[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT OF THE UNIVERSITY OF MANITOBA]

The Action of Carbon Dioxide and of Carbon Monoxide on Manganese

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In the course of experimental work in this Laboratory, Mr. T. H. Martin had occasion to use carbon dioxide in scavenging apparatus containing heated metallic manganese. He found that the issuing gas was inflammable and recognized it to be carbon monoxide, the only source of which could be reduction of the carbon dioxide by the metallic manganese. Accordingly, a systematic investigation of this reaction was undertaken by the present authors.

A search of the literature revealed the following. Guntz[1] prepared metallic manganese by distilling off the mercury from a mercury amalgam, produced by electrolysis. It is important to notice that the manganese so obtained was pyrophoric, or at least had a very small particle size. He heated this manganese to 400° in a current of carbon monoxide. The manganese burned with sufficient liberation of heat to raise the mass to white heat. The carbon monoxide was absorbed so rapidly as to cause a partial vacuum in the apparatus, no carbon dioxide being formed. Guntz gives the equation

$$Mn + CO = MnO + C + 34{,}500 \text{ cal.}^2$$

He then tried the reaction with carbon dioxide, using the same procedure, and observed the same results, in accordance with the equation

$$2Mn + CO_2 = 2MnO + C$$

Nishibori[3] heated pure manganous oxide with carbon monoxide at 780°. The analysis of the gas phase gave the equilibrium proportions: $CO = 93.5\%$, $CO_2 = 6.5\%$. Presumably the equilibrium here is

$$CO + MnO \rightleftarrows Mn + CO_2$$

Lorenz and Heusler,[4] working at low temperatures in the vicinity of 350°, made observations in agreement with those of Guntz. Insofar as their manganese was highly impure, containing 7% carbon, further detail seems inappropriate. In connection with our own observations, however, it should be mentioned that they heated the manganese in a stream of carbon dioxide, and on opening the apparatus the front end of the boat in which the manganese was heated was found to have been eaten away and a brownish manganese glass formed.

Charpy[5] has studied the reaction with carbon monoxide at 1000°, employing metallurgical products, metallic manganese and rich ferromanganese. The solid products consisted of a mixture of manganese monoxide and carbon. Heller[6] found that manganese begins to react with carbon monoxide at 330°, at 350° the reaction is fast, and at 410° very fast.

Both the reactions under consideration are heterogeneous, but they differ fundamentally from the frequently studied catalytic type, where the solid phase remains unchanged throughout. We may, however, accept the view that reaction is preceded by adsorption of the gas on the solid surface. If the adsorption is slight, the velocity measurements comply with the formula for a unimolecular reaction. When the saturation limit is approached, on the other hand, the rate of reaction is apparently independent of the concentration or pressure of the gas, until the concentration of the gas has decreased considerably. Such reactions are said to be of zero order.[7]

In the cases under consideration here, the matter is complicated by a further factor. When carbon dioxide, or carbon monoxide, reacts with metallic manganese, MnO is known to be formed. This must accumulate in an ever thickening layer around the manganese particle, and through this layer all carbon dioxide, or carbon monoxide, subsequently reacting with the manganese, must diffuse. In addition, where carbon monoxide is a product of the reaction, it must diffuse out through it. The velocity measurements give the resultant speed of three processes going on simultaneously: (1) adsorption, (2) diffusion, (3) reaction. If one process is slower than the others, its speed will be the effective speed of the three, no matter how great the velocity of the others. Diffusion may be slower, but can never be faster, than adsorption, for adsorption supplies the diffusing

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(1) A. Guntz, *Compt. rend.*, **114**, 115 (1892).

(2) For some reason not obvious, this value is about one-half that calculated from the heats of formation of reactants and products.

(3) E. Nishibori, Anniversary Volume dedicated to Masumi Chikashige, Kyoto Imp. University, 1930, pp. 295–8.

(4) Lorenz and Heusler, *Z. anorg. Chem.*, **3**, 225 (1893).

(5) G. Charpy, *Compt. rend.*, **148**, 560 (1909).

(6) W. Heller, "Beiträge zur Theorie des Eisenhochofenprozesses," (Marburg, 1905), p. 33.

(7) Hinshelwood, "Kinetics of Chemical Change in Gaseous Systems," Oxford University Press, 1929.

molecules. Similarly, reaction may be slower, but never faster than diffusion. If, in the cases under discussion, the slow process is that of diffusion, Fick's law of diffusion shows that the velocity measurements should comply with the formula of a unimolecular reaction, but we are faced with the further complication that Fick's law requires a diffusion layer of constant thickness, whereas here the layer of MnO is constantly increasing; the relative effect of increasing thickness would be greatest at first, subsequently decreasing with the thickness of the layer. Failure to comply with the unimolecular relationship will not therefore constitute evidence that diffusion is not the slow process. Furthermore, in the case of the carbon dioxide reaction, the carbon monoxide generated must diffuse out through the oxide layer, and this will have a retarding effect on the inward diffusion of carbon dioxide. It is evident from all this that any interpretation of the velocity measurements will be complicated, but certain predictions can be made. When the manganese is fresh, the oxide layer will be so thin that diffusion will produce no appreciable retardation. Accordingly, velocity measurements will give the resultant speed of adsorption and reaction together, and curves obtained by plotting composition of the gas phase against time will be similar to those for catalytic changes. When the manganese is old, and the layer of oxide thick, the increment in thickness as the reaction goes on will hardly affect the rate of diffusion. Then Fick's law will give the rate of diffusion of carbon dioxide through the layer quite accurately. This rate will be slower than the rate of reaction, which will therefore appear to be unimolecular.

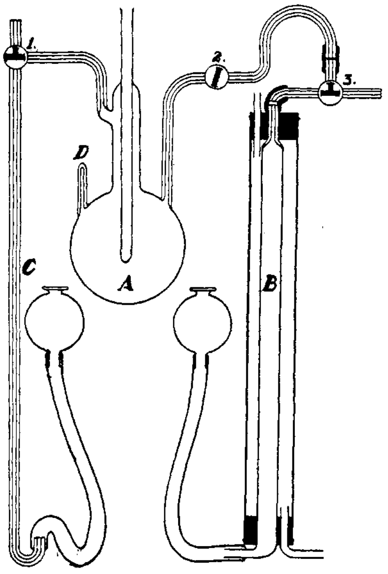

Fig. 1.

Experimental

Figure 1 is a diagram of the apparatus. The reaction chamber, A, was built from a Pyrex distilling flask of roughly 550 cc. total capacity. For temperature measurement inside this chamber an iron–constantan junction was used, the thermocouple leads running down the long tube in the neck of the flask. For measuring pressure an open manometer, C, was used, connected to the flask through the three-way cock 1; the manometer was read with a cathetometer. The free outlet of stopcock 1 led to a Hyvac pump. B is the gas buret for measuring samples taken for analysis; it was water-jacketed. The flask was filled with carbon dioxide through cock 3. After filling, the gas analysis pipets were connected to 3. An electric furnace was constructed such that flask A could be immersed completely in it, leaving only capillary tubing at uncontrolled temperature (about 0.3% of total volume). Temperatures were measured with a Leeds and Northrup potentiometer indicator, having an accuracy of 1 to 2 °F. As a check on the factory calibration, the cooling curves of pure zinc and of pure lead were taken with the instrument.

The side-arm D has the function of permitting additions of fresh manganese, without dismantling the apparatus. Carbon dioxide was prepared from limestone and hydrochloric acid and purified by passage through silver nitrate solution, calcium chloride, and phosphorus pentoxide. Carbon monoxide was prepared from sulfuric acid and sodium formate, and purified by passage through concentrated sulfuric acid, potassium hydroxide solution, calcium chloride, and phosphorus pentoxide.

The gas buret contained mercury, by lowering the level of which, samples of the gas phase could be removed and measured. The measured sample was then displaced through 3 to the gas pipets. That carbon monoxide is the sole gaseous product of the reaction was first determined by combustion with oxygen in a slow-combustion pipet. After this had been demonstrated, subsequent analyses were performed simply by determining the carbon dioxide with a potassium hydroxide pipet and obtaining carbon monoxide by difference.

Pyrophoric manganese was not used. The metal was obtained from the Johnson, Matthey Company of Toronto in the form of a powder and had the analysis: Mn, 96.84%; Fe, 1.74%; Si, 0.61%; C, 0.12%. The manganese was not in truly pulverized form but was very finely crushed and apparently had been screened to a uniform size after crushing. The mean diameter of the particles was 0.096 mm., but there were many particles much larger (> 0.16 mm.).

To determine whether or not the reaction represented by the equation

$$CO_2 + Mn = MnO + CO$$

was the sole one taking place, the flask was loaded with manganese and carbon dioxide, and its temperature gradually raised. Temperature and pressure were recorded every five minutes. Departure from Gay-Lussac law behavior began near 350° and became marked at 600°. Evidently, then, carbon dioxide is converted not only to carbon monoxide, but to a non-gaseous substance as well, for if the reaction were simply that formulated above, there would be no departure from Gay-Lussac law behavior.

That carbon monoxide is formed is beyond doubt. After one hour of heating at 600°, during which time the pressure fell over 400 mm., a sample of the gas contained only 1.0% carbon dioxide. Judging by the pressure drop, about 250 cc., at normal pressure, of gas remained. As previously mentioned, in similar preliminary experiments the carbon monoxide was determined directly by slow combustion, and it was found to correspond to 100% conversion.

After the completion of the preliminary experiments, systematic work was commenced at 600°, but owing to the frequent collapse of the flask under vacuum at this temperature, it was possible to bring only two runs to completion. The method of procedure followed throughout was to evacuate the flask, raise it to the required temperature, then fill it with the appropriate gas. The two successful runs gave the following results

Run	Duration, hr.	% CO_2 unchanged	Approximate initial press., mm.	Final press., mm.
2	1	0.0	831	646
3	0.5	0.0	869	727

The ratio of the change in pressure to the initial pressure gives the proportion of the whole going in the side reaction. This was 20.5% for run 2, and 16.3% for run 3. Since there was complete conversion to carbon monoxide in both cases, it appears to follow that the side reaction is slow compared to the main reaction, but that this deduction is not entirely justified will be seen in the sequel.

An experiment was now carried out at 500°, using 10.0021 g. manganese and 556 cc. carbon dioxide. At the end of two hours the pressure had dropped from 760 to 734 mm. and therefore the fraction of the whole being removed by the side reaction was 3.4%. The gas analysis at the end of the run showed no carbon dioxide remaining, which means that in two hours at 500°, with fresh manganese, the conversion of dioxide to monoxide is complete.

A series of runs was now undertaken in a somewhat different manner. Samples of the gas phase were withdrawn from time to time for analysis, and the whole experiment continued uninterruptedly until complete conversion was attained. Occasionally a run was carried out with carbon monoxide as starting gas, in an attempt to reach the equilibrium, if any, from the other side. Six experiments were carried out at 500°, and six at 400°, pressure readings being taken throughout, for the purpose of following the side reaction. Fresh metallic manganese was not used for each run, but a fresh charge occasionally was added to what was already present. Unimolecular "constants" were calculated for periods between consecutive analyses, and also for the period between the start and each analysis, the values being referred by calculation to a standard charge of 10 g. manganese.

The results showed that the relative speed of the side reaction is still less at 400 than at 500°. From the pressure drop, the fractions of the charge going to the side reaction are calculated as 7.3% in one and one-half hours at 500° and 4.0% in the same period at 400°. The unimolecular "constants" are by no means constant throughout any run. This can be seen from the plot of composition–time, where the curves appear to be much straighter than is required for unimolecular behavior. Figure 2 shows the composition–time curves for three runs. In each of these fresh manganese had been added recently. Runs A and B were at 500°, and run C at 400°. The curves show very well the greater speed at the higher temperature. Run B was faster than A, because the quantity of manganese was larger.

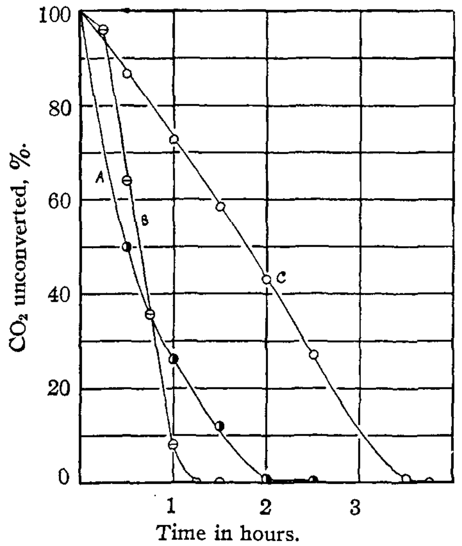

Fig. 2.—Conversion of CO_2 to CO in presence of manganese.

The form of the curves is similar to that of a zero order reaction. The long straight section shows a constant rate of conversion, indicating that adsorption of carbon dioxide is great. When conversion is nearly complete, the rate falls off because there is not enough carbon dioxide left in the gas phase to maintain the concentrated adsorption film.

When the manganese had been used for previous runs, its age began to have a retarding effect on the reaction rate. The "constants" showed this, being less numerically, with increasing use of the manganese. They did, however, show an approach to constancy with increasing use. This approach to constancy with age of the manganese was predicted in the introduction on the basis of diffusion.

In the runs that were followed right through, the final state was always one of complete conversion of carbon dioxide to the monoxide, so it was concluded that there was no appreciable equilibrium. As a check on this, two runs were carried out with carbon monoxide as the starting gas, one run for four hours at 500° and one for nineteen hours at 400°. In neither case was any carbon dioxide generated. Therefore, there is no appreciable equilibrium at 400 or 500°.

A number of runs in the neighborhood of 300° were vitiated from the following cause. A fresh supply of manganese had been obtained from Merck. This came in the form of a solid lump which was pulverized in a rock crusher. During the pulverizing, the manganese took fire for a moment. Subsequent examination showed it to contain manganese dioxide. In all attempts to use this powder it was characterized by extreme sluggishness of reaction. Apparently, then, the presence of a relatively small quantity of dioxide in the manganese insulates it more or less completely from being attacked by carbon dioxide. Fortunately there still remained some of the original manganese which was used in three experiments at 350°. These experiments showed that the reaction goes to completion at 350°.

To study the falling off in the rate of conversion with age of the manganese charge, an extended run was carried out at 500°. The reaction flask was cleaned out and 5.000 g. of fresh manganese introduced. The flask was then filled with carbon dioxide at 500° and the run continued until conversion to monoxide was just complete. The flask was then evacuated immediately and refilled with carbon dioxide. This process was repeated three times. The slowing down is illustrated by the curves of Fig. 3. Here composition is plotted against the logarithm of time, to shorten the diagram. The curves show progressively slower reaction rate with age of the manganese. When plotted against time and not log time, curve 1 has a straight portion like a zero order curve. The others curve at first and then flatten out to a line that is not far from horizontal for 3 and 4, and which approaches 0% CO_2 far out on the time axis. These curves come closer together with age of manganese, as the layer of oxide on the manganese particles becomes thicker. This increasing proximity of the curves for successive runs shows that a uniform rate of reaction is being approached, as was predicted in the introduction. Unimolecular "constants" were calculated for 3 and 4. The figures bear out what is evident from the curves, that the rate of reaction is not yet the same for successive runs. Were the manganese to be exhausted before the layer became sufficiently thick, this stage would never be reached. Comparatively coarse manganese would be more likely to give this effect.

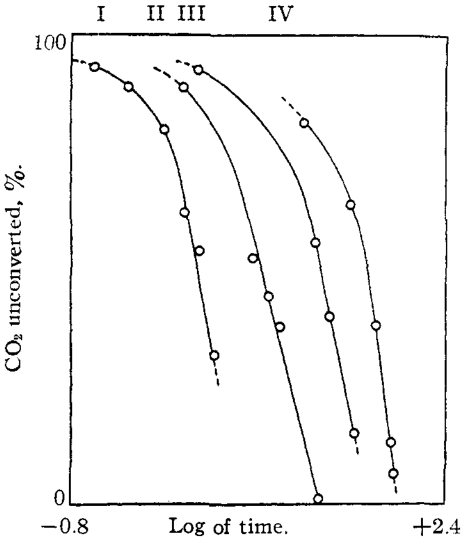

Fig. 3.—The effect of continuous use on the velocity of conversion.

Reaction between Manganese and Carbon Monoxide.—It was thought that this reaction would only attain measurable velocity above 600° and therefore a fresh apparatus was constructed. This consisted of a silica reaction flask connected to a hard glass manometer by a ground joint. The flask was embedded in a furnace capable of giving 800°. The capacity of the flask was 155 cc. and it was charged with 10 g. of manganese. The procedure was otherwise as before, except that no analysis was necessary, the course of the reaction being very simply followed by the drop in pressure.

For this work, the first consignment of manganese having been almost entirely exhausted and the second unsuitable, a third consignment was obtained from the Johnson, Matthey Co. Its analysis was much the same: Mn, 97.22%; Fe, 1.70%; Si, 0.55%; C, 0.11%, but the particle size was found to be much smaller. The average particle diameter was found to be 0.032 mm., as against 0.096 mm. for the manganese used in the earlier experiments.

Experiments were carried out at 600 and 500°. The results showed the reaction, which has been styled the "side reaction," to be unexpectedly rapid. This is undoubtedly due, at least in part, to the finer particle size. Considering consecutive experiments in which the same manganese was used, the speed of the reaction falls off rapidly with use, that is, with increasing thickness of the manganous oxide layer. The data do not comply with the requirements of a first order reaction. The reaction rate is much slower at 500 than at 600°.

An experiment was now carried out with the temperature rising from cold, to determine the temperature at which reaction became appreciable. On plotting pressure against temperature, it was seen that the reaction became rapid between 460 and 470°.

Because of the unexpected rapidity of the carbon monoxide reaction, a run was carried out at 600°, using the original coarser manganese. As was expected, the rate was much slower. Experiments were also carried out at 500°, using the coarser manganese. The velocity was less, although fresh manganese was used.

At all temperatures there is complete decomposition of the carbon monoxide by the manganese. The retarding effect of age is greater with the coarse manganese than with the fine, as would be expected.

The question now arose of whether, using the fine manganese, the same results, qualitatively at least, could be obtained, in respect of the conversion of carbon dioxide to carbon monoxide by manganese. For example, one of the early experiments gave complete conversion of carbon dioxide in two and one-half hours, using a fresh charge of 10 g. of coarse manganese at 500°. The experiment was therefore repeated at the same temperature, using the finer manganese. Pressures were read from time to time, and, after two and one-quarter hours, a sample of the gas phase was drawn off and analyzed for carbon dioxide. Conversion was practically complete and the pressure drop in two hours was 500 mm., whereas in the corresponding experiment with coarse manganese the drop in pressure was only about 40 mm. in the same time. This shows very clearly how the fineness of subdivision favors the reaction with carbon monoxide.

Presumably, if manganese is left in contact with either carbon dioxide or carbon monoxide, for a sufficient length of time, at a temperature of 500° or higher, complete decomposition of the gaseous phase to give manganous oxide and carbon, with production of zero pressure, will result. To test this point, an experiment was carried out at 600°, using carbon dioxide, and 10 g. of fresh fine manganese. Zero pressure was attained in thirty minutes.

Finally an experiment was carried out at 400°, using a carbon monoxide filling and 10 g. of the finer manganese. After two hours there was no change in pressure, indicating zero reaction velocity. It should, however, be mentioned that the manganese had been used in three previous experiments. At all events, the reaction velocity of the carbon monoxide reaction is very small at 400°. This is by no means the case with the carbon dioxide reaction.

As general conclusions to the latter part of this work, we would stress the effect of particle size. With pyrophoric manganese, at temperatures of 500° and above, it is possible that no carbon monoxide would be obtained from carbon dioxide by the action of manganese.

The Solid Phase

2.0364 grams of metallic manganese was heated in a stream of pure dry carbon dioxide in a porcelain boat contained in a wide silica tube, in an electric furnace at 600°. The charge was heated for five one-hour periods, at the end of each of which it was cooled in a stream of carbon dioxide and weighed. By the end of the fifth period the increase in weight was constant at 34.7% of original weight. The increase required for Mn–MnO is 29.2%.

The solid remaining had the characteristic dark green color of manganous oxide. An analysis of the solid product was then carried out. This gave the following figures: total Mn, 76.8%; free Mn, 4.87%; MnO_2, 1.1%; Mn as MnO_2, 0.7%; O_2 as MnO_2, 0.4%.

Mn as MnO = Total Mn − (Mn as MnO_2) − (free Mn) = 71.23%

O_2 required for MnO	21.1%
Carbon	1.45%
	99.75%

No other oxide contains O_2 and Mn in proportions to fit the analysis. It is apparent that carbon dioxide converts metallic manganese to manganese monoxide. The reaction is therefore

$$Mn + CO_2 = CO + MnO$$

The analysis shows an increase in the amount of carbon over that of the original manganese, which contained only 0.12% carbon. This increase can be explained by the side reaction

$$CO + Mn = MnO + C$$

When the tube was removed from the furnace the section where the boat had been was found to have a frosted appearance inside as if the silica had been acted on. This is of interest as Lorenz and Heusler[4] concluded that manganese was volatile in carbon monoxide at white heat and was deposited as a dust on the interior of the tube. It seems to us more likely that a volatile and very unstable carbonyl is formed.

For study of the reaction between carbon monoxide and manganese a similar apparatus was used, except that the carbon monoxide was stagnant and a manometer was introduced to indicate absorption.

A charge of 3.0015 g. of manganese was heated for five days at 700°, then for a short period at 870°, after which there was no further indication of a drop in pressure. When the cooled furnace was opened, it was found that the interior of the silica tube was covered here and there with a greenish black deposit, while adhering to the porcelain boat was a pink deposit, which rendered weighing useless. This is further evidence supporting the contention of Lorenz and Heusler that manganese is volatile in carbon monoxide. The charge in the boat, in addition to possessing the characteristic greenish color of manganese monoxide, contained shining crystalline granules, presumably graphite. When the silica tube was removed from the furnace, it broke in two where the boat had been. This was apparently due to the silica having been attacked, for a pink layer fully 2.5 mm. thick now constituted most of the wall of the tube: only a thin shell of unchanged silica remained. The pink material was crystalline and is perhaps manganese metasilicate, $MnO\cdot SiO_2$. The mineral rhodonite has this composition and is pink in color. Either manganese is volatile in carbon monoxide, as claimed by Lorenz and Heusler, or it reacts with it so violently as to be almost explosively dispersed. This latter alternative does not seem likely, as no signs of excessive activity were observed in the experiments.

Total carbon in the product was determined by direct combustion, and free carbon by treatment with 50% hydrochloric acid and burning the residual carbon. Both determinations gave the same result, indicating that all the carbon is free, and not existing as carbide. The results of the analysis were:

Free carbon (= total carbon) = 14.3%
Total Mn = 66.0%
O_2 by difference = 19.7%

This corresponds to C = 14.3%; MnO = 85.7%. The reaction

$$Mn + CO = MnO + C$$

requires a percentage composition of C, 14.5%; MnO, 85.5%.

Discussion

By the use of non-pyrophoric manganese, the reaction of carbon dioxide with metallic manganese has been shown to take place in two stages, viz.,

$$CO_2 + Mn = MnO + CO \text{ (first stage)}$$
$$CO + Mn = MnO + C \text{ (second stage)}$$

The net result: $CO_2 + 2\,Mn = 2\,MnO + C$.

Lorenz and Heusler, as well as Guntz, were aware of these reactions, but did not recognize them to be stages of one reaction. Guntz used pyrophoric manganese, and the reaction was so fast that he failed to observe the first stage, and from his results formulated an equation identical with that obtained by uniting the first and second stages, as above. Lorenz and Heusler used manganese that contained so much carbon that it corresponded to the formula Mn_3C, so that it cannot be claimed that their results represented the action of metallic manganese on carbon dioxide and carbon monoxide. They did, however, observe the conversion of carbon dioxide to carbon monoxide. They also observed, as did Guntz, that manganese monoxide and carbon are formed when carbon monoxide is used.

This work has established that the only products are those indicated by the equations. It also appears that metallic manganese is volatile in carbon monoxide. This can only mean that manganese unites with carbon monoxide to form a volatile compound, presumably a carbonyl, which is almost immediately decomposed. Lorenz and Heusler stated that a carbonyl is not formed, by which they mean a carbonyl having some degree of stability. Their spectroscopic examination of the gas issuing from their apparatus showed manganese to be absent, and this proves that, if carbonyl is formed, it must be extremely unstable.

The speed of reaction depends not only on the temperature, but on the age and quantity of the manganese. With fresh manganese, reaction is fast between 500 and 600°. It is slower at 400°, and extremely slow at temperatures approaching 300°. The carbon dioxide reaction is of the zero order type, when the manganese is fresh, as shown by the curves of Fig. 2. When the layer of manganese monoxide becomes of appreciable thickness, the rate of conversion is no longer dependent on adsorption, but on the rate of diffusion through the layer. Hence, when the manganese monoxide layer becomes very thick, the reaction appears to be of the first order.

Nishibori found an equilibrium between carbon dioxide and carbon monoxide at 780°, in the presence of manganese monoxide. At the lower temperatures at which the present experiments were carried out, no such equilibrium exists. Conversion of carbon dioxide to carbon monoxide was always complete, except in experiments near 300°, where the reaction is so slow that a false equilibrium seemed to exist. It is not possible, therefore, to calculate the heat of reaction from the van't Hoff isochore. The heats of reaction can, however, be calculated from the known heats of formation, whence we obtain

$$CO_2 + Mn = MnO + CO + 22{,}800 \text{ cal.}$$
$$CO + Mn = MnO + C + 64{,}400 \text{ cal.}$$
$$CO_2 + 2Mn = 2MnO + C + 87{,}200 \text{ cal.}$$

These figures show that both forward reactions are exothermic and hence the back reaction is favored by raising the temperature. Nishibori obtained 6.5% carbon dioxide at 780°, while our work shows that there is no equilibrium at 600°. Somewhere between these two limits of temperature, appreciable equilibrium sets in.

Summary

It has been shown that the reaction previously formulated

$$2Mn + CO_2 = 2MnO + C$$

really consists of two consecutive stages

$$Mn + CO_2 = MnO + CO \qquad (a)$$

and

$$Mn + CO = MnO + C \qquad (b)$$

At temperatures of 400° and less reaction (a) predominates almost exclusively. At temperatures higher than 400°, the velocity of reaction (b) increases very rapidly, and, using pyrophoric manganese, this probably would result in the complete removal of the carbon monoxide formed by (a), at least above 500°.

The velocities of both reactions are principally conditioned by the rate of diffusion through the manganous oxide layer. Apparently, manganous oxide is more pervious to carbon dioxide than to carbon monoxide.

Both reactions are exothermic but no indication of a back reaction was detected up to 600°.

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