

EQUILIBRIUM RELATIONS BETWEEN CARBON STEEL
AND PREPARED ATMOSPHERES

by

TENNYSON IRL COLLINS

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INTRODUCTION

A prepared atmosphere, as used in the treatment of metals is a mixture of gases with a closely controlled composition, formed by the combustion of a fuel gas and air. The proportions of various gases in the mixture will vary, depending upon the gas and the air-gas ratio used in preparing the atmosphere. With a high air-gas ratio the combustion is self supporting and gives off heat, therefore, it is known as an exothermic atmosphere. A mixture having a lower (below 4 or 5) air-gas ratio will not burn by itself and heat must be added to cause the reaction to go to completion.

This endothermic reaction may be hastened by filling the generator combustion chamber with charcoal or a catalyst. The atmosphere thus formed may be used directly from the furnace or further processed by adding or removing a specific gas before used in the heat treating furnace.

It was the purpose of this investigation to study the action of a charcoal-formed endothermic atmosphere upon heated steel, and to compare the results with published data on catalytically formed atmospheres.

REVIEW OF LITERATURE

The process of carburizing (or "carbonizing," as it was known until the 1920's) is among the oldest of the ferrous arts (2). After the complex operation of reducing the ore to a useful metal was mastered, the process of heating iron

packed in a carbonaceous material followed very shortly. Metallographic examination of knives found in tombs indicate the Egyptians were quite advanced in this knowledge as early as 1200 B.C.(1).

In Europe and Asia during the 16th century the iron industry was under the control of the government and usually became a royal monopoly. The workers knew how to produce a surface case, but did not know the reason behind it, and therefore attributed it to magic. For the carburizing medium such things as "black ox blood, toade oyle, fen moss, viper flesh or mummy powder," were usually recommended. As time passed the element of magic disappeared and better carburizing compounds were discovered, such as ground bone, leather and charcoal.

The method of pack carburizing was universally used until early in the 20th century when research performed by Giolitti (2) did much to bring about the development of furnaces using a gas to supply the carbon to the iron. Commercial development began in the United States in 1906, when the first gas carburizing furnaces were put into service (Wyzalek and Folkner, 18). These furnaces were of the rotary batch type, using city gas as the carburizing agent. In 1913 continuous carburizing was brought about by the use of a spiral ribbed retort which automatically moved the work to the discharge end of the furnace. Until about 1920, the processes used always formed a hard dense layer of carbon on the surface of the work, thereby

effectively stopping the carburizing action. This layer was continuously broken off by the tumbling action of the rotary furnace.

In this same period of time much work was done by private companies in an effort to adapt gas carburizing to a particular problem such as the tests run by the Timken Roller Bearing Company on roller bearing parts. In 1913, shortly after Giolitti's investigations became available, a furnace was constructed containing a retort three feet in diameter by twelve feet high. This retort was built of firebrick joined with fire clay and heated by natural gas. The atmosphere was natural gas, carbon monoxide and methane. It was reported (2) that a new retort would hold up about two or three hours before the fire clay would begin to fall out, allowing leakage of gas. Different retorts were tried, including tongue and groove firebrick, fire clay and Carborundum cylinders. They all failed because of leaks or being too fragile. As a last resort a cast nichrome cylinder was used but failed because of leakage at the joints and through the body. At this point the project was abandoned as a commercial possibility until 1925 when satisfactory retorts were developed.

Shortly after 1930 methods were discovered to carburize without the formation of soot deposits. The intermittent surge method (Cowan, 3) was one system. This consisted of a turbulent gas flow at high speed for a short while, with a longer period of no flow. This was especially suitable for

gases of high carbon content which would normally form excessive deposits of soot. Another method was to dilute the hydrocarbon gas with such agents as steam, charcoal producer gas, nitrogen or air. Considerable difficulty was experienced with both methods because of lack of control of the gases.

Several different gases were studied in an attempt to improve the quality of the work. Raw natural gas was used only in batch type rotaries. In continuous furnaces the natural gas was diluted half and half with flue gas formed by the perfect combustion of natural gas. To prevent decarburization during cooling pure raw gas was introduced. Diluted propane and butane were used to some extent. The gas was mixed with about 8 parts of air and externally heated to a higher temperature than the furnace in order to crack the hydrocarbons without the formation of tar or soot.

Another setup used a mixture of dried partly burned gas, partially cracked natural gas and raw natural gas. It was reported that when it did work the results were very satisfactory, but a laboratory man was required to run it (Gillett, 8).

From that period to the present time most of the development work consisted of exploring the effect of different temperatures, gases and ratios upon various steels.

THEORY

When prepared atmospheres are used in metal treating furnaces they may be divided into four classes (Perrine, 14)

according to the action which they have upon the metal.

- (1) Inert or neutral
- (2) Oxidizing
- (3) Reducing
- (4) Metallurgically active

The first class is so named because no reaction occurs between the metal and the surrounding atmosphere. The simplest protective atmosphere for treating steel is a pure inert gas such as Argon or Helium. These are not practical for use in a commercial furnace, because they lack self-protection against impurities which would react with the steel. Another disadvantage is the high cost of these gases.

The second class of atmospheres contain the gases O_2 , CO_2 or HOH . The amount of gas which can cause oxidation is

O_2	Above 0%
CO_2	Above 5%
HOH	Above 3% or 75° F dew point
(Varies with the amount of H_2 present)	

The use of this type of atmosphere is normally to be avoided.

The reducing type of atmospheres contain a gas which will react with an oxide at elevated temperatures to form the pure metal. Three widely used reducing gases are CO , CH_4 and H_2 . The composition may vary from 8-20 percent for CO , 1-10 percent for CH_4 and 2-100 percent for H_2 . This type of gas is used in such processes as the continuous galvanizing of steel strip and the copper brazing of steel assemblies (Hotchkiss and Webber, 11).

The most widely used atmospheres belong to the fourth class, or those which are metallurgically active. These atmospheres contain gases which add or take away a constituent from the part being treated. The reaction of most importance is that of iron and carbon. In any steel treating operation the possibility of carburization or decarburization is of extreme importance.

Equilibrium relations between iron, carbon and atmospheric gases can be used to choose the proper mixture of gases for a given job. The curves shown in graph 1 of Plate I show the relationship between iron and iron oxide with various ratios of HOH with respect to H_2 and of CO_2 with respect to CO. The equations for these reactions are.



Reaction (b) is very important because the water vapor content of an atmosphere gives a very close indication of the carburizing potential of the atmosphere (Groves, 9). The higher the dew point, the lower the potential to carburize. This principle is widely used in industry to determine the proper gas ratios to be used in a furnace and in the automatic control of those ratios.

The area above the solid line is in the oxidizing range and below is in the reducing range. The area above the dotted line is reducing, below is oxidizing. All four of these gases will be present in the products of a partially combusted hydrocarbon gas, and the amount of each gas will determine

whether a steel will be oxidized (colored) or reduced at a given temperature.

If an atmosphere contained four percent CO_2 and 10 percent CO along with hydrogen and water vapor, the CO_2 / CO ratio would be 0.4. This mixture is strongly reducing due to the CO at 1600°F and more so at lower temperatures.

For the reaction between iron and carbon monoxide the theoretical equation is



This shows that a certain ratio must exist between CO_2 and CO. The ratio depends not only upon the temperature but on the carbon content of the steel. As shown in the curves in graph 2 on Plate I, a given ratio of CO_2 / CO is necessary to carburize or be neutral to steel at any given temperature. If the temperature were to be changed, the equilibrium would change accordingly.

Among the most active of the carburizing gases is methane. The reaction with iron is



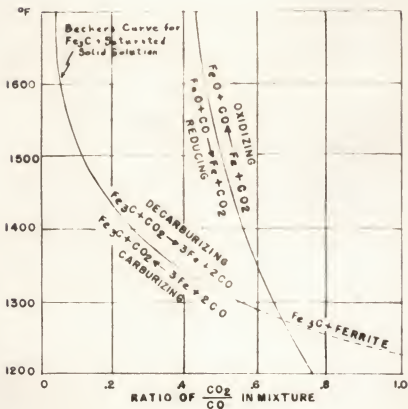
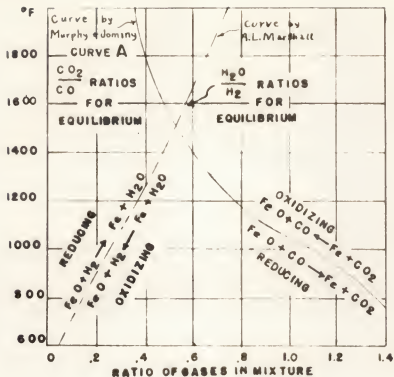
In Plate II the curve shows how the carbon-steel equilibrium point changes with the temperature and CH_4 / H_2 ratio. This reaction also varies with the carbon content of the steel. If the gas ratio and temperature give a point on the right of the curve for a given steel, the steel will be carburized. Hydrogen added to the mixture will tend toward decarburization, but the higher the temperatures, the more hydrogen is required,

Explanation of Plate I

No. 1 Equilibrium curves for iron with various CO_2 / CO and $\text{H}_2\text{O} / \text{H}_2$ ratios.

No. 2 Equilibrium curves showing how the CO_2 / CO ratios affect the carbon content and oxidation of iron.

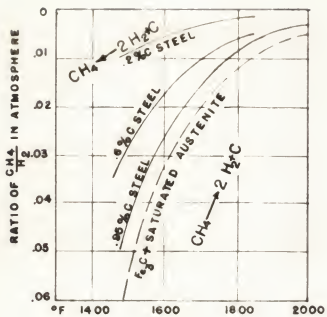
Plate I



Explanation of Plate II

Equilibrium curves showing the effect of temperature and CH_4 / H_2 ratio on the carbon content of steel.

Plate II



therefore, a small amount of methane would cause a shift toward carburization.

While the curves and chemical equations shown are quite accurate when taken alone, it is very difficult to calculate the curves when more gases are present (Gier, 5). An easier method is to run tests on the individual furnace and atmosphere using the steels and temperatures which will be used in actual practice.

As noted above, methane is a good carburizing gas, but it cannot be introduced into a heat treating furnace alone because of the layer of soot which is deposited on the work according to equation (d). The methane may be diluted with other gases in order to eliminate the sooting but the diluent must be carefully chosen. Air is not completely satisfactory because of the CO_2 and HOH formed. Unless balanced by sufficient H_2 , the HOH is extremely oxidizing and decarburizing. It is the most troublesome impurity in most atmospheres (Gillett, 6).

Nitrogen would seem to be suitable with but one exception. Unpurified tank nitrogen contains enough water vapor and oxygen to unbalance the carburizing reaction.

An early method (Wyzałek and Folkner, 18) used to provide a carburizing atmosphere without the bad effects just mentioned, was a gas generator in which city gas was passed over hot charcoal or peat moss. While a satisfactory atmosphere could be produced by this method, it was more expensive to prepare, and the generator required close control, lest the gas ratios

change and ruin a batch of parts. In time the charcoal in the generators was replaced with a catalyst and better controls were devised to hold the proper ratios.

The more important variables in the production of an atmosphere are the temperature, gas ratios, total flow and the particular fuel gas used. As an example of the accuracy required in the gas ratios, for an atmosphere neutral to a 1.15 percent carbon steel at 1700^o F an error of 0.1 percent in the percentage of CO₂ would change the atmosphere to be neutral to a 0.6 percent carbon steel. Therefore, an ordinary Orstat apparatus could not be used. Although the HOH / H₂ ratio is as important as the CO₂ / Co ratio, the water vapor may be measured quite accurately by means other than the Orstat. The dew point of a gas may be determined by several methods to an accuracy of one or two degrees with comparatively inexpensive instruments (Koebel, 12).

EQUIPMENT AND PROCEDURE

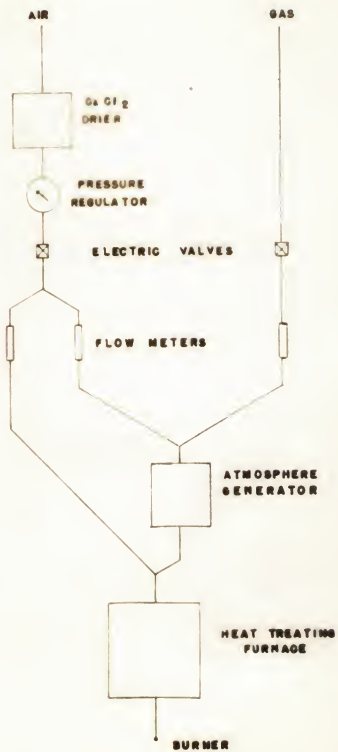
The equipment used in this investigation consisted primarily of a heated combustion tube or generator, in which to burn the air and gas, a heat treating furnace, and the necessary controls and instruments. Both generator and furnace were electrically heated. A flow chart of the set up is shown on Plate III, and a photograph of the equipment is shown on Plate IV.

The air used was dried to a dew point of -10^o F over calcium chloride and the pressure held at five psi with a

Explanation of Plate III

Flow chart of carburizing equipment.

Plate III

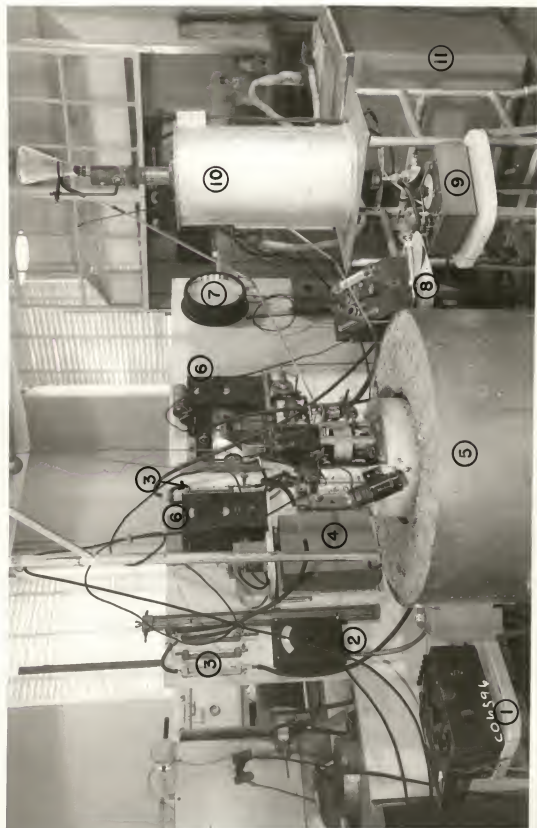


Explanation of Plate IV

Photograph of Research Equipment

- (1) Thwing Potentiometer
- (2) Furnace Rheotrol
- (3) Flowmeters
- (4) Time clock and control panel
- (5) Heat treating furnace
- (6) Foxboro temperature controllers
- (7) Foxboro Dewcel recorder
- (8) Alnor Dew Pointer
- (9) Wheatstone Bridge
- (10) Atmosphere generator
- (11) Refrigeration unit

Plate IV



pressure reducing regulator. The natural gas was used directly from the line and was supplied by the Kansas Power and Light Company. According to the Company, the analysis of the gas was

CH ₄	81.18%
C ₂ H ₆	10.98%
CO ₂	00.04%
O ₂	00.28%
Residue.	7.52%

The dew point of the gas was approximately -50° F.

The generator combustion tube shown in Plate V, was constructed of 0.062 inch thick Inconel sheet formed into a 2.5 inch diameter tube 30 inches long and the seam gas welded. Threaded sections of two inch iron pipe six inches long were brazed to each end to accept pipe caps in which the gas and thermocouple pipes were welded. This tube was surrounded by chromel heating elements and insulated with about five inches of Sil-O-Cel insulation made by the Johns-Manville Company of New York. The insulation was held in place by a sheet metal cylinder.

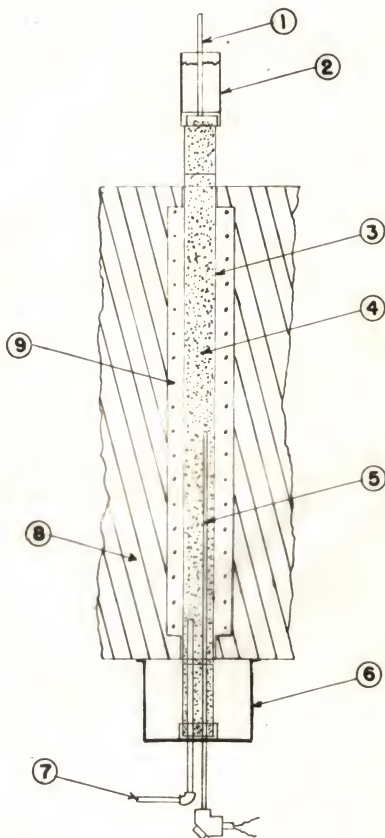
In order to get a more complete reaction between the air and gas, the generator tube was filled with ground charcoal which had been screened to remove all particles below 1/8 inch and above 1/4 inch across. It was found that the charcoal would absorb so much water from the air that it would take two to three hours after each charcoal addition to dry the atmosphere sufficiently to use in the furnace. In order to reduce

Explanation of Plate V

Diagram of Atmosphere Generator

- (1) Outlet tube
- (2) Water cup
- (3) Combustion tube
- (4) Granulated charcoal
- (5) Thermocouple tube
- (6) Combustion tube support
- (7) Inlet tube
- (8) Insulation
- (9) Heating elements

Plate V



this time the charcoal was preheated to 1400° F for about eight hours, then allowed to cool in a closed container. The charcoal was removed from this container as needed. The generator was recharged with charcoal every two to three days. The cup of water was placed on top of the tube for two reasons, primarily to quench the gases as they left the furnace. A rapid quench at this point helped prevent changes in the gas composition (Gier, 5). The water also helps keep the exit tube cool enough to avoid burning the rubber hose leading to the furnace.

The furnace retort as shown in Plate VI was also constructed of 0.062 inch thick Inconel sheet. The dimensions are 11 inches in diameter by 21 inches deep. The lip around the upper edge held very fine sand for the purpose of providing a gas tight seal while still allowing easy removal and replacement of the lid. A 3600 RPM motor was mounted on the lid to drive a fan which was necessary to agitate the gases within the furnace (Ponte, 16). A fan was also put on the shaft above the lid to help cool the shaft bearings.

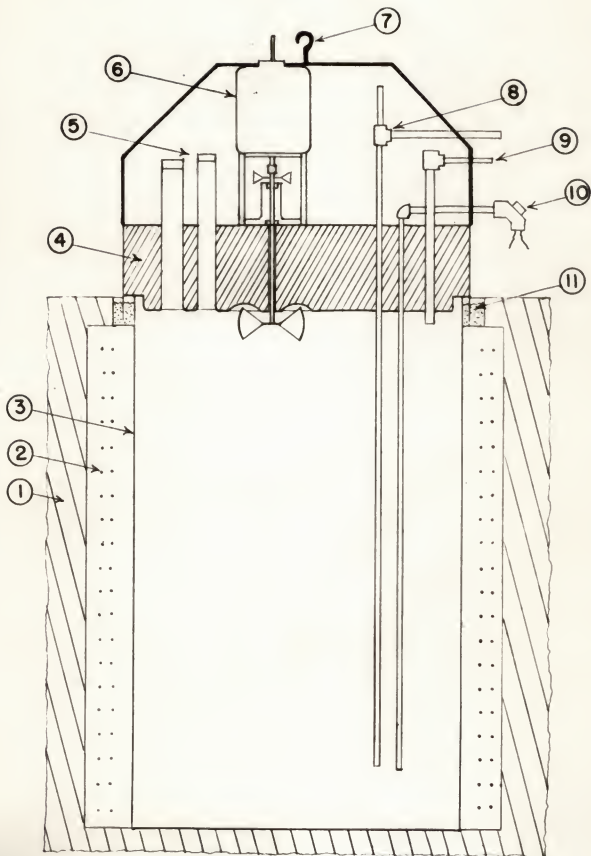
The large openings in the lid allow smaller samples to be inserted into and removed from the furnace without raising the lid. Two 1/4-inch pipes through the lid serve as inlet and outlet for the gases. A third pipe contained the thermocouple. Both thermocouple and inlet tubes were made of Inconel. The furnace retort was heated by chromel resistance elements surrounded by six inches of Sil-O-Cel insulation.

Explanation of Plate VI

Diagram of heat treating furnace.

- (1) Insulation
- (2) Heating elements
- (3) Retort
- (4) Lid insulation
- (5) Tubes for placing samples in furnace
- (6) Fan motor
- (7) Hook for lifting lid
- (8) Inlet tube
- (9) Outlet tube
- (10) Thermocouple tube
- (11) Sand seal

Plate VI



The temperature of the generator and furnace was controlled by Foxboro controllers made by the Foxboro Company of Foxboro, Massachusetts.

In order to bring the generator and furnace up to temperature as rapidly as possible, a rather high current input was used. After the operating temperature was reached, this high input caused considerable over and under shooting of the nominal temperature. To avoid this, a Rheotrol model 624 (Wheelco Instrument Company, Chicago) was placed in the furnace control circuit, and the Foxboro unit controlling the generator was modified to provide a controllable current interruptor similar to the Rheotrol. To bring the furnaces up to temperature the controls were set at 100 percent on and reduced to about 50 percent on to hold at operating temperature.

A Thwing Potentiometer made by the Thwing Albert Instrument Company of Philadelphia, was used to check the accuracy of the two Foxboro controllers.

Because it was desirable to have the furnace at operating temperature by 8 o'clock in the morning, a time clock was installed which would turn the equipment on early enough to have it at temperature at 8:00 a.m. The clock also was set to turn everything off at the close of the day.

In addition to the relays for the heating elements a third relay was used to prevent the air and gas electric valves from opening until the generator and furnace had time to come to temperature. This was done to avert any possible chance of an explosion occurring if an explosive mixture of air

and gas accumulated in either the generator or furnace while their temperature was below 1400° F. Above 1400° F there is no danger of an explosion (Smith, 17).

A diagram of the automatic control circuit is shown on Plate VII.

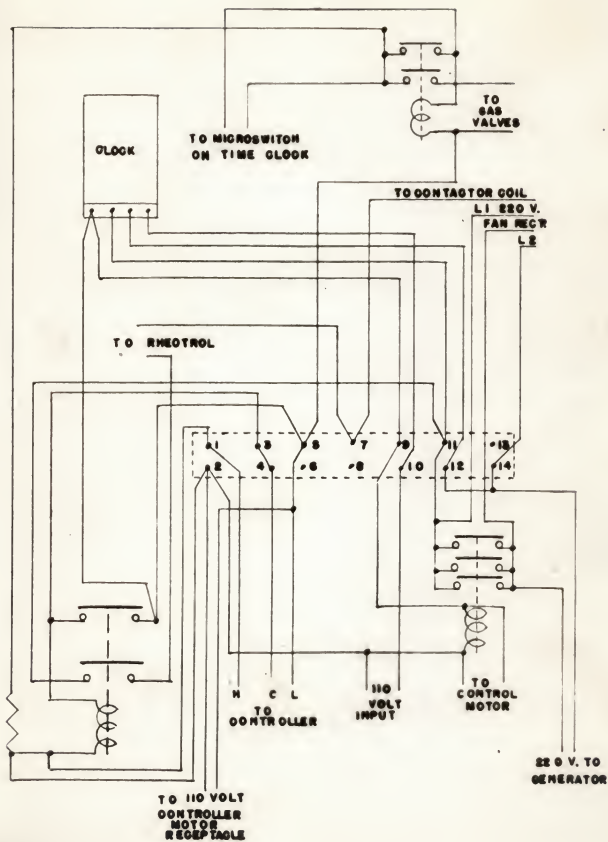
Two instruments were used to measure the dew point of the gas in the furnace. The first, a Foxboro Dewcel gave a continuous recording of the dew point. The principle of this recorder is the change of electrical conductivity of a salt as the moisture content varies. The temperature of the sensing unit or Dewcel had to be kept within a certain range for a given dew point, therefore, the dew cell container was cooled with ethylene glycol circulated through a refrigeration unit. The second measuring device used was an Alnor Dew Pointer, which formed a fog when a compressed sample of gas was suddenly expanded. The dew point of a gas could be found very rapidly with this instrument. After the chambers were purged, three readings a minute could easily be taken. The Dew Pointer was made by the Illinois Testing Machine Company of Chicago.

A third method was occasionally used as a check on these two instruments. This was a small stainless steel box contained within a clear glass beaker. One side of the box was polished to a mirror finish and an opening in the top was provided to admit ice and water or dry ice and alcohol and a thermometer. In use, the atmosphere was circulated around the box and the temperature at which moisture condensed and evaporated from the

Explanation of Plate VII

Wiring diagram of control panel.

Plate VII



mirror surface was noted. This method always checked the others very closely, but because of the longer time required it was not used regularly.

The carbon content of the test samples was measured in two ways. The first and most accurate method was by weighing a pure iron wire before and after carburization and calculating the percent carbon from the increase in weight. All weights were made with a Chainomatic Analytical Balance made by the Becker Instrument Company of New York.

The other method was with steel blocks of different carbon contents which were polished on the standard laboratory equipment.

In addition to recording the dew point and carbon content of the samples, a third reading was taken--the electrical resistance of a short length of pure iron wire carburized in the furnace and quenched. From tests made by the Westinghouse Electric Company, it is known that the resistance increase of a quenched steel sample would give a direct indication of the amount of carbon present. In order to measure this small resistance change a wheatstone bridge was constructed using a pure iron slide wire, balanced by the wire to be tested. The bridge was set up with three contact points to hold the wire to be measured. Point one and three were 20 cm. apart and were used to measure wire having a resistance from one to two and one-half times that of pure iron. Points one and two were 10 cm. apart and were used to measure wire having a resistance of two to five times the uncarburized wire. The scale was read

on the basis of the 10 cm. length. When the 20 cm. length was used for the lower carbon samples the scale reading was divided by two.

When the furnace had been operating for a long enough period of time for the temperature and gas composition to come to equilibrium (usually about four to five hours from the time it was turned on) as indicated by the Dewcel recording, three samples were put into the furnace. First, the wire used for the weight determination; second, three small steel blocks; and third, a wire used for the resistance measurement. The samples were prepared in the following manner. To get reasonable accuracy in the weighings of the weight wire without using an excessive amount of wire, approximately 0.35 grams of wire was used. This represented about three feet of the 0.009 inch diameter wire. The wire was measured out on a measuring stick and wrapped around three of the operators fingers to form a coil which could be easily handled. In the early part of the experiments this coil was washed in carbon tetrachloride until it was discovered that moisture was not completely removed. The next solvent tried was dioxane. This chemical cleaned the wire satisfactorily, but because of the low volatility, a much longer time was required to dry the wire. Finally ethyl alcohol was tried and successfully used in the rest of the tests. In order to insure complete washing of the sample it was placed in a four ounce bottle half filled with alcohol and the bottle rapidly shaken for a few seconds. The sample was then removed

with a pair of tweezers and dried in the warm air from the fan on the furnace. The weight of the wire was found to the nearest 0.1 milligram and the coil suspended in the center of the furnace with a short length of alumel wire. Alumel was used because it would not become embrittled by carburization of the effect of H_2 or CO (Hotchkiss and Webber, 11). The wire was left in the furnace for about 20 minutes to allow time for full carburization to the center of the wire (13). At the end of this time the wire was pulled up into the tube to cool in the furnace atmosphere, removed and weighed.

The three blocks used were 1/2 inch diameter rod cut about 3/4 inch long. For this series of runs, steels of five different contents were selected. They were 0.18, 0.45, 0.73, 1.01, 1.30 percent carbon. After the carbon content was determined by chemical analysis the blocks were stamped with a number to indicate the composition. The 0.18 samples were all marked number 1, the 0.43 number 2, up to 5 for the 1.30 percent carbon blocks. The samples were kept in a dessicator to prevent rusting until use.

If it were known from previous experience that the atmosphere would be neutral to about a 0.8 percent carbon steel, the 0.43, 0.73 and 1.01 percent carbon blocks would be placed in the furnace for a period of one hour. After a slow cool to obtain coarse pearlite formation, the blocks were removed and a serial number stamped on each one. The first step in the polishing procedure was to cut about 1/8 inch from one end to

get to the base metal. The samples were then mounted in a ring shaped holder and held in place with a set screw. By polishing the blocks in this holder, the edges were not rounded off enough to obscure the case detail. The samples were polished in the usual manner, being finished with number 600 grit on a felt wheel. After polishing the samples were removed from the holders and etched in four percent Nital and examined under a microscope. Because of the thin case it was difficult to estimate the carbon of any one sample, but by comparing the three blocks the carburizing potential of the atmosphere could be determined quite accurately. Plate VIII shows photographs of three different steels treated in the same atmosphere, exhibiting the effect of an atmosphere neutral to a medium carbon steel on low and high carbon steels.

The wire used for the resistance measurement was the same size as that used for the weight determination. A piece was cut off long enough to reach the bottom of the furnace retort. It was put in and removed from the furnace at the same time as the weight wire. The wire was quenched by rapidly pulling it into the air and waving it around for a few seconds. It was found the wire would quench properly in this manner after trials in which it was pulled through wet cotton. The opening in the lid through which the wire was placed in the furnace was a piece of 1/2 inch pipe. At first the wire was weighted with a paper clip or a cotter key. But it was found occasionally the weight would catch on the bottom edge of the pipe as the wire was pulled out. When this happened the wire either broke

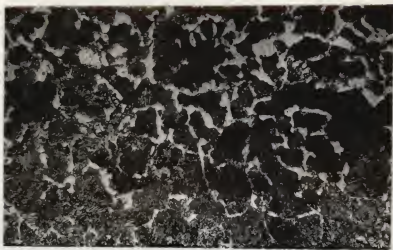
Explanation of Plate VIII

Fig. 1 0.43% carbon steel showing carburized case after being treated in an atmosphere neutral to 0.73% carbon steel. 500x

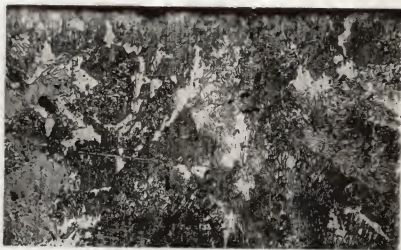
Fig. 2 0.73% carbon steel showing no change after being treated in a neutral atmosphere. 500x

Fig. 3 1.01% carbon steel showing decarburized case after being treated in an atmosphere neutral to 0.73% carbon steel. 500x

Plate VIII



No. 1



No. 2



No. 3

or stretched to such a point that the resistance was not accurate. The only satisfactory way to prevent this was to straighten the wire and bend a loop on one end to keep the wire from catching on the inside of the pipe as it was inserted into the furnace. This procedure worked very well and no further trouble was experienced with the resistance determinations.

The observations and measurements taken for each run are shown as follows:

Resistance ratio
Weight percentage of carbon
Block percentage of carbon
Serial number of the blocks
Date
Furnace temperature
Amount of additional air added
to the furnace
Alnor dew point
Dewcel dew points

As the tests were run the points were plotted on two graphs, dew point vs. carbon, and carbon vs. resistance ratio. When enough points had been found at one temperature to allow a curve to be drawn the temperature was changed and another series of tests begun.

The furnace temperatures used were 1500° F, 1600° F and 1700° F. Lower temperatures were not used because of the slow diffusion rate of carbon (13) and higher temperatures could

not be used because of limitations of the furnace heating coils.

The generator was operated at a constant 1700° F after tests indicated the lower temperatures caused erratic gas composition. The air-gas ratio into the generator was two and the total gas flow was held at 4500 cc per minute. Tests with the generator alone indicated moderate changes in the air-gas ratio and total flow had little effect on the dew point of the gas coming out. But experience with the furnace has shown that the dew point of the gas in the furnace rises rapidly with an increase in the generator air-gas ratio. This is believed to be due to the extra amount of methane in the gas. Time did not allow a more detailed study of that variable.

An analysis of the gases produced by the generator compared with an analysis from a catalytic generator (Perrine, 14) is as follows:

	Charcoal	Catalyst
CH ₄	8%	0.9%
H ₂	28.7%	39.6%
CO	21.2%	20.3%
O ₂	00.0%	00.0%
CO ₂	00.0%	00.0%
Balance N ₂		

These are the average values taken with a generator temperature of 1700° F and air-gas ratio of two. The analyses were made

with a Burrell gas analysis apparatus produced by the Burrell Technical Supply Company, Pittsburgh, Pennsylvania.

The experiments were interrupted several times during the course of the research because of failure of the equipment. The most common failure was the furnace elements burning out. This occurred three times. Each time a new section of chromel wire was gas welded to the burned ends and the work resumed. The Inconel generator tube was replaced once, when the old tube was broken in an attempt to straighten it, after the repeated heating and cooling cycles had caused a rather severe bend.

At a point about midway through the experiments one of the six blades of the furnace fan broke off. As an emergency repair the opposite blade was removed and the fan used in this manner for about a month. In this same period some difficulty was encountered due to sections of the insulation in the furnace lid falling out. The cooling effect that this caused, together with the inefficient fan, was later believed to have been the cause of poor results obtained at this time. After new insulation was cast in the lid, and the fan replaced, the furnace temperature was much more uniform.

The ball bearings on the fan shaft were replaced two times in the course of the work. The first set lasted about 3000 hours, but the second set, installed just prior to the repairs of the lid, failed in less than 200 hours. It is believed some grit from the refractory cement seeped into one of the bearings, although measures were taken to prevent that. The

third set is still operating quietly after approximately 1000 hours.

During the early experimental runs rubber burner hose was used to carry the gas between the flowmeters, generator and furnace. Later it was found that the rubber would absorb moisture from a high dew point gas and slowly release it to a dryer gas, causing serious errors in the dew point readings. To reduce this error, glass tubing was used to carry the atmosphere gas. The glass tube was cut into 24 inch lengths and connected with short lengths of rubber hose, allowing enough flexibility that no breakage occurred. This arrangement proved to be very satisfactory.

It was only after making the above mentioned changes and much refinement of technique that it was possible to duplicate the results in this problem.

DISCUSSION OF RESULTS

The graphs of the results of this investigation are shown on Plates IX and X.

Plate IX shows the plot of furnace dew point vs. the carburizing potential of the atmosphere. As the graph shows, the temperature of the furnace had little if any effect upon the carbon content of a steel at a given dew point. This is in contrast to the results obtained from a furnace using an atmosphere formed over a catalyst rather than charcoal. The curve shown, representing the temperatures 1500° F, 1600° F and 1700° F, coincides nearly exactly with the published

(Perrine, 15) curves found at 1700° F. A furnace operating at 1500° F with a catalytic generator has a carbon potential of about 1 percent at 45° F dew point, while at 1700° F both generator types give a potential of approximately 0.3 percent carbon.

The reason for this discrepancy is believed to be the methane produced by the charcoal filled generator since the methane content is the only major difference between this gas and a catalytically formed gas. It is believed the 7 percent or 8 percent excess methane reacts in the furnace, with the final composition depending upon the temperature, therefore, at 1700° F the methane is reduced to below 1 percent, or the same amount as formed with a catalyst. A continuation of this problem would be to determine the carburizing potential with furnace temperatures higher than 1700° F, and to repeat the original runs with a catalytic rather than charcoal generator.

The graph of carbon percentage vs. resistance ratio is shown on Plate X. With the use of a very inexpensive bridge circuit the carburizing potential of an atmosphere may be found directly without determining the gas composition or dew point. This has a definite advantage because a change in the atmosphere, such as an increase in methane, may not greatly change the dew point but would affect the carburizing potential. The difference between the curve on Plate IX and the published literature is an example of this.

In drawing the curves the carbon percentage used was that found by the weight method, with the blocks used only as a check. The dew point used was that of the Alnor Dew Pointer rather than the Dewcel. It may be noted the latter gave readings approximately 8° - 12° F higher than the Dew Pointer. This difference was believed to be due to maladjustment of the recorder, since the error was consistent over the entire range used.

CONCLUSIONS

- (1) A satisfactory case, controllable from 0-1.2 percent carbon, may be formed on steel, using an atmosphere prepared in a charcoal generator.
- (2) The air-gas ratio into the generator is not critical as compared to a catalytic unit.
- (3) Natural gas available in Kansas is a suitable carburizing agent.
- (4) A tenacious layer of soot was not formed on the samples.
- (5) If the charcoal level falls below a certain level for a given gas flow, the dew point will rise.
- (6) A change in furnace temperature within the range of 1500° F to 1700° F will not change the carburizing potential of the atmosphere.
- (7) The gases in the furnace retort must be rapidly agitated to obtain good results.

(8) The furnace retort must be well insulated to avoid cold spots.

(9) The increase in resistance of a quenched steel sample may be used to determine the carbon content of the sample.

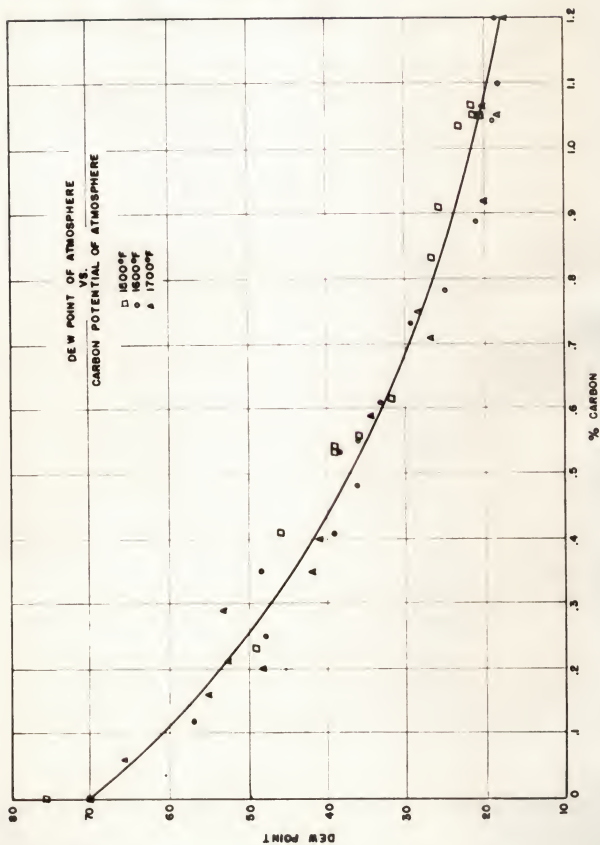
Table 1. Tabulation of results.

Date	F : Temp. :	% C : Wt. :	% C : Blocks :	Res : 10 cm :	Air : cc/min :	DP : Alnor :	DP : Foxboro :	Remarks
9-2	1500	0.0	---	10	1370	76	--	4F2
9-7	"	0.23	---	10.2	--	49	--	
9-30	"	0.83	---	0.2	0	27	34	
10-4	"	0.0	---	10	650	70	70	
10-5	"	0.54	---	17	275	39	45	
10-6	"	0.62	---	20	175	32	43	
10-6	"	0.91	---	33	0	26	35	
10-6	"	0.56	---	20	300	36	44	
10-6	"	0.41	---	15.5	400	46	53	
10-11	"	0.53	---	18	400	39	47	
10-11	"	1.07	---	33	0	22	32	
10-11	"	1.05	---	31	0	21	32	
11-18	"	1.05	---	36	400	22	--	
11-18	"	1.03	---	37.5	400	23	--	
8-19	1600	--	0.55	17.5	425	36	40	7D8
8-19	"	0.35	---	13.5	780	48	60	7D9
8-31	"	0.48	---	18	780	36	--	
10-12	"	1.2	---	36	0	18	25	
10-13	"	1.1	---	36	0	18	27	
10-13	"	1.2	---	37.5	0	18	27	
11-21	"	1.04	---	32	0	19	29	
11-21	"	0.89	---	29	1000	21	35	
11-22	"	0.78	---	23	600	25	32	
11-22	"	0.73	---	25	1000	29	37	
11-23	"	0.06	---	10	1060	66	72	
11-29	"	0.61	---	23	500	33	45	
11-29	"	0.53	---	18	850	38	50	
11-29	"	0.41	---	15	850	39	52	
11-29	"	0.25	---	12.5	950	50	60	
11-29	"	0.12	---	11.5	1000	57	70	
11-29	"	0.0	---	10	1000	70	80	
8-26	1700	0.2	0.2	12	800	48	--	8E6
8-30	"	0.92	0.83	30	910	20	30	8E8
8-31	"	1.07	---	34.5	--	20	17	
11-7	"	0.71	---	21	0	27	35	
11-7	"	0.35	---	15	0	42	--	
11-9	"	0.21	---	12	500	55	--	
11-9	"	0.16	---	12.5	500	55	63	
11-9	"	0.29	---	12.5	400	53	57	
11-30	"	1.2	---	38	0	20	--	
11-30	"	1.05	---	33	350	21	31	
11-30	"	0.75	---	28	625	28	32	
11-30	"	0.59	---	21.5	800	34	39	
11-30	"	0.4	---	15.5	1000	41	48	
11-30	"	0.06	---	11	1400	66	78	

Explanation of Plate IX

The Dew Point of atmosphere vs. the carburizing potential of atmosphere at temperatures of 1500° F, 1600° F and 1700° F.

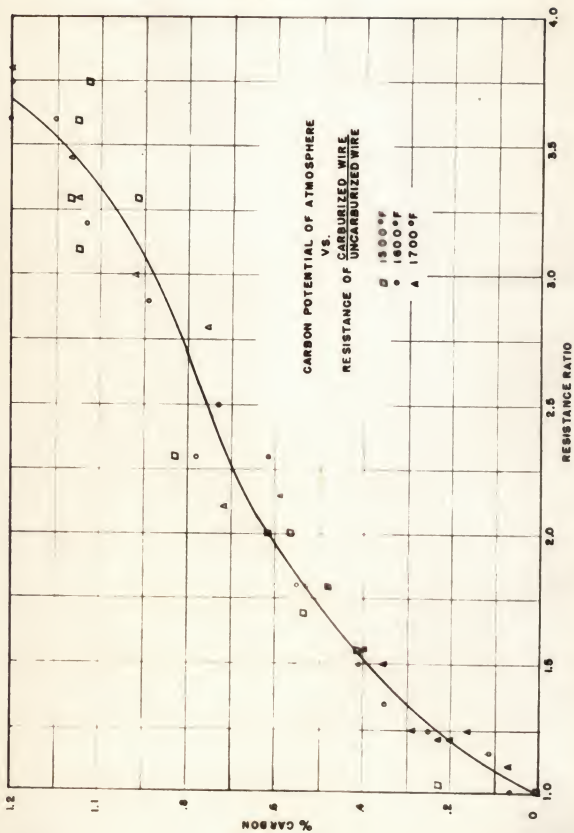
Plate IX



Explanation of Plate X

The carburizing potential of atmosphere vs.
resistance of carburized wire at temperatures
uncarburized wire
of 1500° F, 1600° F, and 1700° F.

Plate X



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EQUILIBRIUM RELATIONS BETWEEN CARBON STEEL
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by

TENNYSON IRL COLLINS

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AN ABSTRACT OF A THESIS

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An investigation was made to determine the equilibrium relations between iron and carbon in a prepared atmosphere. The atmosphere used was formed by passing air and natural gas over hot charcoal in the generator combustion tube. Tests were made with furnace temperatures of 1500° F, 1600° F and 1700° F, and furnace dew points ranging from 18° F to 75° F. The air-gas ratio, total gas flow and generator temperature were held constant. The carburizing potential of the atmosphere, or the highest percentage of carbon which a steel will attain in the atmosphere, was measured by the increase in weight of a pure iron wire after carburization in the atmosphere. This method was checked by exposing steels of known carbon content to the atmosphere and examining the polished section under a microscope to determine the amount of carburization or decarburization.

In addition to finding the equilibrium data, tests were made to determine the effect of carbon content on the electrical resistance of a carburized iron wire. This was done by rapidly quenching an iron wire carburized in the furnace and measuring the resistance increase with a wheatstone bridge.

The results of this investigation were plotted in two graphs, one showing the dew point of the atmosphere vs. carburizing potential of the atmosphere. The other graph shows the carburizing potential of the atmosphere vs. the ratio of resistance of the carburized wire as compared to the uncarburized wire.