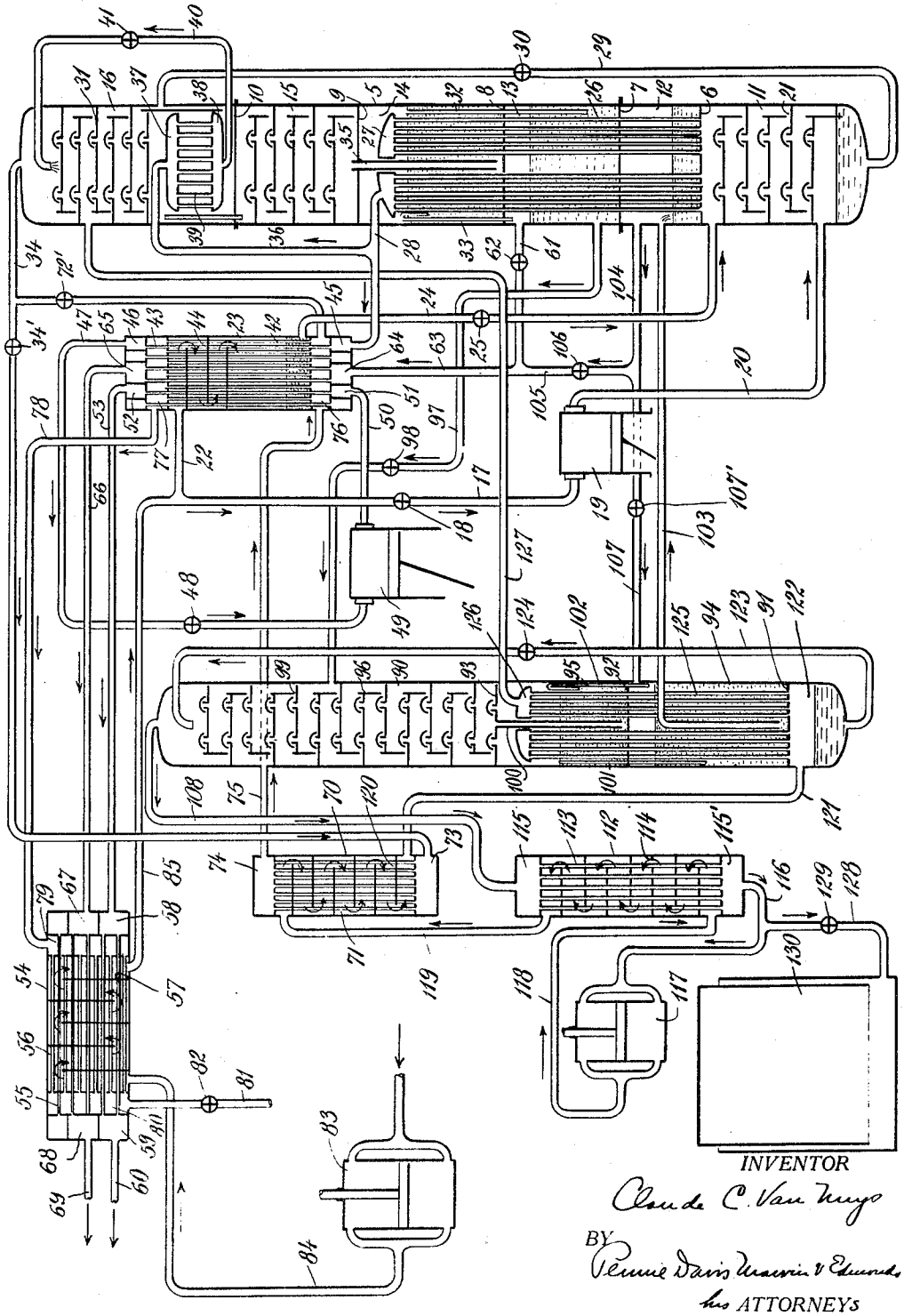
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SEPARATION OF THE CONSTITUENTS OF GASEOUS MIXTURES

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SEPARATION OF THE CONSTITUENTS OF GASEOUS MIXTURES.

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This invention relates to the liquefaction and separation of ternary gaseous mixtures for the purpose of recovering the constituents thereof in a theoretically and commercially economical manner. The method employed is particularly adapted for the separation of the principal constituents of air, although it may be applied for that purpose to other ternary mixtures, the constituents of which have different boiling points.

It has been proposed heretofore to separate by liquefaction and subsequent rectification the constituents of a ternary gaseous mixture such as air, which, for the purpose of this disclosure, is considered to be composed of oxygen, nitrogen and argon, thereby disregarding the minute quantities of rare elements present. Methods as heretofore practiced have, however, relatively low efficiency when compared with the theoretical possibilities. For example, such methods dissipate eight to ten times as much energy as that theoretically required to separate the constituents in substantial purity, and it has been found impossible to actually recover more than one constituent in substantially pure condition.

It is the object of this invention to eliminate many of the sources of energy loss and to otherwise improve methods as heretofore practiced by avoiding as far as possible all thermodynamically irreversible operations in connection with the production of the refrigerative effect required in the liquefaction cycle, and at the same time, by a rational correlation of the steps of rectification with those employed for the production of the necessary refrigerative effect, to recover all three constituents in substantial purity, without any serious loss in the recovery thereof.

A further object of the present invention is the provision of a method of and apparatus for the production of argon from the atmosphere in an economical and efficient manner, accompanied by the recovery of oxygen of higher purity than has heretofore been possible in liquefaction operations owing to the difficulty experienced in separating argon therefrom.

Further objects and advantages of the invention will be apparent as it is better understood with reference to the following specification and accompanying drawing diagrammatically illustrating an apparatus which is adapted for use in practicing the invention.

It is to be understood that in the drawing no attempt has been made to illustrate those details of liquefaction apparatus which are well known to those skilled in the art, the purpose of the drawing being merely to assist the reader to a complete comprehension of the essential features of the invention.

The separation of the three constituents is accomplished, according to the present invention, in three successive steps, each of these steps embodying fractional condensation and separation. The first step consists in separating the compressed and cooled air into two parts by selectively liquefying a portion thereof, employing for that purpose in the greatest possible degree the method of "backward return." This step results in the separation of a fraction, consisting approximately of half by volume of the air treated, composed of substantially pure nitrogen, the other fraction being a ternary mixture of oxygen, argon and nitrogen in the liquid state, with the percentages of the two former constituents substantially greater than in air, for example, oxygen 45%, argon 2% and nitrogen 53%. A portion of the nitrogen is liquefied and utilized in the second step and the balance of the nitrogen fraction which is available at a pressure of five to six atmospheres is not further treated, but after being brought into indirect contact with succeeding portions of the incoming air, is employed as a working fluid in an expansion engine, whereby it attains an extremely low temperature, the refrigerative effect of which is thereafter applied in an efficient manner.

The second step of the separation consists in separating by a suitable rectification the portion enriched in oxygen and argon into two sub-portions, one of which is a gaseous effluent having a composition of substantially pure nitrogen while the other contains from 93 to 95% oxygen and practically all of the argon content of the original air. The low temperature of the nitrogen effluent is utilized by means of suitable interchangers to cool the system, and is thereby restored to substantially the original air temperature. This sub-portion is available at atmospheric pressure, and after giving up its cold to the system it is rejected or utilized for any desired purpose.

The sub-portion of 93 to 95% oxygen is available in the liquid state according to the method herein described and is delivered to an intermediate point of an auxiliary rectification column. In this auxiliary column the third and last step of the separation is accomplished, this step consisting in the production of oxygen of high purity in the liquid condition, and an argon product containing a small amount of oxygen and only a very minute quantity, if any at all, of nitrogen. A small amount of substantially pure nitrogen is also separated in this step as a residual uncondensed gas, and is returned at a suitable level to the primary rectification column by means of which the second separation is accomplished.

In common with my co-pending application, Serial No. 465,518, a feature which distinguishes the present invention from prior methods is the direct return to the primary column of substantially the liquid equivalent of the liquid which passes from the primary column to the auxiliary. In the method described in said co-pending application, however, no special provision is made for compensating for the losses of liquid in the auxiliary column due to the inleakage of external heat, so that in the operation of that method the liquid returning from the auxiliary to the primary column is not exactly equivalent to the liquid entering the auxiliary from the primary column, being less by an amount equal to the liquid losses in the auxiliary due to the inleakage of external heat and the entrance to the auxiliary liquefaction cycle of that portion of the heat of compression which is not removed by the inter- and after-coolers of the auxiliary compressor.

In the operation of the method described in said co-pending application the liquid entering the auxiliary rectification column from the primary column has a composition of substantially 95% oxygen, the remaining 5% being chiefly argon. The liquid returning from the auxiliary to the primary column to be evaporated therein by indirect contact with the incoming air ascending in the tubes of the "backward return" condenser constitutes, after evaporation and restoration to atmospheric temperature, the oxygen product of the separation. The losses of liquid in the auxiliary liquefaction cycle due to heat leakage may amount to as much as or more than 5% of the liquid entering the auxiliary column. Hence in the operation of the method described the amount of the gaseous oxygen product may be somewhat less than the oxygen contained in the liquid entering the auxiliary column from the primary column. To obtain the maximum possible production of oxygen it would be necessary in that case to add to the oxygen product obtained as described substantial amounts of the oxygen vapors ascending from the base of the auxiliary column. These vapors, however, are not of equal purity with the vapors obtained from the liquid returning from the auxiliary to the primary column, and thus the purity of the final oxygen product is somewhat reduced.

In the operation of the method which forms the subject of the present disclosure, provision is made for efficiently applying a sufficient amount of refrigerative effect directly to the auxiliary liquefaction cycle to overcome the effects of heat leakage therein as above described so that the liquid oxygen returning to the primary from the auxiliary column is somewhat greater than the amount necessary to constitute the total oxygen product of the separation. Hence in the operation of the present method, instead of deriving a portion of the oxygen product from the base of the auxiliary rectification column, it is possible to cause a portion of the vapor from the liquid delivered to the primary column and resulting from evaporation therein to return to the base of the auxiliary rectification column and assist in the rectification of the liquids descending therein.

The refrigerative effect necessary in the auxiliary liquefaction cycle to produce the result just described is obtained from any suitable source, for example, by circulating in an auxiliary interchanger or "liquefier" in indirect contact with the gases entering the auxiliary cycle from the auxiliary compressor all or a portion of the gaseous effluent from the primary rectification column before the effluent is applied to the cooling of incoming gases or all or a portion of the exhaust gases from an expansion engine or turbine supplied with residual nitrogen from the first step of the separation. Further details of the arrangement of apparatus necessary to produce the results described will be pointed out later in connection with the detailed description of the method.

In the operation of the method described in said co-pending application, it is necessary in order to produce sufficient refrigerative effect for both primary and auxiliary cycles to operate the primary rectification column at a pressure sufficiently high for the effluent leaving the top of the primary rectification column to pass through an expansion engine before it is returned to the primary compressor. Rectification under pressures substantially greater than atmospheric, although it requires apparatus somewhat smaller in size than when accomplished at atmospheric pressure, possesses some disadvantages, chief among which is that due to the fact that the composition of co-existing liquid and vapor phases of mixtures of oxygen and nitrogen are somewhat closer together at higher pressures than at atmos-

pheric pressure, and thus the rectification at such pressures is relatively somewhat unfavorable.

In the method forming the subject of the present application, I am able to accomplish the rectification in both the auxiliary and primary columns at substantially atmospheric pressure, and at the same time to obtain efficiently the refrigerative effect necessary in both primary and auxiliary cycles. A portion of this refrigerative effect is obtained by expansion with external work in an engine or turbine of a part of the ingoing high pressure air entering the primary liquefaction cycle, the expanded air being delivered to the primary column below the tubular "backward return" condenser. The remaining part of the ingoing air is diverted to a primary "liquefier" wherein it is liquefied by indirect contact with outgoing separated gases. The liquid obtained is delivered onto the rectification trays located in the primary column below the tubular condenser as described in my copending application, Serial No. 409,197, and combining with the liquid produced in those tubes by selective liquefaction flows downwardly over the trays in direct contact with the expanded air. I thus avoid reducing the maximum possible oxygen enrichment obtainable by the "backward return" effect by the addition to the enriched liquid delivered at the bottom of said tubular condenser of the unenriched liquid air coming from the primary "liquefier" as in the method described in co-pending application, Serial No. 465,518. The expansion of the residual uncondensed nitrogen leaving the top of the tubular "backward return" condenser at a pressure of five to six atmospheres has been noted previously. The combination of the refrigerative effect produced by the expansion of the high pressure air and of the residual nitrogen, as above described, is sufficient to maintain the necessary temperature in both the primary and auxiliary cycles. Further details of the operation of the method will be pointed out hereafter.

For the purpose of description, the apparatus may be divided into two sections, the first including the primary column and the appurtenant apparatus and the other including the auxiliary column. In the primary column the first steps of separation are accomplished, and in the treatment of air, for example, oxygen of relatively high purity sufficient for many commercial purposes may be obtained. The auxiliary column is employed for the purpose of separating argon in the treatment of air, although obviously it may be used in connection with the analysis of any ternary mixture in which the constituents bear relations similar to those of the constituents of air. Many of the distinctive features of the present invention may be utilized in connection with the primary column whether or not the auxiliary column is employed.

Referring to the drawing, 5 indicates the primary column which is separated by partitions 6, 7, 8, 9 and 10 into a lower rectifying compartment 11, a lower vaporizing compartment 12, upper vaporizing compartments 13 and 14, and upper rectifying compartments 15 and 16, the several purposes of which will hereinafter more fully appear as the description follows the details of operation of the apparatus.

The gaseous mixture, e. g., air, is compressed and cooled in the usual compressor and heat-interchangers hereinafter described and is divided into two portions. One portion passes at the initial pressure through a pipe 17 controlled by a valve 18 to an engine or turbine 19 where the air is expanded with external work and thereby cooled. The cold expanded air passes through a pipe 20 to the bottom of the compartment 11 of the primary column and thence passes upwardly through a plurality of trays 21 of the usual type in direct contact with the liquid flowing downwardly over the trays. A portion of this liquid is derived from the liquefaction of the balance of the compressed air which is delivered through a pipe 22 to a "liquefier" 23 wherein it is subjected to indirect contact with cold gaseous products as hereinafter more fully set forth. The resulting liquid, having substantially the composition of the entering air, is delivered through a pipe 24 controlled by a valve 25 to the compartment 11 above the trays 21. This liquid is augmented by liquid resulting from selective liquefaction of the air in tubes 26 which communicate with the compartment 11 and extend upwardly through the compartments 12, 13 and 14 wherein a supply of cold liquid at a lower pressure than that of the gaseous mixture is maintained.

The passage of the combined liquids downwardly over the trays 21 in contact with the incoming gaseous mixture results in a rectification with the resulting enrichment of the liquid in the less volatile constituent of the gaseous mixture and a corresponding impoverishment of the liquid in the more volatile constituent. The liquid thus tends to approach a composition of 47% oxygen when air is being treated, liquid of this composition being in phase equilibrium with the incoming air. The gaseous mixture impoverished in oxygen, for example, in passing through the tubes 26, is selectively liquefied, the oxygen, for example, returning with a portion of the nitrogen in the liquid in contact with further quantities of the gaseous mixture in accordance with the principle of "backward return". The

operation results in a residual gas which, when air is treated, is substantially pure nitrogen, and which is delivered from the tubes 26 to a header 27 whence it is withdrawn through a pipe 28.

The enriched oxygen liquid accumulating at the bottom of the primary column is delivered through a pipe 29 controlled by a pressure-reducing valve 30 to the upper rectifying compartment 16 of the column which is provided with trays 31 of the usual type. As the liquid flows downwardly over the trays in the lower portion of the compartment 16, it is subjected to rectification by direct contact with the vapors arising from the compartments 13 and 14 which are connected by a liquid overflow pipe 32 and a vapor pipe 33. In passing over the trays the liquid is enriched in oxygen and the production of an effluent which is substantially pure nitrogen and escapes through a pipe 34 at the top of the column. The liquid passes downwardly through a pipe 35 into the compartment 14 and overflows therefrom through the pipe 32 into the compartment 13. Vapor from the compartment 13 is permitted to pass upwardly through the pipe 33 into the compartment 14 where it joins the vapor in that compartment.

The residual gas escaping from the column through the pipe 28 is divided and a portion thereof is delivered by a pipe 36 to a condenser disposed in the compartment 16 of the column and preferably comprising headers 37 and 38 connected by tubes 39. The residual gas is liquefied in the tubes 39 and the liquid is conveyed by a pipe 40 controlled by a valve 41 to the top of the column where the substantially pure nitrogen liquid produced by heat-interchange with the liquid surrounding the tubes serves as a rectifying agent in the compartment 16. The balance of the residual gas is delivered by the pipe 28 to the liquefier 23 which consists of a casing enclosing a plurality of tubes 42 and 43 which communicate with suitable compartments at the ends of the liquefier. Baffles 44 within the liquefier cause the gaseous mixture entering through the pipe 22 to circulate about the tubes, thereby insuring thorough contact therewith.

The residual gas escaping through the pipe 28 enters a compartment 45 at one end of the liquefier and passes thence through the tubes 43 to a compartment 46 at the opposite end of the liquefier. Thence the residual gas passes through a pipe 47 controlled by a valve 48 to an expansion engine or turbine 49 where it is expanded with external work and thereby cooled. The energy recovered in the expansion engine 49 as well as that supplied by the engine 19 may be utilized in any suitable manner, as for example, in assisting in compression of the incoming gaseous mixture. The cold residual gas escapes from the engine or turbine through a pipe 50 and may be delivered to a compartment 51 at the end of the liquefier 23. Thence the residual gas passes through tubes 43 to a compartment 52 at the opposite end of the liquefier and is withdrawn through a pipe 53 which conveys the expanded gas to an exchanger 54.

This exchanger serves to cool the incoming gaseous mixture after compression and consists of a casing enclosing tubes 55 and 56 which terminate in suitable compartments at the ends of the exchanger. Baffles 57 cause the incoming gaseous mixture to circulate about the tubes. The expanded residual gas enters a compartment 58 at the end of the exchanger 54 and passes through the tubes 55 to a corresponding compartment 59 at the opposite end of the exchanger. The gas is withdrawn from the compartment 59 to a pipe 60 which may deliver it to the atmosphere or to a suitable storage receptacle.

The vapor from the compartment 13, consisting in case air is treated and when the auxiliary cycle is not operated of relatively pure oxygen, may be withdrawn through a pipe 61 controlled by a valve 62 and is delivered through a pipe 63 to a compartment 64. From the compartment 64 the gas passes through tubes 43 to a compartment 65 at the opposite end of the liquefier whence it escapes through a pipe 66 and is delivered to a compartment 67 at one end of the exchanger 54. In the exchanger the gas passes through tubes 55 to a compartment 68 and is withdrawn through a pipe 69 which may convey the gas to a suitable storage receptacle such as a gasometer.

The effluent from the primary column, consisting, for example, of substantially pure nitrogen, if the auxiliary cycle is used, is delivered by the pipe 34 controlled by a valve 34′ to an auxiliary liquefier 70 which supplies the excess refrigeration required for the auxiliary cycle. This liquefier comprises a shell with compartments at its ends and tubes 71 connecting the compartments. The effluent enters a compartment 73 at the lower end of the liquefier and passes through the tubes 71 to a compartment 74 at the opposite end of the liquefier. Thence the effluent, after giving up a portion of its cold in the liquefier, passes through a pipe 75 to the liquefier 23 where it enters a compartment 76, travels through the tubes 42 to a compartment 77 and is withdrawn to a pipe 78 which conveys it to the exchanger 54. The effluent which has been considerably raised in temperature, owing to its passage through the two liquefiers, enters a compartment 79 of the exchanger 54 and passes through tubes 56 therein to a compartment 80. From the compartment 80 the gas is withdrawn

through a pipe 81 controlled by a valve 82 and is rejected or utilized for any purpose.

The incoming gaseous mixture is compressed in the compressor 83 and is delivered therefrom through a pipe 84 to the exchanger 54 where it is caused to circulate by the baffles 57 about the tubes 55 and 56. From the exchanger 54 the cooled gaseous mixture is delivered by a pipe 85 to the pipe 17 leading to the engine or turbine 19. A portion of this cool gaseous mixture is withdrawn from the pipe 85 and is delivered by the pipe 22 to the liquefier 23 in the manner hereinbefore described.

In the foregoing description the gaseous mixture is considered, primarily, as consisting of two constituents, for example, oxygen and nitrogen. In the treatment of air, however, a third constituent, argon, must be considered since the removal of argon is a principal requisite of the production of oxygen of the highest purity. The operation as hereinbefore described may be carried on to produce an oxygen which, though of substantially commercial purity, is contaminated with argon because the major portion of argon is carried in the liquid which descends into the compartment 13 and is vaporized in that compartment with the oxygen.

The separation of the argon is accomplished in an auxiliary column 90 which is divided by partitions 91, 92 and 93 into compartments 94 and 95 and a rectifying chamber 96. The enriched oxygen liquid containing argon and nitrogen is withdrawn from the compartment 13 by a pipe 97 controlled by a valve 98 and is delivered at an intermediate point in the rectifying chamber 96 of the auxiliary column. The rectifying chamber 96 is provided with trays 99, and the liquid flows downwardly thereover in direct contact with vapors arising from the compartment 95 of the column. The rectification thus accomplished results in the further enrichment of the liquid in oxygen with accompanying separation of a gaseous mixture containing substantially all of the nitrogen and argon with some oxygen. The liquid product of the rectification, principally oxygen, enters the compartment 95 through a pipe 100 and overflows through a pipe 101 into the compartment 94. Vapors from the compartment 94 pass upwardly through a pipe 102 into the compartment 95 where they mingle with the vapors formed in that compartment and thence pass upwardly to the rectifying chamber.

The liquid oxygen accumulating in the compartment 94 is withdrawn through a pipe 103 and is delivered to the compartment 12 of the primary column where it is vaporized. This vapor is substantially pure oxygen in case air is treated and is delivered through a pipe 104 to a pipe 105 which is in turn connected to the pipe 63. A valve 106 in the pipe 105 permits the control of oxygen which is withdrawn from the compartment 12 of the primary column, and when this valve is open the valve 62 should be closed, thus preventing contamination of the oxygen. A pipe 107 controlled by a valve 107′ connects the pipe 104 with the compartment 94 of the auxiliary column so that surplus vapors may be returned to the auxiliary column for use in the rectifying compartment of that column. The substantially pure oxygen withdrawn from the primary column through the pipe 104 follows the course hereinbefore outlined in connection with oxygen vapor from the compartment 13.

The effluent from the rectification in the auxiliary column escapes through a pipe 108 to an exchanger 112. This exchanger comprises a shell with tubes 113 extending therethrough and connecting the compartments at opposite ends thereof. Baffles 114 direct the gas within the shell about the tubes 113. The effluent entering the chamber 115 passes through the tubes 113 to a chamber 115′ at the opposite end of the exchanger. Thence the effluent is withdrawn through a pipe 116 and is delivered to a compressor 117 where it is recompressed. Owing to the provision of the exchanger 112, the effluent has been warmed prior to its entrance to the compressor. It is further heated by the compression and is delivered through a pipe 118 to the exchanger 112 wherein it passes about the baffles 114, being thereby caused to circulate about the tubes 113. After cooling in the exchanger 112 the effluent is delivered through a pipe 119 to the liquefier 70 wherein it is caused by the baffles 120 to circulate about the tubes 71 in indirect contact with the cold gaseous products traveling through the tubes. By this contact the effluent is wholly or partially liquefied, the necessary refrigeration for this purpose being supplied by the effluent from the primary column which passes through the liquefier in the manner hereinbefore described. The liquid or mixture of vapor and liquid is withdrawn from a liquefier 70 through a pipe 121 and is delivered to the compartment 122 at the base of the auxiliary column 90. The liquid thus accumulated is delivered through a pipe 123 controlled by a valve 124 to the upper end of the rectification chamber 96 and passes downwardly over the trays 99 to assist in the rectification of the vapors rising therethrough. This liquid eventually joins the liquid delivered to the auxiliary column from the primary column. The vapors which enter the compartment 122 pass upwardly through tubes 125 which extend through the compartments 94 and 95 of the auxiliary column. In these tubes the gas-

eous mixture is subjected to liquefaction with backward return by indirect contact with the liquids accumulated in the chambers 94 and 95.

The liquid formed accumulates with liquid from the liquefier 70 in the chamber 122 and is utilized as hereinbefore described. The uncondensed vapors, principally nitrogen in case air is treated, are delivered to a head 126 and pass therefrom through a pipe 127 to the upper part of the primary column where they enter the rectification compartment and assist in the rectification of the liquids descending therein. Any uncondensed vapors escape with the effluent from the column through the pipe 34.

In the secondary rectification substantially pure oxygen is produced which accumulates in the compartment 94 and is delivered to the primary column through the pipe 103 as previously described. The residual nitrogen, consisting of substantially all of the nitrogen entering the auxiliary column, escapes through the pipe 127. The balance of the gases form the effluent which circulates in the auxiliary cycle and consists of argon, oxygen and possibly small amounts of nitrogen. When the column has been in operation for a sufficient period to produce the desired enrichment in argon, a portion of the circulating gases may be withdrawn through a pipe 128 controlled by a valve 129 and delivered to a suitable receptacle such as a gasometer 130.

As hereinbefore noted, the argon cycle is not necessarily utilized in connection with certain features of the invention since oxygen of commercial purity may be produced by the method described without the removal of argon. The advantages of employing expansion of the gaseous mixture before liquefaction and of the residual unliquefied gas after selective liquefaction are the assurance of sufficient refrigerative effect with the minimum application of energy in the initial compression. In accordance with the method described, rectification may be carried out at substantially atmospheric pressure as is most desirable, and at the same time the maximum of energy may be recovered in the operation. Starting at relatively low pressures the separation is effected at a minimum expense, particularly where a large proportion of the energy may be recovered. The apparatus employed may be relatively light in construction as compared with high pressure systems, and economy of investment is thus added to economy of operation.

When argon is to be separated and recovered with the consequent advantage of the production of oxygen of extremely high purity, the auxiliary cycle is employed and utilization of the gaseous product of the primary column ensures the maintenance of the necessary refrigerative effect in the auxiliary cycle with a minimum of effort. Unavoidable losses resulting from heat leakage into the auxiliary column are automatically made up by the transfer of cold from the gas escaping from the primary column, and the proper volumes of liquids in the auxiliary column are thus constantly assured. The only gases leaving the cycle are substantially pure nitrogen, substantially pure oxygen and argon containing small amounts of oxygen and possibly traces of nitrogen. The conservation of argon is thereby assured.

Obviously the details of the invention may be varied within the scope of the accompanying claims without departing therefrom or sacrificing any of the advantages hereinbefore set forth.

I claim:—

1. A method of separating the constituents of gaseous mixtures, which comprises partially expanding a portion of the cold compressed gaseous mixture with external work, subjecting it to selective liquefaction, thereby producing a liquid and separating an unliquefied gaseous residue, liquefying another portion of the compressed gaseous mixture by indirect contact with colder media, combining this liquid with that produced from the expanded portion, and rectifying the combined liquids by direct contact with the partially expanded gaseous mixture.

2. A method of separating the constituents of gaseous mixtures, which comprises partially expanding a portion of the cold compressed gaseous mixture with external work, subjecting it to selective liquefaction, thereby producing a liquid and separating an unliquefied gaseous residue under pressure, liquefying another portion of the compressed gaseous mixture by indirect contact with colder media, combining this liquid with that produced from the expanded portion, rectifying the combined liquids by direct contact with the partially expanded gaseous mixture, expanding the unliquefied gaseous residue with external work, and utilizing the cold thus produced in the liquefaction of further quantities of the gaseous mixture.

3. A method of separating the constituents of gaseous mixtures, which comprises partially expanding a portion of the cold compressed gaseous mixture with external work, subjecting the expanded portion to selective liquefaction, thereby producing a liquid and separating an unliquefied gaseous residue, liquefying another portion of the compressed gaseous mixture by indirect contact with cold gaseous products, combining this liquid with that produced from the expanded portion, expanding the unliquefied gaseous residue, utilizing the cold thus produced in the liquefaction of further quantities of

the gaseous mixture, and rectifying the combined liquids by direct contact with the partially expanded gaseous mixture.

4. A method of separating the constituents of gaseous mixtures, which comprises compressing and cooling the gaseous mixture, partially expanding one portion thereof with external work, subjecting the expanded portion to selective liquefaction, thereby producing a liquid and separating an unliquefied gaseous residue, expanding the unliquefied gaseous residue, liquefying the other portion of the compressed gaseous mixture by subjecting it to indirect contact with colder gases, utilizing the liquid thus obtained for compensating losses due to inleakage of heat by combining it with the liquid produced by selective liquefaction, and subjecting the combined liquids to rectification by direct contact with the partially expanded gaseous mixture.

5. A method of separating the constituents of gaseous mixtures, which comprises compressing and cooling the gaseous mixture, separating it into two portions, a working portion and a supplementary portion, partially expanding the working portion with external work, subjecting the expanded working portion to selective liquefaction by indirect contact with a colder liquid, withdrawing and expanding the unliquefied gaseous residue, utilizing the refrigeration thus produced in liquefying the supplementary portion, combining the liquid thus produced with the liquid resulting from the selective liquefaction and rectifying the combined liquids.

6. A method of separating the constituents of gaseous mixtures, which comprises compressing and cooling the gaseous mixture, separating it into two portions, a working portion and a supplementary portion, partially expanding the working portion with production of external work, subjecting the expanded working portion to selective liquefaction by indirect contact with a colder liquid, withdrawing and expanding the unliquefied gaseous residue, liquefying the supplementary portion, combining the liquid thus produced with the liquid resulting from the selective liquefaction, and rectifying the combined liquids by direct contact with the expanded working portion.

7. A method of separating the constituents of gaseous mixtures, which comprises compressing the mixture, partially expanding a portion thereof with external work, liquefying another portion by indirect contact with colder gaseous products, recombining the liquid and gaseous portions under conditions of rectification, subjecting the gaseous portion to selective liquefaction by indirect contact with the liquid product at a lower pressure, the liquid thus formed returning in direct contact with the entering gaseous mixture, subjecting the combined liquids to further rectification, and withdrawing and expanding the unliquefied gaseous residue.

8. A method of separating the constituents of gaseous mixtures, which comprises compressing the mixture, expanding a portion thereof with external work, liquefying another portion by indirect contact with colder gaseous products, recombining the liquid and gaseous portions under conditions of rectification, subjecting the gaseous portion to selective liquefaction by indirect contact with the liquid product at a lower pressure, the liquid thus formed returning in contact with the entering gaseous portion, and subjecting the resulting liquid to rectification, whereby the constituents are further separated.

9. A method of separating the constituents of gaseous mixtures, which comprises compressing the mixture, expanding a portion thereof with external work, liquefying another portion by indirect contact with colder gaseous products, recombining the portions under conditions of retification, subjecting the gaseous portion to selective liquefaction by indirect contact with the liquid product at a lower pressure, the liquid thus formed returning in contact with the entering gaseous portion, expanding the unliquefied gaseous residue, and rectifying the combined liquids by direct contact with the expanded gaseous mixture.

10. A method of separating the constituents of gaseous mixtures, which comprises compressing the mixture, expanding a portion thereof with external work, cooling another portion by indirect contact with the colder gaseous products to liquefy that portion, recombining the expanded and liquefied portions with rectification to separate the more volatile gases from the liquid, subjecting the gaseous mixture resulting from the rectificaion to selective liquefaction, the liquid thus formed returning in direct contact with the entering gaseous mixture and further separating the constituents of the liquid by rectification.

11. A method of separating the constituents of gaseous mixtures, which comprises compressing the mixture, partially expanding a portion thereof with external work, cooling another portion by indirect contact with the colder gaseous products to liquefy that portion, recombining the expanded and liquefied portions with rectification to separate the more volatile gases from the liquid, subjecting the gaseous mixture resulting from the rectification to selective liquefaction, the liquid thus formed returning in direct contact with the entering gaseous mixture, expanding the unliquefied gaseous residue, utilizing the cold thus produced to maintain the

required refrigeration, and subjecting the liquid formed to further rectification.

12. A method of separating the constituents of gaseous mixtures, which comprises compressing the mixture, partially expanding a portion thereof with external work, cooling another portion by indirect contact with the colder gaseous products to liquefy that portion, recombining the expanded and liquefied portions with rectification by direct contact with the partially expanded gaseous mixture to separate the more volatile gases from the liquid, subjecting the gaseous mixture resulting from the rectification to selective liquefaction, the liquid thus formed returning in direct contact with the entering gaseous mixture, expanding the unliquefied gaseous residue, utilizing the cold thus produced to maintain the required refrigeration, and subjecting the liquid formed to further rectification.

13. A method of separating the constituents of gaseous mixtures, which comprises partially expanding a portion of the cold compressed gaseous mixture, subjecting it to selective liquefaction, thereby separating a liquid and an unliquefied gaseous residue, expanding the gaseous residue, liquefying another portion of the compressed gaseous mixture by indirect contact with colder media, combining and rectifying the liquids, withdrawing the liquid product of the rectification, subjecting it to a further rectification, and utilizing the cold expanded gaseous residue of the selective liquefaction to compensate the losses due to leakage of heat into the system.

14. A method of separating the constituents of gaseous mixtures, which comprises expanding a portion of the cold compressed gaseous mixture, subjecting it to selective liquefaction, thereby separating a liquid and an unliquefied gaseous residue, withdrawing the gaseous residue, liquefying another portion of the compressed gaseous mixture by indirect contact with colder media, combining and subjecting the liquids to a primary rectification, withdrawing the liquid product of the rectification, subjecting it to an auxiliary rectification, and utilizing the cold effluent from the primary rectification in maintaining the refrigerative effect in the auxiliary rectification.

15. A method of separating the constituents of gaseous mixtures, which comprises subjecting the compressed and cooled mixture to liquefaction and a primary rectification to separate a liquid and an effluent gaseous mixture, subjecting the liquid product to an auxiliary rectification, and utilizing the cold effluent from the primary rectification in maintaining the refrigerative effect of the auxiliary rectification.

16. A method of separating the constituents of gaseous mixtures, which comprises subjecting the compressed and cooled mixture to liquefaction and a primary rectification by contact with the incoming gaseous mixture to separate a liquid and an effluent gaseous mixture, subjecting the liquid product to an auxiliary rectification, utilizing the cold effluent from the primary rectification in maintaining the refrigerative effect of the auxiliary rectification.

17. A method of separating the constituents of gaseous mixtures, which comprises subjecting the gaseous mixture to selective liquefaction, thereby separating a liquid and an unliquefied gaseous residue, withdrawing the gaseous residue, subjecting the liquid to a primary rectification to separate a liquid and an effluent gaseous mixture, subjecting this liquid to an auxiliary rectification, and utilizing the effluent from the primary rectification in maintaining the refrigerative effect of the auxiliary rectification.

18. A method of separating the constituents of gaseous mixtures, which comprises subjecting the gaseous mixture to selective liquefaction, thereby separating a liquid and an unliquefied gaseous residue, withdrawing the gaseous residue, subjecting the liquid to a primary rectification to separate a liquid and an effluent gaseous mixture, subjecting this liquid to an auxiliary rectification and maintaining the refrigerative effect of the auxiliary rectification by cold gaseous products of the primary operation.

19. A method of separating the constituents of a gaseous mixture, which comprises subjecting the compressed and cooled gaseous mixture to liquefaction and a primary rectification to separate a liquid, subjecting the liquid to an auxiliary rectification and maintaining the refrigerative effect of the auxiliary rectification by cold gaseous products of the primary operation.

20. A method of separating three constituents from a gaseous mixture thereof, which comprises partially expanding a portion of the cold compressed mixture, liquefying another portion thereof, subjecting the liquid and gaseous portions to contact under rectifying conditions to impoverish the gaseous mixture in the less volatile constituents, treating the gaseous mixture to selective liquefaction to separate an unliquefied gaseous residue consisting of one constituent, expanding the gaseous residue, subjecting the combined liquids to rectification, thereby separating a gaseous effluent consisting substantially of the most volatile constituent and a liquid containing chiefly the two less volatile constituents, and withdrawing and rectifying the liquid to separate substantially all of the more volatile constituents from a liquid consisting substantially of the least volatile constituent.

21. A method of separating three constituents from a gaseous mixture thereof, which comprises partially expanding a portion of

the cold compressed mixture, liquefying another portion thereof, subjecting the liquid and gaseous portions to contact under rectifying conditions to impoverish the gaseous mixture in the less volatile constituents, treating the gaseous mixture to selective liquefaction to separate an unliquefied gaseous residue consisting of one constituent, expanding the gaseous residue, subjecting the combined liquids to rectification, thereby separating a gaseous effluent consisting substantially of the most volatile constituent and a liquid containing chiefly the two less volatile constituents, returning the gaseous effluent for recompression and further treatment, and further rectifying the liquid to separate substantially all of the more volatile constituents from a liquid consisting substantially of the least volatile constituent.

22. A method of separating the constituents of gaseous mixtures, which comprises subjecting the mixture to selective liquefaction, thereby producing a liquid portion and an unliquefied gaseous residue, rectifying the liquid by direct contact with the partially expanded gaseous mixture and liquefying the gaseous residue nonselectively for use as reflux in the further rectification of the liquid product of the first-mentioned rectification.

23. A method of separating the constituents of gaseous mixtures, which comprises subjecting the mixture to selective liquefaction by heat exchange with a liquid product of the separation, thereby producing a liquid portion and an unliquefied gaseous residue, rectifying the liquid portion by direct contact with the mixture to be selectively liquefied when it is no longer subject to the cooling effect required for selective liquefaction, liquefying the uncondensed gaseous residue nonselectively and utilizing the liquid thus produced for use as reflux in a further rectification of the liquid product of the first rectification.

In testimony whereof I affix my signature.

CLAUDE C. VAN NUYS.