THE KINETICS OF SLAG METAL REACTIONS INVOLVING CARBON MONOXIDE EVOLUTION

by

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ABSTRACT

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The rate of reduction of ferrous oxide by carbon saturated iron was studied. The volume of carbon monoxide evolved during reaction was measured by following the pressure increase in a constant volume system. The reaction was initiated by dropping molten carbon saturated iron from an upper carbon crucible into a slag containing ferrous oxide in a lower alumina crucible. Mechanical stirring was provided by rotating the bottom crucible against a stationary paddle suspended from the top crucible.

The reaction varied from a first order reaction for a highly agitated melt to a second order reaction for one with no mechanical stirring. The reaction is probably transport controlled at low stirring rates where the thickness of the boundary layer, through which the ferrous ions must diffuse, is a function of the rate of carbon monoxide evolution. At high stirring rates giving a first order reaction the data cannot be used to tell whether the rate is controlled by the phase boundary reaction or by a transport process.

Dr. T. B. King
    Professor of Metallurgy

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INTRODUCTION

The thermodynamics of the various systems of interest in steelmaking have been studied for many years and there is a great deal of data available though much work still remains. It is in keeping with these times when interest is being more and more turned toward speed and efficiency that steelmaking research is becoming more directed toward kinetic problems. The results of such research may well improve production rates and possibly even point toward the development of new methods or processes.

There are many slag-metal reactions that result in the evolution of carbon monoxide. All reduction reactions in which a slag containing a reducible oxide comes in contact with iron containing carbon produce carbon monoxide. In the blast furnace these correspond to the direct reduction reactions that take place when slag contacts carbon or carbon saturated iron in the bosh or hearth. The reduction of ferrous oxide, manganese oxide, silica, phosphorus and the transfer of sulfur from metal to slag are examples. The extent to which these reactions take place in comparison to indirect gaseous reduction by carbon monoxide is quite uncertain and varies from furnace to furnace.

Carbon monoxide evolution plays an even bigger role in the open hearth and other steelmaking processes. Here iron oxide acts mainly as a transfer medium for getting oxygen from the furnace atmosphere to the bath. The mechanism is usually postulated to be oxidation of ferrous oxide to ferric at the gas-slag interface, diffusion of the ferric oxide to the slag-metal interface where it reacts with carbon to give carbon monoxide and ferrous oxide which diffuses back to the gas-slag interface for reoxidation.

These very important reactions from the point of view of actual tonnage of oxide reduced are not the main ores that prompted a study of their kinetics. A much more practical consideration is the effect of the oxygen potential of the slag on the sulfur transfer reaction. Recent studies on the rate of sulfur transfer have shown that a study of the rate of iron oxide reduction would be necessary before a definite mechanism could be proven for sulfur transfer.

The purpose of this thesis is to define the conditions governing the rate of iron oxide reduction from slags. The measurement of carbon monoxide evolved during the reaction is used to follow the extent of the reaction.

LITERATURE SURVEY

The literature on kinetic studies of steelmaking systems is not extensive since most of the research effort in the past has been devoted to thermodynamic investigations.

Equilibrium studies of reactions involving carbon monoxide evolution are quite plentiful in the literature, and much is known of the conditions favoring the reduction of various oxides. The equilibrium of sulfur between metal and slag has received much attention. This is due to the necessity of reaching low sulfur contents, and the difficulty of attaining these low sulfurs consistently. The factors affecting the ratio of sulfur in the slag to sulfur in iron have been reasonably well defined. One factor that has a large and definite effect on the sulfur ratio is the iron oxide content or more exactly the oxygen potential of the slag. This was studied by Rocca, Grant and Chipman[1]. They found that the equilibrium sulfur content of the iron was an inverse function of the oxygen potential of the slag within a certain range. In the same regard Fisher and Cohnen[2] found that low carbon irons favored high sulfur contents due to an increased equilibrium iron oxide content of the slag. They also reported that deoxidizers added to the system lowered the sulfur content of the metal. Taylor and Stobo[3] have reported essentially the same results. Grant, Kalling, and Chipman[4] added manganese oxide to the slag and caused sulfur to revert into the metal.

Hatch and Chipman[5] melted blast furnace type slag and metal together in a carbon crucible and found sulfur levels much lower than found in practice. Filer and Darken[6] demonstrated this more definitely by remelting blast furnace slag and metal in a graphite crucible and obtaining further desulfurization. The increased desulfurization in both cases was due to a lowering of the oxygen potential of the slag by contact with the carbon crucible.

There is great disagreement in the literature on the equilibrium iron oxide content of slags in contact with carbon saturated iron. Hatch and Chipman[5] report 0.03 percent, Grant, Kalling and Chipman[4] about 0.1 percent and Taylor and Stobo[3] from 0.1 to 0.3 percent. The discrepancies may be due in part to differences in the methods used to remove free iron from the slags, since chemical analysis cannot readily differentiate between free iron and iron oxide.

All the above investigations point to the importance of oxygen potential on desulfurization equilibria. It would therefore also be expected that the iron oxide content of the slag would have an effect on the kinetics of desulfurization, and this has been found.

Ramachandran[7], and Ramachandran, King and Grant[8] in previous work with the apparatus used in this thesis found that iron oxide did play a role in the kinetics of desulfurization. In nearly all their runs the iron oxide content of the slag rose at the beginning of the sulfur transfer reaction, then fell as the rate of sulfur transfer decreased and the iron oxide had a chance to be reduced by the carbon in the iron. This suggests that the rate of reduction of iron oxide may have a limiting effect on the rate of sulfur transfer and that faster rates of iron oxide reduction would give faster desulfurization. Silicon was also found to transfer from metal to slag against its equilibrium value in a carbon saturated system. At the slag metal interface during sulfur transfer there is a high oxygen potential with oxygen being competed for by carbon, iron and silicon. It is not surprising then that iron is successful in capturing some of the oxygen since it is also at unit activity. Silicon or aluminum in the metal in excess of that in equilibrium with the slag were found to increase the speed of desulfurization by keeping the oxygen potential of the slag lower since they form oxides of very low oxygen activity, and are capable of reducing the oxides of iron or manganese.

One run was tried in which iron oxide was added to the slag with no sulfur present. The rate of reduction was found but no conclusions were drawn from the limited data.

Dancy[9] has made a study of the kinetics of iron oxide reduction by high carbon pig iron. He melted pig iron in a rotating magnesia crucible in a method similar to that used by Taylor and Chipman[10]. The parabolic depression that forms in the iron due to centrifugal force was used to contain the iron oxide and prevent its contact with the highly absorbent magnesia crucible walls. The melt was brought to temperature and the iron oxide dropped into the depression in the molten iron. This was done in nitrogen at a pressure of about ten centimeters of mercury. A low inertia pressure gauge was used to measure the carbon monoxide evolved on reaction. The pressure gauge and a stop watch were photographed simultaneously with a movie camera at 8 frames per second over the course of the reaction. Reduction was usually complete in ten seconds.

The rate of reduction of ferrous oxide was of first order, that is it is proportional to the first power of the amount of ferrous oxide present for the first 80 percent of the reaction. Magnetite reduction was of first order for the initial 30 percent of its reduction. The rate of reduction of ferrous oxide increased by 8 percent for a ten degree centigrade rise in temperature while the rate for magnetite increased by 5 percent for a ten degree temperature rise. An activation energy for the ferrous oxide-carbon in iron reaction of 43,100 plus or minus 10 percent calories per mole was found, and for magnetite reduction the value was 37,300 plus or minus 10 percent.

Philbrook and Kirkbride[11] have studied the rate of reduction of ferrous oxide from a slag by carbon saturated iron. They melted carbon saturated iron and a lime-alumina-silica slag in a stationary graphite crucible. A high ferrous oxide slag was added when the desired temperature had been reached, and the rate of reduction was followed by taking samples of the slag at intervals. The initial FeO content was approximately 5 percent. They found the rate of reduction proportional to the square of the iron oxide concentration so that the reaction was of second order but were unable to suggest a mechanism explaining this order. They compared rates of reaction at the slag-metal and slag-graphite interface and found the slag-metal reaction to be approximately five times as fast. This they attributed possibly to the difficulty of nucleating iron at the graphite-slag interface. They had insufficient data over a range of temperatures but estimated the activation energy for the reaction at about 10 kilocalories.

Arkharov and co-workers[12] studied the solid state reaction of powdered iron oxides and carbon. They found the rate determining step was the nucleation of free iron which supports the reasons given by Philbrook and Kirkbride[11] for the slower iron oxide reduction at the slag-graphite interface.

APPARATUS AND PROCEDURE

A. Apparatus

A perspective drawing of the apparatus is shown in Figure 1. It consists of three main sections: the furnace section, the blank volume section, and the pressure measuring and recording section.

1. The Furnace Section

The furnace section is shown in detail in Figure 2. It consists of a fused silica tube 4-1/2 inches inside diameter by 14 inches long with a 3/16 inch thick wall. On both ends water cooled brass heads are fitted. Silicone rubber gaskets and silicone high vacuum grease are used to make a seal between the silica tube and the brass head.

The brass heads are held against the silica tube by wing nuts on six bolts which run through holes in both top and bottom heads. The bolts are attached to an asbestos board frame which also supports the induction coil as shown in Figure 2.

The top head has three openings fitted with gas-tight seals. One opening, 3/8 inch in diameter is at an angle and is used for sampling from the upper graphite crucible. A black rubber O-ring and silicone grease are used to keep the opening gas tight. An O-ring seal on the other side of the water-cooled head leads in a 9 millimeter Vycor tube. This tube connects the furnace to the blank volume section. In the center a universal vacuum seal (made by the National Research Company of Cambridge, Massachusetts) introduces the grade 304 stainless steel sighting tube (A in Figure 2) into the furnace. The sighting tube A is 5/8 inch in diameter and is fitted with a magnetically operated shutter and sight glass as shown in Figure 2. Optical temperature

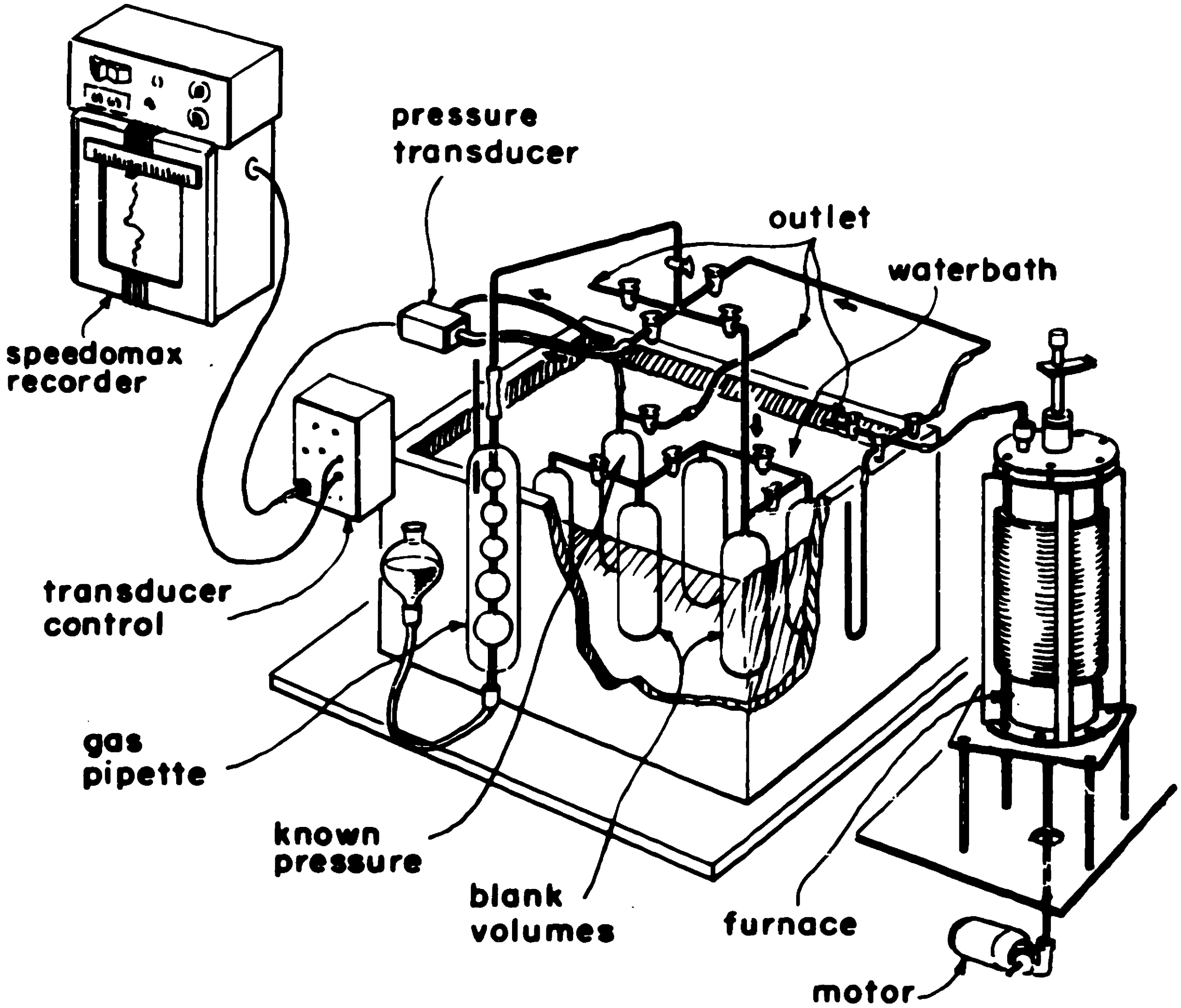


FIG.1 SKETCH OF APPARATUS

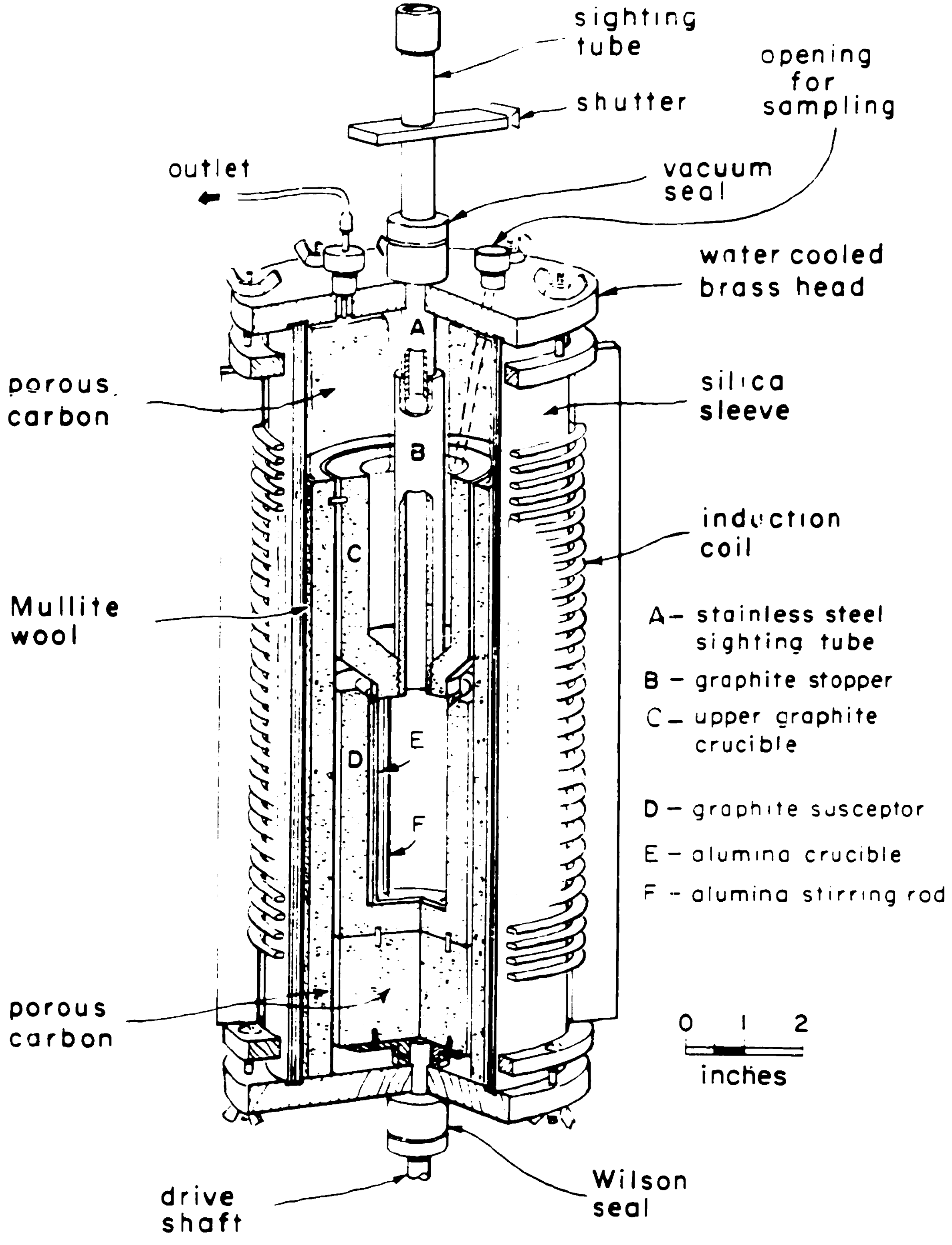


FIG.2-SCHEMATIC DRAWING OF FURNACE

readings of the lower alumina crucible E are made by sighting through this tube into the surface of the slag in the crucible, but they are used only to determine when temperature has been reached. A platinum-platinum 10 percent rhodium thermocouple is inserted through the sight tube to measure the true temperature of the crucible. The sight tube opening is also used to take samples from or make additions to the lower alumina crucible. The sighting tube screws into the graphite stopper B (Figure 2). The sighting tube is used to unscrew the graphite stopper and allow the metal to run into the slag filled lower crucible.

The bottom brass head has a Wilson seal at its center which introduces a 1/4 inch drive shaft from the variable speed electric motor below (Bodine Electric Company, 115 volts, 0.7 amperes). The shaft is attached to a brass table inside the furnace which rests on the bottom brass head. Four vertical 1/4 inch brass studs on the periphery of the table connect it to a porous carbon cylinder 2-7/8 inches outside diameter by 2-1/2 inches long. The lower graphite susceptor D is placed on top of the porous carbon cylinder and attached to it by four 1/4 inch diameter graphite studs. Thus rotation of the drive shaft by the electric motor rotates the lower crucible.

The dimensions of the upper graphite crucible, the lower graphite susceptor, alumina crucible, alumina stirring rod, and graphite stopper are given in Figure 3.

The alumina crucibles were made by the Ceramics Division of the Metallurgy Department at Massachusetts Institute of Technology. They were slip cast from Norton Grade 38x - 220 F alumina powder and fired at 1830°C.

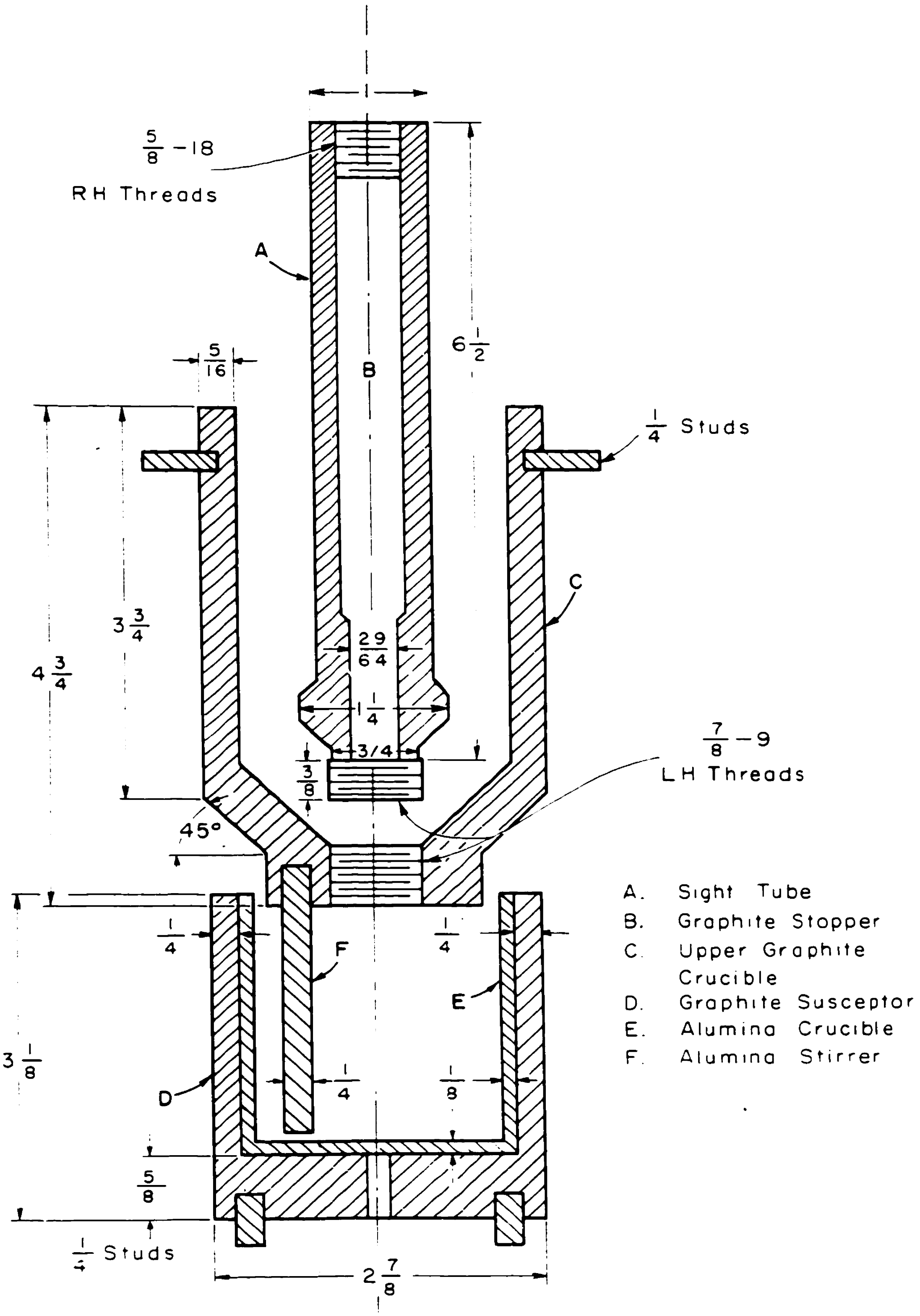


FIG. 3 - SKETCH OF CRUCIBLE ASSEMBLY

The alumina rods were made by the Norton Company of Worcester, Massachusetts and are of extra high purity alumina Grade RA 7232. The alumina rods are of slightly higher density and purity than the crucibles so that most solution of alumina by the slag takes place at the crucible walls and so lessens attack on the stirring rods.

The graphite susceptor is machined to an inside diameter such that the alumina crucible must be forced into it by slight pressure. This plus the slightly greater coefficient of linear expansion of alumina prevents the crucible from slipping in the susceptor during rotation. A hole is drilled through the bottom of the graphite susceptor so that a rod may be inserted to push the alumina crucible out of the susceptor after a run has been completed.

The alumina rod is cemented into the hole in the bottom of the upper crucible with a small amount of alundum cement that fires to a hard refractory during the heating up of the furnace.

The graphite stopper B screws into the hole at the bottom of the upper graphite crucible C and the stainless steel sighting tube A screws into stopper B. A small stainless steel bushing on the sight tube allows it to be screwed into the graphite stopper about 1/2 inch before binding and making further rotation relative to the two impossible. The stopper has a left hand thread at its bottom and a right hand thread at its top. Thus clockwise rotation of the sighting tube tightens its connection with the graphite stopper and unscrews the stopper from the upper graphite crucible.

The upper graphite crucible is supported and keyed in place by four 1/4 inch diameter graphite rods inside the porous carbon tube as seen in Figure 2. The porous carbon tube 3 inches inside diameter, 4 inches outside diameter and 10-1/2 inches long is used for insulation. The volume between the porous carbon tube and the silica tube is filled with mullite wool for additional insulation.

Between the upper graphite crucible and the top head is a porous graphite cylinder 4-1/2 inches in diameter and 3 inches long, with a 1-1/4 inch diameter hole in the center for the sight tube and stopper. A 3/8 inch hole at an angle allows sampling from the upper crucible.

The assembly is heated by an induction coil as shown in Figure 2. Power is supplied by an Ajax Westinghouse motor generator set of 60 kilowatts capacity at 1920 cycles.

2. The Blank Volume Section

The arrangement of the blank volumes is shown in Figure 1.

The outlet from the furnace is connected to the mercury manometer, the series of blank volumes, and the mechanical vacuum pump. By turning stopcocks these can be arranged in any combination.

The tube from the furnace to the blank volumes also connects to the pressure transducer, the gas pipette and an outlet. This outlet leads to a tank of nitrogen so that the system may be filled with nitrogen as desired. The five blank volumes are connected in series with stopcocks between each one so that any number may be included in the system. The blank volumes are placed in a copper lined tank that is insulated from the room and filled with water to minimize temperature fluctuations.

The gas pipette consists of a series of glass bulbs of known volume, also enclosed in a water bath. A mercury thermometer placed in the water bath measures the temperature of the gas inside the bulbs. The gas pipette is used to calibrate the system.

3. The Pressure Measuring and Recording Section

The pressure in the system is measured by a differential pressure transducer made by Statham Laboratories, Incorporated of Los Angeles, California, model number P6-4D-350, specification number 3456 with a range of plus or minus 4 pounds per square inch pressure difference.

The transducer is a bellows and strain gauge device that converts pressure differences into electrical potentials. The unit has a standard resistor built into it. When the resistor is put into the circuit the transducer produces a voltage equal to that produced by a pressure difference of two pounds. The value of this voltage can be changed by turning the "Standardize Turn" knob, so that a convenient voltage can be chosen to indicate 2 pounds pressure. The value of the voltage equal to two pounds pressure difference may be found at any time by pressing the "Standardize-Push" button. It is necessary to do this from time to time during a run since the value drifts slightly due to the drain on the batteries. The output of the transducer is linear throughout its entire pressure range.

One leg of the transducer is connected to the blank volume system, the other to atmosphere. The other leg may be connected to a resevoir at any known pressure and the pressure increase in a system at any pressure level may be measured as long as the pressure difference at no time exceeds 4 pounds per square inch.

The electrical input to the transducer is regulated by the transducer control (see Figure 1). The output of the transducer is fed to a Leeds and Northrup Speedomax Recorder. However the voltage range of this instrument is only 0 to 2 millivolts. To record the pressure, which is usually in the order to 10 millivolts a backing potentiometer capable of extending the range to 110 millivolts if necessary is incorporated in the circuit of the Speedomax. The recorder is also used to record the temperature of the slag in the alumina crucible using a platinum-platinum 10 percent rhodium thermocouple.

B. Procedure

1. Materials

A premelted lime-alumina slag was used. It was made by melting a mixture of chemically pure lime and alumina in a graphite crucible. The molten slag was poured into a cold graphite crucible, cooled, crushed and analyzed. For runs at a very high temperature some pure alumina was mixed with the premelted slag before charging so that attack on the alumina crucible would not be as serious. Magnesia was added as the chemically pure oxide to the slag mixture.

The carbon saturated iron was made by melting Armco iron and graphite in a graphite crucible. It was then poured onto a flat graphite plate giving a slab about 1/2 inch thick which was broken up into pieces small enough to charge into the top crucible.

For some of the earlier runs the iron oxide slag was made by melting a mixture of ferric oxide and alumina in an alumina crucible heated by a graphite susceptor in an induction furnace. A nitrogen atmosphere was used to prevent reduction.

For the rest of the runs a lime-iron oxide slag was used. It was made by melting a lime-ferric oxide mixture in an open iron crucible. The crucible was heated from below by an air-gas Meker burner and from above by an oxygen-gas torch. Only the area directly under the torch was melted but by adding small amounts of the mixture to the crucible it was finally filled with a fused mass which was cooled, crushed, screened to minus 8 plus 40 mesh and analyzed.

TABLE I

ANALYSES OF MASTER SLAGS AND METAL

Metal

% Carbon	5.29
% Sulfur	.030
% Silicon	.002

Slags

	Lime Alumina	Alumina Iron Oxide	Lime Iron Oxide
% CaO	49.70	-	24.07
% Al_2O_3	50.48	47.8	-
% FeO	-	46.07	14.50
% Fe_2O_3	-	4.02	60.66

2. Experimental Procedure

The furnace is assembled by inserting an alumina crucible in the graphite susceptor and fixing the assembly on the insulating carbon block in the furnace by means of graphite studs. The alumina stirring rod is cut to the proper length and cemented in place in the top crucible. The top crucible is placed in the furnace suspended by the four horizontal graphite studs as shown in Figure 2. A weighed amount of premelted lime-alumina slag is charged through the hole in the top crucible into the bottom crucible using a funnel. The graphite plug is then screwed into place and a weighed amount of carbon saturated iron put into the top crucible. The top insulating carbon block is put in on top and the brass head put on and tightened. The furnace is evacuated and power is applied gradually to heat the crucibles slowly and avoid cracking of the alumina. The temperature is checked constantly with the optical pyrometer. It usually took five to six hours to reach a constant temperature. The furnace is heated under vacuum to remove moisture and volatile substances from the system. This procedure gives low and consistent blanks.

The system is now filled with nitrogen and the sight glass removed. The Speedomax recorder and bucking potentiometer are standardized. The platinum-platinum 10 percent rhodium thermocouple is inserted through the sighting tube to within 0.5 centimeters of the bottom of the alumina crucible. The voltage produced is measured by the Speedomax recorder. The tip of the thermocouple is bare since it is not contaminated by the slag. The rest of the thermocouple is protected by an alumina protection tube. The temperature keeps within plus or minus 5°C of the measured value over extended periods of time.

The gas inlet from the nitrogen tank is closed and the desired number of blank volumes are included in the system. The stopcock isolating the pressure transducer is opened and the zero of the transducer control unit adjusted. The value of the voltage equivalent to two pounds per square inch pressure difference is found by pressing the "Standardize Push" knob of the control unit. This voltage is checked at intervals during the run as it decreases by about 1 percent per hour due to drain on the batteries.

A blank reading on the system is made by closing all outlets to the atmosphere and noting any increase or decrease of pressure with time. An unreasonably high blank may be due to insufficient degassing or reactions inside the furnace. In most instances the blank is negative, that is the pressure decreases to below atmospheric. This may be due to readsorption of gas on the surface of the porous carbon insulation or due to the carbon deposition reaction $2\ CO \rightarrow C + CO_2$ if any carbon monoxide is present in the system. At the start of a run the gas is nearly pure nitrogen and the magnitude of this negative blank decreases with time so it seems reasonable to assume that this is due to readsorption of gas after the extended heating under vacuum. A check on gas samples after evolution of carbon monoxide showed only slight traces of CO_2 in an Orsat gas analyzer.

If the blank is reasonable the system is calibrated using the following procedure. The gas pipette (see Figure 1) is filled with nitrogen at atmospheric pressure. The temperature of the pipette is read from a thermometer in the water bath surrounding it, and the absolute pressure is found by taking a barometer reading. The gas is pushed into the system by displacement with mercury and the pressure increase is recorded on the Speedomax. Since gas pressure, temperature and volume are known the change in voltage (or pressure) for a certain increase in the total moles in the system is found. This is the calibration that is required.

The run is now ready to be started. The addition head is filled with a weighed amount of iron oxide slag. It is a one inch glass bulb with its opening fitted into a short piece of tygon tubing. The other end of the tubing is fitted over a small brass fixture which screws onto the top of the sighting tube in place of the sight glass assembly. The iron oxide slag is placed in the head and the tubing bent through 180° and held in place by a rubber band. The slag is added to the lower crucible by removing the rubber band and letting the tubing spring back to a vertical position. A small amount of carbon monoxide is evolved and measured. The stirrer is started after a few minutes and the pressure is watched until it again becomes constant. The slag and metal are sampled to get the initial analyses. The graphite stopper is unscrewed allowing the carbon saturated iron to fall into the slag containing iron oxide. Again the pressure is recorded on the Speedomax recorder. The run is continued until carbon monoxide evolution ceases and the pressure becomes constant. The recorder is on at all times and notes are made on the chart paper so that a complete log of the run is obtained.

The addition head is removed and in some runs s sample of slag and/or metal is taken. With the stirrer on a 3/8 inch graphite rod is inserted into the bottom crucible to resaturate the metal. It was found that about five minutes was necessary to approach saturation. During a run the carbon content of the metal usually drops about 0.2 percent.

The addition head is refilled with iron oxide slag and placed on the sight tube. After checking the blank and the voltage equivalent to two pounds per square inch the second addition of iron oxide slag is made. Carbon monoxide evolution is immediate since the slag is in contact with carbon saturated iron. The procedure is continued in the same way as for the first addition. From one to seven additions were made in the various runs. From start of one addition to start of the next usually takes about 1-1/2 hours.

By using the calibration data the millivolt readings are converted into the amount of carbon monoxide evolved.

Slag samples are analyzed for iron oxide and in some cases calcium oxide, alumina and also magnesia if present. The metal samples are analyzed for carbon and a check was made on a few samples for silicon and sulfur.

3. Sampling Techniques and Analytical Procedure

The metal is sampled with a 6 millimeter Vycor tube fitted with an aspirator bulb. The sample is crushed in a steel mortar to minus 40 mesh for analysis.

Slag samples are obtained by dipping a clean 1/4 inch copper rod into the slag. Because the slag is to be analyzed for small amounts of iron oxide special care is taken to avoid any contamination with iron. For this reason a copper rod is used instead of the usual iron rod. To avoid any oxidation of the small iron pellets always found in the slag it is immediately quenched in water. The slags are crushed to minus 100 mesh and the larger iron pellets removed with a small alnico hand magnet. A very powerful electromagnetic separator with an automatic feeder is used to remove the last traces of free iron. Crushing the slag to an even finer size would facilitate separation of iron from the slag, but the very fine particles are susceptible to oxidation by air. It is unlikely that part of the iron oxide is removed by the electromagnetic separator but this cannot be proven. Some slag always sticks to the metal so analysis of the removed iron for total iron content would not prove anything.

All chemical analyses were carried out by members of the Chemical Laboratory of the Department of Metallurgy at Massachusetts Institute of Technology under the direction of Mr. Donald L. Guernsey.

A brief description of the analytical procedures used follows.

a. Slag analyses

Method for alumina.--The slag dissolved in a mixture of hydrofluoric and nitric acids in a platinum dish. It is dehydrated with perchloric acid. The dehydration is repeated twice to eliminate the last traces of hydrofluoric acid. It is dissolved with dilute hydrochloric acid and the aluminum hydroxide precipitated with ammonia. The precipitate is redissolved with dilute hydrochloric acid and reprecipitated with ammonia. The precipitate is ignited and the alumina is weighed. A correction is made for iron using standard colorimetric methods.

Method for calcium oxide.--The filtrate from the alumina determination is used. Calcium is precipitated as calcium oxalate with ammonium oxalate. The precipitate is dissolved, reprecipitated as before and filtered. The precipitate is dissolved in dilute sulfuric acid and the oxalate ion is titrated with potassium permanganate.

Method for total iron as ferrous oxide.--The sample is dissolved in hydrochloric acid, and hydroquinone added to reduce the iron, after which ortho-phenanthroline is added. The pH of the solution is adjusted to 4. The solution is allowed to stand overnight and the iron is determined colorimetrically.

Method for ferrous oxide.--The sample is dissolved in a hydrochloric acid solution with sodium bicarbonate. The carbon dioxide evolved is used as a blanket atmosphere to prevent oxidation by the air. A solution of manganous sulphate, sulphuric acid and phosphoric acid is added and the solution titrated with potassium permanganate.

Method for ferric oxide.--The sample is dissolved as in the method for ferrous oxide. A solution of ammonium thiocyanate is added and it is titrated with titanium trichloride.

Method for magnesia.--The filtrate from the calcium oxide determination is used. A solution of diammonium phosphate is added, then ammonium hydroxide until basic. The solution is allowed to precipitate overnight, then filtered, washed, redissolved and reprecipitated in the same manner. The precipitate is filtered, ignited and weighed as magnesia.

b. Metal analyses

Method for sulfur.--The standard combustion method, using a Leco Induction unit is used. The sample is melted with a weighed amount of standard low sulfur iron and tin under a stream of oxygen. The gas is absorbed in weakly acid solution and is titrated with standard potassium iodide solution using starch as an indicator.

Method for carbon.--Standard combustion carbon procedure is used.

Method for silicon.--The sample is dissolved in concentrated hydrochloric and nitric acids, dehydrated with perchloric acid, diluted with hydrochloric acid and filtered. The precipitate is ignited and weighed.

PRESENTATION OF RESULTS

A. Diagrams and Tables

All experiments are presented graphically in Figures 4 to 15. In these graphs the amount of carbon monoxide evolved as a function of time is plotted. On many of the runs a three-way stoichiometric balance was made on the system; carbon removed from the iron, iron oxide reduced from the slag, and carbon monoxide evolved. In the earlier runs the check between carbon monoxide evolved and iron oxide reduced was very poor and a reasonable explanation for these discrepancies has not been found. Later runs however, gave a good check between iron oxide reduced and carbon monoxide evolved.

The overall reaction taking place in the crucible is

$$(FeO) + \underline{C} \rightarrow Fe + CO.$$

The reaction of carbon and iron oxide to produce carbon dioxide at this temperature is thermodynamically impossible since the pressure of CO_2 in equilibrium with carbon at 1500°C is extremely low.

It has been stated previously that the blank for many of the runs was negative at the start. This might be attributed to the carbon deposition reaction

$$2\ CO \rightarrow C + CO_2$$

which is favored by a temperature of about 500°C and traces of iron. Orsat analysis of the gas however revealed only a small trace of carbon dioxide.

The negative blank was found even when the apparatus was filled with pure nitrogen, and so has been attributed to the readsorption of gas on the relatively large surface of the porous carbon insulation.

The chemical analyses of all slag and metal samples are given in tables in the appendix. Samples were not always taken before and after each addition because of the change this would have made in the weights of slag and metal reacting, and the large number of chemical analyses necessary. Since all additions during any one run were made at the same temperature and at approximately the same carbon content in the iron the equilibrium iron oxide content should be the same for all additions, and this has been assumed for all runs.

B. Sources of Experimental Error

Most of the conclusions drawn from this work are taken from the carbon monoxide evolution curves so that the most important errors are those affecting these curves.

Errors in the measurement of carbon monoxide evolved are relatively minor. The standardization of the system checks to within less than 1 percent. Somewhat more in error however is the correction due to blanks. This may be serious in runs of a long duration where the total value of the blank may amount to 5 percent of the carbon monoxide evolved. The pressure measurement itself is very accurate and any error in it is insignificant.

Errors in weighing the slag and metal charge, and in estimating the increase in slag weight due to solution of the alumina crucible are important but difficult to estimate. The weights of slag and metal samples is another source of error since loss of part of the sample is almost unavoidable during quenching and removal from the sampling rod or tubes.

Temperature measurement with a platinum - platinum 10 percent rhodium thermocouple is expected to be within ± 2°C of the true temperature. However temperature variations in the crucible may be as high as 15°C due to the large thermal gradients in the whole system. It is not possible to check the temperature constantly during a run but temperature variations should be slight since the temperature does hold very constant before the run as read by the optical pyrometer. Any large temperature variation during a run is immediately detected as a discontinuity or large change in the slope of the carbon monoxide evolution curve.

An overall experimental error of 15 percent can be expected for most of the results. Results should be much better where comparisons are made between different additions in a single run. Many errors are the same for each addition so that for example the comparison of the effect of stirring rates should be quite good. This is borne out by the duplicate additions in Figure 17.

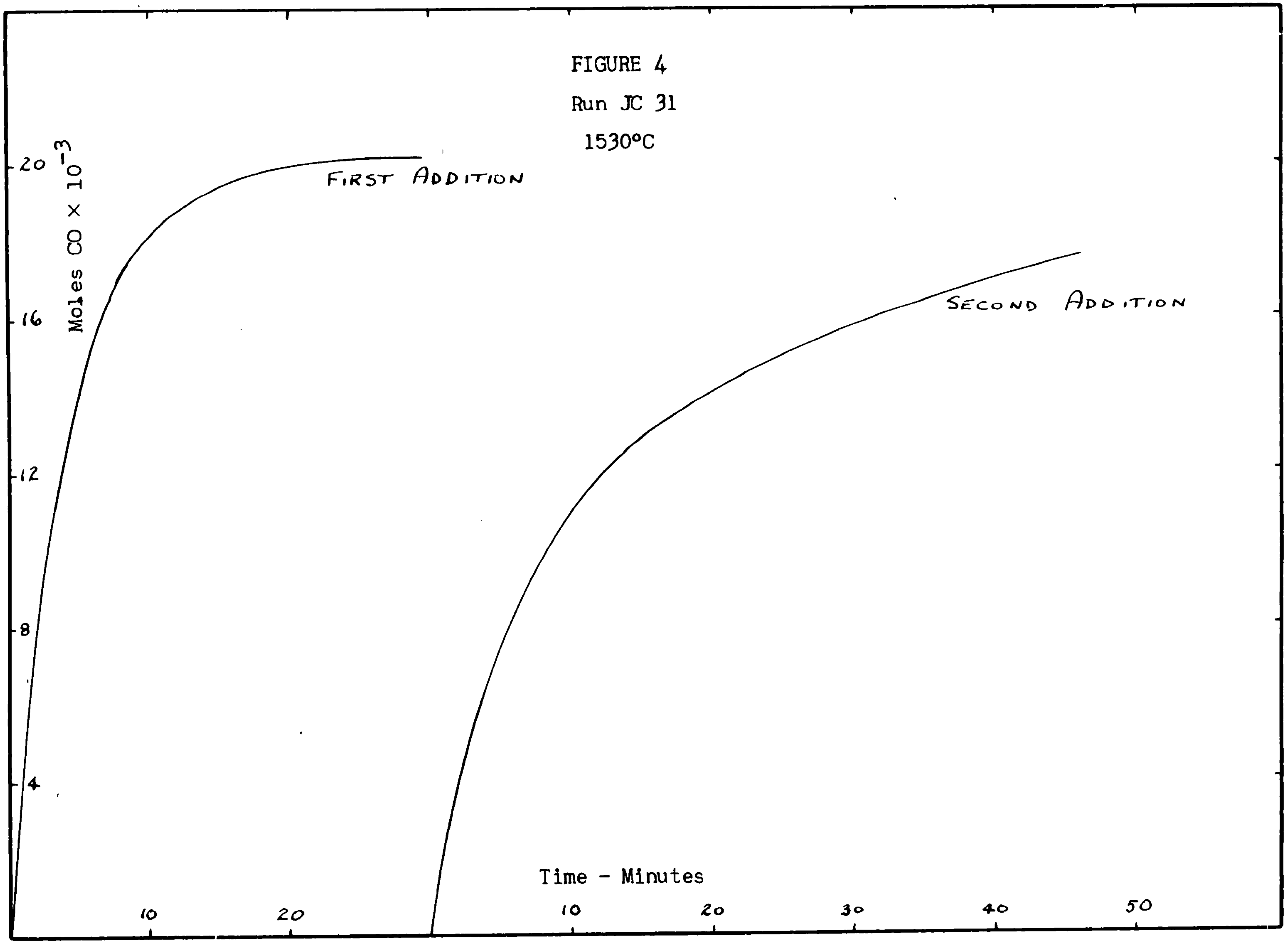


FIGURE 4
Run JC 31
1530°C

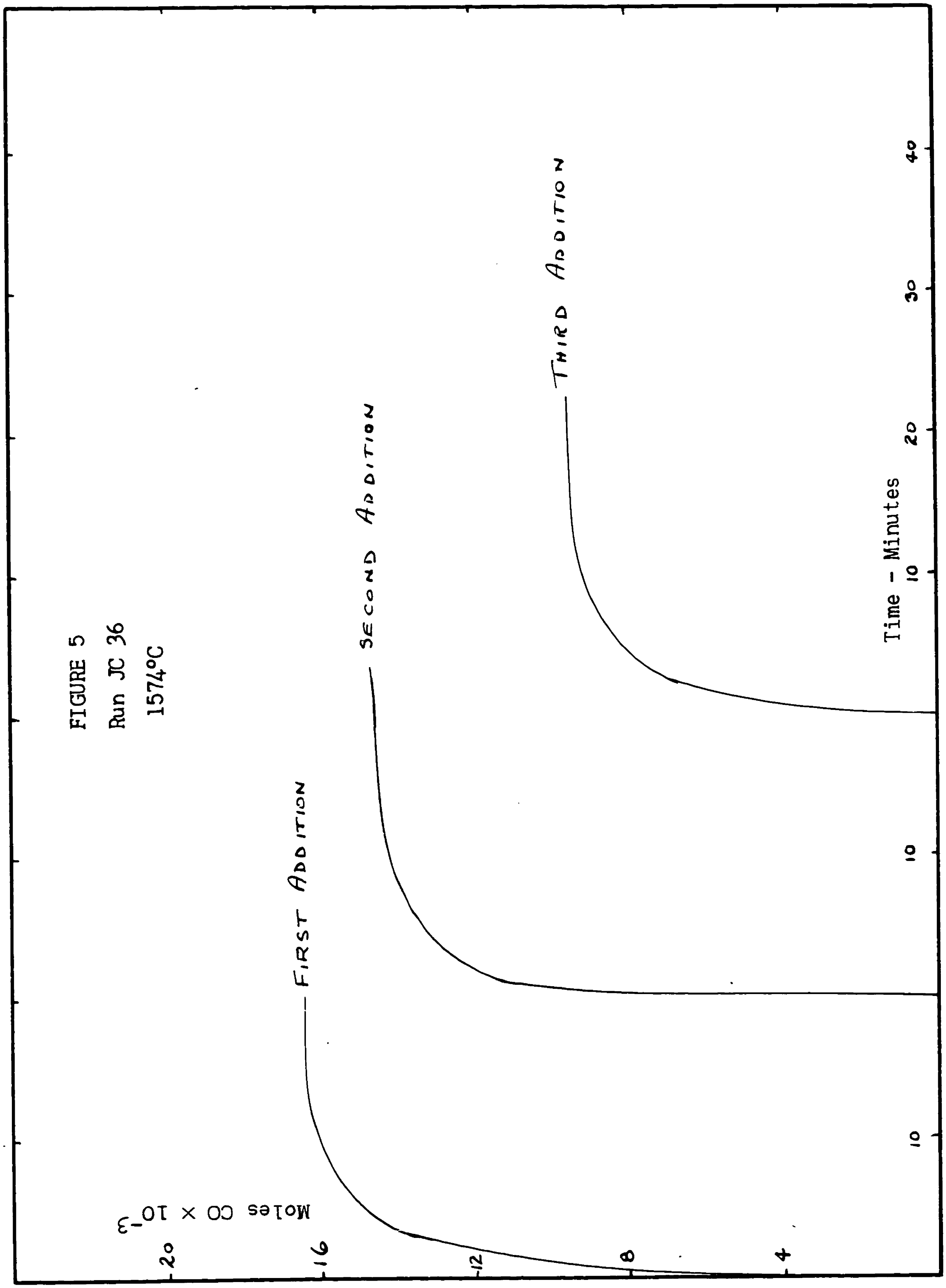
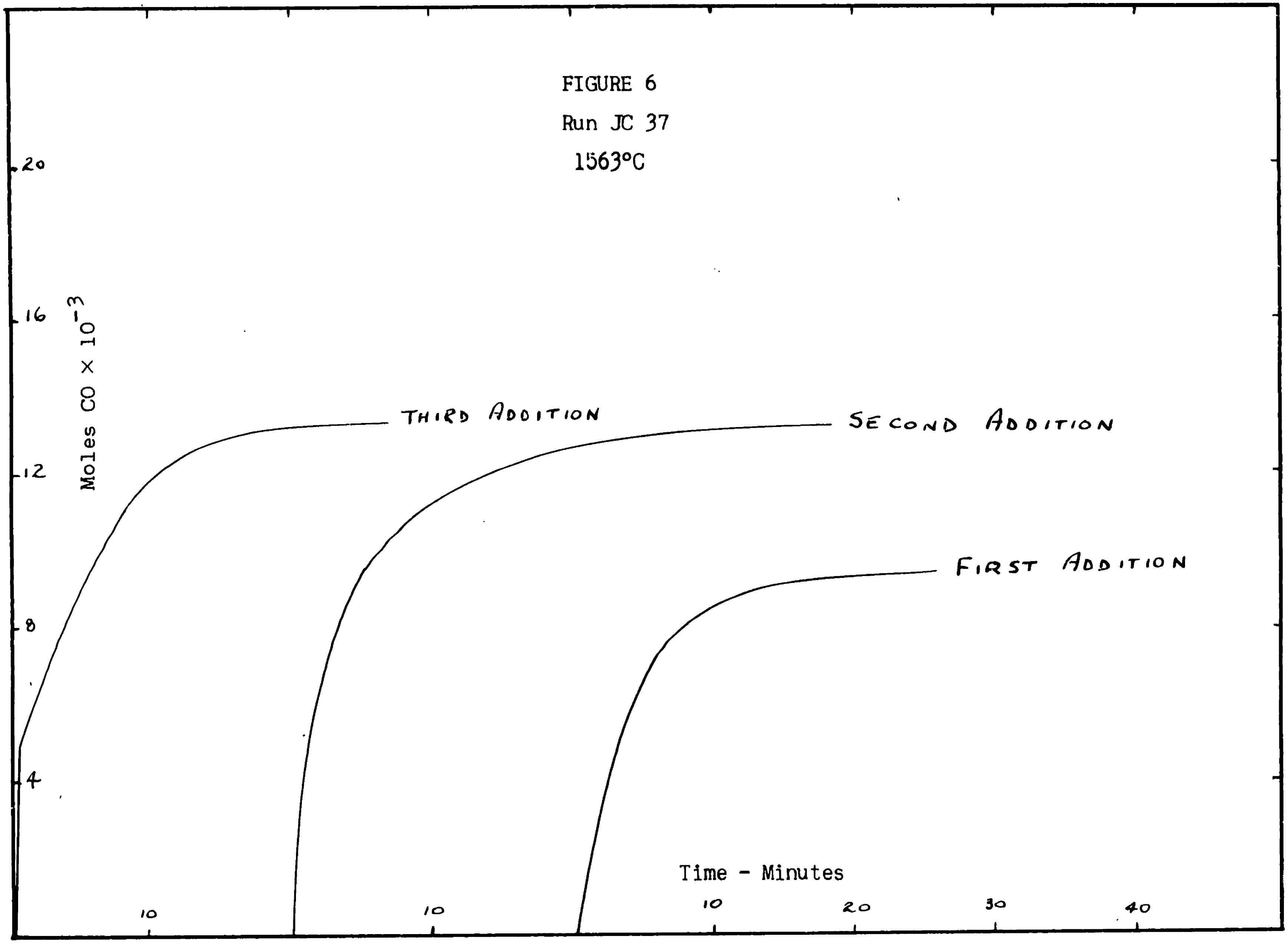


FIGURE 5
Run JC 36
1574°C

FIGURE 6
Run JC 37
1563°C



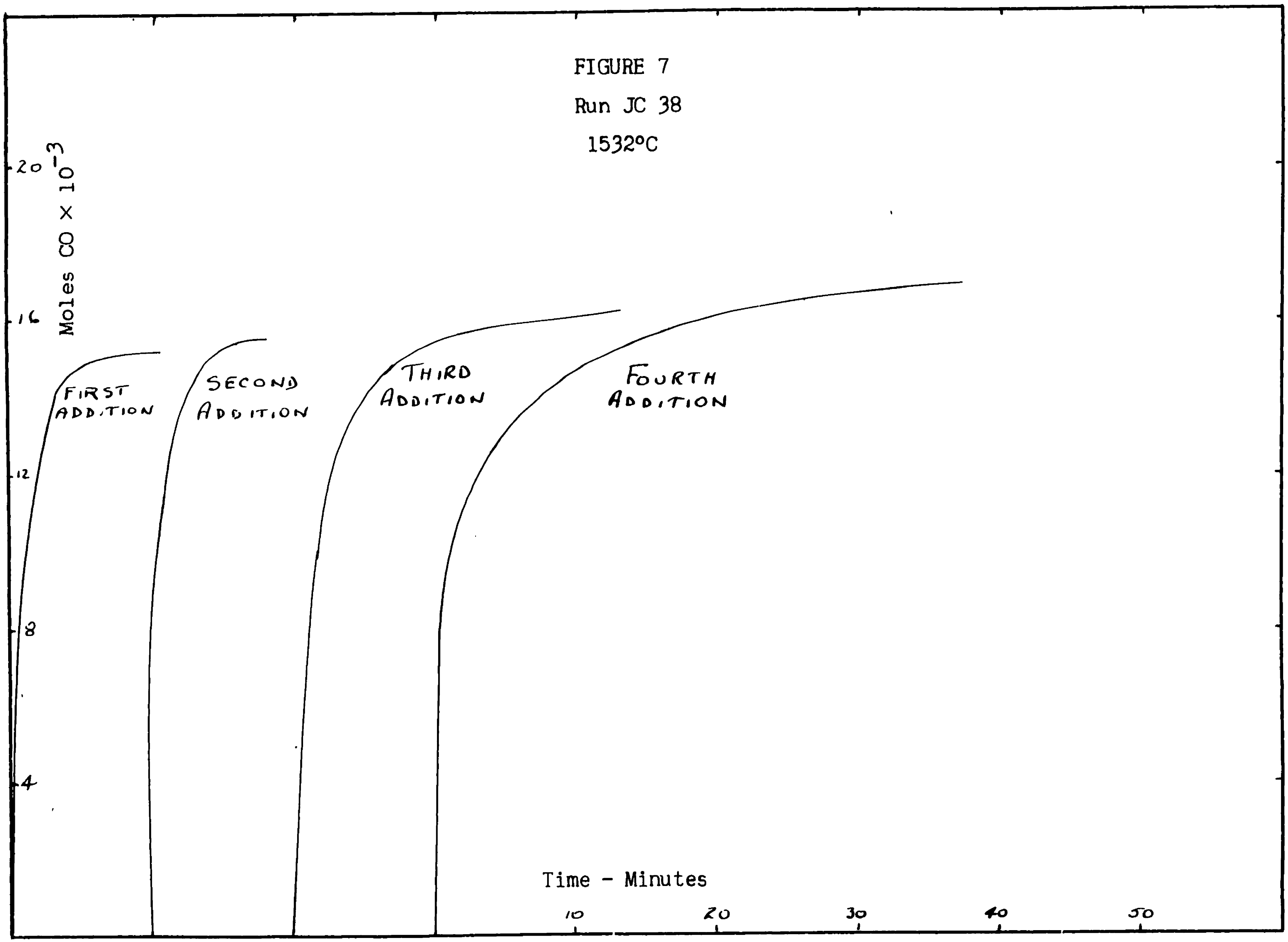


FIGURE 7
Run JC 38
1532°C

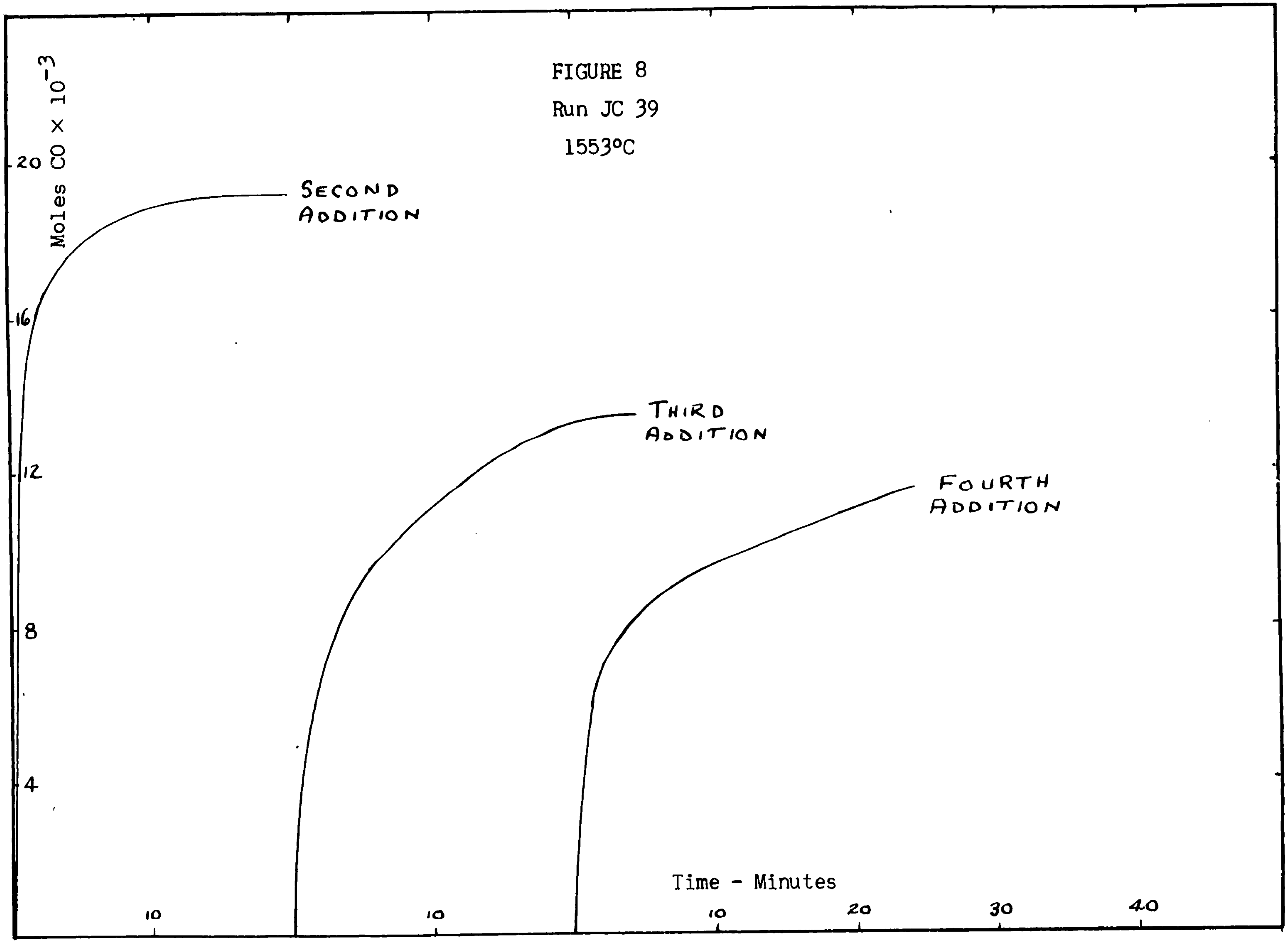


FIGURE 8
Run JC 39
1553°C

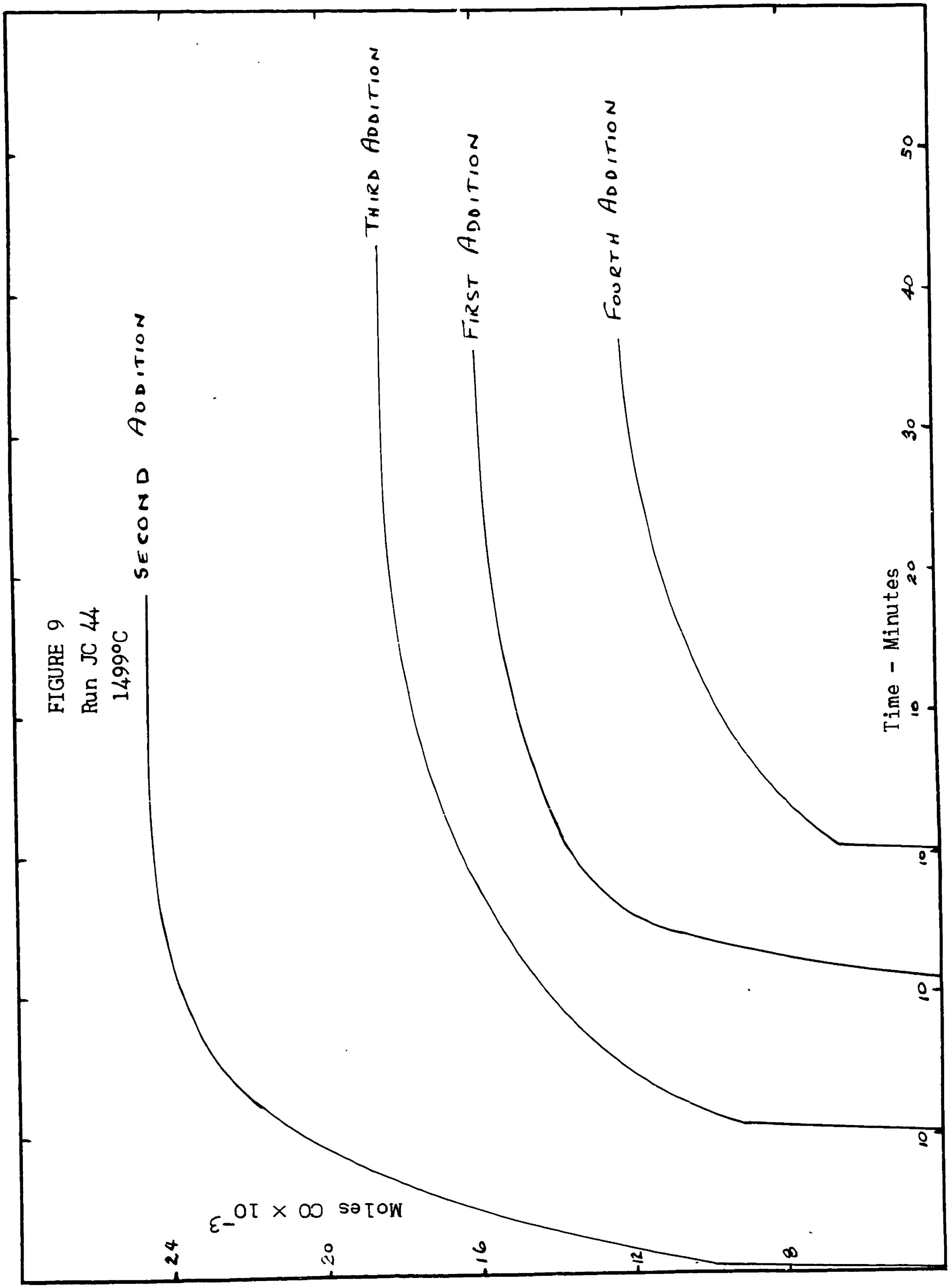


FIGURE 9
Run JC 44
1499°C

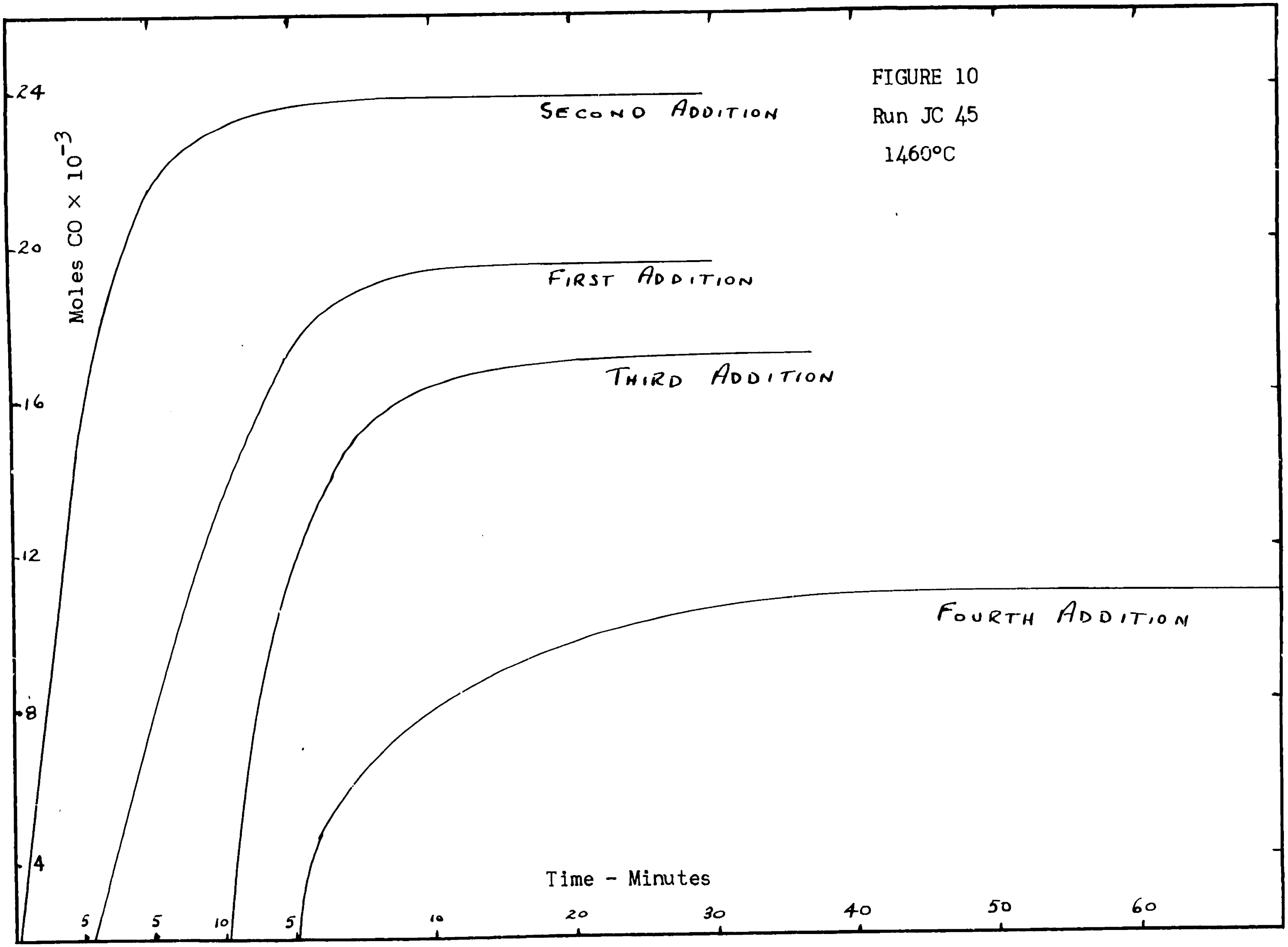


FIGURE 10
Run JC 45
1460°C

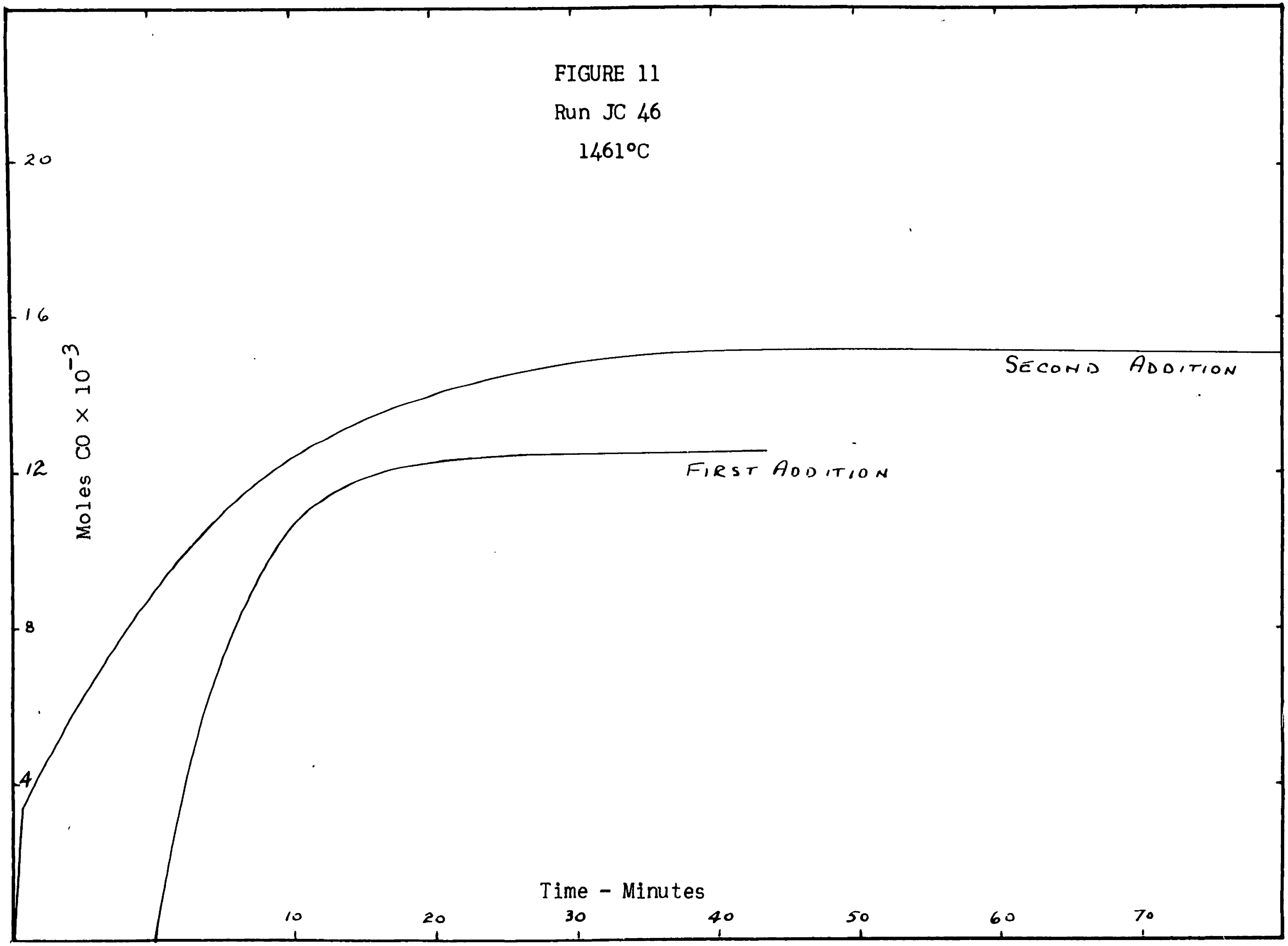


FIGURE 11

Run JC 46

1461°C

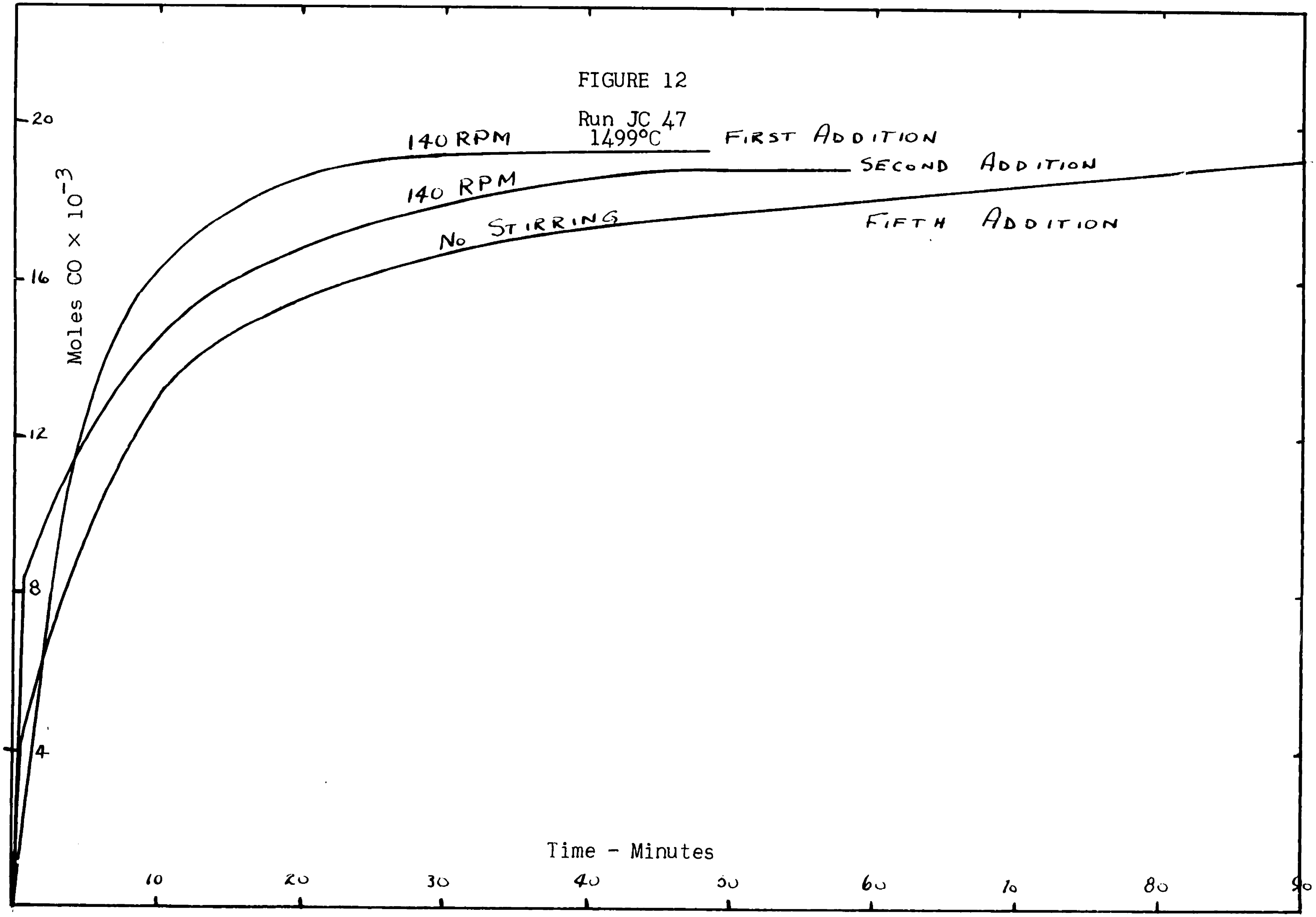


FIGURE 12

Run JC 47
1499°C

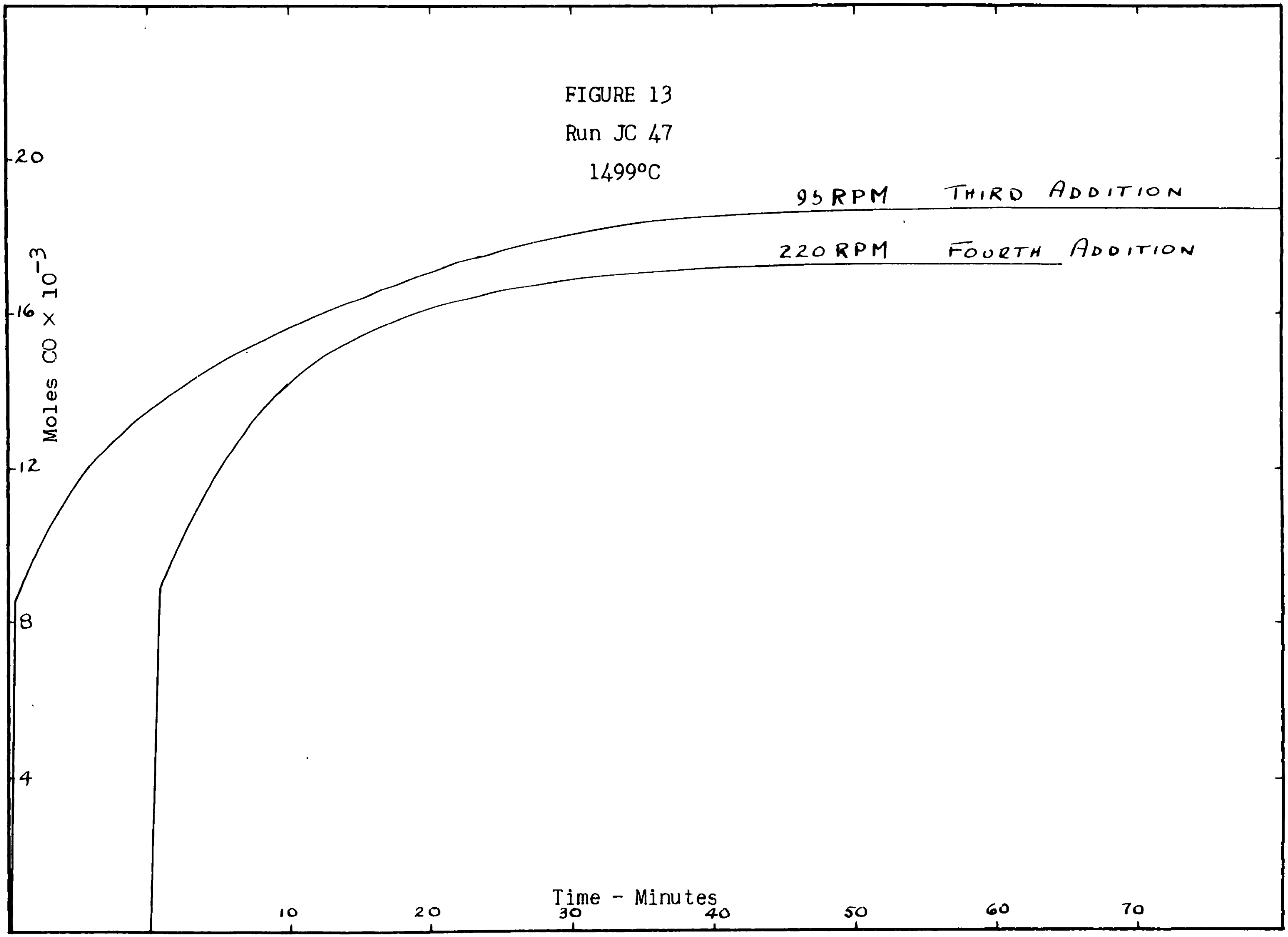


FIGURE 13
Run JC 47
1499°C

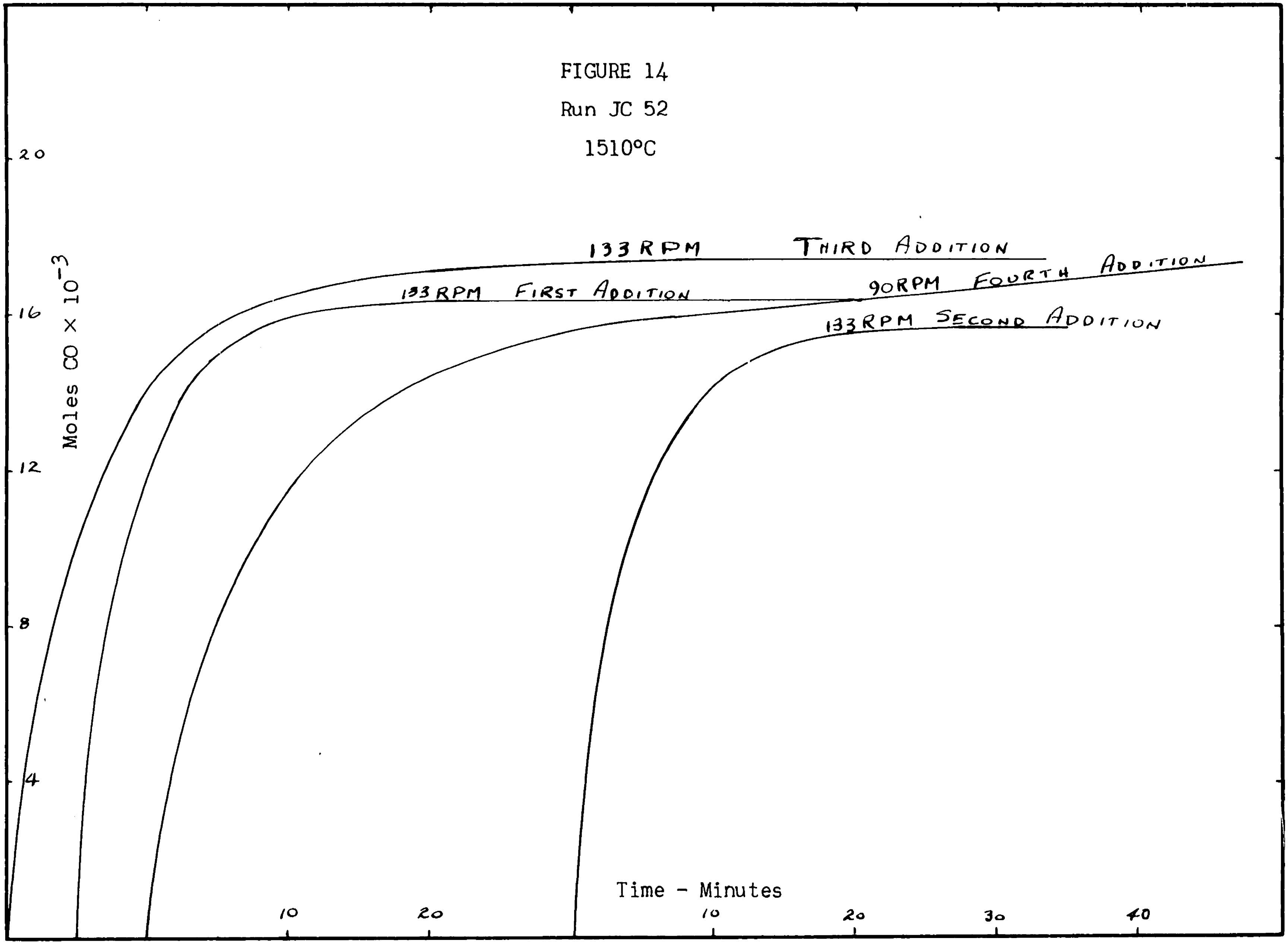


FIGURE 14
Run JC 52
1510°C

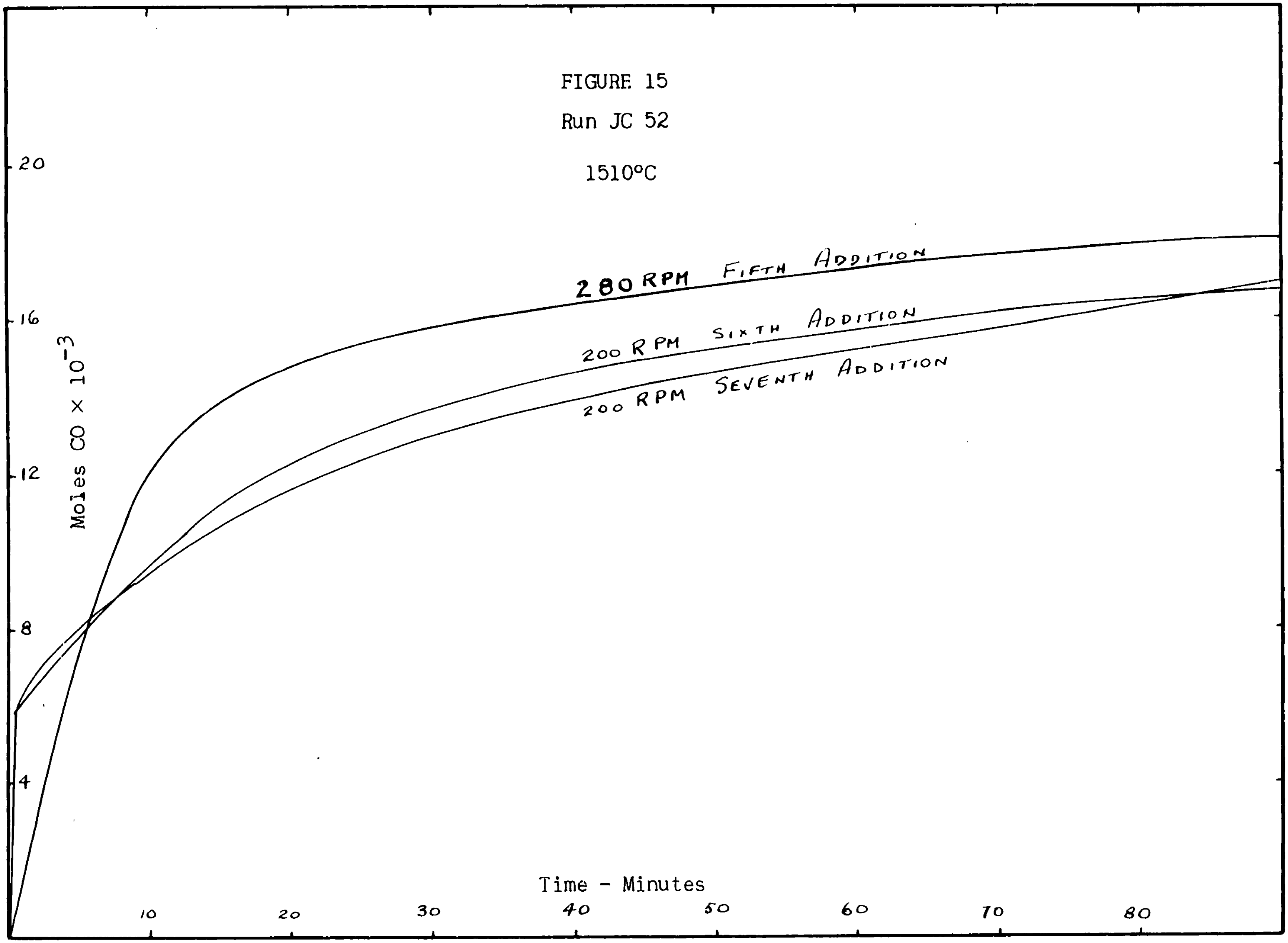


FIGURE 15

Run JC 52

1510°C

DISCUSSION OF RESULTS

A. Runs at the same Stirring Rate

Runs JC 31 and JC 46 (Figures 4 to 11) were all done at the same stirring rate of 140 revolutions per minute. Temperature, the size of the iron oxide additions and concentration of carbon were the main variables. Magnesia was added to the slag in the runs at high temperatures to lower the slag viscosity.

1) Effect of temperature

If Figures 4 to 11 are arranged in order of decreasing temperature the effect is immediately noticeable. The rate of reaction falls off with decreasing temperature with a few exceptions. For the runs above 1530°C the initial evolution of carbon monoxide, when the slag first contacts the carbon saturated iron, is extremely fast and does not fit in with the rest of the evolution as a smooth curve.

Data on reaction rates at different temperatures can be used to calculate activation energies. The evolution curves were therefore recalculated and replotted as the log of the ferrous oxide concentration above equilibrium versus time (a so called semi-log plot). The slope of such a plot is a measure of the reaction rate. If a straight line is obtained on a semi-log plot it indicates that the reaction is first order, that is, that the rate is proportional to the first power of the concentration of the particular reactant. Straight lines were not obtained.

A log-log plot can be used to obtain reaction orders. The slope of the plot is a direct measure of the reaction order. The data were recalculated and replotted as the log of the rate of change of ferrous oxide concentration with time versus the concentration of ferrous oxide above the equilibrium value. Straight lines with slopes varying from 1.3 to 1.6 were obtained. This means that for the particular conditions the reaction was intermediate between first and second order.

The rate of carbon monoxide evolution at a given ferrous oxide concentration can be used to determine the reaction constant.

Let,

$$\frac{d\ V_{CO}}{dt} = K' (\%\ FeO)^x \tag{a}$$

where $\frac{d\ V_{CO}}{dt}$ is the rate of carbon monoxide evolution in cubic centimeters per second

K' is the reaction constant

% FeO is the ferrous oxide content

x is a constant

but $-\frac{d\ C_{FeO}}{dt}$ is proportional to $\frac{d\ V_{CO}}{dt}$ so -

$$-\log \frac{d\ C_{FeO}}{dt} = \log K + x \log \%\ FeO \tag{b}$$

at unit concentration of FeO the term log % FeO = 0 so

$$K = -\frac{d\ C_{FeO}}{dt} \tag{c}$$

The value of the activation energy can be found if the value of K at different temperatures is known according to the equation

$$\log K_1 - \log K_2 = -\frac{E}{4.57} \left(\frac{1}{T_1} - \frac{1}{T_2}\right) \tag{d}$$

where E is the activation energy and T is the absolute temperature.

This has been done and an activation energy of 80,000 calories per mole found. The data used to calculate this value were rather limited and it would be dangerous to draw any conclusions. It is approximately equal to the activation energy for diffusion of constituents in slags.[15]

2) Size of iron oxide addition

The effect of varying the size of the iron oxide addition is as would be expected. The larger addition extends the curve in the initial stages making the first evolution more violent and the total evolution greater. The shape of the curve is similar for all additions (see Figures 5, 8, 9, and 10). This is to be expected since temperature, stirring rate and reaction order are the same so that K the rate constant should be the same also.

An additional reason for the discontinuity in the evolution curves just after addition may be the ferric oxide in the slag. This must first be reduced to ferrous oxide and its reduction rate would be expected to be quite rapid.

3) Effect of carbon content

In runs JC 31 to JC 39 (Figures 4 to 8) the metal was not resaturated with carbon after each iron oxide addition so that the carbon content decreased appreciably. This is well illustrated by run JC 39, Figure 8, where the carbon content decreased from 5.4 percent before the first addition to 4.1 percent at the end of the fourth addition. The reaction has definitely become slower at the lower carbon contents. This is evident in Figure 7 and to a lesser extent in Figures 5 and 6.

B. Effect of Varying Stirring Rate on Reaction Order

As has been shown in section A-1 a plot of the rate of carbon monoxide evolution with time versus the ferrous oxide concentration above equilibrium will yield the reaction order directly. The curves as drawn plot the rate of change of ferrous oxide concentration with time but this is directly proportional to the rate of carbon monoxide evolution.

It will be remembered from the literature survey that two reaction orders had been found for the reduction of ferrous oxide. Philbrook and Kirkbride[11] found that in a stationary crucible the rate of reduction of ferrous oxide was proportional to the square of the ferrous oxide concentration. That is, the reaction was second order. Dancy[9] on the other hand found that the same reaction was first order. This means the rate of reduction was proportional to the first power of the ferrous oxide concentration. Dancy, however, used a rapidly rotating crucible.

Since these two investigations had found different reaction orders and since previous runs in this work had given orders intermediate between the two it was decided to study the effect of stirring rate on the order of reaction.

In runs JC 47 and JC 52 additions were made at different stirring rates. The carbon monoxide evolution curves for these runs are given in Figures 12 to 15 and the log - log plots in Figures 16 and 17. Figure 16 shows very clearly the effect of stirring on the reaction order. Curve 5 from Run JC 46 was for a highly agitated melt in which stirring was provided by the alumina rod plus four pieces of 1/4 inch graphite rod about 3/4 inch long. This violent stirring gave a reaction order of exactly 1.0. The other curves, 1, 2, 3, and 4 are from Run JC 47 at a slightly higher temperature than Run JC 46. The slope and therefore the order of reaction is seen to increase as the stirring rate is decreased; at 220 revolutions per minute the reaction order is

FIGURE 16

5 Run JC 46 First Addition 1461°C 140 RPM Slope 1.00

1 Run JC 47 Fourth Addition 1499°C 220 RPM Slope 1.17

2 Run JC 47 Second Addition 1499°C 140 RPM Slope 1.30

3 Run JC 47 Third Addition 1499°C 95 RPM Slope 1.61

4 Run JC 47 Fifth Addition 1499°C No Stirring Slope 2.06

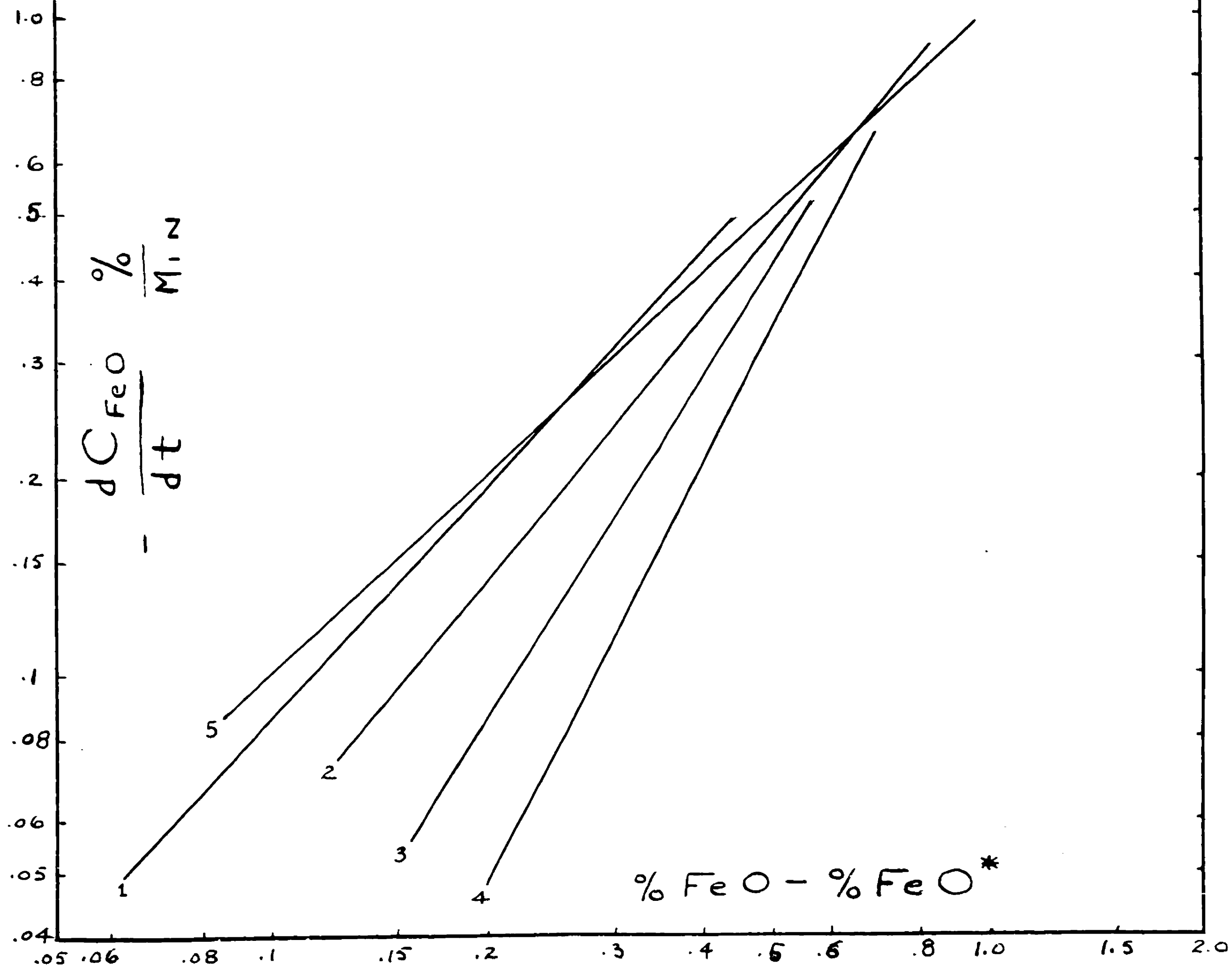


FIGURE 17

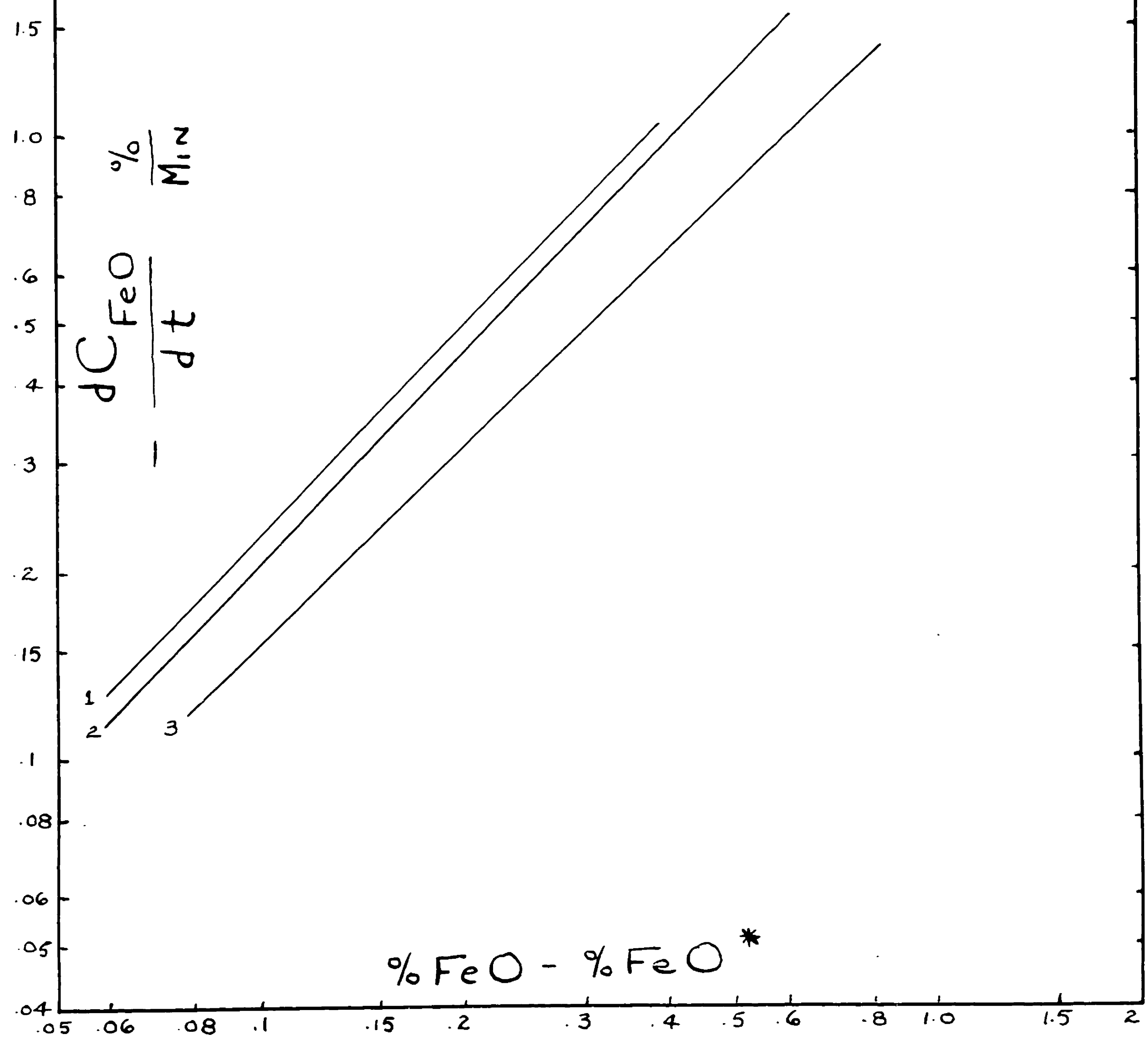
Run JC 52

1510°C

1 First Addition Slope 1.11

2 Second Addition Slope 1.12

3 Third Addition Slope 1.04



1.17, at 140 revolutions per minute it is 1.30 and at 95 revolutions per minute it is 1.61. For the stationary crucible the order is 2.06 in very good agreement with the results of Philbrook and Kirkbride.

The results of the later additions in Run JC 52 are unreliable since when the furnace was taken apart it was found that the stirring rod was completely eroded at the slag line. The first three additions are on a log - log plot in Figure 17 to show how well the slopes of the three curves check for identical stirring conditions of 133 revolutions per minute. As is noted at the top of the figure slopes of 1.11, 1.12, and 1.04 were obtained. This indicates a higher degree of agitation than in the second addition of Run JC 47 where the stirring rate was 140 revolutions per minute and a reaction order of 1.30 was obtained. Differences in slag viscosity and temperature may explain this discrepancy.

C. Theory

1) The reaction

The overall reaction for ferrous oxide reduction may be written as

$$\underline{C} + FeO \rightarrow CO_{(g)} + Fe. \qquad (1)$$

Carbon in the metal and ferrous oxide in the slag react to produce carbon monoxide gas and free iron in the metal.

Let the equilibrium constant for the reaction be K'. Then

$$K' = \frac{p\,CO \cdot a_{Fe}}{a_c \cdot a_{FeO}} \qquad (2)$$

p CO is the pressure of carbon monoxide in atmospheres.

a_{Fe} is the activity of iron in the metal.

a_C is the activity of carbon in the metal.

a_{FeO} is the activity of ferrous oxide in the slag.

a_{Fe} and a_c are assumed to be constant since the solvent is iron, saturated with carbon so

$$K = \frac{p\ CO}{a\ FeO} \tag{3}$$

Actually ferrous oxide exists in the slag as ferrous ions and oxygen ions (Fe^{++} and $O^{=}$).

During reaction carbon, ferrous ions and oxygen ions must all be transported to the slag-metal interface, and carbon monoxide and iron must be removed. Transport or diffusion of oxygen ions in the slag and carbon and iron in the metal as rate controlling steps may be eliminated because of their high concentrations. However, ferrous ion transport may be rate limiting.

The other possible rate limiting step is nucleation of carbon monoxide which has been shown by Ramachandran, King, and Grant to take place at the interface.[8]

2. Transport control

Fick's first law is as follows

$$J = -AD\frac{dc}{dx} \tag{4}$$

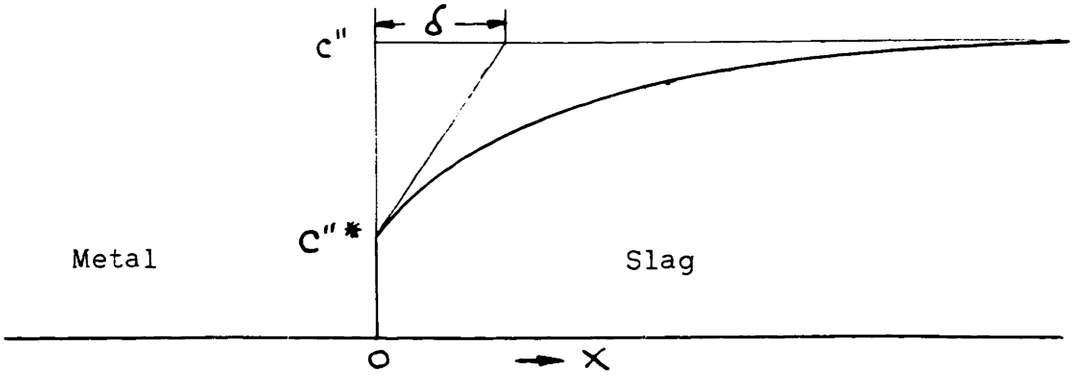
J = the rate of diffusion in moles per unit time.

A is the cross sectional area through which the diffusion is taking place.

D is the diffusion coefficient in units of $\text{length}^2\ \text{time}^{-1}$.

Transport of ferrous oxide in the slag to the slag metal interface is effected by both diffusion and convection. The concentration of ferrous oxide is relatively uniform in the bulk of the slag and the concentration gradient is appreciable only at the interface. (see sketch)

FIGURE 18



Schematic Diagram of Boundary Layer Diffusion

At x = 0 (the slag metal interface) transport is wholly by diffusion, and the flux J is given by (4)

$$J = - AD \left(\frac{dC}{dx}\right)_{x = 0} \tag{4a}$$

from the diagram it can be seen that

$$\left(\frac{dC}{dx}\right)_{x = 0} = \frac{C'' - C''^{*}}{\delta} \tag{4b}$$

Applying this to the transport of iron in the slag and inserting the proper symbols and units we obtain

$$\frac{\dot{\eta}_{Fe}}{A} = \frac{D_{Fe}''}{\delta_{Fe}''} (C_{Fe}'' - C_{Fe}''^{*}) \tag{5}$$

If $\dot{\eta}_{Fe}$ is the number of moles of iron oxide reduced from the slag per second.

D_{Fe}'' is the diffusion coefficient of ferrous ions in the slag in square centimeters per second.

A is the interface area in square centimeters.

δ_{Fe}'' is the effective thickness of the boundary layer through which the ferrous ions must diffuse in centimeters.

$C_{Fe''}$ is the concentration of ferrous ions in the slag in moles per cubic centimeter.

$C_{Fe''}^{*}$ is the concentration of ferrous ions at equilibrium in moles per cubic centimeter.

To preserve electroneutrality in the system

$$\dot{\eta}_{Fe} = \dot{\eta}_{CO} \tag{6}$$

where $\dot{\eta}_{CO}$ is the number of moles of carbon monoxide evolved per second. Then,

$$\frac{\dot{\eta}_{CO}}{A} = \frac{D_{Fe''}}{\delta_{Fe''}} \left(C_{Fe''} - C_{Fe''}^{*} \right) \tag{7}$$

but,

$$\frac{\dot{\eta}_{CO}}{A} = \frac{1}{22,400\ A} \frac{d\,V_{CO}}{dt} \tag{8}$$

where 22,400 is the number of cubic centimeters in a mole and $\frac{d\,V_{CO}}{dt}$ is the rate of carbon monoxide evolution in cubic centimeters per second.

Also

$$C_{Fe''} = \frac{\%\ FeO\ \rho_s}{100 \times 72} \tag{9}$$

where % FeO is the concentration of ferrous oxide in the slag in percent.

ρ_s is the density of the slag in grams per cubic centimeter.

100 is a factor to convert percent to ratio.

72 is the molecular weight of ferrous oxide.

Substituting the results of Equations (8) and (9) in (7) we obtain

$$\frac{d\,V_{CO}}{dt} = \frac{3.11\ A\ D_{Fe''}\ \rho_s}{\delta_{Fe''}} \left(\%\ FeO - \%\ FeO^{*} \right) \tag{10}$$

Since A, D_{Fe}'' and ρ_s are constants they may be combined with the numerical constant as a new constant M. Equation (10) then becomes

$$\frac{d\ V_{CO}}{dt} = \frac{M}{\delta_{Fe}''} (\%\ FeO - \%\ FeO^*) \qquad (11)$$

For a transport controlled reaction the phase boundary reaction is assumed to be in equilibrium so that Equation (3) may be rearranged as

$$a_{FeO} = \frac{p\ CO}{K} \qquad (12)$$

At low ferrous oxide concentrations a_{FeO} is proportional to % FeO. The ferrous oxide content of the slag at equilibrium has been given the symbol % FeO* so

$$\%\ FeO^* = \frac{p\ CO}{K'} \qquad (13)$$

Substituting in Equation (11)

$$\frac{d\ V_{CO}}{dt} = \frac{M}{\delta_{Fe}''} (\%\ FeO - \frac{p\ CO}{K'}) \qquad (14)$$

The rate of this transport controlled reaction is therefore proportional to the first power of the ferrous oxide concentration.

3. Phase boundary control

a. Direct Reaction

If the rate of the phase boundary reaction is the slow step then the concentrations of all reactants at the interface are nearly equal to their concentrations in the bulk. The reaction is that of Equation (1)

$$\underline{C} + FeO \rightarrow CO_{(g)} + Fe \qquad (1)$$

The rate of the forward reaction is determined by the ferrous oxide concentration since the concentration of carbon is high and constant. The rate of the backward reaction is essentially a constant, determined by the carbon monoxide pressure and the activity of iron. The rate equation is then

$$\frac{d\ V_{CO}}{dt} = N\ (\%\ FeO - Z) \tag{15}$$

where N and Z are constants, which is identical with Equation (14) if δ_{Fe}'' is assumed to be constant.

From a measure of the reaction order and rate alone we cannot distinguish between a diffusion controlled and a phase boundary controlled reaction.

b. Electrochemical control

An additional possibility is that the reaction is an electrochemical one in which two reactions take place at different locations simultaneously. The only requirement is that electroneutrality is preserved.

$$C + O^{2-} \rightarrow CO_{(g)} + 2\ e^{-} \tag{16}$$

$$2\ e^{-} + Fe^{2+} \rightarrow Fe \tag{17}$$

A theoretical treatment of this reaction by Wagner[13] has shown its rate to be proportional to the square root of the ferrous oxide concentration

$$\frac{d\ V_{CO}}{dt} = R\ (\%\ FeO)^{1/2} \tag{18}$$

where R is a proportionality constant.

D. Application of Theory to Results

If the overall reaction is controlled by the rate of the phase boundary reaction, the electrochemical reaction may be ruled out as a possibility since reaction orders of less than unity have not been obtained. This is to be expected since the reaction is a simple one involving few reactants.

If the reaction is transport controlled it is possible that an electrochemical reaction takes place but it is not the rate limiting step and present results cannot be used to show whether it is an important mechanism or not.

The first order reaction found during violent stirring may therefore be due to a phase boundary reaction or to a diffusion controlled reaction.

Ramachandran, King, and Grant[8] suggest that the phase boundary reaction is the rate limiting step.

Wagner[14] has presented an explanation of the second order reaction found by Philbrook and Kirkbride[11]. The thickness of the boundary layer cannot be assumed to be constant under the varying convection caused by carbon monoxide evolution. Its thickness δ_{Fe}'' is assumed to be a function of the rate of carbon monoxide evolution

$$\delta_{Fe}'' = b\left(\frac{d\,V_{CO}}{dt}\right)^{-\beta} \qquad (19)$$

where b and β are constants.

Substituting in Equation (11) we obtain

$$\frac{d\,V_{CO}}{dt} = \frac{M}{b\left(\frac{d\,V_{CO}}{dt}\right)^{-\beta}} (\%\ FeO - \%\ FeO*) \qquad (20)$$

which rearranged to

$$\left(\frac{d\,V_{CO}}{dt}\right)^{1-\beta} = \frac{M}{b} (\%\ FeO - \%\ FeO*) \qquad (21)$$

if $\beta = 1/2$ we obtain

$$\frac{d\,V_{CO}}{dt} = \frac{M}{b} (\%\ FeO - \%\ FeO*)^2 \qquad (22)$$

This is what Philbrook and Kirkbride[11] have found.

Present results indicate that β is not a constant since the order of reaction varies from one to two depending on the stirring rate. This means that β varies from 0 to 1/2, or that δ_{Fe}'' is a function that asymptotically approaches a constant value as the stirring rate is increased. Stated in another way as the stirring rate is increased the effect of carbon monoxide evolution on the total convection becomes less and less until finally its effect is insignificant and we obtain a first order reaction.

An equation of the following type is possible

$$\beta = Y\left(\frac{1}{RPM}\right)^{X} \tag{23}$$

where Y and X are constants and RPM is the rotation speed of the crucible.

These results do not prove that the reaction is one controlled by transport but most of the evidence points in that direction.

SUGGESTIONS FOR FUTURE WORK

Further investigation into the rates of iron reduction could clear up the doubt that remains as to mechanism and reaction order.

Runs in a graphite crucible would be much simpler to perform and would eliminate the doubt that exists because of working with a slag at its liquidus. Philbrook and Kirkbride[11] have shown that this type of data can be treated by allowing for the slag-graphite interface reaction. The stirring rate could be varied in the same way as in the present work and a check obtained on the conclusions of this thesis.

Other work could more definitely define the effect of carbon content on the rate of reaction. This must be done in an alumina crucible since a graphite crucible would keep the iron saturated with carbon.

Radioactive tracers might also be used to differentiate between a phase boundary limited reaction and a transport controlled reaction.

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APPENDIX

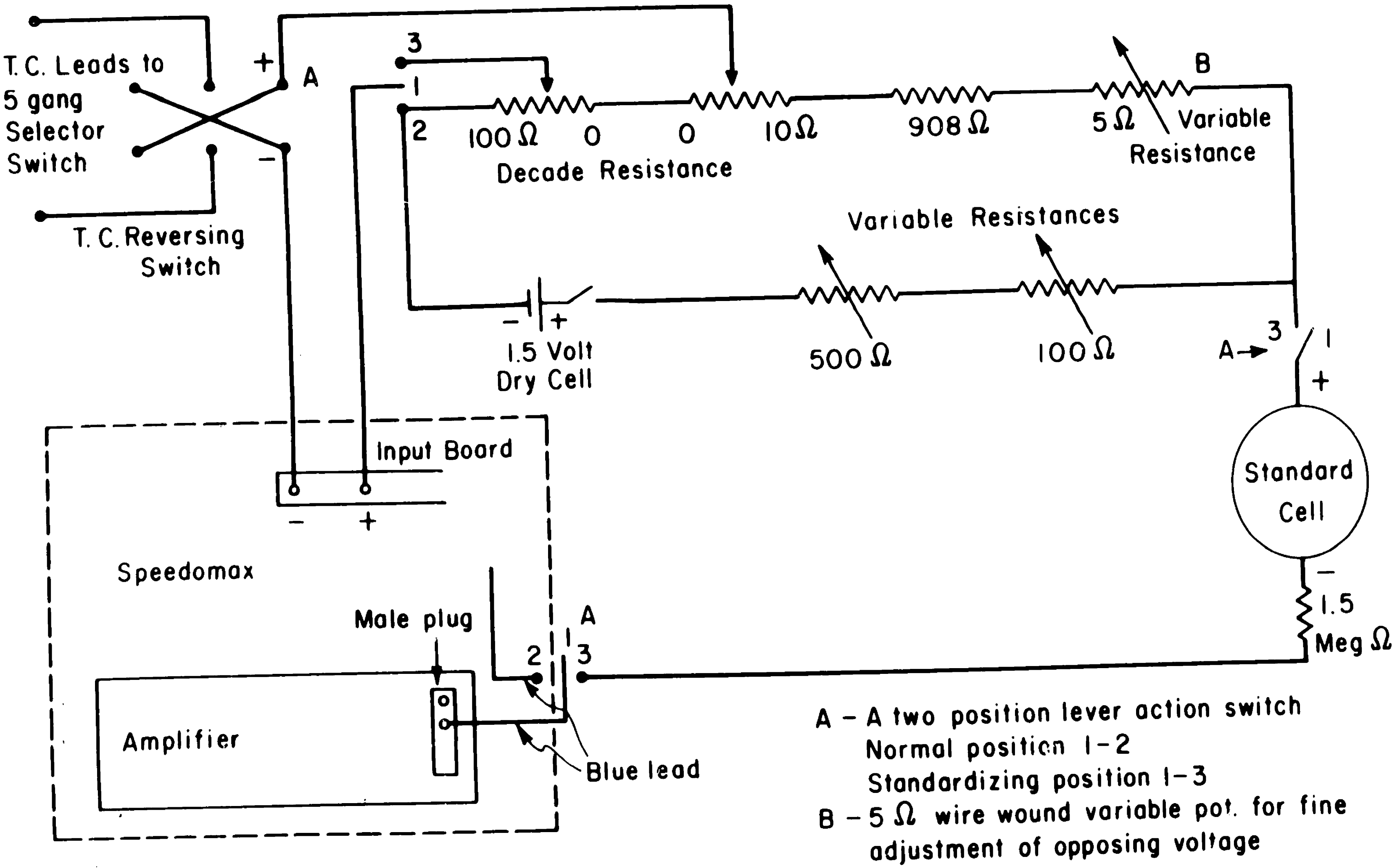
A. The Bucking Potentiometer

A circuit diagram for the bucking potentiometer is given in Figure A 1. It is used in opposition to the Leeds and Northrup Speedomax recorder to extend its range. It is a simple potentiometric circuit from which an opposing voltage variable in steps of one or ten millivolts can be obtained. The Speedomax can measure voltages up to two millivolts to the nearest .01 millivolt. If for example a voltage of 36.8 millivolts is to be measured 35 or 36 millivolts can be set up in the bucking potentiometer leaving the .8 or 1.8 millivolts to be measured by the potentiometer. A bucking potential up to 110 millivolts can be obtained. The decade resistors across which the desired opposing voltage is obtained are in steps of one or ten ohms. When the circuit is balanced the drop across each ohm is one millivolt.

The potentiometer is standardized against a standard cell in the circuit, using the Speedomax to find the null point. The lever action switch (A-A in Figure 1, Standard on the instrument) is pressed down and the variable resistances adjusted until the Speedomax indicates zero. This is done before each run.

The dry cell must be replaced intermittently and the whole circuit readjusted against a standard potentiometer. Fine adjustment is made with variable resistance B (Figure A-1). The potentiometer and Speedomax are checked together by measuring known outputs from the standard potentiometer.

A five position gang switch and a reversing switch are included in the potentiometer circuit so that the voltage from various sources



A – A two position lever action switch
Normal position 1–2
Standardizing position 1–3
B – 5 Ω wire wound variable pot. for fine adjustment of opposing voltage

FIG. A1 – WIRING DIAGRAM OF DECADE POTENTIOMETER can be measured by switching from one to the other. A reversing switch is also included to reverse positive and negative terminals if a wrong connection is made.

B. Standardization and Sample Calculations

The data from a run are of two kinds, data on carbon monoxide evolution, and slag and metal analyses.

The data on carbon monoxide evolution is obtained from the Speedomax chart as millivolts versus time. These are reading of the transducer that converts pressure changes to millivolts. The millivolt readings must be converted into some chemical quantity, in this thesis moles. Since all gas evolved is carbon monoxide this indicates the evolution of carbon monoxide, and is equal to the reduction of ferrous oxide in moles.

The millivolt readings are easily converted to pressure readings. The millivolt reading equivalent to a two pounds per square inch pressure is available at any time simply by pressing the "Standardize Push" knob of the control unit. This voltage, variable from about 16 to 22 millivolts is superimposed on any voltage from the transducer.

The system is standardized by noting the pressure increase of the system for a known increase in the total moles of the system. This is introduced from the gas pipette, which is a series of glass bulbs of known volume. Mercury is used to displace the gas. Total volume of the bulbs is 189.7 cubic centimeters. The initial pressure of both the system and standard volumes is atmospheric. As the gas is displaced into the system the pressure rises.

As an example, V_o = 189.7 the volume of the standard volumes, barometer reading P = 29.58 inches of mercury, standard atmospheric pressure

P_o = 29.96 inches of mercury, gas content R = 82.1 cubic centimeter atmospheres per degree mole, and T = 298.1°C the temperature of the standard volume, then the number of moles in the standard volume

$$N = \frac{\frac{P}{P_o} V_o}{RT} = \frac{\frac{29.58}{29.96} \cdot 189.7}{82.1 \cdot 298.1} = 7.65 \times 10^{-3} \text{ moles}$$

Let M = 3.87 millivolts - the voltage produced when the gas is displaced into the system, and M_o = 16.95, the voltage equal to two pounds per square inch. Then A, the number of moles equivalent to one pound per square inch pressure rise

$$A = \frac{M_o}{2\ M} N = \frac{16.95 \times 7.65 \times 10^{-3}}{2 \times 3.87} = 16.77 \times 10^{-3} \text{ moles}$$

Since the number of millivolts equivalent to a pressure drop of two pounds per square inch decreases slightly with time this enables the system to be calibrated independent of this change. That is, both M_o and M decrease slightly but their ratio always remains the same.

To calculate a run the voltage at various times is read from the Speedomax record. A correction is made to this reading which allows for the initial or zero point of the record plus any blank. The pressure is computed by dividing this voltage by the M_o found just before the addition was made. This pressure is converted into moles of carbon monoxide by multiplying by A - the number of moles equivalent to a pressure difference of one pound per square inch.

The number of moles versus time curves are then plotted. To find the differential $\frac{dC_{FeO}}{dt}$ the slope of the Speedomax curve at the various times is found and converted from a slope of millivolts versus time to percent ferrous oxide versus time. The value of $(C_{FeO} - C_{FeO}^*)$ (where C_{FeO} is concentration of ferrous oxide in percent and C_{FeO}^* is the concentration of ferrous oxide at equilibrium) is found by assuming it to be zero when carbon monoxide evolution ceases. The percentage of ferrous oxide above equilibrium is found by subtracting the moles of carbon monoxide evolved at any time from the moles evolved at equilibrium and converting this to a percentage of ferrous oxide since the weight of slag is known.

TABLE A-1

Figure Number	Run Number	Addition Number	Time Minutes	Slag in Crucible							Metal		
				Weight Grams	Total Fe as % FeO	FeO %	Fe_2O_3 %	CaO %	Al_2O_3 %	MgO %	Weight Grams	C %	S %
4	JC 31	1	0	145		4.60	1.28	37.33			94	5.23	
		1	30	145							94	4.95	
		2	45	140	1.48			41.27			88	4.34	
5	JC 36	1	0	114		3.23	.56	30.91	59.71	2.08	93	5.43	
		1	20	114							93	5.24	
		2	25	114							86	4.90	
		3	25	114							73	4.58	
6	JC 37	1	0	115		1.94	.39	30.68	63.18	2.53	85	5.40	.033
		1	30	112	1.07						85	5.12	.029
		2	40	110	1.09						81	4.80	
		3	25	106	2.02						76	4.58	
7	JC 38	1	0	116		4.30	2.01	30.29	60.32	2.53	148	5.45	
		1	10	116							148	5.25	
		2	10	116	1.03						141	5.09	
		3	25	115	1.10						137	4.91	
		4	40	114	1.22						131	4.62	
8	JC 39	2	0	120	0.67			29.23			135	5.40	
		2	20	120	0.82			28.63	62.43	3.66	135	4.28	
		3	25	118	1.00			29.76			130		
		4	25	114	1.78			30.13			130	4.10	
9	JC 44	1	0	125							135	5.30	

TABLE A-1 (continued)

Figure	Run	Addition	Time	Slag in Crucible							Metal		
Number	Number	Number	Minutes	Weight	Total Fe	FeO	Fe_2O_3	CaO	Al_2O_3	MgO	Weight	C	S
				Grams	as % FeO	%	%	%	%	%	Grams	%	%
9	JC 44	4	35	125							135	4.97	
10	JC 45	1	0	117		.96	1.13	45.60			133	5.16	
		4	70	117	.28						133	4.97	
		4	90	117	.21						133	4.95	
11	JC 46	1	0	116		.99	.81	46.05			143	5.19	
		2	100	116	.18						143		
12, 13	JC 47	1	0	125							138	5.10	
		5	110	125	.11						138	4.83	
14, 15	JC 52			120							133		

Explanation of Table A-1

The first three columns are self-explanatory. Time in minutes refers to the time the sample was taken in relation to the time of the addition.

"Weight - grams" is the weight of slag in the crucible. It is found by calculating the weight of slag from a calcium oxide analysis and the weight and composition of the master slag. From the weight is subtracted the weight of the sample, except if a sample is taken after a run in which case the sample weight is not subtracted.

"Total Fe as % FeO" is the total iron content of the magnetically cleaned slag calculated as percent ferrous oxide.

"FeO %" and "Fe_2O_3 %" refer to a chemical analysis that distinguishes between these two oxides. This analysis was performed on the initial samples only. The other analysis columns are self-explanatory.

"Weight - Grams" of metal is the weight of carbon saturated iron charged minus the weight of metal left in the top crucible and the weight of any previous samples.

Analyses are again self-explanatory.

The weights of all additions are considered to have a negligible effect on the weights of slag and metal compared to the possible errors in calculating these weights.

C. Equilibrium Run

The term equilibrium iron oxide concentration as used in these experiments is a rather indefinite one. Samples were usually taken a few minutes after carbon monoxide evolution had fallen to an immeasurably low value. Analyses of these samples from earlier runs however showed ferrous oxide contents as high as one percent. Thermodynamic calculations indicate a value orders of magnitude lower than this. Later runs of an hours duration or longer gave values of about 0.2 percent iron as ferrous oxide when carbon monoxide evolution had ceased.

To check the iron oxide content of a slag in equilibrium with carbon a run was made in a graphite crucible using a 60 percent alumina, 40 percent calcium oxide slag. This enabled the slag to be held at a temperature much above its liquidus and eliminated the uncertainty present in all the other runs due to the high slag viscosity at the liquidus.

For this run carbon monoxide evolution became negligible in about 30 minutes. 20 minutes later a sample was taken and analyzed 0.017 percent iron as ferrous oxide. A sample 25 minutes later analyzed 0.013 percent iron as ferrous oxide. All samples were thoroughly cleaned in the electromagnetic separator to remove the last traces of free iron before analysis.

This run adds additional data to that already gathered by others on the very low iron oxide content of slags in contact with carbon.

The high ferrous oxide content of the slags in contact with carbon saturated iron in this work is hard to explain. The great defect in the whole system is using a slag at its liquidus. The system is then disturbed by adding a flux to the slag in the form of a lime-iron oxide slag. This at first moves the slag away from the liquidus but some of the alumina crucible dissolves to resaturate the slag. Part of the flux is then removed as the iron oxide is reduced by carbon and there is danger that alumina begins to precipitate from the slag, or at least that the slag increases in viscosity. This could finally make the viscosity so great that diffusion and convection would be greatly diminished and the reaction, even at relatively high ferrous oxide concentrations would become extremely sluggish.

Another reason that was suspected to contribute to the high ferrous oxide contents was the fact that the iron was not quite saturated with carbon when carbon monoxide evolution had ceased. This was proved false by adding carbon pellets to the slag as was done in run JC 46, Figure 11. A sample taken after carbon monoxide evolution had ceased analyzed 0.18 percent iron as ferrous oxide, approximately the same as for slags in contact with iron whose carbon content was about 0.3 percent below saturation.

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