, there must be some lattice reorganisation or sintering which converts an unsaturated into a nearly completely saturated surface. The mobility of the atoms in the lattice of manganese oxide must be appreciably greater than is the case for ZnO,Cr_2O_3 or Cr_2O_3 at the same temperatures.

When carbon monoxide is adsorbed on the oxidised surface, the adsorption is followed by a slow evolution of heat. The same behaviour is shown by ZnO,Cr_2O_3 (cf. Garner and Veal, *loc. cit.*, Table III), but in this case the rearrangement resulting in the evolution of heat takes place considerably more slowly than in the case of Mn_2O_3. This is shown by the fact that the length of the time interval between admissions does not affect the heat in the latter case whereas there is a marked effect with ZnO,Cr_2O_3. In spite of the secondary development of heat, which apparently reaches completion within 20—25 mins. in the case of manganese oxide, the surface is still more active towards oxygen than one from which carbon dioxide has been expelled by baking out at 450°. This is shown by the fact that the heat of adsorption of oxygen on the carbon monoxide-treated surface is 14 kg.-cals. greater than on a partly reduced surface, and is 24 kg.-cals. greater than on an oxidised surface. In the removal of carbon dioxide from the surface, there must be some destruction of the surface activity towards oxygen.

In the case of chromium oxide, as Dowden has shown (results to be published shortly), carbon monoxide is adsorbed with a heat of 29—22 kg.-cals. with no secondary development of heat, and one of us (T. W.) has shown that this adsorption is chemisorption, since when the temperature is raised the gas is desorbed entirely as carbon dioxide. The heat of adsorption of oxygen on the carbon monoxide-treated surface of chromium oxide is 55 kg.-cals. higher than on the same surface from which carbon dioxide has been removed by evaporation, indicating that a very large amount of unsaturation is present on the surface treated with carbon monoxide. Bearing in mind the fact that the unsaturation is less on the carbon monoxide-treated surface of Mn_2O_3 than for Cr_2O_3, and that in the former case a slow evolution of heat follows the adsorption of carbon monoxide, it seems likely that the latter heat arises as a result of the destruction of surface unsaturation. By taking account of this surface unsaturation and its disappearance in certain processes, it is possible to provide a consistent explanation of many features of the heats of adsorption recorded in the experimental part of this paper.

The processes occurring during the adsorption of carbon monoxide on an oxide surface can be represented by the following scheme :

where X is a lower form of the oxide. This scheme postulates van der Waals adsorption followed by chemisorption with the production of a carbonate ion and unsaturation of the surface. The number of unsaturated places on the surface produced in the formation of carbonate should be equal to the number of carbon monoxide molecules adsorbed, and this was proved to be the case for ZnO,Cr_2O_3, if the oxygen were admitted along with the carbon monoxide. It is suggested that these places of unsaturation in the case of Mn_2O_3 and ZnO,Cr_2O_3 decrease in number at room temperature as a result of lattice rearrangements, but that this does not occur for Cr_2O_3. This rearrangement would be accelerated if the carbonate ions were mobile and moved over the surface to build a carbonate lattice, in which event the stability of the unsaturation in the case of Cr_2O_3 would be due to the lack of mobility of the CO_3'' ions.

In view of the occurrence of secondary processes in the adsorption of oxides, it is of interest to employ the above figures on heats of adsorption in an attempt to determine if there is any energy unaccounted for in the conversion of carbon monoxide and oxygen into carbonates. The heats of adsorption for the first admissions of carbon monoxide, carbon dioxide, and oxygen are utilised in three schemes. In the first scheme, the carbonate is formed by the addition of carbon monoxide and oxygen separately to the oxidised surface. In the second, the carbon monoxide and oxygen are admitted together, and in the third carbon dioxide is adsorbed directly on the oxide surface.

$$\begin{array}{lll}
\text{I.} & a.\ 2XO + CO \longrightarrow XCO_3 + X + 67 \text{ kg.-cals.} & \multirow{2}{*}{$\left.\right\}$ 91 kg.-cals.} \\
 & b.\ XCO_3 + X + \tfrac{1}{2}O_2 \longrightarrow XCO_3 + XO + 24 \ \ ,, & \\
\text{II.} & \quad 2XO + \tfrac{1}{2}O_2 + CO \longrightarrow XCO_3 + XO + 82 \ \ ,, & \\
\text{III.} & a.\ CO + \tfrac{1}{2}O_2 \longrightarrow CO_2 + 68 \ \ ,, & \multirow{2}{*}{$\left.\right\}$ 91 kg.-cals.} \\
 & b.\ CO_2 + 2XO \longrightarrow XCO_3 + XO + 23 \ \ ,, &
\end{array}$$

There is good agreement between the total heats of I and III which shows that little energy has been lost in the course of *a* and *b* in scheme I. The fact that the heat in II is less than that in III is of interest, for it indicates that when oxygen and carbon monoxide are adsorbed simultaneously, there remains appreciable although variable unsaturation on the surface. This is probably caused by the rapidity of the adsorption process which leads to a haphazard distribution of adsorbed molecules and places of unsaturation over the surface. Table III shows that the amount of unsaturation after the adsorption of carbon monoxide and oxygen in first admissions is variable, due to some factor not under control, and that where, owing to any cause, unsaturation is left after the first admission, there is an increase in the heat of the second admission.

It will be in accord with the above theory of the surface processes to ascribe the greater values obtained for the heats of adsorption (Table II) on partly reduced surfaces to the occurrence of a higher degree of surface unsaturation in these cases.

In the formation of carbonates, there are three successive stages occurring during the adsorption : (1) van der Waals adsorption, (2) the formation of surface carbonates, and (3) the destruction of the oxide lattice and the formation of the carbonate lattice. In the present investigation, it has been shown that the heat of adsorption of carbon dioxide on the oxidised surface of the manganese oxide ranges from 23 to 18 kg.-cals. according to the surface density employed, and Krustinsons (*loc. cit.*) has shown that the heat of dissociation of crystals of manganous carbonate is 25·4 kg.-cals. The agreement between these two values is sufficiently close to indicate that a carbonate is formed on the surface when carbon dioxide is adsorbed. The heat of desorption of carbon dioxide from the surface carbonate is the same as the heat of adsorption within experimental error; therefore the activation energy for carbonate formation in this case is very small. This is in accord with the earlier work on the adsorption of carbon dioxide on zinc oxide, where the activation energy must be small also. Zawadsky and Bretsznajder (*loc. cit.*), from a study of the thermal decomposition of carbonates (calcium, silver carbonates, etc.), conclude that there is little activation energy involved in the formation of carbonates. It is, however, unwise to generalise from these results that there is no activation energy involved in any cases of carbonate formation, for it was found in the previous paper that carbon dioxide adsorbed on ZnO,Cr_2O_3, although occurring with the low heat of 15—13 kg.-cals., could not be desorbed at appreciable rates at room temperature on evacuation. In this case, there is probably some activation energy needed since, according to the Polanyi–Wigner equation, which fits the facts of reversible non-activated adsorption fairly well, the adsorbed gas should be readily desorbed if the heat of adsorption is less than 20 kg.-cals.

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