THE HIGH TEMPERATURE SORPTION OF NITROGEN BY MANGANESE

by

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Dedicated

TO DR. A. N. CAMPBELL to whom I shall ever be grateful for the suggestion of this problem and for his kind and patient supervision.

Acknowledgment.

I am indebted to Dr. Louis Slotin for many helpful suggestions on the design and construction of apparatus.

Contents

THEORETICAL INTRODUCTION

This work consists of a Phase Rule study of the two component system Nitrogen-Manganese. The components are gaseous and solid respectively. In dealing with a system of this type several variations are possible. These variations are tabulated and described in Alexander Findlay's "The Phase Rule and its Applications" (Longmans, Green and Co.) as follows:-

Case (a) The gas is not absorbed by the solid but when the pressure reaches a certain value, combination of the two components can result.

Such a system can be expressed graphically by an isothermal diagram of the type shown in Fig. 1. The ordinates represent the gas pressures and the abscissae represent the relative concentrations of the gaseous component, which have been taken up by the solid phase. The horizontals AB and CD show that the concentration increases at constant pressure. They, therefore, represent the formation of compounds. Corresponding to any point on each of these horizontals, an equilibrium, exists which may be represented generally as:-

Solid compound $\rightleftharpoons$ Solid component + gaseous component.

If there is no solution there are three phases and, therefore, on applying Gibb's expression for the Phase Rule,

$$F = C - P + 2\ ;\ 2 - 3 + 2 = 1,$$

it is seen that the number of degrees of freedom is 1. Only one variable, then, is at the choice of the experi-

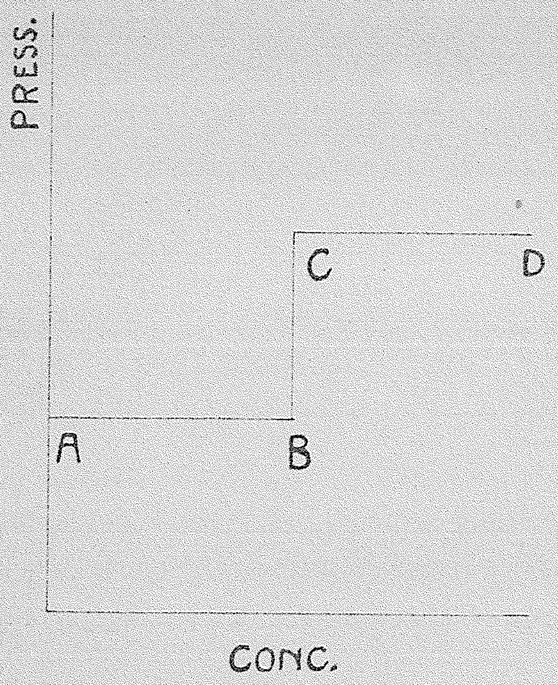


FIG. 1.

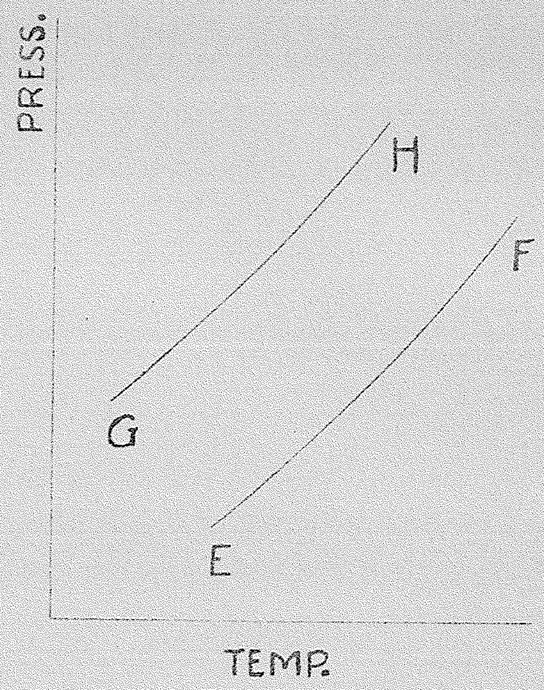


FIG. 2.

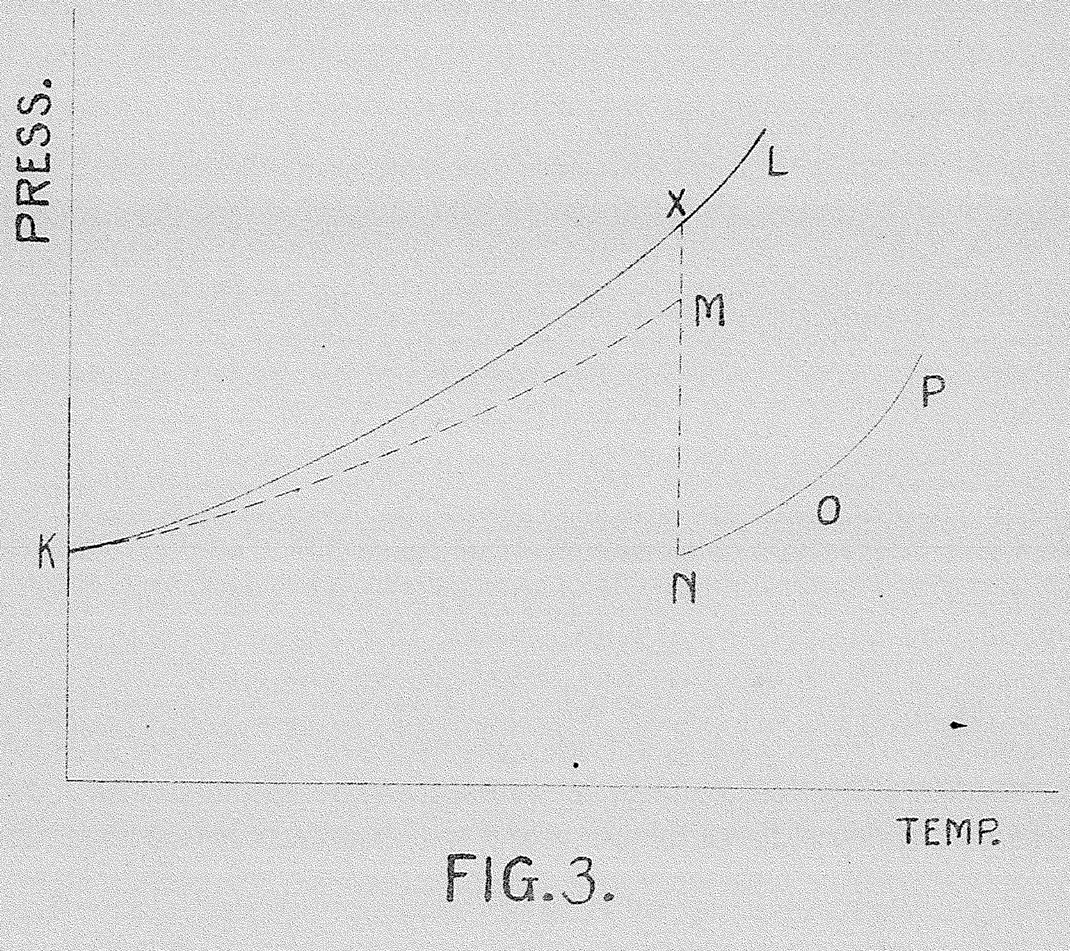


FIG. 3.

menter, and when a value is chosen for one variable the values of the other two are automatically fixed by the nature of things.

If the p - t diagram is drawn it will have the general form shown in Fig. 2. The line EF represents the locus of pressures corresponding to AB, and therefore gives the conditions of temperature and pressure which define, or fix the position of the equilibrium,
Solid compound 1 $\rightleftharpoons$ solid component + gaseous component.
Similarly LH is the locus of all pressures such as CD and gives the conditions governing the position of the equilibrium,
Solid compound 2 $\rightleftharpoons$ Solid compound 1 + gaseous component.
It is seen at once that the possibility exists of the solid compound 2 decomposing directly to the solid and gaseous components without the occurrence of the intermediate compound 1. To be general, at this stage, however, it will be assumed that a trace of the latter compound did appear. EF and LH are the decomposition or dissociation curves of the two compounds. They express univariant behavior and hence are expressed mathematically by the Clausius-Clapeyron equation, as are all univariant curves.

The above curves represent equilibrium conditions for the most simple type of behavior of a two component system. Such behavior is seen only when no solutions occur. The type is exemplified by the salt hydrates and by the ammonia compounds of the silver halides. When solutions are formed the curves differ somewhat.

<u>Case (b)</u> The gas is absorbed by the solid component and no compound is formed.

If absorption of the gas by the solid component takes place with formation of a solid solution there can never be more than two phases present, so that univariant behavior is impossible. From Gibb's expression it is seen that the behavior will be divariant.

The p-c curve will show a gradual increase of concentration with increasing pressure; while the horizontals of Case (a) will be absent since no compound is formed. The corresponding p-t curve is bound to be slightly concave to the temperature axis. It is always possible to spot this type of behavior from the p-t curve, by its departure from the straight line of Charles Law. At every temperature the pressure will be less than that predicted by Charles Law.

<u>Case (c)</u> The gas is absorbed by the solid component and may also form a compound.

This case is merely a combination of the two types of behavior given above so that no new type of curve is introduced. The p-c curve will, at first, show the concentration varying gradually with increasing pressure due to the formation of a solid solution, as for Case (b). When a certain pressure is reached, a compound will form, and hence concentration will increase at constant pressure giving rise to a horizontal in the same manner as in Case (a). The compound will, at every temperature, be in equilibrium with its two components, so that a p-t or decomposition curve, exactly analogous to EF or GH in Fig. 2 and expressed by the Clausius-Clapeyron equation, can be obtained.

Case (d) Absorption of the gas occurs and at a certain concentration the solid solution separates into two partially miscible solid solutions.

The two solid solutions, together with the gas, constitute three phases, so the system will be univariant just as was the case when a compound was formed. Here, then, the p-c curve will be of the same type as for Case (c). The p-t curve, however, although of the same form as for Case (c), is not a decomposition curve, so must differ. The difference between these two p-t curves can be shown by applying the Clausius Clapeyron equation to them. They are both curves expressing univariant behavior so that this equation must express both of them. The equation may be written in the form

$$\frac{dp}{dt} = \frac{Q}{dV} \cdot \frac{1}{T}$$

The slope of the curve is determined by the ratio $\frac{Q}{dV}$. dV must be almost the same for both cases, since the difference of specific volumes of the components and a compound must be very nearly equal to the difference of specific volumes of the components and a solid solution. The values of Q, on the other hand, might differ widely. In the case in which a compound is formed but no solid solution results, the value of Q is given simply by the heat of formation of the compound. If, however, a compound is formed and at the same time a solid solution results, Q will not be simple, but must be the algebraic sum of two quantities, thus

Q = heat of formation of compound + heat of solution.

From this it is seen that the p-t curves of the two cases may have altogether different slopes. Whether or not a solid solution is formed in the Mn - N_2 system, is not known. The heat of formation of at least one of the nitrides of manganese has been determined by another investigator. One of the objects of this work is to determine a decomposition curve accurately and then to apply the above reasoning in the hope of determining whether or not a solid solution is formed.

Getting back to the general discussion, however, it must be pointed out that the solid solution mentioned above is not specified. There is, indeed, some variety of possibility as to what this solution may be. It will be seen that,

(1) gaseous component and solid component
(2) gaseous component and compound
(3) compound and solid component

may be the constituents of the simplest possible solid solutions. Very little can be said about the miscibility of these pairs. It is probable, generally, that there will be an increase of miscibility with increasing temperature in every case. If this is true the horizontals of the p-c diagrams will not always end at the same value of concentration, for different temperatures, but may be lengthened or shortened in the various isothermals. This, of course, can occur only when the gas is one of the constituents of the solution. Such behavior is extremely rare, in fact, the Hydrogen-Palladium system is the only one of this type which has been extensively studied.

There is one statement which may be made at the offset, and that is that if solid solutions do occur, the time factor is of very great importance. Phase diagrams always refer to equilibrium conditions, so that in experimental work it must always be certain that these conditions obtain. Since it is known that solid diffusion (the mechanism of mixing) is a very slow process, the experimenter must have perfect assurance of steady conditions before an observation can be considered to be reliable.

From this general outline of the types of behavior which may be encountered, the method of experimentation will be seen to follow quite simply.

The existance of at least two nitrides of manganese has been known since 1894. Until very recently, however, none of the work done on these substances has been in the nature of a Phase Rule study. The measurements published of such quantities as temperature of formation, temperature of decomposition and even of molecular formulae have shown considerable diversity. Various workers have suggested that some of the nitrides may not be true compounds at all, but may be solid solutions. The object of the present research was to determine, by application of the Phase Rule, which of these combinations are true nitrides and which, if any, are solid solutions; and at the same time to obtain some measurements of the physical quantities mentioned above.

The experimental work was to be carried out in two stages, each in a specially constructed apparatus. The first stage involved the formation of the compound richest in nitrogen, while in the latter stage, this compound was to be decomposed and the decomposition pressures of the lower nitrides measured over as wide a range of temperatures as a glass apparatus would permit.

The formation of the richest nitride was brought about by heating a known quantity of powdered manganese in an atmosphere of nitrogen in a closed system of known volume. The system consisted of a medium sized flask (about 500 c.c.), a system of stop-cocks by which the apparatus could be evacuated and nitrogen admitted, and an open manometer from which the gas pressures were read by means of a cathetometer. The first step in the proceedure of formation was to run a blank; that is to determine the expansion curve characteristic of the apparatus. In a system of this kind the gas pressures cannot be calculated from Charles Law because the enclosed gas is not all at the same temperature. A temperature gradient necessarily exists from the furnace to the parts which are at room temperature. The experimental curve will not be the straight line of Charles Law but is bound to be curved slightly in such a way as to be slightly convex concave to the temperature axis.

This curved analogue of Charles Law, then, was just determined by evacuating the system, admitting pure dry nitrogen and then taking a pressure reading about every 10°C between 0° and 550°C.

The manganese sample was then introduced and the proceedure repeated. As before the temperature was raised by slow stages, care being taken to assure a constant pressure before an observation was recorded. Plotting these points another p-t curve will be obtained. This curve will show deviations from that obtained for the blank apparatus; and from the nature of these deviations it should be possible to determine what changes the system is undergoing.

The processes which, in view of the above discussion of types, are likely to take place, will reveal themselves as follows. If the second curve follows, or runs parallel to that for the blank apparatus, then no absorption of gas is taking place. From this it can be concluded that nitrogen does not form a solid solution in manganese. If however, the second curve lies at lower pressures than that for the blank run, then it is certain that the nitrogen is being taken up by the manganese. Fig. 3 indicates in a general way how this behavior with alter the p-t diagram. KL is the analogue of Charles Law for the blank apparatus. KM shows the curve which will be obtained if nitrogen dissolves in manganese giving rise to a solid solution. Divergence of the two curves will be greater, the higher the temperature since the quantity of gas dissolved in the solid is a function of pressure. KM then, is the nature of the curve which will result from the behavior of the type of case (b).

It now remains to indicate how Case (c) and Case (d) behavior will show up on our experimental p-t diagram. Case (c), as was shown, results in the formation of a compound, while Case (d) results in the formation of two partially miscible solid solutions. If either of these two types of behavior are encountered the curve KM will not continue to diverge steadily from KL but at a certain temperature and pressure a sharp break will occur as shown at M. This inflexion will correspond, in either case, to the formation of a compound; the gas phase will begin to disappear as concentration of gas in the condensed phase increases. Thus the pressure will drop at constant temperature as shown by MN. Points on this line do not, of course, represent equilibrium conditions since with the appearance of the third phase the system becomes divariant. At a given temperature, then, both pressure and concentration can be varied by the experimenter. Corresponding to MN, a p-c or isothermal diagram can be drawn which will be of the type given in Fig. 1.

The pressure cannot continue to drop to zero, however, because eventually a gas pressure will be reached which will be equal to the dissociation pressure of the compound. An equilibrium will then be established which may be represented as,

$$Mn_xN_{\frac{y}{2}} \rightleftharpoons Mn_x + N_{\frac{y}{2}}$$

N represents this point at which equilibrium is first established. Here there are three phases so that the system has again become univariant. N, then, is a point on a univariant curve; this univariant curve must be the decomposition curve of the compound. From here it is easy to obtain other points on the decomposition curve, by simply varying the temperature. Thus if the temperature is raised a little, the equilibrium will shift to the right. When equilibrium conditions are again established, it will be at higher values of temperature and pressure and the point O will be obtained. In a similar manner a further increase of temperature will result in the point N, and so on to as high a temperature as the apparatus will stand. Information as to the formation of a solid solution in addition to the formation of a compound can, it is hoped, be gained from the slopes of these decomposition curves as was indicated above in the general discussion of the Case (d) type of behavior.

Decomposition curves of the lower nitrides, as has already been stated, are to be obtained in a modified apparatus. This comprises the second stage of the work.

The apparatus which has been built for this work is a good deal more complicated, than the previous one. It consists of a small flask, to which is attached a McLeod vacuum gauge, an open monometer and a Toepler pump. The outlet from the pump was drawn out into a capillary and a device for collecting and measuring the ejected gas was made to fit over it. The McLeod Gauge was included because it is altogether probable that the lower nitrides will have very small dissociation pressures even at relatively high temperatures.

The use of this apparatus can be explained most readily, by reference to Fig. 1. The nitride richest in nitrogen is introduced into the flask, and the apparatus evacuated. The temperature of the flask is now raised to some suitably high value, corresponding to which the compound has an appreciable decomposition pressure of, say, ½ to 1 atmosphere. The gas is then pumped off by means of the Toepler pump and the escaping gas collected and measured. If this is done gently, allowing sufficient time, it should be possible to break down the richest nitride to the next richest compound. In other words, the concentration of gas in the condensed phase is slowly lowered to such a point that the nitrogen rich compound ceases to exist. This would correspond to a point such as C in Fig. 1. If the pumping is continued, the pressure should drop along the verticle CD, after which the pressure at a fixed temperature must always be equal to the decomposition pressure of the second nitride, which will correspond to the horizontal AB. The decomposition curve of this compound can then be obtained by varying the temperature, in the same manner as has been described with the first apparatus. The same processes can then be repeated for the lower nitrides. Pressures may be read from the open monometer or from the McLeod gauge as required. This apparatus, it is hoped, can be made to serve two purposes, first, to measure decomposition pressures, and secondly, to determine formulae by measuring, accurately, the volume of nitrogen resulting from the various stages of decomposition.

This then, seems to give a fairly comprehensive view of the aims and methods of the present research. There are other complications and difficulties, but these will be discussed as they are encountered in the text.

- HISTORICAL INTRODUCTION -

reconcile the formation and decomposition of these substances with the predictions of the Phase Rule.

N. H. Warren[1] was the first to observe a reaction between nitrogen and manganese. He investigated the action of ammonia on several of the common metallic elements by the flow method. He noticed that when chromium, nickel, cobalt or manganous oxides were employed a nitride of the metal was obtained. Use of the chloride gave the same affect more readily. He did not, however, analyse for nitrogen in any case but iron, and so did not assign any formulae.

O. Prelinger[2] was unable to confirm Warren's claim of the formation of a nitride when ammonia gas is passed over heated manganous oxide. In the following year he[3] showed, however, that when manganese is oxidized in air some nitride is formed; and that when finely divided manganese obtained by heating the amalgam, is heated in an atmosphere of nitrogen, or the mercury driven off in this atmosphere, manganese pentitadinitride Mn_5N_2 is formed. He describes the substance as having a dull metallic lustre, and when in a finely divided condition is somewhat darker than the powdered metal. On heating in a stream of hydrogen, ammonia is formed, whilst if hydrogen sulphide is substituted for the element ammonium sulphide results. On treatment with ammonium chloride solution, ammonia, hydrogen, and the double chloride of manganese and ammonia were obtained,

$$Mn_5N_2 + 20NH_4Cl \rightarrow 12NH_3 + 2H_2 + 5(NH_4)_2MnCl_4$$

On fusion with caustic alkali a great deal of ammonia was liberated. When this nitride is heated in ammonia it forms manganese tritadinitride Mn_3N_2. Prelinger says that the tritadinitride may also be prepared by substituting ammonia for the nitrogen in the preparation of the pentitadinitride. This nitride is darker in color than is the former, and it readily acquires a bright metalic lustre under pressure. It behaves towards hydrogen, hydrogen sulphide and caustic soda in the same way as does the pentitadinitride. Nitric acid dissolves the tritadinitride only when hot; hydrochloric acid acts on it only in the presence of platinum, aqua regia dissolves it slowly; sulphuric acid acts only when hot, and with the concentrated acid sulphur dioxide is formed; acetic acid has no action and water slowly forms ammonia. When it is heated in nitrogen the pentitadinitride is formed. Prelenger concludes with the assumption that manganese is quinquevalent in the pentitadinitride and tervalent in the tritadinitride.

A. Guntz[4] observed what he believed to be traces of a nitride among the products which resulted when manganese was heated in an atmosphere of nitrogen peroxide. W. C. Hereaus[5] again tried heating the metal in an atmosphere of nitrogen. As a result of this work he concluded that at 1210 to 1220°C a nitride is probably formed.

Three years later Haber and Von Oordt[6] reviewed the subject and criticized the conclusions of Prelinger and the others. They were of the opinion that production of substances having different maximum concentrations of nitrogen on nitrogenation with nitrogen and ammonia was not possible. They attempted to explain the low nitrogen content obtained on nitrogenation with nitrogen by the assumption that residual oxygen in the gas used had partially oxidized the manganese. It may be said, however, that all later researches have confirmed Prelinger's results.

Wedekind and Veit[7], the next workers in this field, verified the existance of the two compounds which Prelinger had described. They $\overset{e}{\text{a}}$ffected preparation by passing dry ammonia gas over the powdered metal which was heated in a porcelain tube. They extended Prelinger's work by trying the preparation at the temperature of the oxyhydrogen flame, and noticed that the resulting body had a pronounced magnetic property. This lead to the conclusion that a new nitride Mn_7N_2 had been formed. This nitride is quite strongly magnetic and shows considerable permanent magnetism. The magnetic property increases with the complexity of the compounds, thus, the heptitadinitride is the most magnetic while the tritadinitride is the least magnetic. When heated the ferromagnetism was destroyed, but returned on cooling.

Henderson and Galletly[8] were the next to investigate the manganese nitrides. They were extending the previous work of Beilby and Henderson[9] who in an attempt to find a material suitable for use in tubes for conducting ammonia at high temperatures had tried several metallic elements. In extending these investigations Henderson and Galletly tried among others, manganese. They found that when manganese in the state of a fine powder was heated to about 800° in a rapid stream of ammonia it is readily converted into a nitride and at the same time a large percentage of the ammonia is decomposed into its elements. Two different specimens of the nitride were found to contain 13.6 and 14.0% of nitrogen respectively; while the formula Mn_3N_2 requires 14.5%. Evidently the conversion of the metal to the nitride is practically complete. With coarse powdered metal and at lower temperatures they obtained products containing 10.1 to 11.8% nitrogen, but these when examined under the microscope were found still to contain particles of the metal, all of which showed rounded edges as if they had been in a partially fused condition. They described the properties of the nitride Mn_3N_2 and showed them to be identical with those previously described by Prelinger.

In the same year Zukov[10] following the lead of

Wedekind and Veit, tried to use the magnetic property of the nitrides to determine the reaction limits. The beginning of the action of nitrogen on manganese was found to occur at 780°C. The equilibrium pressures of nitrogen over different manganese nitrogen preparations were also investigated. From his results he thought he could draw the conclusion that the nitrides consist of solid solutions of nitrogen in manganese. He also investigated the electrical conductivity of the nitrides and found them to be of the same order of magnitude as for the pure metal.

Fischer and Schroeter[11] have prepared a nitride by a method which is altogether different. This is the famous method which they have employed for fixing nitrogen to a great many substances. Nitrogen in contact with manganese was rendered active by passing an electric discharge through it. They made no attempt to analyse their product, but merely dissolved it in acid, added an excess of alkali and noticed that ammonia was given off. Their product was probably a mixture of nitrides.

In 1915 N. Tschischewsky[12] published a paper on the influence of atmospheric nitrogen on iron and steel. In the course of this work he investigated the action of both ammonia and nitrogen on manganese. He used the flow-method but introduced refinements which hitherto had not been used. His aim was, primarily, to shed some light on the question of stability of these nitrides and on the influence of temperature on the course of the reactions. 97.1% manganese, prepared by the Goldschmidt method was used. The apparatus consisted of a long fused silica tube, a portion of which lay within a Heraeus electric furnace. Into one end of this tube the ammonia and nitrogen were introduced after purification, from their respective containers. The gas supplies were controlled by stop-cocks so that a supply of each was available at all times. The other end of the tube was open to the atmosphere to permit the escape of the excess gas. Through this end of the tube the porcelain boat containing the sample of manganese was introduced. Temperatures were measured by means of a thermo-junction, within the tube, and placed immediately above the boat when in its position inside the furnace.

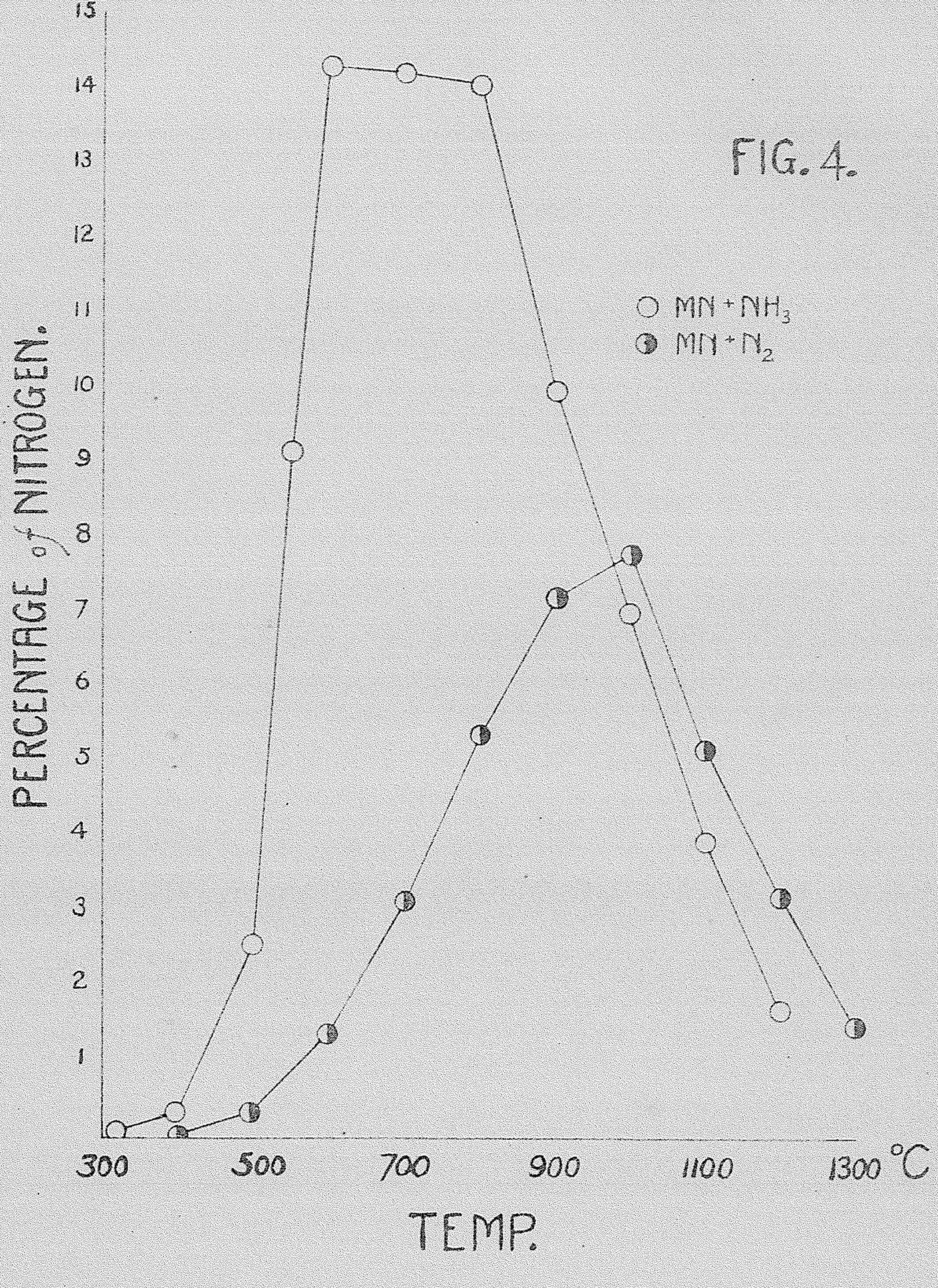
The proceedure followed was; after heating the furnace to a certain temperature, the flow of nitrogen was started and the boat or boats containing the weighed samples of manganese were inserted into the open end of the tube. It was left here for about 5 minutes until all the air was expelled. The flow of ammonia was then started and the nitrogen turned off. After another 5 minutes the boat was pushed into the furnace, by means of a wire, to a position immediately below the thermo-couple. Introducing the cold boat invariably lowered the temperature 50 to 70°. As soon as the furnace had regained its former temperature the time was taken. From this the flow of ammonia was continued for one hour. After this period the boat was drawn into the cool end of tube, and allowed to cool in a stream of nitrogen. The proceedure in the nitrogination with nitrogen itself was the same except that a continuous stream of nitrogen was maintained; that is the metal was heated and cooled in a flow of nitrogen.

Analysis of the product was affected in two ways. First, the increase in mass of the sample was determined by weighing; and secondly, the contents of the boat were dissolved in 10c.c. of concentrated hydrochloric acid, heating slightly if necessary. The nitrogen was determined quantitatively from this solution by means of the Kjeldahl method. Nessler's reagent was used at the conclusion of the distillation to be sure that no ammonia remained in the solution. The quantity of nitrogen determined by titration should, of course, agree with the increase in weight of the sample.

This whole process was repeated at temperature intervals within the range 330° to 1300°C. The results of the nitrogenations with both gases are expressed graphically in Fig. 4.

From the figure it is seen that the curve expressing nitrogenation with ammonia shows a maximum in the neighborhood of 600°C corresponding to 14.39% of nitrogen.

FIG. 4.



15
14
13
12
11
10
9
8
7
6
5
4
3
2
1
PERCENTAGE of NITROGEN.
○ MN + NH_3
◑ MN + N_2
300
500
700
900
1100
1300 °C
TEMP.

This investigator also records the fact that the reaction is strongly exothermic as shown by the observation of spontaneous temperature increases of as much as 10° in the neighborhood of 600°. In this he is in agreement with Haber and Von Oordt[6], above, who has also noticed that the temperature rose as soon as the reaction commenced, producing sufficient heat to cause the solid phase to glow with a dull red incandescence. Tschischewsky also records the very interesting fact that the quantity of nitrogen fixed by the manganese differed by the two methods of determination, viz. the percentage of nitrogen determined by noting the increase of weight of the metal was not in agreement with the amount determined by the Kjeldahl method. The former method indicated a percentage of about 20 in the region of 600°C while the Kjeldahl method as has been shown gave 14.39% of nitrogen at this temperature. He followed this further and proved that on dissolving the product in acid in preparation for the Kjeldahl, gas was evolved. Analysis of the escaping gases showed that the difference of these percentages is actually evolved. It is to be noticed that Fig. 4 expresses nitrogen percentages as determined by the Kjeldahl method. Although Tschischewsky did not himself, indulge in any speculations as to the cause of this evolution of gas, it is obvious that not all the nitrogen is fixed in the same manner by the metal. The 14.39% is no doubt combined with the metal according to the formula Mn_3N_2. As regards the additional 5.6%, however, there are two possibilities. Firstly, this quantity of nitrogen may be dissolved in the solid phase as a solid solution, and secondly, it may be combined in some more complex manner than the above formula indicates. One guess which is not unreasonable is that it is combined in the form of a pernitride, in which case it is concievable that on dissolving in acid the nitrogen so fixed does not react with the acid to produce the ammonium salt, but is evolved as elementary nitrogen. The possibility of a solid solution also may explain the facts because it is well known that elementary nitrogen in contact with acid solutions does not give rise to ammonium salts. Here then is an interesting question which is still open.

As regards the nitrogenation with nitrogen Fig. 4 shows a maximum corresponding to 7.85% nitrogen at about 1000°C. The formula Mn_5N_2 requires 9.24%, so that the agreement here is not so close.

In general, then, Tschischewsky has shown that nitrogenation with ammonia at 600° to 700°C gives rise to a nitride of the formula Mn_3N_2, while nitrogenation with nitrogen at about 1000° results in a nitride of the formula Mn_5N_2. The reason for these two end products, resulting as they do from preparations carried out at the same pressure (atmospheric) does not stand in agreement with the general theory outlined in the introduction. A very plausible explanation has been given by Gunnar Hägg, and will be considered later when his paper is reviewed.

The following year the Japanese investigator, Torajiro Ishiwara[13] again took up the study of the magnetic susceptibility of the manganese nitrides. Various workers had previously made experimental determinations of the susceptibility of metallic manganese and had obtained wide variation in the numerical value. The suggestion had been made that their anomalies may have their explanation in occurrence of nitrides as impurities in the metals. Such nitrides were known to have a magnetic property from the work of Wedekind and Veit and others who have already been mentioned. Manganese is very close to iron in the periodic arrangement, and like iron none of its salts or compounds are magnetic except the nitrides. Ishawara, then, took up the question of the magnetic susceptibility of the nitrides in order to determine whether manganese is really a pseudo ferromagnetic element.

The method of his investigation may be outlined as follows. Samples of nitride were prepared in the usual way, by heating the powdered metal in an atmosphere of nitrogen or ammonia at a given temperature, and chilling before removing the product from this atmosphere. Such a process may result in the simultaneous production of more than one compound as was subsequently shown. The product so obtained was then examined thermo-magnetically; that is, the magnetic susceptibility of the sample was determined over a wide range of temperatures. If a ferromagnetic compound is present, at a certain high temperature it will decompose, and decomposition will be evidenced by a falling off in the value of the magnetic susceptibility. Reasoning backwards then, a decrease in the value of the magnetic susceptibility with time may be taken as indication of the decomposition of a ferromagnetic nitride. In some cases he made use of the reverse process, that is the susceptibility was determined while the compound was being formed.

Ishiwara summarizes the results of his observations as follows:- (1) Manganese and nitrogen give rise to three ferromagnetic substances in the temperature interval 600 to 1600°C.; namely two nitrides and probably a solid solution. One of the nitrides is Mn_5N_2. The composition of the other two could not be ascertained, but they are differentiated from one another by their characteristic thermomagnetic curves and by their critical points.

(2) Ammonia affects manganese at high temperatures in the same way as does nitrogen, an exception being the case of a paramagnetic nitride Mn_3N_2.

(3) In regard to the ferromagnetic substance Mn_7N_2

which Wedekind and Veit obtained by heating manganese in ammonia, we could not confirm its existance.

(4) The various values of susceptibility of manganese by different physicists may well be explained from the present experiments, as due to the effect of nitrogen present in the air or from other sources. As the correct value of the susceptibility of pure manganese we may therefore take 9.66×10^{-6}.

In only one case, then, was the composition determined and this was for the ferromagnetic nitride Mn_5N_2. The method employed was to heat powdered manganese in an atmosphere of nitrogen at 1000°C. At 30 minute intervals the weight of the product and the susceptibility were measured. After 90 minutes the weight increase had become very small, but was still measurable. This small residual increase was considered to be due to oxidation, as the flow-method of preparation can never hope to exclude all traces of oxygen. Calculation revealed 9.96% nitrogen which is trifle too high to conform to the formula Mn_5N_2, for which the value is 9.26% nitrogen.

It is seen that these investigators made no serious attempt to determine the conditions of formation of these compounds.

G. Tamman[14] has made some interesting measurements of the velocity of formation of the nitrides of several elements. The rate of action of a gas on a metal can be determined by observation of the color changes of the metal, which are due to changing thicknesses of the surface layer of reaction product. When the action of the gas on the metal is rapid, such observations determine the rate of diffusion of the gas through the surface layer. Metal surfaces were exposed to pure nitrogen, at different temperatures. Manganese at red heat, it was found, may show all colors up to extreme red, or it may show no change, depending on the original character of the surface. The velocity of layer formation for some cases was given graphically by straight lines when x, the layer thickness is plotted against log t. Unfortunately this was not done for manganese. In general, however, Tamman's curves showed that for the same sample there may be several intersecting lines, a second line describing the thickening of a second layer after the first layer has scaled off. Another cause of uncertain slope of these straight line curves was thought to be the different rates of penetration by the gas through different exposures of the atom grating of the layer.

In 1929 Gabriel Valenski[15 16], published two papers on the action of gases on metals. Both adsorption and high temperature sorption were studied. His high temperature work was carried out along somewhat similar lines to the present research, and is undoubtedly the most comprehensive study of its type that has ever been made of this system. It will, therefore, be reviewed rather fully here.

The Study of Absorption

The method deals, for the most part, with the measurement of volumes and pressures. The apparatus was cunningly constructed in such a manner that by means of a system of stop-cocks, it could be used for both the adsorption and the sorption measurements. By closing the stop-cocks the low pressure instruments were cut off from the rest of the system. Only the part of the apparatus which was used in the sorption determinations will be described.

The measuring instruments consisted of a constant pressure thermometer which differed from the classical type in that the open-air manometer was joined separately to the top of the graduated cylinder. The advantage of this was that the narrow branch of the usual Y-tube was eliminated. The graduated cylinder of this instrument was rather large and for this reason was enclosed in a glass water jacket to insure a constant temperature. The use of the thermometer is simple. The mercury reservoir is simply moved so as to maintain a constant pressure. Volume changes are then determined by observing the change in the position of the miniscus in the graduated cylinder. The cylinder had a volume of 230 c.c. and was calibrated to ·5c.c. This was the only volume calibration necessary. From this instrument a capillary tube, interrupted by a three-way stop-cock, lead to a tube containing the metal which was situated in an electric furnace. The third opening of the stop-cock was used for evacuation and for introducing the pure dry nitrogen. All the connecting tubing, which was at atmospheric temperature, was of capillary size to reduce the error involved in assuming constant conditions for it. The vessel which contained the sample of metal to be studied was of glass or quartz depending on the temperature to be used. It was a tube 35 cm. long, closed at one end, and projecting horizontally into the furnace for a distance of 10 cm. The open end projected out of the furnace a distance of 25 cm. and was joined to the capillary coming from the gas thermometer by means of a cemented joint. This joint was cooled by wicks dipping into water. Temperatures were read by means of a platinum, platinum-rhodium thermocouple.

The first part of Valenski's work deals with a preliminary investigation of the amounts of air and nitrogen which are adsorbed by the glass and quartz tubes in the furnace. In the work on adsorption all observations are corrected for the gas taken up by the tubes. In the case of sorption, however, such corrections are unnecessary since the volumes taken up are sufficiently large to render adsorbed quantities negligible. In general, he finds, that pyrexglass on being heated liberates such a small amount of gas that it can be neglected. Quartz on the other hand, liberates gases in such quantities that an error approaching ·4 c.c. for every 60 sq. cm. of surface is possible.

Sorption was studied by what is admitted to be a 'rapid' method in an attempt to settle;

(1) the boundaries of feeble absorption and those of strong absorption.

(2) to get an idea of the increase in velocity of absorption with increase in temperature.

(3) to get an idea of the number of different compounds which may form.

(4) to examine the question of whether at a certain temperature there exists a pressure below which absorption is impossible.

He made use of a dynamic method which consisted of measuring gas pressures at nearly constant volume, at different temperatures. To prevent the lessening of activity with the progress of the reaction, the temperature was increased rapidly and pressure measurements were made at frequent intervals. The apparatus was not used in the exact form as was described above. The mercury reservoir of the gas thermometer was removed and the bottom of the calibrated cylinder sealed. By so doing the whole volume of the cylinder is available as dead-space. This volume is quite large and if absorptions are small in comparison, then the volume of gas will remain almost constant.

First of all an expansion curve of the apparatus was obtained by admitting nitrogen to nearly atmospheric pressure, then heating and observing the increase in pressure at various temperatures. The results of these experiments are expressed graphically in Fig. 5 in which a b is the expansion curve. The proceedure then was to introduce the sample of metal (3·4 grains), refill the apparatus to 760 mm. with pure nitrogen and start to increase the temperature. The temperature was increased and the new pressure measured every quarter of an hour. In this way four samples of chromium and two of manganese were studied. Fig. 5 shows the results for the two kinds of manganese only, viz. that prepared by the aluminothermic and that prepared by the Moisson process.

In discussing these curves Valenski points out that a reaction, actually, has no absolute beginning. To speak of the beginning of a reaction is to speak relatively, thus the relative beginning depends upon the sensitivity of the method of measuring. In these experiments a pressure drop of 1 cm. in a quarter hour was considered to mark the beginning of the reaction. The sensitivity of this method is admittedly, not sufficient to indicate the zones of weak absorption. Thus the manganese samples both start to react at 460°. The velocities, however, are not the same, but are functions of the origin of the metal as shown by the curves in Fig. 5. The velocity in both cases

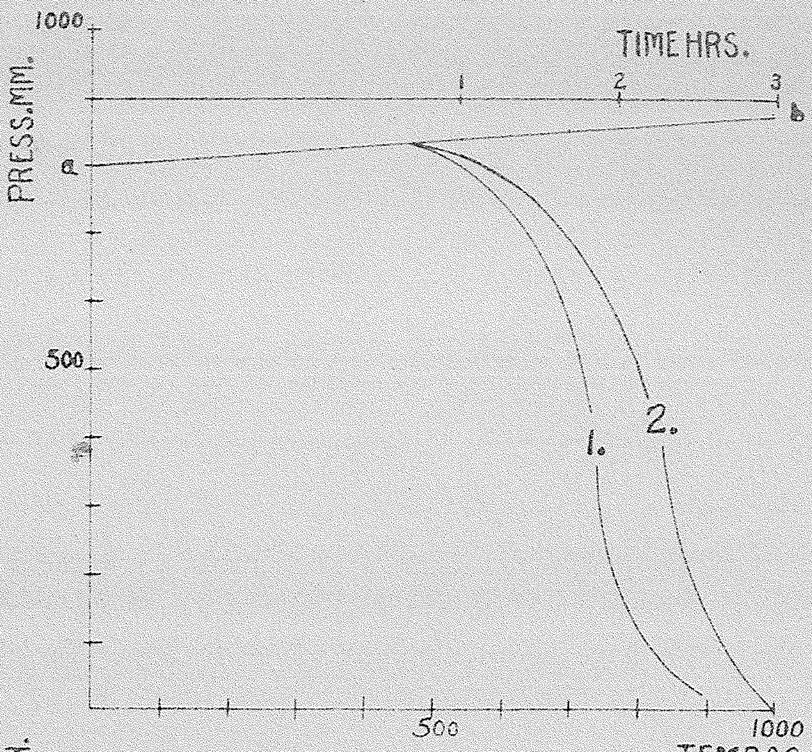


FIG. 5.

ACTION OF N_2 ON MN

1. MOISSON
2. ALUMINOTHERMIC

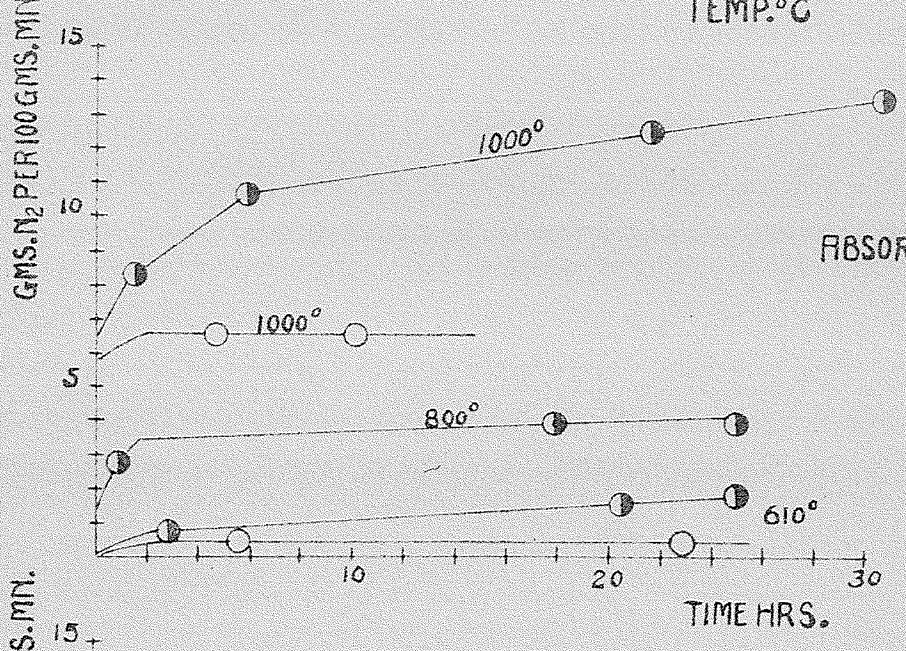


FIG. 6.

ABSORPTION OF N_2 BY COMPACT MN

○ MOISSON
◑ ALUMINOTHERMIC

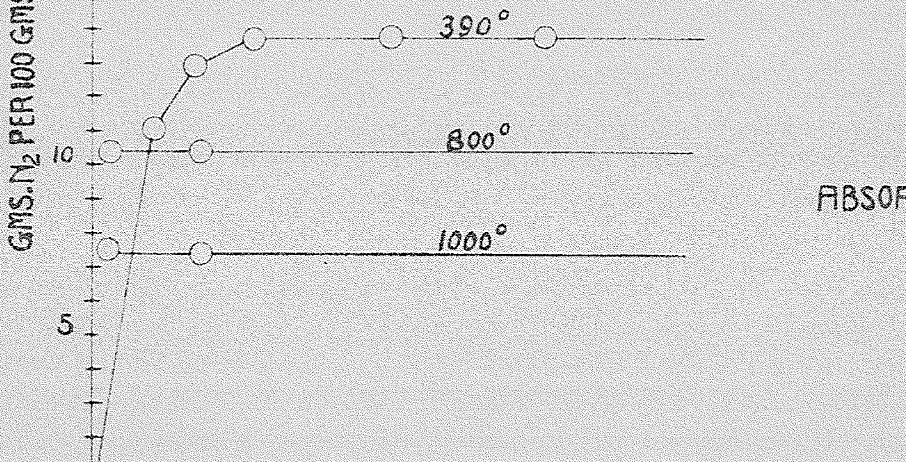


FIG. 7.

ABSORPTION OF N_2 BY PYROPHORIC MN

varies rapidly with temperature. The curves 1 and 2, for Moisson and for aluminothermic manganese respectively are continuous. The velocities are greatest in the neighborhood of the points of inflexion, while the metals are less active between these points. The pressure falls to nearly zero so that it is obvious that the dissociation pressures of the compound or compounds present must be very low. Since the curves are continuous it is impossible to say how many compounds are formed.

The foregoing experiments were preliminary to the more accurate work on absorption. The curves given in Fig. 5 were used as a guide in choosing temperatures for the subsequent experiments. The apparatus used was that described at the offset, that is the mercury was replaced in the gas thermometer, after the completion of the preliminary experiments. By means of this instrument the volumes of gas absorbed were measured. Absorptions were determined by filling the system with nitrogen to 760 mm., raising the temperature to the desired value and maintaining a constant pressure by raising the mercury reservoir of the gas thermometer. In other words absorptions were made at constant pressure and at constant temperature. The temperatures chosen were; for aluminothermic manganese and also for Moisson manganese 610°C; for aluminothermic manganese, 800°C; for aluminothermic and Moisson manganese, 1000 C. Fig. 6 represents graphically the results obtained. Grams of nitrogen per 100 grams of manganese are plotted against the time in hours.

In exactly the same manner the action of nitrogen on pyrophoric manganese was studied at 390°, 800° and 1000°C. These absorptions are represented graphically in Fig. 7.

From these experiments Valenski concludes that the quantities of nitrogen absorbed by the manganese diminishes rapidly as the temperature is raised. At 390°C, 15.4 grams of nitrogen are attached to 100 grams of pyrophoric manganese. This is a product containing 13.3% nitrogen, which is seen to agree fairly well with the formula Mn_3N_2 which requires 14.5% nitrogen. He remarks that since there is no marked discontinuity between the properties of the metal and those of the product, it seems extremely improbable that a definite nitrogen compound is formed under these conditions. This conclusion, however, is make provisionally, to be confirmed by the study of dissociation. Examination of the absorption curves suggests the following;

(1) In comparing the results obtained with the two states of division of the metal (i.e. pyrophoric and compact) it is seen that the curves for the compact metals do not represent the true limits of nitrogenation. Gradually, as the layer which is formed on the surface thickens, the

absorption decreases until it becomes indeterminable. These metals, therefore, broaden the studies of the phenomenon of absorption.

(2) At 1000°C, the Moisson manganese absorbs in less than two hours as much as the pyrophoric manganese.

(3) The aluminothermic manganese, however, presents a very serious anomaly at this temperature, since it fixes 13.8 grams instead of 6.8 grams of nitrogen for 100 grams of the metal. A verification of this fact is seen in the results of Tschischewski (see Fig. 4.), whose experiments lasted only one hour, but yet at 1000 ° gave a result of 7.85% of nitrogen. This anomaly could be explained by admitting the possibility of decomposition of the nitrogen compounds. Such a point of view could be verified by the study of dissociation.

(4) Usually small quantities of impurity may exercise a catalytic action, first, in displacing the start of the absorption reaction and second, in modifying the velocity of the reaction. In general, the aluminothermic metal seems to be more active than the Moisson metal. Differences, however, are lessened with increasing temperature.

So much, then, for the absorption experiments. These conclusions will be given further consideration in the grand summing up, following the account of the dissociation experiments.

The Study of the Dissociation of the Metallic Nitrides.

Before proceeding to the study of dissociation it should be mentioned that a few brief preliminary experiments were made. The experiments consisted simply in evacuating the apparatus used above, containing the product of nitrogenation, and then heating quickly by stages to get some idea of the decomposition pressures which were to be encountered. The paper says very little about the results obtained from these experiments. From them, however, and from the preceeding study of absorption, Volenski says that two classes of facts show the divariance of systems in certain zones of temperature and pressure. These are;

(1) The lowering of the amounts of nitrogen absorbed by the pyrophoric manganese with rising temperatures under 760 m.m., and

(2) The difficulty of decomposing, completely, these products under reduced pressure of 10^{-3} m.m. It was because of these facts that the detailed study of the phenomenon of dissociation has been made at fixed pressure and temperature.

For these experiments the necessity of reducing the dead-space was realized and the apparatus was modified accordingly. The tube containing the nitrogenated sample to be heated was made smaller. A tube 20 cm. long and having an interior diameter of 0.6 cm. was used. Near one end of this tube a short side arm was sealed on, and the end to be inserted in the furnace was sealed off just as in the absorption experiments. There are now two openings. One of these was connected by a cememted joint to the capillary tube coming from the gas thermometer of the apparatus previous described for the absorption experiments. In other words the apparatus was the same as was formerly used, the following additions being made to it.

(1) The other opening of the sample tube was joined by means of a second cemented joint to a tube 820 mm. long and 1.8 mm. in diameter. This long tube was bent close to the cemented joint in such a way that the last 760 mm. were in a vertical position with the open end directed downwards. This open end was dipped into an open vessel containing mercury. A barometer tube (filled with mercury) was dipped into the same mercury vessel, so that the mercury column of the barometer stood beside the long tube, for convenient pressure comparison. In this way the pressure in the apparatus was indicated directly, by the heights of the two mercury columns. A correction was made for the capillary effect in the tube of smaller diameter. Both the tube and the barometer were corrected to 0°C.

(2) The three-way stop-cock was turned so that the gas thermometer was excluded. To the third opening a McLeod gauge and a Geissler pump were attached. A graduated tube was placed over the exhaust orifice of the pump so that

the gases escaping could be collected for analysis.

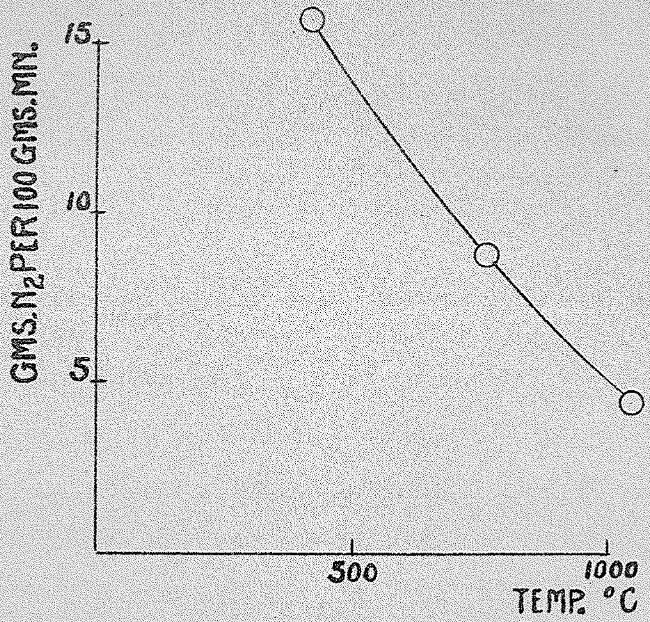
In general the proceedure was as follows. A weighed sample of the nitrogen product was introduced into the tube in the electric furnace. The system was then pumped down to 10^{-3} mm. pressure. The current was then started in the electric furnace, and the temperature increased to a certain value, while the vacuum (10^{-3} mm.) was maintained by the Geissler pump, which, all the while, exhausts the gas into the graduated tube where it is collected over mercury. The temperature was raised only when after two hours, the gas given off was less than 1/30 c.c. The whole of the gas was analysed at the end of each such experiment. Analysis of the gas was carried out by dividing it into two parts by means of a Doyere pipette. Into the first portion a pellet of potassium was added and the shrinkage in volume observed was considered to be the amount of CO_2 present. Pyrogallic acid was then added and the volume of O_2 estimated in the same way. To the second portion a known volume of oxygen was added, and then a pellet of potassium. From this absorption the amount of hydrogen is estimated by noting the difference between this and the former contractions. The non-absorbable gas was then considered to be nitrogen.

In this way the dissociation isobar was obtained. The product richest in nitrogen (13.3%) was heated under a pressure of 760 mm. of nitrogen at rising temperature and the volume of the gas lost was measured. From these the equilibrium concentrations were calculated. Fig. 8 shows the isobare so obtained. The time represents the number of hours at the end of which all variation of volume appeared to have ceased. The equilibrium was demonstrated by varying the temperature, and it was proven possible by so doing to extract nitrogen from, or add nitrogen to the metal. For manganese the quantity of nitrogen absorbed decreased regularly from 15.4 grams per 100 grams Mn at 390°C to 6 grams per 100 grams Mn at 1050° as shown by the isobare in Fig. 8.

The dissociation isotherms were then obtained by altering the pressure and again repeating the whole process until equilibrium was again established. The resulting isothermal curves are shown in Fig. 9; that at 1175° being due to Zukov who was mentioned earlier (reference 10).

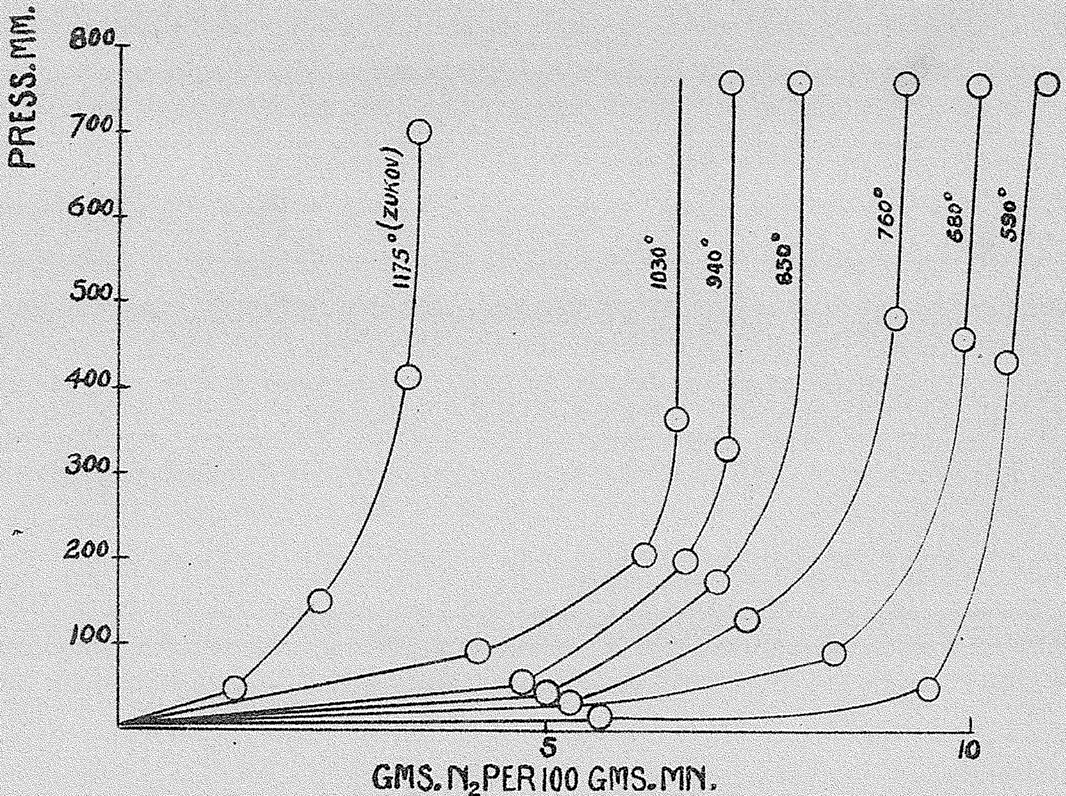
Valenski tabulates his remarks on this work and on the curves obtained as follows:

(1) The time required for the variation in pressure to become negligible varies greatly with temperature. In some cases equilibrium was established in 10 hours, but for low temperatures the time is great; in fact the time required in establishing the 760° curve in Fig. 9 was three months. Temperature, however, is by no means the only factor which controls the time required for equilibrium to become established. Previous thermal treatment,



DISSOCIATION OF MANGANESE NITRIDE UNDER 760 MM.

FIG. 8.



DISSOCIATION ISOTHERMS OF THE NITRIDE.

FIG. 9.

size of the apparatus etc., are other factors which may change the time.

(2) Below 800°C the equilibrium is very difficult to obtain, and it is impossible to get reversibility by lowering the temperature. Because of this the measurements at low temperatures are to be regarded with suspicion.

(3) Experiments with large quantities of nitrides gave erroneous results due to the difficulty of obtaining a temperature which is absolutely constant at all points, the hotter points imposing their tension on the others.

(4) In regard to the importance of the time factor it is pointed out that the speed of the phenomenon may be divided into two components;- (a) the velocity of the reaction between the surface layer of each metallic particle and the gas to produce equilibrium. (b) the speed of diffusion to the interior of each particle to produce homogeniety. If the first factor is the greater, then each particle will show a gradient of concentration (of nitride), decreasing from its centre to its periphery. If this state of affairs obtains the classical definition of the term equilibrium must be modified. Suppose, for instance that at a certain temperature the equilibrium pressure has not been obtained but that the slow diffusion of nitride is going on from the centre outwards towards the periphery. If now the temperature is lowered it is quite possible that a detectable absorption will be observed because the

surface layers have been dissociated and are in a condition to reabsorb. This might be taken to indicate equilibrium, but is not a true state of equilibrium.

The curves shown in Fig. 9 are p-c curves and like Fig. 1 they should show the flat regions corresponding to the decomposition of a compound; that is to say, if three phases are present the system is univariant. Fig. 9, however, does not show these flat regions. Valenski compares these curves to those which he obtained for chronium and which did show the flat regions. The curves of Fig. 9 are he says, analogous to the descending branches of the chronium curves. (i.e. parts of the curves which are at lower pressures than is the flat portion.) This similarity is taken to indicate that the flat portions on the manganese isothermals do occur at higher pressures. The apparatus he used, however, did not permit him to take readings at higher pressures.

Here the paper ends abruptly in its consideration of the manganese-nitrogen system except for the insertion of the final conclusions which are tabulated as follows:

(1) Manganese to a pressure of 1½ atmospheres probably gives only solutions of the nitride in the metal. Comparison with the chronium curves show that the pure nitride exists at greater pressures.

(2) The aluminothermic manganese gave great absorption.

This, then, is a fairly complete account of the work of Gabriel Valenski. It is to be noticed that this worker has not concerned himself with the number of compounds, nor have any of the curves obtained shown discontinuities which are conclusive proof of a definite state of combination. Further remarks, however, will be withheld until the X-ray study of Gunnar Hägg[17] has been reviewed.

The X-ray analysis of the manganese nitrides, prepared by the nitrogenation of manganese with ammonia, has shown that four nitride phases exist. The analysis shows, in general, that the nitrides of the transition elements show great similarity in crystal structure, and are distinguished sharply from the nitrides of the other elements.

The nitrides were prepared by heating the finely powdered metal in a porcelain boat in a tube through which ammonia, or in some cases nitrogen, was passed. The samples so prepared were analysed first by the micro-Kjeldahl method and were then investigated by the X-ray method. The powder technique was used in the X-ray analysis. A preliminary X-ray analysis showed that the samples so produced were unusually heterogeneous, since the photographs showed a great number of very weak lines. In order to get clear-cut photographs it was found necessary to homogenize the samples. Homogenization was brought about by heating the preparations for 135 hours at 600°C in sealed glass tubes. It was noticed that preparations, whose original concentration was greater than 12%, produced a residual pressure in the tubes after the long heating, and showed a loss of weight. This is proof that partial dissociation had taken place. None of the preparations with a content of nitrogen below 12%, showed a loss of weight. The richer nitride must then have a dissociation pressure greater than one atmosphere at 600°C., a fact which appears astonishing when it is remembered that these nitrides had been prepared by nitrogenation with ammonia at 600°C, and under a pressure of one atmosphere. The fact that such nitrides are produced however, has been showen before by a great many investigators of whom Tschischewsky is a good example. See Fig. 4 in this connection. The explanation is given as follows; The fact that nitrides are formed at 600°, which have a dissociation pressure of more than one atmosphere, seems to suggest that the nitrogen fugacity due to the dissociation of ammonia must have been greater than one atmosphere. This is ridiculous because all preparations were carried out under atmospheric pressure. Moreover, it is known that the nitrogen fugacity (or partial pressure) in ammonia at 600°C is about $\frac{1}{4}$ atmosphere. The cause of this apparent contradiction lies in the fact that in the preparation no thermodynamic equilibrium existed. The ammonia streams continuously over the nitride, but because of the very slow rate of decomposition of this nitride very high nitrogen fugacities may arise from it. If, then, the nitrogen fugacity of the nitride is greater than that of the ammonia the nitrogenation may be considered to be the result of two reactions, thus;

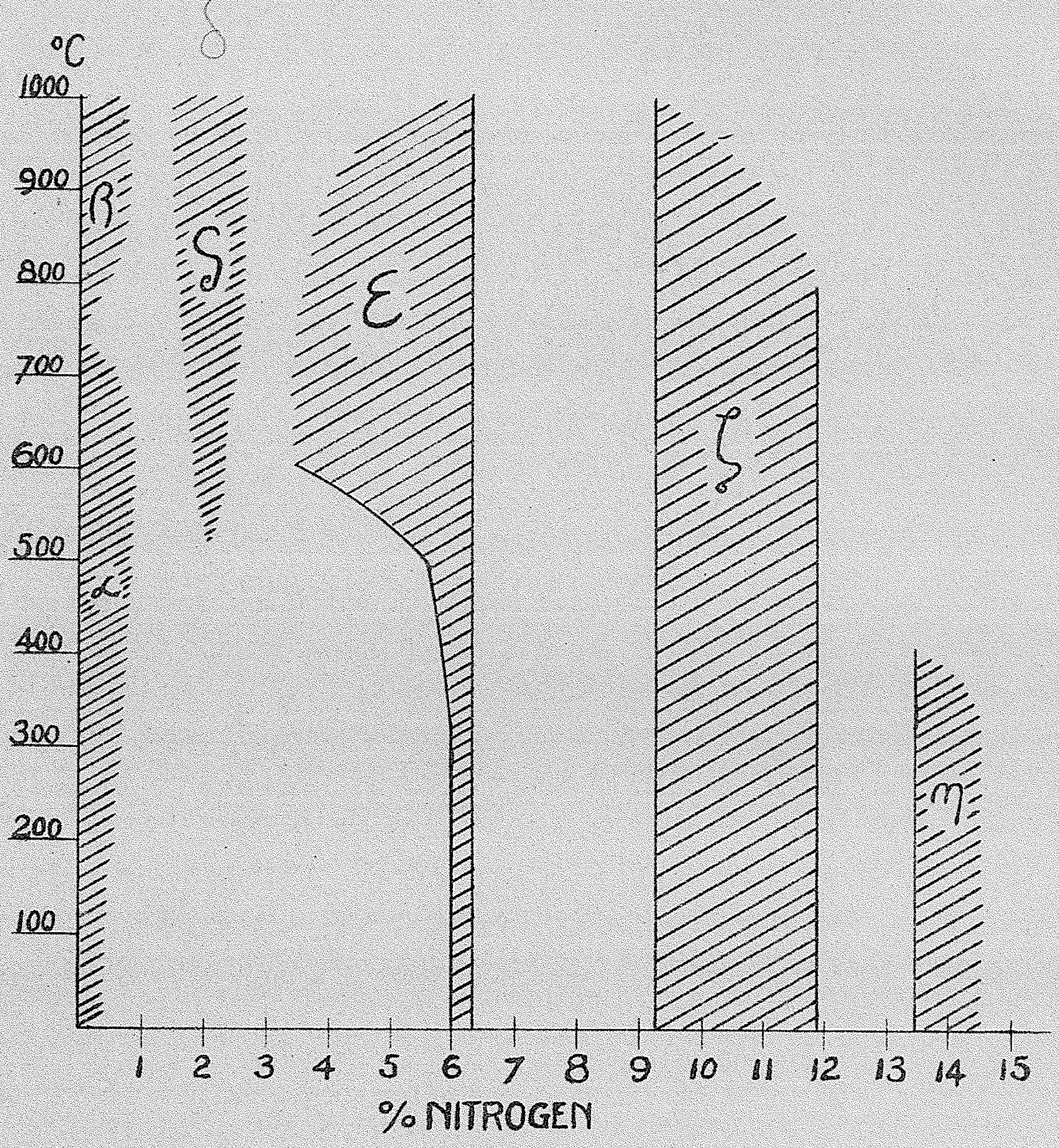
$$Mn + xNH_3 = Mn(N)_x + \frac{3x}{2}\overset{H}{N}_2 \text{ ----(1)}$$

$$Mn(N)_x = Mn(N)_{x-y} + \frac{y}{2}N_2 \text{ -----(2)}$$

If the velocity of (1) is greater than the velocity of (2), then obviously $Mn(N)_x$ is the end product. If, now, it is assumed that for some reason the nitrogen molecule diffuses more slowly through the condensed phase than do the ammonia or hydrogen molecules, then the high nitrogen fugacity is explained. From these assumptions the mechanism of the reaction may be explained as follows. The ammonia diffuses into the metal and there it is practically completely dissociated. The hydrogen resulting from this dissociation diffuses rapidly out into the gas phase where the dissociation equilibrium cannot be established because of the streaming, the hydrogen concentration in the streaming ammonia being very small. The elementary nitrogen on the other hand diffuses very slowly from the solid phase so that its concentration in the solid phase must rise. Hence, the nitrogen concentration (fugacity) in the condensed phase may be great, and so give rise to a nitride which will be rich in nitrogen and have a dissociation pressure greater than the pressure of the reacting gas. This, as far as the candidate is aware is the only explanation given for the experimental fact that nitrogenation with ammonia results in a product richer in nitrogen than does nitrogenation with nitrogen.

The conclusion which have been drawn from the X-ray analysis are illustrated graphically in the schematic phase diagram, Fig. 10. In the neighborhood of 0% nitrogen are shown the two allotropic forms of manganese, alpha and beta. Invwstigation of the concentration changes between 0 and about 14% nitrogen by weight, revealed four crystallographically distinct nitride phases. The nitrogen poorest of these is the delta phase, which showed homogeniety in the region of 2% nitrogen by weight. It exists only above 500°C, decomposing below this temperature to give alpha manganese and the epsilon phase. The epsilon phase occurs in the neighborhood of concentration of about 6% nitrogen by weight. The homogeneous state of the next richest nitride phase, the zeta, begins at about 9% nitrogen. The fourth nitride phase, the eta phase, was found homogenized, only in the preparation, highly nitrogenated with ammonia. It was found to be homogeneous in the region of 14% nitrogen.

It must be understood that the diagram is only tentative. The existances of the four nitride phases is definitely established, but this does not say that they are compounds. Some of them, at least may be solid solutions. The boundaries of the regions of homogeniety which were ascertained with some degree of certainty are represented by lines, while



SCHEMATIC PHASE-DIAGRAM OF THE MN-N_2 SYSTEM.

FIG.10.

those which could not be determined are not ruled to represent a definite boundary.

The region of homogeniety of the delta phase is very uncertain. The diagram merly indicates that in the neighborhood of 2% nitrogen, below about 500°C, no phase exists in a state of homogeniety. It shows clearly that it could not be decided whether at high temperatures this phase coincides with the epsilon phase or not. In order to keep the diagram free from hypothesis, however, these two phases have been drawn separately. For the same reason, the nitrogen poorest limit of homogeniety of the epsilon phase at high temperatures (above about 600°C), is also very uncertain. The other limits of homogeniety, with the exception of those of the manganese phases, are known with a fair degree of certainty. The limits of the manganese phases show, very schematically, the solubility of nitrogen in the alpha and beta manganese respectively.

A large part of this paper is given over to crystallographic data, which need not be mentioned here. The conclusions which are of interest, from the view point of the present problem, are given very completely in the diagram. The formulae which correspond to the various phases may be written as follows:-

eta-phase -- Mn_3N_2 (14.2% nitrogen)
zeta-phase -- Mn_5N_2 (9.2% nitrogen)

epsilon-phase --- Mn_4N (6.8% nitrogen)
delta-phase --- ?

No formula can be written for the delta phase. This is thought to be either a solid solution, or a crystal modification of the epsilon phase. Hägg made an attempt to produce a preparation of nitrogen concentration between those of the two phases, that is between 2 and 6%. It was hoped that such a preparation would show the lines of both phases simultaneously. He was, however, unable to effect the preparation.

This work definitely supports that of the earlier investigators concerning the existance of at least three distinct nitride phases. Aside from the crystallographic data, however, no physical quantities are given.

Still more recently, Dupare, Wenger and Cimerman[18] have investigated the influence of the following factors on the nitrogination of manganese by nitrogen;

(1) Composition and source of the manganese.
(2) Temperature.
(3) The time of the reaction.
(4) Pressure
(5) Catalysis.

This work has shown that the maximum temperature at which the nitride is formed, and also the quantity of nitrogen which is held, depends upon the type of manganese used (i.e. upon the source). In this they are in agreement with Valenski. It is believed that the variation is due to different quantities of aluminum and silica present as impurities in the different manganeses.

The study of the influence of pressure has shown that there is very little increase in the rate of absorption between 0 and 10 atmospheres. There is, however, a definite increase between 10 and 20 atmospheres.

The catalytic affect of lithium nitride was studied. The lithium nitride used (LiN_x) contained 28.9% nitrogen. It was not, then, a homogeneous nitride. The threshold of absorption of a mixture containing 10% LiN_x and 90% Mn was studied as a function of temperature. The positive influence of the catalyst was clearly shown. The threshold temperature of absorption was lowered, and the rate of fixation of nitrogen was increased. Dissociation was also accelerated. The catalytic affect is explained by the fact that the LiN_x dissociates at a lower temperature than does the manganese nitride. The nitrogen so liberated (referred to as nascent nitrogen) then fixes itself to the manganese. The lithium was then removed, renitrogenated, and again dissociated in the presence of manganese. The process was repeated until the manganese was saturated. The absorption threshold for pyrophoric manganese prepared by the method of A. M. Campbell[19] was found to be 500°C, while 740°C is given for compact manganese. The time factor was unimportant. Equilibrium was reached within from one to two hours.

B. Neumann, C. Kröger and H. Haebler[20] have described a new method for determining the heats of formation of nitrides directly. The metal is heated in a small electric furnace, contained in a bomb calorimeter, in nitrogen under pressure. In this way manganese nitride was formed at 500 to 1000°C, under 10 to 25 atmospheres of nitrogen. Analysis showed the compound to be very nearly Mn_5N_2. The heat of formation is given as;

$$5Mn + N_2 = Mn_5N_2 + 57,180(\pm 400)\,cal.$$

The nitride was then burned in oxygen in a bomb calorimeter and the value 62,400 cal. determined. This method is not thought to be as accurate as the former. These experimentally determined heats of formation agree poorly with values calculated from dissociation pressure data. This fact indicates that the dissociation pressures of these nitrides are not known with sufficient accuracy to permit the estimation of the influence of the formation of solid solutions. More accurate dissociation pressure data must be obtained, in order that thermodynamic equations may be used for the calculation of heats of formation.

- EXPERIMENTAL -

The Absorption Experiments

Apparatus:-

The closed glass system which was used in these experiments is shown diagramatically in Fig. 11. This type of system has been described, previously, by Sieverts and Stollenwerk[52], and is really nothing more than a modified dilatometer. It consists, simply, of a flask and an open-air manometer. In the construction, pyrex glass was used throughout. The flask, A, was made from an ordinary 500c.c. distilling flask, the side-arm of which was first bent upward for a distance of about 2 in. and then again bent horizontally. The purpose of these bends was to permit complete immersion in the electric furnace. The neck of the flask was sealed off just above the side-arm and the long tube, a, of 6 mm. internal diameter was fused into the neck to make an internal joint. The length of this tube was so chosen that the sealed end, at a, was situated slightly below the centre of curvature of the flask. This was used as a recess for the thermocouple, in order that gas temperatures could be measured with the greatest possible accuracy. The third tube, b, which was also 6 mm. in internal diameter, was provided in order that the manganese sample could be introduced into the flask without having to cut it from the system.

From the side-arm, a capillary centre section connected the flask to the manometer. At right angles to this, one arm of the tree-way stop-cock, B, was sealed on, making an inverted T-piece. The stop-cock was used in such a manner that the two remaining arms were in a straight line to permit a free passage along this line. (i.e. 1 to 2)

In constructing the manometer rather wide tubing was used. The closed side was made of an 850 mm. length of tubing of 10 mm. inside diameter. The open side was made of tubing 13 mm. inside diameter, and was continued upwards an additional 200 mm. in order that higher pressures could be read. The lower ends of these tubes were joined by a loop of smaller tubing as shown at c.

The flask was heated by an electric furnace which was also built in the laboratory. Two metal cans were used for the rigid parts. The inner can was chosen of such a size that about 1½ in. clearance was obtained between the walls of the can and the walls of the flask at their largest diameter. This can was wrapped with a double layer of asbestos paper over which 18 feet of nichrome resistance wire was wound in the form of a coil. The loose ends of wire were insulated by running them through narrow porcelain tubes, and were lead out to make contact with the 110V power supply. The smaller can was then placed inside a larger one and the space between them packed with powdered asbestos. The outside of the outer can was coated with a layer of asbestos mud. Control of the temperature was affected by including variable resistances in the electrical circuit. The furnace was supported in an

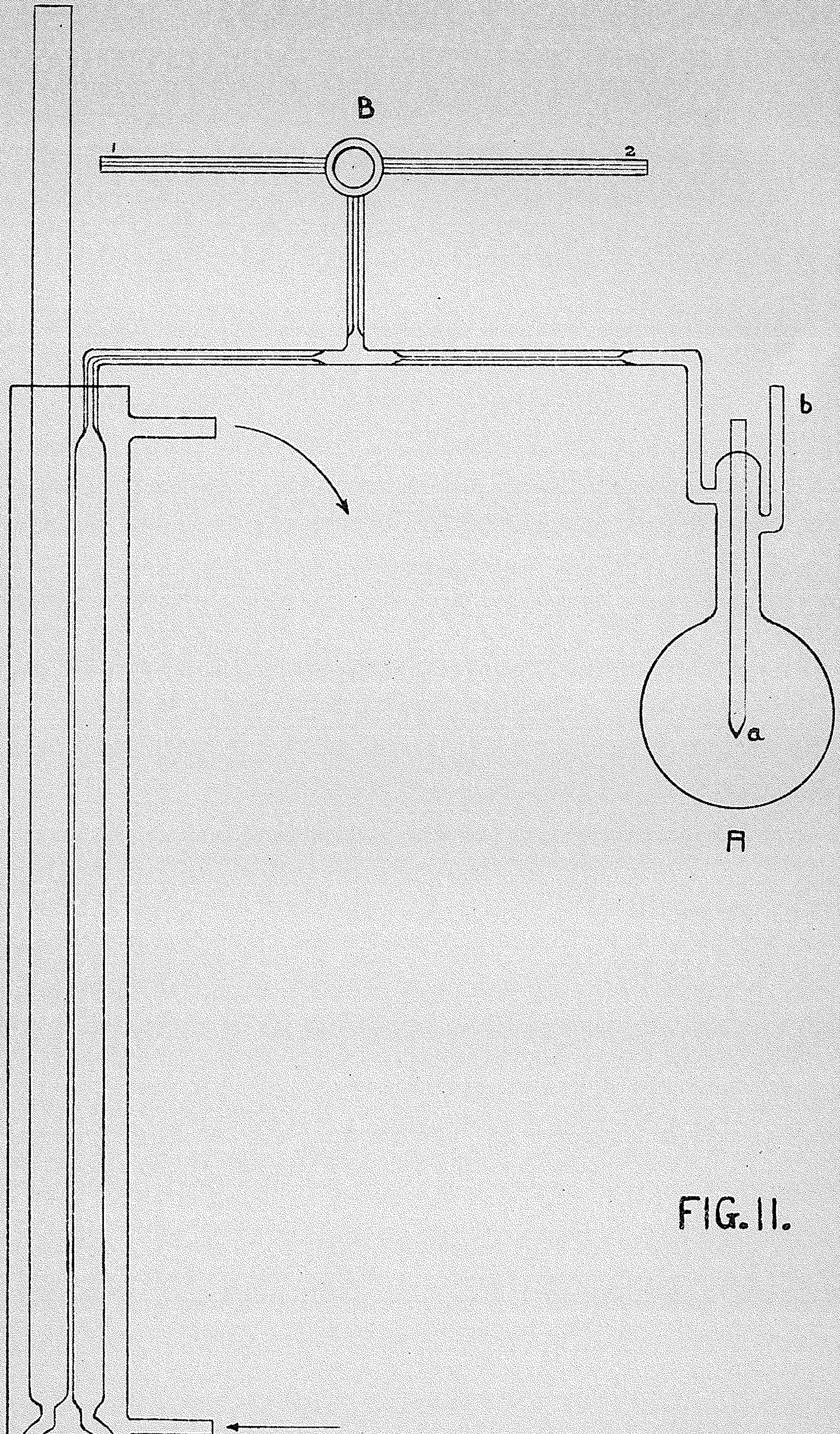


FIG. 11.

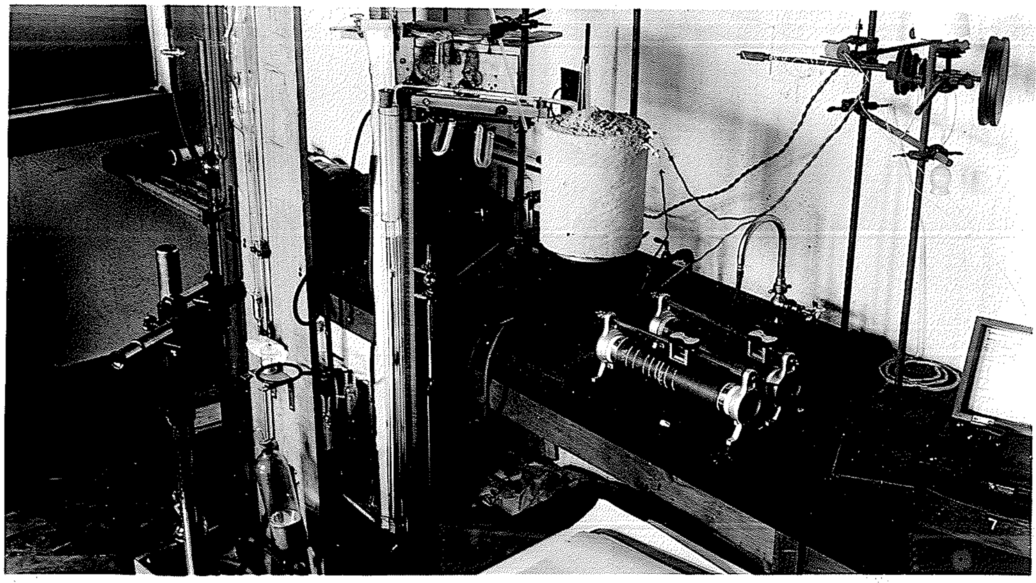
upright position so that the flask was contained in it. All space between the walls of the furnace and the walls of the flask was packed loosely with the powdered asbestos.

Temperatures were measured by an iron-constantan thermocouple, and potentiameter indicator. This instrument is a product of Leeds and Northup and Co. (No. 8658, Cat. 87-34). The wires of the junction are no. 28, d.C.C.. The junction is made by merely twisting the ends of the wires firmly together. Welding is not necessary so that it is a simple matter to renew the junction should the accuracy of the temperature readings become doubtful. The dial of the potentiameter is calibrated every 10°F, but readings can easily be estimated to a tenth part of these divisions. The maximum error due to reading the scale cannot exceed 2°F. The cold junction is provided by a compensator built into the potentiameter unit.

The closed limb of the manometer, as has been said, was made from 10 mm. tubing, and, therefore, it encloses a relatively large volume of gas. Because of this, its temperature had to be controlled. This was done by enclosing the whole manometer in a glass water jacket, made of tubing 3.5 cm. in diameter. No suitable thermostatic control was available. Constant temperature, however, at the time of making observations was all that was required. This was accomplished by cooling to slightly below 10°C by running tap water through the jacket. When the thermometer, immersed in the water, showed a temperature less than 10°C, the flow of water was stopped allowing it to stand stagnant. It thus warmed slowly and uniformly by absorbing heat from the atmosphere. The observation was made when the water in the jacket had reached 10°C. This technique was quite satisfactory since very rarely were more than two observations made in a single day.

The cathetometer used was a product of the Gertner Scientific Corporation, Chicago. This instrument had a range of 0 to 1000 mm., the upright being graduated in mm. The movable scale of the vernier enabled vertical distances to be measured to the nearest 1/10 mm. The levelling bubble was quite sensitive.

Atmospheric pressures had to be known with an accuracy at least equal to that of the manometer readings; that is to 1/10 mm. Three different barometers were used at various times. The first was the standard barometer of the Chemistry Department. This was a very good instrument of the Fortin type, manufactured by the Taylor Instrument Co. It was equipped with a vernier, which enabled pressures to be measured to 1/10 mm. Unfortunately this instrument was at the mercy of everyone in the department with the result that it was broken early in the term. It was necessary , then, to improvise a barometer to replace the damaged one; so an instrument of the syphon type was constructed from 8 mm. glass tubing.



With this, pressures were determined by reading the difference of the heights of the columns with the cathetometer. The improvised barometer was checked against the Meteorological Standard, and was found to read 0.3 mm. too low in the region 735 to 755 mm. This instrument was used for two weeks, during which time, the atmospheric pressure was always well within the above range. During the time that this barometer was in use, 0.3 mm. was added to all pressure observations. An old syphon-type barometer was finally resurrected, which was a great improvement on our improvised instrument. The top of the long column was equipped with a set of two stop-cocks, between which was a mercury trap. This instrument was carefully cleaned and filled with dry mercury. To fill it with mercury the Hyvac pump was applied to the top of the long column while mercury was poured into the short column in an amount sufficient to cause the long column to be filled past the lower stop-cock and into the mercury trap. Both stop-cocks were then closed and some of the mercury subtracted from the short column. This instrument was also read by means of the cathetometer, and in the photograph can be seen standing beside the manometer. Checking against the Meteorological Standard showed very good agreement. This barometer is still in use.

Materials:

The metallic manganese was purchased from the Johnson Matthey Co., Toronto. The manufacturers analysis of the metal was as follows:

Manganese--------96.84%
Iron------------- 1.74%
Silicon---------- 0.61%
Carbon----------- ~~0.21%~~ 0.12

To check this analysis, J. K. Royal made two determinations of the total metallic content. He gives (1) 98.67% and (2) 98.79% as the values obtained from these determinations. Adding the percentages of iron and manganese, given by the manufacturer, it is seen that 98.58% is the value given for the total metallic content. The analysis of J. K. Royal, then, agrees very well with that of the manufacturer.

The metal was delivered in the form of a fine powder. In order to get an idea of the state of division of the metal I have measured some particles by a microscopic method and from these measurements the area per gram of the sample has been calculated. A preliminary examination of some particles showed the 8 mm. objective of the microscope to provide the most suitable magnification, with the ocular micrometer in place. The ocular micrometer then had to be calibrated for use with the 8 mm. objective. This was done with the help of a stage micrometer on which was etched a line divided into ten equal parts. This line was 1/100 mm. in length, so that each small division represented 1/1000 mm. Calibration of the ocular micrometer was affected by using it to measure one small division of the stage micrometer scale. Five measurements were made and the mean taken, thus:

Stage Micrometer	Ocular Micrometer
.001 mm.	2.509 divisions
"	2.505 "
"	2.500 "
"	2.448 "
"	2.486 "
"	Mean = 2.489 "

From this mean value it is seen that,--

.001 mm. = 2.489 scale divisions of ocular micrometer

hence 1 scale div. of ocular micrometer = .000408 mm.

Measurements of particles were made in the following manner. A small quantity of the powdered metal was shaken from a camel hair brush onto a glass slide. This small sample was then searched for the largest particle it contained. When found, the large particle was measured in length and breadth by means of the ocular micrometer. The particles were usually irregular in outline and in making the measurements an attempt was made in every case to obtain an average dimension. In this way the largest particle in each of twelve samples was measured. The values obtained were:-

Length	Width
2.839 divisions	2.298 divisions
4.272 "	2.188 "
4.424 "	2.689 "

Length (con.)	Width
4.888 divisions	3.557 divisions
4.444 "	3.219 "
5.031 "	3.115 "
6.060 "	2.985 "
4.429 "	1.855 "
3.697 "	1.709 "
4.355 "	2.633 "
2.381 "	3.842 "
5.850 "	2.715 "
Mean = 4.389 "	Mean = 2.734 "

Then, multiplying by .000408, the distance which is equivalent to one division of the micrometer scale, we obtain:

Mean length = .0018 mm.

Mean width = .0011 mm.

This is taken to be the largest particle which will be found in any sample of the metal. If, now, the smallest particle is of molecular size, then for the mean particle these dimensions may be halved, giving:-

Mean length = .0009 mm.

Mean width = .0006 mm.

The particles, as has been said, were seen to be very irregular in outline. For this reason the mean particle was considered to be cylindrical, for the purpose of calculation; since a cylinder presents a great many surfaces. Our measurements, then, give the dimensions of this mean cylinder as,--

Radius = .0003 mm.

Length = .0009 mm.

To find the number of mean particles per gram;

Volume of mean particle $= 3.14(.0003)^2.0009 = 254 \times 10^{-12}$ cu. mm.

and since 1 gm. Mn occupies $\frac{1000}{7.42} = 134.8$ cu. mm.

then no. of mean particles per gram $= \frac{135}{254} \times 10^{12} = 5.32 \times 10^{11}$

To find the area of the mean particle;-

area of the curved surface $= 2 \times 3.14 \times .0003 \times .0009 = 16.96 \times 10^{-9}$

area of the two ends $= 2 \times 3.14 \times (.0003)^2 = 5.65 \times 10^{-9}$

Total area $= 2.26 \times 10^{-10}$ sq. mm.

Therefore, the area per gram;

$2.26 \times 10^{-10} \times 5.32 \times 10^{+11} = 120.2$ sq. mm.

The nitrogen used in the nitrogenation of the metallic manganese was ordinary 'tank' nitrogen, obtained from the Canadian Liquid Air Co. Before being admitted to the apparatus it was run through a purifying train which contained the following: two sulphuric acid traps to remove moisture and traces of compressor oil; a spiral of copper gauze, heated in a combustion tube by a small electric furnace, to remove traces of oxygen; and finally, a straight piece of combustion tubing on the bottom of which was a layer of phosphoric anhydride, to remove any remaining traces of moisture. From here the purified nitrogen was conducted to the apparatus by a piece of pressure tubing attached to one arm of the three-way stop-cock.

Experimental

For the purpose of determining its volume, the apparatus was considered in three parts, the flask, the capillary connecting tube and the closed limb of the manometer. The volume of each of these was determined separately. The flask was weighed first, when dry and again when filled with distilled water at 19.2°C.

Weight of flask + water at 19.2°C = 701.82 gms.

Weight of dry flask ------------- = 159.22 gms.

From which the volume was calculated to be 542.49 c.c. The capillary section was calibrated by filling it with mercury and draining the mercury into a weighed beaker and again weighing. This gave;

Weight of beaker + Hg at 21.0°C - 93.2148 gms.

Weight of dry beaker ------------- 38.1724 gms.

from which the volume was calculated to be 4.07 c.c. A meter rule was screwed to the board on which the manometer was mounted in such a manner that the zero mark on the meter stick was at the point where the capillary from the flask was joined to the top of the closed limb of the manometer. The volume calibrations of the limb of the manometer were made with reference to the lengths measured downward, on the meter stick. The method was to drain successive 10 cm. into a weighed beaker and weigh. The data obtained was;

Length of closed limb	Weight of beaker + Hg at 21.0°C	Weight of beaker
10 cm.	148.20 gms.	38.1724 gms.
20 "	256.91 "	"
30 "	364.10 "	"
40 "	472.00 "	"
50 "	581.21 "	"
60 "	689.91 "	"
70 "	798.47 "	"
80 "	903.95 "	"

The following table gives the total volume of the system when various lengths of the manometer are included:

Length of closed limb	Total volume of system
10 cm.	554.7 c.c.
20 "	562.8 "
30 "	570.7 "
40 "	578.7 "
50 "	586.8 "
60 "	594.8 "
70 "	602.9 "
80 "	610.7 "

The quantities given in this table were plotted graphically so that the volumes corresponding to intermediate lengths could be interpolated quickly.

TABLE I.

TEMP. OF MANOMETER	TEMP. OF FURNACE	BAROMETER M M.	MANOMETER M M.	PRESSURE M M.
10°C	99°C	740·3	1·9	742·2
"	104	743·6	3·5	747·1
"	116	745·9	23·2	769·1
"	126	747·4	34·6	782·0
"	155	754·4	71·1	825·5
"	192	747·5	131·4	878·9
"	227	740·1	185·9	926·0
"	254	743·0	219·3	962·3
"	287	742·6	263·0	1005·6
"	302	744·9	280·2	1025·1
"	330	744·3	313·6	1057·9
"	386	739·9	383·7	1123·6
"	420	738·0	422·1	1160·1
"	446	737·7	448·2	1185·9
"	482	745·3	481·0	1226·3
"	508	751·1	501·9	1253·0
"	543	751·5	532·3	1283·8
"	573	752·3	553·1	1305·4

The Expansion Curve

The first stage in the experimental work was to find the curve expressing the expansion of the gas in the system. This curve, as has been pointed out in the introduction, (see Kh in Fig.3) will vary from the straight line relation of the gas laws because, as pressure increases, the volume of the system also increases with the fall of the mercury miniscus in the closed limb of the manometer. The curve, therefore, will be characteristic of the apparatus and must be determined experimentally.

The Hyvac pump was connected to the arm 2, Fig. 11, of the three-way stop-cock, and pumping was continued for two hours to be sure that all moisture was removed from the glass walls. The stop-cock was then moved to the position which closed the system but, at the same time, left a passage through the stop-cock from 1 to 2. Nitrogen from the tank was run through the purifying train and through the stop-cock in the direction from 1 to 2. The flow of nitrogen was continued for ½ hour to expell all air from the purifying train and connecting tubing. The stop-cock was then moved to the position which provided a passage from 1 into the system. Care was taken that the rate at which gas was admitted to the system was slow. By so doing the pressure in the purifying train was always above 1 atmosphere, and hence no air could leak into it. In this way dry nitrogen was admitted to the

TABLE II

DATE	TIME	TEMP. OF FURNACE °C	PRESS. MM.
	1st Charge of N_2 (See Fig. 12)		
Feb. 2	—	118	787.9
" 3	—	126	798.1
" 3	—	138	809.1
" 4	—	144	820.0
" 4	17.05	166	849.0
" 5	9.15	162	851.5
" 8	17.00	177	863.5
" 9	17.00	186	877.2
" 10	17.15	201	897.8
" 11	10.30	218	920.5
" 15	9.30	238	947.9
" 15	17.00	249	963.7
" 16	17.00	270	992.0
" 17	17.10	284	1012.2
" 18	17.00	298	1029.5
" 19	17.00	308	1042.6
" 22	16.30	327	1063.7
" 23	10.15	343	1082.2
" 24	9.20	365	1108.0
" 25	17.00	386	1136.3
March 1	10.15	404	1145.7
" 9	17.00	425	1155.6
" 15	9.30	444	1163.9
" 17	9.25	455	1164.7
" 19	9.20	480	1178.7
" 22	10.00	495	1137.7
" 23	16.20	511	1115.3
" 25	16.50	511	1041.3
" 31	9.45	512	783.7
April 7	13.15	508	572.1
Absorbed N_2 - 3.6% - calculated from -			
—	—	103	314.4

DATE	TIME	TEMP. OF FURNACE °C	PRESS. MM.
	2nd Charge of N_2 (See Fig. 13)		
—	—	100	841.1
—	—	125	882.0
—	—	154	927.0
April 9	9.30	509	1371.1
" 10	9.30	516	1355.7
" 14	8.45	516	1234.1
" 19	12.00	526	1148.7
" 29	13.30	513	965.0
Absorbed N_2 - 5.8% - calculated from -			
—	—	111	563.6
	3rd Charge of N_2 (See Fig. 13)		
—	—	108	787.5
—	—	134	829.2
May 3	17.00	521	1313.2
" 5	10.15	554	1280.0
" 6	10.00	582	1194.8
" 6	17.00	615	1162.0
" 7	10.00	624	914.5
" 10	10.00	625	722.7
" 10	17.00	625	720.7
Absorbed N_2 - 7.1% - calculated from -			
—	—	111	374.6

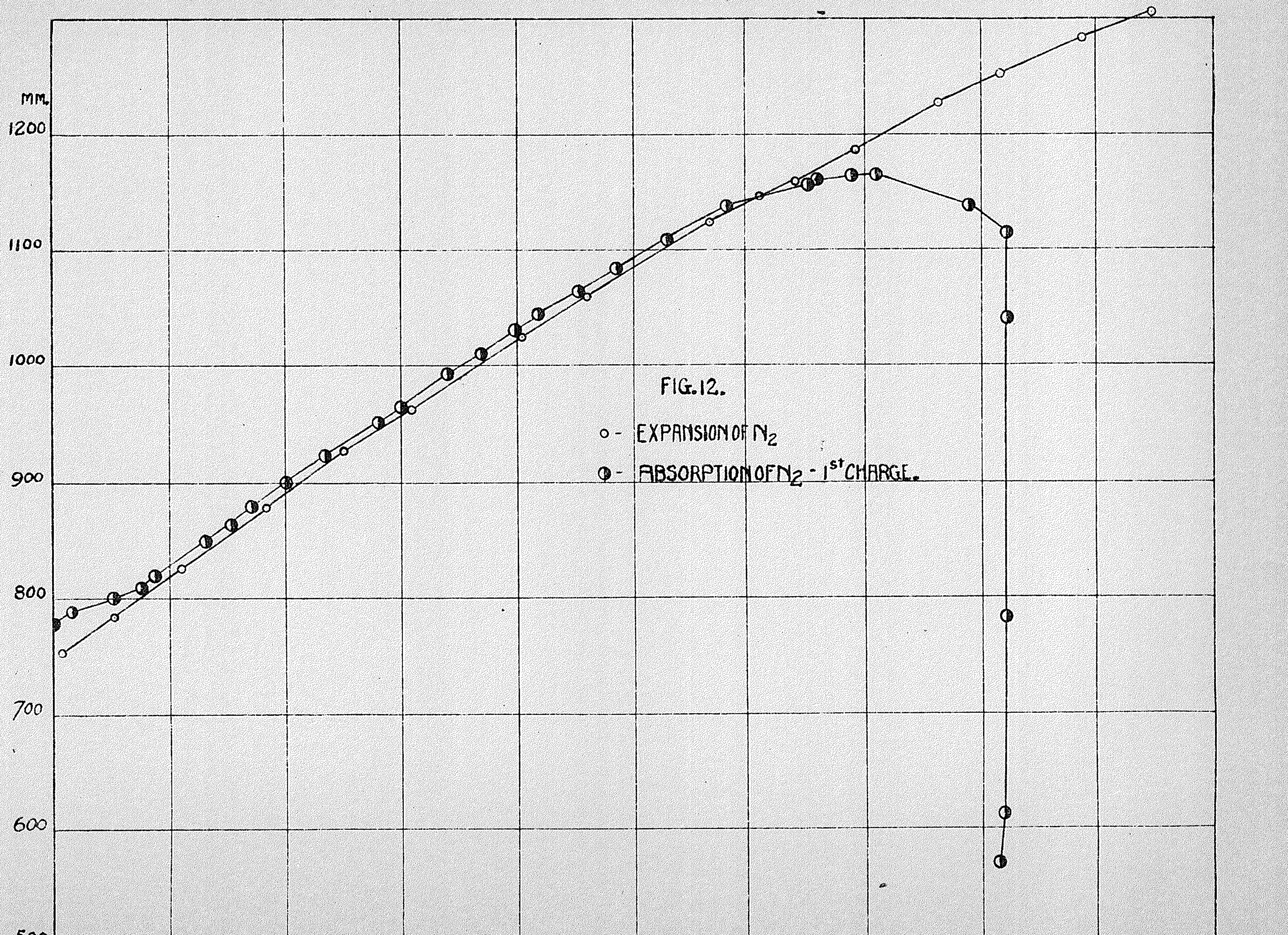


FIG. 12.

○ - EXPANSION OF N_2
◐ - ABSORPTION OF N_2 - 1st CHARGE.
MM.
1200
1100
1000
900
800
700
600
500
200
300
400
500
600 °C

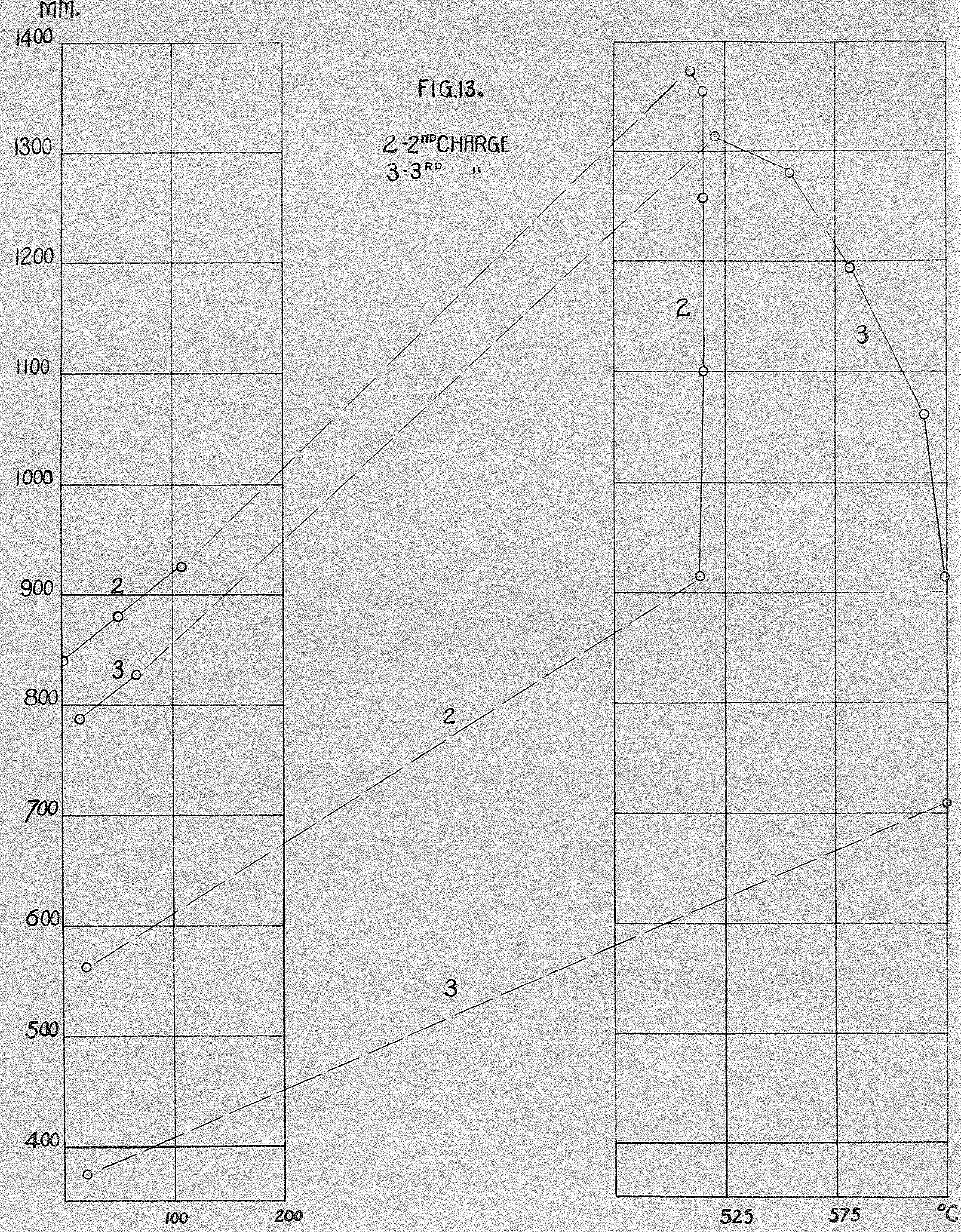
then resealed. The weight of the manganese sample was:-

Wt. of Mn + watch glass---15.4777
Wt. of watch glass--------- 5.4776
Wt. of Mn -----------------10.0001 grams.

The system was then evacuated and charged with nitrogen to about 1 atmosphere in the same manner as for the expansion curve. The proceedure of heating and measuring the corresponding pressures was carried on as before. Here, however, a greater period of time was allowed at each temperature, to be sure that no slow process was taking place.

The most important of the data obtained is given in Table 11 under the heading of 1st charge of Nitrogen. The great length of time required for these experiments indicates the slow rate of the reaction at these temperatures. The data is expressed graphically in Fig. 12.

The apparatus was designed to enclose a comparatively small volume of nitrogen in order to enhance its sensitivity. The possibility of the formation of solid solutions was realized, and in consequence, an attempt was made to have an apparatus as sensitive to absorptions of small volumes of gas as was compatable with the object of ultimate nitrogenation of the metal. For this reason it was calculated that four charges of nitrogen, each representing a pressure drop of ½ atmosphere due to nitrogenation, would be required for a 10 gram sample of the metal. These calculations were based


MM.
1400
1300
1200
1100
1000
900
800
700
600
500
400
100
200
525
575
°C
FIG.13.
2-2ND CHARGE
3-3RD "
2
3
2
3
2
3

on the assumption that Mn_3N_2 represents the ultimate product, with 14.5% of nitrogen. I have numbered these charges 1, 2, etc. as shown in Table 11. The data obtained for the 2nd and 3rd charges is shown graphically in Fig. 13.

The form of the curve obtained for the 1st charge of nitrogen indicates that absorption proceeds with appreciable velocity at a temperature of 510°C. For subsequent charges of nitrogen the temperature was raised quickly to this value since repetition of the whole curve; as was done for the 1st charge; was an obvious waste of time. Thus, the regions of the curves in Fig. 13, which are drawn with a broken line, were not determined by experiment but were swept through by raising the temperature quickly to a high value. The regions shown as a solid line, however, are plotted from the experimental data. The regions of the curves which represent the experimental figures are, first, a short length in the neighborhood of 100° to 200°C; second, the vertical portion at high temperature representing the decrease in pressure due to absorption; and third, a single point to which the system was cooled after the rate of absorption had decreased to such a low value as to warrant the discontinuation of nitrogenation for this particular charge. This single point was used to calculate the amount of nitrogen present in the condensed phase after nitrogenation (i.e. before recharging with nitrogen.)

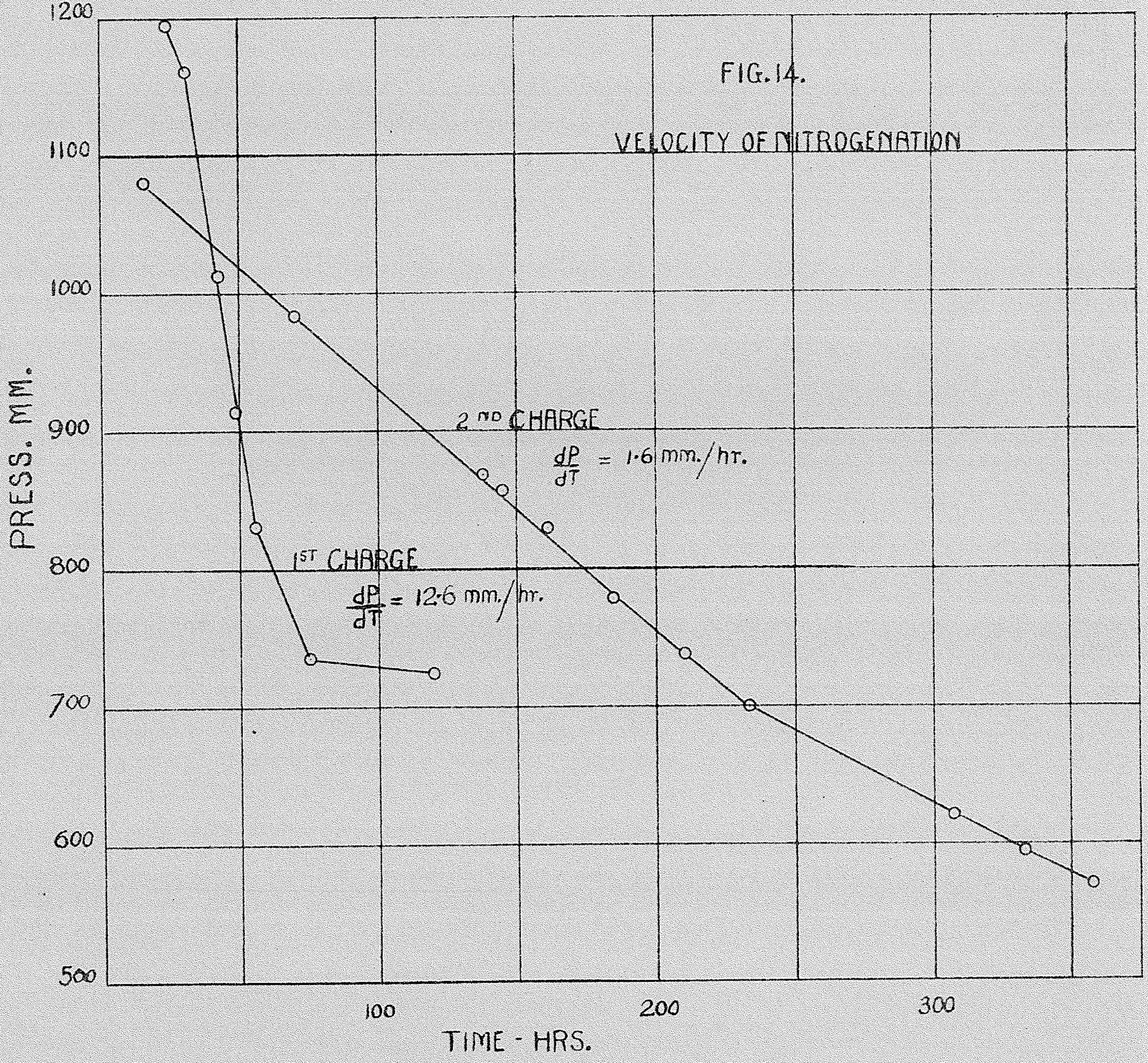


FIG. 14.
VELOCITY OF NITROGENATION
2ND CHARGE
$\frac{dP}{dT}$ = 1·6 mm./hr.
1ST CHARGE
$\frac{dP}{dT}$ = 12·6 mm./hr.
PRESS. MM.
1200
1100
1000
900
800
700
600
500
100
200
300
TIME - HRS.

The velocity curves, shown in Fig. 14, for the 1st and 2nd charges were also plotted from the data. These curves represent the decrease in gas pressure as a function of time at constant temperature. In the case of the 3rd charge no such curve has been plotted, because here, the temperature was raised in an attempt to increase velocity. The attempt was successful in that the velocity was increased and, as Fig. 13 shows, the pressure actually fell below 1 atmosphere in reasonable time. Unfortunately, however, the pyrex glass softened and collapsed. The fact that the flask was distorted, and hence its volume calibration destroyed, did not reveal itself until the 4th charge of nitrogen was being heated. The rapid increase in temperature then caused the flask to crack. This put an end to the first attempt to attain maximum nitrogenation. It appears from this that a pyrex flask at 625°C (gas temperature) has softened to the point where a pressure of 50 mm. causes it to become distorted.

Before proceeding to summarize the conclusions which can be drawn from these experiments, there is another matter which deserves attemtion. This is the manner in which the amount of absorbed nitrogen was calculated, at the end of each charge. These calculations can be explained best, by referring to Fig. 13. These curves illustrate how, for each charge of nitrogen, the system was carried through a sort of cycle. Initially, the nitrogen was admitted, at about 100°C, to a pressure of approximately one atmosphere. In this region a few points were obtained, and a short section of the p-t curve was plotted. From the coordinates of any point on this short curve, and the volume of the system, the amount of gas present in the system before any absorption had taken place, can be calculated. This, however, was never done until after the final point at low pressure (i.e. after absorption) had been obtained because the temperature of this final point could never be adjusted, conveniently, to an exact value.

After the short length of the p-t curve had been obtained the temperature (and hence the pressure) was raised to a high value. Absorption then took place with disappearance of the gas phase and, consequently, the pressure decreased. When it was seen that absorption would proceed no further, the temperature was then brought back to some low value and a final point determined which lay beneath the initial short length of the p-t curve. In other words, there had to be some point on the initial curve which had the same ordinate as the final point. Then, having obtained such a point, the pressures, before and after absorption, could be compared at the same temperature. The initial pressure was interpolated from the short length of the p-t curve. This could be done quite accurately since a large piece of graph paper was employed. On this the experimental curve was plotted on a scale sufficiently large that each small division of the paper represented 1 mm. pressure.

Thus, fractions of a millimeter had to be estimated. The error due to interpolation of the graph could not have exceeded 0.5 mm.

The volume of the apparatus, then, is the sole remaining factor which is necessary for making the calculations. This also was variable because the length of the closed limb of the manometer changes with changing pressure. In the section describing the calibration of the apparatus the volumes corresponding to different lengths of the manometer were given. The slope of the curve which was plotted from this data was found to be 0.080. That is, for every mm. change in pressure the volume of the system changes by 0.080 c.c. The volume of the apparatus, then, was determined as follows. At the same time that the final low temperature point was determined, an observation was made of the length of the closed limb of the manometer which was included in the system. From this length measurement the total volume of the system was interpolated from the length--volume curve. This gave the volume of the system after absorption had taken place. The values obtained for the three charges were:

Length	Total Volume
23.1 cm.	565.3 c.c.
32.1 "	572.5 "
21.1 "	563.8 "

Then multiplying the pressure drop due to absorption by 0.080 (the slope of the length-volume curve) the decrease in volume accompanying the decrease in pressure is obtained. This decrease in volume, when added to the final volume gives the initial volume of the system at the comparison temperature. This method of determining the initial volume had to be resorted to because, as had been said, it was not convenient to set the temperature of the furnace to a preconcieved value.

The sources of error in the estimation of the amount of absorbed nitrogen are:

(1) An error caused by including the volume of the capillary centre-section with that of the furnace for the purpose of calculation. The temperature of this small volume of 4.1 c.c. could not be determined, since a temperature gradient existed from the furnace to the manometer. This error may amount to 0.7 c.c. at the temperatures in the region in which volumes were measured, and will result in a volume too great. The volume of the system, at these pressures, was about 580 c.c. so that the error may be estimated as about 1 in 580.

(2) Two small errors due to interpolation of the two graphs. The direction of these cannot be determined. The error in reading the length-volume graph cannot exceed 1 in 580, while that in reading the p-t curve will be very small, about 1 in 900.

(3) An error due to reading the temperature from the potentiometer indicator, which cannot exceed $1^{\circ}C$. This error must not be greater than 1 in 390.

(4) There is another possible source of error which is very difficult to estimate. The gas in the flask may be at a higher temperature at the walls of the flask than at the centre of curvature where the thermo-junction is separated. The flask, however, was quite large and for this reason convection should be efficient.

From the above it will be seen that the calculated quantities of absorbed nitrogen must be quite accurate. Assuming that the first three errors are in the same direction, then adding, it is estimated that the maximum error due to the first three causes cannot exceed 1 per cent.

Unfortunately, however, the failure of the pyrex flask during the heating of the third charge renders the **final** percentage of nitrogen doubtfull. If time permits it will be checked by analysis. The percentages of nitrogen in the condensed phase after the 1st and 2nd charges, on the other hand, must be accurate.

Discussion of Results and Conclusions

Although these experiments failed in that the object of ultimate nitrogenation was not achieved, there are, nevertheless, several conclusions which can be drawn from the data:

(1) The first indication of disappearance of the gas phase occurred at 126°C. This is revealed in Fig. 12, by the small initial drop in pressure. Following this small initial drop, however, the p-t curve again runs parallel to the expansion curve until a temperature of about ~~510~~ 390°C is reached. Thus, continued nitrogenation for some reason is inhibited. It is probable that the surfaces of the manganese particles become covered by a skin of nitride which is impermeable to nitrogen. In this skin the concentration of nitride is high so that, in accordance with the Law of Le Chatelier, further reaction is prevented. Nitrogenation at this low temperature has never before been observed. If it does represent compound formation, one would expect the pyrophoric metal to form a nitride at this temperature. G. Valenski, however, gives 390°C.

The mass of nitrogen corresponding to this small decrease in pressure has been estimated. This was done by cooling back and comparing gas pressures, before and after absorption, in the manner previously described. The calculation gave .1134 gms. as the mass of nitrogen absorbed. From this and the following data;

Area of Manganese Sample = 1219 sq. meters

Effective area of N_2 molecule = 772×10^{-16} sq. mm.

Avogadro's Number = 6.06×10^{23}

the number of layers of nitrogen was calculated to be 5700. When the crudity of the measurement of the area of the sample is taken into account, this figure may well be accepted as evidence in favor of the 'skin theory' given in the previous paragraph.

(2) Progressive nitrogenation was found to take place with appreciable velocity at 510°C. Fig. 14 shows the velocity curve for this temperature. The p-t curve, however, had commenced to bend downward at 390°C. (see Fig. 12). It is interesting to note that this latter temperature corresponds to that cited by G. Valenski for the pyrophoric metal.

(3) The velocity of the change is lessened progressively as more nitrogen is fixed. The velocity of the reaction below a composition of 3.6% nitrogen is quite rapid. As Fig. 14 illustrates, a pressure decrease of 12.6 mm./hr. was observed. When the pressure had fallen to about 750 mm., however, the curve broke sharply. It was hoped that the greater pressure, after the introduction of the 2nd charge, would again hasten the reaction. This was not the case, however, for the velocity remained constant some 200 hrs. at 1.6 mm./hr. Both curves show the same form, that is a straight

portion which slopes off asymptotic to the axis of time. After some 360 hrs. treatment, the rate for the 2nd charge became so slow that it was revealed by an approximation that about 2½ years would be required to fix 14.5% nitrogen. Recharging the third time did not greatly increase this rate. Because of this higher and higher temperatures were tried resulting finally in the failure of the pyrex flask. The maximum rate obtained at these higher temperatures was 3.5 mm./hr.

(4) No nitride phase of a composition less than 8% of nitrogen gives rise to a solid solution by dissolving gaseous nitrogen. This is concluded from the fact that all the p-t curves were of the form of Fig. 12. The two final curves were not obtained in full, but by comparing the earlier high temperature points (i.e. before appreciable absorption had taken place) with the expansion curve, it was shown that the curves had been parallel. The curves of Figs. 12 and 13, then, are of the type of K x L of Fig. 3 of the theoretical introduction.

The Silica Apparatus

The first attempt to produce maximum nitrogenation, as has been seen, ended in the failure of the pyrex flask. The reaction, at the highest temperature that the pyrex flask would stand, was extremely slow. With the hope of increasing the velocity by obtaining higher temperatures, a silica flask was constructed for the apparatus.

The design of this flask had to be modified because of the limited amount of quartz tubing available. The recess for the thermo-junction was sealed through the curved part of the flask, below the neck, rather than through the neck. The tube by which the flask was connected to the apparatus was sealed to the neck. The manganese sample was introduced through this latter tube before the flask was attached and in consequence of this the other side-tube, formerly used for this purpose, was omitted.

Attachment to the apparatus was accomplished by the use of a short piece of pressure tubing which was wired securely over the ends of the glass and silica tubes. Heating of the rubber pressure tubing was feared, because the silica tube was quite short. In order to prevent this a small water jacket was fitted over the joint and cold water was run through it whenever the furnace was hot. It was necessary to use the furnace in a horizontal vertical position with this flask.

The accompanying photograph shows the new arrangement.

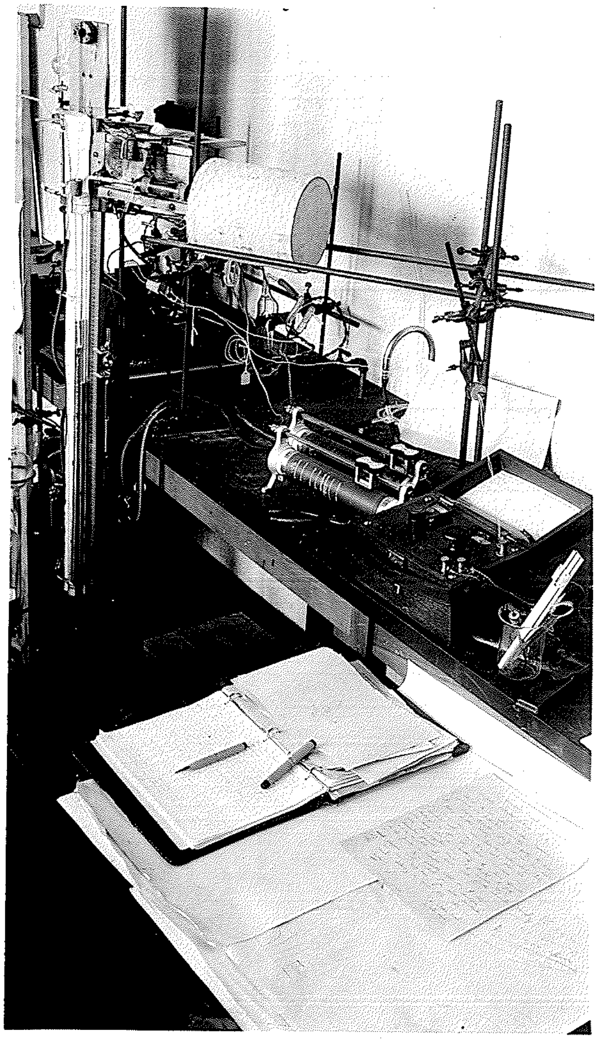


TABLE III

DATE	TIME	TEMP. OF FURNACE °C	PRESS. MM.
	1st Charge of N_2		
May 20	—	132	725·1
" 20	—	172	782·4
" 21	10·30	520	845·7
" 21	17·00	596	768·9
" 22	10·15	594	373·1
" 24	—	594	167·7
" 25	—		
Absorbed N_2 - 4·8 % - calculated from -			
		129	81·3
	2nd Charge of N_2		
" 25	—	128	813·5
" 25	—	177	887·1
" 28	14·15	598	693·8
" 28	17·00	615	668·6
" 29	11·45	607	649·4
" 31	10·00	595	605·8
Absorbed N_2 - 7·8 % - calculated from -			
" 31	—	133	311·8
	3rd Charge of N_2		
" 31	—	126	747·1
" 31	—	149	795·4
June 1	11·30	604	1233·9
" 1	17·00	677	1181·5
" 2	12·30	663	1143·1
" 2	17·00	677	1130·5
" 3	14·00	688	1071·1
" 3	17·00	688	1061·6
" 4	11·45	717	1059·8

DATE	TIME	TEMP. OF FURNACE °C	PRESS. MM.
Absorbed N_2 - 9·3 % - calculated from -			
June 4	—	146	551·9
	4th Charge of N_2		
" 4	—	125	769·9
" 5	10·30	696	1326·2
" 7	11·20	080	1105·5
" 8	17·00	693	1033·1
" 9	14·30	710	1188·1
Absorbed N_2 - 10·1 % - calculated from -			
" 10	—	127	665·0
	5th Charge of N_2		
" 10	—	119	859·4
" 10	17·00	711	1635·2
" 11	13·45	573	1460·8
" 13	11·30	699	941·9
" 14	11·00	682	889·1

The small water-jacket enclosing the pressure tubing can be seen quite clearly.

The quartz flask was smaller than was the pyrex flask. Its volume, which was calibrated with water as before, was found to be 471.6 c.c. From this and from the volumes of the other parts of the apparatus, a volume-length curve, similar to that for the former apparatus, was plotted.

Procedure:- The expansion curve was not repeated for this apparatus. The manganese sample was introduced, at once, into the flask. The flask was attached to the apparatus and after obtaining the short, low-temperature section of the curve, the temperature was raised to a high value. The mass of this fresh sample of manganese was,

Wt. Manganese + watch glass = 16.2189
Wt. watch glass ---------- = 8.2170
Wt. of Manganese --------- = 8.0019 gms.

The experimental mthod was exactly the same as that described for the curves of Fig. 13. A smaller sample of the metal was taken because the volume of the new system was less and, therefore, the amount of nitrogen available for each charge, was less.

Data:- The experimental values are shown in table III, and are expressed graphically in Fig. 15. Not all of the experimental figures are reproduced, but just enough to give the curves of Fig. 15. The table shows that the nitrogenation has been

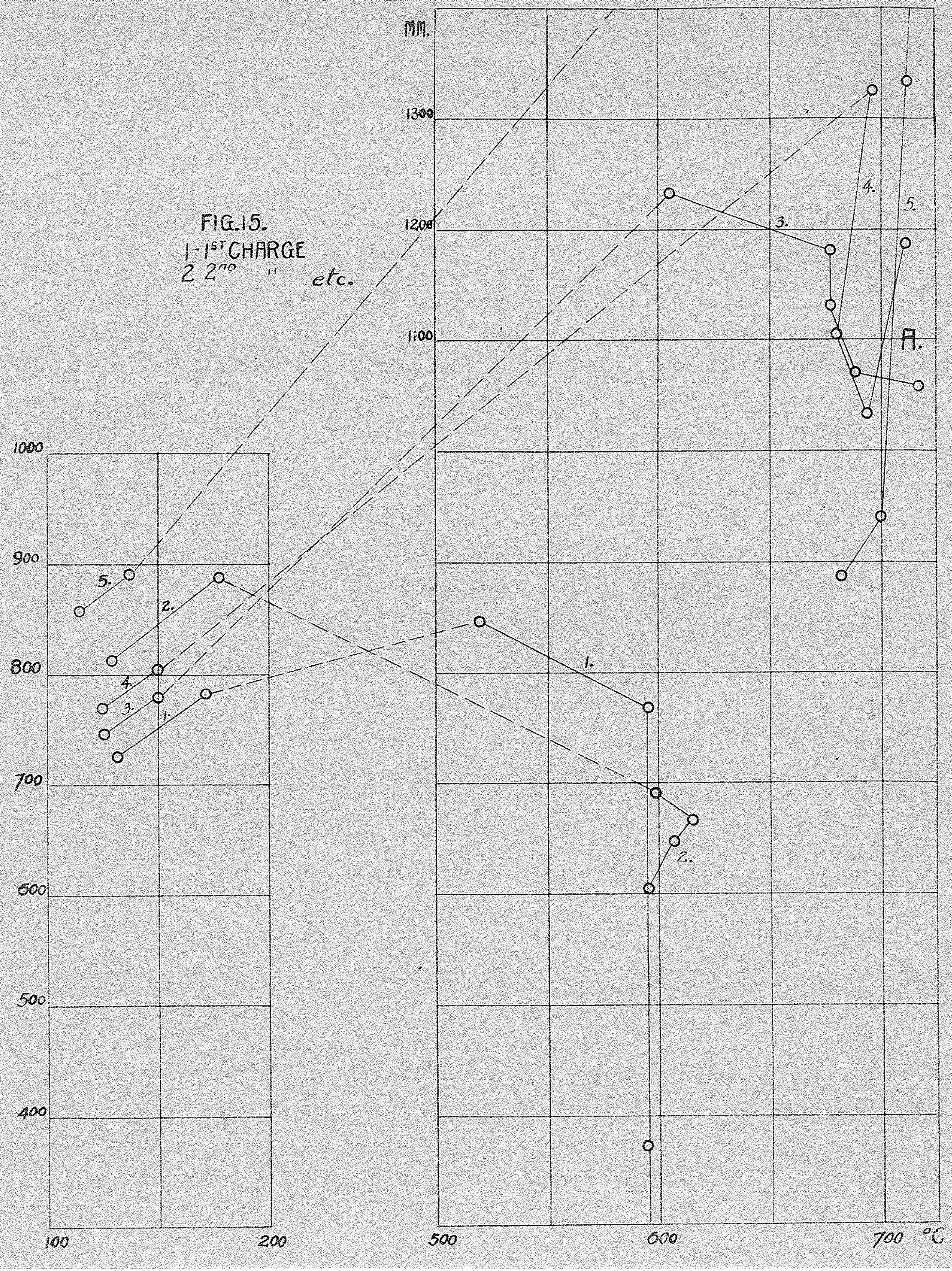


FIG.15.
1-1st CHARGE
2 2nd " etc.

carried to five charges of the system. Actually, two more charges were made, but the data obtained had to be discarded for reasons which will appear later.

Discussion of the data: The velocities of absorption for the 1st and 2nd charges were much higher than for the corresponding charges of the former apparatus. This is remarkable because the temperatures were not greatly different in the two cases. In this fact, confirmation is seen, of the conclusion of G. Valenski, that the velocity of nitrogenation depends upon the previous history of the metal. Thus, in the first apparatus the metal was subjected to prolonged heating before progressive nitrogenation set in, while in the latter temperature was raised at once, to a high value. Manganese does undergo an allotropic change, but as G. Hägg's X-ray study has shown (see Fig. 10), not below 750°C. That beta manganese reacts with nitrogen at a slower rate than does alpha manganese, then, cannot explain the different rates. It is, in all probability, a surface phenomenon.

Velocity curves, are not given because the temperature varied during the course of the nitrogenation. A velocity curve, of course, must be obtained for constant temperature in order to be of theoretical significance. The curves 1 and 2 of Fig.15 show the first of the high temperature points in the neighborhood of 1 atmosphere pressure. This indicates how the pressure fell, during the course of a single night, by more than an atmosphere. By use of the expansion curve, however, the avergge velocities have been approximated as 13.9 mm/hr for the 1st and

11.2 mm/hr. for hte 2nd charge. These approximations are based on the total time of nitrogenation and must not be confused with the $\frac{dp}{dt} = 12.6$ mm/hr. shown for charge 1, in Fig. 14, which refers only to the linear part of the curve.

It is to be noticed that in the second apparatus a closer approach to ideal behavior was obtained, than in the first apparatus. On recharging the apparatus with nitrogen the second time, the velocity was again increased because of the increased gas pressure, in accordance with the Law of Le Chatelier.

On proceeding to the 3rd charge it was found that the velocity had greatly decreased. The averaged velocity here was about 2.1 mm/hr. Because of this the temperature was raised to 677°C, then to 688°C and finally to 717°C. At this latter temperature the rate was very slow. Curve 3 shows an almost flat portion between 688°C and 717°C which indicates an approach to equilibrium conditions. The calculated nitrogen content here is 9.32%, which (see Fig. 10) indicates that a good deal of Mn_5N_2 is present. The final point, then, must represent a gas pressure in the system which is nearing the dissociation pressure of this nitride at 717°C.

The velocity during the 4th charge was slightly greater, amounting to 3.7 mm/hr. This increase was due, no doubt, to the higher initial pressure. Here, reversibility was observed for the first time. This was shown by the rising pressure at the high temperature end of the curve 4. The final point must represent a dissociation pressure. The coordinates of this point are: temperature 710°C, pressure 1188.1 mm. This corresponds to a compostition of 10.1% nitrogen. Reference to Fig. 10 shows that this composition lies in the region of homogeniety of the Mn_5N_2 phase.

It was decided, for the next and 5th charge, that a very high initial pressure be used in an attempt to bring the composition into the region of heterogeniety between the Mn_5N_2 and the Mn_3N_2 phases. It was hoped that a dissociation pressure in this region would furnish some information as to the question of solid solution. Unfortunately, however, the high pressure appears to have caused a very slow leak in the apparatus, probably in the rubber connection. The curve obtained drops across those of the two previous charges without showing any sign of dissociation. This is seen in Fig. 15 in the neighborhood of A.

The fact that the apparatus was leaking could not be decided at once. The velocity of nitrogenation increased to 8.3 mm/hr. This appeared suspicious but could not be regarded as conclusive proof of leakage because there is a plausible explanation. This explanation is as follows. The decomposition pressure which has been measured corresponded to composition of 10.1% nitrogen. The formula Mn_5N_2, however, requires 9.56% nitrogen. Therefore, the dissociation pressure, which is high, may be due to the dissociation of a layer of a higher nitride on the periphery of each particle. This layer will be rich in the nitride Mn_3N_2 and hence will have a high dissociation pressure. Subsequent heating may cause this layer to diffuse inward, resulting in a solid solution having a lower dissociation pressure. There are, then, two opposing tendencies; formation of the nitride tends to produce heterogeniety, while diffusion tends to produce homogeniety. A preponderance of the former could account for the high dissociation pressure. This, then, is a possible explanation of the failure of curve 5 to indicate dissociation.

Because of this explanation the experiment was not stopped immediately. It was not until after two more charges of nitrogen were admitted that the apparatus was definitely shown to be faulty. As the experiments were continued the leak became greater until finally, all doubt was removed. Subsequent analysis of the nitride has shown it to be rather badly oxidized. It appears also, that in the tests and experiments subsequent to the 5th charge, some of the nitrogen was either given off or, replaced by oxygen.

Conclusions:- The only conclusions which can be added to those already given are:

(1) The velocity of the nitrogenation process depends upon the previous heat treatment which the system has received below 600°C.

(2) The dissociation pressure corresponding to a composition of 10.1% nitrogen is 1188.1 mm at 710°C.

Analysis of the Two Samples of Nitride.

The nitrogen was estimated by the Kjeldahl Method. The usual technique was modified slightly. Copying the princile employed in the modified method used in estimating traces of nitrogen in iron and steel, the acid solution of the nitride was added drop by drop, from a tap-funnel, to the boiling alkali. This modification was adopted after several poor results were obtained by the usual method.

The total metal was estimated by the method given by Cumming and Kay in Quantitative Chemical Analysis. By this method the metal is precipitated as phosphate, ignited and weighed as pyrophosphate.

In the case of the nitride taken from the quartz apparatus, which was known to be oxidized, a pyrolusite determination was made. The method, taken from the text book mentioned above, was that by which oxalic acid is oxadized by the dioxide. It is not a good method for the estimation of traces of pyrolusite, but was the best available. The oxygen content of this nitride will be in error on this account. The complete analysis gave;

For the sample of the glass apparatus,-

Manganese and Iron......	91.50%	
Nitrogen................	8.34 %	
Silicon.................	.16%	.61
Carbon..................	.12%	
	100.12%	

The carbon and silican are the manufacturers' values. The manganese and nitrogen are the averages of two estimations.

For the sample from the quartz apparatus,-

Manganese and Iron.........	88.00%
Nitrogen....................	8.36%
Oxygen......................	.90%
Silican.....................	.16%
Carbon......................	.12%
	97.54%

The Oxygen is probably too low because of the difficulty of estimating small quantities of MnO_2.

The analytical percentages of nitrogen agree very badly with those calculated during the absorption experiments. In the case of the quartz apparatus 10.1% nitrogen was calculated at the end of the 4th charge. It was not until after this, that the apparatus became faulty. The analysis, however, shows 8.36% nitrogen. It appears that nitrogen has been lost. Furthermore, it is a strange coincidence that both final products should have so nearly the same nitrogen percentage.

At first it was thought that dissolved nitrogen was present, which could not be determined by the Kjeldahl method. This lead to the performance of several decomposition experiments. In one of these experiments a weighed sample of the nitride in a porcelain boat, was decomposed in a quartz tube around which a small electric furnace was built. The nitrogen resulting from the decomposition of the nitride was displaced into a Schiff Azotometer by means of a stream of dry CO_2. The method is given in Cohens' Practical Organic Chemistry. It was discovered, however, that the glowing manganese decomposed the CO_2 and itself became oxidized. Large volumes of CO were collected in the azotometer. For this reason, this type of decomposition had to be abandoned.

A further attempt was made by using the apparatus built for the decomposition experiments. This apparatus will be described later. The apparatus could not be freed of microscopic leaks, and these experiments also failed. Following these failures the only alternative was the complete analysis, the results which have been given. It is quite evident from the analysis that the Kjeldahls have detected all the nitrogen present.

The disagreement between the calculated and the analytical nitrogen percentages can be explained quite satisfactorily.

In the pyrex apparatus, the flask collapsed without leaking, and destroyed the volume calibration. Thus, the calculation was made for a volume too small and gave a value too great. The final nitrogen percentage in Table II is in error.

Subsequent to the 4th charge, in the case of the quartz apparatus, heating was continued for many hours at pressures slightly above 1 atmosphere. Because of the high temperature and the and the low pressure the nitride was decomposed, partially. The liberated nitrogen leaked away, very slowly, and the pressure in the system fell very slowly. The Pressure drop indicated a progressive absorption, but actually, because of leakage, the reverse was true. None of the erroneous values have been included in the data. I believe that all the nitrogen percentages given in Table III are correct to within the error of the calculation.

Density of the Nitride Sample

The sample of the nitride used was that from the pyrex apparatus. This is the unoxidized sample, for which the best analysis was obtained.

The pycnometer used was of the wide mouthed variety, provided with a ground glass stopper through which a good thermometer was fitted. Weighings, with water, were made after the pycnometer had been immersed in a water bath thermostated to 26°C. The air was removed from the powder by means of a water pump. The powder was covered with about ½ in. of distilled water and the pump attached to the capillary side arm. The water was allowed to boil gently for a time, then the pycnometer was cooled in water and pumping continued for not less than 2 hrs. with frequent shaking. Of five determinations, the two which showed the best agreement are given.

(1) Wt. pycnometer + water at 26°C = 55.8073
Wt. pycnometer + nitride = 36.0214
Wt. dry pycnometer = 31.0814
Wt. of nitride = 4.4900

Wt. pyc. + nitride + water at 26°C = 59.8758

Density = 5.6477

(2) Wt. pycnometer + water at 26°C = 55.8088

Wt. pyc. + nitride = 35.9070

Wt. dry pycnometer = <u>30.0814</u>

Wt. of nitirde = 4.8256

Wt. Pyc. + nitride + water at 26°C = 59.7822

Density = <u>5.6444</u>

For purposes of calculation the density will be taken as 5.6. The final figure is doubtful because of the difficulty of removing all the air from the fine powder. If there is an error from this cause, the density will be too low.

Calculation of Shrinkage of the Lattice

The composition of the sample (i.e. 8.34% nitrogen) places it in the region of heterogeniety between two nitride phases as will be seen from Fig. 10. In other words, our sample is a mixture of the two nitrides Mn_4N and Mn_5N_2. Because of this the density of a pure nitride cannot be calculated satisfactorily. There are, however, some empirical calculations which can be made which are of crystallographic interest.

The analysis of the sample has shown 8.34% nitrogen and 89.76% manganese (i.e. 1.74% Iron). If we consider 100 gms. of the sample, 89.76 gms. will be manganese and 8.34 gms. will be nitrogen. The nitride sample has a density of 5.6, therefore,-

Volume of Mn and N_2 in 100 gms of sample = 17.3 c.c.

Similarly for pure manganese which has a density of 7.42,-

Volume of 89.76 gms of pure Mn = 12.1 c.c.

Similarly for solid nitrogen which has a density of 1.03 at -253 C,-

Volume of 8.34 gms of solid N_2 = 8.0 c.c.

Then adding the volumes for pure Mn and N_2 we get 20.1 c.c.

Thus, the volume has decreased in forming compounds by,-

20.1 - 17.3 = 2.8c.c. , or,-

Mn and N_2, together, have suffered a contraction of

$$\frac{2.8}{20.1} \times 100 = \underline{13.9\%}$$

The decrease in density must be due to the resultant of two component volume changes; (1) the Mn structure must expand while

Summary of Conclusions

(1) A small absorption of .1134 gms. of nitrogen by 10 gms. of manganese occurs at 126°C.

(2) Progressive absorption commences at 390°C , and proceeds with appreciable velocity at 510°C.

(3) The velocity of absorption decreases as the composition of nitride increases.

(4) No nitride phase of a composition of less than 8.34% of nitrogen gives rise to a solid solution by dissolving gaseous nitrogen.

(5) The velocity of the nitrogenation process depends upon the previous heat treatment which the system has received below 600°C.

(6) The dissociation pressure corresponding to a composition of 10.1% nitrogen is 1188.1 m.m. at 710°C.

(7) The Kjeldahl method detects all the nitrogen present in a sample which has stood for some time at atmospheric pressure.

(8) The density of a sample containing 8.34 % of nitrogen is 5.6.

(9) The formation of the Mn_5N_2 phase is accompanied by an expansion of the cubic lattice of alpha manganese. This expansion is in the neighborhood of 30%.

- APPARATUS DESIGNED FOR THE DISSOCIATION EXPERIMENTS -

Description of the Apparatus for the Dissociation Experiments

The objects of the dissociation experiments have been pointed out in the theoretical introduction. None of these experiments have been carried out, however, because both attempts to obtain the richest nitride, ended in failure. While the slow process of absorption was going on this apparatus was devised and constructed and is now available to my successor in this work.

The apparatus is shown diagramatically in Fig. 16. A is the McLeod gauge, B is the Toepler pump and C is the device for collecting the gas exhausted by the pump. The flask was made small, D, about 50 c.c., and like those used in the previous experiments was provided with a recess for the thermo-function. The stop-cock 1, is for the purpose of evacuation with the Hyvac pump before commencing to operate the Toepler pump. Both the McLeod gauge and the Toepler pump are common devices and, therefore, need not be described here. The McLeod gauge is a factory made article, but the Toepler pump was constructed in the laboratory. The device for collecting the exhausted gases was also constructed in the laboratory, and may require some explanation.

The exhaust capillary of the pump was bent upward for a short distance and the end drawn down until the opening was very small. This end is immersed in a small dish of mercury

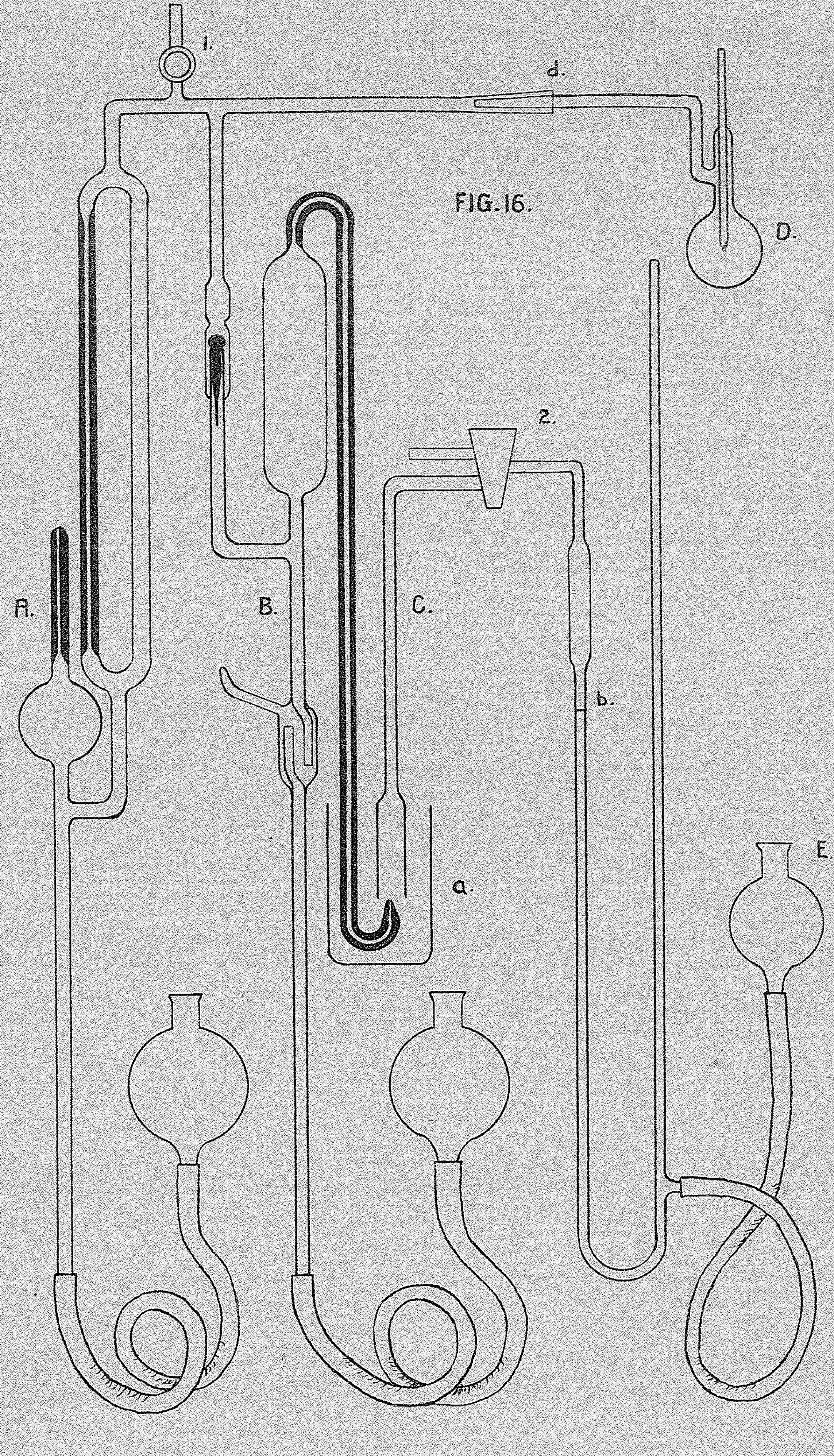
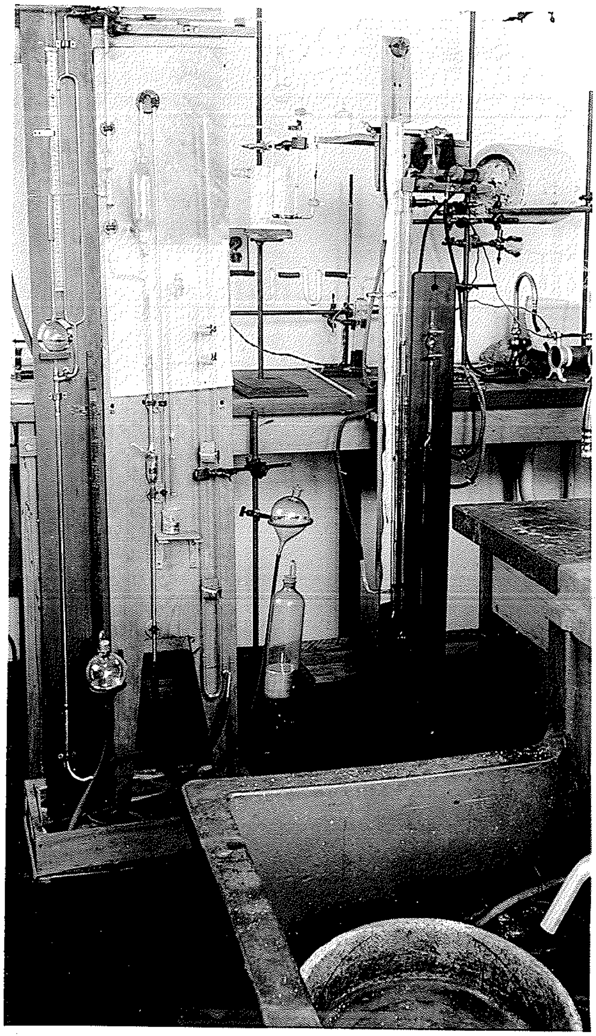


FIG. 16.



and over it the wide end of the left hand limb of the collector is placed. This is shown at a. When this end is immersed in the mercury the whole limb from a to the stop-cock 2 can be filled with mercury by manipulating the reservoir E and the three way stop-cock 2. When the pump is then operated, the exhausted gases are collected by displacement of mercury.

The other two limbs comprise the device for measuring these gases. Near the top of the centre limb is a small bulb. This was made from a 5c.c. pipette the mark of which is at b. The volume, between the stop-cock and b, has been carefully calibrated by weighing the mercury delivered, thus,-

Weighing Bottle + Hg	Weighing Bottle	Hg at 25°C
74.6591	"	59.9881
74.6800	"	60.0090
74.6485	"	59.9775
74.7256	"	60.0546
74.7240	"	60.0530
74.6768	"	60.0058
	Mean =	60.0147 gms.

Therefore, the volume is <u>4.4351 c.c.</u>

Measurement of the amount of gas collected is affected quite simply. The centre limb is evacuated by opening the stop-cock and raising the reservoir E, thereby forcing the air out through the open arm of the stop-cock. E is then lowered and the stop-cock turned so that the gas in the left limb is drawn over into the centre limb. The stop-cock is then closed, and the gas imprisoned in the centre limb is compressed by raising E until the miniscis stands at the mark b. The pressure can then be measured accurately, by means of the cathetometer, from the different heights of the mercury columns in the centre and right hand limbs. Then, knowing volume, pressure, and the room temperature, the mass of gas is easily calculated.

Attempts were made to use this apparatus for quick decompositions for the purpose of analysis of the nitride samples. It was found, however, that the ground glass joint d was faulty. The female part of the joint was made of soda glass and the male part pyrex glass. This was necessary since only the flask, which must stand high temperatures, was made of the pyrex glass. A thin film of picene cement is applied between the ground surfaces. Several different applications of the cement were tried but small leaks always appeared. These leaks were often so small that pressure as low as 10^{-5}mm could be obtained by continued operation of the Toepler pump. Otherwise, the apparatus was found to be very satisfactory. It has been left to the next experimenter to install a more satisfactory joint between the hard and soft glass parts.

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