

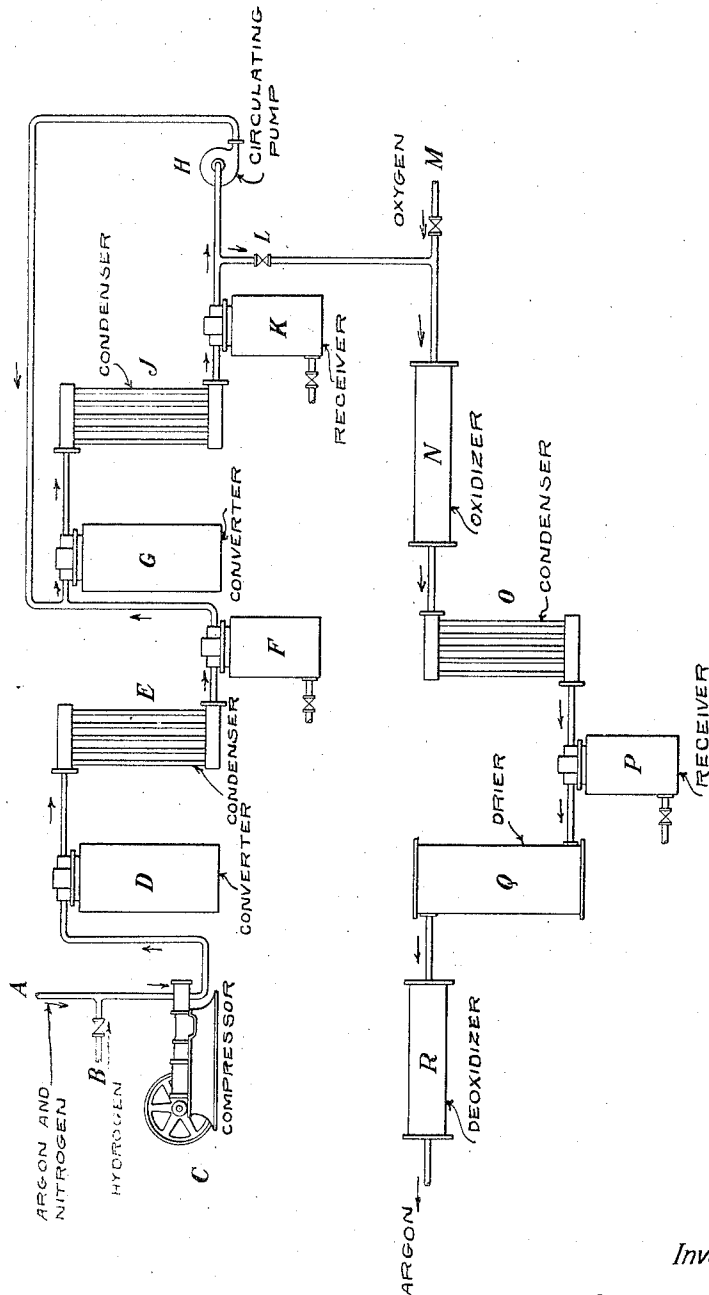
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PROCESS OF OBTAINING ARGON

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PROCESS OF OBTAINING ARGON.

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This invention relates to an improved method of obtaining argon of a high degree of purity from gaseous mixtures containing argon and nitrogen.

Argon for commercial use is at present obtained by the complicated and comparatively costly method of liquefaction of air. The argon obtained in this way is on the average of a purity of about 85%. My invention embodies an economical method of obtaining argon which may be, if desired, of considerably over 85% purity, starting either with commercial argon or with gas of a low argon concentration.

In effecting the separation of argon from the other constituents of the atmosphere by the liquefaction method, by suitably varying the process and apparatus the argon may be made to accompany the oxygen or the nitrogen fraction as may be desired. It would seem that as a general proposition the latter would be more desirable, and, in fact, it appears that when the argon does go with the nitrogen a highly concentrated argon is more readily attainable.

As argon is obtained from the air liquefaction column, in the form of "argon concentrate," it is greatly diluted with nitrogen and oxygen, the relative proportions of which depend upon whether the argon has accompanied the nitrogen or the oxygen fraction. The further concentration of this gas to render it fit for any purpose as argon presents a serious problem. If the principal diluent is oxygen its removal by liquefaction is difficult on account of the fact that there is but a small difference in the boiling points of oxygen and argon. The oxygen may, of course, be removed by burning with admixed hydrogen. The hydrogen for this purpose should be of a high degree of purity. Its cost and the fact that no useful product is obtained as a consequence of the combustion make this oxygen removal step a costly one. Furthermore, when the oxygen has been removed the problem of eliminating the always considerable proportion of nitrogen still remains.

On the other hand, if the major impurity in the argon is nitrogen—which will be true if the argon, as may advantageously be the case, has been separated with the nitrogen—there has been heretofore only one practical method of separation available, namely, rec-

tification. It is true, of course, that for the separation of nitrogen from argon, absorption of the former by heated metallic calcium, magnesium or lithium, by calcium carbide or by lime and magnesium has been proposed, as has been combination of the nitrogen with oxygen to form nitric oxide, under the influence of the electric arc. These methods are, however, of little, if any, practical value.

It is the object of the present invention to provide an improved method for concentrating argon in gaseous mixtures containing nitrogen and argon. While adapted for the separation of argon from any proportion of nitrogen the method is particularly suitable for obtaining argon of high purity from the "argon concentrate" above referred to or from argon of commercial grade, which latter contains approximately 85% argon and 15% nitrogen.

Other objects and advantages of the invention will be apparent as it is better understood by reference to the following specification in which its preferred embodiments are described.

The process consists in causing the nitrogen in the nitrogen-argon-containing gas, from which oxygen has preferably been preliminarily removed by any suitable means, to combine with hydrogen to form ammonia, by submitting the gaseous mixture, repeatedly and preferably under pressure, to the action of a catalyst capable of effecting the desired combination of nitrogen and hydrogen. The ammonia formed is removed, for example, by condensation and the remaining hydrogen is eliminated, for instance, by causing it to combine with oxygen, free or combined. If free oxygen is used, any excess may be taken out by combination thereof with metallic copper. I have found that this method of procedure is effective for the economical concentration of argon. Moreover, an important advantage of the process lies in the fact that a valuable by-product, ammonia, is produced.

It is important for the best results to observe certain precautions regarding the quality of hydrogen used in the process. Thus, particular pains should be taken to avoid the presence of catalyst poisons, and especially sulphur compounds, and oxygen, free or combined. The amount of hy-

drogen added is best at least that theoretically necessary for the complete transformation of all the nitrogen to ammonia.

The combination of nitrogen and hydrogen may be brought about under very high or comparatively low pressures. If the pressure is very high—that is, of the order of magnitude usually referred to as hyperpressures, say 400 to 1000 atmospheres—the catalyst need not be so active as when lower pressures, below 400 atmospheres, are employed; this being due to the more favorable equilibrium conditions at higher pressures. It will, of course, be desirable in any event to suit the activity of the catalyst to the pressure employed, since, the dilution of the nitrogen and hydrogen with inerts being unfavorable to the ammonia equilibrium to begin with, all other conditions should, as nearly as is possible, be arranged to favor the maximum ammonia formation.

I have found that at 1000 atmospheres a catalyst composed of 98 parts of ferrosio-ferric oxide and 2 parts of alumina works satisfactorily, while at 300 atmospheres a catalyst containing in addition 0.75 parts of potassia suits the purpose. Other catalytic materials may, of course, be employed, it being understood that the specific catalysts herein described are old and are not claimed per se.

The nature of my invention will be more fully understood by reference to the following example in which one embodiment of the invention is described with reference to the accompanying drawing, in which—

The figure is a diagrammatic representation of an arrangement of apparatus adapted for the practical application of the invention.

A gaseous mixture containing 2 parts by volume of argon and 22 parts of nitrogen (i. e., containing a ratio of argon to nitrogen over seven times that in air), and free from oxygen and oxygen compounds, enters the system at A under atmospheric pressure. Hydrogen free from catalyst poisons is admitted thru the valve B, which is adjusted so that 66 parts of hydrogen is added to every 24 part of argon-nitrogen mixture. The gaseous mixture is delivered to the compressor C, which compresses it to 900 atmospheres. At this pressure the mixture passes thru the converter D, where it contacts with a catalyst composed of 98 parts ferroso-ferric oxide and 2 parts alumina. During this contact, combination of nitrogen and hydrogen to form ammonia occurs. The ammonia in the gases leaving D is condensed by external water cooling in the condenser E, and withdrawn by way of the receiver F. The gases pass on to a second converter G, employing the same catalytic material as in D. Conjoined to G is a circulating pump H by means of which the gaseous

mixture leaving G—after the ammonia has been condensed in J and collected in K—is recirculated thru the converter G to increase the argon concentration to the value desired. The expansion valve L is adjusted so that the nitrogen content of the gases withdrawn therefrom is not more than 4%. Thru the valve M oxygen is admitted, the valve being set so that at least 7 volumes of oxygen is added to every 100 volumes of the gaseous mixture. In the oxidizer N the gases pass over a heated mass of metallic copper catalyst which serves to effect the combustion of the hydrogen. The resulting water is eliminated in part in the condenser O, to be collected in P, and completely removed in the calcium chloride dryer Q. The dry gases, containing argon, nitrogen and oxygen then pass thru the deoxidizer R, containing heated metallic copper, which removes the oxygen forming copper oxide. The gas leaving R contains over 95% argon, the balance being nitrogen.

The process hereinbefore described affords an economical and satisfactory method of obtaining argon of a high degree of purity from gaseous mixtures containing argon and nitrogen. It will be apparent that a gas containing as high as 95% argon may be prepared by this process and, as already stated, the argon concentration may be increased in a mixture containing initially 85% argon. It will likewise be apparent that other argon percentages may be obtained ranging above 50% argon by the process herein described.

As many apparently widely different embodiments of this invention may be made without departing from the spirit thereof, it is to be understood that the invention is not limited by the foregoing embodiment except as indicated in the appended claims.

I claim:

1. The process of concentrating argon which consists in subjecting a gaseous mixture of hydrogen and nitrogen containing upward of $\frac{1}{10}$ volume of argon per volume of nitrogen to the action of a catalyst active for the formation of ammonia from nitrogen and hydrogen.

2. The process of concentrating argon which comprises subjecting a gaseous mixture of hydrogen and nitrogen containing upward of $\frac{1}{10}$ volume of argon per volume of nitrogen to the action of a catalyst active for the formation of ammonia from nitrogen and hydrogen, removing from the gaseous mixture the ammonia thus formed and eliminating the remaining hydrogen.

3. The process of concentrating argon which comprises subjecting a gaseous mixture of hydrogen and nitrogen containing upward of $\frac{1}{10}$ volume of argon per volume of nitrogen to the action of a catalyst active for the formation of ammonia from nitro-

gen and hydrogen, removing from the gaseous mixture the ammonia thus formed and eliminating the remaining hydrogen by combination thereof with oxygen.

5 4. The process of concentrating argon which consists in subjecting a gaseous mixture of nitrogen and hydrogen containing upward of $\frac{1}{10}$ volume of argon per volume of nitrogen repeatedly to the action of a
10 catalyst active for the formation of ammonia from nitrogen and hydrogen, with removal of ammonia between periods of catalytic contact.

15 5. The process of concentrating argon which consists in subjecting a gaseous mixture of nitrogen and hydrogen containing upward of $\frac{1}{10}$ volume of argon per volume of nitrogen repeatedly to the action of a
20 catalyst active for the formation of ammonia from nitrogen and hydrogen, with removal of ammonia between periods of catalytic contact, the hydrogen in the gaseous mixture thus obtained being removed by combination thereof with oxygen.

25 6. The process of concentrating argon which consists in subjecting a gaseous mixture

of nitrogen and hydrogen containing argon repeatedly to the action of a catalyst active for the formation of ammonia from nitrogen and hydrogen, with removal of
30 ammonia between periods of catalytic contact, the hydrogen in the gaseous mixture thus obtained being removed by combination thereof with oxygen.

7. The process of concentrating argon
35 which consists in subjecting a gaseous mixture of hydrogen and nitrogen containing upward of $\frac{3}{4}$ volume of argon per volume of nitrogen to the action of a catalyst active for the formation of ammonia from nitrogen
40 and hydrogen.

8. The process of manufacturing argon in concentrations above 50% which consists in subjecting a gaseous mixture of hydrogen and nitrogen containing upward of $\frac{1}{10}$ volume of argon per volume of nitrogen to the action of a catalyst active for the formation of ammonia from nitrogen and hydrogen.

In testimony whereof I affix my signature.

WALTER DANNENBAUM.