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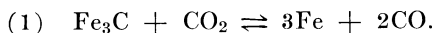
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## REPRESENTATION OF EQUILIBRIUM CONDITIONS FOR THE CARBON MONOXIDE—CARBON DIOXIDE —STEEL SYSTEM.

H. A. WILHELM AND C F GRAY

Proper conditioning of atmospheres for carburizing, for heat treating, and for carrying out other high temperature metallurgical processes depends in general on control of each system with regard to its equilibrium conditions. In connection with steel processing, numerous investigations have been made to determine equilibrium conditions for the most common gas-steel reactions. One such reaction that has been studied extensively takes place when certain mixtures of carbon monoxide and carbon dioxide come in contact with ordinary carbon steel at elevated temperatures. The purpose of this paper is to review some of the methods that have been used to represent equilibrium for this gas-steel reaction and to present a condensed but more comprehensive treatment of equilibrium for the system.

Although differences of opinion exist regarding the actual state of combination of the carbon in steel and regarding the mechanism of the chemical process involved, the equation which is generally used to represent the reaction under consideration is



Here the carbon in the solid state is assumed to be combined with iron and exists as such in solid solution throughout the austenite range of the iron-carbon phase diagram. Whether we do or do not accept this equation as proper representation of the mechanism, the number of variables for the system corresponds to this equation and it will therefore be used in the discussion of the treatment of results of studies on this equilibrium.

An analysis of equation (1) shows that equilibrium depends on a number of factors. In general, temperature change has a very definite influence on chemical equilibrium except in the special case where the heat of reaction over the temperature range is zero or nearly so. Available data show that we are not dealing with such a special case here so temperature must be definitely considered in any treatment of the carbon monoxide-carbon dioxide-steel system. In accordance with the principles of Le Chatelier a change in the total ( $\text{CO} + \text{CO}_2$ ) gas pressure will tend to drive the reaction one way or the other depending upon the change. The

partial pressures of the gases and the composition of the gas phase are related to the total pressure and tend to vary with it to maintain equilibrium. Furthermore, it has been shown experimentally that when only one solid phase (austenite) exists, the composition of the gas phase in equilibrium with a steel depends also on the carbon content of the solid phase and vice versa even though constant temperature and constant total pressure are maintained. Complete representation of equilibrium conditions for the system involving only the one solid phase requires then specification of the four variables, total pressure of the reactive gases, composition of these gases, composition of the solid phase (or the equivalents of these three) and temperature. More specifically the equilibrium constant in terms of activities gives for equation (1) the relation

$$(2)$$

$$K = \frac{A_{Fe}^3 A_{CO}^2}{A_{Fe_3c} A_{CO_2}}$$

For the two phase system, it is evident that specification of all four of the above variables is necessary in order to fix these activities and define the equilibrium.

Investigators have graphically represented the relation between the variables of this system in a number of ways. In practically all cases, however, at least one of the variables is held constant and the graphs, usually consisting of a number of lines, relate the other three variables. Grossmann (1938) has used the data reported by Bramley and Lord (1932) to construct the isotherms of Fig. 1. As an example of the interpretation of these curves, the gas in equilibrium with a steel containing 0.5% carbon at 900°C is approximately 4.5% CO<sub>2</sub> and 95.5% CO when the total (CO<sub>2</sub>+CO) pressure is one atmosphere. In their article, referred to above, Bramley and Lord reported results of work for eight different total pressures ranging from one-fourth of an atmosphere to two atmospheres. Figure 1 is for a total pressure of one atmosphere only. To represent their data completely by this form of graph would require seven more figures constructed on the same plan as Figure 1, each one being for a different value of the total pressure.

Takahashi (1926) represented his data on this system by a series of isotherms similar to Fig. 1. By his method, represented in Fig. 2, allowance is made for changes in the number of solid phases at the boundaries of the austenite area of the iron-carbon

phase diagram. Here again only one total pressure, one atmosphere, is represented and a series of such figures would be required to represent equilibrium conditions for a series of total pressures.

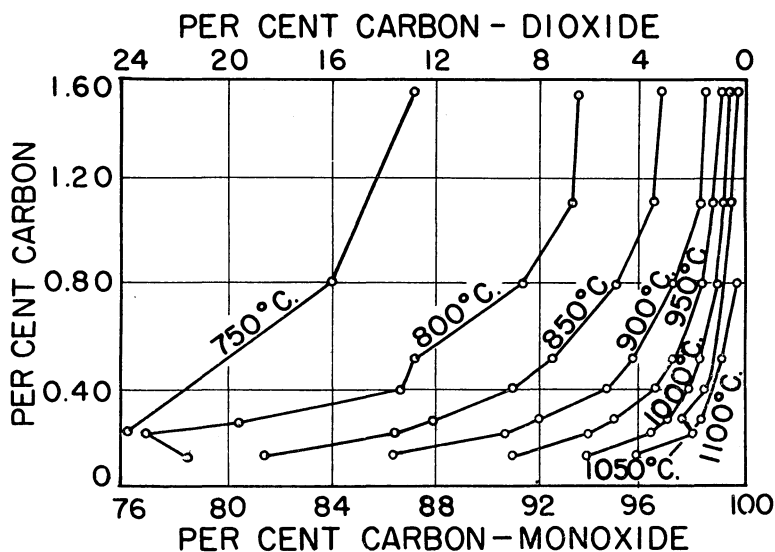


Fig. 1. Isotherms showing equilibria between various CO-CO<sub>2</sub> mixtures and iron with various carbon contents at a series of temperatures. (After Bramley and Lord.)

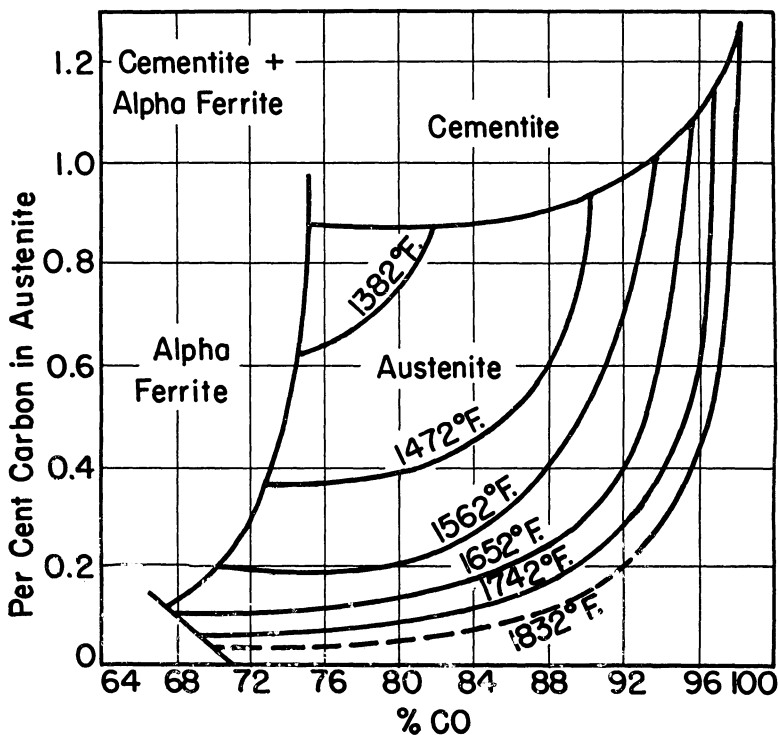


Fig. 2. Takahashi's isotherms for varying percentage of carbon monoxide and carbon dioxide in equilibrium with varying percentage of carbon in austenite.

Fig. 3 represents Takahashi's data (1926) in another manner. In this case the lines are for constant composition of the gas phase at the total pressure of one atmosphere. This method is also limited to a single total pressure per figure.

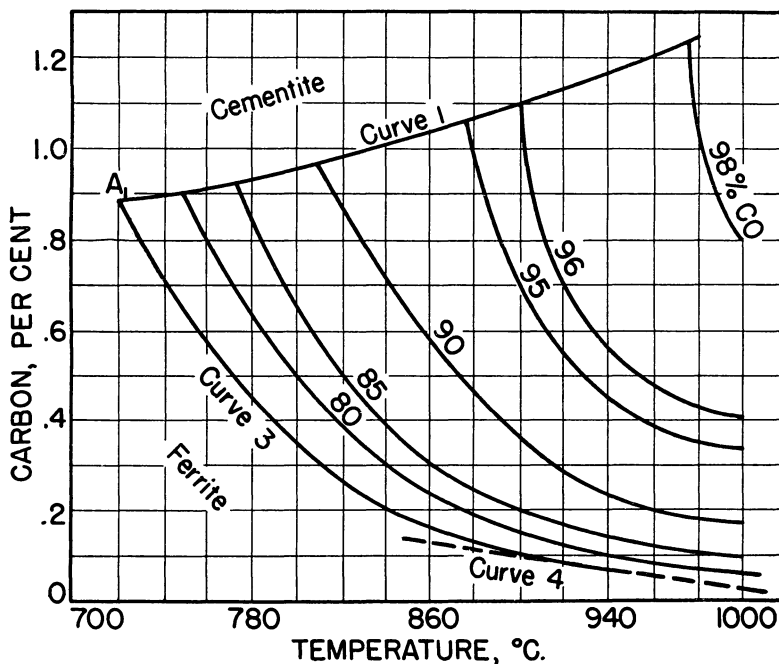


Fig. 3. Lines of constant gas composition in equilibrium with austenite (Takahashi).

Schenck (1926) has represented equilibrium in the CO-CO<sub>2</sub> Steel system at a total pressure of one atmosphere by the curves for constant composition of the austenite phase shown in Fig. 4. Johansson and von Seth (1926) have represented the equilibrium at a CO+CO<sub>2</sub> pressure of 0.4 atmosphere in a similar manner as shown in Fig. 5. This pressure of .4 atmosphere represents closely the pressure of CO+CO<sub>2</sub> that would be formed in air by reacting with an excess of carbon. Neither of these systems of curves represents the system sufficiently for general treatment.

Austin and Day (1940) have calculated values of the equilibrium constant ( $K'$ ) for the reaction under consideration using the data of Becker (1930). Their graphical representation of these values of  $K'$  on a logarithmic scale against temperature on a linear scale is shown in Fig. 6.  $K'$  here is taken as equal to  $p_{CO}^2 / p_{CO_2}$  which represents, referring to relation (2) above, only a part of the true equilibrium constant for the reaction. The activities of the iron and cementite are only indirectly taken into

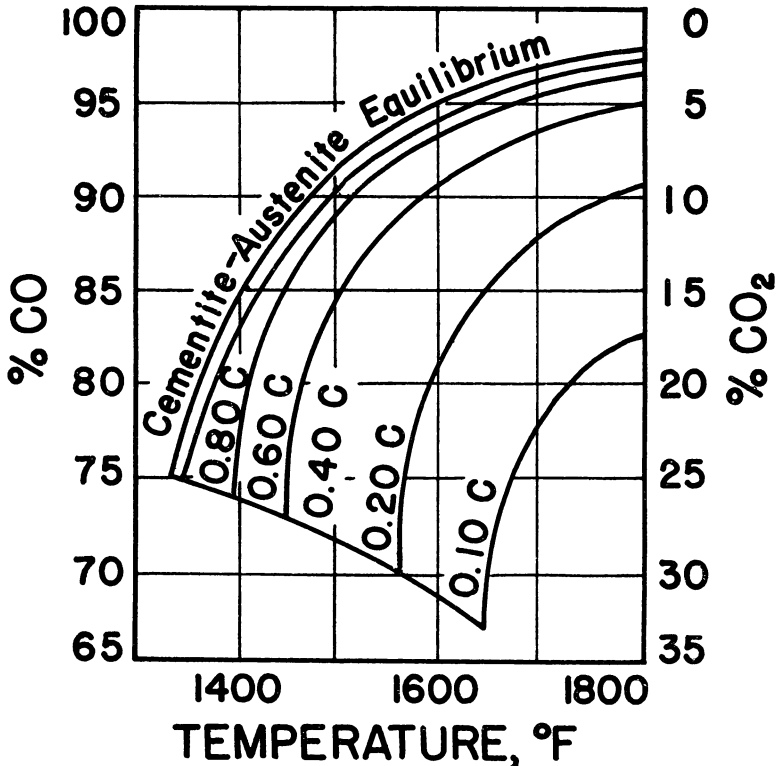


Fig. 4. Schenck's curves for equilibrium of mixtures of carbon monoxide and carbon dioxide with steels of different carbon content.

account in calculating these equilibrium constants. The curves in the figure represent variations of the values of this equilibrium constant with temperature for a number of carbon concentrations in the solid state. This figure is complete in itself for practical use since any partial pressure values of the reacting gases can be employed in its interpretation. This is a decided advantage over

the other graphical method reported above where only one total pressure applied in each case.

In this report an attempt is made to take into account the activities of the iron and the iron carbide in calculating the true equilibrium constant as given in relation (2). The activities of the carbon monoxide and of the carbon dioxide are adequately repre-

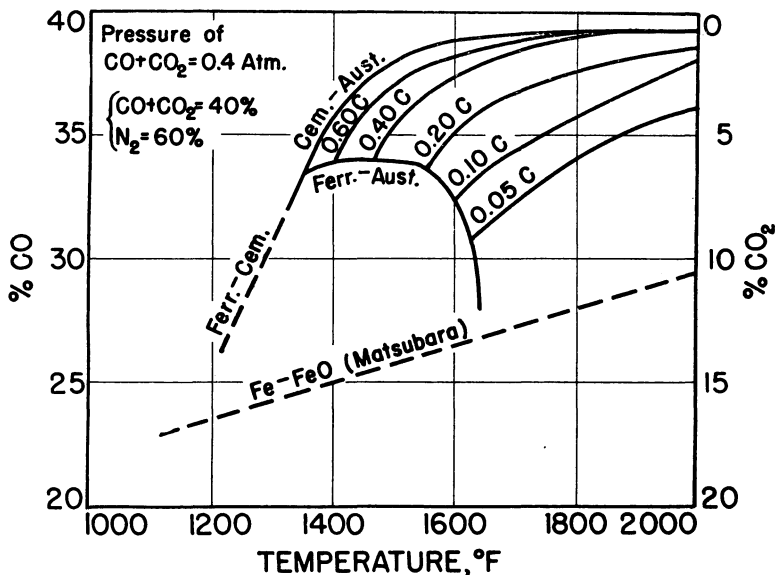


Fig. 5. Johansson-Von Seth curves for equilibrium of mixtures of carbon monoxide and carbon dioxide with steels of different carbon content. These curves were determined experimentally using 60 per cent nitrogen as a dilvent.

sented by their partial pressures in the same manner as used by Austin and Day. The equilibrium constant is then written as

$$(3) \quad K = \frac{A_{Fe}^3}{A_{Fe_3C}} \frac{P_{CO}^2}{P_{CO_2}}$$

Over the temperature range being considered iron carbide is dissolved in gamma iron giving the solid solution austenite. Under these conditions neither the iron nor its carbide can be assumed to have unit activity when only one unsaturated solid phase exists. On the basis of general considerations we can assume that the activity of the iron is equal to, or proportional to, its mol-fraction ( $N_{Fe}$ ) in the solid solution and that the activity of the iron carbide in the solid solution is proportional to its mol-fraction  $N_{Fe_3C}$



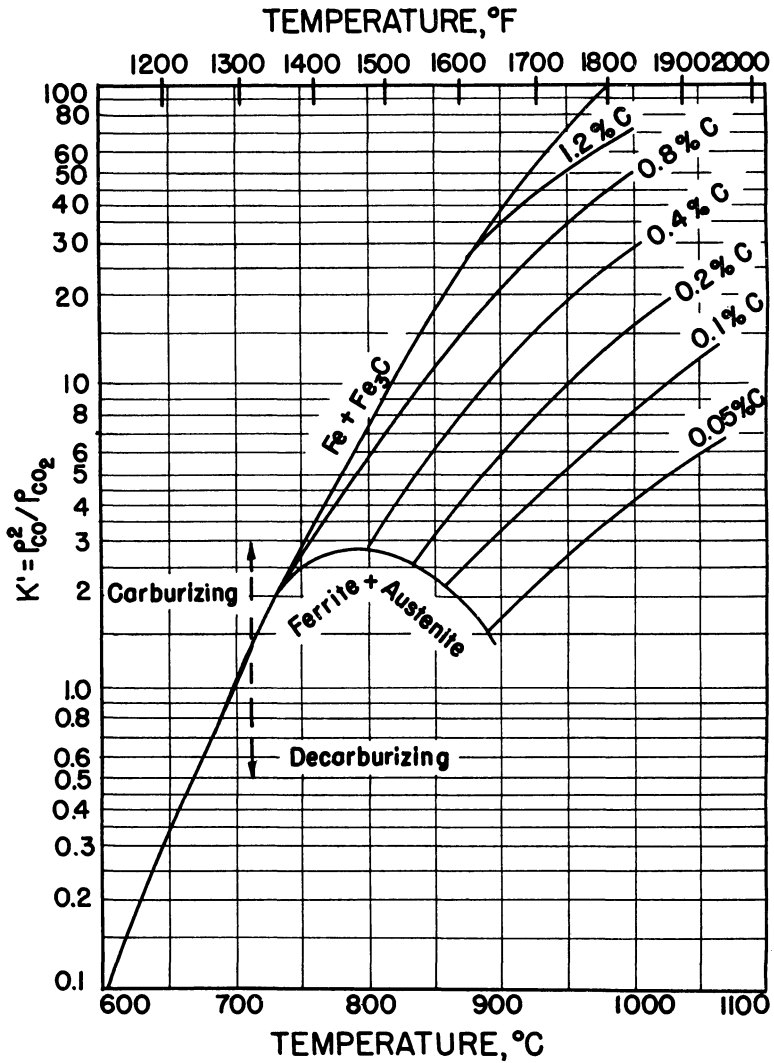


Fig. 6. Values of  $K'$  against temperature. (Austin and Day).

The equilibrium constant for representing equation 1 can then be written

$$(4) \quad K = \frac{N_{Fe}^3}{N_{Fe_3C}} \frac{P_{CO}^2}{P_{CO_2}}$$

Fig. 7 shows the relation between  $N_{Fe}^3 / N_{Fe_3C}$  and the per cent carbon in a steel. This curve is made up from calculated values

and is for convenience in calculations involving equilibrium constants. The data of Bramley and Lord (1932) have been used in evaluating equilibrium constants by equation (4). Their data are fairly complete for equilibrium gas compositions obtained with nine different steels at eight temperatures and under eight different total pressures of the reactive gases.

The calculated values of the equilibrium constants for these steels over the temperature range and at a total pressure of one atmosphere are assembled in table I. The table is divided into three sections according to the phases present in the steel at

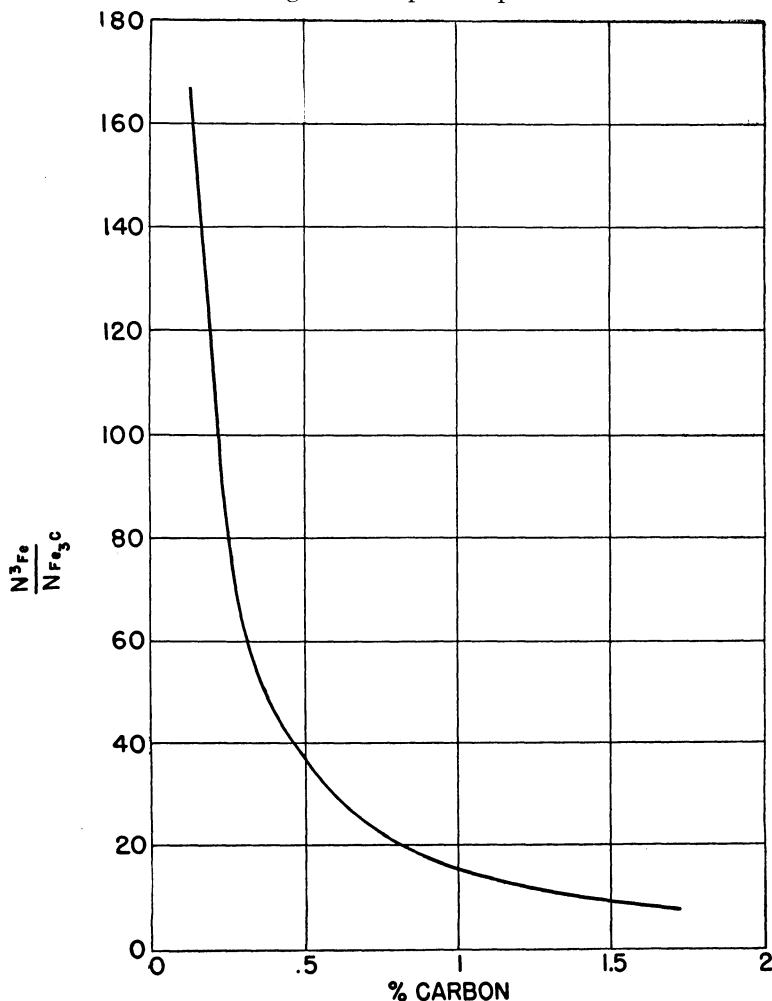


Fig. 7. Graph for conversion of per cent carbon in austenite of value of  $\frac{N^3_{Fe}}{N_{Fe_3C}}$ .

TABLE I  
Equilibrium Constants Calculated from Data for One Atmosphere

$\frac{\%C}{C^\circ \text{ Temp.}}$	.125	.210	.260	.385	.500	.795	1.120	1.550	2.050	Av. K
750	....	69.4	....	....	....	93.9	....	103.7	....	93.9
800	156.	141	180	280	221	207	215	217	225	233
850	431	....	483	463	429	392	379	420	446	426
900	890	863	833	858	797	761	792	851	883	814
950	1540	1430	1390	1380	1310	1400	1230	1560	1240	1380
1000	2420	2510	2650	2400	2100	2620	1930	1520	2170	2200
1050	3690	4970	3290	3650	....	....	....	2460	....	3440
1100	5230	....	4690	....	4650	5050	....	....	....	4950

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temperature. In the upper left section austenite and ferrite are in equilibrium and here the calculation of  $K$  is based on the percentage of carbon in the austenite phase and not on the percentage of carbon in the total solid. Likewise, the values in the area to the right are based on austenite composition and not on the whole solid state which is made up of austenite and free cementite. The composition of the austenite was in each of these cases estimated from the iron-carbon phase diagram. The large central portion represents the unsaturated austenite and only one solid phase. It can be seen that the value of  $K$  is practically constant for the different steels at one temperature. In the last column to the right are the average values of  $K$  for the different steels having only one phase at each of the temperatures; total pressure being one atmosphere.  $K$  values for the two-phase steels were not used in averaging because of the uncertainty of the austenite compositions.

Similar calculations have also been made to obtain corresponding average values of  $K$  for seven other total pressures, and all results are tabulated in table II. The values given for one atmosphere are the values taken from the last column of table I. Inspection of table II shows that the equilibrium constant as calculated by equation (4) is practically independent of total pressure. The last column in the table gives the overall average value of  $K$  for each temperature. Graphical representation of the relation between the equilibrium constants and temperature is presented in Fig. 8.

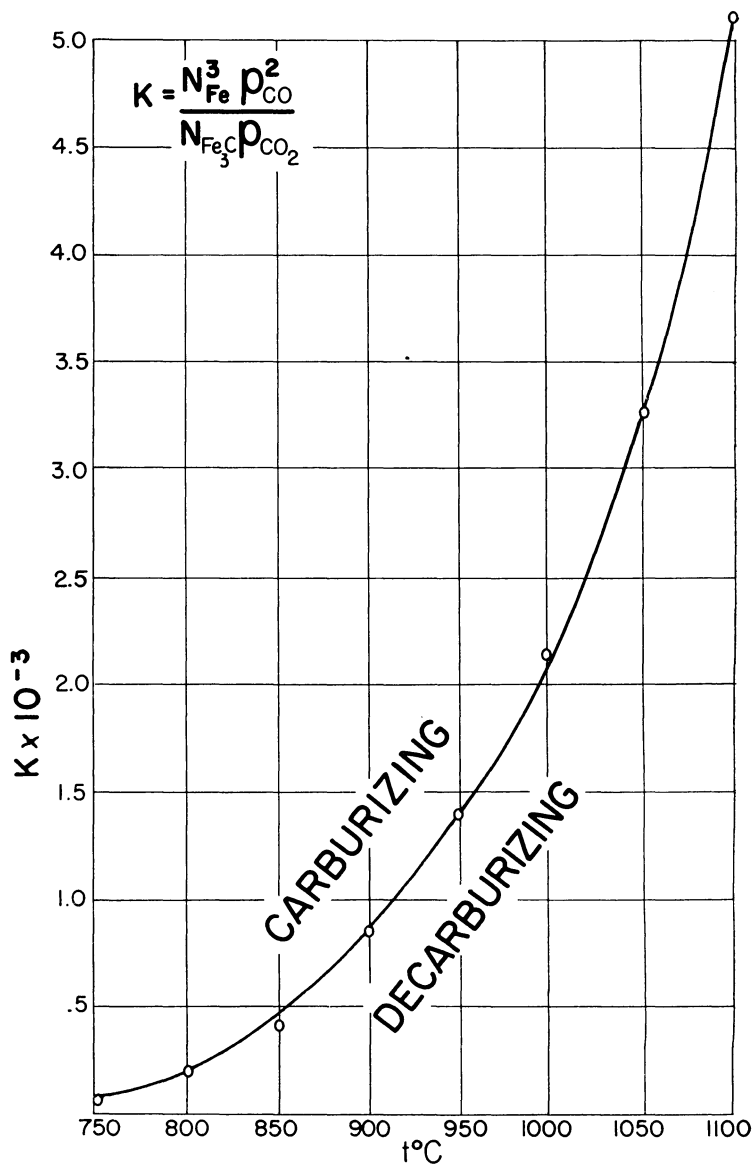


TABLE II  
Average Equilibrium Constants for Eight Total Pressures

°C. Temp.	Press. atm.	0.25	0.50	0.75	1.00	1.25	1.50	1.75	2.00	Overall Av. K
750°		92.0	103.	101.	93.9	101.	92.6	101.	91.7	97.1
800°		227	236	233	233	236	234	234	227	233
850°		418	426	431	426	406	409	420	400	416
900°		860	836	829	814	817	779	775	771	811
950°		1280	1400	1370	1380	1340	1370	1330	1260	1340
1000°		---	2110	2260	2200	2100	2160	2040	2060	2130
1050°		---	3300	3250	3440	3140	3280	3300	3150	3270
1100°		---	5880	5000	4950	5180	4780	4880	5120	5090

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At any temperature, there will be a tendency for the steel to carburize if the mass-action expression for the reaction under the conditions imposed gives a value greater than the mass-action expression for the reaction at equilibrium. That is, conditions that give values above the curve in Fig. 8 are carburizing; furthermore, conditions that give values below the curve are decarburizing to the steel. Suppose, for example, that a steel containing 0.8 per cent carbon is to be annealed at 800°C. and a gas neutral to the steel is desired. Assume that the total active gas pressure is to be 0.34 atmospheres. In Fig. 8 the value of the equilibrium constant at 800°C. is 233, and the value of  $N_{Fe}^3/N_{Fe_3C}$  for an 0.8 per cent carbon steel is 21.9 in Fig. 7. The value of  $P_{CO}^2/P_{CO_2} = 233/21.9 = 10.6$ . In addition,  $P_{CO_2} = 0.34 - P_{CO}$ . Therefore  $P_{CO}^2/0.34 - P_{CO} = 10.6$ . Solving for  $P_{CO}$  gives a value of 0.3297 atmosphere pre-

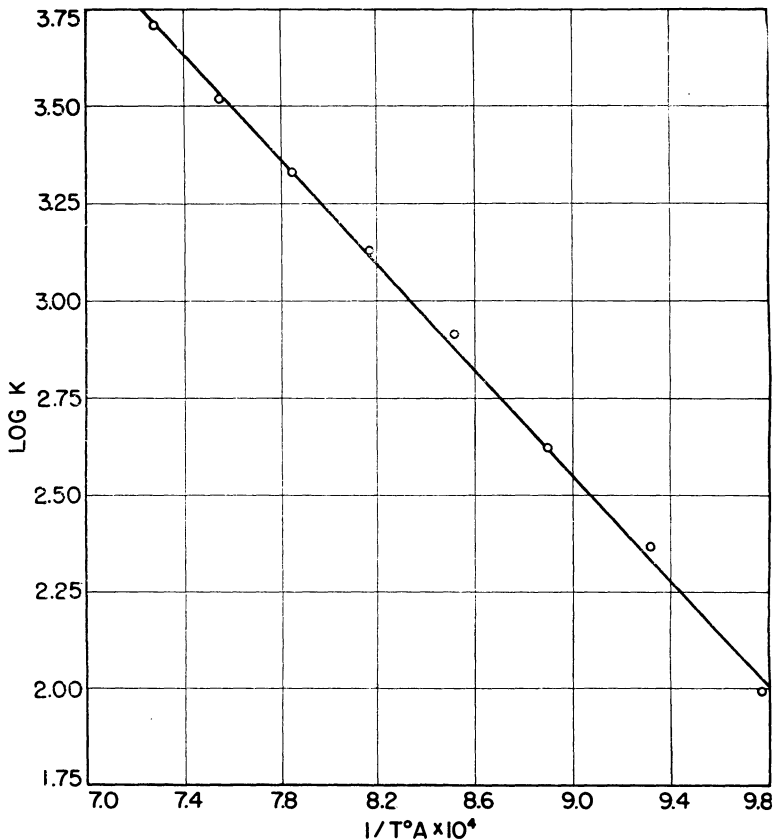


Fig. 9. Values of Log K against 1/T°A.

sure of the CO and 0.0103 atmospheres pressure of CO<sub>2</sub> in the gas to anneal the 0.8 per cent carbon steel at 800° C. without carburizing or decarburizing it.

The equilibrium constants calculated above can be used for the determination of thermodynamic properties in connection with equation (1). Fig. 9 shows a plot of log K against  $1/T^{\circ}A$  and all points fall close to the straight line. Calculation of  $\Delta H$  for reaction (1) from the slope of this line gives a value of about 30,000 calories which is in close agreement with values obtained by other methods of calculation for the same reaction in which the Fe<sub>3</sub>C is in solid solution in gamma-iron.

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