Chemical Equilibrium between Iron, Carbon, and Oxygen

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The problem of the equilibrium between iron, carbon, and oxygen was first carefully investigated by E. Baur and A. Glaessner,[1] who determined the equilibrium conditions of the two reactions

$$Fe_3O_4 + CO \rightleftharpoons 3FeO + CO_2 \qquad (1)$$

$$FeO + CO \rightleftharpoons Fe + CO_2 \qquad (2)$$

within the range of temperature of 350° to 900° C. The next series of investigations was made by R. Schenck and his co-workers,[2] who sought to check the results of Baur and Glaessner's work within the range of 550° to 700° C. and to elucidate the conditions of formation of iron carbide. The equilibrium conditions at the higher temperatures, however, are generally understood to be much more complicated, owing chiefly to the formation of solid solutions between iron, its oxides, and carbide; nevertheless their determination is of much more practical importance than those at the lower temperatures.

It is well known that each of the reactions is reversible; equilibrium is established when the partial pressure of oxygen in the gaseous phase has become equal to the dissociation pressure of magnetic oxide in equation 1 and that of ferrous oxide in equation 2. These equilibria are subsequently designated by "the Fe_3O_4-FeO equilibrium" and "the FeO-Fe equilibrium," respectively.

As the Fe_3O_4-FeO equilibrium has three phases with three components, it must be bivariant. But the reaction involves no pressure change in the gaseous phase, hence the final composition of the latter is practically unaffected by pressure. To know the equilibrium conditions, the compositions of the gaseous phase at different temperatures must be determined. At the higher temperature, however, iron and its oxides dissolve one another in various proportions forming solid solutions; in many cases the content of oxygen in the solid phase becomes a new independent variable.

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[1] *Zeit. phys. Chem.* (1903) **43**, 354.

[2] *Ber.* (1905) **38**, 2132; (1907) **40**, 1704.

If a solid phase containing an excess of free carbon is subjected to a certain temperature in vacuo, an equilibrium is established when each of the reactions

$$\mathrm{Fe_3O_4 + CO \rightleftharpoons 3FeO + CO_2}$$

and

$$\mathrm{2CO \rightleftharpoons C + CO_2} \tag{3}$$

has acquired equilibrium at that temperature. The equilibrium condition may be made evident by measuring the pressure and composition of the resulting gaseous phase; but this method is available only for temperatures lower than about 700° C. Because the equilibrium pressure increases rapidly with increase of temperature, a temperature is soon reached at which the pressure is so great that a special apparatus is required.

It is necessary, therefore, to determine the conditions governing the formation of solid solutions, employing oxides or oxide mixtures, of various average oxygen content, as the solid phases, and CO or $\mathrm{CO_2}$ content, as the initial gaseous phases, and then to find the equilibrium conditions of the reactions (1) and (2) when the solid phases are in proper composition showing no objectionable phenomenon of the formation of solid solution.

EXPERIMENTS

Materials Used

Ferric oxide was prepared from carefully purified hydroxide. Ignition of the hydroxide at too high temperatures spoils the preparation: the oxide tends to become sintered, and, as may be judged from the dark reddish brown color, the resultant oxide is contaminated with lower oxides, formed at high temperatures, which to some extent remain unchanged at lower temperatures because of rapid cooling. Rather low temperatures were therefore used for the ignition and the fine powder was cooled slowly in a current of oxygen.

Metallic iron was prepared by heating its oxalate in a stream of hydrogen at about 600° C. Samples of the reduced commercial iron containing but a small amount of uncombined silica, but with no trace of manganese, were also used.

Carbon dioxide was produced by the action of dilute sulfuric acid on sodium bicarbonate suspended in water and was subsequently dried by passing it through concentrated sulfuric acid and phosphoric oxide.

Carbon monoxide was prepared by the action of concentrated sulfuric acid on oxalic acid; traces of oxygen were removed by heating it over yellow phosphorus, and other impurities were removed by passing it through a series of towers of concentrated caustic potash solution with and without pyrogallol, then through concentrated sulfuric acid; it was finally dried over phosphoric oxide.

Arrangement of Apparatus

The apparatus is diagrammatically represented in Fig. 1. A porcelain tube *v*, 2.3 cm. inside diameter and 40 cm. long, closed at one end and glazed both inside and out, in which a small kaolin plate supports a small magnesia boat of known weight and containing a weighed amount of iron oxide, was inserted into an ordinary Heraeus' furnace *f* in such a position that the boat was in the middle of the furnace and the open end of the vessel projected about 11 cm. A glass cup *g* was sealed to this end by Canada balsam that had been freed from easily volatile substances. During the experiments, the outside of this portion was cooled by circulating water.

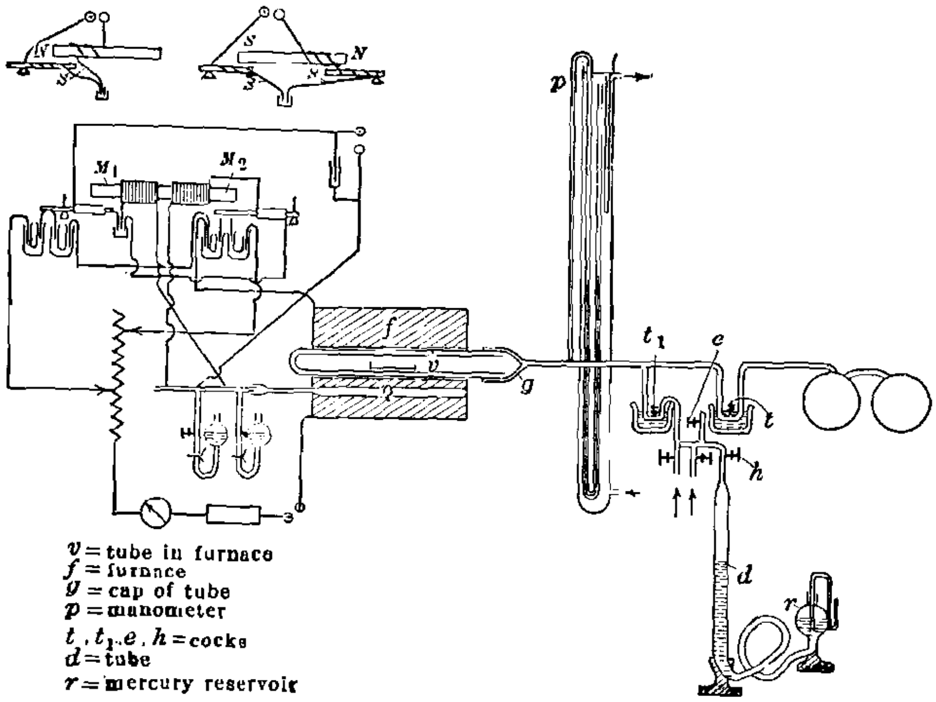

Fig. 1.—Apparatus used in experiments.

The thermojunction of a Le Chatelier pyrometer, which was standardized against five metals, rested at the middle of the furnace and was in contact with the outside of the tube *v*. The end of the thermojunction was connected with a Siemens-Halske millivoltmeter graduated for each 10° C. Correction of temperature in the furnace was made by repeating Boudouard's experiment[3] and by determining the composition of the gaseous phase in equilibrium with amorphous carbon at various temperatures, at nearly one atmosphere, and then determining the average temperatures in the furnace by the result of Boudouard.

The glass cup *g* was connected with a Gaede molecular vacuum pump by a capillary glass tube having a cock *t*. One of the two capillary branches of the capillary tube was connected with a manometer *p*, and

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[3] *Ann. chim. et phys.* (1901) **7**, 24, 5.

the other was fitted with the cock t_1 that controlled the passage of the gases. The manometer p consisted simply of a U-shaped capillary tube 80 cm. in height, the lower halves of which were filled with mercury, dipping vertically into a large glass tube through which a stream of water was allowed to flow slowly upwards. One arm of the U-tube was sealed, leaving a space filled with dry air, while the other was connected with the tube v by a capillary tube. The gas introduced in the porcelain tube v was once taken into an eudiometer d; it could also have been charged directly from the generators. A special device, shown at the left of Fig. 1, made it possible to maintain the temperature of the furnace constant within the range of 5° at 950° C. and 3° at 750° C.

Manipulation

After a weighed amount of ferric oxide was charged into the boat, the end of the porcelain tube v was sealed with the glass cup g, cocks t_1 and e being left open; cock h was opened and the eudiometer was filled with mercury, after which cocks h and e were closed and the whole system was evacuated. Cocks t and t_1 were then closed and the temperature of the furnace was raised to 400° or 500° C., where it was kept for about 2 hr.; any gas evolved was pumped off. The temperature was then increased, the gas to be charged was brought into the tube d and cocks t_1 and h opened; the gas was forced into the reaction vessel by raising the mercury reservoir r until the desired pressure was reached, when the cocks were closed and the reaction was allowed to proceed. To establish equilibrium properly requires roughly 2 hr. at 1100° C. and 14 to 20 hr. at 850° C. After the required length of time, the gas was drawn into the eudiometer and analyzed for carbonic acid, carbon monoxide, and, if necessary, nitrogen. From the result of the analysis, the actual volume of carbon monoxide that had entered the reaction could be calculated; this gave the weight percentage of oxygen in the solid phase, which stood in equilibrium with the gas phase.

After the repetition of these determinations, the boat was removed from the porcelain tube and weighed, so as to check the percentage of oxygen remaining in the solid phase. This percentage did not differ considerably from the calculated value and was taken as the correct number. Another check was made by direct analysis of the solid phase according to Margueritte's method, using Newth's apparatus, modified to introduce sulfuric acid into the flask without opening it. Samples containing metallic iron were determined, first, according to Milner-Merk's method[4] and then the amount of ferrous and total iron were determined as usual.

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[4] *Zeit. anal. chem.* (1902) **41,** 710.

Results of Experiment

The results are graphically represented in Figs. 2, 3, and 4. All the curves are first parallel with the abscissa, rise suddenly, become more

TABLE 1.—*Experiment Series* 1

(*Temperature,* 1070° *C. Initial solid phase,* 5.3946 *gm.* Fe_2O_3)

No.	Gaseous Phase				Solid Phase						
	Equil. Comp., Per Cent. CO	CO Charged		CO Entering the Reaction, c.c. (N.T.P.)	Oxygen Removed from Solid Phase (Cal.), gm.	Oxygen Remaining, gm.		Total Weight, gm.		Per Cent. O	
		Temp., ° C.	Vol., c.c.			Calculated	Found	Calculated	Found	Calculated	Found
1	0	21	84.58	78.54	0.05608	1.5648		5.3378		29.32	
2	0	22	94.40	87.37	0.06238	1.5024		5.2754		28.48	
3	0	21	88.00	81.74	0.05834	1.4441	1.4430	5.2171	5.2160	27.68	27.66
4	5.10	20	74.75	66.10	0.04719	1.3958		5.1688		27.00	
5	15.58	21	74.04	58.04	0.04144	1.3544		5.1274		26.41	
6	14.61	21	73.12	57.08	0.04140	1.3130	1.3603	5.0860	5.7333	25.82	26.50
7	13.37	21	71.55	57.56	0.04110	1.0755		4.1723		25.78	
8	14.36	21	75.95	60.40	0.04312	1.0324		4.1292		25.00	
9	24.55	21	75.95	53.21	0.03799	0.9944		4.0912		24.31	
10	29.50	20	75.95	23.80	0.01699	0.9774		4.0742		23.99	
11	38.17	20	75.90	17.84	0.01274	0.9647	0.9720	4.0615	4.0688	23.75	23.89
12	54.40	20	66.47	28.24	0.02016	0.8111		3.4597		23.44	
13	61.50	20	66.61	11.57	0.00826	0.8028		3.4514		23.26	
14	72.75	20	69.12	7.03	0.00502	0.7978	0.8013	3.4464	3.4499	23.15	23.23
15	72.25	20	70.60	18.25	0.01303	0.7087		3.0939		22.90	
16	72.45	20	70.60	10.21	0.00729	0.7014		3.0866		22.72	
17	71.05	20	70.34	18.97	0.01355	0.6879		3.0731		22.38	
18	72.42	20	72.16	18.54	0.01324	0.6747		3.0599		22.05	
19	72.59	20	73.96	18.89	0.01349	0.6612	0.6552	3.0464	3.0404	21.70	21.55
20	72.13	20	75.19	19.53	0.01394	0.5902		2.7893		21.16	
21	72.51	20	75.56	19.35	0.01382	0.5764		2.7755		20.77	
22	72.33	20	74.95	19.32	0.01379	0.5626		2.7617		20.37	
23	72.89	20	94.46	23.86	0.01704	0.5456	0.5414	2.7447	2.7405	19.88	19.76
24	72.06	20	73.77	19.20	0.01371	0.4728		2.4482		19.31	
25	72.00	20	74.07	19.32	0.01379	0.4590		2.4344		18.85	
26	72.95	20	72.49	18.27	0.01304	0.4460		2.4214		18.42	
27	72.30	20	84.82	21.90	0.01564	0.4304		2.4058		17.89	
28	72.57	20	81.44	20.82	0.01487	0.4155		2.3909		17.38	
29	72.78	20	93.67	23.76	0.01696	0.3985		2.3739		16.79	
30	72.41	20	97.10	24.96	0.01782	0.3807		2.3561		16.16	
31	72.98	20	72.20	18.18	0.01298	0.3275		2.0941		15.64	
32	72.38	21	71.31	18.29	0.01306	0.3144		2.0810		15.11	
33	73.01	21	99.27	24.87	0.01776	0.2966		2.0632		14.38	
43	85.60?						0.0698		1.8032		3.87
44	79.43	22	67.78	13.94	0.00995	0.0383		1.2376		3.10	
45	82.10	22	68.46	12.25	0.00875	0.0296		1.2289		2.41	
46	86.22	21	67.37	9.28	0.00663	0.0229	0.0224	1.2223	1.2217	1.88	1.83
47	88.07	21	67.26	8.02	0.00573	0.0167		1.2160		1.37	
48	90.66	21	68.53	6.40	0.00457	0.0121		1.2114		1.00	

At this point, the apparatus was damaged and the solid phase was oxidized in some degree.

49	90.91	21					0.0116		1.2109		0.95
54	95.43						0.0080		1.2073		0.66

TABLE 2.—*Experiment Series 2*

(*Temperature,* 1175° *C. Initial solid phase,* 4.3539 *gm.* Fe_2O_3)

No.	Equilibrium Composition of		No.	Equilibrium Composition of	
	Gas Phase, Per Cent. CO	Solid Phase, Per Cent. O		Gas Phase, Per Cent. CO	Solid Phase, Per Cent. O
1	0.37	29.36	5	15.36	26.37
2	0.46	28.63	6	14.95	25.59
3	0.60	27.89	7	17.04	24.79
4	15.53	27.14	At this point, the apparatus was damaged.		

TABLE 3.—*Experiment Series 3*

(*Temperature,* 1175° *C. Initial solid phase,* 1.3271 *gm.* Fe_2O_3)

No.	Equilibrium Composition of		No.	Equilibrium Composition of	
	Gas Phase, Per Cent. CO	Solid Phase, Per Cent. O		Gas Phase, Per Cent. CO	Solid Phase, Per Cent. O
1	0.67	27.68	33	94.75	1.58
2	15.14	25.51	34	95.70	1.37
3	32.60	23.54	35	96.64	1.21
4	65.08	22.72	36	96.43	1.03
5	75.62	22.03	37	96.66	0.87
6	75.21	21.32	38	95.61	0.66?
7	75.84	20.57	39	97.09	?
9	75.00	19.05	40	97.39	?
11	75.53	17.45	41	96.83	?
17	75.71	12.27	42	97.10	?
21	76.35	8.41	43	97.93	?
24	80.87	5.87	44	97.61	0.79[a]
25	81.13	5.08	45	96.53	?
26	82.32	4.27	46	94.74	?
27	87.04	3.71	48	95.93	?
28	89.93	3.18	49	96.25	?
29	91.10	2.78	50	96.37	?
30	91.94	2.43	51	95.77	?
31	93.50	2.09	54	96.72	?
32	94.46	1.83	56	97.03	?

[a] Calculated from the weight.

or less horizontal, rise, again become horizontal, and then rise gradually. Each of the lowest horizontals corresponds to a practically irreversible reaction

$$3Fe_2O_3 + CO = 2Fe_3O_4 + CO_2 \tag{4}$$

At this period, the dissociation pressure of Fe_2O_3 containing Fe_3O_4 as solid

TABLE 4.—*Experiment Series 4*

(*Temperature,* 863° *C.* *Initial solid phase,* 3.7774 *gm.* Fe_2O_3)

No	Equilibrium Composition of		No.	Equilibrium Composition of	
	Gas Phase, Per Cent. CO	Solid Phase, Per Cent. O		Gas Phase, Per Cent. CO	Solid Phase, Per Cent. O
1	1.40	29.09	14	68.25	15.64
2	0.97	28.09	15	70.92	13.67
3	24.52	27.33	16	67.80	11.37
4	26.02	26.56	17	78.54?	9.75
5	25.18	25.82	18	70.89	7.44
6	25.71	25.00	19	84.93?	6.21
7	31.45	24.24	20	74.89	4.02
8	52.58	23.71	21	84.88	2.70
9	63.92	23.31	22	81.22	0.99?
10	67.48	22.95	23	80.00	?
11	67.40	22.58	24	89.66	?
12	65.47	19.75	25	86.39	?
13	67.89	17.73			

solution is so great that it does not permit the existence of carbon monoxide in the gaseous phase. From the data given by R. B. Sosman and J. C. Hostetter[5] concerning the dissociation pressure of the solid solution

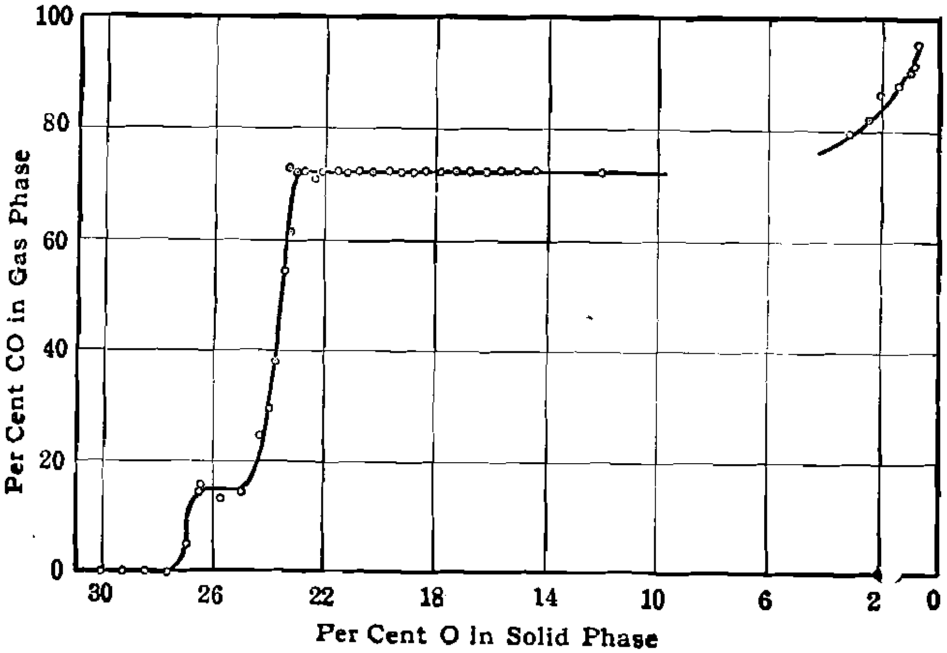

FIG. 2.—EXPERIMENT SERIES 1. TEMPERATURE 1070° C.

of Fe_3O_4 and Fe_2O_3 and the approximate formula of Nernst for the dissociation of CO_2

$$\log \frac{[CO]\cdot[O_2]^{1/2}}{[CO_2]} = -\frac{14,753.8}{T} + 1.221 \log T - 0.00037\, T + 1.3016 \quad (5)$$

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[5] *Jnl.* Am. Chem. Soc. (1916) **38**, 807.

we find that until the percentage of oxygen in the solid phase decreased to about 28.12, the above chemical reaction should be practically irreversible and the measurement of the dissociation pressure in the iron-oxygen system by this method is impossible at 1100°C. and in the neighborhood of atmospheric pressure.

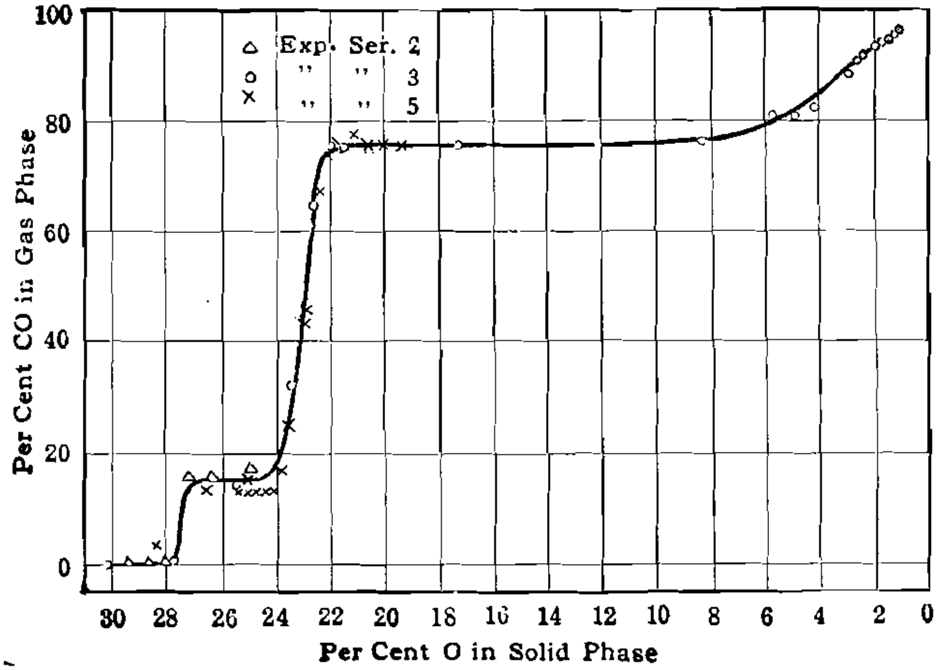

FIG. 3.—EXPERIMENT SERIES 2, 3 AND 5. TEMPERATURE 1175° C.

Figs. 2, 3, and 4 show a measurable carbon monoxide percentage when the percentage of oxygen in the solid phase has fallen to about 27.5, 27.6, and 28.0, respectively, at 1175°, 1070°, and 863°.

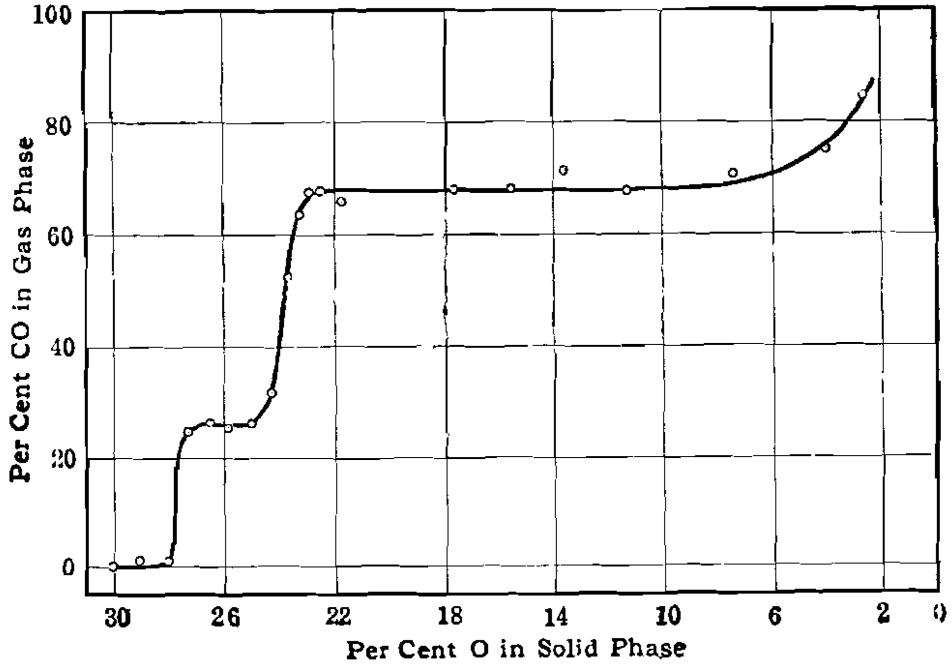

FIG. 4.—EXPERIMENT SERIES 4. TEMPERATURE 863° C.

As the percentage of oxygen decreases, the percentage of carbon monoxide rapidly increases; this upward sloping curve represents a condition in which the solid evidently consists of a single phase. When the oxygen content has been slightly lowered from this limit the curve again becomes horizontal, indicating that the solid consists of two phases and that the new phase must be FeO, with which the solid has become saturated at the transition point from the sloping to the horizontal portion of the curve. The end of this horizontal portion indicates the disappearance of Fe_3O_4 as a distinct phase; the solid phase is now a saturated solution of Fe_3O_4 in FeO. The next almost vertical portion of the curve represents the gradual decomposition of Fe_3O_4 and the subsequent production of Fe, first dissolved in FeO and then appearing as a separate phase at the transition point of the steep slope to the new horizontal. The last change in direction of the curve indicates the transition from a bivariant to a trivariant system; FeO has disappeared as a separate phase and the solid has become a saturated solution of FeO in Fe. The uppermost slope of the curve represents the equilibrium condition of the new trivariant system in which the unsaturated solution of FeO in Fe is the solid phase.

Reversibility of Reactions

In order to make sure of the reversibility of the reactions, the following experiments were made:

Experiment Series 5.—Starting from a solid phase composed of pure Fe_2O_3, the system was brought up to the FeO-Fe horizontal portion of the curve by reduction, when it was oxidized by successive charges of CO_2 at 1175° C. Fig. 3 shows that the reactions in both directions give practically identical results. The small deviations at the transition points of the horizontals to the slopes may be ascribed to lack of time necessary to ensure the complete equilibrium.

Experiment Series 6.—A solid phase whose oxygen content corresponded with the FeO-Fe horizontal of the equilibrium curve at certain temperatures was subjected to the action of CO_2 and then to that of CO. The results are given in Table 5.

TABLE 5.—*Experiment Series* 6

(*Initial solid phase,* 7.1679 *gm. of oxides*)

No.	Temperature, Degrees C.	Equilibrium Composition of Gas Phase (Per Cent. CO)	
		Charged With CO_2	Charged With CO
1	1078	72.42	72.40[a]
2	1075	72.35[a]	
3	963	68.90	69.15
4	863	66.14	[b]
5	720	60.66	60.60

[a] Averages of three determinations. [b] See experiment series 4.

Experiment Series 7.—Similar experiments were made at the Fe_3O_4-FeO horizontal of the equilibrium curves; the results are given in Table 6

TABLE 6.—*Experiment Series* 7

(*Initial solid phase*, 1.6437 *gm. of oxides containing* 24.81 *per cent. oxygen*)

No.	Temperature, Degrees C.	Charged With	Equilibrium Composition of	
			Gas Phase, Per Cent. CO	Solid Phase, Per Cent. O
1	1070	CO_2	16.42	25.27
2	963	CO_2	20.40	25.65
3	863	CO_2	25.49	26.27
4	627	CO	43.40	27.61[a]
5	627	CO	43.60	?[a]

[a] Vigorous gas absorption occurred.

So far as may be seen, there can be no doubt that the reactions are reversible.

Summary of Results

The data in Table 7 were obtained from the results of the experiments described. These data are plotted in two curves in Fig. 5, the coördinates of which are temperature and gaseous composition (per cent. CO). This graph is subsequently designated as "the *t-x* diagram." The upper curve represents the FeO-Fe equilibrium, and the lower the Fe_3O_4-FeO equilibrium, hence these are afterwards termed the "FeO-Fe curve" and the "Fe_3O_4-FeO curve" respectively.

TABLE 7.—*Summary of Results*

Temperature, Degrees C.	Data Obtained From	Equilibrium Composition of Gas Phase, Per Cent. CO in	
		Fe_3O_4-FeO Equilibrium	FeO-Fe Equilibrium
1175	Fig. 3	15.2	75.5
1078	Experiment series 6		72.4
1075	Experiment series 6		72.3
1070	Experiment series 7	16.4	
1070	Fig. 2	15.0	72.3
963	Experiment series 6 and 7	20.4	69.0
863	Experiment series 6 and 7	25.5	66.1
863	Fig. 4	25.5	67.5
720	Experiment series 6		60.6
627	Experiment series 7	43.5	

The FeO-Fe curve, determined by Schenck and his collaborators at temperatures lower than those used by the author, seems to fit in well with the one given here. On the other hand, the author's experiments indicate that the minimum point seen in Baur and Glaessner's curve is not likely to exist, which opinion Schenck also has expressed.

Baur and Glaessner's Fe_3O_4-FeO curve is correct, due, perhaps, to a suitable selection of charging gas in their experiment, on the one hand, and to the suitable composition and amount of the initial solid phase on the other. The Fe_3O_4-FeO horizontal portions, as shown in Figs. 2, 3, and 4, are comparatively short, hence the employment of CO as the charging gas especially on a small amount of solid phase would easily introduce serious errors in the result.

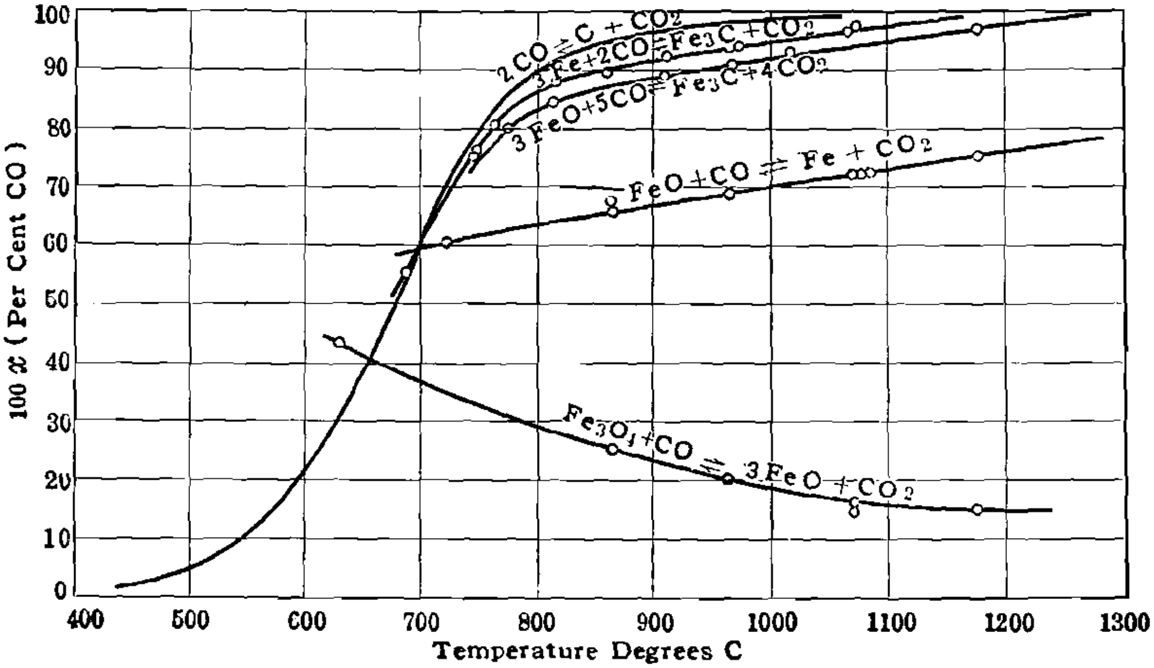

FIG. 5.—*t-x* DIAGRAM. PRESSURE, 1 ATMOSPHERE.

By graphical interpolation, the following may be taken as the correct numbers used in later calculations:

Temperature, Degrees C	Equilibrium Composition of Gas Phase, Per Cent. CO in	
	Fe_3O_4-FeO Equilibrium	FeO-Fe Equilibrium
561		53.6[a]
627	43.5	57.0
662	39.7	58.4[a]
720	35.2	60.7
863	25.5	65.9
963	20.4	69.2
1070	16.4	72.4
1175	15.2	75.5

[a] These two figures are those determined by Schenck and his collaborators.

Let K = equilibrium constant of reaction 3, and x = equilibrium composition of gas phase defined by the equation

$$\text{Per cent. CO} = 100x$$

then

$$K \times \frac{1-x}{x^2} = P \qquad (6)$$

where P = total pressure of system.

According to H. v. Juptner,[6]

$$\log K = 13.68 + 0.001081T - \frac{9037.34}{T} - 1.88 \log T \qquad (7)$$

where T denotes absolute temperature.

Substituting the experimental values of x and the calculated values of K in the left side of equation 6, we obtain the values of equilibrium pressure found in Tables 8 and 9.

TABLE 8.—*Values for FeO-Fe Equilibrium*

Temperature		x	Log K	Log P	P
Degrees C.	Degrees T.				
561	834	0.536	$\bar{2}.2530$	$\bar{2}.4618$	0.029
662	935	0.584	$\bar{1}.4400$	$\bar{1}.5263$	0.336
720	993	0.607	0.0181	0.0461	1.112
863	1136	0.659	1.2085	1.1035	12.7
963	1236	0.692	1.8914	1.6997	50.1
1070	1343	0.724	2.5218	2.2432	175.0
1175	1448	0.755	3.0618	2.6999	501.0

TABLE 9.—*Values for Fe_3O_4-FeO Equilibrium*

Temperature		x	Log K	Log P	P
Degrees C.	Degrees T.				
627	900	0.435	$\bar{1}.0574$	$\bar{1}.5325$	0.341
720	993	0.352	0.0181	0.7366	5.453
863	1,136	0.255	1.2085	2.3763	236.8
963	1,236	0.204	1.8914	3.1730	1,489.0
1,070	1,343	0.164	2.5218	4.0143	10,335.0
1,175	1,448	0.152	3.0618	4.6265	42,320.0

These values of P represent the equilibrium pressure of the system containing amorphous carbon.

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[6] *Das Chem. Gleichgewicht* (1910) 243.

DISSOCIATION PRESSURE OF FeO AND Fe_3O_4

Dissociation of FeO

The dissociation of FeO may be expressed by the reaction

$$FeO \rightleftharpoons Fe + \tfrac{1}{2}O_2 \tag{8}$$

and that of CO_2 by

$$CO_2 \rightleftharpoons CO + \tfrac{1}{2}O_2 \tag{9}$$

Equilibrium is established when the oxygen pressure of FeO becomes equal to that of the gaseous phase. From equation 5,

$$\log [O_2] = -\frac{29{,}507.6}{T} + 2.442 \log T - 0.00074T + 2.6032 - 2 \log \frac{[CO]}{[CO_2]} \tag{10}$$

Then,

T	x	$[O_2]$	T	x	$[O_2]$
834	0.536	5.41×10^{-27}	1236	0.692	4.60×10^{-16}
935	0.584	2.05×10^{-23}	1343	0.724	2.75×10^{-16}
993	0.607	7.06×10^{-21}	1448	0.755	7.84×10^{-13}
1136	0.659	4.75×10^{-18}			

These data may be represented well by the equation

$$\log [O_2] = -\frac{28{,}752}{T} - 1.79 \log T + 13.427 \tag{11}$$

Comparing the values of log $[O_2]$ calculated from this equation with those measured:

T	LOG $[O_2]$ CALCULATED	LOG $[O_2]$ MEASURED	DIFFERENCE
834	−26.2767	−26.2667	+0.0100
935	−22.6415	−22.6876	−0.0461
993	−20.8922	−20.9063	−0.0141
1136	−17.3520	−17.3235	+0.0285
1236	−15.3698	−15.3373	+0.0325
1343	−13.5811	−13.5609	+0.0202
1448	−12.0872	−12.1055	−0.0183

Finally, for the dissociation pressure of FeO calculated from equation 11:

T	(O_2)	T	(O_2)
800	1.95×10^{-28}	1800	4.23×10^{-9}
1000	2.02×10^{-21}	2000	1.39×10^{-7}
1200	9.02×10^{-17}	2200	2.37×10^{-6}
1400	1.81×10^{-13}	2400	2.49×10^{-5}
1600	5.27×10^{-11}		

These values must be somewhat smaller than true ones, because the measurements in reality were concerned with the dissociation of FeO saturated with Fe.

By calculation in the same manner as with FeO, for the dissociation pressure of Fe_3O_4

T	x	$[O_2]$	T	x	$[O_2]$
900	0.435	3.91×10^{-24}	1236	0.204	3.54×10^{-14}
993	0.352	1.00×10^{-20}	1343	0.164	4.92×10^{-12}
1136	0.255	1.94×10^{-16}	1448	0.152	2.32×10^{-10}

These data may be represented by the equation

$$\log [O_2] = \frac{32,254}{T} + 1.75 \log T + 7.23485 \qquad (12)$$

Comparing the values of log $[O_2]$ calculated from this equation with those measured, gives the following:

T	Log $[O_2]$ Calculated	Log $[O_2]$ Measured	Difference
900	−23.4341	−23.4077	+0.0264
993	−20.0019	−19.9986	+0.0033
1136	−15.8108	−15.7112	+0.0996
1236	−13.4496	−13.4516	−0.0020
1343	−11.3074	−11.3085	−0.0011
1448	− 9.5086	− 9.6348	−0.1262

Calculating the dissociation pressure from this equation gives the following:

T	$[O_2]$	T	$[O_2]$	T	$[O_2]$
800	9.95×10^{-29}	1400	5.03×10^{-11}	2000	7.67×10^{-4}
1000	1.70×10^{-20}	1600	4.82×10^{-8}	2200	2.65×10^{-2}
1200	6.03×10^{-15}	1800	1.03×10^{-5}	2400	5.14×10^{-1}

It must be remembered that Fe_3O_4 was saturated with FeO in these experiments.

EQUILIBRIUM SYSTEM OF IRON WITH OR WITHOUT OXYGEN, CARBURIZED IRON AND GAS CONSISTING OF CARBON MONOXIDE OR CARBON DIOXIDE OR BOTH

General Method of Investigation

A solid phase, consisting of a solid solution of FeO in Fe, and a gas phase, consisting of CO and CO_2, form a trivariant system in which the final composition of the gas phase is practically independent of the pressure of the system. But if the amount of oxygen in the solid phase is decreased to a very small quantity by successive reduction with CO, a new chemical reaction begins, as shown by the decrease of pressure in the system when the reaction vessel is charged with fresh CO. Although the original pressure is soon recovered, in the case of a solid phase insufficiently reduced, the recovery is slower after each experiment. When duced pressures.

Under such conditions of solid phase, the composition of the gaseous phase that stands in equilibrium with the solid tends to show some irregularity: the percentage of CO in the total amount of CO and CO_2 is sometimes decreased and sometimes increased according to the magnitude of the final pressure in the equilibrium system. But, when the pressure is practically the same, the composition of the gas phase seems to be practically constant. The latter fact was shown in the third experiment series, in which the final composition of the gas is practically 97 per cent CO, since the final pressures were nearly one atmosphere.

If the solid phase is examined under this condition, it is apparent that carburization has taken place and that the solid phase contains, besides oxygen, some combined carbon.

The reaction of carburization may be considered to occur according to either of the following equations, which have been proposed by many authors

$$3Fe + 2CO \rightleftarrows Fe_3C + CO_2 \tag{13}$$

$$3FeO + 5CO \rightleftarrows Fe_3C + 4CO_2 \tag{14}$$

If K_1 and K_2 are the equilibrium constants of these reactions,

$$K_1 = \frac{[CO]^2}{[CO_2]} = \frac{x^2}{1-x} \times P \tag{15}$$

$$K_2 = \frac{[CO]^5}{[CO_2]^4} = \frac{x^5}{(1-x)^4} \times P \tag{16}$$

If either K_1 or K_2 is constant for various values of P and x, the corresponding carburizing reaction should be the probable one to occur in the system. As long as no better explanation of the phenomena is given, it is reasonable to believe that the reaction coincides with that equation, at least in its final result, no matter how complex the intermediate reactions may be.

Experiments

The arrangement of apparatus and the manipulations were the same as in the previous experiments, except that the final pressures were carefully registered in each case. The establishment of equilibrium was ensured by watching the manometer, as the pressure ceases to change when equilibrium is attained.

Interpretation of Results

After experiment 11, the percentage of CO in the gas phase, instead of rising gradually in each experiment, became practically constant (about 91 per cent.) when the pressure was approximately one atmos-

TABLE 10.—*Experiment Series 8*

(*Initial solid phase,* 7.7344 *gm. of reduced iron containing* 2.01 *per cent. of oxygen, but no trace of manganese. Charging gas,* CO)

No.	Temperature, Degrees C.	Equilibrium Condition in Gaseous Phase		Per Cent. O in Solid Phase, Calculated
		Pressure, Atmospheres	Per Cent. CO	
1	965	1.0778	70.72	1.81
2	965		72.27	1.60
3	965		75.20	1.43
4	965		78.92	1.27
5	965		82.28	1.13
6	965		83.87	1.01
7	965		85.04	0.90
8	965		87.23	0.79
9	965		88.50	0.71
10	965		88.79	0.62
11	965	0.9785	91.14	0.57
12	965	0.8893	91.27	
13	965	0.9665	90.73	
14	965	0.6159	91.65	
15	965	0.9941	90.81	
16	965	0.3176	93.78	
17	965	0.5327	92.20	
18	965	1.0270	91.22	
19	743	0.7710	79.46	
20	743	0.9334	76.84	
21	857	1.0253	86.27	
22	857	1.0107	87.12	
23	857	0.9973	87.25	
24	1070	1.1284	96.87	
25	1070	0.9783	97.39	
26	968	0.9727	94.41	
27	968	1.0221	93.77	
28	744	0.8908	77.67	
29	857	1.0058	89.05	
30	857	0.9905	89.89	
31	857	0.9148	90.29	
32	761	0.9272	81.77	
33	814	1.0668	85.18	
34	814	0.9006	88.08	
35	814	0.9487	87.69	
36	814	0.8729	89.33	
37	814	0.8783	89.25	
38	963			
39	963			
40	963			
41	963	0.9487	98.54	
42	963	0.9506	98.03	
43	963	0.9550	97.92	
44	686	1.0096	57.51	
45	814	0.9169	86.60	
46	814	0.8931	88.22	

NOTE.—Experiments 1 to 3 of experiment series 8 were reductions accompanying no pressure change; at the beginning of experiment 4, some decrease in pressure was noticed. The amount of this decrease gradually became larger, but, until experiment 8, the reduced pressures nearly regained their initial magnitude although the recovery became more and more difficult. Pressure remained depressed in experiment 9 and afterwards.

An examination of the solid phase at the end of experiment 18 showed that strong phere, and it seemed to increase with decrease of pressure. The calculated values of K_1 and K_2 corresponding to 965° C. are as follows:

No.	P	x	Log K_1	Log K_2
16	0.3176	0.9378	0.6523	$\bar{4}.1873$
17	0.5327	0.9220	0.7639	$\bar{3}.9818$
14	0.6159	0.9165	0.7921	$\bar{3}.9134$
12	0.8893	0.9127	0.9087	$\bar{3}.9367$
13	0.9665	0.9073	0.9336	$\bar{3}.9056$
11	0.9785	0.9114	0.9626	$\bar{3}.9994$
15	0.9941	0.9081	0.9504	$\bar{3}.9348$
18	1.0270	0.9112	0.9883	$\bar{4}.0381$

Apparently there is a serious gradation in the column of log K_1; the numbers in the column of log K_2 agree well with one another. Therefore the reaction that took place during these experiments coincides with reaction 9, at least in its final result.

Iron carbide produced in this way might have dissolved to a certain extent in the pre-existing solid phase at the earlier stage, but at last the carbide or some other substance rich in carbon made its appearance as a separate solid phase. As a result, the equilibrium system must have changed to a divariant one.

The mean value of log K_2 is $\bar{3}.987$, from which equilibrium pressures corresponding to any desired value of x can be calculated, thus

x	P	x	P	x	P
0.1	6.36×10^8	0.8	4.74×10	0.95	0.079
0.2	1.24×10^7	0.9	1.644	0.96	0.030
0.3	9.59×10^5	0.91	1.021	0.97	0.009
0.4	1.23×10^5	0.92	0.603	0.98	0.002
0.5	1.94×10^4	0.93	0.335	0.99	0.0001
0.6	3.20×10^3	0.94	0.172	1.00	0.0
0.7	4.68×10^2				

By graphic interpolation, 0.9105 is found to be the value of x corresponding to $P = 1$. Consequently, at the temperature of 965° C. and under a pressure of one atmosphere, an equilibrium will be established when the gaseous composition becomes 91.05 per cent. CO.

The results of experiments 19 and 20 give

No.	P	x	Log K_2	Log K_1
19	0.7710	0.7946	2.1374	0.3748
20	0.9334	0.7684	1.9391	0.3765

This time log K_1 gives a more constant value than log K_2, showing that the reaction was either carburization, according to reaction 8, or soot deposition, in accordance with reaction 3. From the mean value of

$\log K_1$, $x = 0.7549$ for $P = 1$. This equilibrium point deviates slightly from the carbon curve wrought out by Boudouard. Hence the equilibria should have been those of carburization.

Experiments 21 to 23 were made under the pressures of practically one atmosphere. The first result differs slightly from the following two: the gaseous composition acquired its constant value first in experiment 22. Hence the last two numbers are to be taken as those representing the true divariant equilibria at 857° C. The mean gaseous composition is 87.19 per cent. CO, but the nature of this reaction cannot be decided from these data. However, as shown in Fig. 6, this equilibrium point lies exactly on the equilibrium curve of reaction 9, which is afterwards wrought out from other data. The solid phase must have been oxidized during the experiment at 743° C. because formerly it was so well reduced that its oxygen pressure admitted of carburization during the experiment at 965°, and the same solid phase is incapable of being carburized at 857° without previous reduction. It is also clear that the solid phase which stood in equilibrium of reaction at 965° was capable of being carburized according to reaction 9 at 743°.

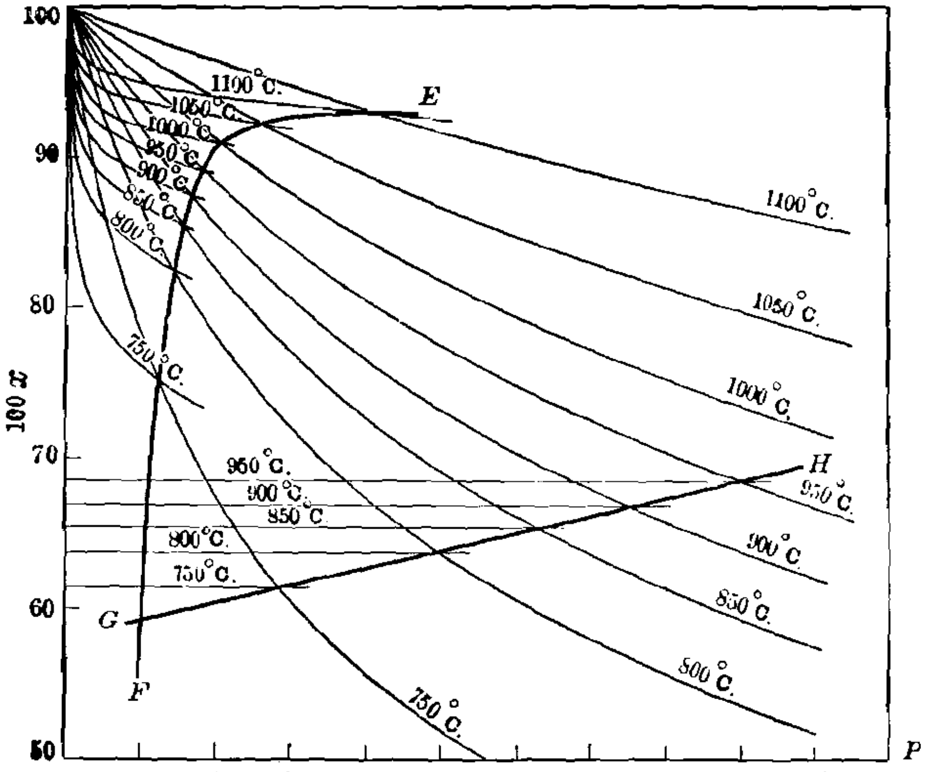


FIG. 6.—P-x DIAGRAM.

Experiments 24 and 25 give the following results:

No.	P	x	LOG K_3	LOG K_1
24	1.1284	0.9687	6.0013	1.5293
25	0.9783	0.9739	6.2665	1.5509

The mean value of $\log K_1$ is 1.540, which gives $x = 0.9727$ for $P = 1$. This equilibrium point deviates in a marked degree from the carbon curve of Boudouard; therefore the reaction was that of carburization in accordance with reaction 8. It must be remembered that the solid phase was brought from 857° to 1070°. Perhaps the amount of charging gas was so large, compared to the amount of solid in experiment 24, that the former reduced the latter sufficiently to establish Fe-Fe_3C equilibrium at 1070°.

Experiments 26 and 27 give the following results.

No.	Log K_1	Log K_1
26	4.7534	1.1606
27	4.5521	1.1591

The mean value of log K_1 is 1.1599, which gives $x = 0.9390$ for $P=1$; this point is not on the carbon curve.

Experiment 28 gives $x = 0.7600$ for $P = 1$ if the reaction is assumed to be that of carburization; which is a reasonable assumption because the solid phase showed the carburization equilibrium of reaction 8 to be 980° in the previous experiment. The calculated equilibrium point agrees with the results of experiments 19 and 20.

Experiment 29 shows apparently a transitional equilibrium resulting from oxidation of the solid phase in the previous experiment at 744°. But the solid phase was well reduced and carburized at higher temperatures during experiments 24 to 27 and it was exposed to 744° in only one experiment. Therefore the result of oxidation was not so serious as in experiment 21. The mean value of log K_1, which is constant in experiments 30 and 31, is 0.8920; this gives $x = 0.8968$ for $P = 1$.

From experiment 32, $x = 0.8081$ for $P = 1$, on the assumption that log K_1 is a constant. This assumption is permissible because the solid phase is brought from 857° to 761°.

Experiments 33 to 37 furnish an interesting example of the transition of reactions.

No.	P	x	Log K_1
33	1.0668	0.8518	0.7179
34	0.9006	0.8808	0.7680
35	0.9487	0.8769	0.7728
36	0.8729	0.8933	0.8148
37	0.8783	0.8925	0.8135

The first is obviously a transitional equilibrium resulting from the oxidation of the solid phase in the previous experiment. The second and the third give one group of vicinal numbers as log K_1; they must correspond to the equilibrium of reaction 8. The mean value of log K_1 is 0.7704 from which $x = 0.8712$ for $P = 1$. The fourth and fifth experiments give another group of vicinal numbers as log K_1; this group corresponds to the reaction of soot deposition because the mean value of log K_1 is 0.8141, which gives $x = 0.8809$ for $P = 1$, which point lies exactly on the carbon curve of Boudouard. Hence it is known that the solid phase, or at least its surface layer, was saturated with carbon at the beginning of experiment 36, and the equilibrium point had been displaced toward the carbon curve before the end of that experiment.

After the repeated carburization of the solid phase, experiments 41 to 43 were made to determine the position of the carbon curve at 963°. The calculated results are:

No.	P	x	Log K_1
41	0.9487	0.9854	1.8000
42	0.9506	0.9803	1.6663
43	0.9550	0.9792	1.6437

There is a gradation in the column of log K_1, but the absolute values are much larger than those corresponding to the equilibrium of Fe, Fe_3C, CO, and CO_2. This shows that only the surface layer had acquired the composition of pure cementite by the rapid reaction of fresh carbon monoxide during the previous carburizing operation. Hence, in experiment 41, the gaseous phase in equilibrium was so rich in CO that soot was deposited upon the cementite crust, because the calculated value of x corresponding to $P = 1$ is 0.9846, which is on the carbon curve. The next two equilibria seem to be transitional ones, the position of the equilibrium point depending entirely on the carbon content of the surface layer of solid phase.

The equilibrium pressure in experiment 44 was nearly one atmosphere and the equilibrium point lies nearly on the carbon curve.

Experiments 45 and 46 give the following results:

No.	P	x	Log K_1
45	0.9169	0.8660	0.7103
46	0.8931	0.8822	0.7709

Log K_1 in the second experiment exactly coincides with the equilibria of Fe, Fe_3C, CO, and CO_2 determined by experiments 34 and 35, hence the solid phase was again oxidized during the previous experiment at 686°. The equilibrium in the first experiment was only a transitional one.

This series of experiments shows:

1. The first period of carburizing reaction coincides, at least in its result, with

$$3FeO + 5CO \rightleftharpoons Fe_3C + 4CO_2 \tag{14}$$

and at the later period with

$$3Fe + 2CO \rightleftharpoons Fe_3C + CO_2 \tag{13}$$

2. There exist the transitional equilibria between the above two, between the first and FeO-Fe equilibrium, and between the second and carbon equilibrium.

3. Equilibria at lower temperatures occur with more oxidized form of solid phase than at the higher temperatures even in the same carburizing reaction.

Confirmatory Experiments

The following experiments were made as a check on the previous experiments on reaction 14 at various temperatures and under a pressure of practically one atmosphere. Account was taken of the variation in the composition of the solid phase: in most cases, a solid solution of FeO in Fe containing a large amount of oxygen was used as the initial solid phase. The equilibrium composition of gas phase, after successive experiments, became constant when the experiment at that temperature was finished. If the deviation of equilibrium pressure from one atmosphere was not negligible, the equilibrium constant was calculated and from this the gaseous composition corresponding to one atmosphere was obtained as usual.

TABLE 11.—*Experiment Series* 9

(*Temperature,* 907° *C. Initial solid phase, solid solution of FeO in Fe containing* 2.01 *per cent. oxygen. Charging gas, CO*)

No.	Equilibrium Conditions		Remarks
	Pressure, Atmospheres	Composition of Gas, Per Cent. CO	
1	1.1764	82.38	
2	0.9863	83.70	
3	1.0753	85.49	
4	1.0716	86.70	
5	1.0919	87.19	
6	1.1539	87.54	
7	0.9838	89.04	Average 89.15
8	0.9884	88.71	
9	0.9793	89.31	
10	0.9979	89.55	

TABLE 12.—*Experiment Series* 10

(*Temperature,* 772° *C. Initial solid phase, solid solution of FeO in Fe containing* 2.01 *per cent. oxygen. Charging gas, CO*)

No.	Equilibrium Conditions		Remarks
	Pressure, Atmospheres	Composition of Gas, Per Cent. CO	
1	0.8204	77.72	
2	1.0910	75.23	
3	0.9029	79.06	Average 80.22
4	0.9977	80.00	
5	1.0023	81.26	
6	0.9848	80.56	

TABLE 13.—*Experiment Series* 11

(*Temperature*, 810° *C*. *Initial solid phase, end product in experiment series* 10. *Charging gas, CO*)

No.	Equilibrium Conditions		Remarks
	Pressure, Atmospheres	Composition of Gas, Per Cent. CO	
1	1.0080	85.22	
2	0.9458	86.06	
Vessel was evacuated, filled with CO, closed, and allowed to stand for 1 hr., then evacuated. This process was repeated three times, when the reaction with CO was allowed to go on as before.			
3	0.9375	82.60	
4	0.9818	84.64	Average 84.58
5	1.0204	84.51	

TABLE 14.—*Experiment Series* 12

(*Temperature*, 1014° *C*. *Initial solid phase, end product in experiment series* 17. *Charging gas, CO*)

No	Equilibrium Conditions	
	Pressure, Atmospheres	Composition of Gas, Per Cent. CO
1	1.0118	96.95
Solid phase was subjected to oxidizing action of CO_2 as in experiment series 11.		
2	0.9501	81.56
3		87.20
4	1.0181	88.79
5		
6		
7		
8	0.9843	92.18
9	0.9759	92.57
10	0.9799	92.82
11	0.9623	93.16
12	0.9601	93.20

The average value of log K_2 calculated from the last two results is 4.4943; this gives $x = 0.9312$ for $P = 1$.

This time log K_1 gave more constant values than log K_2; hence the conditions of equilibrium of reaction 9 have not been determined. From the last three data, $\bar{1}.852$ is the average value of log K_1, which gives $x =$

TABLE 15.—*Experiment Series* 13

(*Temperature,* 685° *C. Initial solid phase, end product in experiment series* 12. *Charging gas, CO*)

No.	Equilibrium Conditions		Log K_1	Log K_3
	Pressure, Atmospheres	Composition of Gas, Per Cent CO		
1	0.6389?	61.73	$\bar{1}.8036$	0.4265
2	0.7086	56.43?	$\bar{1}.7142$	0.0512
3	0.4170	70.46	$\bar{1}.8456$	0.9782
4	0.6385	64.00	$\bar{1}.8612$	0.6109
5	0.4239	70.36	$\bar{1}.8500$	0.9764

of Boudouard; but as there was no sign of soot deposition in the solid phase or on the wall of the vessel, the reaction was presumably that of carburization.

The following experiments were made as a check for the equilibrium conditions of reaction 13, employing various forms of iron with no oxygen content as the initial solid phase.

Experiment Series 14.—No. 1. Temperature, 909° C. Initial solid phase, 7.0368 gm. of reduced iron. Charging gas, CO. Composition of gas in equilibrium, 92.97 per cent. CO. Equilibrium pressure, 0.9187 atmosphere. Calculated composition of gas corresponding to an equilibrium pressure of 1 atmosphere, 92.45 per cent. CO.

No. 2. Temperature, 963° C. Initial solid phase, 19.1430 gm. of white pig iron of the following composition: 3.708 per cent. C, 0.063 per cent. P, 0.028 per cent. S, 0.084 per cent. Si, trace of Mn. Charging gas, CO_2. Composition of gas in equilibrium, 91.18 per cent. CO. Equilibrium pressure, 1.5440 atmosphere. Calculated composition of gas corresponding to an equilibrium pressure of 1 atmosphere, 93.9 per cent. CO.

No. 3. Temperature, 1065° C. Initial solid phase, 5.1295 gm. fine piano wire. Charging gas, CO. Composition of gas in equilibrium: (*a*) 96.50 per cent. CO; (*b*) 96.64 per cent. CO. Equilibrium pressures: (*a*) 0.959 atmosphere; (*b*) 1.100 atmospheres. Calculated composition of gas corresponding to an equilibrium pressure of 1 atmosphere: (*a*) 96.35 per cent. CO; (*b*) 96.93 per cent. CO; mean 96.64 per cent. CO.

No. 4. Temperature, 968° C. Initial solid phase, 1.3938 gm. of reduced iron. Charging gas, mixture of CO and CO_2; CO in charging gas: (*a*) 100 per cent.; (*b*) 100.0 > < 95.6 per cent.; (*c*) 100.0 > < 94.74 per cent. Equilibrium pressures: (*a*) 0.9349 atmosphere; (*b*) 0.9232 atmosphere; (*c*) 0.9443 atmosphere. Calculated composition of gas corresponding to an equilibrium pressure of 1 atmosphere: (*a*) 94.62 per cent. CO; (*b*) 94.74 per cent. CO; (*c*) 94.49 per cent. CO. From these data:

Experiment	Log K_1	$100x$ ($P = 1$)
a	1.1915	94.28
b	1.1974	94 35
c	1.1847	94.20
		94.28 average

TABLE 16.—*Equilibrium Points of Carburizing Reactions*

Experiment Series	Temperature, Degrees C.	$100x$ Corresponding to $P = 1$ in Equilibrium	
		$3Fe + 5CO \rightleftharpoons Fe_3C + 4CO_2$	$3FeO + 2CO \rightleftharpoons Fe_3C + CO_2$
13	685		55.48
8	743		75.49
8	744		76.00
8	761		80.81
10	772	80.22	
11	810	84.58	
8	814		88.09
8	857		89.68
9	907	89.15	
14	909		92.45
14	963		93.90
8	965	91.05	
8	968		93.90
14	968		94.28
12	1014	93.12	
14	1065		96.64
8	1070		97.27
3	1176	97	

Summary of Results

The equilibrium points of carburizing reactions may be summarized as shown in Table 16. These equilibrium points are plotted in two curves in Fig. 5. They are subsequently designated as "carburization curves" and to distinguish one from the other they are marked "Fe-Fe_3C curve" and "FeO-Fe_3C curve."

Influence of Pressure on Equilibria

The equilibrium constant at any required temperature in either of the two carburizing reactions can be calculated from the *t-x* diagram. Thus for the Fe-Fe_3C equilibrium:

Degrees C.	x	Log K_1	Degrees C.	x	Log K_1
1100	0.981	1.7046	900	0.917	1.0057
1050	0.967	1.4524	850	0.897	0.8927
1000	0.951	1.2662	800	0.866	0.7479
950	0.935	1.1287	750	0.783	0.4511

and for the FeO-Fe_3C equilibrium:

Temperature, Degrees C.	x	Log K_1	Temperature, Degrees C.	x	Log K_1
1200	0.977	6.5025	900	0.889	3.5632
1150	0.964	5.6952	850	0.868	3.2103
1100	0.950	5.0927	800	0.838	2.7781
1050	0.937	4.6613	750	0.762	1.9034
1000	0.922	4.2553	700	0.620	0.6428
950	0.906	3.8931			

TABLE 17.—*Value of P for Fe-Fe_3C Equilibrium*

x	Temperature, in Degrees C.							
	1100	1050	1000	950	900	850	800	750
	Equilibrium Pressures, in Atmospheres							
0.98	1.056	0.590	0.384	0.280	0.211	0.164	0.117	0.059
0.96	2.198	1.230	0.801	0.584	0.440	0.339	0.243	0.123
0.94	3.439	1.924	1.253	0.913	0.688	0.530	0.380	0.192
0.92	4.787	2.678	1.744	1.271	0.958	0.738	0.529	0.267
0.90	6.253	3.498	2.279	1.660	1.251	0.964	0.691	0.349
9.88	7.849	4.391	2.860	2.084	1.570	1.210	0.867	0.438
0.86	9.588	5.364	3.494	2.546	1.918	1.479	1.059	0.535
0.84	11.49	6.426	4.185	3.050	2.297	1.771	1.269	0.641
0.82		7.586	4.941	3.601	2.712	2.091	1.498	0.756
0.80		8.855	5.768	4.203	3.166	2.441	1.749	0.823
0.78		10.25	6.674	4.864	3.664	2.825	2.024	1.022
0.76			7.669	5.589	4.210	3.246	2.326	1.174
0.74			8.763	6.386	4.810	3.709	2.657	1.341
0.72			9.969	7.265	5.472	4.219	3.023	1.526
0.70			11.30	8.234	6.203	4.783	3.427	1.730
0.68				9.308	7.011	5.406	3.873	1.955
0.66				10.50	7.908	6.097	4.369	2.205
0.64					8.904	6.866	4.919	2.484
0.62					10.02	7.722	5.533	2.793
0.60						8.680	6.219	3.139
0.58						9.753	6.988	3.527
0.56						10.96	7.853	3.964
0.54							8.829	4.457
0.52							9.935	5.015
0.50							11.14	5.650

TABLE 18.—*Value of P for FeO-Fe$_3$C Equilibrium*

x	Temperature, in Degrees C.									
	1150	1100	1050	1000	950	900	850	800	750	700
	Equilibrium Pressures, in Atmospheres									
0.98	0.070	0.022								
0.96	1.556	0.389	0.144							
0.94	8.753	2.186	0.810	0.318	0.138					
0.92	30.8	7.693	2.849	1.119	0.486	0.227	0.101			
0.90		20.97	7.765	3.049	1.324	0.620	0 275	0.102		
0.88			18.02	7.073	3.072	1.437	0.638	0.236		
0.86				14.70	6.386	2.987	1.325	0.490	0.126	
0.84					12.25	5.732	2.543	0.940	0.227	
0.82						10.36	4.596	1.700	0.391	
0.80							7.925	2.929	0.650	
0.78							13.17	4.868	0.650	
0.76								7.851	1.048	
0.74								12.36	1.649	
0.72									2.543	
0.70									3.858	
0.68									5.774	
0.66									8.544	0.469
0.64									12.52	0.687

The equilibrium pressures corresponding to various values of x at various temperatures may be calculated from the constants just obtained. These equilibrium points are plotted in isothermals in Fig. 6, x and P being the coördinates; these curves are designated "P-x isothermals." To distinguish one from the other they are marked "Fe-Fe$_3$C isothermal" and "FeO-Fe$_3$C isothermal." "The FeO-Fe isothermals," which should be straight lines, are also represented.

The point of intersection of an Fe-Fe$_3$C isothermal with the corresponding FeO-Fe$_3$C isothermal is the point where the two kinds of carburization equilibria are established simultaneously, *i.e.*, carburization in Fe and FeO may be effected at the same time: these points are plotted in a curve *E-F*. The point of intersection of a FeO-Fe$_3$C isothermal with the corresponding FeO-Fe isothermal is the point where the reduction and carburization of FeO may be effected at the same time; these points are plotted in a curve *G-H*. The three kinds of equilibrium should be established simultaneously at the intersection of *E-F* and *G-H*, the coordinate of which point seems to be approximately $P = 1$ and $x = 0.59$. The disposition of the two carburization curves in the t-x diagram shows the same fact. The carbon curve of Boudouard on the same diagram should also pass through the same point because the FeO-Fe curve in the t-x diagram intersects with the carbon curve at the point $x = 0.593$ and $t = 695$. This at once shows that the four kinds of equilibrium, namely the carbon equilibrium, two carburization equilibria, and FeO-

Fe equilibrium, are established at the same time at a point $P = 1$, $x = 0.593$, and $t = 695°$ C.; and that both the carbon isothermal and Fe-Fe_3C isothermal in the P-x diagram coincide in their entire length with each other at 693° C.

Phenomena of Pressure Change during Carburization and Decarburization

If a current of CO is rapidly passed over crystals or fragments of crystals of the mineral magnetite at a temperature of about 800° to 1000° C.; or if a closed reaction vessel is used, if the charging and withdrawing of CO are rapidly repeated, the surface and fissures of the oxide are quickly reduced and carburized so that it becomes covered by thin crusts, the composition of which ranges from high-grade oxide, in the inner layer, to highly carburized iron in the outer layer. Even a rich deposition of soot upon the surface may be effected by a sufficiently rapid supply of fresh CO. But if the supply of CO is stopped and the whole system is allowed to stand with the reaction taking place in a confined space and kept at a definite temperature, the carbon content of the solid, phase is gradually oxidized by oxygen produced by dissociation of the solid and the pressure of the system is gradually increased. The following experiments show the manner of pressure-change with regard to time.

EXPERIMENT SERIES 15

No. 1. Temperature, 907° C. Initial solid phase, 17.7414 gm. of fragments of magnetite crystal not larger than grains of corn, surface being previously reduced and carburized. Initial gas phase, CO.

In the tables h is reading of mercury column in right side of capillary tube of manometer; t is time, in minutes; P is pressure, in atmospheric units.

t	h	P	t	h	P	t	h	P
0	467	1.3312	50	462		105	469	1.3344
2	460		55	463		110	469	
5	457		60	466		115	469	
10	455	1.2707	65	467		120	469	
15	455		70	467.5	1.3270	125	469	
20	455		75	467.5		130	469	
25	455		80	467.5		150	474	1.3606
30	455		85	467.5		165	474	
35	455.5		90	467.5		180	474	
40	459		95	467.5		190	474	
45	460		100	468		200	474	

A gas analysis at the end gave 79.01 per cent. CO.

No. 2. Temperature and initial conditions, same as in No. 1.

t	h	P	t	h	P	t	h	P
0	475	1.3691	45	468		90	475.6	
5	467		50	471		95	475.6	
10	466.5	1.3252	55	472.5		100	478.5	
15	466.5		60	473	1.3546	105	480	
20	466.5		65	473		110	481.5	
25	466.5		70	473		115	482.5	1.405
30	466.5		75	474		120	482.5	
35	467		80	474.4		150	482.5	
40	467.5		85	475.6	1.3601			

A gas analysis at the end gave 84.44 per cent. CO.

No. 3. Temperature, 853° C. Initial conditions, same as in No. 1.

t	h	P	t	h	P	t	h	P
0	443	1.2069	40	428		120	431	
2	433		50	428		130	432	1.1542
5	427	1.136L	60	428		140	432	
10	427		70	428		150	432	
15	427		80	430		160	432	
20	427		90	431	1.1481	170	432	
25	427		100	431				
30	428	1.1362	110	431				

A gas analysis at the end gave 76.70 per cent. CO.

These results are graphically represented in Figs. 7 and 8, which represent the same type of pressure change. First, the pressure falls with remarkable speed, then after remaining stationary for some time, it increases rapidly; after a second pause, it again increases; a third pause is succeeded by the third increase; after the fourth pause there is no further pressure change. Many similar experiments were made by the writer and graphs of similar type were always obtained.

The first horizontal seems to represent an equilibrium state of reaction 3. If the reaction starts from pure CO and if P_0 is the initial pressure of the system,

$$xP = P_0 - 2(P_0 - P) \tag{17}$$

where P = total pressure and x = gaseous composition as before.

The intersection of this hyperbola in the P-x plane with the carbon isothermal should be the point where an equilibrium is established between soot and the gaseous phase. Exactly the same statement holds true with the reaction

$$3Fe + 2CO \rightarrow Fe_3C + CO_2$$

in which the point of intersection of the hyperbola with the Fe-Fe_3C isothermal is where the above equilibrium is actually established.

Fig. 5 shows that an equilibrium is established between carbon and its oxides at 907° C. when $x = 0.972$ and $P = 1$. This gives 33.742 as the equilibrium constant, from which $x = 0.9649$ when $P = 1.2707$ and $x = 0.9636$ when $P = 1.3252$. From equation 17,

$$P_0 = (2 - 0.9649) \times 1.2707 = 1.315, \text{ in experiment 1}$$

and

$$P_0 = (2 - 0.9636) \times 1.3252 = 1.373, \text{ in experiment 2}$$

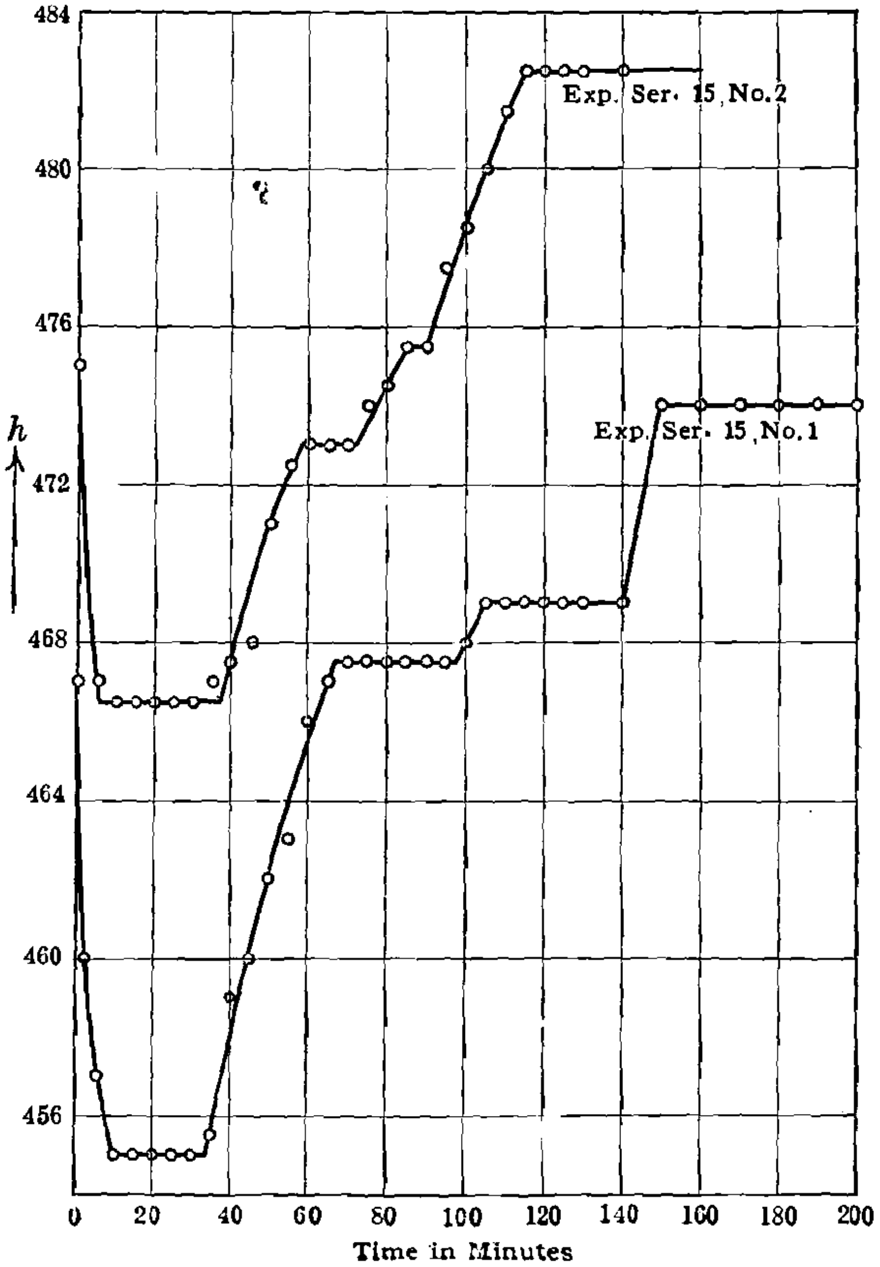


Fig. 7.—Experiment Series 15. Temperature 907° C.

These values of P_0 should be equal to the initial pressure in each experiment, respectively, if it is assumed that the first horizontals in Fig. 7 represent the equilibrium states of soot and gases. Comparing these values with those actually measured, it is found that their agreement is

No.	P_0 Calculated	P_0 Measured	Difference
1	1.315	1.331	−0.016
2	1.373	1.369	+0.004

As 0.918 is the value of x corresponding to the Fe-Fe_3C equilibrium at 907° C., in Fig. 5, $x = 0.8999$ for $P = 1.271$. P_0 in experiment 1 would then be 1.398 if the first horizontal in Fig. 7 is assumed to be an equilibrium state of the system Fe-Fe_3C, and gases. As there seems to be no other possible explanation, our first assumption should be correct. This is also the case with experiment 3, where 15.601 is obtained as the equilibrium constant of the carbon equilibrium. Then $x = 0.9362$ when $P = 1.136$ and $P_0 = 1.136 \times (2 - 0.9362) = 1.208$; by actual measurement P_0 was 1.207.

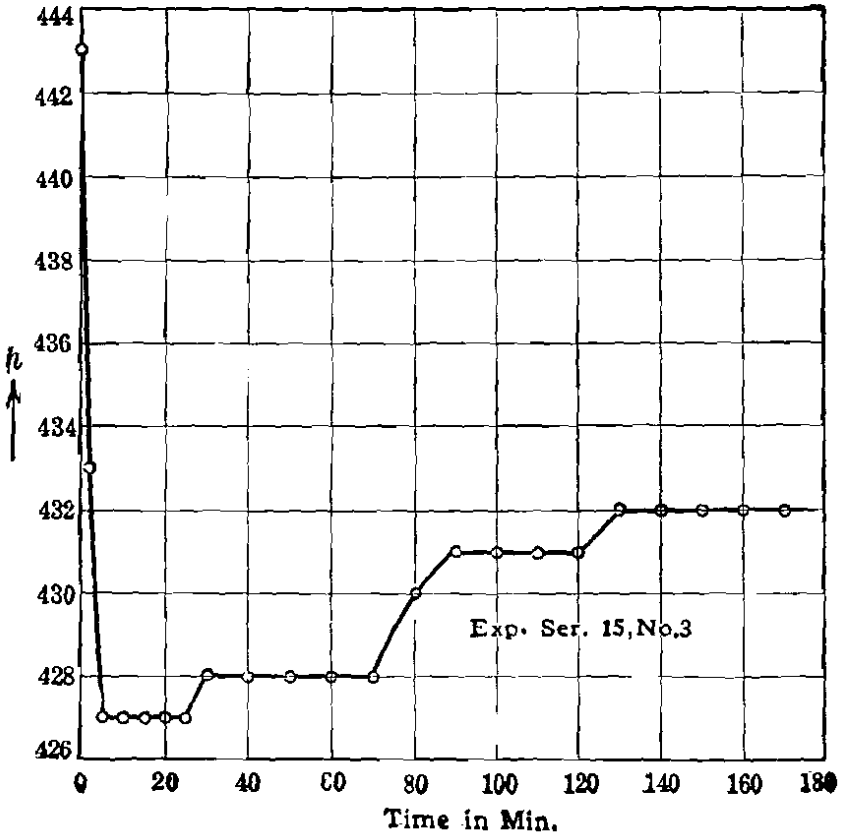


Fig. 8.—Experiment Series 15. Temperature 853° C.

The last (fourth) horizontals in Figs. 7 and 8 apparently correspond to the period during which reduction of iron oxide is effected without pressure change. Then the remaining horizontals (the second and the third) are presumably the equilibrium states of carburization; if that is assumed, a reasonable explanation may be made of the whole process of pressure change. The succession of reactions, considered in this way, may be expressed as follows:

Period of pressure decrease .... $2CO \rightarrow C + CO_2$

Period of first pause .... $\left\{ \begin{array}{l} 2CO \rightleftharpoons C + CO_2 \\ FeO + CO \rightarrow Fe + CO_2 \end{array} \right.$

Period of first increase .... $\left\{\begin{array}{l} 2CO \leftarrow C \quad + CO_2 \\ FeO + CO \rightarrow Fe + CO_2 \\ 3FeO + 5CO \rightarrow Fe_3C + 4CO_2 \\ 3Fe + 2CO \rightarrow Fe_3C + CO_2 \end{array}\right.$

Period of second pause .... $\left\{\begin{array}{l} 3Fe + 2CO \rightleftharpoons Fe_3C + CO_2 \\ FeO + CO \rightarrow Fe + CO_2 \end{array}\right.$

Period of second increase .... $\left\{\begin{array}{l} 3Fe + 2CO \leftarrow Fe_3C + CO_2 \\ 3FeO + 5CO \rightarrow Fe_3C + 4CO_2 \\ FeO + CO \rightarrow Fe + CO_2 \end{array}\right.$

Period of third pause .... $\left\{\begin{array}{l} 3FeO + 5CO \rightleftharpoons Fe_3C + 4CO_2 \\ FeO + CO \rightarrow Fe + CO_2 \end{array}\right.$

Period of third increase .... $\left\{\begin{array}{l} 3FeO + 5CO \leftarrow Fe_3C + 4CO_2 \\ FeO + CO \rightarrow Fe + CO_2 \end{array}\right.$

Period of fourth pause .... $FeO + CO \rightarrow Fe + CO_2$

In Figs. 9 and 10, the changes in gaseous state are roughly represented by arrowhead curves in the *P-x* diagrams, which are made out of the equilibrium constants obtained from the *t-x* diagram.

The last (final) equilibrium may be a trivariant in which a solid solution of FeO in Fe constitutes the solid phase, or it may be the divariant equilibrium corresponding to the FeO-Fe horizontal or even to the Fe_3O_4-FeO horizontal, such as in Fig. 3, according to the conditions of the experiment. In all these cases, the final pressure should not be lower than the initial pressure. If the final equilibrium is the trivariant in which the solid phase is an oxygen-bearing iron containing some carbon, as in experiments 9 and 10 of series 8, the final pressure is lower than the initial.

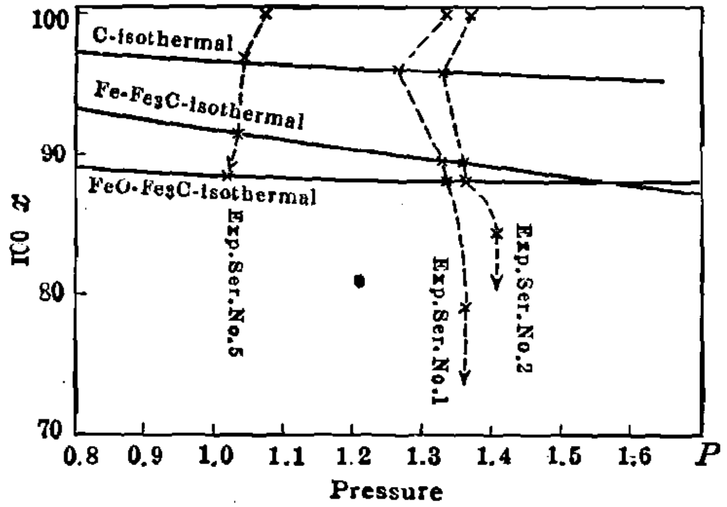


FIG. 9.—TEMPERATURE 907° C.

The lowest pressure does not always occur in the carbon equilibrium; it may happen during any of the carburization equilibria. The following results illustrate this statement. This result is represented in Fig. 11, to which the corresponding P-x diagram is attached.

Experiment Series 15—(*Continued*)

No. 4. Temperature, 772° C. Initial solid phase, 7.0848 gm. reduced iron containing 2.01 per cent. oxygen previously reduced and carburized with CO.

t	h	P	t	h	P	t	h	P
0	487	1.444	12	451		28	441	
1	470		13	451		29	441	
2	465		14	451		30	441	
3	460		15	448		35	441	
4	457		16	446		40	441	
5	455		17	445		50	441	
6	453		18	443.5	1.225	89	441	
7	451	1.257	19	443.5		90	444	1.223
8	451		20	443.5		100	444	
9	451		25	443.5		120	444	
10	451		26	443.5		150	444	
11	451		27	441	1.210			

In this case, the value of P_0 should be corrected from that corresponding to the supposed carbon equilibrium, as the fall of pressure at the beginning is so rapid that a delay of the initial time by a couple of seconds would cause an appreciable error in the result of measurement.

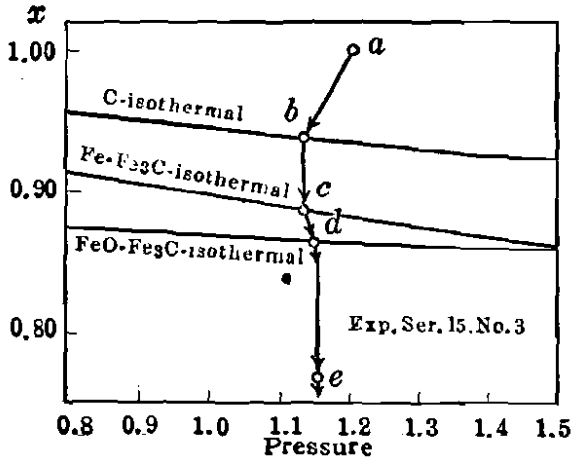


Fig. 10.—Experiment Series 15, No. 3. Temperature 853° C.

Since the coördinates of the point b in the P-x diagram are $x = 0.8295$ and $P = 1.257$,

$$1.257 \times (2 - 0.8295) = 1.471$$

is the corrected value of P_0 on an assumption that no oxidation had taken place during the soot deposition.

The second pause of pressure change occurs at a point the coördinates of which are $x = 0.8045$ and $P = 1.225$. This requires

$$P_0 = 1.225 \times (2 - 0.8045) = 1.465,$$

if the point c lies on the Fe-Fe$_3$C isothermal. This value of P_0 agrees accurately with the corrected value of initial pressure. As there are no other explanations to the phenomena, the assumptions should be correct. As a matter of fact, the curves *ab* and *bc* in Fig. 11 make a continuous curve, the equation of which is $xP = 1.471 - 2(1.471 - P)$. Then, the third pause in pressure change in this experiment must correspond to the period of FeO-Fe$_3$C equilibrium, and the pressure is lowest at this period, as shown in Fig. 11.

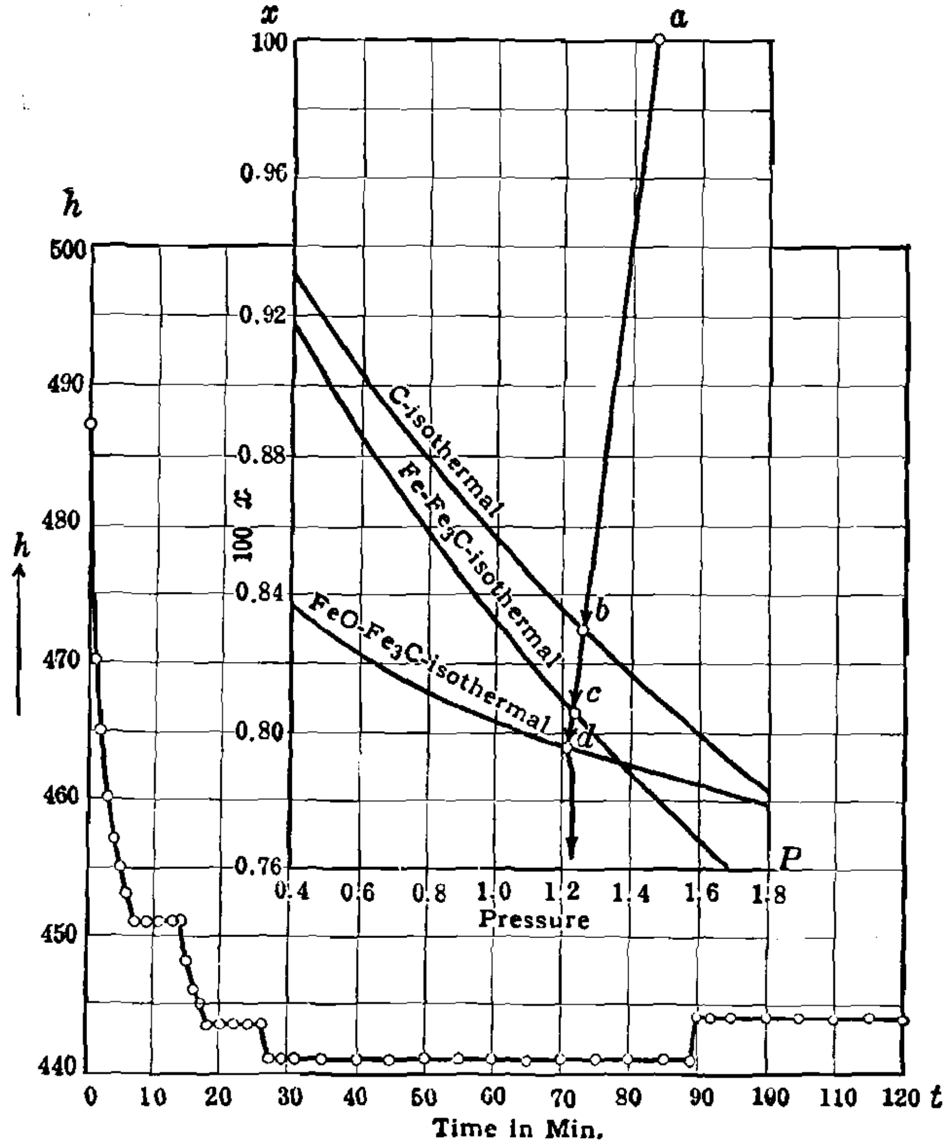


FIG. 11.—EXPERIMENT SERIES 15, NO. 4. TEMPERATURE 772° C.

The actual magnitude of pressures in various states of equilibrium in this series of experiments may perhaps be complex functions of the composition of the solid phase, temperature, velocities of several reactions, etc. In general, the larger the oxygen content of the solid phase, the more pronounced is the displacement to the right of the equilibrium points in the *P-x* diagram, and the increase in pressure begins at the earlier period, hence the lowest pressure occurs at the earlier reaction of the series. A higher oxide of iron, especially when it is in a finely divided form, causes scarcely any depression of pressure at the instant when it is covered by CO in a confined space. If a solid phase contains such a small quantity of oxygen that it causes a FeO-Fe_3C equilibrium when it is covered by CO, the third pause in the pressure change is the final state and the pressure always decreases from the first pause toward the last. When the solid phase is suitable to establish an Fe-Fe_3C equilibrium, the second pause is the final state, the pressure of which is always smaller than the first. An example is given below.

EXPERIMENT SERIES 15—(*Continued*)

No. 5. Temperature, 907° C. Initial solid phase, a well reduced and carburized iron oxide.

t	*h*	*P*	*t*	*h*	*P*	*t*	*h*
0	411	1.072	200	401.2		400	398
20	409.3		220	401.2		420	398
40	408		240	401.2		440	398
60	407		260	398	1.020	460	398
80	404.5		280	398		480	398
100	403	1.041	300	398		500	398
120	403		320	398		520	398
140	401.2	1.033	340	398		540	398
160	401.2		360	398		560	398
180	401.2		380	398		600	398

This result is expressed in the *P*-*x* diagram in Fig. 9. All these facts concerning the pressure change may be explained from the nature of the carburization equilibria, hence, vice versa, the former may be said to afford a proof to the latter.

Discussion of Result

The chemical equilibrium on the FeO-Fe_3C curve in the *t*-*x* diagram is one of the divariant system having three components and phases. Equilibrium is established when the oxygen-dissociation pressure of one of the two solid phases becomes equal to that of the gaseous phase, hence that solid phase must show a definite dissociation pressure at a definite temperature and pressure. For the sake of simplicity, this solid phase is denoted by S_1 and the other by S_2. But S_1 may be a solid solution of FeO in Fe and S_2 carburized iron, or S_1 may be an intermediate product of carburization containing Fe, C, and O, while S_2 is a solid solution of FeO in Fe with or without carbon content.

According to the first view, the ratio FeO:Fe in the solid solution is constant at a definite temperature and pressure, but increases with increase of pressure and temperature. When CO acts upon this, some part of it may be reduced and carburized, but the remaining part retains the original ratio of FeO:Fe. For instance, if the ratio is expressed by $3:x$, the reaction may be represented by the equation

$$\underset{\substack{\text{solid solution}\\ S_1}}{3\mathrm{FeO}.x\mathrm{Fe}} + 5\mathrm{CO} \rightleftharpoons \underset{\substack{\text{solid solution}\\ S_2}}{x\mathrm{Fe}.\mathrm{Fe_3C}} + 4\mathrm{CO_2}$$

where x varies with temperature and pressure.

When nearly all of the S_1 is thus transformed to S_2 the remaining trace of S_1 may be dissolved by S_2. In that case the system increases its freedom by one and shows the transitional equilibria from the lower to the upper carburization curve. The only difficulty in this mode of interpretation is the assumption that $3FeO.xFe$ must react like a compound and that neither FeO nor Fe can react separately upon the surrounding gases.

According to the second view, S_1 is an intermediate product of carburization containing Fe, C, and O. It may be a solid solution of FeO with carburized iron, or Fe (or FeO) containing some quantity of the surrounding gas dissolved. If S_1 is such a substance, it can be easily imagined that its oxygen content, and consequently its oxygen pressure, varies concurrently with temperature and pressure. So long as S_1 exists in the system and its oxygen-dissociation pressure is larger than that of the surrounding gas, CO must first attack S_1; the latter must be reduced and CO_2 produced. This will, of course, alter the composition of S_1, and some amount of carburized iron must be separated. As no more than two solid phases can exist this carburized iron should go over the S_2 phase. S_2 is also attacked by CO as long as its oxygen pressure is larger than that of the gas phase. This will deprive S_2 of its oxygen (or FeO) content and supplies the S_1 phase with the new reaction product. The S_2 phase, in this way, loses its oxygen content step by step; hence its oxygen pressure is lowered in the same manner, but as long as it contains sufficient oxygen, some S_1 must be produced which keeps the composition of the gas phase constant if temperature and pressure are fixed.

The mechanics of reaction may be expressed as shown in Fig. 12. The mechanics of decarburization is exactly the reverse as shown in Fig. 13. The Fe-Fe_3C equilibrium is also one of the divariant system, but no solid phase showing oxygen pressure is on the left side of the equation

$$3\mathrm{Fe} + 2\mathrm{CO} = \mathrm{Fe_3C} + \mathrm{CO_2}$$

Therefore the existence of some solid phase showing a definite oxygen-dissociation pressure at a definite temperature and pressure must be assumed. Let this substance be designated R_1, and the other solid phase R_2. As to the composition of R_1 and R_2 and the parts played by them in the course of carburization, two possibilities may be considered. The first is to assign R_1 to a solid solution of FeO in Fe, and R_2 to carburized iron. The ratio FeO:Fe in R_1 and, hence, the composition of gas standing in equilibrium with it are to be considered constant if temperature and pressure are fixed. The mechanics of reaction are represented as follows:

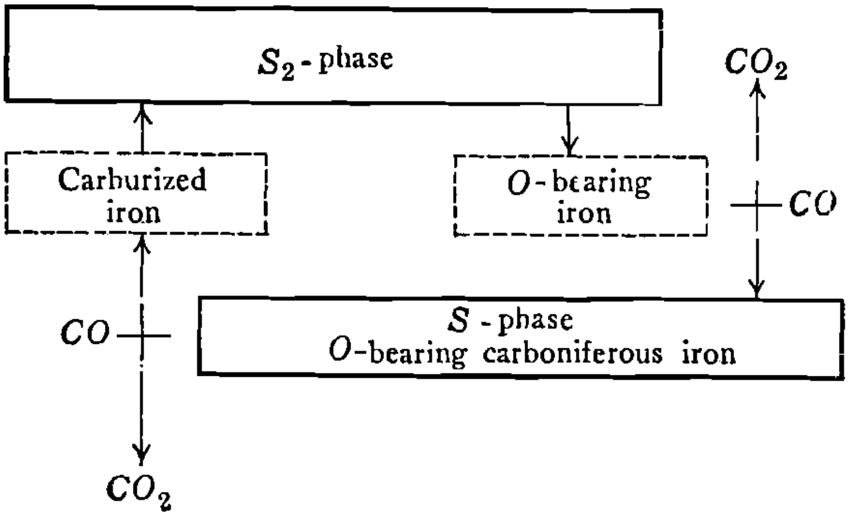
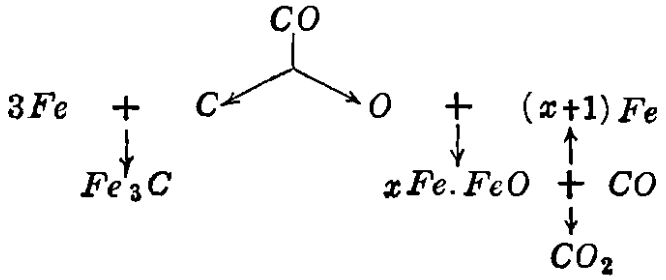


FIG. 12.—MECHANICS OF CARBURIZATION.

$$
\begin{aligned}
x\text{Fe}.\text{FeO} + \text{CO} &= (x+1)\text{Fe} + \text{CO}_2 \\
\text{CO} &= \text{C} + \text{O} \\
(x+1)\text{Fe} + \text{O} &= x\text{Fe}.\text{FeO} \\
3\text{Fe} + \text{C} &= \text{Fe}_3\text{C} \\
\hline
\text{summing up } 3\text{Fe} + 2\text{CO} &= \text{Fe}_3\text{C} + \text{CO}_2
\end{aligned}
$$

Diagrammatically represented,



However, oxygen-bearing iron and carburized iron dissolve each other to a certain extent, as was proved by the existence of the trivariant carburization equilibria in experiment series 8. Then the existence of C in the R_1 phase considered in this way must be accepted.

According to the second view, R_1 contains carbon and is a solid solution of the type $x\text{Fe}.(u\text{Fe}.v\text{C}.w\text{O})$. This solid phase is attacked by CO as long as its oxygen-dissociation pressure is larger than that of the surrounding gas. But the reaction product should not constitute a separate phase—it must go over into R_2 phase. This at once shows that the new product is carbon-rich iron, which is dissolving into the phase of carburized iron (R_2). If one gram-atom of C is transferred to the R_2 phase as the result of the action of one molecule of CO, then R_1 phase requires one molecule of CO to compensate for the loss of one gram-atom has been deprived; the latter should be supplied by the R_2 phase. In other words, one molecule of CO combines with the proper amount of iron

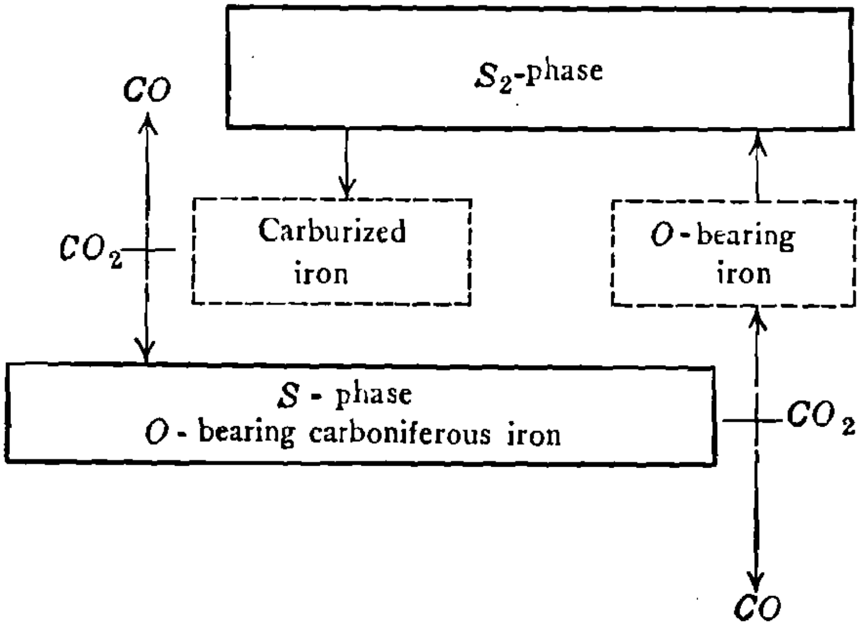


FIG. 13.—MECHANICS OF DECARBURIZATION.

of R_2 phase and joins with the remaining part of the R_1 phase to correct its dissociation pressure, which is constant in the system as long as the two solid phases exist therein. Then the result exactly coincides with the reaction

$$3\mathrm{Fe} + 2\mathrm{CO} = \mathrm{Fe_3C} + \mathrm{CO_2}$$

Then the part played by R_1 is entirely catalytic and the mechanism of the reaction may be expressed as follows:

$$(m\mathrm{Fe}.v\mathrm{C}.w\mathrm{O}) + \mathrm{CO} = [(m - a)\mathrm{Fe}.(v - 1)\mathrm{C}.(w - 1)\mathrm{O}] + (a - 3)\mathrm{Fe}.\mathrm{Fe_3C} + \mathrm{CO_2}$$

$$a\mathrm{Fe} + \mathrm{CO} = \mathrm{CO}.a\mathrm{Fe}$$

$$[(m - a)\mathrm{Fe}.(v - 1)\mathrm{C}.(w - 1)\mathrm{O}] + \mathrm{CO}.a\mathrm{Fe} = (m\mathrm{Fe}.v\mathrm{C}.w\mathrm{O})$$

where

$$x\mathrm{Fe}.(u\mathrm{Fe}.v\mathrm{C}.w\mathrm{O}) \equiv [m\mathrm{Fe}.v\mathrm{C}.w\mathrm{O}] \text{ and } m \geq a \geq 3$$

or as shown diagrammatically in Fig. 14. The reaction will continue until the supply of non-carburized iron from the R_2 phase is stopped when the remaining R_1 phase is destroyed by CO and is finally dissolved by R_2.

The existence of oxygen-bearing carboniferous iron is not altogether imaginary. H. M. Caron[7] proved the existence of oxygen in the carburized iron produced by the action of CO upon pure reduced iron. L. Gruner[8] obtained a similar result by employing iron wire instead of reduced iron. F. Giolitti and F. Carnevali[9], during the process of carburization of iron blocks, obtained thick crusts of oxygen-bearing

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[7] *Compt. rend.* (1864) **59**, 335.

[8] *Compt. rend.* (1872) **74**, 226.

[9] *Jnl.* Iron and Steel Inst. (No. 2, 1911) 331.

iron covering the inner core of the carburized iron and intermingled with carbon. P. Georens[10] extracted gases from commercial steels by heating the latter in vacuum at high temperatures, and found the quantity of gas evolved to be three to four times the volume of steel when it was previously deoxidized and the chief constituent of the extracted gas to be carbon monoxide. This fact might well be explained by occlusion, but it may also be assigned to a decarburizing action of oxygen evolved by dissociation of a certain substance chemically combined with oxygen.

The present writer made the following experiment upon this point. About 20 gm. of pure iron oxalate was placed in a hard glass tube and well reduced by a slow current of hydrogen at a temperature slightly below 550° C., after which a slow current of CO was passed through, the tube being kept at the same temperature. At the first stage, the gas was vigorously absorbed by the iron so that none of the gas escaped from the end of the tube. After 1 hr. about one-fifth of the entering gas escaped from the tube. Though the absorption continued for several hours it gradually decreased. The escaping gas was introduced into a hard glass tube which was heated by a gas flame to below dull redness; this caused a black substance to be deposited at the hot part of the second tube. This black substance was strongly attracted by a magnet and some of it dissolved in aqua regia with evolution of gas leaving carbon flakes. The solution then showed iron content.

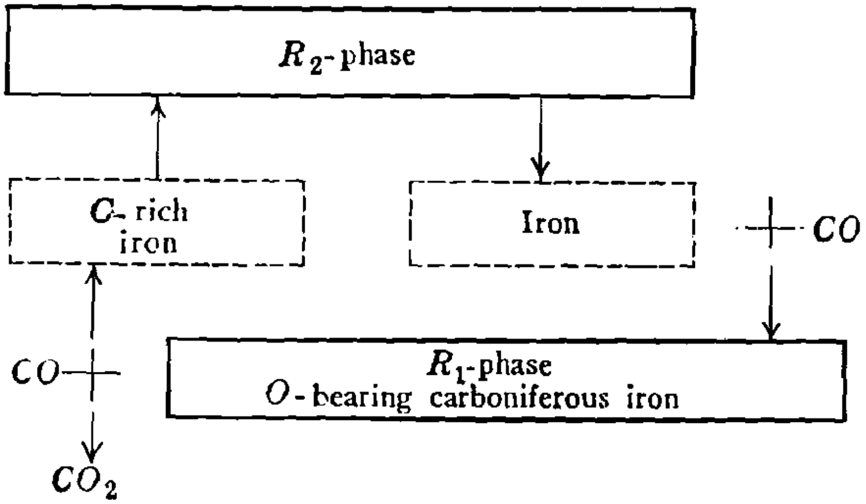

Fig. 14.—Mechanics of carburization.

The black deposit was apparently a decomposition product of some volatile substance resembling iron carbonyls in character. At the hot part of the first tube, the decomposition should have been strong and several complicated reactions between gas and solid may be supposed to have taken place; only a small part of reaction products might have escaped into the second tube.

All of these facts, especially the phenomenon of gas absorption together with the indication of gas reaction upon reduced iron in the above

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[10] *Mitteilungen aus den Eisenhüttenmannischen.* Institut der Königl. Tech. Hoch-

experiment, induced the author to believe that the formation of the oxygen-bearing carboniferous iron, such as R_1 or S_1, is possible, for the reaction under the above conditions of experiment is, in some respect, the same as that which takes place at the higher temperature and under very high pressure as is easily understood from Fig. 6.

Limit of Carburization Temperature and Pressure

The disposition of the FeO-Fe_3C curve in Fig. 5 shows that the latter will approach very closely to a horizontal $x = 1$ at a temperature of about 1300° C. This shows the following facts:

1. At a temperature of about 1300° C., the oxygen dissociation pressure is equal to that of pure CO if the pressure is one atmosphere.

2. At a temperature higher than about 1300° C., the carburizing action of CO does not occur; carburized iron is oxidized to FeO-Fe solid solution even by a current of pure CO under a pressure of one atmosphere.

3. The above limit of temperature increases slightly with increase of pressure.

The Fe-Fe_3C curve in Fig. 5 seems to approach very closely to a horizontal $x = 1$ at a temperature of about 1200° C. Then

1. At a temperature of about 1200° C. the dissociation pressure of R_1 is equal to that of CO, and neither carburization nor decarburization occurs even in a current of pure CO if the pressure is one atmosphere.

2. At a temperature between 1200° and 1300°, and under a pressure of one atmosphere, the dissociation pressure of pure CO is larger than that of R_1 but is smaller than that of S_1; carbon-bearing iron is decarburized even by a current of pure CO, but oxygen-bearing iron may be carburized by the same gas; both reactions end in the formation of oxygen-bearing carboniferous iron proper to that temperature.

3. At a temperature between 1200° and about 695° C., a gas richer in CO than corresponds to the Fe-Fe_3C curve in Fig. 5 will carburize iron under a pressure of one atmosphere or more. Under the lower pressures, both the lower and higher boundaries of temperature are correspondingly decreased, but under the higher pressures the reverse holds true.

4. The lower the pressure, the larger is the value of x at equilibrium, hence purer gas (richer in CO) is required for carburization; the higher the pressure the easier is the carburization; *i.e.*, the same degree of carburization may be accomplished by less pure gas, compared with the case of lower pressure—if the same gas is employed, the velocity of reaction is greater in the case of higher pressure.

5. Under a pressure higher than that corresponding to the curve ***E-F*** in the *P-x* diagram (Fig. 6), the first carburizing reaction taking place after the reduction of oxide with CO is

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

Under a pressure higher than that corresponding to the curve *G-H* in the same diagram, the carburizing reaction according to the above equation occurs upon iron oxide the oxygen pressure of which is higher than that corresponding to a saturated solution of Fe in FeO.

6 At a temperature below 695° C and under a pressure of one atmosphere or more, the carbon isothermal sinks beneath the two carburization isothermals in the *P-x* plane, and no carburization, in the ordinary sense, can occur.

7. All the conditions of decarburization are just the reverse of those of carburization.

APPLICATIONS OF THEORY OF CARBURIZATION

Casehardening

That part of the casehardening theory of Giolitti and Carnevali[11] that is related to the present research may be summarized as follows:

1. As iron carbide dissolves in iron above 700° C., the mixed crystal may show several carburization curves, according to the content of carbon in iron as represented by *a*, in Fig. 15.

2. One of these curves may coincide with the carbon isothermal throughout its entire length; the mixed crystal of that composition is designated as the "Σ-mixed crystal."

3. If the gaseous condition in the reaction vessel always corresponds to a point on the carbon isothermal, the carburizing action of the gas converts the whole iron into the Σ-mixed crystal.

4. Under a pressure higher than the point *O*, Fig. 15, the formation of magnetic oxide must accompany that of the Σ-mixed crystal; within the range of pressure between *O* and *Q*, the formation of ferrous oxide must accompany that of the Σ-mixed crystal; under a pressure lower than *Q*, the Σ-mixed crystal alone is formed, hence the carburization must be performed under a pressure lower than *Q*.

5. Curves *3*, *4*, and *5* displace toward the right concurrently with rising temperature as the result of which *O* and *Q* displace toward the right and higher pressure: therefore carburization may be performed at higher pressures without oxidation. The displacement of *O* and *Q* is controlled by the composition of the iron.

It is at once evident that there can be no such *P-x* diagram as that shown in Fig. 15. The meeting of curves *1*, *2*, and *3* at one point occurs only at 695° C. and curve *5* also passes through the same point. The carbon isothermal lies to the left of one or both of the carburization curves under a pressure of one atmosphere or more at temperatures lower than 695° C.; in this case no carburization is possible. This error is due to the basing of these curves upon the theory of Schenck that curves *1*, *2*,

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[11] *Jnl.* Iron and Inst. Steel (No 2, 1911) 307–352.

and *3* must always pass through a common point. Therefore, Giolitti and Carnevali's Σ-mixed crystal, which, at the temperatures suitable for carburization, should be nothing other than iron saturated with carbon, was always obliged to show a higher oxygen pressure than that corresponding to the Fe-Fe_3C isothermal. The oxygen pressure should be reduced to that of the carbon isothermal when the carburization is finished.

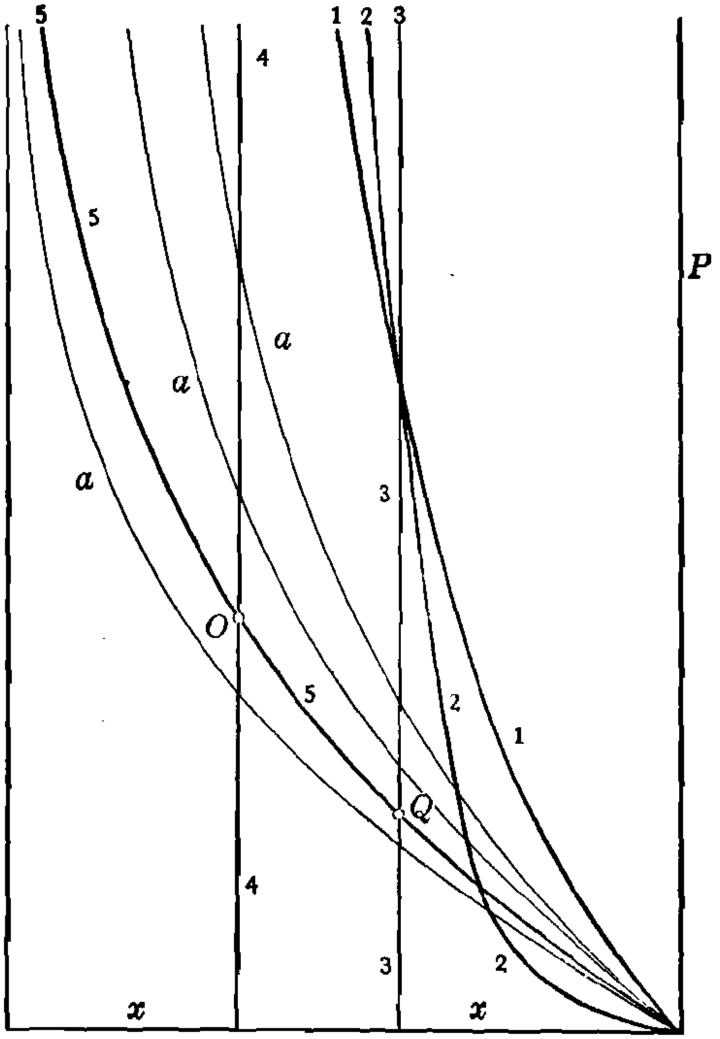

FIG. 15.—FROM GIOLITTI AND CARNAVALI.

1. Fe-Fe_3C isothermal.
2. FeO-Fe_3C isothermal.
3. FeO-Fe isothermal.
4. Fe_3O_4-FeO isothermal.
5. C isothermal.

The present author offers as a typical *P-x* diagram for carburization temperatures Fig. 16, which is a *P-x* diagram for 950° C.; the upper three isothermals were plotted from the corresponding equilibrium constants. Carburization of iron is possible at 950° C., for instance, in a CO and CO_2 mixture containing more than about 75 per cent. CO and less than six atmospheres total gaseous pressure; under a pressure of twelve atmospheres, the necessary amount of CO decreases to about 63 per cent. If the mixed gas is richer in CO than that corresponding to any point on the carbon isothermal, there is soot deposition together with carburization.

In other words, a point on the carbon isothermal represents those values of P and x at which soot can exist in the system.

It is highly probable that some substance showing the same oxygen pressure as that of the gaseous phase is formed in the solid phase if an equilibrium is established at any one point on the carbon isothermal. But if the gaseous phase is always richer in CO than that corresponding to that point equilibrium is never established there, hence any fixation of oxygen in the solid phase is avoided even under the pressure represented by the same point. For instance, the point Q never represents the pressure under which FeO should be formed in carburized iron under every circumstance of the gaseous phase. Then why has Giolitti and Carnevali's experiment proved the formation of a thick stratum of compact crust of magnetite on the carburized iron?

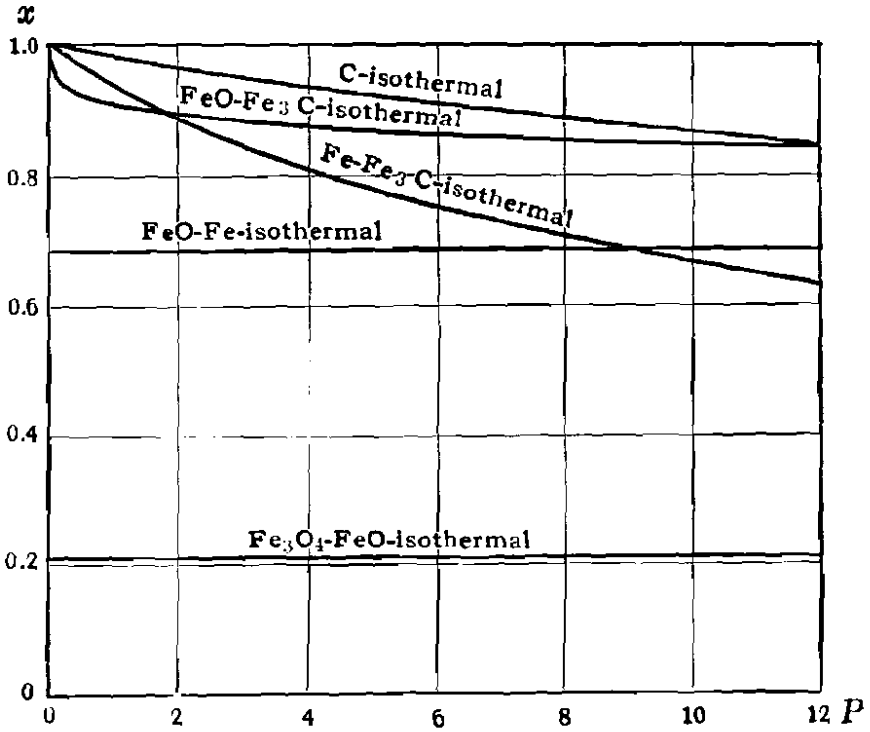

FIG. 16.—P-x DIAGRAM FOR 950° C.

In order to solve this problem, let us make a few calculations. As their experiments were made between 890° and 960° C., assume that it was fixed at 900°. Then, calculating from the value of K_1, it is known that R_1 must show a dissociation pressure corresponding to $x = 0.47$ under the pressure of 25 atmospheres. Even if it is assumed that R_1 is pure iron oxide, its oxygen content does not exceed 23.5 per cent. at 1075° C., and 23.9 per cent. at 863° C. (see Figs. 3 and 4); by graphic interpolation, it is found to be about 23.8 per cent. for 900° C., hence the iron content of the oxide, which is a solid solution of Fe_3O_4 in FeO, must be at least 76.2 per cent. If any higher oxide is present in the system, no carburization should be possible.

An analysis of the crust made by the same authors, however, showed carbon and the oxygen pressure of the former must have been decreased by the latter, otherwise the gas must have acted as a decarburizer instead of a carburizer.

If it was magnetic oxide, or very nearly magnetic as reported by the authors, this might be due to their method of carburization. Giolitti and Carnevali's method of casehardening is accomplished by the action of a so-called mixed agent on heated iron. The mixed agent consists of charcoal, which surrounds the iron block, and a current of CO_2 passed through the reaction vessel with a definite velocity. This mixed agent may produce CO quickly, but the gaseous currents, rich in CO_2, have every chance to touch the heated iron before they are converted to CO causing serious oxidation of the iron. Of course the carburization may go on as long as the gas that touches the surface of the iron is richer in CO than corresponds to the Fe-Fe_3C isothermal, but a gas with a large CO_2 content not only facilitates the formation of R_1, but also decreases the carburization velocity in a marked degree because the difference between the percentage of CO in the gaseous current and that of the gaseous phase in its equilibrium state in a closed vessel should be a factor in determining the velocity of the reaction. As a matter of fact, the reducing action of carbon upon CO_2 is not completed as instantaneously as was expected by the authors, especially at a temperature of 900° or 800° C.

The best practical method is the rapid introduction of CO, instead of CO_2, upon the heated iron with or without carbon enclosure (according to the result required) under as high a pressure as possible. The remaining problem is then the industrial preparation of pure CO. Fortunately the percentage of CO_2 in the escaping gas from the reaction vessel is very small, especially when the velocity of the passing gas is large; hence if the CO_2 content of the escaping gas is reduced by passing this gas through a furnace filled with highly heated carbon, CO_2 may be completely reduced in a short time. The resulting CO is then returned into the reaction vessel. In order to accomplish this operation quickly and completely, the furnace must be kept at high temperature. But the temperature of the carburization vessel should not be kept very high for the carburized iron should not be brought to melting. Moreover, even in the temperature range of 1100° to 1200° C., carburization by the gas reaction is difficult unless we work under fairly high pressures. From the practical standpoint, too, the heating of the carburization vessel to a high temperature like 1100° is not easy to carry out.

On the other hand, the pressure in the furnace for the purification of gas should be low, otherwise the prepared gas would be impure, as is easily understood from the disposition of the carbon isothermals, while the pressure in the carburization vessel should be high enough to facilitate the quick carburization. Therefore the claims of these two reactions are, to some extent, contradictory to each other; they should not be carried out in the same vessel.

Malleable Casting

That which it is desired to oxidize in the practice of malleablization is iron carbide and not iron itself. The reaction should, therefore, be confined to

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

and not to be extended to

$$Fe + O = FeO, \text{etc.}$$

Then, it is clear that the oxygen-dissociation pressure of the gas surrounding the cast iron that is to be malleablized should be always a little higher than corresponds to the Fe–Fe_3C curve in the t-x diagram proper to the adopted pressure; any large excess of oxygen pressure should be avoided, as otherwise iron would be oxidized. This regulation of pressure can be performed by one of the following methods:

1. By the regulation of the velocity at which CO_2, O_2, or air is introduced into the reaction vessel.
2. By the regulation of the composition of the oxidizing gas; for instance, the ratio of $CO:CO_2$ when a mixture of these gases is employed, the ratio of $O_2:N_2$ when air is employed, etc.
3. By the combination of these methods.

By the analysis of the escaping gas the oxygen pressure of the reacting gas is easily determined, it is only necessary to determine the ratio $CO:(CO + CO_2)$ in the gas, for the volume percentage of oxygen is negligible.

Reactions Between Iron, Oxygen, and Carbon in an Iron Blast Furnace

This discussion will be confined chiefly to gas reactions taking place between Fe, O, and C, and will take into consideration neither the influences of the other substances nor the reactions arising between them. Moreover, the study is, in a sense, of a special nature, being confined to an individual furnace, for the conditions may vary in different furnaces; even in the same furnace, they may differ in accordance with the nature of the charges and the mode of operation. Hence only an example, to show the method of investigation, will be given. In this case three kinds of data relating to the conditions of the blast furnace come into consideration: (1) Distribution of pressure, (2) distribution of temperature, and (3) gaseous composition with regard to the height in the furnace. The first was neglected by several previous investigators owing chiefly to the difficulty of measurement; therefore a few approximate assumptions must be made. The iron blast furnace of Gutehoffnungshütte in Oberhausen, whose blast-furnace diagram was determined by W. A. Schlesinger,[12]

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[12] *Stahl u. Eisen* (1911), 1182.

is adopted. It is regretted that the author did not report the percentage of CO and CO_2 in the total gas taken in analysis. In some furnaces this percentage decreases from the lower part toward the top while in others the reverse is the case. Commonly it varies between 34 and 38 per cent.—a variation that has little significance in the calculation of partial pressure of these two gases as compared with the error arising from the calculation of the total pressure. Therefore, it will be assumed to be 36 per cent. and that no variation in this percentage took place throughout the height of the furnace.

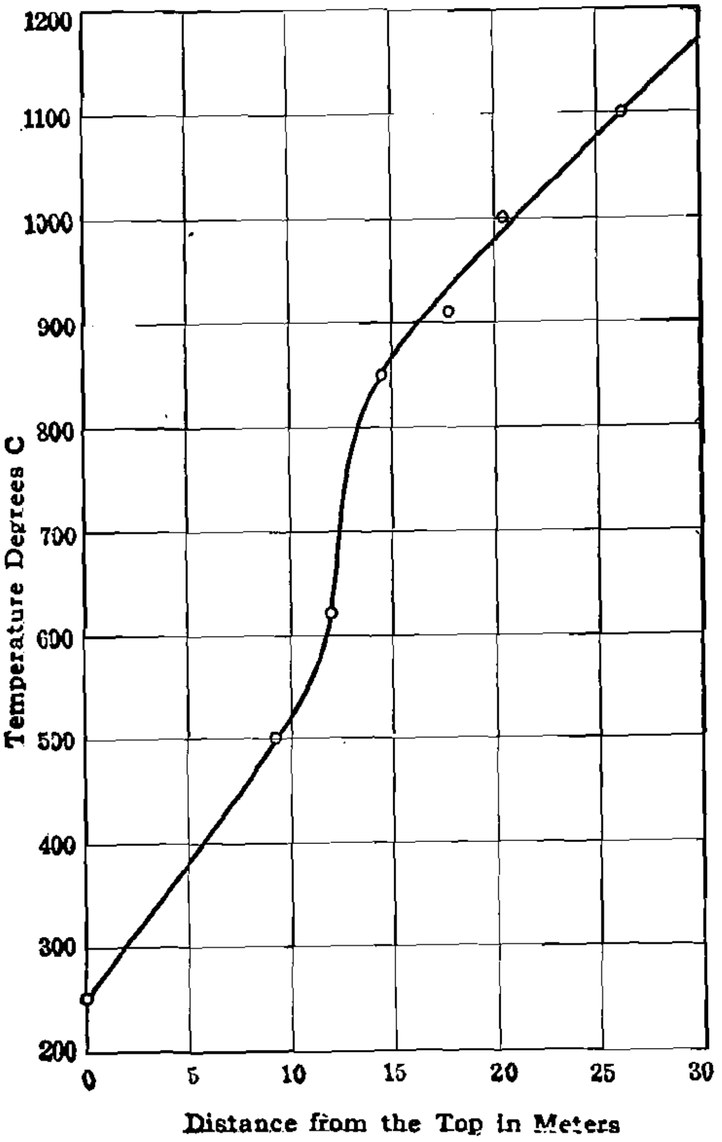

FIG. 17.—DISTANCE-TEMPERATURE CURVE.

The pressure of the blast was reported to have been about 60 cm. (Hg), which corresponds to 1.776 atmosphere in net value; the wind pressure at the top of an ordinary blast furnace having this blast pressure may properly be assumed to be about 200 mm. in water column;[13] this corresponds to a net value of 1.019 atmosphere. The decrease of pressure is, therefore, 0.757 atmosphere. Assume that the pressure at the tuyere level is 1.776 atmosphere and that the decrease of pressure is

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[13] Osann: *Eisenhüttenkunde* (1915) **1**, 380.

proportional to the height of the furnace as a first approximation although it may perhaps be a complex function of temperature, distance from the tuyere level, inner diameter of the furnace, velocities of the chemical reactions, etc. The accompanying table specifies the pressure distribution in this furnace at the time that Schlesinger made his measurement.

Distance from Top, Meters	Temperature, Degrees C.	Total Pressure, Atmospheres	Partial Pressure of CO-CO_2 Atmosphere
27.8		1.776	
26.2	1100	1.732	0.624
20.4	1000	1.574	0.567
18.5	950	1.523	0.548
16.4*	900	1.466	0.522
14.5	850	1.414	0.509
13.5*	800	1.387	0.499
12.8*	750	1.367	0.492
12.4*	700	1.357	0.489
12.1*	650	1.348	0.485
12.0	620	1.346	0.485
11.7*	600	1.338	0.482
9.2	550	1.269	0.457

* These numbers were found from the distance-temperature curve shown in Fig. 17.

The equilibrium gaseous compositions of several reactions occurring at the various heights of the furnace may be found by interpolation from Figs. 5, 6, and 13.

Distance from Top, Meters	Temperature, Degrees C.	Equilibrium Composition of Gas, Per Cent. CO in CO-CO_2 in				
		Fe_3O_4-FeO Equilibrium	FeO-Fe Equilibrium	FeO-Fe_3C Equilibrium	Fe-Fe_3C Equilibrium	C Equilibrium
26.2	1100	15.8	73.0	95.6	98.9	
20.4	1000	19.8	70.0	92.9	97.0	99.6
16.4	900	23.5	67.0	90.3	95.4	98.3
14.5	850	26.2	65.4	88.6	94.5	97.0
13.5	800	29.6	63.8	86.0	92.3	94.4
12.8	750	33.2	62.2	79.0	87.0	88.3
12.4	700	36.7	60.2			73.8
12.1	650	40.4	60.0			50.3
11.7	600		55.6			30.3
9.2	550		52.9			

Each of the equilibrium curves may be plotted from this table on the blast-furnace diagram drawn by Schlesinger as shown in Fig. 18:

Curve I is an equilibrium curve of reaction $Fe_3O_4 + CO \rightleftarrows 3FeO + CO$

Curve II is an equilibrium curve of $FeO + CO \leftrightarrows Fe + CO_2$

Curve III is an equilibrium curve of $3FeO + 5CO \rightleftarrows Fe_3C + 4CO_2$

Curve IV is an equilibrium curve of $3Fe + 2CO \rightleftarrows Fe_3C + CO_2$

Curve V is an equilibrium curve of $2CO \rightleftarrows C + CO_2$.

Curve VI represents the actual gaseous composition measured by Schlesinger.

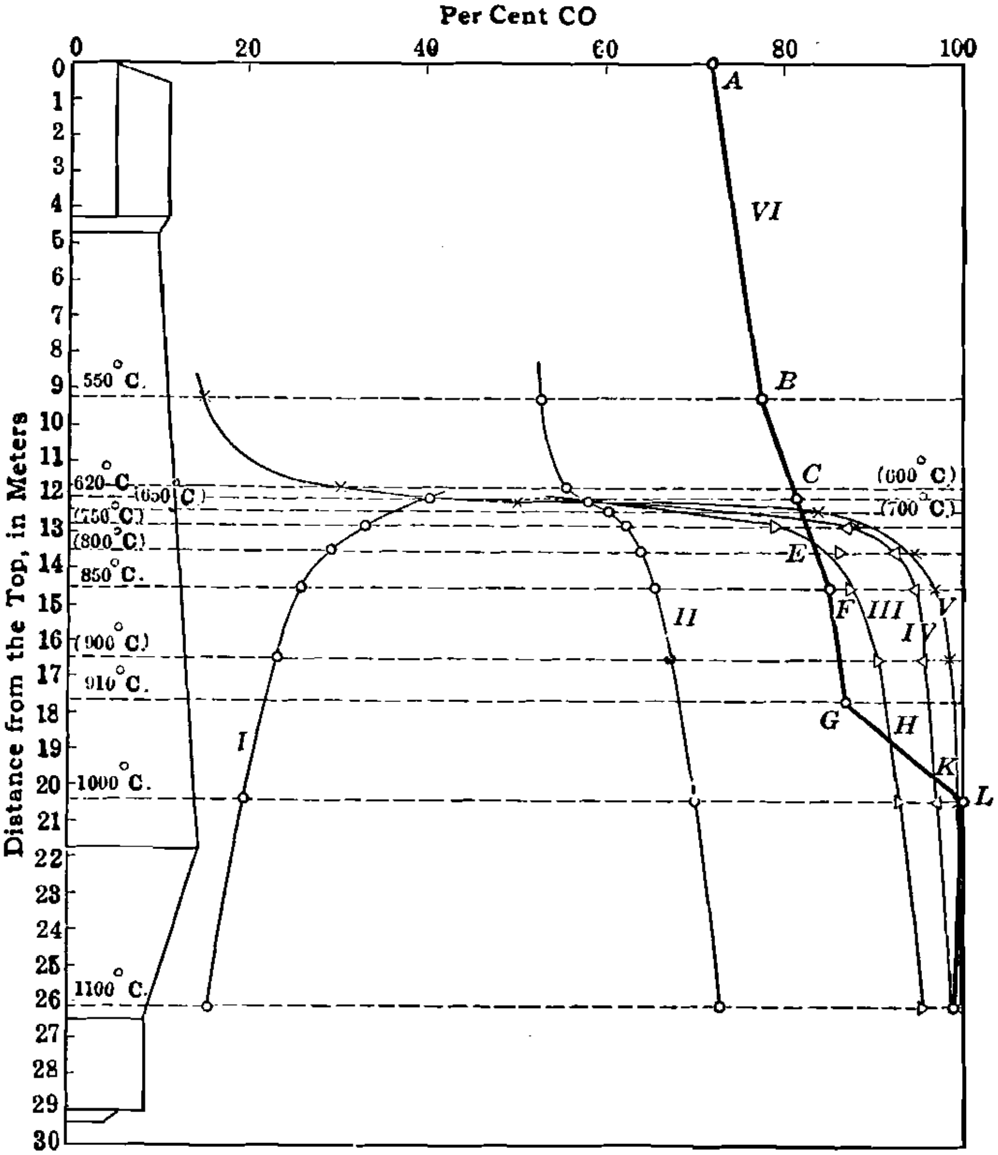

FIG. 18.

That part of curve VI corresponding to temperatures lower than 910° C. is quite similar to the FeO-Fe curve, showing that the main part of the reducing power of this blast furnace is used for the reduction of ferrous oxide. Ferrous oxide is difficult to reduce owing to its low dissociation pressure, while the reductions of ferric oxide and magnetic oxide are easier because of their high dissociation; the removal of oxygen, corresponding to about 24 per cent. of the original oxygen content will convert the latter wholly into a mixture of ferrous oxide and iron.

The form of the curve IV, however, must be affected by the following factors: (1) Evolution of CO_2 from limestone; (2) reaction of soot deposition; (3) reduction of higher oxides; (4) carburization; (5) reducing action of C upon CO_2.

For the dissociation pressure of $CaCO_3$, J. Johnstone[14] gave the following numbers:

Temperature, Degrees C.	Pressure, Mm. Hg.	Temperature, Degrees C.	Pressure, Mm. Hg.
1000	2710	750	68.0
950	1490	700	25.3
900	773	650	8.2
850	373	600	2.35
800	168		

Comparing these values with the partial pressure of CO_2 and the total pressure of the gaeous flow in the blast furnace, gives the values shown in the accompanying table where the partial pressures of CO_2 were calculated from curve VI.

Distance from Top, Meters	Temperature, Degrees C.	Partial Pressure of CO_2, Mm. Hg.	Total Pressure, Mm. Hg.	Dissociation Pressure of $CaCO_3$ Mm. Hg.
26.2	1100	10	1316	
20.4	1000	0	1192	2710
18.5	950	38	1158	1490
16.4	900	56	1114	773
14.5	850	58	1075	373
13.5	800	63	1054	168
12.8	750	66	1039	68
12.4	700	67	1031	25
12.1	650	70	1025	8
11.7	600	70	1017	2
9.2	550	78	964	

By graphic interpolation, it is known that the decomposition of limestone begins at about 12.8 m. from the top and that the strong decomposition begins at about 17.3 m. (very near to zone *G*). Since there is no partial pressure of CO_2 at zone *L*, Fig. 18, the decomposition should be finished at least before the charge reaches that zone. Hence the interval between these two zones *G* and *L* should be a zone of strong decomposition of limestone. The sudden fall of curve VI at this zone causes the belief that there may be some connection between these two facts. A number of other blast-furnace diagrams show this kind of break in the curve, and the type of curve shown in Fig. 18 seems to represent the most common and normal state of an iron blast furnace. A diagram of a blast furnace in Oberschlesich made by Nietz (Doktor Dissertation, Aachen) and the diagrams quoted by C. Brisker[15] show this kind of break in the curves

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[14] *Jnl.* Amer. Chem. Soc. (1910) **32,** 944

[15] *Stahl u. Eisen* (1908) **1,** 391.

although the degree and position of the break may differ in different furnaces according to the velocity of wind, distribution of temperature and pressure, nature of charge, etc.

Another possible explanation of that portion of curve VI is that it corresponds to the uppermost steep portion in the equilibrium curves in Figs. 2, 3, and 4; in other words, ferrous oxide ceases to be a definite solid phase at the point *G* and the subsequent reduction is that of the solid solution of ferrous oxide in iron, which should cause a gradual rise of the curve VI. This transition, however, takes place gradually, as in Fig. 4, etc., so that it may not cause such a sudden change of the gaseous composition though it may have some influence upon it. Therefore this break of the curve is presumably an indication of the sudden deterioration in the quality of gas resulting from sudden decomposition of limestone.

The reaction of soot deposition takes place about 12 m. from the top of the furnace. "Das Hängen," if any, must occur in or above this zone. This reaction may have some influence on curve VI, as C. Brisker has generalized from the instances of several other furnaces, but it must be remembered that the deposited soot is oxidized immediately after the charge has traversed the zone about 12.5 m. from the top so that the effect of this reaction on the gas flow may compensate that of the soot deposition. That part of the latter which lies above point *G* seems to be determined chiefly by the disposition of the Fe-FeO curve.

The reduction of higher oxides may occur even in that part of the zone in which the soot deposition begins. But the reaction cannot be conspicuous and its effect on the form of curve VI is naturally very small because curves I and II are high and the velocities of reactions are small on account of low temperatures. The strong reduction of the higher oxides begins as soon as the charge has passed through the zone at which the oxidation of soot begins. The reaction may be finished in a short distance on account of its enormous velocity; the nature of the reaction resembles that of the decomposition of limestone. Perhaps the steep inclination of the curve between points *B* and *F* has an intimate relation with this reaction.

The reactions of carburization may take place 12.5 to 13 m. from the top (*C* to *E*). Any carbon fixed in this zone is thoroughly oxidized afterward and no carburization occurs until the charge arrives at zone *H*, which is about 18.7 m. from the top. Here the carburization of FeO may begin while at zone *K*, which is about 19.75 m. from the top, the carburization of iron may take place. At the tuyere level, the temperature is too high for the existence of iron carbide, so the carbon content in iron may be oxidized by the blast. But the reaction between carburized liquid iron and the surrounding gas is entirely beyond the scope of the present research.

As the result of the rapid carburization at the lower part of the furnace, a large quantity of CO_2 may be produced; this may have some influence upon the sudden depression of that part of curve VI between *G* and *L*.

At the lower part of the furnace, coke is able to convert oxygen or CO_2 into CO very rapidly on account of the high temperature. According to van Voltens[16] the free oxygen, which is so strongly blown in, can exist as such only in a space 60 cm. in diameter around the tip of the tuyere; the region in which CO_2 can exist seems to be a little larger. At any rate, the combustion of free carbon, together with the velocity of the blast, must be the most potent factors determining the position of curve VI, while the reduction of ferrous oxide and the decomposition of limestone are other prominent factors which determine the disposition of the same curve.

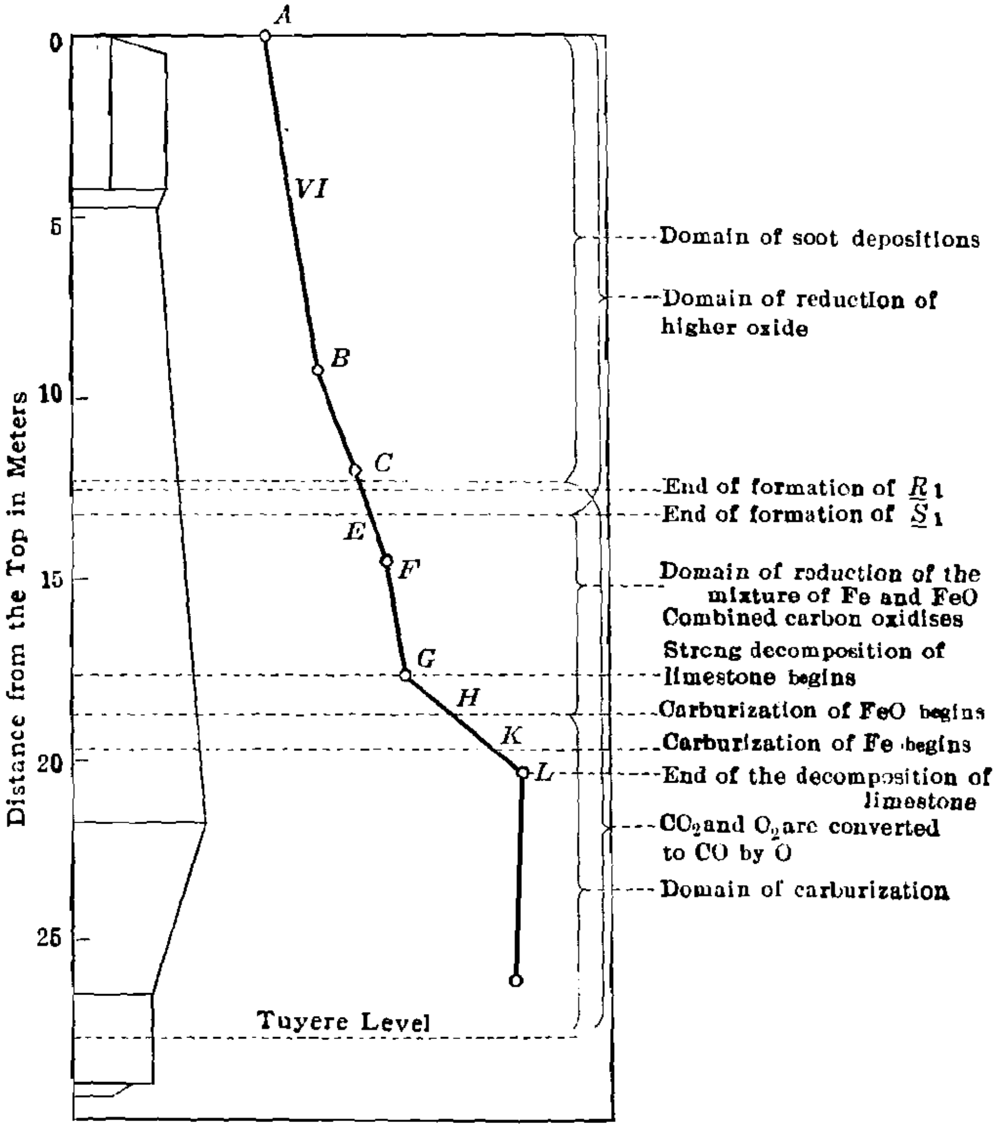

FIG. 19.

The foregoing may be summarized in the diagram shown in Fig. 19. It must be remembered that all the boundaries of reactions must devi-

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[16] *Stahl u. Eisen* (1893) 26.

ate in some degree from those represented in this diagram according to the velocity of the blast. In other words, curve VI, which illustrates the reactions, should lag upwards.

Problem of Quick Smelting

It is well known that increasing the blast pressure accelerates smelting. In some modern American iron blast furnaces, especially those built during the war, such pressures as 1200 gm. per sq. cm. are said to have been adopted in order to increase the capacity of the furnace. There may be many reasons why smelting is accelerated by increasing blast pressure, but here it will be considered only from the standpoint of the gas reactions.

By increasing the blast pressure, the following changes in the gas flow may be expected to occur: The velocity of gas flow in the furnace is increased; the partial pressure of the reacting gas is increased; and the range of high temperature in the furnace is extended toward the top.

It is scarcely worth while to consider that the range in which the free oxygen or CO_2 exists around the tip of the tuyere is extended by increasing the blast pressure, for, should this happen, it would be a negligible enlargement of the space especially when the temperature of the glowing carbon is increased by that operation.

The increased velocity of gas flow displaces the actual gas-composition curve in the blast-furnace diagram upward and leftwards; consequently it enlarges the distances from that curve to every other equilibrium curve, and these enlargements should increase the reaction velocities. Moreover, the increased velocity of gas flow extends the zone in which final carburization may be effected, which necessarily results in quicker smelting.

The extension of the high-temperature zone increases that part of furnace where the reduction and the carburization can be made effectively, thus shortening the "pass-through time."

The increase of the partial pressure of $(CO + CO_2)$ is also desirable for it lowers the position of the carburization curves and hence causes the increase of carburization velocity. Even the simple reduction of oxides should be accelerated by this change on acount of the increase of concentration of CO in $(CO + CO_2)$.

Perhaps the quick smelting in some modern furnaces is attributable chiefly to the combined effect of the conditions enumerated. However, the introduction of nitrogen in the furnace is not advisable, if considered from a purely scientific standpoint. Oxygen or the exhaust gas mixed with a suitable quantity of oxygen instead of air, would be effective, because, in this way, it is possible to maintain the partial pressure of (CO +

tion of carburization curves in the blast-furnace diagram in a marked degree. Moreover, the ratio of CO_2 produced by the reactions to that of CO would always be very small, hence the actual gas composition curve would be raised much higher than the ordinary position. In an electric iron smelting furnace the realization of this condition is relatively easy.

Summary

1. Equilibrium compositions of gas phase in the system CO, CO_2, and Fe containing more than a few per cent. of oxygen were measured at 863 C., 1070 C., and 1175 C.

2. Equilibrium compositions of gas phase in the system (*a*) CO, CO_2 FeO (saturated with Fe), and Fe (saturated with FeO) and (*b*) CO, CO_2, Fe_3O_4 (saturated with FeO), and FeO (saturated with Fe_3O_4) were measured at several temperatures higher than 700 C.

3. Pressures in the above two equilibrium systems containing free carbon as a permanent solid phase were calculated.

4. Dissociation pressures of FeO (saturated with Fe) and Fe_3O_4 (saturated with FeO) were calculated.

5. Equilibrium composition of gas phase in the systems (*a*) FeO, Fe_3C, CO, and CO_2 and (*b*) Fe, Fe_3C, CO, and CO_2 were measured in a temperature range of 700° to 1100° C. The formation of oxygen-bearing carboniferous irons and the mechanism of carburization were inferred.

6. The compositions of gas phase in the carburization equlibria under various temperatures and pressures were calculated.

7. Some applications of the carburization theory on the practice of casehardening, malleable casting, and the explanation of blast-furnace diagram etc. were treated.

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DISCUSSION

Haakon Styri,* Philadelphia, Pa.—It is interesting to see that Mr. Matsubara's data on the dissociation pressures of FeO confirm calculations made by Professor LeChatelier about ten years ago. I have

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used LeChatelier's data to calculate the equilibrium conditions in the steel furnace for various concentrations of oxygen, carbon, manganese, and silicon. We are greatly in need of more accurate data about these equilibrium conditions and it would be extremely valuable if Mr. Matsubara, or somebody else, could undertake to establish equilibrium at higher temperatures than were here experimented with, including temperatures higher than the melting point of iron.

J. W. RICHARDS,* South Bethlehem, Pa.—Mr. Styri says that we should know the equilibria at higher temperatures. If the equilibria pressures at lower temperatures are known, it is possible, in general, to make a pretty good estimate of the pressures at the higher temperatures. The dissociation pressures of iron oxides will follow the same type of formula; *viz.*, $\log p = -\frac{A}{T} + B$. If the logarithm of the pressure is plotted against the reciprocal of the absolute temperature, the dissociation pressures will lie on a straight line, and can be readily extrapolated from low temperatures to higher ones.

G. K. BURGESS,† Washington, D. C.—That applies, I understand, where you have one phase. These temperatures were for substances in a solid state. If you go from the solid to the liquid phase, would you not get the same sort of a curve we had before, and might that not lead you into error?

J. W. RICHARDS.—Certainly; one formula is only valid for substances in the same physical state. If the physical states change, another formula of the same form but with different constants appears.

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