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# A study of the graphitization of iron carbide

Frank Ireland
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UMI

# A STUDY OF THE GRAPHITIZATION OF IRON CARBIDE

by

FRANK IRELAND

A Thesis Submitted to the Graduate Faculty
for the Degree of

DOCTOR OF PHILOSOPHY

Major Subject Physical Chemistry

Approved:

In charge of Major Work

Head of Major Department

Dean of Graduate College

Iowa State College
1936

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# INTRODUCTION

In the heat treatment of steel the formation and decomposition of iron carbide plays a very important role. Probably for this reason investigations were first carried out to determine its stability.

In the past few years many investigations have been made upon the graphitization, free energy, heat of formation, heat capacity and entropy of iron carbide. Not only are there wide discrepancies in the results of the various investigators, but also in the results from the different experiments of the same investigator.

From the standpoint of the physical metallurgist, graphitization and carburization are very important. Knowing the value for the change in free energy, $\Delta F$, of the reaction,

$$3\ Fe + C \longrightarrow Fe_3C\ ,$$
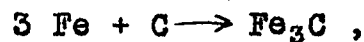
one can determine immediately whether iron carbide is stable or meta-stable, that is, whether carburization or graphitization occurs. If the free energy of the compound is greater than the sum of the free energies of its elements, that is, if $\Delta F$ is greater than zero, the compound is meta-stable. If $\Delta F$ is less than zero, the compound is stable.

There are three general methods of obtaining the

change in the free energy of chemical reactions.

One of these methods involves the relationship between the free energy change and the electromotive force of a galvanic cell in which the reaction takes place. This relationship is expressed by the equation,

$$\Delta F = -NFE$$

where E is the electromotive force of the cell, F is the Faraday equivalent and N is the number of such equivalents passing through the cell. However, as no one has been able to devise a cell in which the reaction,

$$3 \ Fe + C \longrightarrow Fe_3C \ ,$$
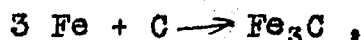
takes place reversibly, this method is of no value in this investigation.

Another method makes use of the relationship between free energy and the heat of reaction. The equation expressing this relationship is,

$$\Delta F = \Delta H - T\Delta S \ .$$

$\Delta H$ is the heat of formation, T the absolute temperature and $\Delta S$ is the change in entropy. The heat of formation, $\Delta H$, can be determined by subtracting the heat of combustion of the compound, from the sum of the heats of combustion of the elements in the compound, or by other less direct methods. By definition,

$$ds = \frac{dq}{T} = \frac{C_p dT}{T} \ ,$$

where $C_p$ is the heat capacity at constant pressure. Therefore the entropy at any temperature is,

$$S = S - So = \int_0^T \frac{cp}{T} \, dT,$$

since, by the third law of thermodynamics,

$$S = 0.$$

S is obtained by finding the difference in S for any two different temperatures. If the free energy is to be determined by the use of the above equations the heat of formation and heat capacity will have to be determined experimentally.

A more direct method of determining the free energy change would be to make use of the following expression for the change of free energy,

$$\triangle F^° = -RT\ln K,$$

where R is the gas law constant, T the absolute temperature, and K the equilibrium constant for the reaction.

The free energy change of the reaction,

$$3Fe + C \longrightarrow Fe_3C,$$
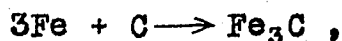
can be determined if the equilibrium constant, K, for the reaction is known. This constant can be determined indirectly. Assuming that the following reactions represent the mechanism for the graphitization and carburization of pure iron carbon compounds,

1. $3Fe + 2CO \longrightarrow Fe_3C + CO_2$

2. $C + CO_2 \longrightarrow 2CO$

$$3. \quad 3Fe + C \longrightarrow Fe_3C$$
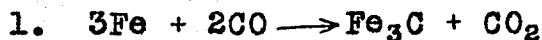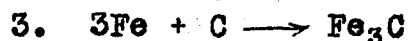
it is seen that reaction (3) proceeding toward the right is the sum of reactions (1) and (2) proceeding toward the right. If $\Delta F_1$, $\Delta F_2$ and $\Delta F_3$ represent the change in the free energy of reactions (1), (2) and (3) respectively, then,

$$\Delta F_1 + \Delta F_2 = \Delta F_3 .$$

Both $\Delta F_1$ and $\Delta F_2$ can be determined experimentally, however the equilibrium data for equation 2, in the International Critical Tables will be used in this investigation to obtain $\Delta F_2$.

$\Delta F_1$ can be obtained by determining the equilibrium constant, $K_1$, for equation (1), and substituting in the equation,

$$\Delta F_1 = -RT \ln K.$$

The expression for the equilibrium constant, $K_1$, for equation (1) is,

$$K_1 = \frac{P_{CO_2}}{P_{CO}^2} .$$

The immediate objective of this work is to determine values of $K_1$ at various temperatures. Values of $\Delta F$ and $\Delta H$ for the reaction,

$$Fe_3C \longrightarrow 3Fe + C ,$$
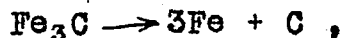
will then be calculated from these data.

## HISTORICAL

Of the investigations upon iron carbide, the heat of formation has received the most attention. Four distinct methods have been used and the resulting values for $\Delta H$ range from -27,000 to +78,750 calories. Table I contains in chronological order the names of the investigators, the values of $\Delta H$ and $\Delta F$ obtained by them, and the temperature at which the experiments were performed.

Campbell (1) dissolved iron and iron carbide, in cupric chloride solutions. He assumed the iron and iron carbide to be dissolved according to the reactions,

$$3Fe + 6CuCl_2 \longrightarrow 3FeCl_2 + 6CuCl$$

$$Fe_3C + 6CuCl_2 \longrightarrow 3FeCl_2 + 6CuCl + C.$$
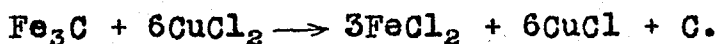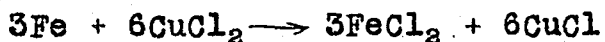
However, as hydrochloric acid was used to obtain complete solution, some of the combined carbon was probably converted into hydrocarbons. Since he assumed that the carbon be left as the element carbon, his results will necessarily be incorrect.

Brodie, Jennings and Hayes (7), Baykoff (3), Jerimilow (4), Ruff and Gersten (5), Roth (10), and Watase (9), all obtained values for $\Delta H$ by direct combustion in bomb calorimeters.

## TABLE I

Chronological Survey of Work Done on $Fe_3C$

| Date | Author | Temp. of Reaction | $\Delta H$ | $\Delta F$ |
|------|--------|-------------------|-----------|-----------|
| 1901 | Campbell (1) | Room Temp. | +8,494 | |
| 1907 | Schenck, Semillar and Falcke (2) | 650 to 700°C. | +8,940 | |
| 1911 | Baykoff (3) | Room Temp. | +1,430 | |
| 1911 | Jerimilow (4) | Room Temp. | +2,270 | |
| 1912 | Ruff and Gersten (5) | Room Temp. | -15,100 | |
| 1924 | Maxwell and Hayes (6) | 650 to 700°C. | -19,160 | 3,138 2,281 |
| 1926 | Brodie, Jennings and Hayes (7) | 30°C. | -13,580 | |
| 1927 | Schenck (8) | 700 to 900°C. | -15,405 | |
| 1928 | Watase (9) | Room Temp. | -4,800 | |
| 1929 | Roth (10) | Room Temp. | -3,900 | |
| 1931 | Pingualt (11) | 740°C. | -27,500 | |
| 1931 | LaCraft (12) | 700 to 800°C. | +78,750 | 3,784 cal. |
| 1932 | Janeoke (13) | 650 to 1050°C. | -6,500 | |
| 1932 | Yap and Liu (14) | 30°C. | 12,300 | 9,300 |
| 1934 | Naeser (15) | Room Temp. | -4,000 | |
| 1935 | Andes (16) | 25°C. | | 11,598 |

Schenck (8) used gaseous mixtures of hydrogen and methane in equilibrium with iron carbide and iron according to the equation,

$$Fe_3C + 2H_2 \rightleftharpoons CH_4 + 3Fe \ .$$
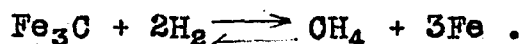
His method has the disadvantage, however, in that at high temperatures, methane decomposes and deposits carbon.

Schenck, Semillar and Falcke (2), used carbon monoxide-carbon dioxide equilibria reactions according to the equations,

$$3FeO + 5CO = Fe_3C + 4CO_2$$

$$3FeO + 3CO = 3Fe + 3CO_2$$
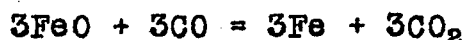
However, they used gas equilibrium values to calculate the heat of formation which have since been found erroneous.

Maxwell and Hayes (6) employed a static method using a gaseous mixture of CO and $CO_2$ in equilibrium with Fe and $Fe_3C$.

Janecke (13), Pingault (11) and LaCraft (12), each used $CO-CO_2$ mixtures in equilibrium with Fe and $Fe_3C$ and employed a dynamic method. Pingault states that above 740°C., $CO_2$ in the gaseous state varied between 0 and 28% and $Fe_3C$ was formed; between 740°C. and 700°C., $CO_2$ varied from 28% to 42% and $Fe_3C$ was oxidized to Fe and CO; below 700°C., $CO_2$ became sufficient to oxidize the iron.

Naeser (15) pointed out that the discrepancies in

the values of $\triangle H$ might be ascribed to the difference in the state of the carbon formed or used. By using graphitic carbon, calorimetric data were obtained which would indicate the value for $\triangle H$ to be -4,000 calories. In some earlier work carbon was produced in an amorphous state. The data obtained from this experiment yield a value of +8,000 calories for $\triangle H$.

The investigation of Evans and Hayes (17) in this laboratory using a static method, resulted in iron carbon alloys of rather high purity being graphitized in the presence of a gas mixture of CO and $CO_2$ at a pressure of fine atmospheres within the temperature interval of 700 to 1080°C. They did not calculate the heat of formation.

Schwartz (18) and Yap and Liu (14) consider the work of Brodie, Jennings and Hayes (7) the most reliable. Yap and Liu obtained their values of $\triangle H$ and $\triangle F$ by re-calculating the date of Brodie, Jennings and Hayes.

By determining the heat capacity of iron carbide and using the value of $\triangle H$ obtained by Yap and Liu, Andes (16) calculated the change in free energy for the formation of iron carbide to be 11,596 calories.

# EXPERIMENTAL

## Preparation of Materials

Iron turnings, approximately one millimeter in thickness and of an average length of perhaps ten millimeters were used. These turnings were secured by means of a lathe from an Armco iron rod one and one-half inches in diameter. This piece of iron was also used in the construction of the furnace which served as the reaction chamber in this investigation. The furnace and its construction will be described later.

The iron-carbon alloy turnings used in this experiment, were obtained from a steel slug which was prepared from pure Armco iron and pure carbon. The iron and carbon were melted in a magnesia crucible. C.P. magnesium oxide was sintered to about 1800°C. in a carbon crucible. This sintered magnesia was then ground to about 100 mesh, moistened with just enough of a one per cent magnesium chloride solution to make it stick together and made into a crucible. This magnesia crucible was made by packing the moistened magnesia into a carbon crucible six and one-half inches long and one and one-half inches of inside diameter. A piece of one inch glass

tubing, closed at the ends, was held in the center of the
carbon crucible. The magnesia was pressed between the walls
of the glass tubing and the walls of the carbon crucible. The
crucible was dried slowly at 100°C. in a muffle furnace and
then heated to 1800° C. in an induction furnace. After cooling
the crucible was filled with the correct amount of Armco
iron and carbon. The carbon was in electrode form and by
spectrographic analysis was found to contain only insignificant
traces of impurities. The crucible and contents were heated
again until the mixture became molten. It was kept molten
for about five minutes and then allowed to cool. The slug
thus obtained was examined microscopically and no free carbon
could be detected. The turnings from this slug were about
the same size as those of the pure iron. By analysis it was
found that the alloy contained 1.55% carbon.

The carbon dioxide was obtained from the Pure
Carbonic Company, Incorporated, of Chicago, Illinois and
certified by them. This gas after being passed through drying
towers was found, by Orsat analysis to contain no impurities.

The carbon monoxide was prepared from sulphuric
acid and sodium formate. C.P., concentrated, Grasselli,
sulphuric acid of 1.84 specific gravity and 95.60% $H_2SO_4$
was dropped from a dropping funnel upon reagent sodium formate,
which was prepared by the General Chemical Company of New

York. The sodium formate was in a three liter round bottom flask.

The nitrogen used, was from a cylinder secured from the Air Reduction Sales Company.

The calcium chloride used in the drying jars was eight mesh analytical reagent, obtained from the Mallinckrodt Chemical Works.

The anhydrous cuprous chloride used in the Orsat apparatus to absorb the CO, was prepared by mixing cupric sulphate and sodium chloride solutions and passing in $SO_2$ until no more precipitate was formed. The solution was filtered, the precipitate washed and redissolved in hot hydrochloric acid. Precipitation was again effected by dilution and passing in more sulphur dioxide. The precipitate was dehydrated by washing with glacial acetic acid. It was then dried in an oven and made into a 15% solution, using boiled hydrochloric acid solution, one part acid to one part water.

The potassium hydroxide used to absorb the $CO_2$, was a 40% solution of C.P. potassium hydroxide.

## Apparatus

The $CO_2$ cylinder, Figure 1, was equipped with a needle valve, V, so that the rate of flow of $CO_2$ gas could be more easily controlled. The delivery tube from this cylinder was an 8 m.m. Pyrex glass tube. It was connected
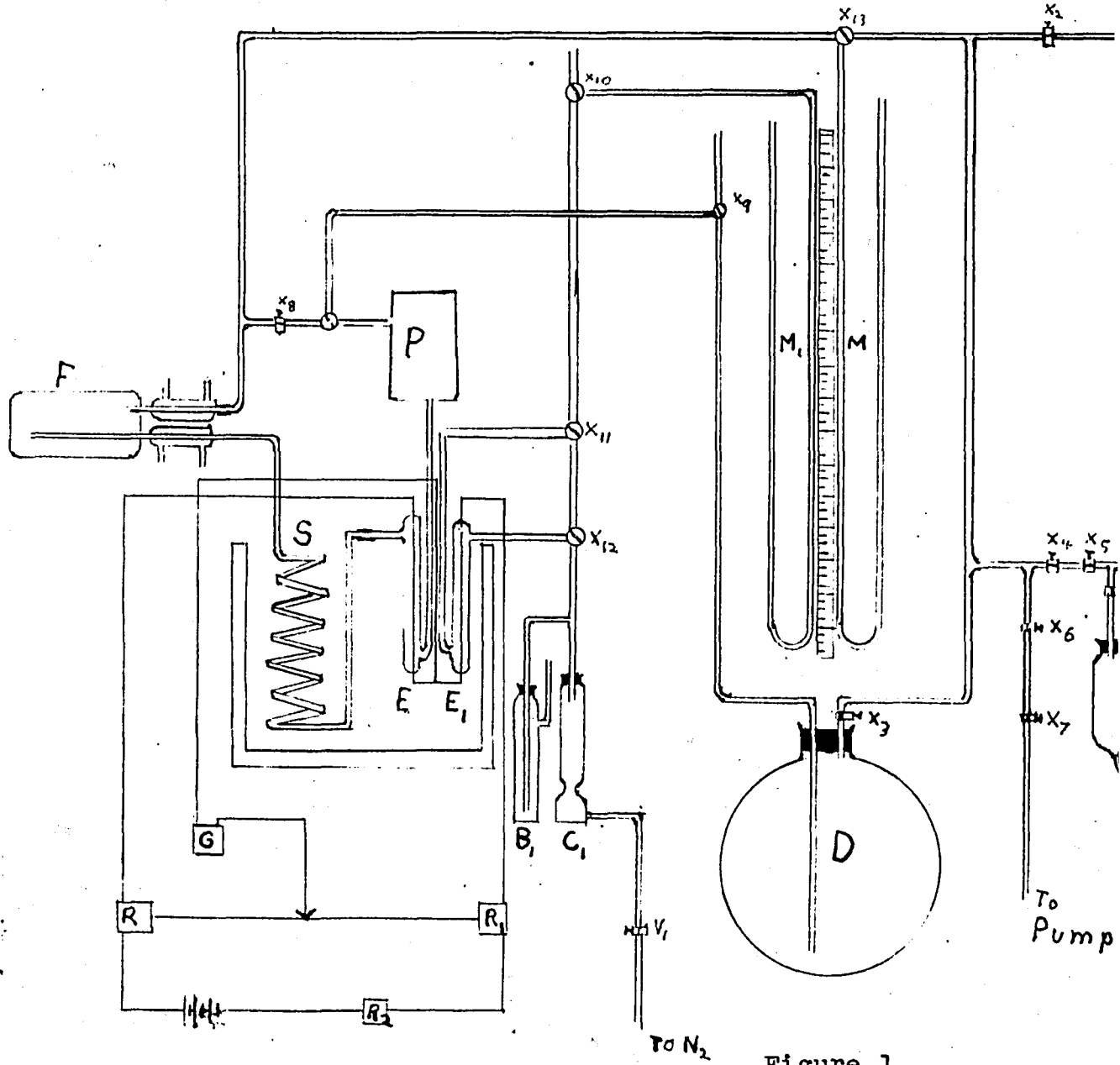
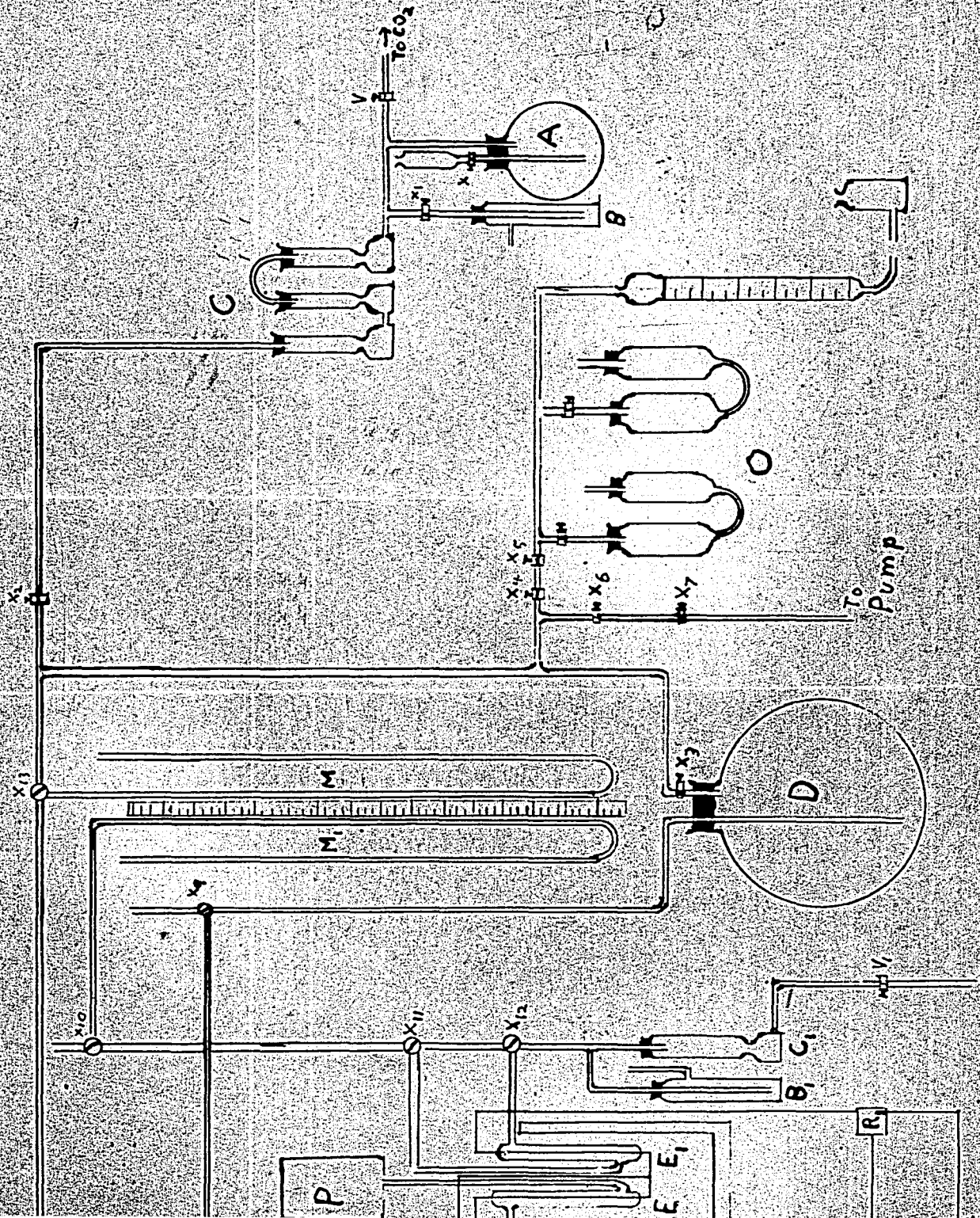Figure 1
GAS EQUILIBRIA APPARATUS

Figure 1

GAS EQUILIBRIA APPARATUS

to the $CO_2$ needle valve by means of pressure tubing and
thoroughly sealed with sealing wax.

The carbon monoxide generator, A, was a three liter
round bottom flask fitted with a two hole rubber stopper.
A dropping funnel extended through one of the holes of the
stopper to the bottom of the flask. A 7 m.m. glass tube,
forming a T seal with the $CO_2$ delivery tube, extended through
the other hole of the stopper into the flask so that the one
delivery tube served both the $CO_2$ cylinder and the CO generator.

Just beyond the CO generator another T seal was
made into the delivery tube. A Drechsel gas washing bottle,
B, was connected through stop cock $X_1$, to the delivery tube.
This bottle was partially filled with mercury and was used
as a safety trap.

Three drying jars, C, filled with $CaCl_2$ were next
inserted into the delivery line. The gases, after leaving
the drying jars, entered the gas reservoir, D.

This reservoir in which the carbon monoxide and
carbon dioxide were mixed, was a round bottom flask with a
capacity of twelve liters. The flask, carrying a two hole
rubber stopper, was wrapped loosely with cheese cloth and
placed in a wooden box as a safety precaution against shattered
glass in the event the flask should collapse during evacuation.
The delivery tube from the $CO_2$ cylinder and the CO generator
extended about three inches, through the stopper, into the

flask, D. The 8 m.m. Pyrex glass tube, conducting the gas from the pump, P, extended through the other hole in the stopper practically to the bottom of the flask.

An Orsat apparatus, O, was connected into the system just above, stop cock $X_3$. The 7 m.m. glass tubing containing stop cocks $X_6$ and $X_7$ connected the entire system to a "Cenco Megavac" mechanical pump.

$V_1$, a needle valve similar to V, controls the flow of gas from the nitrogen cylinder. $C_1$ is another drying jar, also filled with $CaCl_2$. $B_1$ is a safety trap similar to B. X, $X_1$, $X_2$, $X_3$, $X_4$, $X_5$, $X_6$, $X_7$, and $X_8$ are two way Pyrex stop cocks. $X_9$, $X_{10}$, $X_{11}$, $X_{12}$ and $X_{13}$ are three way Pyrex stop cocks. M is a mercury manometer made of 6 m.m. glass tubing, which registers the pressure of the carbon monoxide-carbon dioxide mixtures. $M_1$ is another manometer which measures the pressure of the nitrogen in the thermal conductivity cell, $E_1$.

P is an electromagnetic pump used to circulate the gaseous mixture through the system. It is somewhat similar to the one described by Treadwell and Hartnagel (19). A more detailed drawing of it is found in Figure 2. W is a steel slug, 2.5 inches long and turned down upon the lathe until it fits snugly into the glass tube A, whose inside diameter is 5/8 inch. This slug suspended by a steel spring, S, acts as the piston. This piston is motivated by a magnetic wire C.
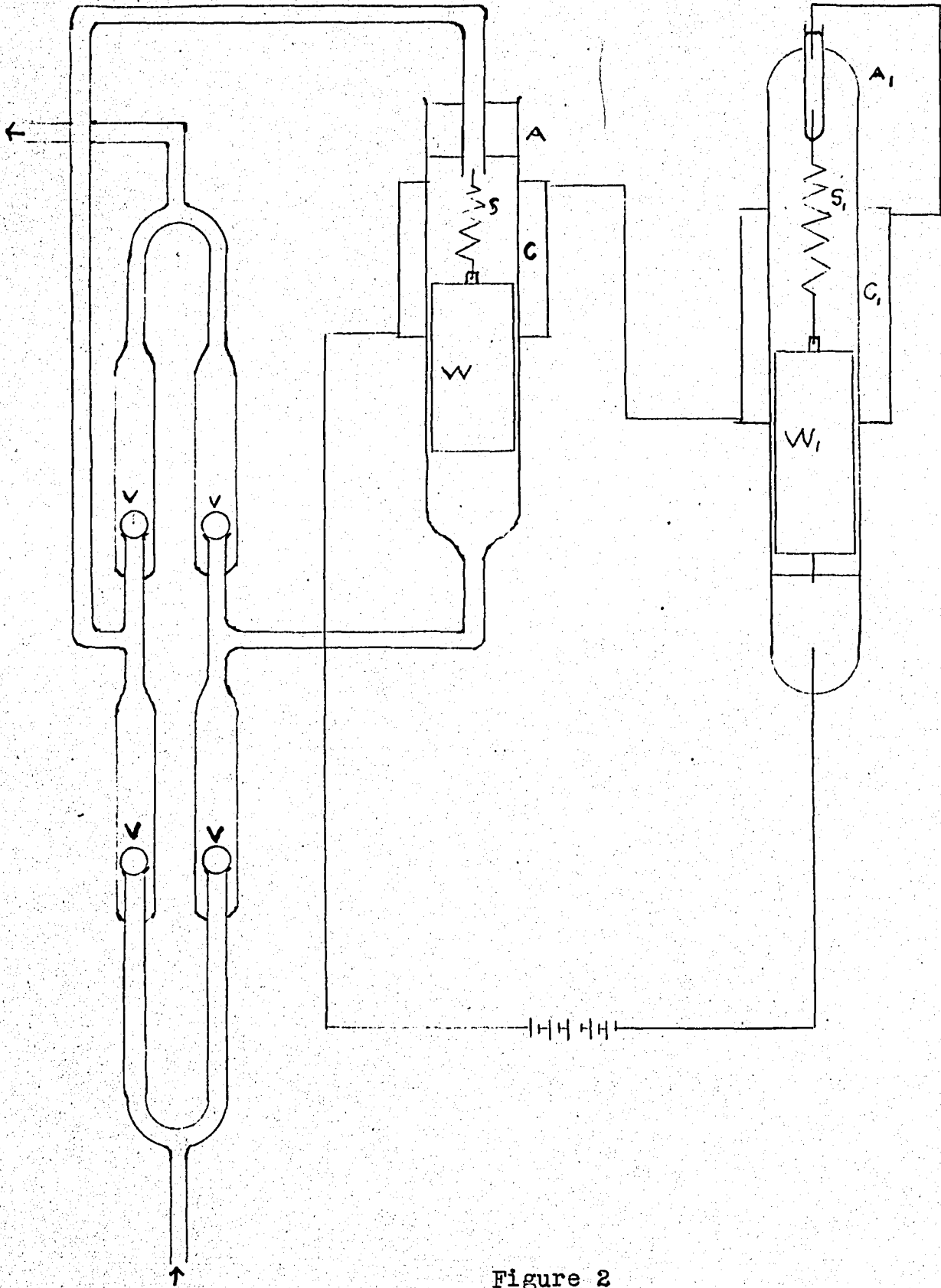
Figure 2

Electromagnetic Pump

This coil consists of about 2,000 turns of insulated, No. 32, copper wire. It is wound upon a thin wooden spool whose inside diameter allows it to fit snugly around the glass tube A. When a current flows through the coil C, piston $W$ is jerked upward, when the circuit is broken the piston drops down again. This vibration of the piston opens and closes the valves, V, forcing the gas upward through the pump.

The four valves, V, are steel balls, 6 m.m. in diameter. The ends of the glass tubing upon which they rest were flanged out and ground down with carborundum until the balls were seated very snugly. This grinding process was greatly lessened by pressing the ends of the glass tubes, while still hot over the steel balls, thus causing the glass to assume the proper size and shape. This glass tubing was 5 m.m. in diameter. The larger tubing surrounding the 5 m.m. tubing was 10 m.m. in diameter.

To make and break the circuit, another glass tube, $A_1$, similar to A, and containing a steel piston, $W_1$, was used. Unlike $W$, however, $W_1$ was a hollow cylinder. A piece of No. 18 copper wire was brazed onto the lower end of it so that when spring $S_1$ was supporting the weight of $W_1$, the wire made contact with the mercury in A. Electrical contact was made with the mercury through a piece of tungsten wire sealed through the bottom of tube $A_1$. The coil of wire, $C_1$, similar

to C, was connected in series with coil C. When piston $W_1$ makes contact with the mercury a current flows through both coils, the pistons are pulled up, this breaks the circuit and the pistons drop back again. 110 volt A.C. was used to operate the pump. The rate of flow of the gas through the pump can be controlled by adjusting the position of the coils C and $C_1$. To prevent oxidization of the mercury, tube $A_1$ was evacuated and filled with nitrogen gas.

The furnace used in this experiment, Figure 3, was made from a piece of Armco iron rod 1.5 inches in diameter and 10 inches long. A hole 1.25 inches in diameter was drilled co-axially through the center of the iron to a depth of 8.5 inches. A lid cut from the same piece of iron, was ground with carborundum and rouge upon the open end of the iron core until there was no gas leakage between them when the lid was fastened to the core. The lid has two 6 m.m. copper tubes hard soldered through it. Tube A, which conducted the gases into the furnace, extended one inch into the chamber. Tube B, which conducted the gases out of the furnace, extended within 1/4 inch of the outside of the thermocouple well. The length of the tubes on the outside of the furnace was about nine inches. A copper jacket was soldered around each so that cold water could be passed around the tubes, thereby keeping them cool. The lid carrying the tubes was fastened to the core by means of six screws. A heating unit,
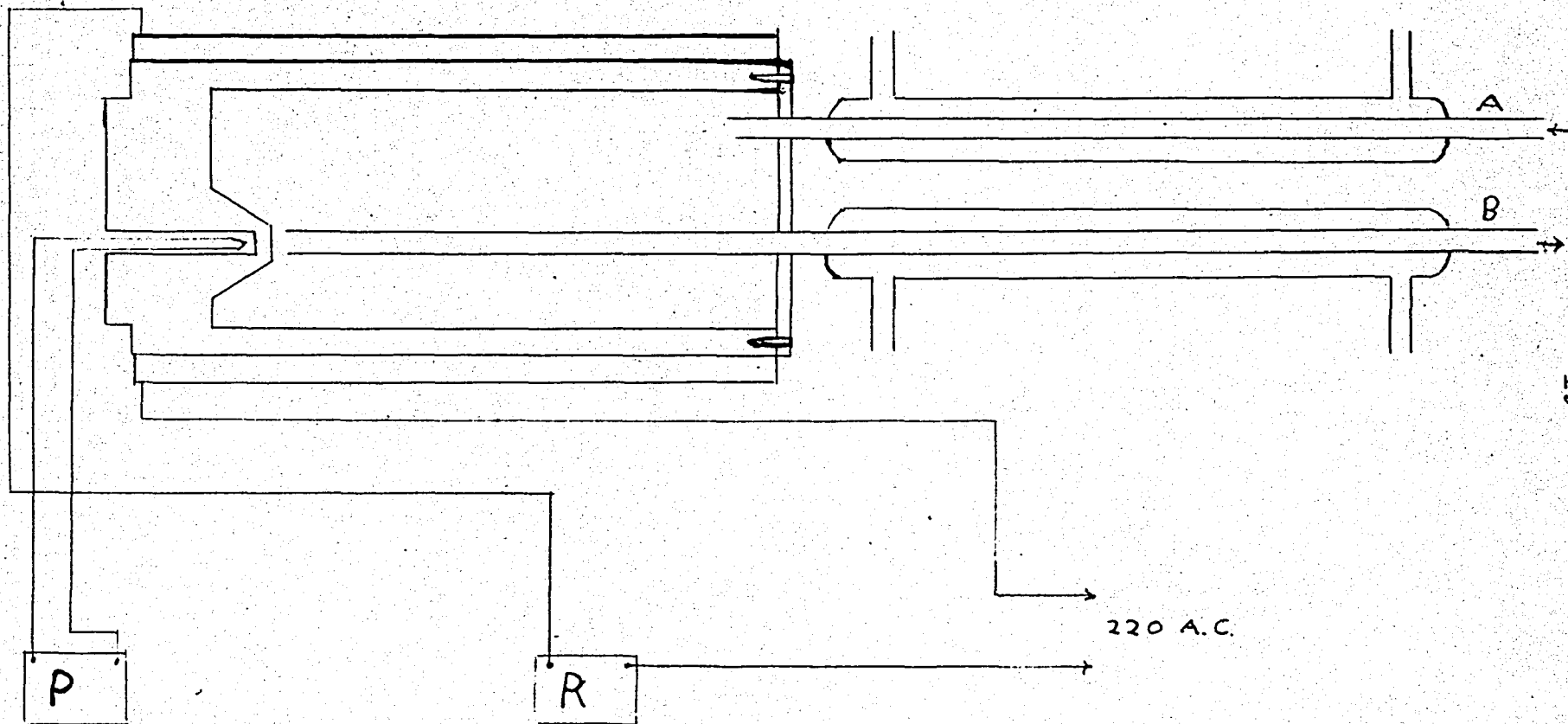
Figure 3

Furnace

Type 123, made by the Nevi Duty Electric Company, was used.
The unit and furance were then wrapped in several layers of
asbestos. The temperature was controlled by a rheostat, R,
built especially for this purpose. The thermocouple well
was drilled into the rear end of the furnace, as shown in
Figure 3. The thermocouple was made of No. 18 chromel and
No. 18 alumel wire. The electromotive force, produced by
the thermocouple was measured by a Leeds and Northrup
thermocouple potentiometer, P, which could be read to the
nearest microvolt.

The composition of the gases were measured by means
of the hot wire conductivity bridge, similar to the bridge
described by Daynes (20). The two cells, C and $C_1$, Figure 4,
are of Pyrex glass tubing, 10 inches long, with an inside
diameter of 12 m.m. A platinum wire 200 m.m. long and 0.05
m.m. in diameter was mounted co-axially in each of the tubes.
Tungsten wire was sealed through each end of the glass tube,
The platinum wire was connected directly to the tungsten at
one end; at the other end it was connected to a spring made
of platinum-iridium alloy, wire 0.008 inches in diameter,
which in turn was connected to the tungsten.

At each end of the cell a hole was blown in the side
wall of the glass tube and a 6 m.m. glass tube sealed on to
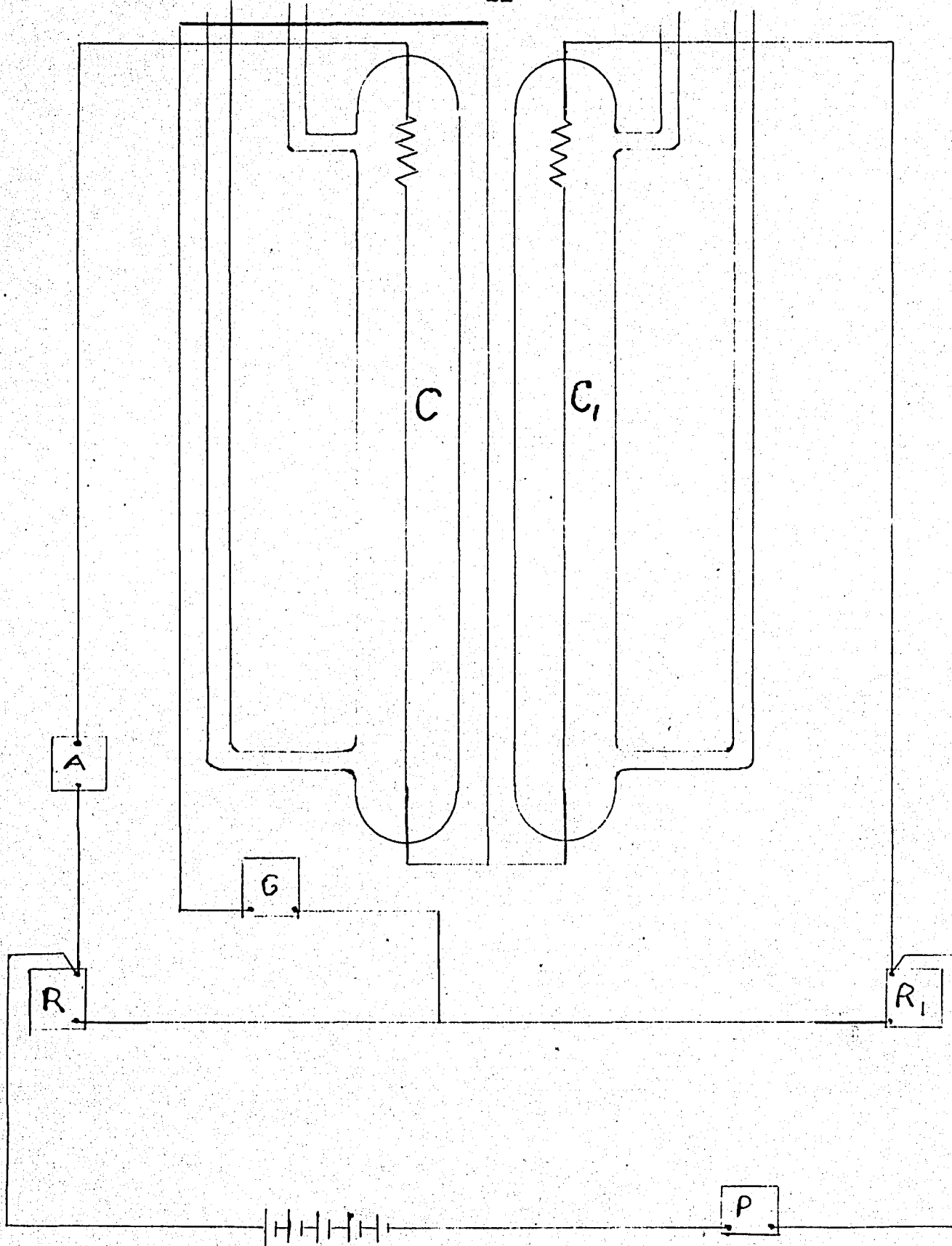provide for entry or exit of the gas. The gas was caused to

Figure 4
Conductivity Meter

flow through the cells at a rate of about 20 c.c. per minute. The unknown mixture of CO and $CO_2$ from the furnace flowing through cell $C_1$. These two cells are two of the resistance arms of a Wheatstone bridge. Two decade dial resistance boxes, R and $R_1$, are the other resistance arms of the bridge, and are connected by a bridge wire which forms part of the resistance of R and $R_1$.

Six dry cell batteries supplied the current. A 20 ohm radio rheostat, P, was used to control the current. The current, flowing through the cells, was measured by means of a millimeter, A, which could be read with an accuracy of one or two tenths of a milliampere. A Leeds and Northrup galvanometer, G, Type No. 2420, was used.

The cells were kept at a constant temperature of 24.7°C. in the thermostat, shown in Figure 1. The temperature of the thermostat was controlled by means of a Hiergesell Brothers, red top, thermo regulator, a Cenco dry cell relay, and a nichrome heating unit. The stirrer used on the thermostat was a Robinson Rochester Corporation, " Quick Mix" stirrer.

### Method of Procedure

Calibration of the conductivity meter.

Approximately 8 grams of pure iron turnings were

placed in the furnace, F, which served as the reaction chamber. The CO generator flask, A, was charged with sodium formate. The apparatus was then assembled as shown in Figure 1. The system was evacuated by closing stopcocks X, $X_1$, and $X_9$, and opening $X_6$ and $X_7$ to the Cenco pump. The other stopcocks were so turned that the entire system was open to the pump but not to the outside. The apparatus was then filled with $CO_2$ at atmospheric pressure. This process was repeated three times in order to rid the system of all nitrogen or oxygen.

Carbon monoxide was generated and mixed with the carbon dioxide in the gas reservoir. The pressure in the system was maintained in slight excess of the atmospheric pressure, so that, should there be a leakage, air would not get into the system. This excess pressure was so adjusted that the pressure on the inside was 748 m.m. The approximate desired composition of CO and $CO_2$ was obtained by allowing the CO to build up pressure and the excess gas to escape at intervals through stopcock $X_9$. Stopcocks $X_2$ and $X_6$ were closed while stopcock $X_1$ was open. Circulation was effected through the entire system by pump, P; stopcock $X_8$ was closed so that the gases, upon leaving the pump, entered aspirator D; from there they passed through the furnace F; then through the coil of copper tubing, S; next passing through the thermal conductivity cell, E; and back to the pump again.

More rapid mixing was secured by drawing the gases into the
gas burette of the Orsat apparatus and flushing them back
into the aspirator again. Accurate adjustment of the pressure
was obtained by opening stopcock $X_7$ to the pump, keeping
$X_6$ closed, evacuating, closing stopcock $X_7$ and opening
stopcock $X_6$.

Nitrogen was passed at a constant rate of 20 c.c.
per minute through cell E, and then permitted to escape
through $X_{10}$.

The resistance bridge was balanced for each gas
composition by changing the resistance of two of the arms,
R and $R_1$, by adjustment of the sliding contact on the slide
wire. The resistance change necessary to effect this balance
was taken as a measure of the change of composition. The
rheostat, $R_2$, was regulated so as to keep a constant current
of 200 milliamperes flowing through the cells.

After waiting a sufficient length of time for the
gases to form a homogeneous mixture, the position of the
sliding contact on the slide wire was noted. Samples of the
gas were drawn into the Orsat and analyzed. At first the
$CO_2$ was absorbed by a potassium hydroxide solution and the
CO was absorbed by a cuprous chloride solution, in order to
assure that no gases other than CO and $CO_2$ were present.
Later, however, only the $CO_2$ was absorbed and the CO obtained
by difference.

Readings were taken for mixtures varying from 56.4 to 93% CO. The readings of the slide wire and per cent composition are given in Table II, while Figure 5 shows the calibration curve obtained by plotting the bridge readings against per cent CO.

TABLE II

| Bridge Reading | % CO | % $CO_2$ | Temp. of Furnace | Temp. of Thermostat |
|---|---|---|---|---|
| 27.5 | 93.0 | 7.0 | 905°C. | 24.7°C. $\pm$ .05° |
| 32.8 | 89.7 | 10.3 | Room Temp. | " " |
| 37.8 | 87.0 | 13.0 | " " | " " |
| 40.0 | 85.0 | 15.0 | " " | " " |
| 44.5 | 80.8 | 19.2 | " " | " " |
| 46.6 | 78.0 | 22.0 | " " | " " |
| 50.5 | 72.6 | 27.4 | " " | " " |
| 53.6 | 67.0 | 33.0 | " " | " " |
| 55.0 | 65.6 | 34.4 | " " | " " |
| 58.5 | 60.6 | 39.4 | " " | " " |
| 61.8 | 56.4 | 43.6 | " " | " " |

Investigation of the reaction, $3Fe + 2CO = Fe_3C + CO_2$, using iron.

As carburization of iron is a very slow process and carbon does not penetrate the iron to a great depth at
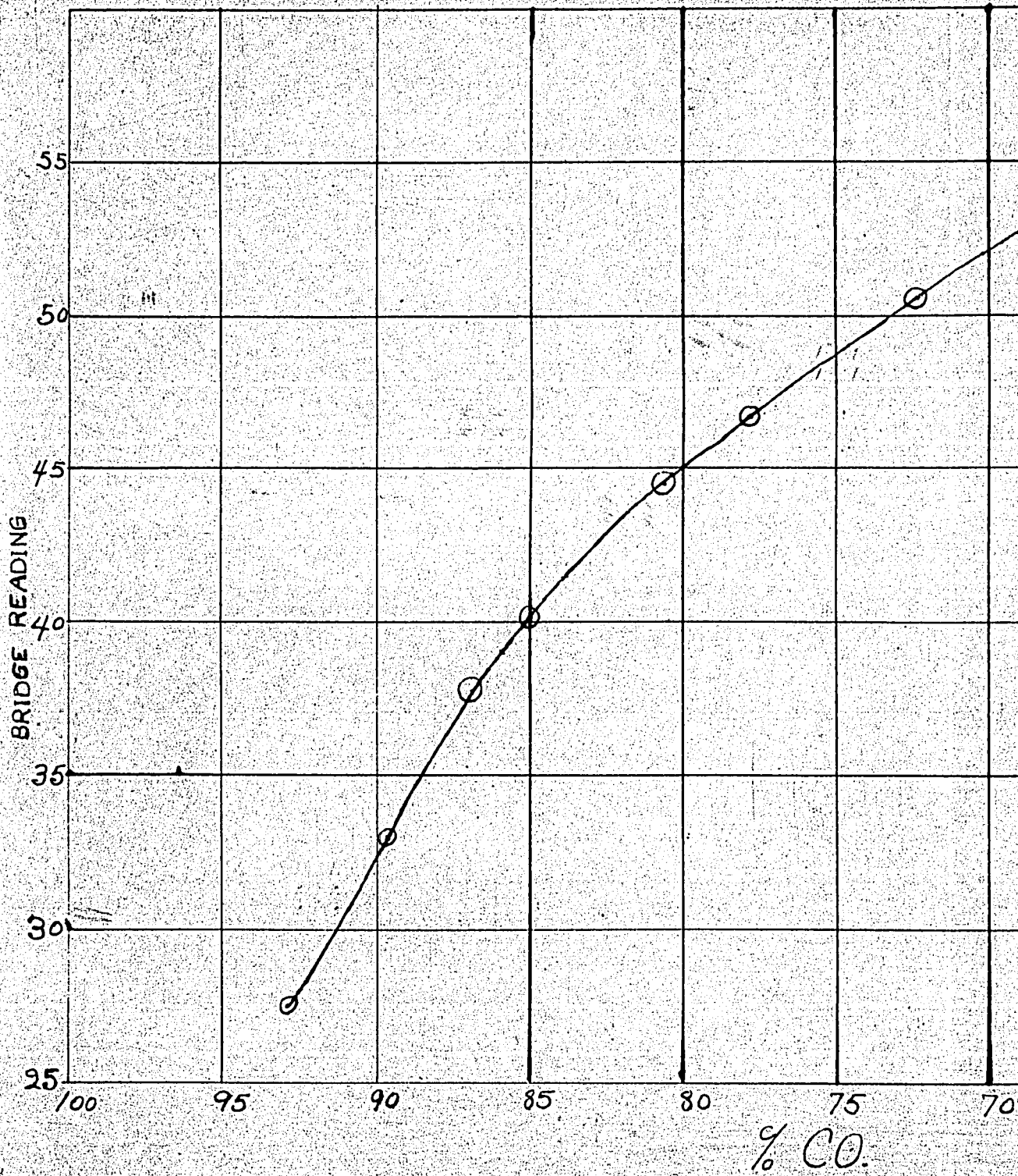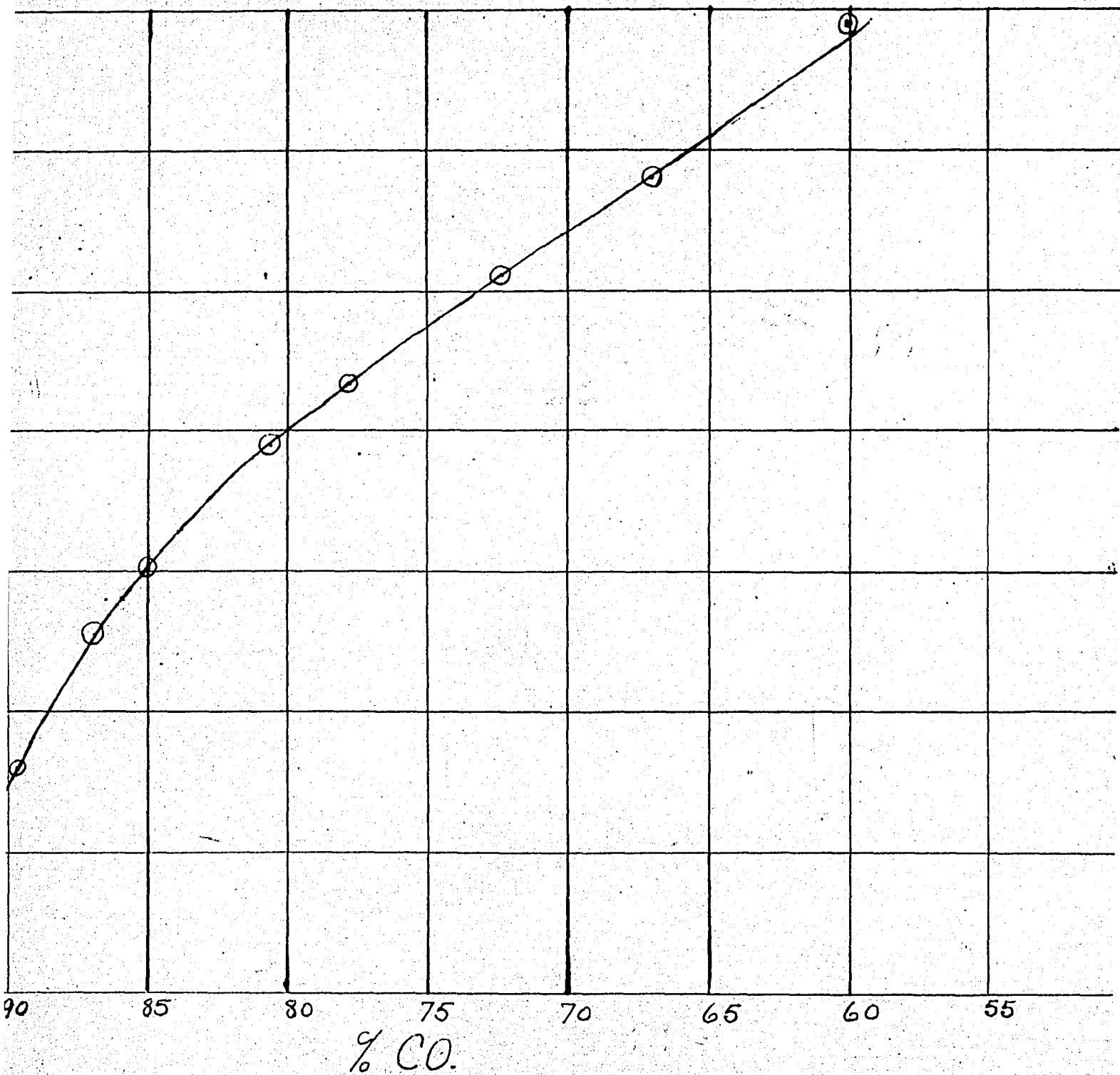
Figure 5

% CO.

Figure 5

temperatures of 700°C. or lower (21) the furnace, containing

about 8 grams of iron was heated to about 910°C. for

approximately 48 hours. The gas had previously been enriched

with carbon monoxide until the mixture was 95% CO. During this

time stopcock, $X_8$, was closed so that the pump circulated

the gas through the entire system. At the end of the 48

hours the bridge reading was recorded and a sample of the

gas drawn off and analyzed in the Orsat apparatus. These

data were used in the calibration of the bridge but not in the

equilibrium data for the carburization reaction, as there

might not have been a sufficient amount of iron exposed to

the gas mixture for the reaction to reach equilibrium.

With this in mind, the mixture was enriched in $CO_2$,

the gas circulated through the whole system and the reading

of the bridge noted. By closing stopcocks $X_9$ and $X_{13}$ to the

aspirator, and opening stopcock $X_8$, the gas was now circulated

only through the furnace, cell and pump. From the direction

of the change of the sliding contact on the bridge wire,

necessary in order to keep the bridge balanced, it was

quickly determined whether the temperature of the furnace was

smaller or greater than that demanded to maintain the original

gas ratio. The furnace temperature was then adjusted so that

the change in CO content would be small. When the reaction

had reached equilibrium, the bridge reading and furnace

temperature were recorded. The temperature of the furnace was now lowered a few degrees and after equilibrium was again reached, the corresponding data recorded. Successive temperatures and bridge readings were thus obtained until the CO content had changed about four or five per cent; the $CO_2$ in the gas reservoir was increased, the gas allowed to circulate through the entire system for awhile, and the above process repeated. Readings were thus obtained from 896 to 576°C.

These data and the per cent composition of the gases, which were obtained from the bridge calibration curve, are given in Table III. Figure 6, shows the CO per cent from the reaction,

$$3Fe + 2CO = Fe_3C + CO_2$$

plotted against the temperature.

Table IV contains the data secured in the same manner by taking readings at intervals while the temperature of the furnace was being raised from 576 to 905°C. Data from this table were used to show graphically, Figure 7, the change of carbon monoxide with temperature.

Data for Table V and Figure 8, were obtained by taking readings while the temperature was changed from 905 to 590°C.

During all this work the temperature of the thermo-

## TABLE III
### Run 1

| Bridge Reading | Temperature of Furnace | % CO | % $CO_2$ |
|---|---|---|---|
| 36.8 | 896 | 87.6 | 12.4 |
| 37.0 | 878 | 87.4 | 12.6 |
| 37.2 | 865 | 87.3 | 12.7 |
| 37.3 | 850 | 87.2 | 12.8 |
| 39.0 | 796 | 86.0 | 14.0 |
| 41.4 | 806 | 84.0 | 16.0 |
| 41.0 | 784 | 84.4 | 15.6 |
| 40.3 | 750 | 84.9 | 15.1 |
| 44.5 | 735 | 80.8 | 19.2 |
| 46.6 | 724 | 78.0 | 22.0 |
| 53.2 | 705 | 68.3 | 31.7 |
| 53.0 | 685 | 67.0 | 33.0 |
| 56.1 | 670 | 64.2 | 35.8 |
| 56.6 | 638 | 63.6 | 36.4 |
| 58.5 | 592 | 60.6 | 39.4 |
| 58.6 | 576 | 60.5 | 39.5 |

## TABLE IV
### Run 2

| Bridge Reading | Temperature of Furnace | % CO | % CO$_2$ |
|---|---|---|---|
| 58.6 | 576 | 60.5 | 39.5 |
| 55.7 | 658 | 62.2 | 37.8 |
| 50.5 | 710 | 72.6 | 27.4 |
| 46.7 | 728 | 77.7 | 22.3 |
| 44.8 | 730 | 80.3 | 19.7 |
| 40.2 | 757 | 85.2 | 14.8 |
| 37.4 | 815 | 87.1 | 12.9 |
| 37.4 | 836 | 87.1 | 12.9 |
| 37.2 | 842 | 87.3 | 12.7 |
| 37.2 | 867 | 87.3 | 12.7 |
| 37.2 | 880 | 87.3 | 12.7 |
| 36.9 | 905 | 87.6 | 12.4 |

Figure 6

CO-CO₂ Equilibria Diagram for Run 1

% CO.

Figure 6

CO-CO$_2$ Equilibria Diagram for Run 1

Figure 7

CO-CO$_2$ Equilibria Diagram for Run 2

%CO.
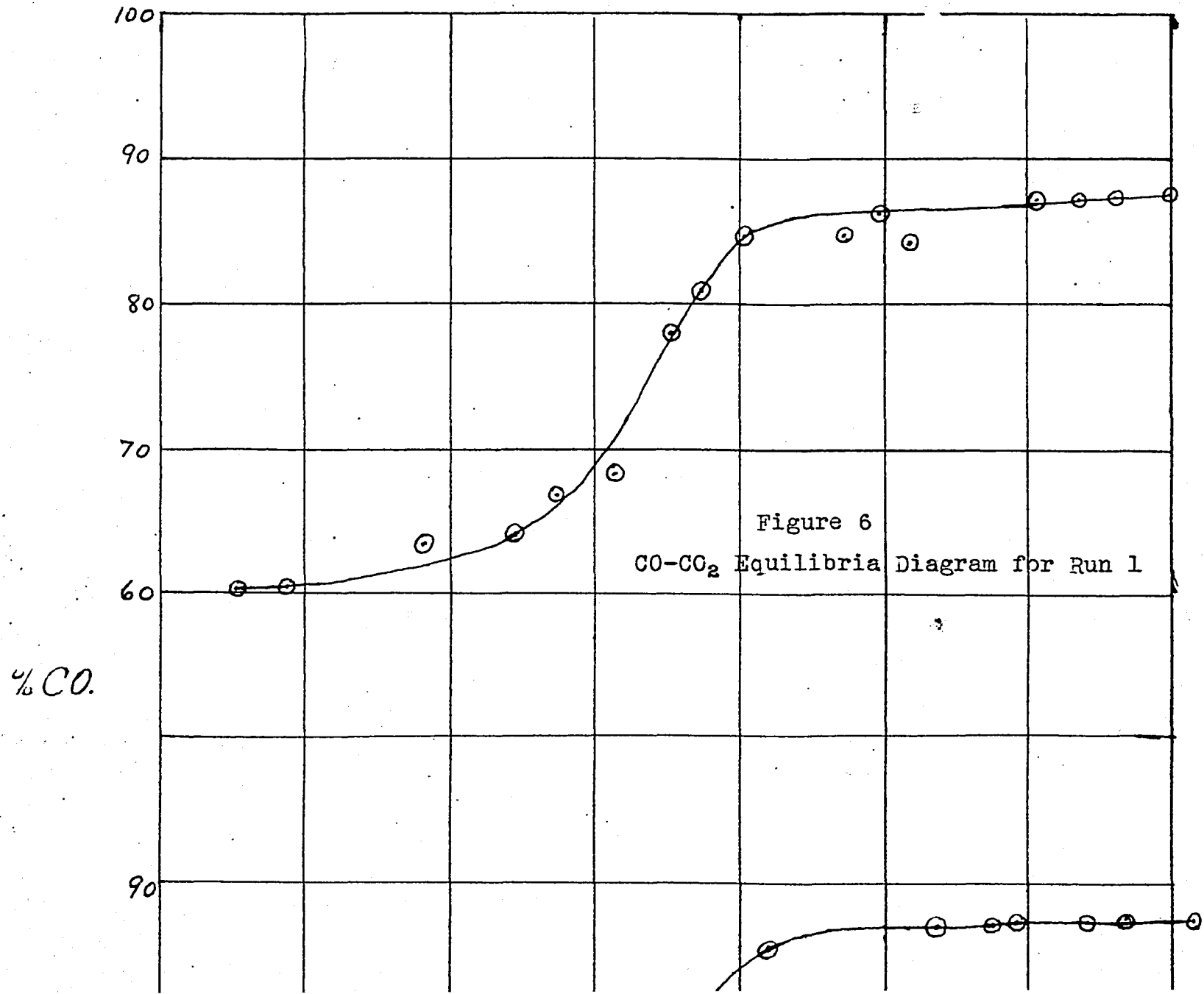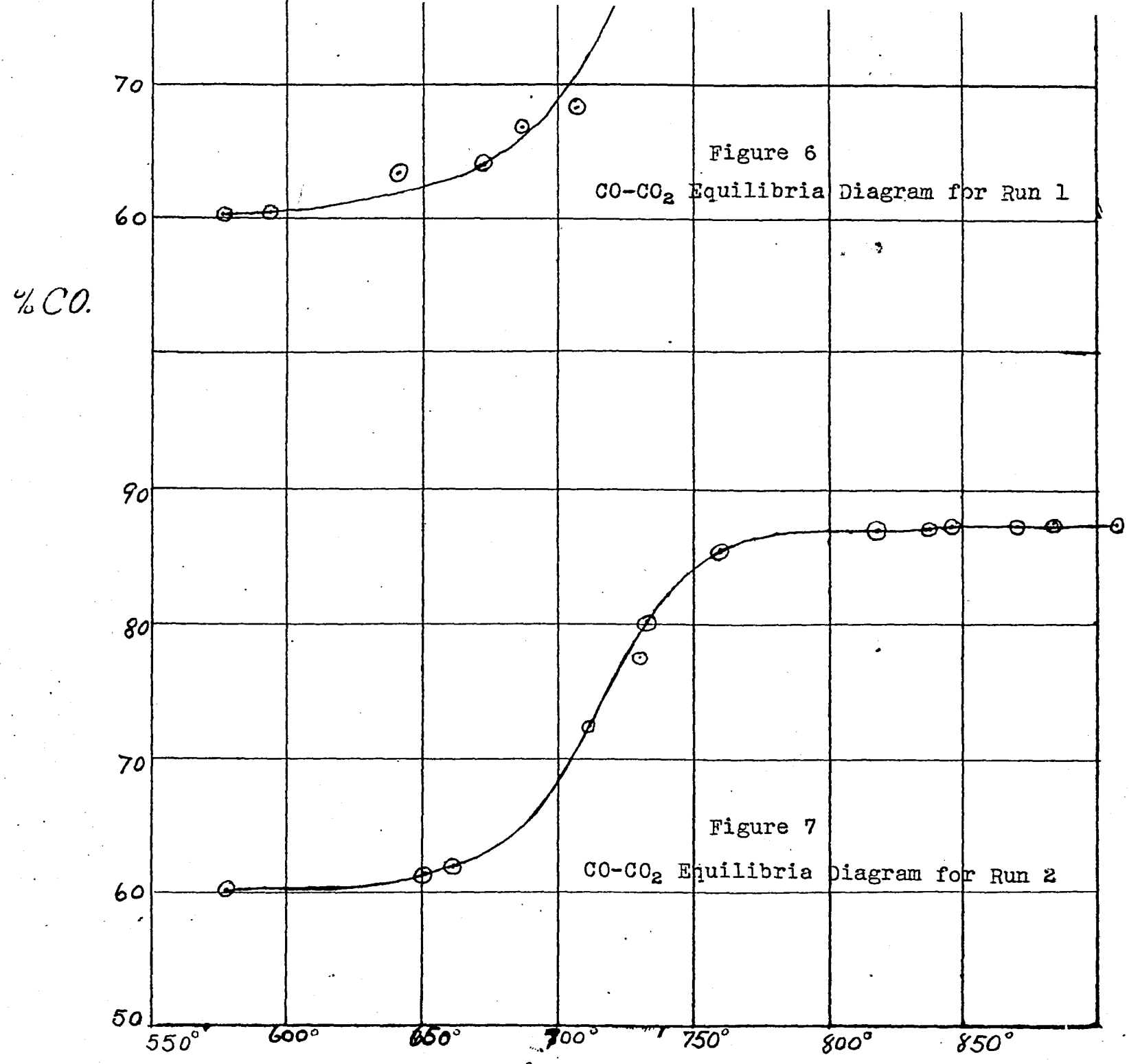
## TABLE V
### Run 3

| Bridge Reading | Temperature of Furnace | % CO | % CO$_2$ |
|---|---|---|---|
| 36.9 | 905 | 87.6 | 12.4 |
| 36.9 | 893 | 87.5 | 12.5 |
| 36.4 | 880 | 87.75 | 12.25 |
| 37.3 | 845 | 87.2 | 12.8 |
| 37.3 | 820 | 87.2 | 12.8 |
| 37.4 | 798 | 87.1 | 12.9 |
| 37.4 | 788 | 87.1 | 12.9 |
| 40.0 | 760 | 85.2 | 14.8 |
| 41.5 | 743 | 84.0 | 16.0 |
| 44.6 | 725 | 80.6 | 19.4 |
| 46.2 | 676 | 78.5 | 21.5 |
| 52.5 | 703 | 69.4 | 30.6 |
| 58.2 | 672 | 62.0 | 38.0 |
| 58.0 | 630 | 61.8 | 38.2 |
| 60.7 | 590 | 58.4 | 41.6 |

Figure 8

$CO-CO_2$ Equilibria Diagram for Run 3

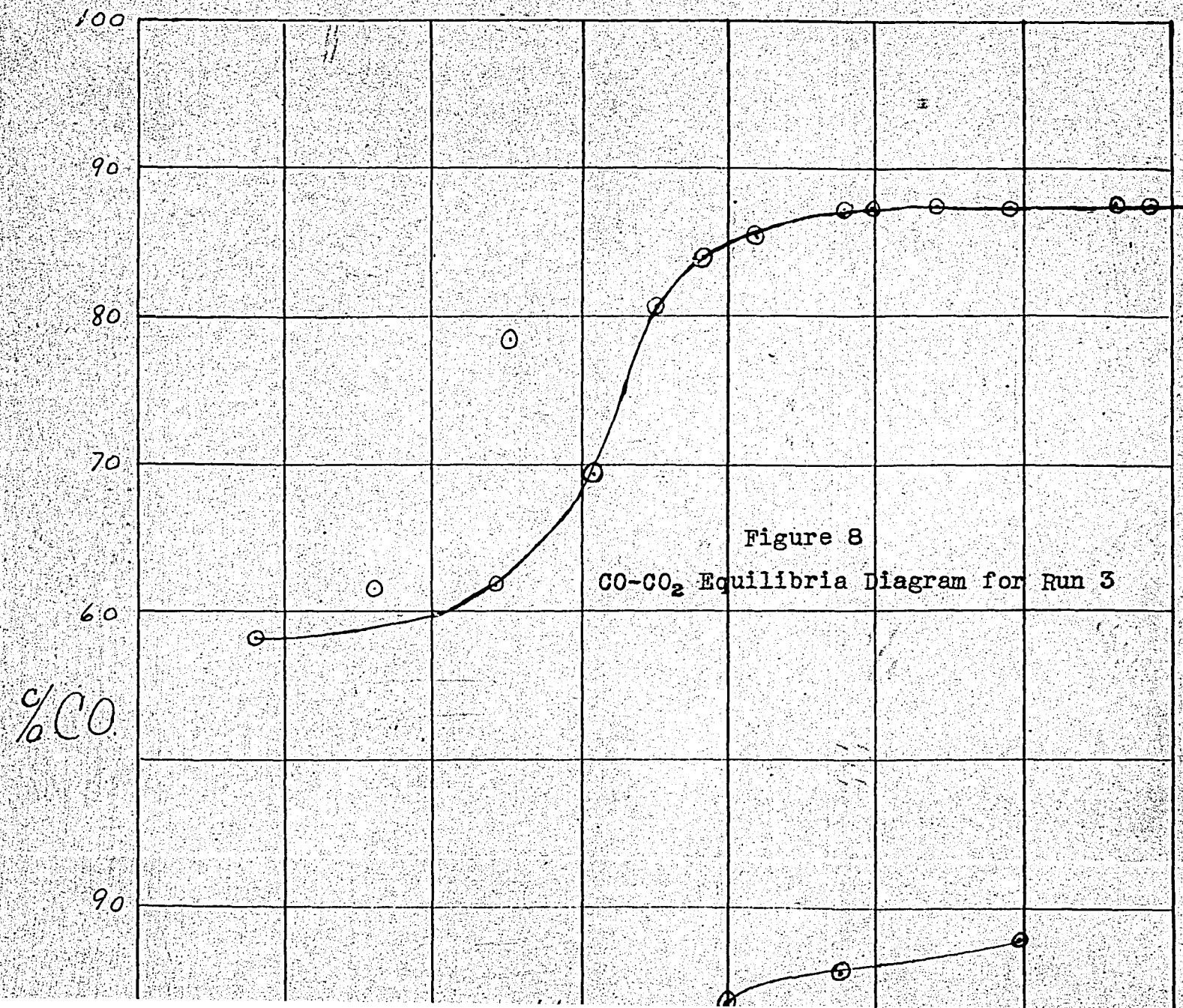Figure 8

$CO-CO_2$ Equilibria Diagram for Run 3

Figure 9

$CO-CO_2$ Equilibria Diagram for Run 4
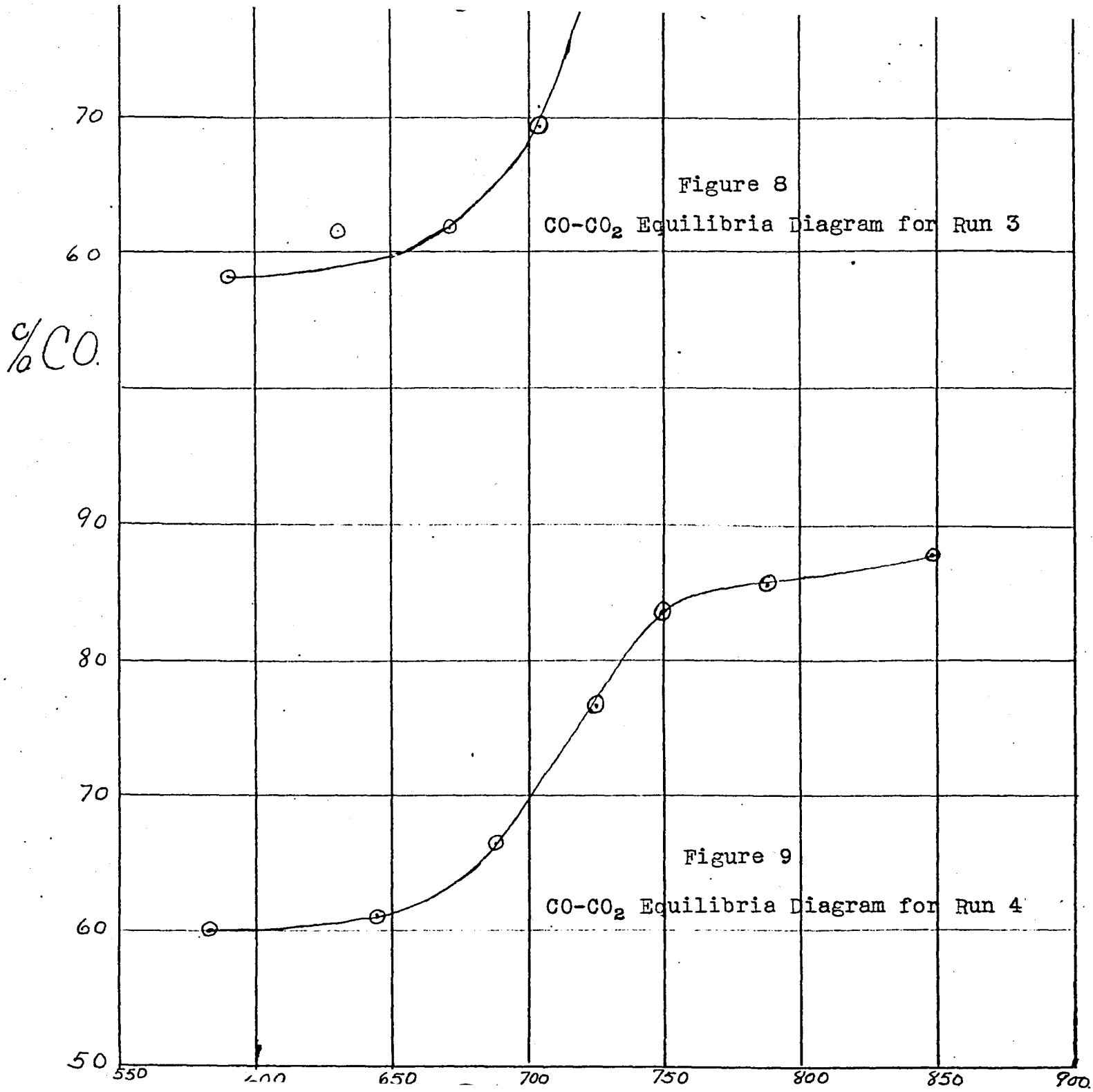
stat in which the cells of the conductivity meter were placed, was maintained at 24.7°C, the current flowing through the cells at 200 milliamperes, a constant rate of about 2,000 of c.c. per minute of gas flowing through the cells and a pressure of 748 m.m. The pressure was kept constant by putting gas from the reservoir into the cell and furnace as the pressure decreased and by allowing the gas to escape into the reservoir when the pressure in the cell and furnace exceeded 748 m.m.

## Investigation of the reaction $3Fe + 2CO = Fe_3C + CO_2$ using iron-carbon alloy.

The furnace was disconnected from the system and refilled with about 25 grams of the iron-carbon alloy turnings. The lid was placed on securely and hydrogen gas passed through it for approximately thirty minutes after the furnace had attained a temperature of 300°C. This was done in order to reduce any oxide which might have been present. The hydrogen was displaced by nitrogen and the furnace allowed to cool. When cool it was again connected into the system and all the gases flushed from it. The system was refilled with a $CO-CO_2$ mixture of about 60% CO. Readings were taken as previously described and the data obtained included in Table VI. The per cent of monoxide plotted against the temperature is shown in Figure 9.

## TABLE VI

### Run 4

| Bridge Reading | Temperature of Furnace | % CO | % CO$_2$ |
|---|---|---|---|
| 60.0 | 585 | 60.2 | 39.2 |
| 58.7 | 648 | 61.3 | 38.7 |
| 54.5 | 688 | 66.4 | 33.6 |
| 47.7 | 725 | 76.6 | 23.4 |
| 41.5 | 750 | 84.0 | 16.0 |
|  | 788 | 85.2 | 14.8 |
|  | 847 | 87.8 | 12.2 |

## CALCULATIONS AND RESULTS

Curve 1, Figure 10 was obtained by plotting the per cent CO as ordinates against temperature as abscissae. The combined data of Tables III, IV, V, and VI were used. Curve 2 of the same figure was taken from Garran (22). It represents the results of equilibrium studies of the reaction,

$$C + CO_2 = 2CO .$$
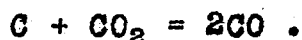
At temperatures of 775°C. or above, the partial pressure of carbon monoxide is higher in equilibrium with carbon than it is in contact with the iron and iron carbide. Also the partial pressure of carbon dioxide is greater in contact with iron carbide than with carbon. Therefore, in the presence of a mixture of CO and $CO_2$ gas, iron carbide will be stable above 775°C. and meta-stable below this temperature.

Concentrations of CO were obtained at intervals of 25° from Figure 8. The concentrations were changed to partial pressures and these values substituted into the equation,

$$K_1 = \frac{P_{CO_2}}{(P_{CO})^2} .$$

These data and the values of $K_1$, thus obtained, are listed in tabular form in Table VII. The change in free energy for reaction (1) was obtained by substituting these values of $K_1$
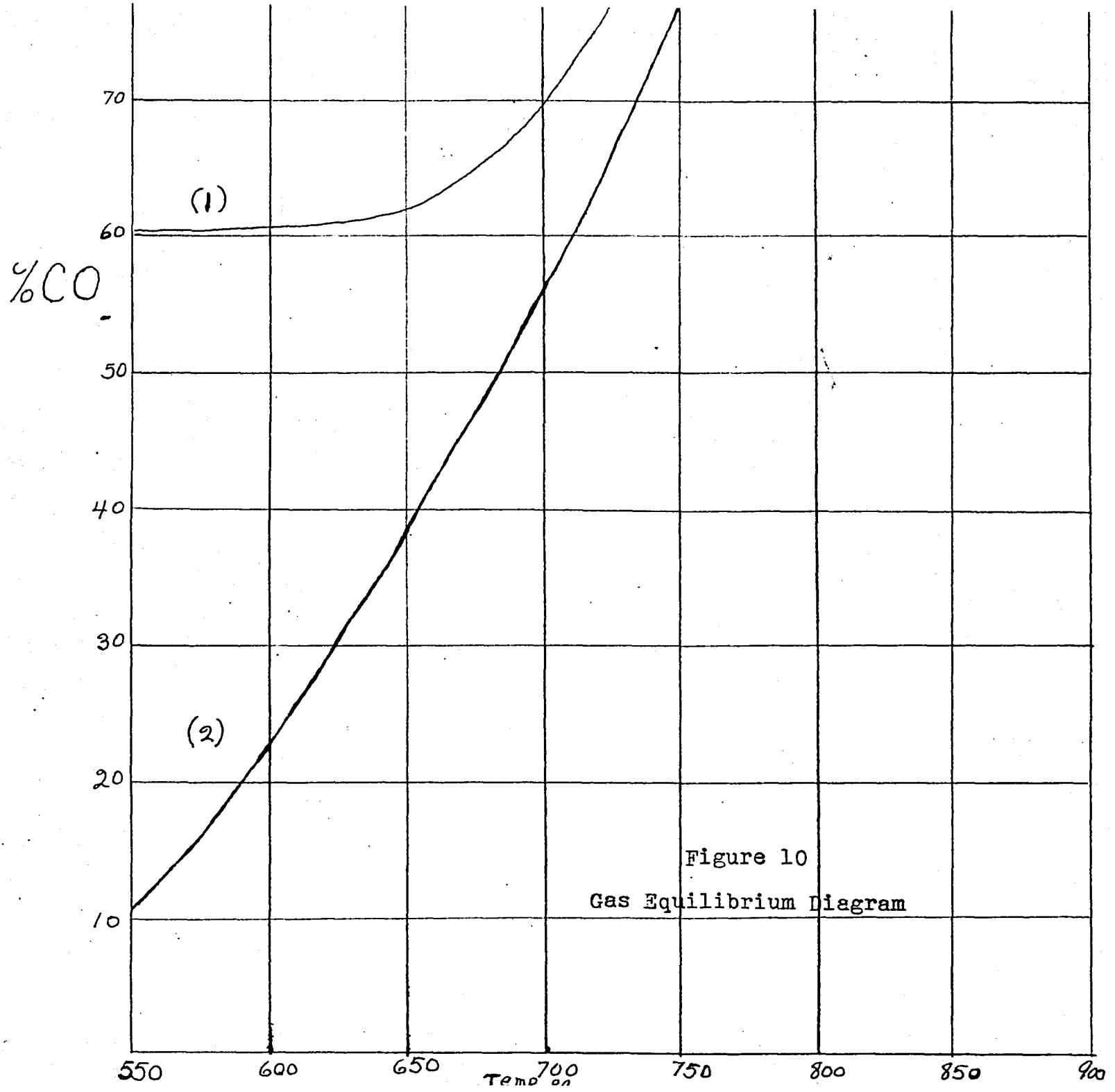
CO%

100 90 80 70 60 50 40

(1)
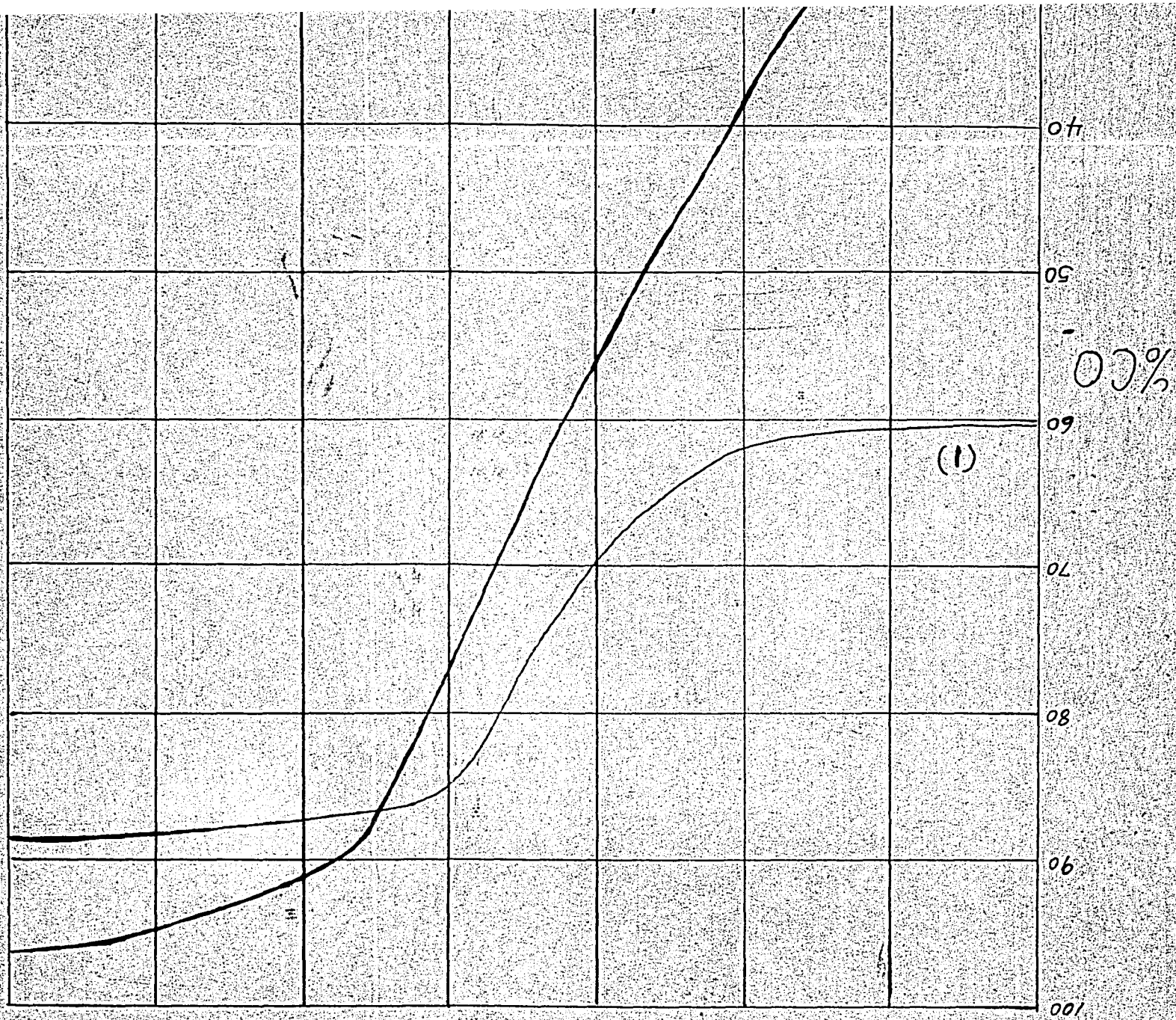
Figure 10

Gas Equilibrium Diagram

## TABLE VII

### Partial Pressures of CO & $CO_2$

| Temp. °C. | % CO | % $CO_2$ | $P_{CO}$ | $P_{CO_2}$ | Log $K_1$ | $K_1$ |
|---|---|---|---|---|---|---|
| 550 | 60.0 | 40.0 | .590520 | .393680 | .052673 | 1.12896 |
| 575 | 60.4 | 39.6 | .594456 | .389744 | .042542 | 1.10292 |
| 600 | 60.6 | 39.4 | .596425 | .387775 | .037437 | 1.0905 |
| 625 | 60.8 | 39.2 | .598394 | .385806 | .032393 | 1.07742 |
| 650 | 61.6 | 38.4 | .606267 | .377993 | .012153 | 1.02838 |
| 675 | 64.6 | 35.4 | .635793 | .349407 | $\bar{1}$.936699 | 0.864370 |
| 700 | 69.4 | 30.6 | .683035 | .301165 | $\bar{1}$.809919 | 0.645532 |
| 725 | 76.8 | 23.2 | .755866 | .228334 | $\bar{1}$.601685 | 0.399655 |
| 750 | 84.2 | 15.8 | .828696 | .155604 | $\bar{1}$.355227 | 0.226583 |
| 775 | 86.7 | 13.3 | .853301 | .130899 | $\bar{1}$.254730 | 0.179750 |
| 800 | 87.4 | 12.6 | .860191 | .124009 | $\bar{1}$.223588 | 0.167336 |
| 850 | 88.0 | 12.0 | .866096 | .118104 | $\bar{1}$.197138 | 0.157448 |
| 900 | 88.5 | 11.5 | .870817 | .113383 | $\bar{1}$.174694 | 0.149518 |

into the equation,

$$\Delta F_1^o = - RT\ln K_1 .$$

The change in free energy, $\Delta F_2^o$, for the reaction,

$$C + CO_2 = 2CO ,$$
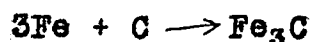
was obtained from free energy data taken from the International Critical Tables (23). The equation used was

$$\Delta F^o = +40,910 - 4.90 \ln T - .00495T + .00000051T^2 + 12.66 .$$

The change in free energy, $\Delta F_3^o$ , for the reaction,

$$3Fe + C \longrightarrow Fe_3C$$

was obtained by adding $\Delta F_1^o + \Delta F_2^o$ .

The heat of formation of iron carbide was then calculated by substituting the values of $\Delta F_3$ into the equation,

$$\frac{d\frac{\Delta F}{T}}{d\frac{1}{T}} = \Delta H$$

and solving by a graphical method, i.e., by plotting the values of $\frac{\Delta F}{T}$ as ordinates and $\frac{1}{T}$ as abscissae. The slope of the curve so obtained gives $\Delta H$ directly.

The calculated values for the free energy change and the heat of reaction are recorded in Table VIII.

## TABLE VIII

### Heat of Formation of $Fe_3C$

| Temp. °C. | $\Delta F_1$ | $\Delta F_2$ | $\Delta F_3$ | $\angle H$ |
|---|---|---|---|---|
| 550 | -298.3 | +6,241 | +5,943 | +34,200 |
| 575 | -188.7 | +5,401 | +5212 | +35,300 |
| 600 | -149.5 | +4,318 | +4,168 | +38,000 |
| 625 | -133.1 | +3,237 | +3.104 | +40,700 |
| 650 | -51.2 | +2,105 | +2,054 | +34,600 |
| 675 | +274.5 | +1,076 | +1,351 | +35,900 |
| 700 | +846.1 | -2 | +844 | +14,700 |
| 725 | +1583.9 | -1,076 | +508 | + 5,450 |
| 750 | +3,017.5 | -2,150 | +867 | |
| 775 | +3,573.0 | -3,223 | +350 | |
| 800 | +3,811.1 | -4,471 | -661 | +29,400 |
| 850 | +4,030.6 | -6,543 | -2,512 | +32,600 |
| 900 | +4,427.7 | -9,376 | -4,948 | |

## DISCUSSION

The values for the heat of formation of iron carbide, as obtained by various investigators, range from -27,500 to +78,750 calories. The values calculated from the experimental data secured in this investigation indicate a range of 5,450 to 40,700 calories over a temperature range of 550 to 850°C.

There is a noticeable break at about 760°C. in the curve obtained by plotting $\frac{\Delta F}{T}$ against $\frac{1}{T}$ from which the values of $\Delta H$ were read. That this break occurs at approximately the same temperature that $\alpha$ iron changes to $\beta$ iron, is not inconsistent with what might be expected, since the heat of transition of $\alpha$ iron $\longrightarrow$ $\beta$ iron should produce a noticeable effect upon the heat of formation of $Fe_3C$.

The values obtained for the free energy change of the reaction,

$$3Fe + C \longrightarrow Fe_3C ,$$

vary from +5,943 at 550° to -4,948 at 900°C. Values obtained by other investigators, range from 11,598 calories to 2,281 calories, the temperature range being from 25 to 700°C.

The results obtained by using the free energy data in the International Critical Tables indicate that $Fe_3C$ is

stable above 780°C. and meta-stable below this temperature. By the use of data taken from Garran, the results would indicate $Fe_3C$ to be stable above 775°C. and meta-stable at temperatures below this value.

The majority of the investigators consider iron carbide to be in a meta-stable condition below temperatures ranging from 740 to 770°C., and stable above these temperatures.

## SUMMARY AND CONCLUSIONS

1. Equilibrium values for CO and $CO_2$ in contact with Fe and $Fe_3C$ over a temperature range of 550 and 900°C. have been determined.

2. By means of these data, values of +5,943 and -4,948 were obtained for the change in free energy content accompanying the reaction,

$$3Fe + C \longrightarrow Fe_3C \; ,$$

at temperatures of 550°C. and 900°C., respectively.

3. Values ranging from 5,450 to 40,700 were calculated for the heat of formation of $Fe_3C$.

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