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The Reaction of Carbon Monoxide on Molybdenum Oxides

BY HUGH M. SPENCER AND JOHN L. JUSTICE[1]

The original aim of this investigation was to supply the carbon monoxide–carbon dioxide ratios over molybdenum dioxide–molybdenum, which would permit an indirect calculation of the water-gas equilibrium. Calculations based on the water vapor–hydrogen ratio[2] and the accepted value for the water-gas equilibrium constant[3] indicated that temperatures could be conveniently selected for which the compositions would preclude the direct decomposition of carbon monoxide.[4] Preliminary experiments showed, however, that molybdenum dioxide reacts with carbon monoxide to form molybdenum carbide (Mo_2C) and carbon dioxide, and that the reaction is reversible. Thus the possible reactions of all ratios of carbon monoxide and carbon dioxide over the various pairs of solid phases: the molybdenum oxides, metallic molybdenum, molybdenum carbides and the various conceivable solid solutions are of interest.

The results of the earlier experiments are in some cases conflicting, or at least are susceptible of different interpretation in light of more recent work. Though the statement is made in the literature[5] that Debray used a mixture of carbon monoxide and carbon dioxide as the reducing agent in transforming molybdenum trioxide to molybdenum dioxide, the original article, while showing the reversibility of reduction equilibria over iron–ferrous oxide with mixtures of hydrogen and water vapor or of carbon monoxide and carbon dioxide, and predicting the generality of such reactions, merely reports the oxidation of the red oxide (molybdenum dioxide) to molybdenum trioxide by water vapor.

Muthmann,[6] however, who passed carbon monoxide over molybdenum trioxide, and analyzed only for molybdenum, showed progressive reduction up to 82.71% molybdenum in the course of three hours. He stated that after ten hours ignition the mass was homogeneous and gray and the reduction complete, but as he gave no analysis, his final product, in light of the present and other recent work, may have been molybdenum carbide. The reverse reaction was studied by Vandenberghe.[7] He passed carbon dioxide over molybdenum at 700° and found that the carbon dioxide was reduced to carbon monoxide. He made no analysis of the solid phase but assumed that the molybdenum was oxidized through the lower oxides to molybdenum trioxide. The course of the oxidation was followed by observation of the appearance of the solid phase. The colors reported indicate that the oxidation was carried only to the dioxide.

The action of carbon monoxide on molybdenum has been the subject of a number of investigations.[8] Smith and Oberholtzer observed no reaction when molybdenum was heated to a red heat in an atmosphere of carbon monoxide. The results of Hilpert and Ornstein indicate that, at 1000°, carbon monoxide passed over finely divided molybdenum leads to the carbide Mo_2C, at 800° to a higher carbide or solid solution (between MoC and Mo_3C_4). At 800° they also obtained a carbide of high carbon content by the action of carbon monoxide on molybdenum trioxide. Westgren and Phragmén in their study of molybdenum carbides prepared some of their samples by carburizing filaments in an atmosphere of carbon monoxide at 1500°. Their samples prepared in various ways yielded solid solutions of 30 to 39 atomic per cent. carbon and gave some indication of carbides of higher carbon content.

While this work was in progress Tutiya's paper concerning the catalytic action of molybdenum

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(1) Du Pont Research Fellow 1932–1934.

(2) G. Chaudron, *Ann. chim.*, [9] **16**, 246 (1921).

(3) A. R. Gordon, *J. Chem. Phys.*, **2**, 65 (1934).

(4) The values of the equilibrium constant for the reaction $2\,CO = C + CO_2$ have been measured by many investigators, but the results are not in agreement. The recent papers of F. J. Dent and J. W. Cobb [*J. Chem. Soc.*, 1903 (1929)] and of E. Jänecke [*Z. anorg. allgem. Chem.*, **204**, 249 (1932)] may be consulted for summaries and discussions of the problem. As an approximate guide the following data from G. Meyer and F. E. C. Scheffer [*Rec. trav. chim.*, **46**, 754 (1927)] are quoted:

Temp., °C.	650	700	750	800	850	900	1000
% CO_2	61.5	42.3	24.7	12.6	6.0	2.8	0.7

(5) J. W. Mellor, "Comprehensive Treatise on Inorganic and Theoretical Chemistry," Longmans, Green and Co., London, 1931, Vol XI, p 527; (a) H. Debray, *Compt. rend.*, **45**, 1 018 (1857).

(6) W. Muthmann, *Ann.*, **238**, 108 (1887).

(7) A. Vandenberghe, *Z. anorg. Chem.*, **11**, 397 (1896).

(8) E. F. Smith and V. Oberholtzer, THIS JOURNAL, **15**, 206 (1893); S. Hilpert and M. Ornstein, *Ber.*, **46**, 1669 (1913); A. Westgren and G. Phragmén, *Z. anorg. allgem. Chem.*, **156**, 27 (1926); H. Tutiya, *Bull. Inst. Phys. Chem. Research* (Tokyo), **11**, 1136 (1932), (Abstracts (in English) published with *Sci. Papers Inst. Phys. Chem. Research* (Tokyo), **19**, Nos. 384–392).

and molybdenum carbides on the decomposition of carbon monoxide was published. According to his results Mo_2C is the only carbide formed between 450 and 600°, and the carbide alone will bring about the decomposition of carbon monoxide at 600°. At 650 to 700° a metastable carbide phase was formed, and at 750° another carbide phase was noted, probably MoC. From 750 to 800° the decomposition of carbon monoxide is not dependent upon the presence of metallic molybdenum.

This communication presents several of the more interesting preliminary studies of the reactions of the molybdenum and carbon oxides and a study of the reversible equilibrium

$$2MoO_2 + 6CO = Mo_2C + 5CO_2 \qquad (1)$$

by a dynamic method.

Experimental Methods and Materials

The dynamic method used was in most respects similar to that described by Emmett and Shultz.[9] The silica reaction tube was 80 cm. long, and for half its length the internal diameter was 20 mm., the remainder being 6 mm. It was similar to the one described by the same authors.[10] In the final measurements the 20-g. samples of molybdenum dioxide used occupied a length of 6.5 cm. in the wide part of the tube ending at the point where the tube was constricted. The exit gas passed through the constricted portion of the tube.

In the preliminary experiments temperature was measured by a 650° thermometer, but in the study of Reaction 1 a platinum-90% platinum 10% rhodium thermocouple in conjunction with a Leeds and Northrup Type K potentiometer and Type R galvanometer was used. The thermocouple was calibrated by the method of Roberts,[11] using salts of reagent quality which had been further recrystallized once. The following salts were used: potassium dichromate, 30.5% sodium chloride and 69.5% sodium sulfate, sodium chloride and sodium sulfate.

The part of the reaction tube containing the sample was about midway of the 30 cm. length of the furnace. The thermocouple was embedded in the center of the sample where temperatures were maintained constant to within less than 2° except as noted in Tables I, II and III. At 810°, though the middle two-thirds of the sample was quite uniform in temperature, the ends differed as much as 10° from the middle.

The inlet gas compositions were metered in by carefully calibrated flowmeters similar to the carbon dioxide flowmeter used by Emmett and Shultz,[9] except that no bypasses were provided. The carbon monoxide flowmeter was checked at seven values of head (50 to 455 mm. Nujol) by Method 2 of their paper, the carbon dioxide flowmeter at five values of head (80 to 285 mm.), three by Method 1 (ascarite used as absorbent) and two by Method 2. In Method 2 a solution saturated with sodium chloride and carbon dioxide was displaced from an aspirator bottle at such a rate that the pressure in the gas space was equal to atmospheric pressure. Water was used for the carbon monoxide. Since the gases passed through the flowmeter dry and were collected over solution (or water) corrections were applied for the vapor pressure. The resulting calibration curves at 25° were straight lines through the origins.

Since the inlet composition and the inlet volume are of importance in the treatment of the data, rather than serving merely as a rough control, further explanation of the treatment of the data is called for. The theory of flowmeters has been discussed by Benton.[12] Using capillary-tube flowmeters with pressure heads sufficiently small the flow is streamline (as in the present investigation), and with temperatures 25 ± 4° (mostly ±2°) and pressures 760 ±10 mm., the results may be simply interpreted with the required accuracy. From Meyer's equation

$$p_1v_1 = p_2v_2 = \frac{\pi r^4 t}{16\eta l}(p_1^2 - p_2^2)$$

where p_1, v_1 and p_2, v_2 are the pressures and volumes at the inlet and outlet ends of the capillary, respectively, η is the viscosity, and r and l are the radius and length of the capillary, it may be seen that at constant temperature the volumes transmitted and measured at the pressure concerned are related by

$$\frac{v_2'}{v_2} = \frac{p_2(2p_2' + h)}{p_2'(2p_2 + h)}$$

and thus for a head of 30 mm. of Hg(=400 mm. of Nujol) and $p_2' = 750$, $p_2 = 760$ mm., the ratio is practically unity (1.00025). Therefore the volumes transmitted in calibration runs and in later use of the flowmeters need not be corrected to standard pressures.

For a given flowmeter and constant inlet pressure and head, it follows also from Meyer's equation that the volume transmitted is inversely proportional to the viscosity at the temperature concerned. Thus the volume transmitted at T and measured at p_2 and T, v_T, is given by

$$v_T = \eta_{298.1}\, v_{298.1}/\eta_T$$

Plots of the ratios $\eta_{298.1}/\eta_T$ were derived from Sutherland's equation[13]

$$\frac{\eta_1}{\eta_2} = \frac{\sqrt{T_1}\,(1 + c/T_2)}{\sqrt{T_2}\,(1 + c/T_1)}$$

using $c = 102$ for carbon monoxide and 240 for carbon dioxide. No appreciable correction is necessary for the inlet gas composition since the gases are metered in at the same temperature and the ratios are not very different. Where the temperatures are three degrees removed from 25°, the temperature for which the calibration was made (or was being made), corrections of 0.77 and 0.95% were necessary in the calculations of the inlet volumes (or volumes delivered in calibration) of carbon monoxide and carbon dioxide, respectively.

Carbon monoxide, prepared by the method of Thompson,[14] and passed over soda lime to remove any acid spray

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[9] P. H. Emmett and J. F. Shultz, THIS JOURNAL, **52**, 1782 (1930).

[10] P. H. Emmett and J. F. Shultz, *ibid.*, **52**, 4268 (1930).

[11] H. S. Roberts, *Phys. Rev.*, [2] **23**, 386 (1924).

[12] A. F. Benton, *Ind. Eng. Chem.*, **11**, 623 (1919).

[13] F. H. Newman and V. H. L. Searle, "The General Properties of Matter," The Macmillan Co., New York, 1933, pp. 211-217.

[14] J. G. Thompson, *Ind. Eng. Chem.*, **21**, 389 (1929).

that might be present, was led into two 5-gallon carboys which had previously been evacuated. To sweep the generator free of air it was first operated for several hours before the stopcock was partially turned, thus permitting a slow escape into the carboys without danger of drawing a vacuum on the generator. The process of evacuating and filling the carboys was carried out four times to remove all air from the storage bottles. In passing the gas into the system the flow of carbon monoxide was maintained by having the carboys under a pressure about 10 mm. of mercury in excess of atmospheric pressure.

Carbon dioxide was prepared by dropping 33% sulfuric acid solution into a concentrated solution of sodium bicarbonate. The spent bicarbonate solution could be removed and replaced by fresh solution without getting air into the system. This apparatus was similar to one used in this Laboratory by Dr. E. C. Markham. The method of filling the carboys and that of passing the gas into the system was the same as that used in working with carbon monoxide.

The molybdenum trioxide used in the preliminary experiments was prepared from Baker analyzed ammonium molybdate by treating a concentrated solution of the molybdate with concentrated nitric acid. The precipitated molybdenum trioxide was filtered with suction, washed and dried on a hot plate. Purified crystals, thin glassy plates having a yellow tint, were prepared by sublimation of the dry powder in a current of air.

It proved impractical to prepare the larger quantities of molybdenum trioxide required for the preparation of molybdenum dioxide by sublimation. The molybdenum trioxide used in the preparation of the dioxide was a yellow powder made by heating ammonium molybdate in air. The powder was placed in a Pyrex tube and reduced by hydrogen at 420 to 470° for fifty-six hours. During the last twelve hours of heating the gain in weight of the calcium chloride tube attached to the furnace exit was 55 mg. Four analyses of the product, following the procedure given by Randall,[15] gave a mean value of 75.49 ± 0.13% molybdenum (calcd., 75.00%).

Preliminary Experiments

Several interesting results came out of the attempts to prepare molybdenum dioxide from molybdenum trioxide by reduction with carbon monoxide. A sample of the sublimed molybdenum trioxide was first heated in a stream of carbon monoxide at 300° for six hours. Only a slight darkening of the crystals resulted. In the hope of providing a more active surface than that possessed by the flat glassy plates of the sublimed molybdenum trioxide, 5 g. of ammonium molybdate was heated in a porcelain boat at 400° in a stream of carbon monoxide. After four hours of heating, the substance had the appearance of the blue oxide, and after six hours it had the reddish-brown color of molybdenum dioxide. Ascarite tubes were attached to the furnace and the heating was continued to see if carbon dioxide was still being evolved. In four hours 0.1399 g. of carbon dioxide was absorbed. The oxide was found to have a molybdenum content of 69.1%. In spite of the change in surface color the material was still largely molybdenum trioxide.

A 5-g. sample of the sublimed molybdenum trioxide was packed in a Pyrex tube with glass wool and heated in a stream of pure carbon monoxide (10 cc. per minute) at a temperature between 550 and 580°. The heating was continued intermittently for a total of more than fifty hours, checks on the carbon dioxide evolved being made for periods averaging five hours. During the last five hours of the run 0.1179 g. of carbon dioxide was evolved, much less than the amount obtained for any previous equal period. The reduced oxide was dark gray, almost black. The molybdenum analysis was low due to loss by creeping in the long solution process. The results were: molybdenum, 81.07%; carbon, 14.19%; glass wool, 2.55%. In light of Tutiya's work these results indicate that molybdenum trioxide is reduced to molybdenum carbide (Mo_2C) by the carbon monoxide and the molybdenum carbide then catalyzes the decomposition of carbon monoxide. The decrease in the amount of carbon dioxide leaving the reaction tube may be due to a decrease in the carbide–gas interface resulting from the deposition of free carbon.

Two grams of molybdenum dioxide in a porcelain boat was heated to a bright red heat in a stream of carbon monoxide and the heating was continued with a mixture 81% carbon monoxide and 19% carbon dioxide. The product was gray in color and analyzed 92.5% molybdenum, 4.8% carbon. The theoretical value for Mo_2C is 94.12% molybdenum. One gram of this product was heated to a bright red heat in a stream of carbon dioxide for one hour. The product for the most part had the characteristic color of molybdenum dioxide, though a small amount along the bottom of the boat was still gray. It analyzed 80.4% molybdenum. Though the exact temperature was unknown, it may be safely stated that it was about 800°, well within the range where separation of free carbon from a gas mixture of the composition used would be impossible. The conclusion that molybdenum dioxide reacts with carbon monoxide to form molybdenum carbide (Mo_2C) and carbon dioxide and that the reaction may be reversed was substantiated in the following experiments.

Final Measurements

A 20-g. sample of molybdenum dioxide was studied with mixtures of carbon monoxide and carbon dioxide containing at least enough carbon dioxide to prevent the separation of free carbon. The material was always heated and cooled in an atmosphere of carbon dioxide. Before any analyses were made a gas mixture containing nearly the maximum amount of carbon monoxide was passed over the oxide for about ten hours in order to ensure the presence of both solid phases. Several times during the course of the measurements when there was little difference between the inlet and exit compositions of the gas, this precaution was again taken; for it was thought that the continued heating and cooling in carbon dioxide might have led to the complete removal of the reduced phase.

The first analysis of the exit gas was not made until one hour after the gas mixture had been flowing. After the carbon dioxide was absorbed by passage through two tubes containing ascarite, the carbon monoxide was mixed with carbon dioxide-free air and drawn over hot cupric oxide. The resulting carbon dioxide was absorbed in a second series of ascarite tubes. Nine runs, made with

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(15) D. L. Randall, *Am. J. Sci.*, [4] **24**, 313 (1907).

analyses for only one of the components, had indicated the approximate equilibrium composition. Table I presents the first series of the final measurements.

TABLE I

Temp., °C.	Rate of flow, cc. per min.	Volume, cc. In	Volume, cc. Out	Composition, % CO_2 In	Composition, % CO_2 Out
812	25.05	501	500	46.6	48.0
814	24.44	489	489	47.6	48.2
815	20.17	605	611	49.1	49.0
815 ± 2	10.03	401	405	49.8	49.3

Three blank runs made at this point showed that the small differences between the inlet and outlet compositions were significant.

It appeared that the reaction rate was not quite sufficient to establish equilibrium compositions. The various sets of experiments shown in Table II were carried out with approximately constant compositions of inlet gas in order to see if the composition of the exit gas changed with time, and with various carbon dioxide proportions in order to determine the true equilibrium compositions. Though the runs are arranged in the order of increasing inlet carbon dioxide compositions, they were not all carried out in the same order. During the runs the ascarite tubes were connected for twenty minutes, and the rate of flow was approximately 20 cc. per minute. The time is measured from the beginning of the first analysis, which was not made until the gas mixture had been passing the hot sample for at least one hour.

In order to gain more information about the reaction which was occurring, the molybdenum dioxide was completely reduced. Table III presents the conditions under which the reduction was carried out on six consecutive days. In cases such as the present ones, where the outlet composition differs considerably from the inlet composition, it is possible to calculate rather satisfactorily the decrease in volume to be expected if Reaction 1 is occurring. In the first experiment 20 cc. of carbon dioxide passed into the reaction tube during the period of twenty minutes, as determined by the flowmeter setting. During the same time 89 cc. of carbon dioxide left the reaction tube; therefore 69 cc. of carbon dioxide was formed in the reaction tube. According to Reaction 1 82.8 cc. of carbon monoxide would furnish the 69 cc. of carbon dioxide, yielding a calculated contraction of 13.8 cc. The postulated course of the reaction is borne out by the other comparisons of contraction, as well as by the analysis of the final product. The mean of six analyses for molybdenum was 93.79 ± 0.39%, and that of seven analyses for carbon was 5.45 ± 0.15. The percentage of molybdenum in molybdenum carbide (Mo_2C) is 94.12.

Discussion

The first four series of measurements of Table II show a decrease in the concentration of carbon dioxide with increase in time of heating. It may be that the molybdenum dioxide formed by the heating and cooling in carbon dioxide was reduced with greater speed than the bulk of the material, but it hardly seems probable that an effect of this kind would last for such a long time.

TABLE II

Time in hours	Temp., °C.	Volume, cc. In	Volume, cc. Out	Composition, % CO_2 In	Composition, % CO_2 Out
0.0	813	401	397	35.4	42.6
2.5	813	402	401	35.5	41.1
4.5	814	397	392	34.9	40.6
6.5	815	402	398	35.5	40.4
0.0	811	419	422	40.1	43.2
2.0	813	420	422	40.3	42.2
4.0	812	397	397	40.3	42.2
6.0	813	398	398	40.0	42.1
0.0	815	401	400	41.8	45.5
2.0	812	402	404	41.8	44.0
4.0	812	402	403	42.0	43.4
6.0	811	398	397	41.6	43.35
9.5	814 ± 1.1	417	416	41.6	43.22
11.5	813	418	417	41.8	43.22
0.0	812 ± 2.7	395	393	43.4	46.1
3.0	811	380	378	43.3	44.7
4.5	812	395	396	43.4	44.5
0.0	811	401	402	44.5	45.2
2.0	810	397	399	44.3	44.9
4.0	811	398	397	44.6	45.2
0.0	811	399	397	45.1	45.8
2.5	810 ± 1.2	397	397	45.0	45.6
4.5	813	417	418	44.9	45.5
0.0	811 ± 4.2	421	425	47.2	48.4
2.0	812	401	401	47.1	47.8
4.0	813 ± 2.0	400	[a]	47.2	48.7
5.5	811 ± 2.0	400	[a]	47.2	47.5
0.0	813	395	403	47.3	47.2
2.0	811	397	398	47.3	48.0
4.0	813	398	392	47.3	48.0
0.0	812	394	399	48.2	48.2
2.0	811 ± 2.0	396	399	48.1	47.9
4.0	813	391	394	48.0	48.0
0.0	810	398	399	49.1	49.3
2.0	811	398	400	49.4	49.4
0.0	810	402	400	49.3	49.1
2.5	811	400	400	49.2	49.1
4.5	811	395	395	48.6	48.1
0.0	811	503	520	49.5	47.6
2.0	812	401	405	49.4	48.8
3.0	812	496	498	48.9	48.6
0.0	812	405	404	53.1	50.1
2.0	814	399	408	52.3	50.3
4.0	812	397	404	52.2	50.3

[a] No carbon monoxide analysis was made.

TABLE III

Temp., °C.	Rate of flow, cc. per min.	Volume, cc. In	Volume, cc. Out	Composition, % CO_2 In	Composition, % CO_2 Out	Contraction, cc. Calcd.	Contraction, cc. Obs.
975[a]	13.80	276	264	7.3	33.6	13.8	12
896	14.16	283	263	5.1	34.9	15.6	20
850	14.65	293	283	6.3	32.3	14.6	10
898	13.75	261	252	6.3	32.1	13.0	9
900	13.28	265	262	6.4	27.8	12.2	3
888	13.84	277	280	7.23	7.16	0.0	−3

[a] Approximate, due to limits of calibration.

An approximate value of the gas composition at equilibrium was obtained from a plot of the percentage of carbon dioxide in the inlet gas against the percentage of carbon dioxide in the exit gas (see Fig. 1), using the final value in each series of Table II and the values of Table I as representative of a steady state. The best curve drawn through the data of Table II crosses the diagonal of the graph at 48.1% carbon dioxide. The data of Table I give approximately a straight line crossing the diagonal at 48.9%. The average of these two values, 48.5% carbon dioxide, is taken as the composition at equilibrium, a value which obviously is subject to considerable error.

The temperature coefficient of the reaction is not known, but it should hardly introduce appreciable error to consider that the analyses give the gas composition at 810°. The equilibrium is dependent upon pressure. The majority of the experiments were made when the barometer reading was close to 750 mm. Using this figure for the pressure the equilibrium constant is $K_{1083} = 1.46$. If a pressure of one atmosphere were used in the calculation the value of K would be 1.44. Errors due to the uncertainty in the temperature and pressure are negligible in comparison with the error in the determination of the composition of the gas mixture at equilibrium.

One would expect so complicated a reaction as Reaction 1 to take place in steps, but the following considerations indicate that the formation of metallic molybdenum on a macroscopic scale as an intermediate step in the reduction is impossible. Chaudron[2] has measured the equilibrium constant for the reaction

$$\frac{1}{2}MoO_2 + H_2 = \frac{1}{2}Mo + H_2O \qquad (2)$$

from 700 to 1100° by a static method. From these results, at 810°, $\log K_{1083} = -0.276$.[16] There may be considerable error in the experimental values.[17] A plot of the values calculated for the water-gas reaction

$$CO + H_2O = CO_2 + H_2$$

by Gordon[3] gives $\log K_{1083} = 0.016$. This value can hardly be in error by more than 3%. Combining this with the value derived for Reaction 2, yields for the reaction

$$\frac{1}{2}MoO_2 + CO = \frac{1}{2}Mo + CO_2 \qquad (3)$$

$K_{1083} = 0.550$. Such a value of K indicates that mixtures containing less than 64.6% carbon monoxide would be incapable of reducing molybdenum dioxide to molybdenum in the same form that resulted in Chaudron's experiments (*i. e.*, irrespective of whether it be metallic molybdenum or molybdenum dissolved in molybdenum dioxide). In other words, assuming the accuracy of this value of K, the intermediate formation of molybdenum could not have taken place under the conditions given in Table II, with the exception of part of the first run. The formation of molybdenum as a first step in the reaction may be a partial explanation of the greater speed of reaction noted in Table III.

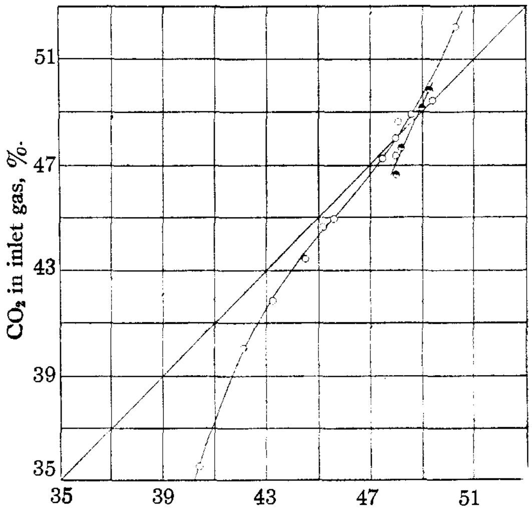

Fig. 1.—○ Data from Table II; ● data from Table I.

Schenck, Kurzen and Wesselkock[18] have studied

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[16] The averages of Chaudron's oxidation and reduction values were fitted to the equation

$$\log K = a/T + b$$

(in the absence of reliable heat capacity data) by the method of least squares. Thus $a = -1559.2$ and $b = 1.1634$. This equation gives for values of observed less calculated K, five plus values totaling 0.148, and three negative values totaling 0.130, and in view of the difference in the oxidation and reduction values, the equation seems satisfactory.

[17] P. H. Emmett and J. F. Shultz [THIS JOURNAL, **55**, 1376 (1933)] have recently pointed out that the values of equilibrium constants obtained by the static method are subject to a large error due to thermal diffusion. They found Chaudron's values of the water vapor–hydrogen ratio over iron and ferrous oxide to be from 0 to 40% higher than their own values and attribute this discrepancy to thermal diffusion. Since at 800° Chaudron's value of the ratio for the iron–ferrous oxide system is about the same as his value for the molybdenum–molybdenum dioxide system (approximately 0.5), one would expect about the same percentage error in both measurements if thermal diffusion was the main source of error in both cases. However, Emmett and Shultz's explanation of the discordance in the equilibrium measurements cannot account for all of Chaudron's measurements, for half of the latter's values of the water vapor–hydrogen ratio over magnetite and ferrous oxide deviate from the former's in a manner opposite to what one would expect if the deviations were due to thermal diffusion.

[18] R. Schenck, F. Kurzen and H. Wesselkock, *Z. anorg. allgem. Chem.*, **203**, 159 (1931).

the carburization of molybdenum by methane at 700 and 850° and have shown that an abrupt phase change occurs at about 5.9% carbon, *i. e.*, when molybdenum carbide (Mo_2C) is completely formed. Whereas at 700° subjection to further carburization leads to a metastable carbide of higher carbon content, at 850° equilibrium involving direct decomposition to free carbon (to which the carbide of higher carbon content is metastable) sets in. These results are compatible with those of the present contribution.

The value of the equilibrium constant for their reaction

$$2Mo + CH_4 = Mo_2C + 2H_2 \qquad (4)$$

may be calculated from those of Reactions 1 and 3, and that of the reaction

$$CH_4 + CO_2 = 2CO + 2H_2$$

The value for the latter, $K_{1083} = 216.2$, was derived by interpolation of the combination of Kassel's[19] values of $R \ln K$ for the formation of methane and of Gordon's[20] values of $R \ln K$ for the decomposition of carbon monoxide into graphite and carbon dioxide. These lead to K_{1083} for Reaction 4 equal to 3454, and $N_{CH_4} = 0.0003$. The results of Schenck, Kurzen and Wesselkock indicate values of approximately 0.004 and 0.001 at 700 and 850°, respectively. In view of the different character of the latter's experiments and the number of steps combined the agreement is satisfactory.

Summary

1. At 400° the reduction of molybdenum trioxide by carbon monoxide is very slow. The end-product of the reduction is apparently molybdenum dioxide, but no runs were made to establish this conclusion definitely.

2. At 560° molybdenum is reduced by carbon monoxide to molybdenum carbide and the carbide catalyzes the decomposition of carbon monoxide.

3. At 810° molybdenum dioxide is reduced to molybdenum carbide (Mo_2C). The over-all reaction is reversible and may be represented by the equation

$$2MoO_2 + 6CO = Mo_2C + 5CO_2$$

The equilibrium constant, K_p, at 810°, calculated on the assumption that the measurements were at 750 mm. pressure, is 1.46.

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(19) L. S. Kassel, THIS JOURNAL, **55**, 1357 (1933).

(20) A. R. Gordon, *J. Chem. Phys.*, **1**, 308 (1933).

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Equilibrium in the System Vanadium Tetroxide–Carbon Monoxide–Vanadium Trioxide–Carbon Dioxide

BY HUGH M. SPENCER AND JOHN L. JUSTICE[1]

There has recently been published a study[2] of equilibria in which the reactions are assumed to be

$$\tfrac{1}{2}V_2O_2 + H_2 = V + H_2O \qquad (1)$$
$$V_2O_3 + H_2 = V_2O_2 + H_2O \qquad (2)$$

which may prove to be a satisfactory means of defining the free energies of formation of vanadium compounds. The dissociation pressure of vanadium pentoxide[3] has also been studied, and values have been reported[4] for the reactions

$$V_2O_4 + H_2 = V_2O_3 + H_2O \qquad (3)$$
$$V_2O_5 + H_2 = V_2O_4 + H_2O \qquad (4)$$

This latter work appears to be unsatisfactory and the present investigation, in which the reversible equilibrium

$$V_2O_4 + CO = V_2O_3 + CO_2 \qquad (5)$$

was studied over the temperature range 750 to 896° by a flow method, was undertaken as part of a program of determining the free energy relations of the vanadium oxides. These are of interest in vanadium oxide catalysis involving oxidation, as well as that involving reduction where the method of production of the catalyst indicates the presence of the lower oxides.[5]

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(1) Du Pont Research Fellow, 1932–1934.

(2) M. Kobayashi, *Bull. Chem. Soc. Japan*, **8**, 231 (1933).

(3) E. F. Milan, *J. Phys. Chem.*, **33**, 498 (1929).

(4) H. Müller, W. Biltz's Festschrift, Hannover, 1927, quoted in J. W. Mellor's "Comprehensive Treatise on Inorganic and Theoretical Chemistry," Longmans, Green and Co., London, Vol. IX, 1929, pp. 741 and 744.

(5) J. M. Weiss, C. R. Downs and R. M. Burns, *Ind. Eng. Chem.*, **15**, 965 (1923); (a) O. W. Brown and C. O. Henke, *J. Phys. Chem.*, **26**, 272 (1922); and H. A. Doyal and O. W. Brown, *ibid.*, **36**, 1549 (1932). Incidentally it may be noted that the first-named authors used an incorrect form of the Nernst approximation equation (in which the heat effect was not doubled in expressing log p_{O_2}) in the calculation of the dissociation pressures of vanadium pentoxide and vanadium tetroxide.