234. *The Reduction of Oxides by Hydrogen and Carbon Monoxide.*

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The previous investigations on the heats of adsorption of hydrogen, carbon monoxide, oxygen, and carbon dioxide on ZnO, $MnO_{1.5}$, Cr_2O_3 and their mixtures have been summarised. These oxides are semi-conductors and there is considerable mobility of ions in the oxide lattice at the temperature of reduction. The adsorption at room temperature takes place on a surface which may be the result of an equilibrium set up in a lattice defect structure at higher temperatures.

Reversible chemisorption of carbon monoxide occurs on metal-rich oxides with negative holes, and irreversible chemisorption on oxides with positive holes. The two types of chemisorption are not readily interconvertible. The reversible adsorption of carbon monoxide on zinc oxide, and the adsorption of carbon dioxide on the oxides of the transition elements occur without appreciable activation energy. It is suggested that when carbon monoxide is adsorbed irreversibly, there is set up a resonating system involving the S and D shells of the transition element. This system is moved in the direction of the carbonate ion, when the stoicheiometric quantity of oxygen is adsorbed on the surface. The ease with which the carbonate ion is dissociated is thus determined by the number of unpaired electrons in the D and S shells of the transition element.

INVESTIGATIONS on the reduction of metallic oxides by hydrogen and carbon monoxide have shown that the reaction proceeds through a number of intermediate stages to yield hydroxides and carbonates which decompose to produce the lower oxide or metal (Garner and Kingman, *Trans. Faraday Soc.*, 1931, **27**, 322; Garner and Veal, *J.*, 1935, 1436, 1487; Dowden and Garner, *J.*, 1939, 894; Garner and Ward, *J.*, 1939, 858; Ward, following paper). The processes which precede the evolution of water or carbon dioxide include (*a*) van der Waals adsorption, which is specially predominant at low temperatures, and also (*b*) several types of chemisorption. The rate of chemisorption on oxides increases rapidly with increase of temperature, which led Taylor (*J. Amer. Chem. Soc.*, 1931, **53**, 578) to designate this type of process as " activated " adsorption. The heats of chemisorption of carbon monoxide and hydrogen on a number of oxides range from 15 to 70 k.-cals./mol., according to the oxide. It is found that if the heat of adsorption is below 20 k.-cals./mol., the gas can be desorbed unchanged on raising the temperature, but when the heat is greater than this value, the adsorption is usually irreversible, in the sense that, on warming, carbon dioxide or water is evolved. The results have been obtained on oxides which are reducible with difficulty. They may, however, be capable of application to easily reduced oxides, where the various stages in the reaction may proceed too quickly for them to be readily isolated from one another.

Chemisorption of Carbon Monoxide and Hydrogen.—In Table I are summarised the heats of adsorption of the two gases on a number of oxides at room temperature. On zinc oxide, carbon monoxide is adsorbed reversibly and carbonates are not formed, the activation energies and heats of reaction being unfavourable for the formation of carbonates in this case. For a mixture of zinc and chromium oxides, the adsorption of hydrogen or carbon monoxide is partly reversible and partly irreversible, the proportion of the two types of chemisorption depending on the state

TABLE I.

Heats of adsorption (in k.-cals./mol.) of CO and H_2 on oxidised and on reduced surfaces.

	H₂.		CO.		
Substance.	Reduced.	Oxidised.	Reduced.	Oxidised.	Remarks.
ZnO	No appreciable adsorption		20	18 → 13	Reversible desorption of CO at room temp.
Cr_2O_3	36	72	29 → 22	28 → 12	Hydrogen very difficult to remove, even by long treatment at 450°; CO evolved as CO_2 at 70—400°.
$MnO_{1.5}$	44	30	67	62	
ZnO, Cr_2O_3	13 → 10	48 → 13	15 → 11	44 → 16	Partial desorption of CO and H₂ at room temp.
$MnO_{1.5}$, Cr_2O_3	No appreciable adsorption		33	47	CO not desorbed at room temp.

of reduction of the oxide. On heating the oxide on which hydrogen or carbon monoxide is reversibly chemisorbed to 100—200°, the gas is evolved unchanged. The pressure rises to a maximum and then falls to zero. On further heating to 400° the gas is evolved as water or carbon dioxide respectively. It is clear that the direct conversion from reversible to irreversible chemisorption does not occur, since the surface reaction is hindered by a high potential energy barrier which is greater than the heat of desorption of the gas (see Fig.). This may be due to the two states of adsorption taking place on different centres. For the other oxides quoted in Table I, the adsorption is, for the most part, irreversible.

Formation of Carbonates.—Information relevant to the formation of carbonates on the surface of the oxides is given in Table II. The oxides were treated with oxygen at 450°, then evacuated and cooled to room temperature. Measurements were made of the heats of adsorption of carbon monoxide, oxygen, and carbon dioxide, and of mixtures of carbon monoxide and oxygen.

When the carbon monoxide is adsorbed irreversibly, carbon dioxide can be liberated on raising the temperature, but it is difficult to desorb this gas at room temperature. On the other hand, if carbon dioxide is adsorbed on the oxide, the heat of formation of the carbonate is of the order of 20 k.-cals., and the gas can be usually desorbed at room temperature, at a rate given by the Polanyi–Wigner equation, $r = \nu \cdot Ne^{-Q/RT}$, where Q is the heat of adsorption, N is the number of molecules adsorbed on 1 cm.² of the surface, and $\nu = 10^{13}$ sec. The absence of appreciable activation energy in the formation and dissociation of carbonates is in agreement with the conclusions of Zawadzki and Bretsznajder (*Z. Elektrochem.*, 1935, **41**, 215) and Spencer and Topley (*J.*, 1929, 2633). It is, however, clear that when carbon monoxide is adsorbed on an oxide, the product differs in some way from the carbonate formed from carbon dioxide.

TABLE II.

Heats of adsorption (in k.-cals./mol.) of CO and $\frac{1}{2}O_2$ on oxidised surface.

|	1.	2.	3.	4.	5.	6.	7.
	Substance.	CO.	$\frac{1}{2}O_2$ after CO.	CO + $\frac{1}{2}O_2$.	CO_2.	Total heat.	$\frac{1}{2}O_2$ on reduced surface.
ZnO		18	—	—	13	—	—
Cr_2O_3		29	55	84 †	18	66	40—50
		61 *	38 *	—	—	—	—
$MnO_{1.5}$		67	24	82	23	68(59)	31
ZnO,Cr_2O_3		44(18)	22	66	15	51	22
$MnO_{1.5}$,Cr_2O_3		47	39	85	20	65	52 *
							19

      * Oxide containing hydrogen as hydroxide.   † Calculated.

The surface after adsorption of carbon monoxide (col. 2) is, however, unsaturated with respect to oxygen, and a quantity of oxygen can be taken up with the liberation of the heats shown in col. 3. These heats are quite large and depend on the previous history of the oxide as well as on its nature. For Cr_2O_3 the heats are lower if hydrogen is present in the oxide. The observations made with $MnO_{1.5}$,Cr_2O_3 are instructive. The adsorbed carbon monoxide cannot be removed by evacuation at room temperature, but after the adsorption of oxygen or after the adsorption of CO + $\frac{1}{2}O_2$ (col. 4), carbon dioxide is liberated on evacuation with a heat of desorption equal to the heat of adsorption of carbon dioxide (col. 5). In order to produce a carbonate from carbon monoxide with the same properties as that formed from carbon dioxide,

it is necessary to reoxidise the surface with the stoicheiometric quantity of oxygen. It will be noted that the total heats given in col. 6 correspond in most cases with the heat of the reaction, $CO + \frac{1}{2}O_2 \longrightarrow CO_2$, which provides a good check on the accuracy of the measurements.

Formation of Hydroxides.—The position with regard to the formation of hydroxides is not so clear, since the results at room temperature were not sufficiently complete. " Activated " adsorption of hydrogen does not readily occur on some of the oxides at room temperature. It was shown, however, in a number of cases that the surface reduced with hydrogen was not unsaturated to the same extent as with carbon monoxide. Also, the hydrogen adsorbed irreversibly is so tightly held that it is difficult to remove it completely without sintering the oxide. Thus no information could be obtained with regard to the heat of desorption of water. For Cr_2O_3, the hydrogen cannot be completely removed, even at 450°. It can, however, be removed in the course of the reduction by carbon monoxide, which mobilises the adsorbed hydrogen. The residual hydrogen in the case of Cr_2O_3 is found to increase materially the heat of adsorption of carbon monoxide.
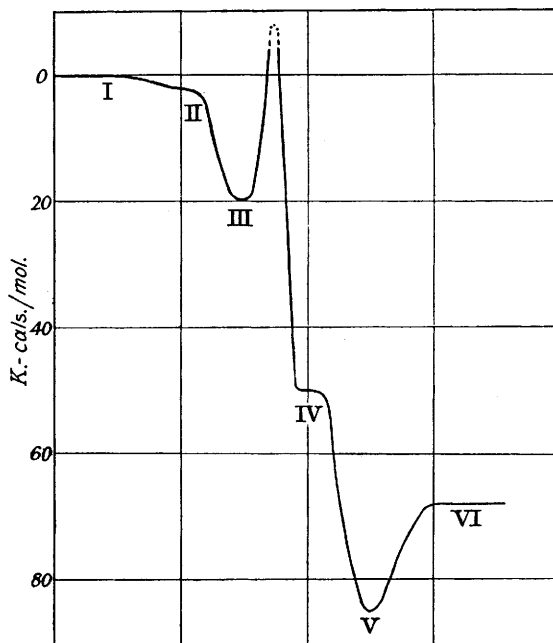
The reduction of oxides by carbon monoxide.

Energy Levels.—The energy levels formed during the reduction of the oxides are set out schematically in the figure. This only gives a very approximate representation of the results of Table II, since the position of the levels varies with the oxide. The levels from left to right are : I, $CO + \frac{1}{2}O_2$; II, van der Waals adsorption of CO; III, reversible chemisorption of CO; IV, irreversible adsorption of CO, leading to an unsaturated surface; V, adsorption of $CO + \frac{1}{2}O_2$; and VI, carbon dioxide. There is an activation energy between II and III and carbon monoxide may be desorbed unchanged on raising the temperature if this activation energy is greater than the heat of desorption. This is the case for the adsorption of carbon monoxide on ZnO, Cr_2O_3. The overall change from I to VI is the conversion of carbon monoxide and oxygen into carbon dioxide.

Lattice Irregularities.—These oxides belong to the class of semiconductors, the electrical conductivity being due to a defect or excess of some ion in the lattice. Zinc oxide dissolves zinc, giving negative holes in the lattice. Oxides of manganese give a series of partially miscible solid solutions of MnO, Mn_3O_4, and Mn_2O_3, which can only be produced at the expense of some lattice irregularity. In this case, oxygen is in excess, which probably gives rise to positive holes in the lattice. It is thus similar to the cuprous oxide, which has been thoroughly investigated by Wagner (cf. Mott and Gurney, " Electronic Processes in Ionic Crystals ", 1940), who shows that there is considerable mobility of the ions at high temperatures. On removal of oxygen by

reduction, negative holes will be produced on the surface, and if the temperature is sufficiently high, these negative holes will migrate into the interior of the lattice, their place on the surface being taken by oxygen ions. The surface reduction of oxides might therefore at sufficiently high temperature lead to a movement of oxygen from the interior of the lattice to the surface.

A phenomenon of this type possibly occurs at 450°, when the oxides are undergoing reduction. The extent to which the reduction occurs at this temperature and the quantities of gas which can be absorbed on the reduced surface are shown in Table III.

TABLE III.

Reduction of surfaces of oxides.

| Substance.	Wt., g.	Gas used in reduction.	Vol. of gas used up at 400—450°.	Gases adsorbed on reduced surface at saturation, in c.c. at room temp.			Remarks.
				H_2.	CO.	O_2.	
ZnO,Cr_2O_3	14·8	H_2	200	3·0	1·4	9·0	
ZnO	6·0	H_2	3 c.c./hr.	V. small	0·35	—	Zn volatilises on reduction
$MnO_{1·5}$	11·2	$\{$CO	64	—	2·0	—	
		H_2	243	0·17	—	—	
Cr_2O_3	16·1	CO	57	V. small	32·3	30·0	
$MnO_{1·5},Cr_2O_3$ ...	19·7	CO	28	V. small	1·0	0·10	

If the surfaces are reduced stepwise, only a relatively slow change in the character of the surface occurs as the reduction proceeds. Thus with ZnO,Cr_2O_3 the reduction by 50 c.c. of hydrogen out of a total possible of 200 c.c. made no significant difference to the volume of hydrogen adsorbed or to its heat of adsorption at room temperature. A similar result also was obtained with $MnO_{1·5}$; the adsorption and heat of adsorption of carbon monoxide was not appreciably affected by the partial reduction of the oxide. Also, the amount of oxygen adsorbed and the heat of adsorption of oxygen on Cr_2O_3 only increases slowly as the surface is reduced. The amount of oxygen adsorbed by manganous–chromic oxide is only slightly affected by the reduction process. As oxygen is removed from the surface during the reduction, there is evidently some compensating factor which keeps the properties of the surface unchanged. This may well be the diffusion of oxygen ions from the lattice to the surface.

At room temperature the mobility of the oxygen ions within the lattice is probably very low, so that the oxide under these conditions would be expected to be a frozen form of the equilibrium set up at higher temperatures. The adsorption of hydrogen and carbon monoxide at room temperature may therefore take place on lattice irregularities caused by the establishment of equilibrium in a lattice defect structure at higher temperatures. The bearing of lattice defects on the reduction of oxides and for catalysis generally has not yet received much attention, and no researches appear to have been directed specifically to clear up this point.

Activation Energy during the Reduction of Oxides.—Carbon monoxide is adsorbed on oxide surfaces in two ways, (1) reversibly and (2) irreversibly. The first type occurs on ZnO, on ZnO,Cr_2O_3, and only to a small extent on the other oxides. On zinc oxide the heat of adsorption is 18 k.-cals. and the gas can be completely desorbed at room temperature within 20 minutes. The rate of desorption is given by $N v e^{-E/RT}$, where N = number of adsorbed molecules per cm.^{2}, $v = 10^{13}$ as a maximum value, and E = the energy required to evaporate the molecule from the surface. Calculation shows that E is approximately the same as the heat of adsorption within a few calories. The reversible adsorption is thus not appreciably activated.

On ZnO,Cr_2O_3, both types of adsorption occur, but the passage from reversible to irreversible adsorption does not readily occur on the surface. On heating, carbon monoxide first evaporates and then condenses to give an adsorption complex from which carbon dioxide can be liberated. It is very probable, therefore, that different centres are involved in the two types of adsorption process.
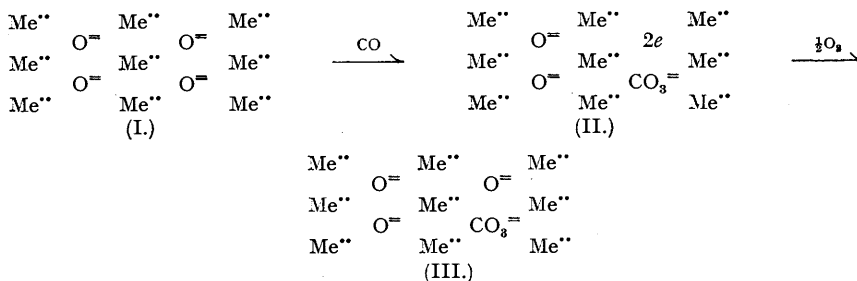
On oxides of the transition elements and their mixtures, carbon monoxide reacts with two oxygen ions or atoms on the surface to give $CO_3^=$ ions, liberating two electrons :

$$(1) \quad CO + 2O^= \longrightarrow CO_3 + 2e$$
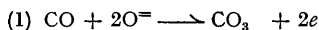
The surface has become unsaturated with respect to oxygen, which can be added in stoicheiometric quantities, *viz.*, $\frac{1}{2}O_2$ to each CO :
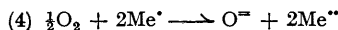
$$(2) \quad \tfrac{1}{2}O_2 + 2e \longrightarrow O^=$$
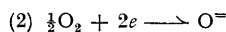
The process is shown schematically below for a bivalent metal ion.

$$
\begin{array}{ccccc}
\text{Me}^{\cdot\cdot} & \text{Me}^{\cdot\cdot} & \text{Me}^{\cdot\cdot} & & \text{Me}^{\cdot\cdot} & \text{Me}^{\cdot\cdot} & \text{Me}^{\cdot\cdot} \\
& O^{=} & O^{=} & \xrightarrow{\text{CO}} & & O^{=} & 2e \\
\text{Me}^{\cdot\cdot} & \text{Me}^{\cdot\cdot} & \text{Me}^{\cdot\cdot} & & \text{Me}^{\cdot\cdot} & \text{Me}^{\cdot\cdot} & \text{Me}^{\cdot\cdot} \xrightarrow{\frac{1}{2}O_2} \\
& O^{=} & O^{=} & & & O^{=} & CO_3^{=} \\
\text{Me}^{\cdot\cdot} & \text{Me}^{\cdot\cdot} & \text{Me}^{\cdot\cdot} & & \text{Me}^{\cdot\cdot} & \text{Me}^{\cdot\cdot} & \text{Me}^{\cdot\cdot} \\
& (\text{I.}) & & & & (\text{II.})
\end{array}
$$

$$
\begin{array}{ccc}
\text{Me}^{\cdot\cdot} & \text{Me}^{\cdot\cdot} & \text{Me}^{\cdot\cdot} \\
& O^{=} & O^{=} \\
\text{Me}^{\cdot\cdot} & \text{Me}^{\cdot\cdot} & \text{Me}^{\cdot\cdot} \\
& O^{=} & CO_3^{=} \\
\text{Me}^{\cdot\cdot} & \text{Me}^{\cdot\cdot} & \text{Me}^{\cdot\cdot} \\
& (\text{III.})
\end{array}
$$

The following qualitative picture can be given in explanation of the experimental results. The electrons set free in (II) will be held in the neighbourhood of the carbonate ion. They will possibly be accommodated in the S or D shells of the transition element,* which, together with the $CO_3^{=}$ ion, can form a resonating system :

$$(3) \quad CO + 2O^{=} + 2Me^{\cdot\cdot} \rightleftharpoons CO_3 + 2Me^{\cdot}$$

The addition of $\frac{1}{2}O_2$ in (III),

$$(4) \quad \tfrac{1}{2}O_2 + 2Me^{\cdot} \longrightarrow O^{=} + 2Me^{\cdot\cdot}$$

will have the effect of moving the resonating system in (3) to the right, *i.e.*, in the direction of the formation of $CO_3^{=}$ ion, which would explain the observation that CO_2 is evolved more readily from state (III) than from state (II).

The carbonate ion can be dissociated to give carbon dioxide. Measurements of the rates of desorption show that within a few calories the activation energy is the same as the heat of adsorption. The process of dissociation involves the displacement of the carbon atom as in (5), and the transference of the two electrons to an oxygen atom and the metal ions associated

$$(5) \quad O-C{\overset{\textstyle O}{\underset{\textstyle O}{\diagup}}} \longrightarrow O^{=} + CO_2$$
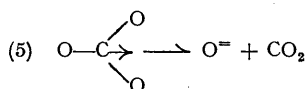
with it in the lattice. An activation energy might be expected for this step, but it may be small,† especially if there is some choice among the levels of the D and S shells of the transition element, in the formation of the bond between the oxygen ion and the surrounding metal ions. If there is a broad band of electronic levels in the shells of the transition element, which are suitably placed with respect to the levels of the oxygen and carbonate ions, then the electron transfer reactions (3)—(5) would be facilitated. The effectiveness of the transition metals for catalysis generally may depend on a suitable distribution of the electron levels in the catalyst.

When carbon monoxide is adsorbed reversibly on zinc oxide, the surface does not become unsaturated with respect to oxygen, and no additional oxygen can be adsorbed after carbon monoxide. This is in accord with the view that reversible and irreversible adsorption of carbon monoxide occur on different centres.

Conclusions on the Reaction of Carbon Monoxide with Oxides.—It has been demonstrated that reversible adsorption of carbon monoxide occurs on metal-rich oxides with negative holes in the lattice, and irreversible adsorption on oxides defective in metal ion with positive holes. The two types of adsorption are not readily inter-convertible and probably occur on different types of centre. Reversible chemisorption may take place on sites where electrons can be donated to the adsorbed molecule, and irreversible adsorption on sites which can abstract electrons from the molecule. The reversible adsorption is not appreciably " activated ".

It is suggested that the resonating system $CO + 2O^{=} + 2Me^{\cdot\cdot} \rightleftharpoons CO_3^{=} + 2Me^{\cdot}$ may play an important part in the irreversible adsorption. The carbon monoxide is held in an intermediate state on the way to a $CO_3^{=}$ ion. This system will move to the right if the number of unpaired electrons in the shells of the metal ion is increased, so that the extent to which the

* The transition elements are most effective as catalysts when their magnetic susceptibility is highest, indicating that the unpaired electrons in the D shell play an important part in heterogeneous catalysis (Hüttig, *J. Amer. Chem. Soc.*, 1935, **57**, 2470; Hofer, Peebles, and Dieter, *ibid.*, 1946, **68**, 1953; Selwood, Hill, and Boardman, *ibid.*, p., 2055).

† I am indebted to Dr. F. C. Frank for this suggestion.

carbonate ion is formed can be increased by the adsorption of oxygen simultaneously with carbon monoxide, $\frac{1}{2}O_2 + 2Me^{\cdot} \longrightarrow O^{=} + 2Me^{\cdot\cdot}$. This is in accord with the fact that the carbonate ion is more readily dissociated when the surface is saturated with oxygen.

The dissociation of the carbonate ion has been shown to possess an activation energy approximately equal to the heat of adsorption of carbon dioxide, so that the formation of carbonate ions from carbon dioxide requires no appreciable activation energy. In explanation of this fact, it is suggested that the activation energy for the dissociation may be small if the electronic levels of the shells of the metal ions lie in a broad band which is suitably placed with respect to the electronic levels of the oxygen and carbonate ions.