XXIV.--Equilibria in the Reduction of Oxides by Carbon.

By ROLAND EDGAR SLADE and GEOFFREY ISHERWOOD HIGSON. Equilibria of some reactions of the type:

metal $oxide + carbon \rightleftharpoons carbon monoxide + metal$

or

metal oxide + metal carbide \rightleftharpoons carbon monoxide + metal

have been investigated.

In either of the above systems there are three components, namely, metal, carbon, and oxygen, and four phases, namely, metal, metal oxide, carbon (or carbide), and carbon monoxide (gas). The number of degrees of freedom is thus 3+2-4=1. Therefore at one temperature there is one pressure of carbon monoxide which determines the equilibrium of the system

The following experimental method was adopted. A small quantity of the metal was heated in a vacuum to a certain temperature, and carbon monoxide was then admitted until the pressure was greater than the equilibrium pressure. The reaction proceeded in the direction from right to left, and carbon monoxide was absorbed until the equilibrium pressure was attained. Some carbon monoxide was then removed, when the reaction proceeded from left to right until the equilibrium pressure was again attained. If the carbon formed in the first part of the experiment did not remain as a separate phase either as a carbon or as a carbide, but formed a solid solution with the metal, there would be only two solid phases present with the gas phase; the system would there SLADE AND HIGSON: EQUILIBRIA IN THE

fore have two degrees of freedom, and the pressure of carbon monoxide would depend on the relative amounts of metal and carbon present, as well as on the temperature. When the equilibrium was attained from left to right, there was less carbon monoxide present than when the equilibrium was attained from right to left, therefore the equilibrium pressures would have been different in these two cases if there were only two solid phases present.

The equilibrium may be calculated from the heat of reaction by making use of the Nernst heat theorem. In the reaction

$$\mathbf{M} + \mathbf{CO} \rightleftharpoons \mathbf{MO} + \mathbf{C} + Q_t \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

where M is the weight in grams of any metal combining with 16 grams of oxygen, and Q_t is the heat of reaction; in all cases Q_t is positive, so that increase in temperature will cause the formation of M+CO. That is to say, $p_{\rm CO}$ increases with the temperature. This quantity of heat, Q_t , may be considered as the differences of two quantities of heat, Q_1 and Q_2 , for if we write

$$\mathbf{M} + \mathbf{O} = \mathbf{MO} + Q_1 \qquad \dots \qquad \dots \qquad (2)$$

$$\mathbf{CO} = \mathbf{C} + \mathbf{O} + Q_2 \quad \dots \quad \dots \quad \dots \quad \dots \quad (3)$$

then, on addition, $M + CO = MO + C + (Q_1 + Q_2)$. Q_2 , the heat of dissociation of carbon monoxide, is -29,000 calories, therefore

$$Q_t = Q_1 - 29,000$$
 (4)

Neglecting terms containing T^2 , the Nernst heat theorem requires that

$$\log p_{\rm co} = \frac{-Q_0}{4.571 \ T} + 1.75 \ \log T + 2.6 \qquad . \qquad . \qquad (5)$$

where Q_0 is the heat of reaction at absolute zero.

The thermodynamic constant used for carbon monoxide is the value given by Weigert in Abegg's "Handbuch." The relation between Q_0 and Q_t is given by the equation

Limits of the Investigation.—The equilibrium mentioned above could only be determined at temperatures at which the equilibrium,

$$2CO \rightleftharpoons CO_2 + C$$
,

is practically completely in the left-hand direction. Rhead and Wheeler (T., 1910, 97, 2187; 1911, 99, 1140) have investigated this equilibrium, and from their results it is possible to calculate the partial pressure of carbon dioxide in equilibrium with carbon monoxide at 760 mm. or 50 mm. These values are given in table I.

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TABLE I.

Pressure of carbon dioxide in mm. when pressure of carbon monoxide is 760 mm	Pressure of carbon dioxide in mm. when pressure of carbon monoxide is 50 mm
15 100 11111	13 00 11111.
53.8	0.23
17.6	0.076
4.6	0.0020
0.90	0.00082
0.46	0.00020
	Pressure of carbon dioxide in mm. when pressure of carbon monoxide is 760 mm. 53.8 17.6 4.6 0.90 0.46

From these figures, it is seen that if the equilibrium pressure is as low as 50 mm., there is no complication due to the presence of carbon dioxide at temperatures from 850° upwards. If, however, the pressure is as great as 760 mm., the amount of carbon dioxide present is appreciable up to 1200°. If a carbide is present instead of free carbon, the ratio of carbon dioxide to carbon monoxide will be greater, for we have

$$\frac{p^2_{\rm co}}{p_{\rm co_2}p_c} = K,$$

and p_c (partial pressure of carbon vapour) will be lower over a carbide than over carbon.

In all our experiments, the equilibrium pressures were sufficiently low and the temperature was sufficiently high for the pressure of carbon dioxide to be negligible.

The metals with which we could determine the above equilibrium were only such as would fulfil the following conditions: (1) The metals must not be volatile at the temperature of the experiments. At these temperatures, the vapour pressure of the metal should certainly not be more than 0.25 mm., or it will distil rapidly on to parts of the platinum tube which are at a somewhat lower temperature, and probably attack the platinum. Platinum tubes were, in fact, destroyed by the volatility of boron and manganese. (2) The equilibrium pressure must not be greater than 50 mm. at 850°, or the quantity of carbon monoxide in the gas phase will be appreciable. (3) The equilibrium pressure must be sufficiently great to be measurable. It must be at least 1 mm. at 1300°. Applying the Nernst heat theorem to the equilibrium, we should only expect those elements of which the heat of oxidation, per gramatom of oxygen, lies between 75,000 and 114,000 calories, to give an equilibrium pressure measurable in our apparatus. Of substances with known heats of oxidation, only silicon, boron, and manganese lie within this range. The only likely metals for which

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the heats of oxidation were unknown, and which were readily obtainable, were vanadium, tantalum, and chromium.

Apparatus.-The furnace, which has been described by Slade (Proc. Roy. Soc., 1912, [A], 87, 519), consists of a platinum tube 2 cm. in diameter heated by a current of 300 to 400 amperes at 2 to 4 volts. The furnace is placed in a vessel which can be exhausted to prevent the platinum tube from collapsing under the pressure of the atmosphere. A silver capillary tube is used to connect the furnace with the glass tube leading to the pressure gauge. The temperatures were determined by means of a platinum platinum (90 per cent.)-rhodium (10 per cent.) thermocouple. The couple was calibrated up to the melting point of copper, 1083°, and higher temperatures were determined by extrapolating by means of the formula

 $\log e = 1.22 \log t - 2.65$,

where t is expressed in degrees centigrade and e in millivolts. The cold end of the couple was kept at 0° .

It was found to be impossible to use a platinum boat for any of the substances investigated, for although the temperatures were well below their melting points, they were rapidly alloyed with Accordingly, boats of unglazed Royal Berlin porcelain platinum. were employed.

Pressures were read on a mercury vacuum manometer, behind which was a glass millimetre scale illuminated by a lamp and a milk-glass screen. The readings were made with a telescope, and were accurate to ± 0.05 mm.

The carbon monoxide was prepared by running pure formic acid into concentrated sulphuric acid at 70-80°. The gas, which was first passed through a long tube of soda-lime and then through a similar tube of phosphoric oxide, was collected and stored over mercury in a vessel of 1 litre capacity.

The gas was led from the reservoir to the furnace and pressure gauge by means of a tube, in which were placed two taps separated by a capillary tube of such dimensions that the volume between the two taps was 0.2 c.c. By filling this tube with carbon monoxide at the ordinary temperature, then closing one tap and opening the other, 0.2 c.c. of carbon monoxide was allowed to flow into the exhausted furnace and the tubes connecting the furnace to the gauge and pump. The total volume of this part of the apparatus was about 50 c.c., and when the furnace was heated to about 1200°, its effective volume was about 30 c.c., so that the introduction of 0.2 c.c. under a pressure of one atmosphere caused a rise of pressure of $\frac{0.2}{30}$ atmosphere, or about 5 mm. of mercury.

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In most of the experiments, 0.1 gram of the metal under investigation was introduced into the boat. That this was sufficient may be seen from the following considerations.

If the reaction is

$$M + CO = MO + C$$
,

where M is two equivalents of an element, then two gram-equivalents of the element would react with 22,400 c.c. of carbon monoxide. If the pressure in the furnace was 60 mm., which was the maximum pressure used in several cases, the volume of gas contained in the furnace was 2.4 c.c. when measured at N.T.P., therefore to absorb all this gas, $\frac{2.4}{22,400} \times 2 = 2.2 \times 10^{-4}$ gram-equivalent of the element would be required. If the equivalent were as great as 100, only 0.02 gram would be required. The metal was usually broken into small pieces, as the velocity of the action must be

proportional to the surface exposed. *Experiments with Vanadium*.—As vanadium is a very refractory substance and is difficultly reducible (that is, the oxide has a high heat of formation), it was decided to attempt to measure the reduction equilibrium.

Some preliminary experiments were made on the action of vanadium on platinum and the melting point of vanadium. The vanadium was placed, in very small pieces (about 0.5 mm. in diameter and less), on a platinum strip which was heated in an atmosphere of hydrogen by an electric current. At 1400°, the vanadium adhered to the strip when the heating had been carried on for some three minutes. The temperature was determined by means of a Wanner pyrometer, correction being made for blackbody radiation of the platinum. In another experiment, the strip was dusted with powdered vanadium and heated rapidly until it fused at one point. Examination under the microscope showed that the vanadium had then fused into globules just round the portion of the strip which had fused. The melting point of this vanadium is therefore just below the melting point of platinum, namely, 1760°. The vanadium had been prepared in the electric furnace, and contained 4.6 per cent. of carbon. The carbon probably exists as the carbide, VC, and may be present in solid solution, although the fact that so much carbon is present makes it seem probable that the carbide exists as a separate phase.

Experiments.—0.0636 Gram of the metal was placed in an unglazed porcelain boat in the platinum tube furnace. The furnace was exhausted and left for sixteen hours, when no rise of pressure was noticeable. The temperature was raised to 1000° , and the occluded gas from the boat pumped off; 0.2 c.c. of carbon mon-

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oxide was then admitted, and this raised the pressure to 6 mm., at which it remained. Therefore the equilibrium pressure was greater than this, or the velocity of reaction at this temperature was very small. The latter was found to be the case, for when the pressure of carbon monoxide had been increased to 60 mm., The temperature was then raised to there was still no reaction. 1340°, and maintained at this temperature for four and a-half During this time, the pressure fell at first rapidly, and hours. finally became steady at 1.7 mm. The temperature was then reduced to 1145°, where it was maintained for thirty minutes. The pressure fell rapidly to 0.55 mm., where it remained constant. The temperature was then lowered to 900°, when the pressure fell only to 0.2 mm.

On the following day, the furnace was heated to 1340° and the temperature kept constant. In one hour the pressure rose to 1.2 mm., at which it remained constant for three and a-half hours.

The equilibrium pressure at 1340° was therefore between 1.7 and 1.2 mm. The mean of these values is 1.45 mm. At lower temperatures, the equilibrium was attained too slowly to be determined.

The reaction is probably

$$VO + VC \rightarrow 2V + CO + Q.$$

The value

$$p_{\rm co} = \frac{1.45}{760}$$
 atm. at 1340°

gives, by the Nernst heat theorem, the value

$$Q_0 = 80,875$$
 cals.

Substituting this in equation (5), we find that

 $p_{\rm co} = 1$ atmosphere at 1827°.

This is the temperature at which vanadium oxide would be reduced by the carbide under a pressure of one atmosphere.

There is no direct evidence as to the heat of formation of vanadium carbide, that is, of the reaction

$$V + C \rightarrow VC$$
,

but usually the heats of formation of carbides are small (Wartenberg, Zeitsch. anorg. Chem., 1907, 52, 299), that is to say, not greater than 2000—3000 calories per gram-atom of carbon. If this heat of formation of the carbide is neglected, an approximate value of the heat of oxidation of vanadium at 20° can be obtained:

$$V + O = VO + 111,000$$
 cals.

Not much trust can be placed in this value, however, for the carbide may be in solid solution in the metal and not as a separate phase.

Experiments with Tantalum.—The tantalum used was a portion of a specimen obtained from the late Dr. Werner von Bolton, and used by yon Hevesy and Slade to determine the electrode potential of tantalum. It was in the form of a rolled sheet about 0.25 mm. thick. As only a small quantity of the metal was available, 0.035 gram was used in each experiment. If the tantalum was oxidised to the oxide, Ta₂O, this metal would absorb 3.5 c.c. of carbon monoxide. In the first experiment with tantalum, the metal was in the form of one piece of sheet. At 1000°, 2 c.c. of carbon monoxide were admitted (p=60 mm.); the pressure fell, and in two hours became constant at 0.7 mm. The temperature was then raised to 1200° and 0.6 c.c. of carbon monoxide was admitted, so that the pressure was raised to 14 mm. As the pressure did not fall, more carbon monoxide was admitted until the pressure was 40 mm., but there was still no action. The furnace was therefore exhausted, but no appreciable rise in pressure took place in two It therefore seemed probable that the constant pressure of hours. 0.7 mm. obtained at 1000° was not a true equilibrium pressure, but that the equilibrium pressure, even at 1200° , was very low indeed.

In the next experiment the same quantity of metal was used, but it was cut into as many strips as possible, in order to increase the surface. After pumping out all gases from the boat at 1150° , 0.4 c.c. of carbon monoxide was admitted, so as to raise the pressure to about 13 mm. In half an hour the pressure fell to 0.2 mm., and then became constant, and remained so for half an hour. An attempt was now made to reach the equilibrium from the low pressure side. The furnace was exhausted and the temperature was raised to 1270° . In four hours the pressure rose slightly above 0.1 mm. (perhaps 0.12 mm.), and remained constant for about three hours. Carbon monoxide (about 0.1 c.c.) was then admitted to raise the pressure to 2.5 mm., and in one hour the pressure fell to 0.1 mm. This value is therefore the equilibrium pressure at 1270° .

It was impossible to determine the equilibrium at a higher temperature, because at this stage of the work the platinum tube had become weakened and slowly collapsed when kept exhausted for several hours at 1270° , although the external pressure on the tube was only 30—40 mm. of mercury.

Experiments with Chromium.—The temperature of reduction of chromium sesquioxide was determined by Greenwood (T., 1908, 93, 1438), who found that this oxide was reduced at 1195° under a

pressure of 2 mm. The boiling point of chromium is 2200° (Greenwood), and from this value the vapour pressure of liquid chromium can be calculated to be 0.07 mm. at 1000°, 0.078 mm. at 1100°, 0.7 mm. at 1200°, and 1.12 mm. at 1300°. It was therefore not safe to heat chromium to a much higher temperature than 1200° in the platinum furnace.

The chromium had been prepared by the Goldschmidt method, and therefore contained a trace of aluminium. As aluminium is easily and completely oxidised by carbon monoxide, it is probable that it would only have a very slight influence on the equilibrium.

0.45 Gram of metal, in the form of a coarse powder, was used in the first experiment. The furnace was heated to 936°, and all adsorbed gases were pumped out. Carbon monoxide was then admitted until the pressure was 100 mm. In nine and a-half hours the pressure fell to 22 mm., but did not appear to be approaching a steady value. After remaining for eighty-five hours, the furnace was heated to 1010° and carbon monoxide admitted until the pressure was 50 mm. In six hours the pressure fell to 0.75 mm., and appeared to be constant. After eighteen hours, the temperature was raised to 1292°, and carbon monoxide admitted until the pressure was 63 mm. In forty-five minutes the pressure fell to 6.2 mm., and remained constant. Carbon monoxide was then pumped out until the pressure fell to 5 mm. In fifteen minutes the pressure rose to 6.2 mm., and remained constant. The temperature was then raised to 1339°, and in twenty-five minutes the pressure had risen to 9.1 mm., and become constant. The furnace was then cooled, and next day was heated to 1339°. In twenty minutes the pressure rose to 9.2 mm. The furnace was now cooled to 1292°, and carbon monoxide was pumped off until the pressure was less than 1 mm. In an hour the pressure became constant at 4.4 mm. The furnace was cooled, and the next day was heated to 1292°; the pressure rose to 4.4 mm. Carbon monoxide was then admitted until the pressure was 8.6 mm. In fortyfive minutes the pressure fell to 4.4 mm. The temperature was now raised to 1339°, when the pressure rose to 9.2 mm. In the figure are given some of the time-pressure curves obtained. These show how accurately the results could be reproduced.

A new sample of chromium (0.45 gram) was now introduced into the furnace, and the temperature was raised to 1292°, carbon monoxide being admitted until the pressure was 15 mm. In twenty minutes the pressure fell to 6.2 mm., and remained constant at this value for one hour. The temperature was then raised to 1339°, and the pressure rose to 9.1 mm., but the platinum tube began to leak, owing to its being attacked by the chromium, which had distilled on to it during this and former experiments.

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Table II shows the values for the equilibrium pressure obtained with chromium. All these equilibrium pressures were obtained twice from each side. The high value at 1292° is the value obtained when the furnace had not been raised to a higher temperature. After the temperature had been raised to 1339° and lowered again to 1292° , the equilibrium pressure was 4.4 mm., and this value could be obtained again and again. Since chromium easily forms a carbide, it is probable that the reaction taking place was

 $5\operatorname{Cr} + \operatorname{CO} \rightleftharpoons \operatorname{Cr}_4\operatorname{C} + \operatorname{CrO} + Q.$

Calculating the heat of reaction per gram-atom of oxygen at 1315° from the Nernst formula and the van't Hoff formula, the values given in table II are obtained.

TABLE II.

Temperature.	Pressure of carbon monoxide in mm.	Q_t calculated, Nernst.	Q_t calculated, van't Hoff.
1292°	$6 \cdot 2$	73,600	
1339	9.2	69,200	77 000
1292	4.4	69.200 í	77,000

The value 77,000 calories is the heat of reaction calculated from the integrated form of the van't Hoff equation,

$$Q_t = -4.571 \ (\log p_2 - \log p_1) \frac{T_1 T_2}{T_2 - T_1}.$$

In this method of calculating Q_t , an error of 0.1 mm. in the determination of the equilibrium at 1292° would make a difference of a little more than 1000 calories in the value of Q_t . The assumption on which this formula is based, however, is only that the heat of reaction does not change appreciably between the two temperatures. That two different values were obtained for the equilibrium at 1292°, according to whether the furnace had been heated up to 1339° or not, must be explained by supposing that the substances in equilibrium were different in the two cases. It is very improbable that the first value is due to the presence of a trace of aluminium in the metal, for the presence of aluminium would be expected to lower rather than to raise the equilibrium pressure, and in the two experiments in which the pressure was 6.2 mm., very different amounts of carbon monoxide had been absorbed by the same amount of metal. In the first experiment, 6—7 c.c. of carbon monoxide, and in the second case only 0.6 c.c., were absorbed.

The equilibrium in the gas phase is represented by

$$p_{\rm co} = K \cdot \frac{p_{\rm carbide} \quad p_{\rm oxide}}{p_{\rm metal}}$$

The change in the system caused by raising the temperature to 1339° was to give a lower equilibrium pressure at 1292°, and this must be due to (1) increase in the partial pressure of chromium, (2) lowering of the partial pressure of the carbide, or (3) lowering of the partial pressure of the oxide.

Case (1) might be caused by the existence of a transition point of chromium between 1292° and 1339° . At first, the metal is in the α -form, stable at lower temperatures; on heating, the metal would change to the other, or β -form, and on cooling to 1292° would not revert to the α -form, but remain in the unstable β -form, which would have a higher vapour pressure than the α -form.

Case (2) might be caused by the formation of an unstable carbide in the first instance, which on heating to 1339° changes into the stable form. On cooling now to the lower temperature, the unstable carbide is not formed in the presence of the more stable one.

Case (3) might be caused by the chromium oxide combining with the silica in the boat to form a silicate, but this reaction should not be different after the furnace had been raised to the higher temperature. The first explanation seems the more probable.

This investigation was carried out in the Muspratt Laboratory of Physical Chemistry, University of Liverpool.

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