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PROCESS OF REDUCING FERROUS CHLORIDE IN THE GASEOUS PHASE WITH HYDROGEN TO PRODUCE METALLIC IRON

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The present invention relates to a process of reducing ferrous chloride in the gaseous phase with hydrogen to produce metallic iron. More particularly the present process relates to the reduction of gaseous ferrous chloride at temperatures above the melting point of ferrous chloride with a gas consisting of or containing hydrogen to produce metallic iron in some useable form and particularly to produce powdered iron.

It is known in the prior art that solid ferrous chloride at a temperature below the melting point thereof but substantially elevated in respect to room temperature, may be reduced with hydrogen or a hydrogen-containing gas to produce metallic iron. The reduction of ferrous chloride in a liquid state to form metallic iron and apparatus for use therewith and the peculiar requirements of the process form the subject matter of a co-pending application of Darner et al., Serial No. 188,128, filed October 3, 1950, entitled "Process and Apparatus for Reducing Ferrous Chloride in Liquid Form to Elemental Iron."

From the above it might be presumed, from a cursory consideration, that the reduction of ferrous chloride in the vapor phase to produce metallic iron would be a relatively simple process which could be carried out by any trained chemist. This was found, however, not to be the case. Some time ago experimental work was carried on in search of a practicable commercial process for the reduction of ferrous chloride in the vapor phase with hydrogen. The particular object of this experimental work was to produce metallic iron in a fine state of subdivision for use in the making of certain electronic devices such as cores for coils. The experiment involved the use of a tube-type furnace, which was externally heated and wherein hydrogen was passed through the tube. Located in the tube in a way permitting of movement axially of the tube, was an ampule having but a single opening directed along the tube down stream in respect to the flow of hydrogen. Once the furnace was heated and hydrogen was passed continuously through the tube, the ampule aforesaid, in which was located some solid ferrous chloride, was introduced from a cool part of the tube into a heated part thereof, for the purpose of generating ferrous chloride vapor, which was intended to pass out of the ampule into the tube through a small opening provided for the purpose. It was found, however, that apparently the device did not operate in this manner; but that hydrogen passed into the ampule, with the result that when the ampule was finally removed and examined, following the

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cooling thereof at the completion of the test, much of the ferrous chloride therein had been reduced to metallic iron which was contained in the ampule in a substantially solid body admixed with some unreduced ferrous chloride. The product remaining in the ampule was not a desired finely powdered iron, which was then being sought. Furthermore, the product was all inside the ampule and would have been difficult to remove therefrom and/or to separate the iron produced from the unreduced ferrous chloride. In addition to this, the mass adhered firmly to the inside walls of the ampule and was not easily detached therefrom. The product obviously was not suitable for the principal purpose for which powdered iron was desired. From a theoretical point of view it could not be determined by the tests made, or a study of the product of the test, that the ferrous chloride had not been reduced in a solid state, rather than in the vapor phase, which was the original purpose of the test. For all these reasons, therefore, it was considered that the reduction of ferrous chloride in the vapor phase, either was not at all operative, or would present so many difficulties that further work along this line was abandoned for a considerable time following this test.

Some time later, in conducting research experiments looking toward the development of a process for reducing liquid ferrous chloride with hydrogen, minor explosions occurred, resulting in dislocation of parts of the apparatus. It appeared that these minor explosions might be due to a rapid reaction between hydrogen and ferrous chloride vapor. This has subsequently been proved to be true as the reaction between hydrogen and ferrous chloride vapor occurs quite rapidly, sometimes with explosive violence.

Renewed interest has been established in the reduction of ferrous chloride vapor as a step in a broader process for refining ores containing iron. In this process the reduction of the ferrous chloride vapor rather than the solid was desired, since the ferrous chloride is available as a product of the preceding step in vapor form. This vapor can be condensed to solid only at great expense, resulting from the heat lost. The present process provides a desirable reducing step for this larger process.

As the present vapor phase reduction process involves an exothermic reaction, as distinguished from the endothermic reduction in the liquid or solid phases, it is unnecessary to supply heat for the reaction to the reducing zone, which is advantageous from a practical operating point of

view. In general, it has been found that the same rules do not hold as between the solid, liquid and vapor phases, so that each has had to be investigated separately and each has its own peculiarities and special requirements.

In accordance with the present invention it is desirable to keep all reaction products, except the metallic iron, in the vapor phase to expedite handling and separation, and prevent clogging of the apparatus used. The desired condition may be attained by a proper balance of operating conditions such as to avoid the presence or deposition of ferrous chloride in either the solid or liquid states in the zone in which the reduction reaction is to take place.

It is desirable from many points of view to carry on this reaction in the vapor phase due to the speed of the reaction and also due to the fact that desired products may be produced uncontaminated by undesired ingredients, when the proper precautions are taken, as hereinafter more particularly set forth.

Summarizing the present invention, therefore, it comprises the process of producing elemental or metallic iron in a fine state of subdivision by a reduction of ferrous chloride vapor with hydrogen, or a gas containing hydrogen, and of which hydrogen is the active reducing agent. More particularly, the reaction may be considered from two points of view:

(1) The reaction may be carried on at or above the boiling point of ferrous chloride at the pressure conditions existing. Under these circumstances, all the ferrous chloride present will be retained in the gaseous phase as the temperature alone may be relied on to prevent the condensation of ferrous chloride as a liquid. Further, the reaction will occur very rapidly, but will work toward an equilibrium condition, the exact equilibrium depending upon the conditions under which the reaction occurs. In other words, the reaction is reversible in character and always tends toward the attainment of an equilibrium condition intermediate the terminal conditions possible. This reaction may be expressed by the equation:

$$FeCl_2\ (vapor)+H_2=Fe\ (solid)+2HCl$$

This reaction occurs with the evolution of a substantial amount of heat, so that once the reacting materials are supplied to a reaction zone, no difficulty is experienced in retaining the ferrous chloride as a vapor, even as to the amount of ferrous chloride remaining after substantial equilibrium conditions are attained.

(2) The same reaction also may take place between ferrous chloride vapor and hydrogen, which forms, or is present as a part of the gas used, at temperatures between the melting point (about 1250° F.) and the boiling point (at the pressure condition extant) of ferrous chloride. Under these conditions, if all that is wanted is iron in any metallic form, and if it is not considered necessary to the process that the iron be in powder form, again no particularly special precaution need be taken, although there is always a tendency, under these circumstances, for ferrous chloride to condense out from the vapor as a liquid. Provision may be made, in accordance with the present invention, for the prevention of this condensation of liquid ferrous chloride, so as to enable the process to produce iron in powder form suitable, for example, for powder metallurgy operations, and substantially uncontaminated by liquid ferrous chloride (or by solid ferrous chloride on final cooling). When liquid ferrous chloride is condensed out and mixed with some iron, produced usually in powder form, there is formed a cementitious type mass of iron particles bonded together or in the form of a slurry therewith. This makes the removal of the reaction products from the furnace quite difficult. If the mixed material is heated again sufficiently to vaporize the ferrous chloride therefrom, the remaining iron is left in a massive or sintered condition, rather than as iron powder; and hence is no longer suitable for use in powder metallurgy processes. Basically, the arrangement for prevention of the condensation of liquid ferrous chloride is dependent upon there being a sufficient concentration of hydrogen in the reaction zone, so that the concentration of ferrous chloride vapor is always less than its dew point for the conditions pertaining. It is preferred to evaluate this condition in terms of the relative amounts of hydrogen present with respect to the amount of ferrous chloride vapor simultaneously present. Satisfactory operation has resulted when the ratio of hydrogen concentration to ferrous chloride vapor concentration is at least as great as the ratio expressed in the following equation:

(1) $$\frac{H_2}{FeCl_2}=\frac{1}{2}\sqrt{\frac{d^2}{c^2}+\frac{4}{c}}-\frac{d}{2c}-1$$

wherein H_2 and $FeCl_2$ are both expressed as mols or relative volumes. The factors c and d in Equation 1 may be calculated from the following mathematical equations:

(2) $$c=\frac{V_p}{P}\cdot\frac{K}{4}+\frac{V_p^2}{P^2}\cdot\left(\frac{K}{4}-1\right)$$

(3) $$d=2\frac{V_p}{P}-\frac{V_p}{2P}\cdot K$$

In Equations 2 and 3 P is the sum of the partial pressures of $FeCl_2$, HCl and H_2 expressed in atmospheres; V_p is the vapor pressure of the $FeCl_2$ expressed in atmospheres; and K is the equilibrium constant of the equation

$$FeCl_2\ (vapor)+H_2\rightleftarrows Fe+2HCl$$

V_p and K may be calculated for any given temperature from the equations:

(4) $$\text{Natural logarithm of } V_p=12.46\left(1-\frac{1296}{T}\right)$$

(5) $$\text{Natural logarithm of } K=2.94\left(1-\frac{1260}{T}\right)$$

In Equations 4 and 5, T is expressed in degrees Kelvin (i. e. degrees centigrade absolute).

Considering now the details of the present process and the requirements thereof, it is found that the process may be carried out in any suitable apparatus, which apparatus forms no part of the present invention, so that it is not illustrated herein.

The first essential is that there be produced or available in some way, ferrous chloride vapor. For this purpose ferrous chloride may be heated sufficiently to vaporize it. This vaporization need not be effected at a temperature above the boiling point thereof at the pressure existing, for example, atmospheric pressure, but may take place at temperatures below the boiling point of ferrous chloride, but above the melting point thereof. This is due to the fact that ferrous chloride, similar to many other materials, has a

progressively increasing vapor pressure as the temperature rises, the boiling point being characterized by the vapor pressure becoming equal to the pressure surrounding the material as it is vaporized. At atmospheric pressure the boiling point of ferrous chloride is about 1880° F. At its melting point, the vapor pressure of ferrous chloride is equivalent to about 0.01 atmosphere. For the purpose of the present application, the latter temperature is given as the low limit of temperature for the operation, as below this limit the amount of ferrous chloride present in any gaseous mixture is so low that the reaction is uneconomical.

The reaction of reducing ferrous chloride vapor to metallic iron may take place in the presence of more or less inert gaseous material, such, for example, as nitrogen, the presence of which may sometimes be desirable due to its effect in diluting the reactants and consequently, diminishing the violence of the reaction. Such inert gas may be necessary or desirable, in some instances, as a carrier for enabling the ferrous chloride vapor to be carried from its point of generation or vaporization point to a reaction zone in which the reaction is to take place. From the point of view of the present invention, any gas which will be neutral in respect to the present reaction may be present. It will be found by calculation in Equations 1 to 3 above that the presence of diluent gases tends to lower the value of the ratio

$$\frac{H_2}{FeCl_2}$$

The reducing gas, in accordance with the present invention, is hydrogen. In order to provide such a gas, any gaseous mixture either consisting of, or containing the necessary or a desired amount of hydrogen, may be used; provided that any other gas or gases present do not undersirably affect the reaction. In other words, if desired, the hydrogen may be mixed with some inert gas or gases such as nitrogen or water vapor, but other gases which would use up hydrogen, such as oxygen, are not desired to be present.

Considering now the reaction itself, it is necessary in order to attain the equilibrium possible under the circumstances, that there be reasonably complete or effective mixing between hydrogen and the ferrous chloride vapor. This mixing requirement is not always easy of attainment as ferrous chloride vapor has a much greater density than hydrogen. Various arrangements may be used, the details of which form no part of the present invention, for effecting a substantially complete mixing between the ferrous chloride vapor and the hydrogen. Such mixing may, for example, be attained by the establishment in the reaction zone of a condition of turbulence. For example, such turbulence may be created by the use of a nozzle construction causing relatively intimate mixing of these two gases.

Once the gases have reacted, iron in a solid form, usually in the form of iron powder having very small particle size, will be produced. In general, it is found that in order to produce the finer grades or sizes of iron powder, lower reaction temperatures are more desirable, as the higher temperatures tend to cause powder thus formed to sinter together. For example, when the present reaction is carried on at about the boiling point of ferrous chloride, iron powder having a particle size of about one micron, may be made. As the temperature is increased, the

iron particles sinter as aforesaid. If the reaction zone is of sufficient size, or if the point of impingement of hydrogen and ferrous chloride is spaced somewhat from the walls of the chamber in which the reaction is taking place and defining the reaction zone, the iron is liberated in the form of fine powder in suspension and is not deposited on the wall. Some of this iron powder may also be carried in suspension in the stream of gas leaving the reaction zone and may be separated therefrom by methods known to the art of separating fine powders from a gaseous stream.

When the reaction is to take place at temperatures above the boiling point of ferrous chloride, many difficulties are avoided, as hereinafter set forth, as there is no tendency for the ferrous chloride, under these conditions, to condense to the liquid form. It will be understood, of course, that the boiling point of ferrous chloride is a function of pressure, so that, except for given pressure conditions, no particular data can be given thereon as to an exact boiling point temperature. However, whatever the pressure may be, the reaction will take place, as far as is now known, and seems to require no special catalytic agents or special initiating conditions in order that reaction may carry on. The only requirement in this temperature range (above boiling point) is the requirement for adequate mixing between the ferrous chloride and hydrogen, as aforesaid. The temperature at which the reaction is carried on may be selected, in view of the character of the product to be formed, as aforesaid. However, as the temperature rises, the equilibrium toward which the reaction proceeds is somewhat less satisfactory; that is, as the temperature rises, progressively more of the ferrous chloride vapor will be unreacted with hydrogen at equilibrium. For this reason, therefore, operations at lower temperatures are usually more desirable than operations at higher temperatures. The additional reason tending to have one select lower temperatures for operation, is the cost of maintaining the reaction at the higher temperatures. It may, however, be desirable to operate at least as high as the boiling point of ferrous chloride, so as to avoid the difficulties incident to operations at lower temperatures, as hereinafter more particularly set forth.

Operations at temperatures between the melting point (about 1250° F.) and the boiling point of ferrous chloride, as aforesaid, are quite attractive from many points of view, as it is in this range that the highest efficiencies of conversion of ferrous chloride vapor to iron are attained, due to the equilibrium tending in that direction as the temperature goes down. In any event, at lower temperatures of operation, the tendency of the iron particles to sinter and/or to adhere to the walls of a chamber defining a reaction zone is minimized.

In this low temperature range it is found that as the temperature is lowered, there is an increasing tendency for ferrous chloride to condense out as a liquid. However, it has been found, in accordance with the present invention, that this tendency may be successfully opposed by maintaining a sufficient excess of hydrogen in respect to the ferrous chloride concentration in the reaction zone. For example, at about the melting point of ferrous chloride (about 1250° F.), it is found that a mol ratio or partial pressure ratio of at least about 11.5:1

of hydrogen in respect to ferrous chloride, will result in the effective prevention of the condensation of liquid ferrous chloride. This ratio progressively diminishes as the temperature rises, and becomes zero at the boiling point of ferrous chloride. Various points on the curve of this ratio plotted against temperature have been determined.

This curve may be drawn for any given pressure, such as atmospheric pressure, by calculating the value of desired points in accordance with Equation 1 given above. The correctness of various curves so plotted has been checked by numerous experiments, some of which are set forth in examples herein.

From a broad point of view it is contemplated that ratios (by mol or volume) of hydrogen to ferrous chloride vapor of about 1:1 up to about 50:1 are desirable for use in accordance with the present invention. These limits are chosen as follows: If the ratio of hydrogen to ferrous chloride is less than about 1:1, even at temperatures at or above the boiling point of ferrous chloride, then the efficiency of conversion is so low that the reaction may not be economically carried out. It is desired, also, as previously explained, that this ratio shall be sufficient to avoid difficulties incident to the condensation of liquid ferrous chloride. Thus at temperatures below the boiling point of ferrous chloride the ratio should preferably exceed the minimum critical ratio as expressed by the equation given above to avoid the presence of $FeCl_2$ in the liquid phase in the reaction zone. The high limit of this ratio of hydrogen to ferrous chloride vapor is not critical; but for the purpose of the present application is given as about 50:1 for practical reasons. It will be understood, of course, that the excess hydrogen acts in several ways: (*a*) partly to influence the equilibrium conditions, so that to this extent, excess hydrogen is desired; (*b*) to prevent the condensation of liquid ferrous chloride; and (*c*) as a diluent gas of a character which will not undesirably affect the reaction. On the other hand, as it is usually not desired to waste this hydrogen, it is usual in a process of this kind to recirculate the hydrogen-containing gas. Under these circumstances, the greater the excess of hydrogen present, the greater is the pumping cost and the greater is the inevitable heat loss that will occur in the recirculation cycle in the event that the gas is not maintained hot throughout, so that an economic limit is reached as the percentage of hydrogen is increased.

From a more narrow point of view and as a preferred range, it is usually desirable to have a sufficient excess of hydrogen, so that even at the lowest temperature at which the reaction could reasonably occur, i. e. about the melting point of ferrous chloride, there will be sufficient hydrogen present to prevent the condensation of liquid ferrous chloride. Thus the low limit of the preferred range may be set at about 11.5:1 of hydrogen to ferrous chloride vapor. The high limit of the preferred range may be chosen at about 20:1. The reason for this is that with this concentration of gases, the resulting gaseous products of the reaction will contain about 8% to 9% HCl. This gaseous concentration, while not particularly important from the point of view of the present reaction, is a desired concentration for use in another reaction with which the entire process of the present application is intended to be associated from a commercial point of view. This HCl concentration is also desirable from the point of view of the commercial recovery of HCl, even neglecting the other process just referred to. Thus to a large extent the upper limit of the ratio of hydrogen to ferrous chloride is dictated, not by the requirements of the present process, but rather by the requirements of some other process with which the present process is contemplated to be associated.

One type of operation which may be conducted in accordance with the present invention may be termed "adiabatic," in that all the heat required to start the reaction and to assure its continuance to its final equilibrium condition is supplied as sensible heat of the ingredient materials. This is so on a basis taking into account heat produced by the reaction itself, which as above set forth, is exothermic in character. In some instances the reaction may take place with sufficient heat in the incoming gases to initiate the reaction, following which the exothermic heat of reaction provides excess heat, which may be dissipated during the continued reaction. When practicing this process, for example, it is possible to supply ferrous chloride vapor at about its boiling point and to supply hydrogen for reaction therewith, alone or in a mixture with some one or more inert gases, at a temperature which may be calculated in order that the temperature in the reaction zone shall be adequate for the reaction to carry on on this basis and without the supplying of heat from external sources once the reaction is started. In this way, there may be a substantial or even a large difference between the temperatures of introduction of the ferrous chloride vapor and the hydrogen, amounting to several hundred degrees as demonstrated in actual examples hereinafter given.

From another point of view, it is possible in operating in accordance with this phase of the present invention to decide first upon the general average composition of the end products to be formed, for example, HCl concentration; then knowing this, predetermine the compositions and the temperatures of the ingredient materials, so as to attain substantially the initially predetermined end product composition. This is also demonstrated by the examples hereinafter given.

A particularly desirable embodiment of the present process may be in fact a two-step process. In the first step the reaction may take place at a relatively high temperature, for example, at a selected temperature above the boiling point of ferrous chloride. Under these circumstances, and due to the fact that this reaction proceeds more rapidly in the higher temperature range, equilibrium may be rapidly attained. As a second step of the process, the temperature may be substantially reduced, for example, to a selected point between the melting point and boiling point of ferrous chloride. Under these circumstances, while the rate of the reaction is relatively less, the equilibrium is more desirable than the equilibrium conditions at the higher temperature. Thus the overall efficiency of the two stage process, completed at a lower temperature, is greater than if the process were completed in a single stage at the higher temperature. In this two-stage process, two advantageous results are obtained. In the first place, when operating at the higher temperature, the major part of the conversion of the ferrous chloride to iron is attained, thus utilizing the additional speed available for the reaction at the higher temperature and reducing the amount of ferrous chloride

remaining to be reacted in the second stage. It also avoids the possibility of condensing ferrous chloride in this first stage. At the same time, when the second stage is reached, the greater efficiency, due to the more desirable equilibrium conditions at the low temperature, is attained and again the deposition of ferrous chloride by condensation thereof is avoided. This is due to the fact that while the hydrogen concentration itself has changed but little, due to the relatively large excess of hydrogen usually used, the concentration of ferrous chloride has been largely reduced, so that the ratio of hydrogen concentration to ferrous chloride concentration, which is the critical factor in avoiding the condensation of ferrous chloride, is now greatly increased and will, under substantially all circumstances, exceed the critical ratio, as aforesaid. The operation of the process on at least a two-stage basis or with a descending temperature gradient may be employed to attain substantially the same results as a sharp change from a higher temperature to a lower temperature. From a practical operating standpoint, the descending temperature gradient will probably be the one used, due to the difficulty of attaining sharp changes in the temperature gradient in practical operation.

Example I

In order to illustrate the effect of an increasing temperature between about 1250° F., which is the lowest temperature contemplated for use according to the present invention, and 1884° F., which is the boiling point of $FeCl_2$ at atmospheric pressure, upon the efficiency of the reduction of $FeCl_2$ vapor by hydrogen, Table I is set forth below. This table shows the percentages of $FeCl_2$ converted to metallic iron at various temperatures, and thus shows the effect of temperature upon the equilibrium toward which the reaction proceeds. As is evident from the table, as the temperature rises, the efficiency of the reduction decreases substantially. In all the tests made in this series, pure hydrogen was introduced into a reaction chamber at the rate of one cubic foot a minute and the $FeCl_2$ vapor was introduced at such a rate that the mol ratio of hydrogen to $FeCl_2$ was 11.5:1.

TABLE I

Temperature, °F.	Percentage $FeCl_2$ Converted to Metallic Fe
1,250	83.8
1,350	79.4
1,450	75.2
1,550	72.9
1,650	70.4
1,750	69.0
1,850	68.2
1,884	68.0

In each of these cases the ratio of hydrogen to $FeCl_2$ was high enough to maintain the $FeCl_2$ in a vapor phase during the reduction at each of the temperatures.

Example II

Table II below indicates the effect of varying the mol ratio of hydrogen to $FeCl_2$ introduced into the reaction chamber upon the efficiency of the reduction of $FeCl_2$ to iron by hydrogen. In each of the tests reported in Table II the reaction was carried out at the boiling point of $FeCl_2$, i. e. about 1884° F.

TABLE II

Ratio of mols of Hydrogen per mol of $FeCl_2$ Introduced	Percent Conversion of $FeCl_2$ to Fe
1:1	32.3
4:1	56.0
7:1	68.0
24:1	86.7
50:1	92.2

A comparison is given below of two tests both made at 1920° F. (above the boiling point temperature of $FeCl_2$ at atmospheric pressure). In the first of these tests hydrogen was introduced at a rate of ten liters of hydrogen per minute (measured at standard temperature and pressure) while the $FeCl_2$ vapor was introduced at a rate of 12 grams of $FeCl_2$ per minute. This was equivalent to a mol ratio of $H_2/FeCl_2$ of 4.5:1. The reaction was carried on for a period of 9½ hours, producing powdered iron; and it was found that 61% of the $FeCl_2$ vapor had been reduced to metallic iron in powder form. A second run made at the same temperature differed in conditions only by increasing the rate of hydrogen flow to 21 liters per minute (measured at standard temperature and pressure) so that the mol ratio of $H_2/FeCl_2$ was 9.45:1 rather than 4.5:1. The reaction was carried out in this way for a period of ten minutes, producing powdered iron. During this run 73% of the $FeCl_2$ was reduced to metallic iron in powder form.

At a temperature below the boiling point of $FeCl_2$, namely about 1600° F., the following relations have been determined:

TABLE III

Mol ratio $H_2/FeCl_2$	Percent $FeCl_2$ Converted to Fe
5.57:1	68.0
7.3:1	72.7
12.2:1	81.0
23.9:1	89.2

Example III

It has been stated above that the desired reaction is exothermic in character. Also, the temperature at which the $FeCl_2$ vapor is introduced is a variable, and may be predetermined for any particular operation. It has been found that if it is desired to produce a resulting gaseous mixture having a predetermined HCl concentration, such a result may be attained by introducing a predetermined amount of hydrogen in respect to the amount of $FeCl_2$ being introduced; in other words, by varying the ratio of hydrogen to $FeCl_2$. From the above and from experimental work, it has also been found that it is possible to supply the $FeCl_2$ vapor and the hydrogen at temperatures such that at least enough heat is supplied as sensible heat in the incoming gases, so that no additional heat need be added to the reaction zone for the maintenance of the desired reaction conditions, particularly temperature. This also take into account the amount of heat available from the reaction itself, due to the exothermic character thereof. For example, it is possible to introduce ferrous chloride at a particular temperature, say the boiling point thereof, and to introduce hydrogen at a substantially lower temperature, and yet maintain the temperature in the reaction zone at a relatively high temperature, for exam-

ple, the boiling point of ferrous chloride, due to the exothermic heat aforesaid.

It is also possible in view of the above, to predetermine the temperature of the incoming ferrous chloride vapor and to predetermine the ratio of hydrogen and $FeCl_2$, and then to control the temperature of reaction by controlling the temperature of reaction by controlling the temperature of the incoming hydrogen. This is a useful manner of operation. One particular embodiment of this type of operation is to conduct the reaction on an adiabatic basis, i. e., where heat is neither required to be added, nor is dissipated in any substantial amount. By a predetermined heat balance, the process may be operated at a substantially constant temperature, so that the efficiency of the reaction will be definite and known.

Thus where it was desired to operate the reduction step in an adiabatic manner to produce a product having a ratio of about 9 mols of hydrogen per mol of HCl, hydrogen and $FeCl_2$ vapor were introduced into a reactor at the rate of 15.6 mols of hydrogen per mol of $FeCl_2$ vapor. In order that the reaction be adiabatic, the $FeCl_2$ vapor was introduced at the boiling point of $FeCl_2$, i. e., about 1880° F. and the H_2 at 1105° F. It was found that the reaction proceeded in the desired adiabatic manner, producing a gas containing 1.2% $FeCl_2$ vapor, 88.9% hydrogen and 9.9% HCl. In the course of the reaction 80.0% of the $FeCl_2$ was reduced to metallic iron. After the $FeCl_2$ had been removed in a suitable manner, the gaseous products contained approximately 90% hydrogen and 10% HCl.

In order to produce a product containing about 80% hydrogen and 20% HCl, $FeCl_2$ vapor and hydrogen were introduced into a reactor in the ratio of 5.8 mols of hydrogen per mol of $FeCl_2$. The $FeCl_2$ was introduced at a temperature of 1880° F., while the hydrogen was introduced at 875° F. This reaction proceeded in the desired adiabatic manner, producing a gaseous product containing 5.0% $FeCl_2$ vapor, 19.0% HCl and 76.0% hydrogen. During the course of the reaction it was found that 64.7% of the $FeCl_2$ vapor introduced had been reduced to metallic iron. After separation of the $FeCl_2$ from the gaseous products, a mixture containing the desired composition of about 80% hydrogen and 20% HCl was obtained.

Example IV

In order to illustrate how the advantages of both high and low temperature reduction may be obtained simultaneously by operating the process in two successive stages, the following example is given: $FeCl_2$ vapor and hydrogen were introduced into the reactor at the rate of 4.0 mols of hydrogen per mol of $FeCl_2$ vapor. By maintaining the reaction at a temperature of 1884° F. (the boiling point of $FeCl_2$ at atmospheric pressure), the equilibrium for this temperature was reached very rapidly; and a gaseous mixture containing 8.8 mol percent $FeCl_2$ vapor, 68.8 mol percent hydrogen and 22.4 mol percent HCl was produced. In the course of this reaction, 56.0% of the $FeCl_2$ had been reduced to metallic iron. Instead of removing the iron and separating the products of the reaction at this elevated temperature, the reaction products were cooled to a temperature of 1340° F. before the products were separated. At the end of the first, or high temperature stage of the reduction, the ratio of hydrogen to $FeCl_2$ vapor present in the gaseous mixture was 7.8:1, which is considerably in excess of the minimum molal ratio of hydrogen to $FeCl_2$ vapor of 6.9:1, which is required to maintain the $FeCl_2$ in vapor form exclusively at 1340° F. At this lower temperature, however, the equilibrium conditions are more favorable to the formation of metallic iron than they were during the first or high temperature stage of the reaction. The reaction mixture thus continued to react to form metallic iron and tended toward a new and more desirable equilibrium, producing a gaseous mixture containing 5.6 mol percent $FeCl_2$, 65.6 mol percent hydrogen and 28.8 mol percent HCl. Thus, an overall efficiency, expressed in terms of percent of the $FeCl_2$ reduced to metallic iron of 71.9 was obtained by carrying out the reduction in two distinct stages, the second of which was at a lower temperature than the first.

Example V

In order to illustrate the effects of the presence of a diluent gas such as nitrogen on the reduction process, the following example is given:

When $FeCl_2$ vapor is reduced with hydrogen at a temperature of 1340° F. (without any diluent gas), the minimum ratio of hydrogen to $FeCl_2$ required in order to prevent the condensation of liquid $FeCl_2$ is 7.85:1. When the reduction is carried out using this ratio at the temperature aforesaid, 83.2% of the $FeCl_2$ vapor is reduced to metallic iron. If, however, enough nitrogen is present in the system to make up 25% of the total volume of gas present (the temperature being the same), it is found that the minimum mol ratio of hydrogen to $FeCl_2$ required to prevent condensation of liquid $FeCl_2$ is only 5.75:1. When operating at this temperature and using a mol ratio of hydrogen to $FeCl_2$ of 5.75:1, it has been found that 77.9% of the $FeCl_2$ vapor is reduced to metallic iron.

When the amount of nitrogen in the system is 50% of the total volume of gases present (other conditions remaining the same), it is found that the minimum mol ratio of hydrogen to $FeCl_2$ required to prevent condensation of liquid $FeCl_2$ is only 4.30:1. If reduction is carried out in the presence of this proportion of nitrogen, still at 1340° F., using the minimum mol ratio of hydrogen to $FeCl_2$ aforesaid, it is found that 73.2% of the $FeCl_2$ vapor will be reduced to metallic iron.

Thus, it appears that at a given temperature, when a neutral diluent gas, such as nitrogen, is introduced into the system, the mol ratio of hydrogen to $FeCl_2$ necessary to prevent condensation of liquid $FeCl_2$ decreases. The presence of a diluent gas thus reduces the total pressure factor P, which is one of the factors used in the Equation 1 set forth above for the calculation of the minimum mol ratio of hydrogen to $FeCl_2$ to prevent condensation of liquid $FeCl_2$ for otherwise predetermined conditions.

While there are disclosed herein certain examples illustrating the present process and certain principles by the use of which it may be successfully employed, it is intended that all reasonable equivalents, as may appear to those skilled in the art from the foregoing teachings, shall be considered to be within the scope of the appended claims, which are, therefore, to be construed validly as broadly as the state of the prior art permits.

What is claimed is:

1. The process of reducing ferrous chloride to produce metallic iron solely in powder form, comprising the steps of introducing ferrous chloride solely as a stream of vapor and in a pre-

determined direction into a reaction zone, separately introducing into said reaction zone a stream of a gas, the essential active reducing ingredient of which is hydrogen, predetermining the direction of introduction of said stream of said gas so that it will impinge against said stream of ferrous chloride vapor at a point spaced from any walls defining any boundaries of said reaction zone, and maintaining the temperature in said reaction zone at least about 1250° F., so as to provide a solely gaseous phase reaction in said zone between ferrous chloride vapor and hydrogen to produce metallic iron solely in powder form.

2. The process in accordance with claim 1, wherein the temperature in said reaction zone is less than the boiling point temperature of ferrous chloride at the pressure existing in said reaction zone, and comprising the additional step of maintaining in said reaction zone a ratio of hydrogen to ferrous chloride vapor at least as great as the ratio set forth in the equation:

(1) $$\frac{H_2}{FeCl_2}=\frac{1}{2}\sqrt{\frac{d^2}{c^2}+\frac{4}{c}}-\frac{d}{2c}-1$$

wherein H_2 and $FeCl_2$ are both expressed as mol or relative volumes and wherein the factors c and d may be calculated from the following equations:

(2) $$c=\frac{V_p}{P}\cdot\frac{K}{4}+\frac{V_p^2}{P^2}\cdot\left(\frac{K}{4}-1\right)$$

(3) $$d=2\frac{V_p}{P}-\frac{V_p}{2P}\cdot K$$

wherein in Equations 2 and 3, P is the sum of the partial pressures of $FeCl_2$, HCl and H_2 expressed in atmospheres; V^p is the vapor pressure of the $FeCl_2$ expressed in atmospheres; and K is the equilibrium constant of the equation:

$$FeCl_2 \text{ (vapor)} + H_2 \rightleftarrows Fe + 2HCl$$

and v^p and K may be calculated for any given temperature from the equations:

(4) $$\text{Natural logarithm of } V_p = 12.46\left(1-\frac{1296}{T}\right)$$

(5) $$\text{Natural logarithm of } K = 2.94\left(1-\frac{1260}{T}\right)$$

and wherein in Equations 4 and 5, T is temperature in degrees Kelvin.

3. The process in accordance with claim 1, wherein the temperature in said reaction zone is less than the boiling point temperature of ferrous chloride at the pressure existing in said reaction zone, and wherein hydrogen and ferrous chloride vapor are present in said reaction zone in a mol ratio between about 11.5:1 and about 20:1.

4. The process in accordance with claim 1, wherein the temperature in said reaction zone is at least as high as the boiling point temperature of ferrous chloride at the pressure existing in said reaction zone.

5. The process in accordance with claim 1, wherein during a first reaction period the temperature of the materials in the reaction zone is maintained at a relatively higher value; and in a subsequent period as to said materials in said reaction zone, the temperature of such materials is maintained at a relatively lower value but above 1250° F.

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