

effected without the intervention of the diffusion of the gases but by simple carbon diffusion "by difference in concentration" of the carbon dissolved by direct contact in the surface layers of the steel.

The high concentrations of carbon in the cemented zones which are obtained by starting from steels of considerably high carbon content (such,



FIG. 59.

for example, as the steel *B* above) greatly accentuate the phenomenon of liquation of the cementite, the practical importance of which I have already referred to.<sup>1</sup> The study of the phenomenon in this special case confirms fully the conclusions drawn from the earlier experiments. As an example of the importance which the phenomenon of liquation of the cementite may attain, I reproduce in Fig. 59 the micrograph<sup>2</sup> of the edge of a cylinder of the steel *B*, cemented with methane for three hours at 1100° C. and allowed to cool slowly in the furnace. The great quantity of cementite is clearly seen, accumulated (necessarily as the result of liquation) in the deeper parts of the cemented zone, and leaving *at the periphery* a zone more than a millimeter thick in which the concentration of the carbon does not exceed the value which it originally had in the steel used. We have thus demonstrated the great practical importance of any means which allows of obtaining cemented zones in which the concentration of the carbon does not exceed 0.9% in the surface layers, and varies from these to the deeper layers as slowly and uniformly as possible. These belong to that "intermediate type" which we have defined by referring to the two characteristic types which are obtained by cementing with pure carbon monoxide and with pure ethylene (see p. 82). We have also seen (see p. 108) that the simplest of these means consists in properly utilizing the characteristic carburizing action of carbon monoxide, increasing by means of the addition of other carburizing substances, such as hydrocarbons or solid carbon, the too low

<sup>1</sup> See p. 93.

<sup>2</sup> Enlargement 50 diameters. Etched with picric acid in alcoholic solution.

concentration of carbon which would otherwise be obtained, under ordinary conditions of temperature and pressure.

The importance of an accurate study of the processes of cementation based on the specific action of carbon monoxide is thus made evident. The practical results of such studies and their industrial applications are set forth in the second part of this volume; for the present, I report only the results of some laboratory experiments designed to define precisely the course of cementation effected with carbon monoxide in the presence of free carbon. The results of these studies, which I carried out in collaboration with Doctor Tavanti, are collected in a paper published early in 1910.<sup>1</sup>

The experiments whose results I report were carried out with the usual experimental arrangement already described (see pp. 96 and 116), using cylinders 18 mm. in diameter by 150 in length, of soft steel of the following composition:

Carbon.....	0.14 percent.
Silicon.....	0.03 percent.
Manganese.....	0.80 percent.
Sulphur.....	0.05 percent.
Phosphorus.....	0.02 percent.

The wood charcoal was ground and washed in the usual way, and we used the portion passing through a sieve of 16 mesh per sq. cm. and retained by a sieve of 81 mesh per sq. cm. Instead of carbon monoxide we used carbon dioxide, after having ascertained, by means of some preliminary experiments, that the gaseous mixture of CO and CO<sub>2</sub> resulting from the action of the carbon dioxide on the front layers of carbon had really reached the composition corresponding to complete equilibrium with free carbon. The experiments showed that these conditions of equilibrium are attained when the gaseous mixture has traversed a layer of granular carbon 25 cm. thick, even when giving to the current of gas a velocity (1 liter in 9 minutes) more than four times that used in our cementation tests (1 liter in 40 minutes). Besides its obvious practical advantages, the use of carbon dioxide is preferable to the direct use of pure carbon monoxide because with the former gas we always have "automatically" the mixture of CO and of CO<sub>2</sub> in the exact proportions corresponding to equilibrium with free carbon, while with the latter there is always a small excess of CO which must decompose in contact with the steel, depositing on it "carbon in excess." This makes itself felt markedly when considerable quantities of gas are used.

Fig. 60 reproduces the edge of the section of one of the cylinders thus cemented, enlarged 60 diameters, and polished and etched with alcoholic picric acid. Seven liters of carbon monoxide was used in five hours, at 1050° C.

<sup>1</sup>F. Giolitti and G. Tavanti, *Ricerche sulla fabbricazione dell'acciaio cementato*, VII: Studio di un processo di cementazione fondato sull'azione specifica dell'ossido di carbonio (*Rend. della Reale Accademia delle Scienze di Torino*, 1910).



FIG. 60.

Compare this micrograph with Fig. 38, which reproduces at the same enlargement the edge of the section of a cylinder of the same steel, cemented with *ethylene* under identical conditions (at 1050° for five hours with seven liters of gas).

The comparison of the two micrographs shows at once the profound difference between the strong and sudden variations in the concentration of the carbon which present themselves in the cemented zone obtained with the use of ethylene (Fig. 38), and the continuous and gradual variation of this concentration which manifests itself in the steel cylinder cemented with carbon monoxide and carbon (Fig. 60). In fact, in the former case we first pass suddenly from the external hyper-eutectic zone (with a total thickness of 1.2 mm) to the eutectic zone (0.7 mm. thick), and from this we again pass suddenly to the hypo-eutectic zone, in which the concentration of the carbon falls from 0.9% to the value which it had in the original soft steel, within an interval of less than 0.5 mm. In the second case, on the other hand, the hyper-eutectic zone is lacking, and the purely eutectic zone (about 1.1 mm. thick) gradually connects with the hypo-eutectic zone, in which the concentration of the carbon varies continuously and gradually, through an interval of more than 2 mm., from the maximum value 0.9% (at a depth of about 1 mm.) where the first fine filaments of ferrite begin to appear, to the value which it had in the original soft steel.

These observations therefore fully

confirm the views which I have expressed, both as regards the relations which exist between the distribution of the carbon in the cemented zones before and after the slow cooling,<sup>1</sup> and as regards the more uniform initial—and therefore also final—distribution of the carbon that can be obtained by the use of definite cements.

This explains how, in the cemented zone obtained by the new process, under the conditions just indicated, both the causes of brittleness due to the liquation of the cementite and to the liquation of the ferrite are totally eliminated (*cf.* pp. 108 and 110).

The following table shows the results of a series of cementations carried out under the conditions named, passing 1 liter of CO<sub>2</sub> through the apparatus every forty minutes.

Number	Temperature (degrees C.)	Time of cementation (hours)	Thickness of hyper-eutectic zone (mm.)	Thickness of eutectic zone (mm.)	Thickness of hypo-eutectic zone (mm.)	Total thickness of cemented zone (mm.)
1	1000°	2	.....	0.5	0.5	1.0
2	1000°	6	.....	1.0	1.2	2.2
3	1000°	12	.....	1.5	1.5	3.0
4	1000°	36	2.2	1.0	3.2	6.4
5	1060°	2	.....	0.7	1.2	1.9
6	1060°	6	.....	1.5	1.5	3.0
7	1100°	2	.....	1.0	1.4	2.4
8	1100°	6	.....	1.6	1.9	3.5
9	1100°	12	1.4	1.6	2.5	5.5
10	1200°	2	.....	1.2	2.0	3.2
11	1200°	6	.....	1.8	3.5	5.3

Leaving aside for the present considerations of a practical nature, which we shall consider later, it is seen at once how the data demonstrate that the specific action of carbon monoxide (as "equalizer" of the concentration of the carbon) manifests itself in cementations carried out under widely varying conditions. In the deeper cementations (Experiments 4 and 9) the action of the carbon monoxide can not be exercised completely, and a hyper-eutectic zone, relatively thin, appears. In these cases the equalization of the carbon is produced if we "isolate" for a certain time the action of the carbon monoxide, by making it act alone on the cemented steel after having removed the stronger antagonistic cement, in this case free carbon.

As proof of this I give in the following table the results obtained by reheating twice in succession, at 1000° C., in an atmosphere of pure carbon

<sup>1</sup> It is clear that in the specimen shown in Fig. 60 a certain liquation of the ferrite has also taken place; this is shown by the presence in this specimen of the external zone of pure pearlite. On the other hand, the measure of the liquation varies enormously from the one specimen to the other.

monoxide, a cylinder of soft steel first cemented in such a way as to show a marked hyper-eutectic zone:

	Thickness of hyper-eutectic zone (mm.)	Thickness of eutectic zone (mm.)	Thickness of hypo-eutectic zone (mm.)	Total thickness of cemented zone (mm.)	Total time of heating at 1000° in carbon monoxide (hours)
(a) In original cylinder. ....	2.1	0.9	1.8	4.8	.....
(b) After first heating (7 hours at 1000° C.).	.....	3.7	3.2	6.9	7
(c) After second heating (8 hours at 1000° C.)	.....	.....	8.5	8.5	15

The table clearly shows the efficacy of carbon monoxide as an agent for diffusing or equalizing the carbon in the steel. Of the mechanism of this action, I have already spoken (see p. 86).

It is quite probable that an analogous process of "equalization," observed by Portevin and Berjot<sup>1</sup> in a specimen of cemented steel heated for a long time in a mass of cast-iron turnings, was also due to the agency of carbon monoxide formed by the action of the oxygen of the air occluded in the cast-iron turnings on the carbon of the latter. The paper of Portevin and Berjot contains interesting practical data, which I will review later.

The important part which is taken by carbon monoxide in the process of cementation is shown still better by a second series of experiments, carried out under the same conditions as the preceding ones but using, instead of the granular carbon prepared as we have described above, a fine powder of this same wood charcoal, employing only that part of the carbon which passes through a sieve of 81 mesh to the sq. cm. The results of these experiments are collected in the following table:

Number	Temperature (degrees C.)	Time of cementation (hours)	Thickness of eutectic zone (mm.)	Thickness of hypo-eutectic zone (mm.)	Total thickness of cemented zone (mm.)	Max. concentration of C in hypo-eutectic zone, %	Remarks
1	1000	2	.....	1.0	1.0	0.70	Horizontal furnace.
2	1000	6	.....	1.2	1.2	0.70	Horizontal furnace.
3	1000	2	.....	0.6	0.6	0.60	Vertical furnace.
4	1000	6	0.5	0.4	0.9	0.90	Vertical furnace.

These data prove in a conclusive manner what I have asserted above. It is evident, in fact, that if the diffusion of the carbon into the steel were due to the direct action of the solid carbon placed in contact with it, the cementation should take place considerably more rapidly in the experiments reported in the last table than in those I carried out under identical conditions, reported in the first table; for it is clear that the contact between

<sup>1</sup> *Revue de Métallurgie*, 1910, pp. 61-75.

the steel and the carbon is considerably more intimate when the latter is used in the form of a fine powder than when it is used in granular form. In the cementation reported in the last table the velocity of penetration of the carbon is considerably lower than in the corresponding experiments of the table reproduced on p. 135; this is an evident proof of the slight *direct* action of the carbon (by contact) and of the preponderant action of carbon monoxide as "vehicle" for the penetration of the carbon into the steel. In fact, the velocity of the penetration of the carbon is greater the more freely the carbon monoxide can circulate around the carbon and the steel, with which it must react alternately, as I have before indicated. Further confirmation of this is seen by a comparison of Experiments 1 and 3 of the table above; this comparison shows, in fact, that the cementation is considerably less deep when, keeping all the other conditions equal, the porcelain tube acting as cementation chamber is arranged vertically instead of horizontally. It is evident that while the vertical arrangement favors the contact between the carbon powder and the surface of the steel cylinders, it renders the circulation of the gases in the apparatus considerably more difficult.<sup>1</sup>

These observations explain the results which are obtained in practice in cementation effected with powdered mixtures of wood charcoal and barium carbonate.

There still remained to be investigated one quite important point for the technical application of the process, *viz.*, concerning the limits of "space" in which carbon monoxide can still efficiently exercise its characteristic specific function as "vehicle" in the transportation of the carbon from the solid cementing mass to the mass of steel. The importance of defining practically these limits is evident to anyone familiar with the technique of ordinary cementation carried out with solid cements, for he knows how difficult it is to operate under such conditions as to be absolutely sure that imperfect contact of the cement with any section of the surface of the piece to be cemented will not leave dangerous gaps in the carburized zone.

For this investigation we used the following arrangement: Having arranged our furnace vertically, we placed in the center of it, and along the axis of the cementation chamber, a cylinder of the usual soft steel, 30 cm. long and 10 mm. in diameter. Along a length of the cylinder were made file marks, 1 cm. distant from each other, numbered progressively from 1 to 29, starting from the lower end of the cylinder. Only the lower part of the cylinder was immersed, for a length of 13 cm., in the usual mass of granular wood charcoal; the upper portion, on the contrary, remained entirely free.

While a slow current of carbon monoxide (about 2 liters per hour) circulated through the apparatus, entering from the bottom, we raised the

<sup>1</sup> This last fact is clearly observed when carrying on the experiment.

temperature of the cementation chamber to 980°, keeping it constant there for four hours. Having allowed the apparatus to cool slowly, we cut the steel cylinder longitudinally along a plane passing through its axis, and on the section thus obtained, polished and etched in the usual way, we were easily able to observe under the microscope the variations in structure of the cemented zone along its whole length. I report in the table below the results of some of our observations:

Position of observed section of zone on scale on cylinder	Thickness of eutectic zone (mm.)	Thickness of hypo-eutectic zone (mm.)	Maximum concentration of carbon in hypo-eutectic zone	Remarks
5.0	0.6	1.2	0.9%	Part immersed in the carbon.
10.0	0.6	1.1	0.9	Part immersed in the carbon.
13.0	0.6	1.1	0.9	Part immersed in the carbon.
13.5	0.6	1.1	0.9	Part not immersed in the carbon.
14.5	0.3	1.2	0.9	Part not immersed in the carbon.
16.0	.....	1.5	0.65	Part not immersed in the carbon.
19.0	.....	1.2	0.5	Part not immersed in the carbon.
20.0	.....	1.2	0.4	Part not immersed in the carbon.
26.0	.....	1.1	0.3	Part not immersed in the carbon.

The data contained in the preceding table show clearly how, in the process with which we are dealing, the cementation takes place, by the action of carbon monoxide, with full efficiency even in the sections of the surface of the steel which are not in direct contact with the granular mass of carbon but are about a centimeter distant from it, and that the efficiency of the cementation is diminished only in the parts of the surface of the steel considerably more distant (5-6 cm.) from the carbon.

We shall deal, in the second part of this volume, with the data contained in several other recent publications,<sup>1</sup> for they are data of essentially practical interest; as, for example, the course of the cementation of special steels for deep cementation, the best conditions for tempering cemented steels, etc.

Before closing this chapter, however, I want to report the results of some more recent investigations which, although rather of a theoretical

<sup>1</sup> As an example, among the publications of this period, the contents of which I consider it superfluous to cite here, I call attention to a memoir presented by Grayson before the Iron and Steel Institute (1910, Vol. I, pp. 287-302). In this memoir the author does, in truth, reproduce several "concentration-depth" diagrams; but (even leaving aside the fact that these diagrams appeared a long time after those already published by me and my collaborators), Grayson does not deduce from them any of the important conclusions which we have seen can be drawn from an accurate study of these diagrams.

Moreover, Grayson studies the effects of four solid cements, of which he indicates only the elementary composition but ignores their constitution. It is clear that under these conditions the results obtained can be only of small importance.

character, nevertheless present much interest from the practical point of view.

Referring briefly to some observations contained in a recent work of J. Kirner;<sup>1</sup> they are at present very incomplete, but may probably open the way for interesting researches. The author examines the behavior of two nitrogenous cements and of one free from nitrogen. For the first one, not knowing its constituents, he indicates the composition resulting from analysis; besides the carbon, it contained 41% of sodium chloride, 9% of total nitrogen, 0.5% of sulphur, and 18% of a residue insoluble in water, consisting principally of Fe<sub>2</sub>O<sub>3</sub>, Al<sub>2</sub>O<sub>3</sub> and CaO. This cement he designates by the letter A<sub>1</sub>. The second nitrogenous cement, which he designates C<sub>1</sub>, consisted of leather carbon. The third, a non-nitrogenous cement (B<sub>1</sub>), was of wood charcoal mixed with alkaline carbonates.

At 700° C. both nitrogenous cements (A<sub>1</sub> and C<sub>1</sub>) furnish a thin cemented zone with less than 0.55% C but *very rich in nitrogen*, the percentage of which exceeds 0.5% in the zone obtained with the cement C<sub>1</sub> and 0.6% in that obtained with the cement A<sub>1</sub>. In these cemented zones the author observes a special constituent which he designates by the name "flavite," the proportion of which increases with increase in the content of nitrogen. This constituent appears with "the aspect of a solid solution" (?) in sections of the heated steels etched with picric acid, while it disappears in these steels when hardened.

At 900° C. the cemented zones obtained with cement A<sub>1</sub> contain a much smaller quantity of nitrogen (0.035%) than that contained in the zones obtained under the same conditions with cement C<sub>1</sub> (0.15%). At 1000° C. the proportion of nitrogen absorbed by the steel becomes very small for both cements.

As to the intensity of the carburization, while in the zones obtained with the non-nitrogenous cement B<sub>1</sub> the mean concentration of the carbon increases gradually and continuously with rise in the temperature, in the zones obtained with the two nitrogenous cements (A<sub>1</sub> and C<sub>1</sub>) the mean concentration of the carbon does not increase appreciably when the temperature of the cementation varies from 700° to 900° C., and begins to rise markedly with the temperature only when the latter goes above 950° C.

These experiments appear to show with great probability two things: the possibility that certain nitrogenous cements under definite conditions give rise to the diffusion of considerable proportions of nitrogen into the steel, and the influence exercised by nitrogen on the course of the cementation. It is to be regretted that the authors omit a description of their method for the quantitative determination of the nitrogen.

<sup>1</sup> J. Kirner, *Ueber einige bemerkenswerte Beobachtungen beim Einsatzhärten von Stahl, insbesondere hinsichtlich der Wirkung des Stickstoffs* (Metallurgie, 1911, Vol. VIII, pp. 72-77).

Since even small quantities of nitrogen can exercise great influence on the mechanical properties of steel, it is quite probable that a series of investigations carried out as above would lead to interesting results.

#### CEMENTATION OF NICKEL STEELS

Some recent investigations on the cementation of nickel and of chromium steels are worth citing. The data relative to the first—the nickel steels—are collected in two papers<sup>1</sup> published in the first half of 1911.

Leaving aside a detailed exposition of the data regarding the concentration and the characteristic distribution of the carbon in the cemented zones obtained by working under various conditions with steels of varying nickel content, I here summarize the more general conclusions which can be reached from these data.

The experiments were carried out by cementing successively at various temperatures ranging between 900° and 1100° C., with ethylene, with carbon monoxide and with the *mixed* cement of which I have already spoken (carbon monoxide and carbon), soft steels containing 2%, 3%, 5%, 25% and 30% of nickel, respectively.

The principal conclusions are the following:

1. The course of the cementation of steels with 2 to 3% of nickel is practically identical with that of the cementation of carbon steel equally carburized.

2. When the nickel content exceeds 3%, the maximum concentration of the carbon in the cemented zones decreases with increase in the percentage of nickel contained in the steel.

The following table contains data relative to the maximum concentrations reached by the carbon in the cemented zones when cementing, under various conditions, steels of varying nickel content.

No.	Conditions of cementation	Nickel content				
		2%	3%	5%	25%	30%
1	Carbon monoxide (16 liters) 5 hours at 950° . . . . .	0.38	0.23	.....	0.15	
2	5 hours at 1050° . . . . .	0.35	0.35	.....	0.17	
3	Ethylene 5 hours at 950° . . . . .	1.12	.....	0.93	.....	0.39
4	5 hours at 1050° . . . . .	1.53	1.28	0.84	0.63	
5	Mixed cement 2 hours at 1000° . . . . .	0.70	.....	0.70	.....	0.67
6	2 hours at 1100° . . . . .	0.92	.....	0.74	.....	0.40
7	5 hours at 1000° . . . . .	1.12	.....	0.80	0.64	.....
8	5 hours at 1050° . . . . .	0.83	.....	0.73	0.59	.....
9	5 hours at 1100° . . . . .	1.07	.....	0.83	0.73	.....

<sup>1</sup>F. Giolitti and F. Carnevali, *Sulla cementazione degli acciai al nichelio*, I (*Atti della R. Accademia delle Scienze di Torino*, Vol. XLVI, February 19, 1911); and F. Giolitti and G. Tavanti, *Sulla cementazione degli acciai al nichelio*, II (*Rassegna Mineraria, Metallurgica e Chimica*, Vol. XXXIV, No. 18, June 21, 1911.)

For detailed experimental data relative to the curves of the distribution of the carbon, to the composition of the steels used, etc., and for the particular conditions of the individual experiments, I must refer the reader to the two original papers.

3. Under the same experimental conditions, the variations in the concentration of the carbon in the cemented zones are more gradual and more uniform in nickel steels than in carbon steels. This is one of the reasons which make it advantageous to use nickel steel for cemented pieces which are to be subjected to shocks and which must, therefore, show the minimum brittleness compatible with the required surface hardness. This advantage clearly results from the "exfoliation" of cemented and hardened pieces. The phenomenon just mentioned is due, at least in part, to the fact (proved by microscopical examination) that in nickel steels the phenomenon of liquation in the mixed crystals manifests itself, under equal conditions, with less intensity than in carbon steels.

4. In pearlitic nickel steels, or those belonging to the first transition zone of Guillet's diagram, the region of passage from the hyper-eutectic to the eutectic layer in the cemented zone corresponds to a carbon content (0.6–0.65%) lower than that of the corresponding zone (the eutectic zone) of cemented carbon steels (0.9%).

5. The specific action of carbon monoxide is exercised in the cementation of nickel steels in a manner entirely analogous to that in which it is exercised in the cementation of carbon steels. The use of the mixed cement with carbon monoxide as base presents, therefore, in the cementation of nickel steels the same advantages which we have already seen for the cementation of carbon steels.

6. The "velocity of cementation" (meaning the *depth* reached in a given time by the carburized zone) is, using mixed cement, slightly higher for nickel steels than for carbon steels.

#### CEMENTATION OF CHROME STEELS

Cementation experiments made on a chrome steel with 2.33% of chromium,<sup>1</sup> using successively as cements ethylene, pure carbon monoxide, and the usual mixed cement with carbon monoxide as base (CO + C), showed first of all that the characteristic mode of action of each of the three "typical cements" just indicated is exercised toward chrome steel just as we found it for carbon steels. In general, however (and this presents great interest in practice), it is clearly observed that the presence of the chromium tends to an increase in the maximum concentration of the carbon in the cemented zones, when we take as basis the value which this concentration reaches in carbon steels subjected to cementation under identical conditions.

<sup>1</sup>F. Giolitti and F. Carnevali, *Sulla cementazione degli acciai al cromo* (*Atti della R. Accademia delle Scienze di Torino*, Vol. XLVI, April 2, 1911).

An approximate idea of the extent of this increase may be obtained from the data of the following table, in which are given the maximum concentrations of the carbon in the cemented zones obtained with the steel having 2.33% of chromium and 0.4% of carbon, working under the different conditions indicated in the table. For more precise data on the experimental conditions and on the results (especially as regards the distribution of the carbon in the cemented zones) I must refer back to the original paper.

No.	Cement used	Temperature	Length of cementation (hours)	Maximum concentration of carbon in cemented zone %
1	Ethylene.....	950°	5	1.40%
2	Ethylene.....	1050°	5	1.30
3	Carbon monoxide.....	950°	5	0.60
4	Carbon monoxide.....	1050°	5	0.52
5	Mixed cement (CO + C).....	1000°	2	0.81
6	Mixed cement (CO + C).....	1100°	2	0.91
7	Mixed cement (CO + C).....	1000°	5	1.22
8	Mixed cement (CO + C).....	1100°	5	1.21

#### CEMENTATION UNDER PRESSURE

The course of the cementation of special steels with cements whose carburizing action is due chiefly to carbon monoxide, and of the phenomena of oxidation which often accompany it, is cleared up greatly by a series of recent investigations using the mixed cement of wood charcoal and carbon monoxide under pressures higher than atmospheric.

A part of these results was communicated at a meeting of the Iron and Steel Institute held in October, 1911.<sup>1</sup> We will review them here at some length.

I have already cited on page 126 a series of experiments bearing on the relation between the pressure of the carburizing gas and the depth and the intensity of the cementation obtained, when using cements whose activity is due chiefly to the specific action of carbon monoxide. These gave clear proof of the direct and preponderant function of the carburizing gases (and especially of the carbon monoxide) in the process of the cementation.

The apparatus used in the experiments which I now report is shown in perspective in Fig. 61; it was similar to that already described as being used in the experiments just cited, differing essentially only in the devices which made it more gas-tight. This is essential for the exact determination of the velocity of the current of carbon dioxide which reaches the cementation box.

The longitudinal section is reproduced in the accompanying figure (Fig. 62).

<sup>1</sup>F. Giolitti and E. Carnevali, *On Cases of Hardening by means of Compressed Gases* (*The Journal of the Iron and Steel Institute*, 1911).

A and B are connectors fastened to rods which pass (electrically insulated and gas-tight) through the walls of the cast-iron vessel C and carry the heating current to the spiral of nickel wire D. This spiral is wrapped around

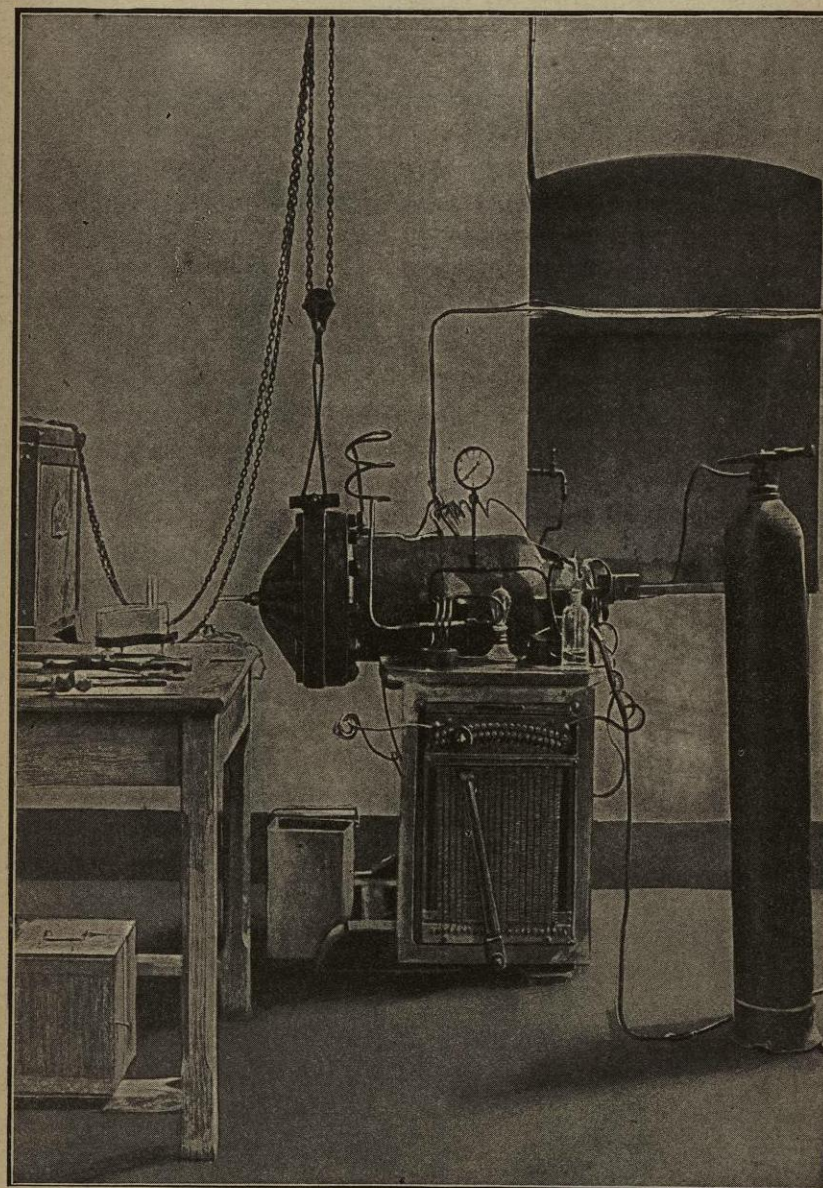


FIG. 61.

the porcelain tube E, which can easily be put in position and removed from the apparatus, in which it is simply placed in a larger tube of refractory earth F.

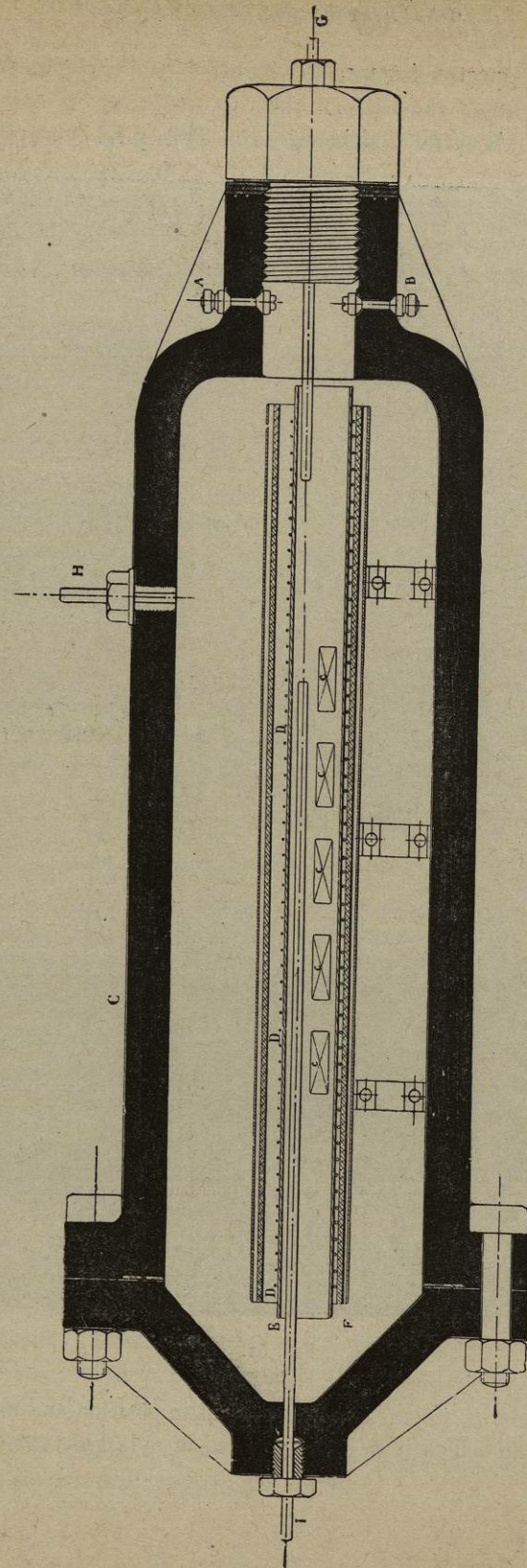


FIG. 62.

The space between the tube *F* and the wall of the cast-iron vessel is filled with asbestos. The gas ( $\text{CO}_2$ ) enters through the tube *G* and issues through the tube *H*. The strong porcelain tube *I* protects the thermo-electric couple for measuring the temperature throughout the whole length of the cementation chamber; near it are placed the pieces *C* to be cemented, wholly surrounded by the granular carbon. The apparatus to regulate and indicate the pressure is seen in Fig. 61. It is identical with that which I have already described on p. 129.

The experiments were carried out similarly to those already described (see p. 130), using granular wood charcoal, carbon dioxide and cylinders of different steels of the following compositions:

1. Ordinary soft carbon steel, which I shall designate as *Steel "C"*:
 

Carbon.....	0.11 percent.
Silicon.....	0.05 percent.
Manganese.....	0.54 percent.
Sulphur.....	0.02 percent.
Phosphorus.....	0.04 percent.
2. Soft steel with 2% of nickel, which I shall designate as *Steel "Ni<sup>2</sup>"*:
 

Nickel.....	2.03 percent.
Carbon.....	0.10 percent.
Silicon.....	0.26 percent.
Manganese.....	0.41 percent.
3. Soft steel with 5% of nickel, which I shall designate as *Steel "Ni<sup>5</sup>"*:
 

Nickel.....	5.02 percent.
Carbon.....	0.118 percent.
Silicon.....	0.20 percent.
Manganese.....	0.47 percent.
4. Steel with 25% of nickel, which I shall designate as *Steel "Ni<sup>25</sup>"*:
 

Nickel.....	24.92 percent.
Carbon.....	0.17 percent.
Silicon.....	0.10 percent.
Manganese.....	0.28 percent.
5. Steel with 2.3% of chromium, which I shall designate as *Steel "Cr"*:
 

Chromium.....	2.33 percent.
Carbon.....	0.41 percent.
Silicon.....	0.15 percent.
Manganese.....	0.60 percent.
6. Chrome-nickel steel, which I shall designate as *Steel "Cr-Ni"*:
 

Chromium.....	1.50 percent.
Nickel.....	3.17 percent.
Carbon.....	0.33 percent.
Manganese.....	0.43 percent.
Silicon.....	0.06 percent.

In all these steels, the contents of sulphur and phosphorus were less than 0.04%.

Table I shows the conditions under which the individual cementations were carried out, and some pertinent observations on the state of the surface of the various steels after the cementation (see Table I below).

The variation of the concentration of the carbon in the cemented zones was determined by microscopic examination for the steels "C," "Ni<sup>2</sup>" and "Cr," for which such an examination can furnish sufficiently precise indications. Table II contains the results of this examination.

TABLE I

Number	Steel used	Length of cementation (hours)	Pressure of gas (kg. per sq. cm.)	Interval of temperature within which cementation is effected	Velocity of gas (CO <sub>2</sub> ) (liters per hour per sq. dm. of surface to be cemented)	Observations on the state of the surface of the cemented steel
I	C	3	15	900°-955° C.	1.5	Surface unchanged.
II	C	3	15	1020°-1050°	1.5	Surface unchanged.
III	C	2:30'	25	890°-960°	1.5	Thick layer of compact oxide.
IV	C	3	25	980°-1015°	3.0	Strong oxidation.
V	Ni <sup>2</sup>	3	15	955°-975°	1.5	Surface unchanged.
VI	Ni <sup>2</sup>	3	15	1035°-1045°	1.5	Surface unchanged.
VII	Ni <sup>2</sup>	2:30'	25	905°-955°	1.5	Slight oxidation.
VIII	Ni <sup>2</sup>	3	25	1030°-1050°	3.0	Surface unchanged.
IX	Ni <sup>5</sup>	3	15	850°-890°	1.5	Surface unchanged.
X	Ni <sup>5</sup>	3	15	945°-995°	1.5	Surface unchanged.
XI	Ni <sup>5</sup>	2:30'	25	840°-930°	1.5	Thick layer of compact oxide.
XII	Ni <sup>5</sup>	3	25	875°-915°	3.0	Thick layer of compact oxide.
XIII	Ni <sup>25</sup>	3	15	870°-930°	1.5	Surface almost unchanged.
XIV	Ni <sup>25</sup>	3	15	1000°-1045°	1.5	Surface unchanged.
XV	Ni <sup>25</sup>	2:30'	25	870°-950°	1.5	Thin layer of non-compact oxide.
XVI	Ni <sup>25</sup>	3	25	942°-980°	3.0	Slight oxidation.
XVII	Cr	3	15	935°-965°	1.5	Slight oxidation.
XVIII	Cr	3	15	1035°-1060°	1.5	Thick layer of compact oxide.
XIX	Cr	2:30'	25	900°-965°	1.5	Thick layer of compact oxide.
XX	Cr	3	25	1010°-1035°	3.0	Thick layer of compact oxide.
XXI	Cr-Ni	3	15	810°-850°	1.5	Strong oxidation.
XXII	Cr-Ni	3	15	875°-915°	1.5	Thick layer of compact oxide.
XXIII	Cr-Ni	3	25	810°-845°	3.0	Thick layer of compact oxide.
XXIV	Cr-Ni	2:30'	25	850°-900°	1.5	Thick layer of compact oxide.

For the three other steels—"Ni<sup>5</sup>," "Ni<sup>25</sup>" and "Cr-Ni"—for which the microscopic examination could not furnish definite results, gravimetric determinations were made on samples obtained by removing successively

from the cemented cylinders coaxial layers about a quarter of a millimeter thick.<sup>1</sup>

Gravimetric carbon analyses were also made in the same manner on layers of the cylinders of the steel "Cr," for the purpose of determining with precision the importance of a strong hyper-increase in the carbon content of the first thin surface zone which the microscopic examination had revealed.

TABLE II

Number of cementation (see Table I)	Thickness of hyper-eutectic zone (mm.)	Thickness of eutectic zone (mm.)	Thickness of hypo-eutectic zone (up to about 0.4% of carbon) (mm.)
I	0.4	0.3	0.5
II	1.3	0.8	0.4
IV	0.7	0.6	0.4
V	0.25	1.1	0.35
VI	0.9	0.8	0.7
VIII	0.9	0.7	0.8
XVII	0.1	1.0	?(a)
XVIII	0.15	1.0	?
XX	0.8	1.7	?

(a) For the chrome steel of the composition of that used by us, the precise microscopic determination of the hypo-eutectic zone is quite difficult.

The results of these analyses are collected in Table III.

TABLE III

Number of cementation (see Table I)	Concentration of the carbon		
	In first layer (0.25 mm.), percent.	In third layer (depth, 0.7 mm.), percent.	In fifth layer (depth, 1 mm.), percent.
IX	0.71	.....	0.12
XIII	0.57	.....	.....
XXI	0.45	.....	0.54
XVII	2.22	.....	1.03
X	0.99	.....	0.29
XIV	0.90	0.32	.....
XXII	0.76	.....	0.49
XVIII	3.1	.....	1.39
XII	0.73	.....	0.36
XVI	0.61	0.37	.....
XXIII	0.54	.....	1.56
XX	2.37	.....	1.40

These experimental data furnish some interesting conclusions, which I summarize here briefly, limiting myself to those which are of general interest.

<sup>1</sup> In order to be able to cut the successive layers of the cemented steels in Experiments IX, X, XII, XX, XXI, XXII, XXIII, it was necessary to reheat them for five hours at about 550° C. in a neutral atmosphere. It is known that heating under such conditions does not modify in any way the characters of the cemented zones.



These conclusions, although of an essentially general character, indicate the methods to be followed in any special case in order to fix with certainty practical rules for avoiding definite disadvantages and for obtaining given results. It is clear that the consideration of special cases which may arise in practice can not be undertaken here.

A first deduction from the experimental data is the effect which variations in the pressure of the carburizing gas exercise on the depth of the cementation, and on the concentration of the carbon in the cemented zones. This fact confirms fully the results of the earlier experiments,<sup>1</sup> extending them to the special steels of various types now in question. The correctness of this assertion is seen clearly from a simple comparison of the data just cited with each other and with those which I cited previously, on page 135, relative to cementations of carbon steels and of special steels carried out with the same mixed cement as used in the present experiments, but working under atmospheric pressure.

The greater pressure of the carburizing gas increases the concentration of the carbon in the cemented zones, and confirms the conclusions drawn previously as to the *direct* function of carbon monoxide in the cementation with the mixed cement.

A second fact results clearly from the comparison of the results of Experiment VI with those of VIII, of IX with XII, of XVIII with XX, and of XXI with XXIII. These comparisons show, in fact, how an increase in the velocity of the current of carbon dioxide tends to cause a decrease in the intensity of the cementation, thus eliminating, in the four pairs of experiments just cited, the effects of the increase in the pressure. These effects, as we have seen, manifest themselves with marked intensity when the cemented zones obtained by working under various pressures (ordinary pressure and pressures of 15–25 kg. per sq. cm.) but with currents of carbon dioxide of equal velocity are compared with each other.

In cementations carried out with cements based on the action of the carbon monoxide, true states of complete chemical equilibrium are never reached, so that the final characteristics of the cemented zones obtained depend to a very marked degree on the relations between the velocity of the individual reactions which take place in the course of the cementation.

The surface oxidation of the cemented steel is a third phenomenon which presents great interest, both from the theoretical and the practical point of view, and which the experimental data reported in the preceding pages (especially in Table I) show to occur with special frequency and intensity in cementations carried out under strong pressures with the mixed cement and carbon monoxide.

An oxidation of this kind had already been observed by Charpy in 1909,<sup>2</sup>

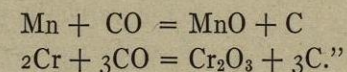
<sup>1</sup> See p. 130.

<sup>2</sup> *Revue de Métallurgie*, May, 1909, Vol. VI, pp. 505–518.

in subjecting to the action of pure carbon monoxide, at 1000° C., chromium, manganese and various chrome steels (containing from 1.99% to 7.71% of chromium) and chromium-nickel steels (containing from 2.08% to 6.45% of nickel and from 0.70% to 7.04% of chromium).

Charpy had observed that in using these special steels as filings the carbon monoxide is decomposed by the chromium and there occurs "*simultaneously the oxidation of the chromium and the carburization of the iron; the two elements behave as if they had been isolated.*" Charpy then adds that "when, instead of working with filings, pieces of considerable dimensions are used, the same phenomena are no longer observed; the oxidation of the chromium is produced only in the surface layer, and below the cementation proceeds regularly by diffusion."

Charpy concludes, on the basis of his experiments, that "the action of carbon monoxide at 1000° C., which is one of cementation for iron, as well as for tungsten and perhaps for nickel, is therefore one of oxidation for chromium and manganese, and may be represented by the equations:



I have already pointed out<sup>1</sup> how these conclusions drawn by Charpy from his most interesting experiments were premature<sup>2</sup> and especially in the fact that they did not take into account at all the results of the important investigations on the action of carbon monoxide on the metals of the iron group which Schenck had published some time before.<sup>3</sup>

In fact Schenck's investigations—the results of which I have used extensively in my technical studies of the cementation of steel—had already led to referring to a single principle the oxidizing action of carbon monoxide on the various metals of the iron group, thus making it possible to greatly simplify the theoretical treatment of the reactions which take place in the systems consisting of the metals, carbon monoxide, carbon dioxide, carbon and the products of the oxidation and of the carburization of the various metals.

Our experiments, the results of which I have summarized in the preceding pages, give concrete form (though certainly not definite and anything but complete) to the general laws which govern the process of the cementation

<sup>1</sup> See p. 112.

<sup>2</sup> We shall see, in fact, in the pages that follow, how also for iron alone the action of carbon monoxide may be *simultaneously* "cementing" and "oxidizing." And so too for chromium and manganese steels, for which it is, in fact, not necessary (nor justifiable) to assume that the iron and the manganese, or the iron and the chromium, "behave as if they were isolated"; for, on the contrary, we shall see later how it is necessary to recognize that the behavior of each of these (iron and manganese, or iron and chromium) is profoundly modified by the presence of the other, with which it is *united* in the state of solid solution.

<sup>3</sup> *Berichte der deutschen chemischen Gesellschaft*, 1903–1907; *Zeitschrift f. Elektrochemie*, 1904.

of special steels with cements whose activity is due to the specific carburizing action of carbon monoxide.

But, before examining these experimental results from this point of view, it is necessary to recall briefly some physico-chemical laws relative to the action of carbon monoxide on metals, to show how these laws can be applied in our case.

If we consider the diagram of complete isothermal equilibrium, studied by Schenck,<sup>1</sup> in the case in which the metal subjected to the action of the carbon

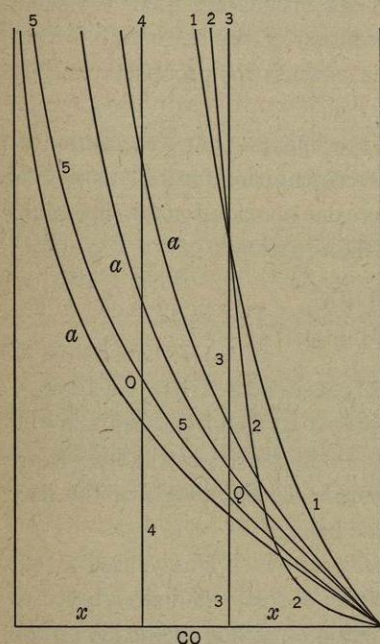


FIG. 63.

monoxide is iron alone and for the temperatures at which solid solutions (mixed crystals) of iron carbide in the iron can not be formed (that is, below  $700^{\circ}$  C.), we find five equilibrium curves corresponding to five distinct reactions. Representing, as usual, on the axis of abscissas the concentration ( $x$ ) of carbon monoxide in the mixture of carbon monoxide and carbon dioxide (varying  $x$  from 0 to 1) and on the axis of ordinates the total pressures ( $P$ ) of the said gaseous mixture, the five curves are those represented in the accompanying figure (Fig. 63) and designated by the numbers 1, 2, 3, 4 and 5.

We will recall here briefly the significance and the equation of each of these curves:

*Curve 1.* Cubical hyperbola  $\frac{x^2}{1-x} P = \mu$  ( $\mu = \text{constant}$ ); corresponding to the conditions of equilibrium of the system ( $\text{Fe}_3\text{C}$ ,  $\text{Fe}$ ,  $\text{CO}$ ,  $\text{CO}_2$ ).

*Curve 2.*  $\frac{x^5}{(1-x)^4} P = \theta$  ( $\theta = \text{constant}$ ); corresponding to the conditions of equilibrium of the system ( $\text{Fe}_3\text{C}$ ,  $\text{FeO}$ ,  $\text{CO}$ ,  $\text{CO}_2$ ).

*Curve 3.* Straight line  $\frac{x}{1-x} = \eta$  ( $\eta = \text{constant}$  of reduction); corresponding to the conditions of equilibrium of the system ( $\text{Fe}$ ,  $\text{FeO}$ ,  $\text{CO}$ ,  $\text{CO}_2$ ).

*Curve 4.* Straight line  $\frac{x}{1-x} = k$  ( $k = \text{constant}$ ); corresponding to the conditions of equilibrium of the system ( $\text{Fe}_3\text{O}_4$ ,  $\text{FeO}$ ,  $\text{CO}$ ,  $\text{CO}_2$ ).

<sup>1</sup>In the French edition of his *Physical Chemistry of the Metals* (Trad. par Lallement, Paris, Dunod et Pinat, 1911), Schenck has summarized with great clearness the results of his most recent investigations on the problem with which we are dealing.

*Curve 5.*  $\frac{x^2}{1-x} P = \zeta$  ( $\zeta = \text{constant}$ ); corresponding to the conditions of equilibrium of the system ( $\text{C}$ ,  $\text{CO}$ ,  $\text{CO}_2$ ).

If, instead, we work at a temperature higher than  $700^{\circ}$  C., the iron carbide will be able to form solid solutions with the iron, and there must appear in the equilibrium diagram, besides the five curves already indicated, the equilibrium curves of the systems resulting from the addition to the preceding constituents of iron-carbon mixed crystals.

To every value of the concentration of the carbon in the mixed crystals, there corresponds an equilibrium curve whose equation (in the case in which the mixed crystals are present in sufficient amount so that their concentration does not vary sensibly with variation—within certain limits—of the pressure of the gaseous mixture) is also that of a cubical hyperbola of the form  $\frac{x^2}{1-x} P = \nu$ ; analogous, therefore, to that of the systems ( $\text{Fe}$ ,  $\text{Fe}_3\text{C}$ ,  $\text{CO}$ ,  $\text{CO}_2$ ) and ( $\text{C}$ ,  $\text{CO}$ ,  $\text{CO}_2$ ). Among all these cubical hyperbolas, constituting a pencil and all passing through the point ( $x = 1$ ,  $P = 0$ ),<sup>1</sup> one presents special interest for our case, in which—the cementation being effected with the “mixed cement”—the reactions take place in the presence of a large excess of free carbon (“granular” wood charcoal); this curve is that corresponding to the particular concentration of the carbon in the mixed crystals for which the constant  $\nu$  has (for the same temperature) the same value as the constant  $\zeta$  of the equilibrium equation of the system  $\text{C}$ ,  $\text{CO}$ ,  $\text{CO}_2$ . It is clear, from what we have said, that such a curve coincides throughout its whole length with the isothermal of equilibrium of the system  $\text{C}$ ,  $\text{CO}$ ,  $\text{CO}_2$ .

If we suppose that all the operations are carried out with sufficient slowness to always attain states of complete equilibrium which we know never really occurs exactly in practice, but which we can assume with sufficient qualitative approximation), the final concentration of the carbon in the mixed crystals will always be that corresponding to a definite value of the constant  $\nu$ , equal to that which, at the same temperature, is assumed by the constant  $\zeta$  of the equation  $2\text{CO} \rightleftharpoons \text{CO}_2 + \text{C}$ . We will designate by  $\Sigma$  the mixed crystals in which the carbon has this particular concentration.

We can therefore infer that in the qualitative study of the reactions which are effected in the cementation with mixed cement, and which are based on the simultaneous action of the carbon and the mixture of carbon dioxide and carbon monoxide in equilibrium with it, we can separate the equilibrium curves into curves corresponding to the various concentrations of the carbon in the mixed crystals, and then consider a single one of these.

In other words, in the case of the cementation carried out with “mixed cement,” the problem is reduced to the same simplicity which it has (as Schenck has shown) when the study of it is limited to temperatures below

<sup>1</sup>Some of these curves are traced in the figure and indicated by the letters  $a$ ,  $a$ , . . .