

C. S. BRADLEY.

PROCESS AND APPARATUS FOR PRODUCING CHEMICAL ACTION IN GASES.

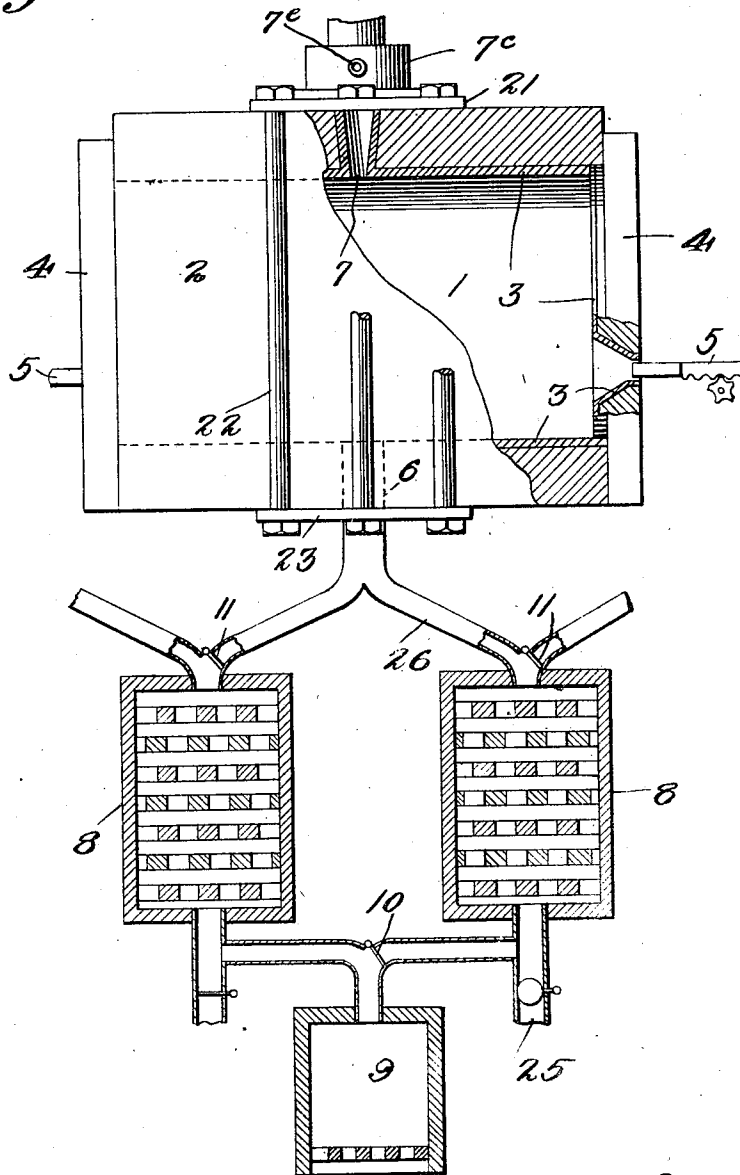
APPLICATION FILED MAY 1, 1909. RENEWED SEPT. 2, 1914.

1,134,583.

Patented Apr. 6, 1915.

4 SHEETS-SHEET 1.

Fig. 1.



Inventor

Witnesses

Joe. F. Collins
J. M. Wykebrook

By

Charles S. Bradley
Knight Bros
Attorneys

C. S. BRADLEY.

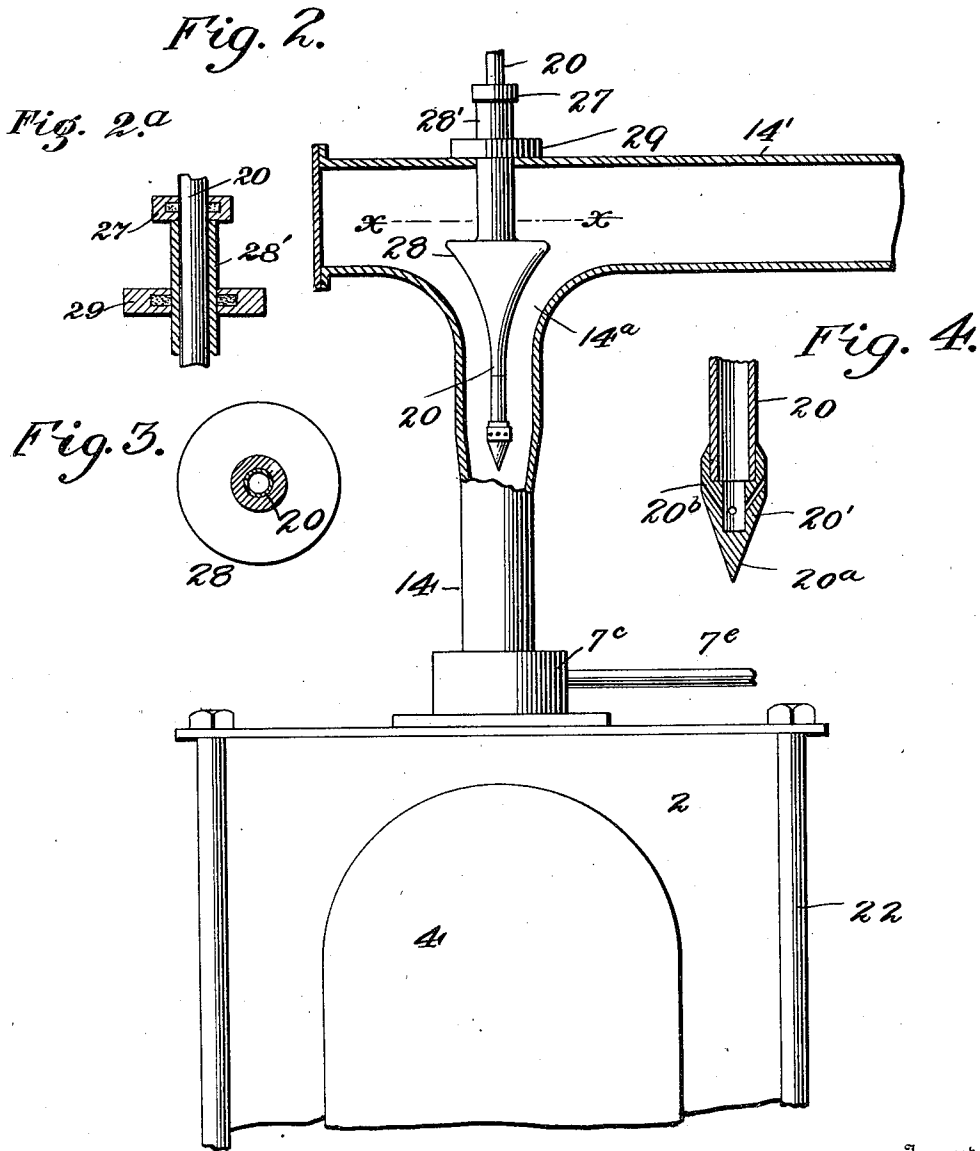
PROCESS AND APPARATUS FOR PRODUCING CHEMICAL ACTION IN GASES.

APPLICATION FILED MAY 1, 1909. RENEWED SEPT. 2, 1914.

1,134,583.

Patented Apr. 6, 1915.

4 SHEETS—SHEET 2.



Inventor

Witnesses

Jos. J. Collins,
J. W. Winkler.

Charles S. Bradley

By

Knight Bros.
Attorneys

C. S. BRADLEY.

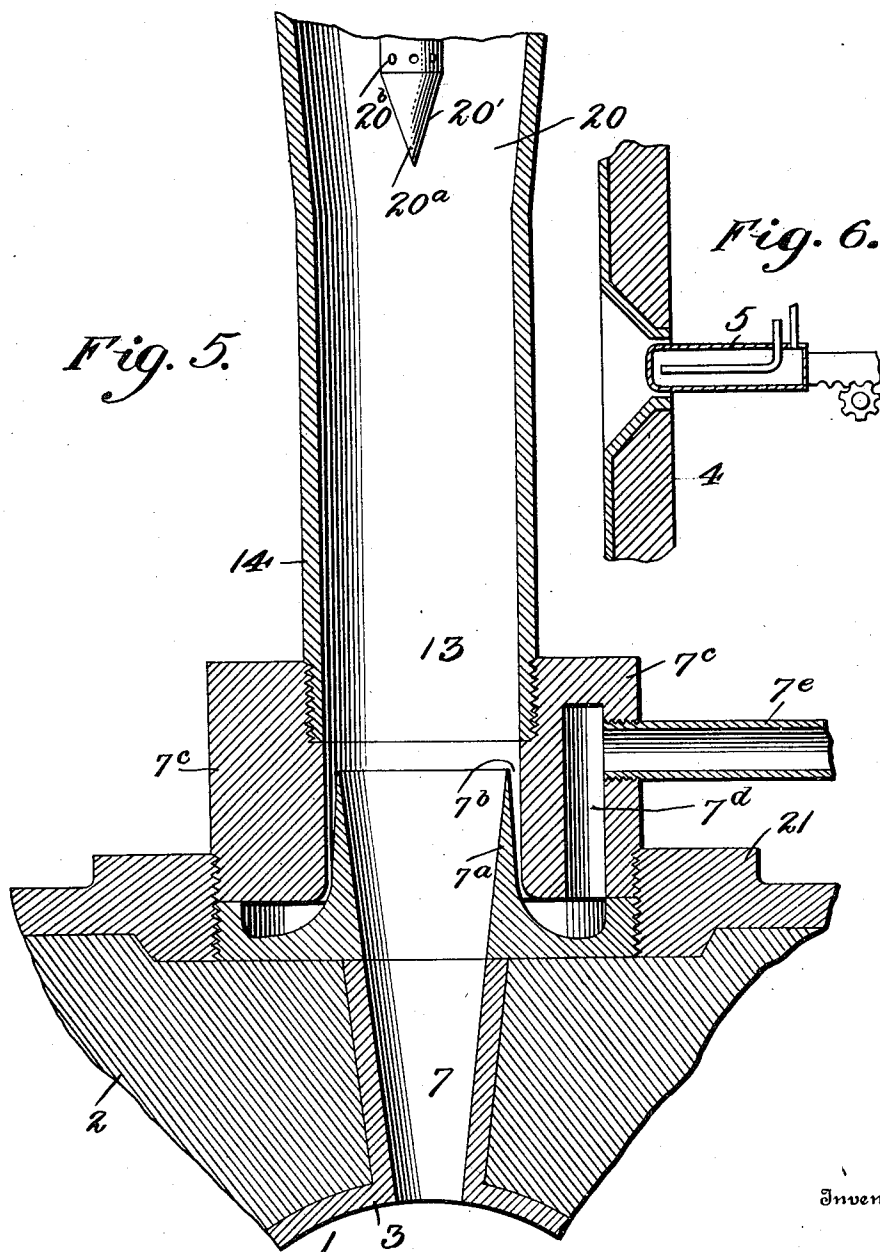
PROCESS AND APPARATUS FOR PRODUCING CHEMICAL ACTION IN GASES.

APPLICATION FILED MAY 1, 1909. RENEWED SEPT. 2, 1914.

1,134,583.

Patented Apr. 6, 1915.

4 SHEETS-SHEET 3.



Inventor

Witnesses

Geo. F. Collins
J. M. Wynkoop

By

Charles S. Bradley,

Knight Bros.
Attorney

C. S. BRADLEY.

PROCESS AND APPARATUS FOR PRODUCING CHEMICAL ACTION IN GASES.

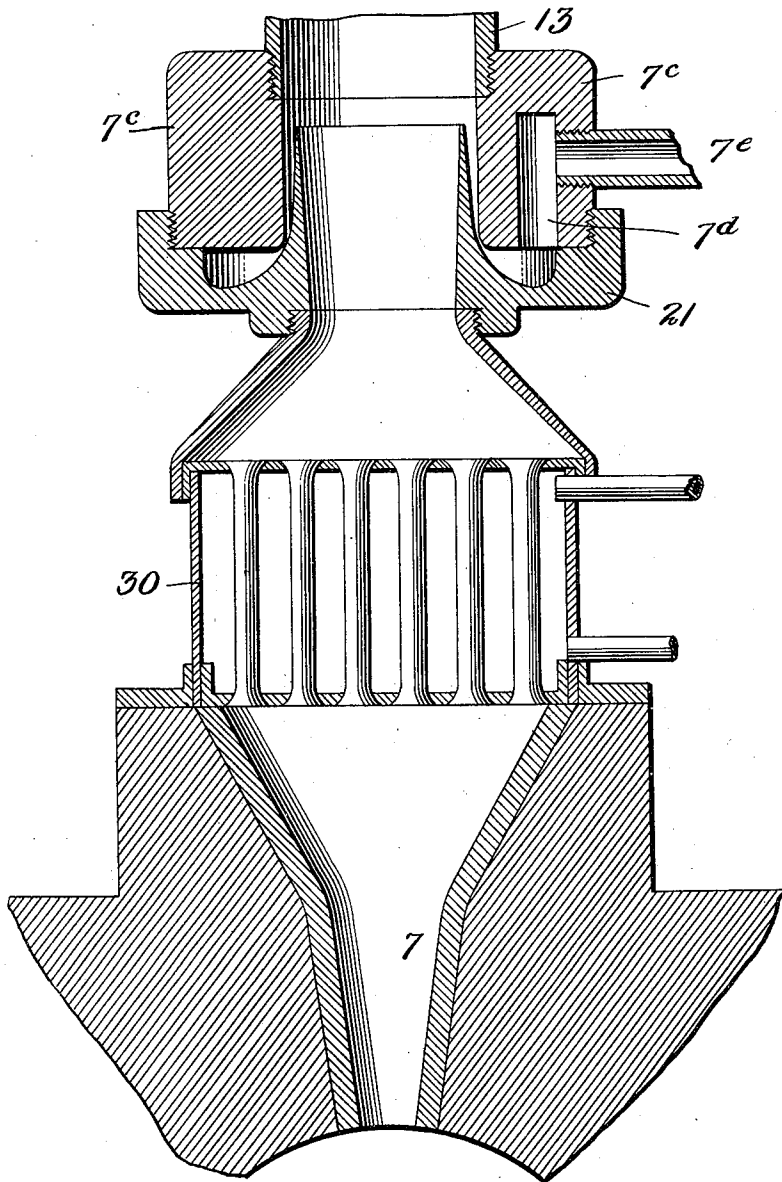
APPLICATION FILED MAY 1, 1909. RENEWED SEPT. 2, 1914.

1,134,583.

Patented Apr. 6, 1915.

4 SHEETS—SHEET 4.

Fig. 7.



Inventor

Witnesses

Jos. F. Collins
J. M. Thompson

By

Charles S. Bradley,

Knight Bros
Attorney

UNITED STATES PATENT OFFICE.

CHARLES S. BRADLEY, OF NEW YORK, N. Y.

PROCESS AND APPARATUS FOR PRODUCING CHEMICAL ACTION IN GASES.

1,134,583.

Specification of Letters Patent.

Patented Apr. 6, 1915.

Application filed May 1, 1909, Serial No. 493,318. Renewed September 2, 1914. Serial No. 859,916.

To all whom it may concern:

Be it known that I, CHARLES S. BRADLEY, a citizen of the United States, and resident of the city, county, and State of New York, have invented new and useful Processes and Apparatus for Producing Chemical Action in Gases, and in order that others skilled in the art may understand and practice the same give the following specification.

The invention relates to process for effecting chemical changes in gases and has for its object to provide a method and apparatus for causing said changes to take place in an efficient manner with a maximum yield of the product sought.

My invention may be explained by reference to processes which have heretofore been disclosed for effecting chemical combination between nitrogen and oxygen, or the synthetic production of nitrogen compounds from the atmosphere, as, for example, in the patents granted to myself and to D. R. Lovejoy, September 30, 1902, numbered 709,867; 709,868, and others. In these and other published processes, the heat required for the reaction was supplied in the form of electric arcs, and a feature of the patented processes referred to was the production of a thin or elongated arc, because such an arc presented a relatively large surface to the surrounding cooler gases and thus their cooling effect was utilized to the best advantage and dissociation of the products or reversion of the reaction was diminished. Other processes which have been published from time to time have sought in various ways to take advantage of the cooling of the products by the surrounding gases.

Further investigation of the subject has led me to the discovery that in the transition from the temperature of the arc to the lower temperature surrounding the arc, dissociation—reversal of the reaction sought—occurred to a considerable extent, whereby the yield was materially reduced. The reaction is for the most part confined to the core of the arc where the reaction temperature is maintained, and the products there formed are dissociated to a considerable extent when they come to the surrounding cooler arc envelop. As the temperature of the products falls gradually in passing from the hot core outward to the cooler arc envelop not only are the products dissociated in considerable

proportion, but the gases suffer repeated combination and dissociation, involving waste of the energy in addition to the loss due to dissociation. These losses in yield and energy are the result of a too slow reduction in temperature from the reaction temperature at the core of the arc to the temperature at which tendency to dissociation ceases and the products become fixed.

Chemical reactions, such as above referred to, involve the absorption of heat energy, part of which is taken up in the chemical change produced, the excess appearing in the high temperature of the products; but in returning to the ordinary conditions of temperature required for handling and utilization of the products reversal of the reaction takes place. By conversion of the excess heat energy into a chemically inactive form of energy at a point before reversion of dissociation of the products takes place, or by eliminating the time interval between the temperature of formation of the products and their return to ordinary temperature, dissociation or reversion of the products is prevented and they become fixed. This I accomplish by converting the excess heat energy into velocity by causing the products to expand suddenly. The velocity will, as will be understood, have no chemical effect on the products. The consequent sudden cooling results in bringing the products to a temperature at which they become fixed and may be utilized and handled. These phenomena apply not only to the fixation of atmospheric nitrogen as in the processes referred to, but also to other reactions subject to reversibility or decomposition of products by reason of heat conditions, as will appear in the following.

In further explanation of my invention, it may be pointed out that in such reactions there are what may be termed three temperature zones. The zone of formation or reaction, the zone of dissociation and the zone of permanence or fixation. When the products are endothermic substances a certain amount of energy in the form of heat must be supplied before reaction can take place. The zone of formation commences where reaction begins and extends to where it is complete. Below and adjacent this zone is the zone of dissociation in which the products formed are dissociated or revert to their components. Lower still in the scale is the

third temperature zone or region in which the products formed in the reaction zone are permanent or fixed—*i. e.* do not tend to dissociate. These zones are not necessarily sharply divided one from the other and in passing from one to another an appreciable interval of time may occur for products existing in one zone to undergo the change in the other. From these considerations it follows that, if all the products formed by bringing the gases to the combining temperature, or first-named temperature zone, could be immediately carried to the third temperature zone or zone of permanence, (overpassing the zone of dissociation) there would be practically no loss from dissociation. And if, in addition to this, the whole volume or charge of the gases, as distinguished from the small fraction thereof actually traversed by the arcs, as in known processes, were brought to the combining temperature, the maximum yield would be secured.

The object of my present invention is to provide both these conditions.

Although, in the foregoing, I have specifically referred to the formation of the oxides of nitrogen, it is to be distinctly understood that this is by way of illustration only, and that my present invention embraces the effecting of reaction in gases generally, including dissociation of such as dissociate at elevated temperature and whose components are stable or permanent at ordinary or lower temperatures, all as will appear in the following.

For the better understanding of my invention and the practical performance of the same I have illustrated in the accompanying drawing a form of apparatus suitable therefor in which—

Figure 1 illustrates in a partly sectional view the reaction chamber and preheating chambers; Fig. 2 is a partly sectional view of the apparatus from the reaction chamber to the duct leading to the recovery apparatus (not shown); Fig. 2^a is a sectional detail view of some of the parts shown in Fig. 2; Fig. 3 is a sectional view of a detail taken on line *x-x* Fig. 2; Fig. 4 is a sectional view on enlarged scale of the end of the water pipe; Fig. 5 is a detail sectional view on enlarged scale showing the expansion apparatus; Fig. 6 is a sectional view of a modified form of electrode; and Fig. 7 is a partly sectional view of a modified form of apparatus.

In Fig. 1, the reaction chamber is indicated by the numeral 1. Said chamber may be conveniently formed of a hollow block 2 of suitable size and of refractory material. The chamber is, for the production of nitrogen oxides, preferably lined with a material, such as thoria, capable of withstanding the high temperature and inert to the gases

treated. Said lining is indicated at 3. The ends of the chamber are closed by slabs or blocks 4 through which enter the electrodes 5—5, which are connected to a suitable source of electrical energy (not shown). The discharge between the electrodes furnishes the heat energy for the reaction. It is not necessary to the invention that the heat be supplied in the form of the electric arc. Any other suitable means of heating the gases to the reaction temperature, such, for example, as heating the walls of the chamber, may be employed, but as the electric arc affords a convenient and direct means of heating it will be found preferable in practice. The gases to be acted upon are admitted to the chamber, in the apparatus illustrated, from below through the inlet 6 and the products are discharged therefrom through the expansion outlet 7. The gases may be admitted directly to the reaction chamber but it is advantageous to preheat them. Accordingly I have shown preheaters 8, 8, interposed in the path of the gases on their way to the reaction chamber. These preheaters are shown of the regenerator type. A furnace 9 supplies the heat, the heated combustion products from which may, by means of valve 10, be directed to either preheater alternately. As will be readily understood, one preheater is being heated by the furnace while the other is imparting its heat to gases going to the reaction chamber. Valves 11, 11 control the discharge of the products of combustion from the preheaters and the admission of the heated gases therefrom to the reaction chamber.

From the reaction chamber 1 the products are suddenly expanded into a chamber or space 13 (Fig. 5) of low pressure, the object being to cause a sudden or immediate expansion of the products and a consequent sudden and immediate cooling thereof from the temperature of the reaction chamber to a temperature below that at which said products would tend to dissociate. Rarefaction or maintenance of reduced pressure in the space 13, is obtained, in the apparatus illustrated, by an expansion nozzle formed by outlet 7 and an ejector or propelling device or mouth 7^b. This expansion nozzle is formed by a mouth piece 7^a which may be of metal, tapered internally and forming (as shown) a continuation of the outlet 7. Surrounding the end of this nozzle is a collar 7^c forming with mouth piece 7^a a tapered annular mouth 7^b. In the collar 7^c is a duct 7^d communicating with the mouth 7^b and to this duct is connected a pipe 7^e for leading in steam or other fluid under pressure. The parts 7, 7^a, 7^b, 7^c, 7^d, and 7^e form the ejector or expansion nozzle. By means of the steam or other fluid delivered under pressure through pipe 7^e and issuing from mouth 7^b

rarefaction is produced in space 13 in the vicinity of the mouth of nozzle 7^a. The steam also serves to absorb some of the heat from the products. In cases where the products would be injuriously or disadvantageously affected by steam, another fluid will be substituted therefor; also, if desired, any other suitable means for producing the required rarefaction may be substituted for the nozzle 7^b such, for example, as a vacuum pump or other rarefaction apparatus. Such modifications are to be regarded as within the scope of the invention.

The parts constituting the expansion nozzle may be secured on the reaction chamber by means of a plate 21 in which are screw-threaded mouth piece 7^a and collar 7^c. Plate 21 is secured in place by means of tie bolts 22 which pass therethrough and through a plate 23 at the bottom of the chamber. The union of the inlet pipes 26 from the preheaters, passes through this plate 23 to inlet 6.

The trunk or pipe 14 into which the products from the reaction chamber and expansion nozzle discharge is threaded in collar 7^c, as shown. Beyond the portion of said pipe which constitutes the rarefaction chamber 13 is arranged an adjustable compression nozzle indicated at 14^a. This nozzle is formed by means of an adjustable tapered valve 28, the stem 28' of which passes through a stuffing box 29 in the wall of the pipe 14. By adjustment of the valve 28 the size of the nozzle 14^a and the degree of compression exerted on the products is regulated. In the vicinity of this compression nozzle is arranged a water jet to absorb the heat due to compression. This jet is provided by means of a pipe 20 passing through stuffing box 27 and axially through valve 28. At its end pipe 20 is provided with a tip 20' provided with upwardly inclined discharging passages 20^b; and the tip is pointed or tapered as at 20^a in order to present little or no obstruction to the flow of the products. To compensate for the space occupied by pipe 20 the trunk 14 is enlarged, as shown, in the vicinity of said pipe. Beyond valve 28 the trunk 14 is enlarged and passes to the absorption devices. These devices form no part of my invention and hence are not shown. They may consist of absorption towers of well known construction, or other absorption or recovery devices, depending upon the nature of the products obtained and the form in which it is desired to absorb or collect them. Provision may also be made for mixing other gases or substances with the products, as for example, by supplying oxygen to convert the lower oxides of nitrogen (where these form the products) into the higher oxides: but the subsequent treatment of the products after their fixation in accord-

ance with my invention is immaterial so far as the present invention is concerned.

In several of the views of the drawings I have illustrated modifications of parts of the apparatus. In Fig. 6 I have shown a metallic electrode, which may be of iron or copper, having its interior hollow or chambered for the circulation of cooling water. The use of such electrodes is advantageous in preventing dilution or contamination of the gases or products by carbon dioxide which might occur in the use of carbon electrodes.

In Fig. 7 is another modification in which a cooler 30 of tubular construction is shown interposed between the expansion nozzle and the outlet of the reaction chamber for the purpose of preventing a rise of temperature due to friction or recompression and at the same time the density of the issuing products is increased and their volume lessened. This permits the steam delivered to pipe 7^c or the pump, as the case may be, to be more effective.

Where nitrogen compounds are to be produced according to my invention, air or a suitable mixture of oxygen and nitrogen is led through the preheaters to the reaction chamber. The preheaters are worked alternately. As shown in Fig. 1 of the drawings, the preheater on the left is being heated by the furnace; and the preheater on the right is giving up its heat to the gases or air entering at the inlet 25 and passing through branch pipe 26 to the inlet 6 of the reaction chamber. The gases entering the chamber in the preheated condition have their electrical conductivity increased thereby, and the arcs will consequently have greater length so that adjustment of the electrodes for striking or maintaining the arc will be unnecessary. It is understood, however, that the electrodes may be adjusted toward and from each other by any well known means as shown. Where carbon electrodes are used, the preheating of the gases enables penetration of the electrodes into the chamber unnecessary, so that the carbon dioxide formed near the tips may pass off without entering the chamber. The electrodes are connected with a suitable source of current which may be either alternating or direct, supplying constant current.

The gases in the chamber are heated to the reaction or combining temperature, the whole charge therein being raised to or somewhat above that temperature. For the production of nitrogen compounds the temperature will be in the neighborhood of 3,000°-3,500° C. In order to insure the requisite velocity of discharge from the chamber the gases may be supplied to the chamber under pressure. From the reaction chamber the products issue through the expansion nozzle into the space 13 of reduced

pressure. Assuming that the velocity of flow of the products from the reaction chamber to the expansion chamber be three thousand five hundred to four thousand feet per second and the length of the expansion opening or nozzle be three inches, the time of expansion would occupy about one fifteen-thousandth ($1/15,000$) part of a second. In this fraction of a second the temperature of the products is reduced, by the sudden expansion, below that at which there is any tendency to dissociation. The resulting temperature after expansion will vary with the degree of expansion and with the heat of reaction or combination of the particular gases treated, and for nitrogen compounds, the heat of the products after expansion will be in the neighborhood of 1500 degrees C. The particular temperature after expansion is not of vital importance so long as it is below the temperature at which the gaseous compounds formed tend to dissociate. The difference in pressure of the gases between that in the reaction chamber and that in the expansion chamber for the above conditions will be in the neighborhood of the ratio of 15:1.33. The cooling being thus instantaneous, the products are obtained with practically no loss and the yield is obviously greatly increased over the processes heretofore known. The effect of the expansion nozzle is to convert the energy of temperature and pressure in the reaction chamber into velocity. The velocity will of course have no influence upon the chemical product formed. The steam delivered through pipe 7^e should have a velocity somewhat in excess of that of the products issuing through the nozzle so as to have a carrying effect upon the same. A steam pressure of 100 to 150 pounds will, in the instance given, be suitable. Where the velocity of the products is such that a high steam pressure is required to have a carrying effect, the employment of a cooling device, as in Fig. 7, in advance of the steam nozzle permits the use of lower steam pressure.

Leaving the rarefaction chamber, the velocity of the products is checked or converted into pressure. This is accomplished by adjustable compression nozzle and valve 28. The heat incident to the compression is absorbed by the water jets from water nozzle 20', the point of their application being adjusted by raising or lowering the pipe 20. From the compression nozzle the products pass to the horizontally arranged portion 14' of pipe 14 to the absorption apparatus. It will be understood that the compression nozzle and pipe 20 will be adjusted to obtain the proper relations between the rate of flow of the products, the temperature and the rate of expansion.

From the foregoing it will be seen that, as distinguished from known processes in

which a slow cooling of the products by heat interchange with the surrounding volume of gases, and the consequent slow transit of the products through what I have termed the zone of dissociation, my invention produces in immediate or instantaneous cooling by which the products are carried at once from the reaction zone or zone of combination to the zone of permanence—the transit of the products through the zone of dissociation being so instantaneous that, for practical consideration, it may be said that the dissociation zone is passed over and the products go immediately to the zone of permanence and suffer no dissociation.

As described in the foregoing the process is continuous, the gases passing into the reaction chamber and the products discharged uninterruptedly. The process may, however, be worked intermittently if desired by treating successive charges of gases.

My invention is not limited to its application to the fixation of atmospheric nitrogen. It may be also employed, for instance, for the production of acetylene. A similar apparatus is employed, carbon electrodes being used, but an atmosphere of hydrogen is supplied to the reaction chamber which, under the influence of the arcs, combines with the carbon of the electrodes, or with the carbon with which the interior of the chamber may be lined, to produce the acetylene. Or, hydrocarbon gases may be supplied to the chamber and the action of the heat from the arcs will cause a portion of the carbon and hydrogen contained therein to unite to form acetylene.

The invention may also be employed upon exothermic substances as for example by dissociating combined gases or compounds into their constituents and maintaining the dissociated condition by the instantaneous lowering of the temperature through the temperature zone in which recombination would take place. For instance, it is well known that steam is decomposed at a temperature in the neighborhood of 2,000° C.; but owing to the impracticability of separating the hydrogen and the oxygen produced in the zone of dissociation, recombination or ignition takes place, water being formed as the products cool. By my invention, ignition or recombination is prevented by the instantaneous lowering of the temperature of the products by sudden expansion and cooling beyond the temperature zone in which recombination takes place. In treating this class of bodies the same principles apply. The reaction is reversible but reversion is prevented by bringing the temperature suddenly to the zone of fixation or permanence. The zones will in these cases have different names. The highest zone in the scale is the zone of dissociation (reaction); the inter-

mediate zone is the zone of recombination, and the lowest zone is, as before, the zone of permanence or fixation.

It will be apparent from the foregoing that the electric arcs are mentioned as only one form of obtaining the necessary reaction temperature for causing the chemical reactions to be produced. Any other suitable form of heat may be substituted, such as incandescent bodies over which the gases may be passed; or the walls of the reaction chamber may be heated up in any convenient and suitable manner to obtain the necessary temperature of reaction. If desired, the pressure in the reaction chamber may be increased by supplying the gases to be combined under pressure.

While I have referred to gaseous bodies as entering into combination to form new products, it will be obvious that substances may be combined which are not gases, but which under the conditions of the reaction form gaseous compounds or products, as in the case of the production of acetylene above mentioned.

While I have described the application of my invention to the several instances above mentioned, it is to be understood that I refer to such instances by way of illustration and that my invention is not limited to any specific embodiment thereof but includes broadly carrying of the products formed under the conditions of reaction instantaneously through what I have termed the zone of decomposition (or recombination) by causing a sudden expansion or reduction of pressure with the consequent drop in temperature below the critical point where the product formed would tend to decompose or revert to its constituents, or vice versa.

Having described my invention, what I claim is:

1. The process of fixing the products of endo-thermic reactions in gases, which consists in heating a volume of the gas to reaction temperature, immediately discharging or removing the products from the area or zone of reaction and simultaneously expanding said products and imparting velocity thereto and thereby rapidly removing said products from the area or zone of reaction and reducing the temperature thereof below that at which they would tend to dissociate or revert to their components.

2. The process of effecting chemical changes in gases which consists in bringing the gases to reaction temperature and immediately imparting velocity to the product and discharging the same into an area of reduced pressure to cause an immediate fall in temperature below that at which the product formed by the reaction would tend to reverse.

3. The process of effecting chemical changes in gases, which consists in continu-

ously charging the gases into an inclosed chamber, heating the charge in the chamber to the reaction temperature, and continuously imparting velocity to and discharging the products formed from said chamber immediately into an area of reduced pressure, to produce a sudden reduction of the temperature of said products below that at which dissociation thereof tends to occur.

4. The process for producing oxids of nitrogen, which consists in charging a mixture of oxygen and nitrogen gases into an inclosed chamber, heating said charge throughout to the combining temperature, immediately imparting velocity to and discharging the products from said chamber in an area of reduced pressure, whereby the temperature of the products is reduced below that at which dissociation tends to occur.

5. The process of producing oxids of nitrogen, which consists in introducing a mixture of nitrogen and oxygen into an inclosed chamber, striking electric arcs in said chamber, imparting velocity to the product to suddenly discharge the same into an area of reduced pressure to reduce the temperature of said product to a point where the product formed is fixed or permanent.

6. The process of forming nitrogen oxids which consist in heating a mixture of nitrogen and oxygen to the reaction temperature, immediately discharging or removing the products from the area or zone of reaction and simultaneously expanding said products and imparting velocity thereto and thereby rapidly removing said products from the area or zone of reaction and reducing the temperature thereof below that at which they would tend to dissociate or revert to their components.

7. The process of producing nitrogen oxids, which consists in heating a mixture of nitrogen and oxygen to the reaction temperature, suddenly expanding the products formed, recompressing said products and absorbing the heat due to recompression.

8. An apparatus for the purpose described, having in combination a reaction chamber, means to introduce gases thereto, means for heating the gases in said chamber, an expansion outlet for discharging and expanding the products formed in said chamber, and means to impart velocity to the products through said outlet.

9. An apparatus for the purpose described, having in combination a reaction chamber, means to introduce gases thereto, means for heating the gases in said chamber, a rarefaction chamber, an expansion outlet leading from the reaction chamber to the rarefaction chamber, and exhaust means for imparting velocity to the discharging gases connected to said reaction chamber.

10. In apparatus for the purpose described, the combination of a reaction cham-

ber, means to introduce gases thereto, means for heating the gases in said chamber, a trunk leading from said chamber, exhaustion means connected to said trunk for exhausting and rarefying the products from said chamber, means in said trunk for recompressing said products and means to absorb the heat due to recompression.

11. In apparatus for the purpose described, the combination of a reaction chamber, means to introduce gases to said chamber, means to heat the gases in said chamber, an expansion nozzle connected to said chamber, means for exhausting the product from said chamber through said nozzle, an adjustable compression nozzle in the path of the products from the expansion nozzle and means to absorb the heat due to compression.

12. In apparatus of the character described, the combination of a preheating chamber, a reaction chamber connected to the preheating chamber, means to heat the gases in the reaction chamber to the reaction temperature, an expansion nozzle and a compression nozzle connected to the reaction chamber and successively arranged in the path of the products from said chamber, an exhaust apparatus for exhausting the products from the reaction chamber through said nozzles and means to absorb the heat due to compression in the compression nozzle.

13. In apparatus of the character described, the combination of a reaction chamber, electrodes arranged to form arcs in said chamber, means to introduce gases into said chamber, an expanding outlet from said chamber, a trunk connected to said outlet, an ejector nozzle in said trunk, means to discharge fluid under pressure from said nozzle to eject or discharge the products from the chamber through the expanding outlet, a compression nozzle in the path of the products from said outlet, and means to discharge a cooling fluid in the vicinity of said compression nozzle.

14. In apparatus for the purpose described, the combination of a reaction chamber, means to introduce gases to said chamber, means to heat the gases in said chamber, an expansion nozzle connected to said chamber, means to absorb heat from the products on their way to the expansion nozzle, means for exhausting the product from said chamber through said nozzle, an adjustable compression nozzle in the path of the products from the expansion nozzle and means to absorb the heat due to compression.

CHARLES S. BRADLEY.

Witnesses:

LAURA E. MONK,
HARRY E. KNIGHT.