

(to which *alone* the equilibrium phenomena observed can be referred) is so evident that it is no longer possible to doubt the very great preponderance of the *direct* action of the carburizing gas in comparison with the direct action of the carbon in contact with the steel or which may be deposited on the surface of the steel as the result of the decomposition of the gas.

The principles which I have developed also allow an explanation of some older observations already referred to. Thus, for example, we easily see the weakness of Mannesmann's reasoning which I have cited on p. 18, based on the alleged absurdity of admitting that the same gas contained in a crucible can on the one hand remove the carbon from the cast iron to yield it on the other to the steel. It is, in fact, quite understandable that a given mixture of carbon monoxide and carbon dioxide should act as an oxidizer on the carbon of the iron-carbon mixed crystals of high carbon content (of the cast iron) and as a carburizer on the mixed crystals of lower carbon content (soft steel). I have already reported the results of experiments which realize very simply and surely just the process considered as absurd by Mannesmann, producing, simultaneously and in the same operation, the decarbonizing of a cast iron and the cementation of a steel.

The same principles explain in a very simple way the phenomenon observed by Forquignon, of the refining of a cast iron ignited in carbon powder, and "therefore subjected to the same treatment which gives rise to the carburization of steel." In fact, my own direct experiments show that certain types of cast irons can be decarburized easily by gaseous mixtures with carbon monoxide as base which are in equilibrium with free carbon.

Finally, I wish to mention the results of some experiments which, on account of their essentially practical interest,¹ I shall examine more in detail in the second part of this volume.

These experiments show that when the cementation with mixtures of carbon monoxide and carbon dioxide in chemical equilibrium with free carbon (for example, with wood charcoal) is carried out under the usual experimental conditions which I have indicated, diluting the gaseous carburizing mixture with nitrogen, there are obtained cemented zones in which the maximum concentration of the carbon is less than that which would be obtained by working under identical conditions but without diluting the gaseous mixture. I shall consider in a subsequent chapter the theoretical and practical importance of this fact.

¹F. Giolitti and G. Scavia, *Sull'impiego dei forni a muffole orizzontali nella cementazione dell'acciaio coi cementi misti* (*La Metallurgia Italiana*, August, 1911).

CHAPTER V

THE PRESENT STATE OF THE THEORY OF THE PROCESS OF CEMENTATION¹

The simple setting forth in the preceding chapters of the theoretical conclusions resulting from the experimental investigations carried out to determine the nature of the process of cementation define the actual state of our knowledge on this subject. It does not, however, seem to me useless to further summarize and briefly classify this knowledge, and to show how the inconclusive and at times apparently contradictory results of the first experimental investigations are clearly explained by results of more recent investigations. This will place still better in evidence the real value of the most recent studies, showing that the experimental foundation of the new theories is considerably more extensive than that on which they were directly constructed.

One of the questions which has been discussed at greatest length and with the greatest interest is the part played in the process of cementation by the various carburizing gases, especially as compared with the *direct* action of the free carbon. And here, it seems to me, one of the principal causes of the discordance of opinions must be sought in the fact that in many cases the various experimenters set themselves, in reality, quite different problems, which could not admit of a common solution. It is easy to see this by examining, for example, the experimental data discussed by Ledebur and by Guillet in their polemic, which I reviewed at length in the preceding pages. Thus, for example, Guillet, among other things, proposed to show that pure carbon, *in the absence of the smallest trace of gas*, can not cement iron, but he admitted explicitly that in industrial practice the carbon monoxide produced by the oxygen of the air contained in the cementation boxes on the carbon of the cement may give rise to a cementation, though "very slow." Now, given this premise, it can not but cause surprise to see Ledebur oppose to Guillet, in proof of the possibility of producing the cementation directly with solid carbon without the intervention of any gas, experiments carried out without the least precaution for eliminating from the medium in which the cementation is effected precisely that gas (air) to which Guillet had, at least partially, attributed the cementation. This fact, otherwise inexplicable, is easily

¹The contents of this chapter have already been published in part in a note which appeared in September, 1911, in the *Rassegna Mineraria, Metallurgica e Chimica*. In the present compilation, however, have been added various considerations relative to many researches carried out since that time.

explained when we note the fundamental difference between the problems which each of them proposed to solve. While Guillet proposed to establish, as a *scientific datum*, the fact that pure carbon can not cement iron when the presence of the slightest trace of gas is excluded, Ledebur wished simply to prove that under the ordinary conditions used in industrial practice, the intervention of the special gaseous compounds named by Guillet (volatile cyanides, carbon monoxide, etc.) need not be considered necessary to obtain a good *technical* result. This explains also the insistence of Ledebur in reproaching Guillet for not having carried out his experiments on a large scale under the conditions of industrial practice; such a reproach would evidently be considered absurd and ridiculous by one approaching the problem from the purely scientific point of view of Guillet.¹

Analogous observations could be made on the polemic between Caron and Margueritte, on the cementing action of carbon monoxide.

Granting this point of view, let us examine briefly, on the basis of the more recent experimental data, the conclusions of various experimenters on the function of the various gases in the process of cementation.

Leaving aside, because of its evident improbability, Laurent's hypothesis (see p. 4), according to which the cementation is due to the action of the vapor of carbon on the iron, we find as early as 1841 the theory of Leplay attributing to carbon monoxide the principal part in the process of cementation with wood charcoal. We have further seen that this hypothesis, slightly changed in form by substituting the conception of continuous reactions tending to a definite state of equilibrium, for that of alternating complete reactions, is in substance fully confirmed by the recent investigations, detailed in Chapter IV. These have shown, in fact, that in the great majority of processes of cementation used in practice the reaction which greatly predominates over any other is carbon monoxide acting as "vehicle" for the diffusion of the carbon into the mass of the steel. But the hypothesis of Leplay was not founded on sufficient known experimental data, and the criticisms by Gay-Lussac five years later (see p. 4), cautioning against the acceptance of hypotheses not based on direct and sure experimental proofs, were perfectly justifiable. The criticisms of Gay-Lussac were the incentive to a long series of experimental investigations, which have only in the last few years led to sure conclusions.

¹ I consider it, in general, absolutely unjustifiable to assert that the course of an industrial process can be cleared up *solely* on the basis of the results of experiments on an industrial scale. In fact, laboratory investigations, if chosen and carried out along proper lines and interpreted rationally, constitute the most valid means (and in many cases the only means) of clearing up the course of very complicated processes, whether industrial or not. Such alone permit of *isolating* the elementary phenomena constituting a complex phenomenon, whose very complexity would render it inaccessible to *direct* investigation. For this reason I believe that the ideas expressed by Mannesmann (see p. 15), by Ledebur (see p. 60), and by others concerning this subject must be regarded as beside the mark.

Among all the various groups of gaseous carburizing compounds, that to which the majority of experimenters attributed the greatest efficacy in the process of the cementation of iron is without doubt the group comprising cyanogen and its derivatives, and especially the volatile alkali cyanides.

That cyanogen and the more or less volatile cyanides can cement iron intensely is beyond doubt. It is sufficient, to prove it, to note the results of the cementation experiments carried out by Caron, using pure ammonium cyanide (see p. 6). Moreover, it is well known that fused potassium cyanide and potassium ferrocyanide are used in the pure state to obtain thin and strongly carburized cemented zones in the case-hardening of machine parts.

But it is inexplicable why accurate experimenters, such as Caron, Guillet and others, observing merely that the isolated alkali cyanides or ammonia in the presence of carbon (see p. 5) can cement iron, inferred directly that cyanides always play the chief part in the carburizing action of the cements in the cementation industry. In industrial practice the cyanides do not exist already formed, but may be formed in very small quantity by the action of the nitrogen of the air (occluded in the cement) on the carbon used and on the small quantities of alkali constituting a part of the ashes of this carbon. Although the formation of small quantities of alkali cyanides can not therefore be wholly avoided in industrial cementation with carbon as base, the part which is played by these traces of volatile cyanides is *certainly negligible* in comparison with that of the carbon monoxide formed by the action of the oxygen of the air on the carbon used as cement. The following facts show certainly and clearly the correctness of this assertion:

1. If the activity of cements with carbon as base were due essentially to cyanides formed by the action of the nitrogen of the air occluded in the carbon on this carbon and on the alkalis contained in its ashes, it is evident that the intensity of the cementation should be greatest when the cement is made to act in an atmosphere of nitrogen, and least when a gas *free from nitrogen*, as, for example, carbon monoxide, is completely substituted for the air occluded in the carbon. But our experiments (see p. 121) have clearly shown the contrary, *viz.*, that wood charcoal in an atmosphere of pure nitrogen gives rise to only a very faint carburization of the iron, while this same carbon, freed from the last traces of occluded nitrogen by repeated ignitions in a current of pure carbon monoxide and kept, before and during the cementation, in an atmosphere of pure carbon monoxide, gives very intense cementation. Thus, from numerous experiments it has been proved that the carburization is considerably more intense when the carbon is made to act on the iron in an atmosphere of carbon monoxide freed from nitrogen than when it is made to act in the presence of air, in which case the nitrogen intervenes together with the carbon monoxide.¹

¹ Charpy also (see p. 113) observed an analogous phenomenon, but his observation is more than a year later than some patents of mine in which this phenomenon is clearly

2. We are led to the same conclusion by discussing the cementations carried out by Ledebur (see p. 61), using carbon whose ash did not contain alkalis capable of forming volatile cyanides.

3. From the experiments of Charpy (see p. 113) it follows that in the majority of cases, using cements with carbon as base, not the least trace of cyanides is formed during the cementation, and this, too, in cases in which the carburization is most intense. Thus, for example, using the cement of carbon powder and barium carbonate, no traces of cyanides appear except at temperatures higher than 1050° C., while the carburizing action of this cement is very intense even at a much lower temperature. It is to be noted that it was particularly on a consideration of the activity of this cement that Caron and then Guillet based their hypothesis of the necessity of the intervention of cyanides in the cementation.

4. Numerous experiments (see pp. 78-81) show that pure hydrocarbons, and especially those freed from the smallest traces of nitrogen, strongly cement iron. This, moreover, Caron himself had been forced to admit, on the basis of his own experiments carried out to confute the theories of Frémy (see p. 7). But Caron maintains that with hydrocarbons there is not obtained true cementation proper, since they always furnish cemented zones so strongly carburized as to constitute true cast irons, not steels. This last assertion, however, does not correspond to the facts, as is clear from a large number of experiments on this head which I have summarized in the preceding chapters.

The only consideration which can justify attributing to cyanides the carburizing action of cements with carbon as base is the double assumption that carbon can not cement the iron directly without the intervention of a gas, and that carbon monoxide has no cementing action whatever on the iron (Caron) or only a very slow and practically negligible carburizing action (Guillet). Admitting the necessity of the intervention of a carburizing gas and excluding the possibility that this gas could be carbon monoxide, it must be recognized that the simplest hypothesis was that of attributing the carburization of the iron to the action of volatile carburized compounds of nitrogen, especially as described. Moreover (as I have already pointed out) not all of Charpy's observations in this memoir are entirely correct. It suffices, for example, to cite those (see *Revue de Métallurgie*, 1909, p. 517) on the different behavior of the carbonates of calcium and barium, from which it almost seems as if the author attributed to the different nature of the two carbonates the different proportions of carbon dioxide and of carbon monoxide which are evolved in their mixtures with carbon. So, too, the observation contained in the note on page 518 of the same memoir on the "limitation" of the cementation carried out in a limited atmosphere of carbon monoxide holds only when the steel subjected to the cementation is in wires or thin plates or in small granules; for we know that in ordinary cases, in which pieces of iron of medium or large dimensions are cemented, even in a limited atmosphere of carbon monoxide, the cementation can reach a great depth (theoretically unlimited), but with the concentration of the carbon in the cemented zone becoming continually smaller.

it had already been proved that not only cyanides already formed but even dry ammonia in the presence of carbon can cement iron. Nevertheless, as we have seen in the preceding chapter, there not only was lacking any direct proof of the new hypotheses, but more recent experiments have since shown that both of the assumptions made the basis of these hypotheses are absolutely without foundation—especially the second, relative to the impossibility of practically cementing iron with carbon monoxide. At present, the action of carbon monoxide suffices to explain perfectly the processes of cementation which earlier experimenters thought it necessary to explain by the intervention of cyanides.

We must however explain the numerous negative results obtained by various experimenters in attempts to show the carburizing action of carbon monoxide on iron.

The first precise experimental investigations to establish whether carbon monoxide can cement iron were those carried out by Caron and by Margueritte in the course of the discussion to which I have already referred.

Caron in all his experiments used specimens of iron of considerable dimensions,¹ and to determine the amount of cementation he contented himself with breaking the specimens, after having forged and hardened them, and examining the "grain" of the fracture. Now, my recent experiments (see p. 78) show that, working under these conditions, and especially if the temperature of the cementation is high and the quantity of carbon monoxide used is not very large, or the gas is not absolutely pure, there are obtained, without the intervention of the slightest traces of cyanides, quite deep cemented zones, but the concentration of the carbon in them is too small to make it possible to recognize the cemented zone from the simple appearance of the surface of fracture.

That this is the cause of Caron's error is proved by the fact that he himself admitted that carbon monoxide can cement iron at dark red heat,² but not (contrary to the assertions of Margueritte) at the higher temperatures at which the industrial process of cementation is always effected.³ We have seen that the knowledge acquired more recently about the conditions under

¹ In general 10 × 10 × 300 mm., dimensions much greater than the mean thicknesses of the carburized zones which are obtained with the usual cements working under the conditions of length and temperature adopted by Caron.

² Wedding also (*Ausführliches Handbuch der Eisenhüttenkunde*, Part 2, Vol. IV, p. 237) asserts that carbon monoxide does not cement iron except at temperatures below 400° C. On the basis of this, and other considerations on the exhaustion of the gases of the cementation boxes, Wedding holds that in practice the gases can at most but "initiate" the cementation.

³ It is clear from what I have said that in the discussion between Caron and Margueritte there occurs a misunderstanding analogous to that between Guillet and Ledebur, already described. We have seen how this misunderstanding was due essentially to the fact that one of the experimenters considered and studied the process of cementation exclusively from the point of view of its technical applications, the other from the scientific standpoint.

which the process of cementation is effected by means of carbon monoxide permits of asserting that in the cementation of specimens of considerable dimensions with carbon monoxide alone the essential difference between the product which is obtained by working at a low temperature (700–800° C.) and that which is obtained at high temperatures (1000–1100° C.) consists chiefly in the *concentration* of the carbon in the cemented zones, a concentration which is the smaller the higher the temperature.¹

This explains the error of Caron, who, however, also reasoned erroneously that because carbon monoxide *alone* does not (as he thought) cement iron, the action of the carbon monoxide is *nil* even in the cementation boxes, where it is in the presence of an excess of carbon. Now, we have already seen on p. 135 that in the presence of the free carbon the carburizing action of the carbon monoxide is modified, becoming more intense, so that it can be used directly in practice with great advantage.

Caron evidently was misled by his premature conclusion when, on the basis of a direct experiment, he asserted that carbon monoxide even in the presence of carbon can not cement iron. In fact, numerous experiments prove the contrary, and the wide technical applications of the carburizing activity of carbon monoxide used together with carbon allow no doubt as to the error of Caron.

To analogous experimental errors must be attributed the assertion of Saunderson, cited by Caron in support of his hypothesis (see p. 6), that the cementation is effected *only* by the simultaneous action of nitrogen (for example, in the form of ammonia) and of carbon, and that, for example, carbon monoxide and ethylene, taken separately, can not cement iron.

Contrary to Caron, Margueritte in his cementation experiments with carbon monoxide always used the iron in the form of thin pieces such as wires, or thin sheets, or filings, or powder obtained by the reduction of iron oxalate. Only in one case did Margueritte use a bar of iron 6 mm. thick. These are thin compared with the thicknesses of cemented zones obtained with the usual cements, working under the same conditions.

Now, under these conditions the carbon yielded by the carbon monoxide can not diffuse deeply into the mass of the iron, as takes place when specimens

¹ The same consideration serves to explain clearly the apparently strange observation of Charpy (see p. 45), according to which "the velocity of the cementation" with carbon monoxide does not increase sensibly for temperatures higher than 900° C. In reality, "the velocity of cementation"—meant as "depth reached by the cemented zone in a given time"—increases with increase in the temperature even much above 900° C., and my more recent experiments (see p. 78) show it clearly. But, given the conditions under which Charpy worked (see the observations made on page 46), the decrease in the *concentration* of the carbon which, for the reasons which I have indicated, gradually manifests itself as the temperature rises above 900° C. is such that the *quantity* of the carbon absorbed in a given time (for a given velocity of the current of carbon monoxide) continues to diminish with rise in the temperature.

of iron of greater dimensions are cemented. In the latter case, as I have already explained, the carbon monoxide lowers the concentration of the carbon at the periphery of the cemented pieces, functioning as a "vehicle" for the rapid diffusion of this carbon toward the deeper parts of the specimens. It is evident, therefore, that when the surface of the iron subjected to cementation is considerable as compared with its mass, the concentration of the carbon in the metal can more quickly reach a high value.

This explains how Margueritte, contrary to Caron, obtained cementation with carbon monoxide, even when working at high temperatures.¹

Margueritte also made some observations which have been clearly confirmed by more recent experiments and the physico-chemical theory of cementation with carbon monoxide. Thus, he observes that in iron wires cemented with carbon monoxide, all other conditions being equal, the concentration of the carbon is the smaller the higher the temperature (between cherry-red and orange-red) at which the cementation was effected. Later he himself properly pointed out that Percy in 1859 had used too small quantities of carbon monoxide to obtain appreciable cementations. This is confirmed by our own results.

Summing up, I believe it can be asserted that the observations of Margueritte, examined in the light of our present knowledge, constitute an excellent refutation of the hypothesis of Caron regarding the necessary and preponderant intervention of cyanides in industrial cementation, and substantiate the active carburizing action of carbon monoxide and of carbon alone on iron.

Other experimenters also, finding that carbon monoxide, acting *alone* on the iron, gives carburizations of slight intensity, or, more correctly, cemented zones of low carbon content, held that in cementation with cements having carbon as base (such as are used in industrial practice) the specific carburizing action of the carbon monoxide was by far less intense than the direct action of the carbon or of the other gases (cyanides, nitrogen, etc.). Their mistake consisted in not knowing that the carburizing action of the carbon monoxide is strongly "intensified" by the presence of the carbon.

In this connection I will also recall the conclusions of Mannesmann (see p. 17). Boussingault pointed out that the quantity of carbon monoxide which can be formed in the ordinary cementation boxes would be sufficient to cement only a very small part of the 13 or 14 tons of steel contained in a box, but we have seen that more recent investigations have proved that under these conditions the carbon monoxide is not exhausted during the cementation, and really constitutes a most efficient vehicle in producing the diffusion of the carbon from the wood charcoal into the mass of the steel.

¹ The same considerations also explain how Charpy (see page 45), cementing iron *wires and filings* with carbon monoxide, obtained strong carburization at high temperatures (1000° C.).

Guillet also (see p. 47) holds that the carbon monoxide which is formed in the cementation boxes (either by the action of the oxygen of the air on the carbon or by the action of this carbon on the carbon dioxide of the carbonates added to the cement) has an action which is but very slow and entirely secondary in the process of industrial cementation. But these considerations of Guillet, also, have been shown to be inexact.

Le Chatelier, even after the decisive experiments of Charpy, limits himself to observing that it is "difficult to admit that the cementing action of carbon monoxide is *nil*." Later, Bruch (see p. 66), on the basis of new experiments, affirms that carbon monoxide can not cement iron.

All these results, partially or totally negative, are explained by the considerations which I advanced in connection with the analogous results of Caron's investigations.

Assuming this, and having established by experimental data that in the ordinary processes of cementation with cements having carbon as base the action of cyanides is not preponderant but is entirely or almost entirely negligible, while the specific action of the carbon monoxide predominates, let us see how the results of the experiments which led to the hypothesis of the preponderant action of cyanides are explained. I shall refer to only two series of more noteworthy facts, for the examination of all these experiments would be long and tedious.

First of all, it is clear that the greater carburizing activity obtained by adding to the wood charcoal the carbonates of the alkali or alkaline earth metals (see, for example, Caron, p. 6, Guillet, p. 49) is explained perfectly by the results of the recent experiments showing the efficacious action of carbon dioxide. This is especially evident for the "inexhaustible" cement, composed of mixtures of carbon and of barium carbonate, proposed repeatedly, for example, by Caron and by Guillet. For this result, the agency of considerable quantities of carbon dioxide is evident, and this not only when the cement is used the first time but also every time this same cement, after having been used, is allowed to stand in contact with air before using again, so as to make possible the "regeneration" of the barium carbonate.

The other hypothesis, evidently untenable since the demonstration of the negligible part played by cyanides in ordinary cementations, is that first advanced by Caron (see p. 11) and then by Guillet (see p. 50), which attributes the "exhaustion" of the cements with carbon as base to the progressive volatilization of the alkali cyanides.¹ It is quite probable that the cause of this "exhaustion" is not a single one, so that it would be necessary to seek

¹ The persistence observed by Guillet in the carburizing action of the carbon in the presence of ammonia can certainly be due to the formation of ammonium cyanide. But here also (analogously to what I have already pointed out on p. 171 of the present chapter) this *in no wise* proves that the exhaustion of the cements is due to the volatilization of the cyanides, whose presence or formation in these cements is, moreover, negated by the experiments of Charpy.

it along different lines, case by case, depending on the composition of the cement considered. It is indeed possible that in some cases the exhaustion may be due (as Margueritte and Mannesmann had already supposed) (see p. 19) to a change in the state of agglomeration of the carbon contained in the cement. This appears the more probable, now that we know the importance of the part which carbon monoxide plays in the cementation, when we consider the fact, demonstrated by Schenck, that with variations in the nature of the carbon its manner of acting with mixtures of carbon monoxide and of carbon dioxide also varies markedly, and this not only as regards the velocity of the reactions but also as regards the final conditions of equilibrium to which these reactions lead.¹

For cements containing easily fusible alkali carbonates and cyanides, it is not improbable that to the causes just indicated there may be added a diminution in the "reacting surface" of the porous carbon, due to the fact that the latter becomes impregnated with the fused salts.

Having now cleared up some of the fundamental points of the theory of cementation, the discussion of which required more detailed consideration, let us try to draw some concrete conclusions from the results of the various experiments described, especially concerning the conditions which are present in practice, on the *direct* cementing action of carbon in ordinary industrial cementation.

And here it is, first of all, necessary to put the matter very clearly, in order to avoid drawing opposite conclusions from the experiments of various experimenters.

Here, put in the most schematic form, are the various partial questions to which the experimental researches of the group with which we are dealing may furnish an answer. Together with each question I add, in succinct form, the answer which can be given to it by the numerous experiments which I have cited in the preceding pages. A few brief references to the facts already developed will then suffice to show how the conclusions correspond well with all the experimental results obtained by the various experimenters.

1. Can *carbon alone*, simply heated in contact with solid iron and without the intervention of any gas, carburize iron?

This question, of a purely scientific character, experiment answers affirmatively.

2. Can *carbon alone*, that is, simply heated in contact with solid iron without the intervention of any gas, give rise to cementation of practically suffi-

¹ Moreover, when we take into account the various facts which I have cited concerning the manner in which carbon monoxide intervenes in the processes of cementation, it is easily understood how a cement formed of practically pure carbon (such as sugar carbon) must be rapidly exhausted owing to the fact that the small quantity of carbon monoxide which can be formed at the expense of the oxygen of the air occluded in it is eliminated either because a part of it passes into solution in the iron or because another part escapes from the cementation boxes, the joints of which are always permeable to gases.

cient intensity under the conditions of time and temperature which are ordinarily present in industrial practice?

This question, of an essentially technical character, experiment answers negatively. The cementation obtained with carbon *alone*, in the absence of any gas, is of practically negligible intensity.

3. What part does the carbon and what part do the gases play in the ordinary processes of cementation used industrially?

To this question it is not possible to give a single answer, holding for all cases. It is necessary, for every type of cement, to examine the specific carburizing action of the gases which may be formed in its use, and to study in what way this specific action is modified by the presence of the free carbon pre-existing in the cement (as, for example, in the cement composed of the mixture of carbon and barium carbonate), or formed during the cementation (as, for example, in the cementation carried out in the presence of hydrocarbons).

I shall examine later from this point of view some of the cases which occur in practice, to show the real technical value of these recent studies.

Beginning with the first of the three questions enunciated above, we can affirm that the fact that carbon *alone*, without the intervention of any gas, cements the iron with which it is kept in contact for a sufficiently long time and at a sufficiently high temperature has been proved with certainty by a number of the experiments which I have described in the preceding chapters. Among the most convincing are those of Mannesmann (see p. 18), carried out with cast-iron turnings "drowned," together with the iron specimens, in fused salt or lead, in which case the exceedingly slow cementation of the iron specimens takes place only at the points at which they come in contact with the cast iron. We can also refer to those of Roberts-Austen (see p. 27), in which the carburization of pure electrolytic iron by the action of a diamond placed in contact with it was effected at bright red heat *in a vacuum*, and after both the iron and the diamond had been ignited for a long time in a vacuum to totally eliminate occluded gases from them. Royston's tests (see p. 30) proved that the carbon diffuses from a piece of highly carburized steel (0.95% C) to one less carburized (0.15% C) with which it is kept in contact *in a vacuum* at a high temperature, and that diffusion ceases as soon as there is no longer *direct* contact between the two specimens of steel. Arnold and MacWilliam (see p. 34) proved the diffusion of carbon from a more highly carburized steel to one less carburized kept in intimate contact *in a vacuum* at a high temperature.¹ The same was proved by more recent

¹ In truth, the experiments of Royston and those of Arnold and MacWilliam (contrary to those of Mannesmann and of Roberts-Austen and the more recent ones) do not furnish a *direct* proof that *free* carbon can cement iron without the intervention of any gas, but only show the fact, which is not entirely equivalent, that the intervention of any gas is not necessary to produce the diffusion of the carbon from one point to another in a mass of solid steel. Really this last process is but one (though the most important one) of the two phases of the process of cementation.

experiments carried out by myself and Astorri (see p. 121), by Guillet and Griffith (see p. 122), and by Weyl (see p. 124).

On the other hand, experiments based on the observation that when carburizing gases are not totally eliminated or absent the cementation is always more intense at the points at which the carbon is in direct contact with the iron have but little evidential value; such are, for example, the experiments carried out by Margueritte with diamond and graphite powder in a current of hydrogen (see p. 8), by Percy (see p. 13), by Mannesmann (see p. 18), by Bell, etc. This is so because experiment shows (see p. 138) that the various gases, and especially that one which acts most efficaciously in cementation, *viz.*, carbon monoxide, act with maximum intensity in the immediate proximity of the free carbon, and their carburizing activity diminishes when the distance between the point at which the carburization of the iron is effected and that at which the gas can be regenerated by reacting with the free carbon increases. This diminution in intensity, which is quite slow when the gas can move freely between the surface of the steel and the carbon which must regenerate it, becomes very great when these movements are obstructed and the carbon is far from the surface of the steel; this happened, for example, in the experiments of Mannesmann cited, in which the surface of the steel not in contact with the carbon was buried in refractory earth, in whose pores the gas circulates only with extreme slowness. Next, the experiments of Ledebur (see p. 60), carried out on a large scale but without care to eliminate the gases occluded in the carburizing powders used for the cementation, prove absolutely nothing when the problem is considered from the more general scientific point of view.¹

Taking up the second question and the answer given, it follows from the same experiments which I have cited above that the "direct" carburizing action of free carbon on the iron, by simple "contact" at a high temperature, acting alone and without the intervention of any gas, if not null,² is at least certainly *exceedingly small*. As to deciding whether this *direct* action of carbon on iron, in the absence of the slightest traces of gases, is *really absolutely null* or only extremely small, the information may present a certain

¹ The small scientific value of these experiments of Ledebur is still more evident now that we know the efficacy of the intervention of the oxygen of the air occluded in the cements (as a generator of carbon monoxide). Guillet did not succeed in showing this in his attempt to point out that Ledebur had not eliminated the possibility of the formation of alkali cyanides, to which chiefly and almost exclusively he attributed the process of cementation.

² Charpy and Bonnerot consider it null, on the basis of the results of some of their recent experiments (see *C. R. de l'Académie des Sciences*, 1st sem., Vol. CL, p. 173). Charpy observes that the fact that temper-carbon redissolves in the iron as the result of prolonged heating (a fact which Le Chatelier (see p. 64) had cited as proof of the possibility of the *direct* diffusion of carbon into iron) may be due to the action of the gases always present in solution in the iron. He holds that "solid carbon outside of a fragment of steel can not penetrate into it without the intervention of a gaseous vehicle."