A STUDY OF THE CO₂-C-CO
EQUILIBRIUM

by

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A thesis submitted in partial fulfilment of the requirements for the Degree of MASTER OF ARTS in the Department of CHEMISTRY

The University of British Columbia
April, 1949.
ABSTRACT

A method is described for determining whether or not the reaction represented by the equation:

\[ 2\text{CO} \rightarrow \text{CO}_2 + \text{C} \]

is a true equilibrium reaction. The procedure consists of placing radioactive carbon dioxide over charcoal at an elevated temperature. When equilibrium is reached, the gas present is comprised chiefly of carbon monoxide. The charcoal was tested for radioactivity after different intervals of time, once the equilibrium had been reached.

It was found that the charcoal had picked up a considerable amount of radioactivity. The activity, however, remained constant even after a prolonged period of heating at the equilibrium pressure.

If carbon monoxide was depositing carbon on to the charcoal surface, the activity of the sample should have increased with time. The absence of any increase indicated that the equilibrium reaction was proceeding by means of some other mechanism, which very probably involved the surface oxides on the charcoal.
I wish to thank Dr. M. J. Marshall for his help and guidance during the course of this research.
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A STUDY OF THE CO₂-C-CO EQUILIBRIUM

INTRODUCTION:

The CO₂-C-CO equilibrium was first studied by Deville (1) in 1864. Deville observed a slight degree of dissociation of carbon monoxide at high temperatures; no dissociation could be detected at temperatures above 1000°C.

Bell, in 1869 (2), found that iron and iron oxide as well as nickel and cobalt and their oxides were capable of decomposing CO. Bell gave the equation for the reaction as: 2CO → CO₂+C

The reaction was also studied by Boudouard (3), who investigated the effect of temperature on the equilibrium. Boudouard used catalysts for the decomposition of carbon monoxide. The results of the work indicated that the reaction was a true equilibrium and the formation of carbon dioxide from the monoxide was favoured at lower temperatures.

Rhead and Wheeler (4) made a quantitative investigation of the reaction in 1910. In experiments where they started with 100% carbon dioxide, they found that at temperatures of 800°C and below, the equilibrium was not attained even after prolonged periods of
heating.

At a temperature of 850° C., they calculated the rates for the forward and reverse reactions and found that the reaction \( \text{CO}_2 + \text{C} \rightarrow 2\text{CO} \) proceeded at a speed 166 times as great as that of the reverse reaction.

Rhead and Wheeler investigated the effects of temperature and pressure on the equilibrium, in a later paper. The results of this investigation indicated that the reaction was a true equilibrium. They studied the effect of pressures which ranged from 3.08 atmospheres to 0.66 atmospheres, and noted a very consistent value for the equilibrium constant. The reaction was studied over a range of temperatures, and they concluded that the reaction proceeded strictly in accordance with Le Chateliers law.

Broom and Travers in 1929 (5), made a thorough investigation of the reaction. The carbon surface was allowed to remain in contact with the two oxides over long periods of time. The reaction was studied at the two temperatures, 705° C. and 746° C., with two kinds of carbon; coconut carbon which had not been heated above 900° C., and sugar carbon which had not been heated to above 1000° C. Broom and Travers obtained a value of 0.225 for the equilibrium constant at 746° C. This value was arrived at both by introducing \( \text{CO}_2 \) and
CO into the reaction bulb.

From their experiments they concluded that the reaction between carbon, carbon monoxide and carbon dioxide is not represented by the equation:

\[ C + CO_2 \rightleftharpoons 2CO \]

but rather by a mechanism which proceeds in two steps:

1) \( CO_2 + \text{carbon} \rightarrow CO \text{(gas)} + \text{carbon-oxygen complex} \)
2) \( CO + \text{carbon} \rightarrow \text{carbon-CO-complex} \)

Broom and Travers also studied the effect of treating the carbon surface beforehand, with oxygen. They observed that the presence of oxygen on the surface increased the initial rate of the reaction of carbon dioxide with the carbon, and the effect depended upon the manner in which the carbon was treated with oxygen.

In a thesis, presented at this university, Brewer observed that when carbon monoxide was placed in contact with outgassed charcoal at 550\(^\circ\) C., no carbon dioxide could be detected after a considerable period of time.

Other work carried on over a period of years in this laboratory indicates that the adsorptive powers of carbon in the form of charcoal are not decreased after the charcoal has been exposed to carbon monoxide for a certain length of time. If carbon is deposited from the gas phase on to the charcoal surface, a decrease in activity would be expected, because the carbon atoms which are depositing have a chance to oriente
themselves in their most stable form. Therefore, any crystal structure or unstable configuration is eliminated, causing a decrease in adsorptive power on the carbon surface.

These observations lead to the possibility that carbon does not deposit on the charcoal from carbon monoxide in the gas phase, in the absence of a catalyst. It is possible that the equilibrium between carbon dioxide and carbon monoxide may take place through an oxide layer on the carbon surface. The reaction may be written -

\[ \text{CO} + (0) \xrightarrow{} \text{CO}_2 \]  

(in surface complex)

In the reverse reaction, carbon dioxide takes up a carbon atom from the charcoal to form carbon monoxide.

The existence of carbon-oxygen complexes on the surface of charcoal has been extensively discussed in the literature, particularly in connection with the mechanisms proposed for the combustion of carbon.

Langmuir (6) observed that carbon monoxide gave no trace of carbon dioxide on a glowing graphite surface. On the other hand, carbon dioxide was distinctly reduced on the surface of a moderately glowing graphite filament, a porous surface favouring the reaction more than a compact one. Langmuir observed that the carbon monoxide found in the carbon dioxide on the surface of the graphite filament comprised only about half of that required by the
chemical reduction process. Langmuir assumed that one oxygen atom from each reduced molecule of carbon dioxide, remained on the surface.

When the temperature of the graphite surface is raised, the spontaneous formation of carbon monoxide increases. If the temperature of the graphite is too low, no measurable carbon monoxide pressure in stationary gas experiments is produced. The carbon monoxide comes off only when the temperature of the graphite surface approaches a critical value. Sihvonen (7) states that this temperature is the temperature at which stable keto groups formed on the surface, break up.

Sihvonen gives the equation for the reaction in which cold carbon dioxide acts upon heated graphite as -

$$2C_x + CO_2 \rightarrow CO + QCO$$

R.F. Strickland-Constable (8) discussed the nature of these surface oxides of carbon. He assumed that the surface oxide complex consists of a series of definite chemical compounds, having a wide range of decomposition temperatures. He also concluded from experimental observations that the complex probably consists of compounds containing

$$\text{CO groups.}$$

These groups are attached to the carbon atoms. Organic compounds like

$$\begin{array}{c}
\text{CH}_3 \\
\text{CO}
\end{array}$$

$$\begin{array}{c}
\text{CH}_3 \\
\text{CO}
\end{array}$$
which contain this group decompose at much lower temperatures than the surface oxides. It is evident then, that the surface oxides are definite co-va lent compounds which may have a variety of possible structures, and which exhibit distinctive chemical properties.

These oxides will play an important part in any reaction between the carbon surface and oxides of carbon like CO$_2$ and CO. It is quite probable then, that the equilibrium between carbon, carbon dioxide and carbon monoxide is greatly influenced by the surface complex. A certain concentration of the complex must be built up on the surface before carbon monoxide can react with the solid phase to give carbon dioxide.

The purpose of this research is to investigate the possibility that the equilibrium is proceeding through the medium of the surface complex rather than the actual carbon lattice in the charcoal.

If radioactive carbon dioxide is placed over charcoal, the carbon surface will be oxidized until equilibrium is attained. Now, if the reaction actually proceeds as indicated by the equation

$$2C0 \rightleftharpoons CO_2 + C$$

it can be seen that the charcoal should pick up more and more radioactive carbon, if the solid phase is far in excess. On the other hand, if the reaction at equilibrium involves only the two oxides and the surface com-
plex, the solid phase should not become more radioactive over a period of time. There is a distinct possibility however, that the surface will pick up radioactive carbon from the gas phase due to adsorption or some mechanism whereby the surface complex is first formed. This activity should remain constant as the equilibrium reaction carries on.

Brandner and Urey (9) observed that there was an isotopic exchange reaction between carbon monoxide and carbon dioxide. Several mechanisms were proposed. The existence of such an exchange will not influence the conclusions of the above experiment, since if the reaction does proceed by means of the reaction:

\[ 2\text{CO} \rightleftharpoons \text{CO}_2 + \text{C} \]

then eventually we would expect the carbon to become increasingly more radioactive.
DIAGRAM I

To Gas Pipette

Position of Furnace

Charcoal
Diagram II

To Load Terminals of Capacitrol

Variac 110 v.

Ammeter

6 amp. fuse

Diagram III

To Furnace
Experimental:

Diagram (1) describes the detail of the quartz bulb and the furnace. The temperature at which the experiment was carried out was 850°C. The temperature was kept constant with the aid of a Wheelco "Capacitrol" (diagram 2).

The carbon dioxide used was stored in a glass bulb (diagram 3), and measured quantities of the gas were admitted to the charcoal tube by means of the gas pipette shown in diagram (4).

The changes in pressure were observed with a mercury manometer.

When the reaction reached equilibrium, the gaseous mixture was removed from the charcoal by means of a special mercury diffusion pump and a Töpler pump. The gases could be stored in a glass bulb, and the charcoal removed from the apparatus. The experimental procedure consisted of measuring the radioactivity of portions of the charcoal sample, at various times after the reaction had come to equilibrium. Several small samples of the charcoal, weighing about 0.37 gms. each, were counted every time the equilibrium reaction was interrupted. The radioactivity of the charcoal was measured with a standard type of Geiger counter.

At this point I would like to acknowledge the assistance and helpful suggestions of Dr. J. G. Hooley, in connection with the handling of radioactive materials.
DIAGRAM IV

To Reaction Chamber ← Vacuum → To Storage Bulb

Mercury Reservoir

DIAGRAM V

Liquid air Trap

Oil Pump
After these samples were counted, the charcoal was replaced in the apparatus and the equilibrium gas mixture was allowed to stand over the charcoal for another period of time.

A micro gas analysis gauge was also added to the apparatus (diagram 5). The equilibrium mixture could be analyzed for carbon monoxide and carbon dioxide. The gauge is essentially the same as a McLeod pressure gauge. A small amount of the gas is admitted and its volume and pressure are accurately recorded. The stop-cock at the top of the capillary is then opened and the carbon dioxide is solidified with liquid air. The carbon monoxide left, is drawn out of the small trap and the volume and pressure are again accurately recorded. The difference in pressure represents the percentage composition of the two oxides in the gas.

Since the gas in the space above the charcoal contains radioactive molecules, it is necessary that some definite procedure be adopted in removing the gas preparatory to the determination of the activity in the charcoal. If the gases were not all removed at 850°C., then when the charcoal was cooled to room temperature, there would be a possibility that some gas would be adsorbed, thus giving an increased activity to the charcoal.

Two alternatives are possible; the first is that all the gas above the charcoal be removed at 850°C., and
the second is that as much of the gas as possible is removed by means of a standard procedure which may be closely repeated for every run. It is practically impossible to remove all the gas, so the second alternative was employed. The gases were removed by means of the Töpler pump, until the pressure could not be read on the manometer. The diffusion pump was then employed for exactly one hour. At the end of this time, the collected gases were again removed. This procedure could be repeated for each run, thus ensuring that any adsorption taking place on cooling would be the same for each determination of the activity of the charcoal.

The charcoal sample consisted of many small particles of varying sizes and shapes. In order to obtain a representative portion of the charcoal for counting, the following procedure was used.

Five samples, of almost the same weight, were weighed out accurately on small aluminum discs. Since the samples were almost the same weight, any variation in activity from one sample to another could be attributed to the varying sizes and surface areas of the particles. The weights of the samples and the average activity of each were added, thus giving the activity of a sample weighing about 1.85 gms. This procedure made it possible to follow any change
in radioactivity of a fairly large sample of charcoal, and at the same time minimizing the error brought in because of the variation in particle size.

PREPARATIONS:

(1) treatment of charcoal - "Columbia Activated Carbon", grade 6 G, size 8-14 mesh, was extracted 72 hours with constant boiling HCL, then washed for four days with distilled water. The sample was dried, and then treated with HF in a platinum crucible. The charcoal was then washed in a Soxhlet extractor for three days with distilled water. A small amount of KOH was added to the water flask in order to neutralize the acid. The sample was subsequently outgassed for 10 hours at 1000° C., then raised to 1100° C. for an additional 2½ hours.

(2) Carbon dioxide - the radioactive carbon dioxide was prepared from 19.4 milligrams of BaCO₃ obtained from Chalk River. The original sample of the carbonate weighed 64 mg. and contained one millicurie. The isotopic ratio C¹⁴/C¹² was 6.8%. Diagram 3 illustrates the apparatus used. The carbon dioxide was generated from the barium carbonate by the drop-wise addition of a mixture of 80% H₂SO₄ (96%), and 20% fuming sulfuric acid. A dry ice-alcohol trap was included in the apparatus. The acid mixture was boiled previously, and the whole generating system evacuated. The active carbon dioxide was led into a large storage bulb.
The inactive carbon dioxide was prepared from dry ice. The carbon dioxide produced in this way was distilled through a dry ice-alcohol trap six times before being passed into the storage bulb. A dry ice-alcohol mixture was also placed around the trap on the storage bulb while the carbon dioxide mixture was first passed onto the charcoal. The above procedure served to remove virtually all of the water vapor present.

RESULTS:

The furnace was raised to a temperature of 850°C before the carbon dioxide was allowed to pass over the charcoal. The initial pressure was 39.7 cm. Hg. The accompanying graph shows how the pressure increased with time. After approximately 100 hours of heating, the pressure had risen to 64.5 cm. of Hg.

At this stage the gas was pumped out of the reaction chamber, and the charcoal was removed. Each sample was counted three times, and the average was taken. The samples were counted for a time of one minute, in each case. Table I gives the results of the first determination of the radioactivity. Table II gives the results of the count after 18\(\frac{1}{2}\) hours of further heating at the equilibrium pressure. Tables III, IV and V give the results after 44, 88 and 142\(\frac{1}{2}\) hours of further heating, respectively.

After the last period of heating, the gases were re-
### TABLE I

<table>
<thead>
<tr>
<th>Sample</th>
<th>Weight</th>
<th>Average counts/min.</th>
</tr>
</thead>
<tbody>
<tr>
<td>#1</td>
<td>0.3700 gm.</td>
<td>3462</td>
</tr>
<tr>
<td>#2</td>
<td>0.3696</td>
<td>3599</td>
</tr>
<tr>
<td>#3</td>
<td>0.3704</td>
<td>3852</td>
</tr>
<tr>
<td>#4</td>
<td>0.3689</td>
<td>3627</td>
</tr>
<tr>
<td>#5</td>
<td>0.3695</td>
<td>3916</td>
</tr>
</tbody>
</table>

1.8484 gms. gives 18,456 counts per minute

### TABLE II

<table>
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<th>Weight</th>
<th>Average counts/min.</th>
</tr>
</thead>
<tbody>
<tr>
<td>#1</td>
<td>0.3705 gm.</td>
<td>3486</td>
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<td>#2</td>
<td>0.3704</td>
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<td>#3</td>
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<td>3788</td>
</tr>
<tr>
<td>#5</td>
<td>0.3698</td>
<td>3603</td>
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</table>

1.8513 gms. gives 18,097 counts per minute

### TABLE III

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<th>Weight</th>
<th>Average counts/min.</th>
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</tr>
<tr>
<td>#2</td>
<td>0.3703</td>
<td>3592</td>
</tr>
<tr>
<td>#3</td>
<td>0.3702</td>
<td>3508</td>
</tr>
<tr>
<td>#4</td>
<td>0.3700</td>
<td>3548</td>
</tr>
<tr>
<td>#5</td>
<td>0.3703</td>
<td>3578</td>
</tr>
</tbody>
</table>

1.8511 gms. gives 17,531 counts per minute
### TABLE IV

<table>
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<th>Sample</th>
<th>Weight</th>
<th>Average counts/min</th>
</tr>
</thead>
<tbody>
<tr>
<td>#1</td>
<td>0.3707 gm.</td>
<td>3726</td>
</tr>
<tr>
<td>#2</td>
<td>0.3704</td>
<td>3807</td>
</tr>
<tr>
<td>#3</td>
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<td>3857</td>
</tr>
<tr>
<td>#4</td>
<td>0.3702</td>
<td>3853</td>
</tr>
<tr>
<td>#5</td>
<td>0.3709</td>
<td>3930</td>
</tr>
</tbody>
</table>

1.8525 gms. gives 19,173 counts per minute

### TABLE V

<table>
<thead>
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<th>Sample</th>
<th>Weight</th>
<th>Average counts/min</th>
</tr>
</thead>
<tbody>
<tr>
<td>#1</td>
<td>0.3698 gm.</td>
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</tr>
<tr>
<td>#2</td>
<td>0.3703</td>
<td>3883</td>
</tr>
<tr>
<td>#3</td>
<td>0.3709</td>
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<td>#4</td>
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<td>3983</td>
</tr>
<tr>
<td>#5</td>
<td>0.3707</td>
<td>3816</td>
</tr>
</tbody>
</table>

1.8516 gms. gives 19,364 counts per minute

### TABLE VI

<table>
<thead>
<tr>
<th>Sample</th>
<th>Weight</th>
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</thead>
<tbody>
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<td>#2</td>
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<tr>
<td>#3</td>
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<td>3770</td>
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<tr>
<td>#4</td>
<td>0.3695</td>
<td>3645</td>
</tr>
<tr>
<td>#5</td>
<td>0.3705</td>
<td>3636</td>
</tr>
</tbody>
</table>

1.8514 gms. gives 18,253 counts per minute
moved and the charcoal was raised to a temperature of 1000° C. At this temperature, the small amount of gas produced, was removed. The charcoal was left under these conditions for 12 hours. The temperature was then raised to 1100° C. for three hours, with the diffusion pump running continuously. Table VI gives the results of the radioactive count after this treatment.

In all cases, the background count was so small that it could be neglected.

The maximum difference between the weights of the samples for the five determinations was about 4 milligrams. This difference in the weights of the samples is too small to cause any appreciable variation in the radioactive counts.
DISCUSSION OF RESULTS

The average count for the first five determinations showed a maximum deviation of about 1830 counts. This represents a percentage deviation of about 9 or 10%. The fifth reading was made 293 hours after the first, and showed an increase of 908 counts or about 4.9%. In between these two determinations, the activity was observed to decrease to a minimum of 925 counts below the initial value.

From the above results, it does not appear that the activity of the charcoal is increasing with time. The variation in the activity, if not caused by carbon depositing from the carbon monoxide in the gas phase, could be caused by two effects.

The first is the source of error inherent in the counting procedure. The samples, as previously stated, varied considerably in size and shape. The Geiger counter is also subject to a statistical error. The maximum percentage deviation in counts between any one of the five samples for the five determinations, ranged from 13.1% to 5.4%. The effect of the varying sizes of the samples thus contributes to a considerable variation in activity.

The other factor which would cause variations in activity, is the possibility that the procedure for removing the equilibrium gas mixture was not consistent.
Another point which must be considered, is that the charcoal may have taken up practically all the radioactive carbon atoms from the gas phase, after only a few hours. This would explain the fairly constant value of the radioactive count. However, this does not seem reasonable, because the pressure increased fairly slowly after the carbon dioxide was initially introduced, indicating that the equilibrium was being approached slowly.

Table VI gives the results of a determination of the activity after the charcoal was outgassed at a higher temperature. The purpose of this outgassing process was to see if the activity of the charcoal decreased. From Table VI it can be seen that although the activity is lower than in the preceding determination, the activity still lies within the same limits as found before. If we assume that the activity is contained in the surface complex, the conclusion is that the complex can withstand very high temperatures without decomposing.

On the basis of the above results, it seems quite possible that the equilibrium reaction is proceeding through the medium of a surface complex rather than by the mechanism represented by the equation -

\[ 2\text{CO} \rightleftharpoons \text{CO}_2 + \text{C} \]

A more definite conclusion could be reached if it were possible to remove the source of error connected with the
counting of the solid samples.

In the counting of solid radioactive samples, an effect often occurs which might alter the conclusions of this experiment. It has been observed that after a sample reaches a certain thickness, the number of counts tends to become constant. This is due to the phenomenon of "self-absorption".

![Graph: Counts per unit time vs. Thickness of sample]

However, charcoal has a very large surface area, and in this case, the thickness of the active layer will always be fairly small. Therefore, we may still conclude that the constant value of the activity of the charcoal indicates that the equilibrium reaction is not proceeding as indicated by the equation:

$$2\text{CO} \rightleftharpoons \text{CO}_2 + \text{C}$$
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