interest from the theoretical point of view but it is a problem of very small, if of any, practical interest.[1]

On the other hand, the solution of the third question which we have set ourselves presents a very great practical as well as theoretical importance. This is the establishment of the part played directly in the process of cementation by the various gases and that played, directly or indirectly, by the free carbon when the gases and the carbon act simultaneously, and in what way the two groups of substances (the solid cement with carbon as base and the gases), acting simultaneously, reciprocally modify each other's specific action.

To treat such a complex problem it is first necessary to examine, at least briefly, the behavior, in the presence of iron and of free carbon, of the individual gases which may be active in the processes in practical use. And, indeed, this examination furnishes the answer to our question for the most frequent cases.

Of the gases which may take part in cementation carried out by the usual processes, let us begin by considering free nitrogen. In all cementations carried out with solid cements there is necessarily present the nitrogen of the air contained in the cementation boxes.

We have already seen (see p. 7) how Frémy's hypothesis that nitrogen acts *directly* on iron, simply "nitrogenizing" it and transforming it into steel, was quickly shown to be false by the experiments of Caron.

Later (see p. 26), Hempel maintained, on the basis of careful experiments, that carbon in the presence of pure nitrogen freed from the smallest traces of oxygen can not cement iron. Considerably more recently, Le Chatelier (see p. 58) held that in the usual processes of cementation nitrogen is the agent which transports the carbon into the mass of the iron. In reality, all the more recent and more precise experiments show that during cementation the nitrogen may diffuse in small amounts into the iron (see p. 139). This may be the cause, as Le Chatelier suggested, of the increase in brittleness sometimes observed in those parts of the steel subjected to cementation which the carburization had not even reached. It is however now certain that the presence of pure nitrogen does not increase except to a minimum extent the carburizing action of free carbon. The cemented zones which are obtained by the simultaneous action of carbon and nitrogen are in particular (see p. 121) characterized by a very low carbon concentration.[2] The explanation of this last phenomenon, which is the cause of the negative results obtained by Hempel, is the fact that the intervention of nitrogen in the process of cementation must be explained in a manner analogous to that of carbon monoxide, that is, by a reaction whose final equilibrium depends also on the concentration of the carbon dissolved in the iron of the cemented zones. But, while the reasons for the specific carburizing action of the carbon monoxide, alone or in presence of free carbon, have been accurately studied and are now known in all their particulars, the reactions (certainly analogous) to which the slight specific carburizing action of nitrogen in the presence of the free carbon is due have been studied considerably less, and we have no precise data about them.

For practical purposes this deficiency in data about the specific action of nitrogen has no importance, for exact experiments have shown that in the technical study of the processes of cementation we do not have to take into account the intervention of the free nitrogen, whose action in the presence of free carbon is certainly too slight to influence practically the results which are obtained with a given cement.

With a second class of volatile carburizing compounds, the cyanides, I have already dealt, in discussing whether the volatile cyanides take a preponderant part in the ordinary processes of cementation. I there showed by rigorous experiments that these cyanides (which, without doubt, exercise on iron at a high temperature an intense specific carburizing action) are never formed in the cements usually employed, or that they are formed only under special conditions, but always in such small amount as to render their action practically negligible. As to those special cases in which solid or fused cyanides or ferrocyanides are used directly for the cementation of steel, alone or mixed in considerable proportions with other carburizing substances, it is certain that their intense specific action is exercised directly on the iron, adding itself to that of the other carburizing substances. In these cases also, therefore, the intervention of the cyanides *as volatile gases* at the temperature of the cementation is absolutely negligible.

We conclude, therefore, that in the examination of the respective parts played by the gases and the free carbon in industrial cementation we need not take into account the cyanides, because experiment shows that these, when they intervene as gases or vapors, produce only a negligible effect. As to the intense action of the solid or fused cyanides, this in no way concerns the part of the problem we are now considering.

Among the gases which usually and efficaciously act in industrial cementation with free carbon are the hydrocarbons. Such gases are really widely used in practice for every kind of cementation from thin cementation of machine parts up to the deepest cementations, such as those which are used for armor for ships. In almost all these cases (see p. 114) a part of the hydrocarbon used for the cementation is decomposed, setting carbon free. Therefore, both in the case in which the hydrocarbons are used alone and where they are

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[1] For this reason it seems to me that there is no justification for the observation of Guillet, who, in reporting some of his communications presented before the Congress of Metallurgy of Düsseldorf (see *Bull. de la Soc. des Ing. Civils de France*, October, 1910), asserts that it would be of extraordinary importance for technology to establish with certainty whether carbon alone can cement iron without the intervention of gases.

[2] This explains, when we consider my explanation of the erroneous conclusions drawn by Caron in connection with the carburizing action of carbon monoxide, why Caron asserted that carbon in an atmosphere of pure nitrogen can not cement iron.

introduced into the cementation boxes (or are formed there by the decomposition of organic substances), in the presence of pre-existing free carbon, we have the problem of establishing what part is played by the direct action of the gases and what by the action of the free carbon which they deposit on the surface of the iron.

And here it is well to make clear what is meant by the *action of the gases* in cementation. Any carburizing gas whatsoever can cement iron only by the action of the carbon which it can set free in decomposing. But this separation of free carbon can take place in two distinct ways:[1]

1. The gas may decompose totally as soon as it comes in contact with the surface of the steel, setting free on this surface all the carbon which it is capable of yielding. In this case it is evident that the carburizing gas exercises no other function than that of carrying the carbon into intimate contact with the steel. As to the process of the cementation proper, or the more or less deep diffusion of the carbon into the mass of the solid steel, this is effected in this case exclusively by the solution of the carbon in the surface layer of the steel and its passage from this layer to the succeeding one through the action of one of those processes of diffusion *by difference in concentration* which have been observed in a large number of alloys formed of solid solutions.[2]

In these cases we properly say that the gas exercises no specific action on the course of the cementation. It may also be asserted that this extreme case never presents itself in practice.

2. The gas may decompose only partially when it comes in contact with the surface of the steel, setting free there only a part of the carbon which it is capable of yielding. The gas, then, as it diffuses into the mass of the steel continues to decompose, setting free in these interior layers of the steel new quantities of carbon which gradually pass into solution *directly* in the metal of the deeper and deeper layers.

In this case, which we have seen occurs with special clearness in the case of carbon monoxide, we say that the gas exercises a direct specific action on the course of the cementation. In this case, all the variations in the conditions (for example, the pressure, the quantity of the gas, etc.) on which the diffusion of the gas into the steel depends or the reaction by which the gas can set carbon free must greatly influence the course of the cementation.

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[1] See also the observations of Le Chatelier (p. 64).

[2] It is interesting to recall in this connection the results of the investigations of many experimenters on diffusion in other metals. I have already referred to the investigations of Roberts-Austen on the diffusion of gold and of platinum into lead, on the basis of which he asserted the complete analogy between these and the process of cementation. The latter would therefore be a simple phenomenon of direct diffusion of the carbon into the iron by difference in concentration

In reality, the "concentration-depth" curves determined by Roberts-Austen for the two pairs of metals Au-Pb and Pt-Pb differ profoundly from the analogous curves which I have reproduced in the preceding pages for the processes of cementation, and especially for those of them based on the action of carbon monoxide. This is explained by the direct action of the carburizing gases and thus constitutes a new proof of their intervention.

In the case of the hydrocarbons with which we are now dealing, there is no doubt that a part of the carburizing action which they exercise on iron at a high temperature is due to the *direct* action of the carbon which they always deposit on the surface of the metal. In fact, we have seen that solid carbon heated in contact with iron cements it, even without the intervention of any gas, and moreover it is quite probable that with pulverulent carbon in a state of extreme division, such as that which is formed in the decomposition of hydrocarbons, the direct action "by contact" is considerably more intense than with powdered wood charcoal, if for no other reason than the more perfect contact between the carbon and the surface of the steel.

But we have seen[1] that in cementation carried out with pure hydrocarbons both the depth reached by the carburization in a given time (velocity of cementation) and the maximum concentration attained by the carbon in the cemented zone increase markedly with increase in the *pressure* of the gas and in the *quantity* of this gas which comes in contact in a given time with a given surface of the steel. These facts show that in cementation with the hydrocarbons there is also a specific action of the gases, or that the diffusion of the carbon into the steel is due also to diffusion into it of the carburizing gases, which react with the steel in the deep zones, there yielding carbon directly. In fact, the variations in the velocity of the cementation and in the concentration of the carbon in the cemented zones can not be due to the free carbon which the gas always deposits in excess on the surface of the steel; for of this carbon the only part which can act directly by contact is that of the first layers formed immediately on the surface of the metal and not that further portion which, through an increase in the pressure or of the quantity of gas used, may eventually be deposited upon the preceding, without increasing the quantity of free carbon which is actually in contact with the surface of the steel.

This explains the expression of Guillet, that in cementation hydrocarbons certainly act "by dissociation" (see p. 48); and we can now say that the way in which hydrocarbons behave in the presence of iron or of free carbon is fully known.

Finally, another carburizing gas, which does not belong to any of the groups which we have just examined, is carbon monoxide. I have spoken at length of its great efficacy in the process of cementation, basing my remarks on the results of numerous experiments reported in the preceding chapters. I have also already spoken of the special manner in which carbon monoxide behaves as cement, either alone or in the presence of free carbon and of hydrocarbons.

First of all, we have seen (see p. 45) that carbon monoxide, acting alone on iron, deposits free carbon on it only at temperatures lower than those ordi-

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[1] See p. 82 and especially the data contained in the tables on pp. 78–81.

narily used in industrial cementation, that is, below about 700° C. At all the temperatures used in cementation practice, carbon monoxide carburizes iron exclusively through its specific action *as a gas*, and this action is not modified by the deposition of free carbon on the surface of the metal, in a state of extreme division.

This fact facilitates enormously the exact study of the characteristic specific action of carbon monoxide, not only in the case in which the carbon monoxide is made to act alone on the iron, but also in the case in which it acts together with other carburizing substances whose specific action is known.

I have already reported in detail the proof of the very slight and practically negligible carburizing action which the ordinary forms of carbon (such as wood charcoal, sugar carbon, etc.) exercise *directly* on iron in the absence of gases. This, with the facts just related, permit of stating at once that when the very efficacious cement composed of carbon monoxide and the ordinary forms of carbon (for example, wood charcoal) acts on the iron, the greatly preponderating action is the specific action of the carbon monoxide, modified and greatly "intensified," in the way which I have explained further back, by the presence of the free carbon.

The same observations show that the carburization obtained with carbon monoxide mixed with such a small proportion of volatile hydrocarbon that during the cementation the gaseous mixture can not set carbon free at the surface of the iron is due exclusively to the specific actions of the two gases; actions which in this case are additive, reciprocally modifying each other in the manner we have seen.

From the facts set forth and the considerations developed we can now draw these conclusions of practical interest:

1. The *direct* action of the carbon in the forms in which it is habitually used in solid cements is exceedingly slight; it is absolutely negligible as far as regards the *technical* results which are obtained with a given cement.

It is barely possible that the direct carburizing action of the carbon in a state of extreme division which some carburizing gases, such as the hydrocarbons, deposit on the surface of the steel may be of appreciable extent.

2. The salts derived from cyanogen (cyanides, ferrocyanides, etc.) exercise on iron a specific carburizing action, which has not yet been studied with precision. At any rate, the most reliable experiments show that, contrary to what various experimenters thought they had proved, the activity of cements containing free carbon and carbonates of the alkali or alkaline-earth metals is certainly not due to the formation of volatile cyanides by the action of the nitrogen of the air on the alkali or alkaline earth carbonates, but to the formation of carbon monoxide by the action of the carbon on the carbon dioxide produced by the dissociation of the carbonates.

3. The carburizing action of nitrogen in the presence of carbon is also technically negligible.

4. In the carburizing action on iron exercised by the hydrocarbons at a high temperature, there certainly occurs to a very considerable extent the *direct* action of the gases. However, experimental data are lacking which would establish the extent of the simultaneous direct action of the finely divided carbon which the hydrocarbons, in decomposing, deposit on the surface of the iron.

5. The carburizing activity of pure carbon monoxide on iron at the temperatures used in the practice of cementation is due exclusively to the direct specific action of the gas.

6. The specific carburizing action of carbon monoxide becomes most intense when the gas acts on iron in the presence of free carbon. This specific action, modified by the other carburizing substances present, such as hydrocarbons, cyanides, etc., is enormously preponderant above all the others in all cements in which carbon monoxide is present or can be formed,[1] among which must be numbered all the most widely used solid cements.

Besides wood charcoal, which we have shown to act exclusively through the action of carbon monoxide, the "inexhaustible cement," first proposed by Caron and then by Guillet and used to-day very frequently for the superficial cementation of machine parts, acts similarly. To the same group belong the cements derived from the last mentioned by substituting wholly or partially for the barium carbonate other carbonates, such as the carbonate of calcium, of sodium, of potassium, etc.

Finally, the cements based on the use of pure carbon in a current of carbon monoxide, pure or diluted with nitrogen, belong to the same group, their activity being due exclusively to the specific action of carbon monoxide.

The carburizing substances containing cyanogen (such as the alkali cyanides, the ferrocyanides, etc.), are at present limited in use to operations of secondary importance, for which the exact knowledge of the way in which the diffusion of the carbon into the steel takes place presents little or no interest. In fact, we shall see that they are used in those cases in which a very hard metallic surface is needed and it does no harm if the cemented zone is very thin and, after the hardening, brittle. Aside from these, only two classes of carburizing substances act directly in all the processes of cementation to-day used industrially:

The first class includes the volatile hydrocarbons, whose specific carburizing action is strongly in evidence when they are used alone, and also in those processes in which they act together with free carbon or other solid carburizing substances.

The second class includes carbon monoxide, whose specific action is greatly preponderant in almost the whole of the cements used to-day in practice.

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[1] This shows the inexactness of the opinions of the various experimenters who considered the carburizing action of carbon monoxide in the processes of cementation negligible as compared with that exercised directly by the carbon or by other carburizing gases or vapors.

It is evident, therefore, that a physico-chemical theoretical study of the process of cementation, whose final and essential object must be to establish precise rules for the practical conduct of the industrial process, must establish first of all the behavior, either alone or in the presence of the ordinary forms of compact carbon, of the two classes of carburizing substances just mentioned. The results of such a study will also furnish practically all the data necessary for the conduct of the actual processes of cementation for we have already seen that the action therein of all the other substances present is practically negligible.

For the case of the hydrocarbons, we may represent schematically the general reaction to which their carburizing effect on iron is due as follows:

$$C_mH_n = C_{m-x}H_{n-2y} + yH_2 + xC.$$

The course of the cementation depends on the velocity of this reaction and the final conditions of equilibrium of the resulting system. Experiment has shown that the course and the final state of the general reaction written above vary within very wide limits, not only with variations in the nature of the hydrocarbon used but also with the smallest variations in the conditions (temperature, pressure, composition of the steel, etc.) under which this reaction is effected.

If we except the cases in which we work at very low temperatures, the reaction schematically indicated above is in reality considerably more complex, because it consists of the aggregate of many analogous reactions and it is not completely reversible, or, at least, in the system corresponding to the final equilibrium the components indicated in the second member predominate enormously. Since we do not usually work at very low temperatures, because of the consequent slowness of the process, cemented zones of *excessively high* carbon content are almost always obtained.

Moreover, even when starting with a pure, chemically definite hydrocarbon, the reaction which takes place in reality never has the simplicity of that schematically written above; thus, for example, the hydrocarbon $C_{m-x}H_{n-2y}$ indicated in the second member is, in practice, replaced by a mixture of various hydrocarbons. And the complexity of the phenomenon increases enormously when, as happens normally in practice, the gas or the vapor used does not consist of a single, chemically definite hydrocarbon but of a mixture of various hydrocarbons.

All these cause the general physico-chemical study of the processes of cementation with hydrocarbons to present enormous difficulties, and lead to results of great complexity.[1]

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[1] For all these reasons we must consider the assertion of Charpy which I have cited on p. 55 to be without foundation. We must consider it as certain that, *in practice*, hydrocarbons used *alone* as cements cannot furnish "automatically limited" cementations, in the sense in which Charpy uses this expression.

Moreover, the same phenomena make it in practice exceedingly difficult, if not impossible, to conduct a cementation with a cement having hydrocarbons as base, in such a way as to obtain a well-defined result, owing to the complexity of the reactions which take place in the cementation boxes. If we work at very low temperatures in order to avoid cemented zones of high concentration of carbon, the process becomes exceedingly slow.[1] For these reasons the use of volatile hydrocarbons is not advantageous in those most frequent and important cases in which it is desired to obtain cemented zones of a certain depth (for example, more than a millimeter), and where a predetermined, well-defined result must be obtained, or where it is important that the concentration of the carbon should not be too far removed from a certain value and that the distribution of this carbon should be as uniform as possible and show no sudden variations.[2]

On the other hand, none of the disadvantages mentioned above is presented by the cements whose activity is due to carbon monoxide. In fact, the reaction to which the carburizing action of carbon monoxide is due, either when acting alone or in the presence of free carbon on iron at a high temperature, is *exclusively* the following:

$$2CO \rightleftarrows CO_2 + C$$

This reaction is simple, perfectly reversible at the temperatures at which the cementation is effected most rapidly, and leads to equilibrium with great rapidity in the presence of the iron, which is, for this reaction, an efficient catalyzer.

Moreover, the conditions of equilibrium of this reaction are exactly such as permit, when working under the conditions best adapted to obtaining in a given time a cementation of maximum depth, of obtaining practically, in the cemented zones, the concentration and the distribution of the carbon usually desired in the cemented articles.

Finally, the course of this reaction, as to the states of equilibrium to which it can lead, under the most varied conditions of temperature, pressure, composition of the steel, etc., are so well known, from such a great series of experimental and theoretical data, as to make possible an exact preliminary determination of the conditions best adapted to obtaining a certain practical result, and thus render easy a rigorous control of the operation.

Since the specific carburizing action of carbon monoxide constitutes the absolutely essential element of all the more important processes of cementation used industrially, and since the general laws which govern this carburiz-

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[1] This had already been observed from the time of the first scientific investigations on cementation; for example, by Caron (see p. 6).

[2] We have seen (see p. 106) how even in cementations carried out at a relatively low temperature it is not possible to avoid at least a sudden variation in the concentration of the carbon in the cemented zone.

ing reaction are known, it seems well to develop here briefly some considerations which it is absolutely necessary to take into account when it is desired to apply these general laws to practical cases such as present themselves in technology.

The reactions concerned in the specific action of carbon monoxide have been the subject of many experimental researches, and the *general* laws which govern their course and the state of equilibrium to which they lead have been enunciated in simple and clear form by Schenck. The theoretical considerations developed by Schenck constitute the necessary foundation for the correct interpretation of these phenomena. For obvious reasons of convenience, we can reproduce these considerations here only in abstract, and I must assume that those who wish to master completely and rigorously the laws which govern the phenomena will study the results of the investigations of Schenck and of his students, or at least as much of them as is reported in Chapters IV and V of his volume on the "Physical Chemistry of the Metals." I therefore limit myself here to making observations on the applicability of Schenck's theories to the practical study of the processes of cementation by carbon monoxide.

First of all, it is necessary to remember that the conclusions of Schenck hold without modification and exactly only in the case in which the various reactions proceed freely until they reach *complete equilibrium.* The course of the reactions which are effected in the system formed of carbon monoxide, carbon dioxide, and iron-carbon mixed crystals hold with exactness only in the case in which the concentration of the carbon is uniform throughout the whole mass of the mixed crystals. But this uniformity can be attained in the time available in practice only when the iron being cemented is subdivided into small masses (wires, granules, filings, etc.), while in the more general practical case of cementation of larger articles, the carburization is limited to the peripheral zone of the pieces and in this zone the concentration of the carbon varies (decreasing) as we pass to the successively deeper layers. It is clear that in this last case we cannot speak of *complete equilibrium.* Also, to the three factors (pressure, temperature and composition of the gaseous mixture) on which in the first case the final result of the cementation depends, are added two others: the velocity with which the gases diffuse into the steel and the velocity with which the carbon diffuses in this steel. Experiment, however, shows that, under the conditions of temperature and of pressure at which the cementation is ordinarily effected, the two new factors act with insufficient intensity to produce a *qualitative* change in the phenomena, and barely sufficient to produce a *quantitative* change in the relation between the maximum concentration of the carbon in the surface layer of the cemented zone and the composition of the gaseous phase.

A proof (among the many which I could cite) of the correctness of these assertions is furnished, for example, by the results of the experiments described on pages 135–136, from which it follows that even when the cementation is limited merely to one zone of the pieces of steel there exists a definite concentration of the mixed crystals, corresponding to that special gaseous mixture which is present, under equal conditions, in equilibrium with the form of free carbon present.

The intervention of the two new factors is, on the other hand, placed in evidence by the fact (see p. 167) that on reducing, by dilution with nitrogen, the partial pressure of the mixture of carbon monoxide and of carbon dioxide acting on the iron, *in the presence of wood charcoal*, all the other conditions being equal (and only for cementations of slight depth), the maximum concentration of the carbon in the cemented zones decreases markedly. In fact, if such variation did not occur in the relation between the velocity of the reactions and the velocity of the diffusion of the carbon and of the gases, no variation whatever could manifest itself in the concentration of the carbon in the mixed crystals, for it is proved[1] that in the diagram of the pressures and compositions of the gaseous phase (at constant temperature) the equilibrium curve corresponding to a given form of free carbon coincides *wholly* (for any pressure whatever of the active gases) with the equilibrium curve corresponding to mixed crystals of a definite concentration.

Similar considerations may be deduced from the fact that Schenck's conclusions hold for reactions which develop in a definite mass of gas kept *entirely* under the conditions (of temperature, of pressure, etc.) considered, and during a time sufficient for the attainment of complete equilibrium, while in the practice of cementation the gaseous mass acts in the form of a *current*, so that at any moment only a portion of the gas used is in a position to react under the normal conditions chosen for the operation. It is evident, therefore, that the velocity of the gaseous current intervenes in practice as another factor modifying the final result of the cementation such as it would be deduced from the laws of chemical statics. This new factor, however, like the two cited before, can give rise to only quantitative and not to qualitative modifications of the results predicted on the basis of the laws of chemical statics. This is because, under the usual conditions of temperatures higher than 800° C. and in the presence of iron acting in this case as an efficient catalyzer, the velocity of the reactions taking place in the gaseous phase is so high that they are practically completed in the interval of time sufficing for the renewal of the mass of gas in the cementation box.[2]

This is also confirmed by the attainment in the cemented zones of a well defined concentration of the carbon, corresponding to the gaseous mixture

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[1] See Schenck, *Chimie physique des métaux*, pp. 199–201.

[2] On the velocity of these reactions see, for example, the investigations of Bell (1869), of Boudouard (1901), of Schenck and Zimmermann (1905), etc., and the recent ones of F. E. Rhead and Richard V. Wheeler (*The Journal of the Chemical Society*, November, 1910, pp. 1140–1153).

in equilibrium with the free carbon, and this even in the case in which the gaseous mixture is made to act in successive portions in the form of a current.

Finally, we have seen how in practice it is necessary to also take into account the unavoidable oscillations in the temperature which may manifest themselves during the cementation. In fact, we have already seen how such oscillations, for the reasons already pointed out by Osmond (see p. 31), and by Charpy (see p. 42), and later better developed by Benedicks and by myself and by G. Scavia (see p. 159), may give rise to very great increases in the concentration of carbon in the cemented zones; increases entirely independent of the maximum value which the concentration of the carbon may attain (in the case of complete static equilibrium) under the conditions under which the cementation is effected. This is shown experimentally in a very clear manner by the experiments cited on page 160.

When the observations which I have just set forth are taken into account, it will be easy for every one to find in the theoretical discussions of Schenck a rigorous scientific explanation of the facts which I have noted and a simple explanation of the special behavior of carbon monoxide in the cementation process.

In connection with the theoretical considerations developed by Schenck, I think it well to make still some observations on another point which may, in some special cases, assume marked practical importance.

In the diagram of complete equilibrium traced by Schenck for temperatures below 700° C., at which the iron-carbon mixed crystals are not formed, there appear also equilibrium curves corresponding to the reactions in which oxides of iron and metallic iron (two by two) act with the gaseous phase. At temperatures higher than 700° C., that is, temperatures at which iron-carbon mixed crystals are formed and which alone are of real practical interest in the study of cementation, Schenck observes that those curves of monovariant equilibrium cease to be of interest because, from 750° C. up, the reaction pressures corresponding to them exceed one atmosphere.

This is certainly correct for the cases occurring most frequently in practice, and, in fact, in the general study of the cementation of ordinary steels with carbon monoxide it is never necessary to consider the case of the formation of an oxide of iron. But there are two cases which I think it well to specially point out here, in which these equilibrium curves present great interest. The first is that of cementation carried out with carbon monoxide (pure or in the presence of free carbon) under pressures higher than atmospheric. We have seen, in fact, that recent experiments have confirmed the great importance which the exact knowledge of the position of these curves has in this case in the determination of the lower limit of temperatures which can be practically used. The second case is that which we have seen presents itself (see p. 156) in the cementation of special steels, when the oxidation curve of the steel subjected to cementation with carbon monoxide is displaced, with respect to that corresponding to pure iron, so far toward the end of the diagram corresponding to pure carbon monoxide that for the former the reaction pressure (corresponding, in this case, to its intersection with the curves of cementation) falls until it re-enters the field of the pressures used for cementation.

This shows itself in industrial practice by the phenomena which every one may have observed and is seen also from the experiments of Charpy (see p. 112) on the cementation of chromium, of manganese, and of chromium and chromium-nickel steels, with carbon monoxide.

I have already pointed out (see p. 149) that the experiments of Charpy just cited were carried out from a practical standpoint, and without taking into account in any way the studies of Schenck. If these studies are taken into account, we can reach a clear and complete interpretation of these phenomena. But from those experiments, besides the pure and simple determination of the fact that the presence of the chromium in the steel lowers (for equal temperatures) the point of intersection of the curves of cementation and of oxidation of the metal, so as to make it correspond to a pressure lower than the atmospheric pressure, there follows another interesting datum, consisting in the empirical observation of Charpy that the oxidation of the metal is limited to a very thin surface layer when the cementation of steels of medium or low chromium content is carried out with carbon monoxide at about 1000° C. This fact, the practical importance of which is evident, is easily explained when we consider that the minimum limiting pressure of oxidation increases with rise in the temperature, so that at 1000° C. the cementation can, for certain steels, proceed under ordinary pressure without being accompanied by oxidation, and only during the initial heating and the cooling which follows the cementation does the system traverse the interval of temperature within which the cementation is accompanied by oxidation. It is clear that under these conditions the oxidation can be only superficial.

From these observations is seen the importance of determining the relation of temperature to the pressures of monovariant equilibrium for the special steels which it is desired to subject to cementation by the specific action of carbon monoxide. The experiments of Schenck and Semiller on the alloys of iron and manganese already furnish precise data on the lowering which the equilibrium point undergoes with increase in the manganese content, and show that this lowering is great for even relatively low manganese contents. It is sufficient to prove it to report three data relative to a temperature of about 950° C.—one of the most frequently used in cementation.

Manganese content	Temperature	Pressure
0.00 percent.	950° C.	Much higher than 2 atmospheres
0.95 percent.	950° C.	802 mm.
4.01 percent.	965° C.	46 mm.
6.38 percent.	956° C.	20 mm.

Analogous variations, though not so great, are observed for many of the alloys of iron most frequently used in practice. This is seen in chromium, and chromium-nickel steels, etc., from the results of my and Doctor Carnevali's experiments which I have cited and examined in detail, also from the point of view of their theoretical interpretation, in the preceding chapter (see p. 146).

The numerous experimental data set forth in the preceding chapter confirm fully these conclusions, showing the ease and the certainty with which the rational use of carbon monoxide in the cementation of steel permits of obtaining cemented zones in which the maximum *concentration* of the carbon does not exceed a definite and pre-established value and varies from one layer to the other of these cemented zones as desired. No other carburizing substance permits of such control. The variety of the types of *distribution* of the carbon in the cemented zones which can be thus obtained permits of obtaining with certainty in any practical case the product which is best suited to its purposes.

It can, therefore, be asserted that the cements with carbon monoxide as base, and, more especially, those whose action may be regulated,[1] are the most perfect cements. They offer the greatest guarantees of well-defined and uniform quality of the product, together with the amplest opportunity of adapting the quality of the product to the conditions which it must satisfy.

Before closing this chapter, I think it well still to review briefly, on the basis of the most recent and reliable experimental data, the results obtained by various experimenters on some other problems in the processes of cementation. I shall omit various questions of secondary practical interest, such, for example, as that of a "reciprocal" phenomenon of the cementation proper, consisting in diffusion of the iron into the carbon (see Colson, p. 25, and Osmond, p. 28), or that, also treated by Osmond (see p. 28), of the eventual necessity that the diamond undergo a "molecular transformation" to be able to cement iron. Thus, too, I shall not deal with questions on which experiment has yet furnished only scarce and uncertain data; such, for example, as the question of electrical cementation (see p. 28).

A series of experimental data of great practical interest is that which concerns the relations between the temperature at which a given process of cementation is effected and the quality of the product obtained. In all this group the only reliable data are those furnished by the more recent researches, the only ones in which the measurement of the temperatures was made with precision.[2]

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[1] This does not happen, for example, in the cements in which the carbon monoxide is a secondary product of the dissociation of a carbonate added to the other components of a solid cement.

[2] See, for example, the observations which I made in connection with the investigations of Mannesmann (see p. 17). Also in the recent investigations of Ledebur (see p. 60) the measurement of the temperature was made exclusively by means of Seger cones, which, as is well known, permit of only a very rough approximation.

A first fact, enunciated successively by many experimenters (see Mannesmann, p. 16, Guillet, p. 47; and very recently Bruch, p. 66) and known by all practitioners from the earliest times cementations were effected, is the great increase which the velocity of cementation undergoes with increase in the temperature, meaning by "velocity" of cementation the "depth" attained by the cemented layer in the unit of time.[1] As to the importance of this increase, that follows from the diagram of Fig. 19 on page 71.[2]

The effects which variations in the temperature produce on the *concentration* of the carbon in the cemented zones have also been the subject of numerous observations. We may recall as examples the investigations of Osmond cited on page 28; those of Arnold (see p. 32), and many others. But in this field also, only the most recent investigations have given precise and concordant results, and this because, contrary to the earlier researches, the new investigations were carried out with cements of simple and well-defined chemical nature, working at constant and exactly measured temperatures, and the results controlled by exact gravimetric carbon determinations made on various successive layers of the cemented zones.

These recent experiments, carried out with more exact methods, have furnished new, precise proof of the practical importance of the relations between the temperature of the cementation and the concentration of the carbon in the cemented zones which are obtained by means of the action of carbon monoxide. These relations are profoundly different from, and in many cases directly opposite to, those which hold for the other cements.

Finally, the study of the relation between the temperature at which the cementation is effected and the result of the operation gives rise to a third question, *viz.*, what is the lowest temperature at which the cementation can be effected.

Many experiments, such, for example, as those of Mannesmann (see p. 17), of Charpy (p. 45), of Bruch (p. 66), etc., would prove that even at relatively low temperatures, below 700° C. and even as low as 500° C., certain cements, and especially carbon monoxide, produce the diffusion of appreciable quantities of carbon into the mass of the steel. But more recent experiments, carried out with more precise means of observation (see p. 88), prove, for example, that with ordinary soft carbon steels a true cementation proper, meaning the formation of a zone of steel of higher carbon content than that of the rest of the metallic mass and endowed with the structure of a true steel proper having this greater carbon content, can be obtained only at temperatures above 780° C., and that, in general, for all steels the cementation assumes its regular and normal course only at temperatures at which the iron assumes

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[1] I have already explained in the footnote on p. 174 the cause of an experimental result apparently contrary to this rule, obtained by Charpy.

[2] The analogous diagrams of Mannesmann do not furnish reliable data on account of the inexactness of his temperature determinations.

the form of γ-iron. This explains the fact that the special steels, for which the transformation points are markedly low as compared with ordinary steel of equal carbon content, can be cemented at lower temperatures than the ordinary, equally carburized steels.

This would explain also the assertion of Guillet (see p. 54) that (γ-iron) polyhedral steels can undergo a true process of cementation (or "diffusion of structural carbon") even at ordinary temperature. The same considerations would explain the influence of the initial carbon content in the steel on the minimum temperature of cementation.[1]

Another group of investigations of great practical importance is the influence of the nature of the cement on the course of the cementation, on the velocity of the penetration of the carbon, on the maximum concentration and on the distribution of the carbon in the cemented zones, etc. Recent experiments, carried out[2] with simple and chemically definite cements so as to isolate the individual processes of carburization, have established quite sure and precise data on the relations which exist between the nature of the cement, the course of the cementation, and the results which it is desired to obtain.

The observation of Caron (see p. 6) of a relation existing between the "decomposability" of the cement and the concentration of the carbon in the cemented zone, and that of Mannesmann (see p. 21), that the "degree of carburization" is proportional to the difference in the "affinity which the carbon has for the iron and for the substances with which it is combined in the cement,"[3] are confirmed in more precise form by the more recent experiments; for example, by those on the carburizing action of carbon monoxide, pure and mixed with volatile hydrocarbons. On the contrary, the assertion of Guillet (see p. 48) that the velocity of cementation varies at first with the nature of the cement but later becomes equal for all the cements when the operation is prolonged beyond a certain time (in general, eight hours at 1000° C.) is not confirmed by the recent experiments with cements having carbon monoxide as base. It is therefore quite probable that the equalization of action observed by Guillet is due to the "exhaustion" of the cements; while it follows with certainty that the velocity of the cementation, even for very long operations,

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[1] We must consider as based on inexact experimental data the observations of Arnold and MacWilliam (see p. 37) on the sudden increase in the minimum temperature of cementation; an increase which, as we have seen, manifests itself when the carbon content of the steel subjected to cementation reaches the value of 0.9 % and which the authors explain by the hypothesis (now proved to be inexact) of the existence, together with the cementite, of a second carbide of iron corresponding to the formula $Fe_{24}C$.

[2] Even in very recent times various experimenters used complicated cements, of undefined chemical nature, in investigations of a scientific character. See, for examples of this, the investigations of Scott (p. 68), of Bannister and Lambert (p. 69), and others which I have cited in the preceding chapters.

[3] The further conclusion drawn by Mannesmann, that the "highest" cementation must be obtained with free carbon, is not justified by the more recent investigations.

varies with variations in the nature of the cement and is a maximum for a current of carbon monoxide acting in the presence of free carbon.

Only recently has attention been given to the relations which exist between the nature of the cement and the distribution of the carbon in the cemented zones, and an exact account taken of this distribution. Among the few and incomplete references to this made by the earlier investigators, the most precise are those of Mannesmann (see p. 15) who observed in the very intensely cemented zones sudden variations in the concentration of the carbon, corresponding to the surfaces of passage from the layer transformed into cast iron to that in the state of steel or of iron.[1] Arnold (see p. 33) gives a few "concentration-depth" diagrams, but he limits himself to deducing that the concentration of the carbon in the cemented zones decreases with increase in the depth of the layers analyzed, calling attention, also, to the existence of "three distinct strata" in the cemented zones. The micrographs reproduced by Arnold, however, show that the three strata observed by him do not coincide with the three characteristic layers (hyper-eutectic, eutectic and hypo-eutectic) which I have studied in the preceding chapter, where I indicated the causes of their formation.

Moreover, even in many of the more recent experimental researches, the gravimetric determinations of the carbon are limited to one layer (see, for example, the investigations of Guillet, in which the first surface layer, 1/4 mm. thick, is analyzed) or to two layers (see Charpy, p. 112).

Quite discordant also are the conclusions reached by various experimenters in regard to the influence which the initial content of carbon in the material subjected to cementation exercises on the course of the cementation. A case of such discordance was the polemic which developed between Guillet and Ledebur with regard to the theory of cementation (see especially pp. 59–63). After it was proved that in practice the specific carburizing action of the gases always has a preponderant importance as compared with the action exercised directly by the carbon "by contact," the complicated arguments of Mannesmann (see p. 22) and others as to why the more highly carburized steels are cemented more rapidly than steels with a lower carbon content lose their point and purpose. This fact, now confirmed by precise experiments, constitutes a further proof of the slightness of the direct carburizing action of carbon as compared with that exercised by the carburizing gases.

Similar discordant results were obtained by various experimenters in investigations on the maximum concentration of the carbon in the steel which can be attained when working under definite conditions. Such are the results of the investigations of Mannesmann (see p. 15), of Osmond (see p. 28), of Roberts-Austen (p. 29) and of Saniter (p. 31).

These discordances have been explained, although in a not entirely exact

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[1] See a more precise study of this phenomenon by Giolitti, Carnevali and Tavanti: *Ricerche sulla fabbricazione della ghisa malleabile*, Nota III (*Rassegna Mineraria*, 1910).

manner, by Osmond (p. 31), and later by Charpy (p. 42) and by Benedicks (p. 159). The latter showed, with very simple reasoning from his experiments, the impossibility of attaining by means of cementation a definite maximum concentration of the carbon, corresponding to saturation of the iron, except by keeping the temperature rigorously constant during the whole of the cementation. Still more recent considerations and experiments (see pp. 160–167) have furnished direct proof and a clear theoretical explanation of the effects which even slight oscillations in the temperature produce on the apparent limit of saturation of the iron by the carbon in cementation experiments.

As to the cementation of the special steels, there is not much to add to what has been said in the preceding chapters. Caron (see p. 9) made the first investigations on the effects in cementation of foreign substances (such as manganese, silicon, etc.) alloyed with the iron. Guillet (see p. 52) studied essentially practical problems, such as the velocity of the cementation in various special steels, and the obtaining of zones of martensitic or polyhedral steel by cementing certain pearlitic steels.

The investigations of Charpy on the cementation of the special steels with carbon monoxide have been already noticed in the present chapter (see p. 191). We have also already reported the more precise data obtained in recent investigations on the distribution of the carbon in the cemented zones, and the exact definition of the conditions under which cements with carbon monoxide as base can be advantageously employed for the cementation of the various types of special steels (see p. 145).

A last group of investigations of great practical importance are the studies on the diffusion of the other elements than carbon into iron at a high temperature but still in the solid state. The experimental data published up to the present on this subject are few and not wholly reliable. We may mention here the experiments of Boussingault on the variations in the concentration of the sulphur contained in iron during cementation (see p. 23); those of Campbell and of Arnold and MacWilliam (see p. 34) on the diffusion of the sulphide and oxysulphide of iron into iron, and those of Arnold and MacWilliam on the diffusion of various metals into solid iron.

In connection with these last experiments, I must point out that recent investigations (to which we will refer in the second part of this book) do not confirm the division made by Arnold and MacWilliam (see p. 35) of the various elements into two classes, the first of which includes the elements capable of diffusing or "migrating" into the mass of the solid iron, while the elements belonging to the second class lack this power. The experiments to which I have just referred prove that the various elements classified by Arnold and MacWilliam in the second class can diffuse into solid iron, under suitable thermal treatment.

PART SECOND

INDUSTRIAL APPLICATIONS OF THE PROCESS OF CEMENTATION