

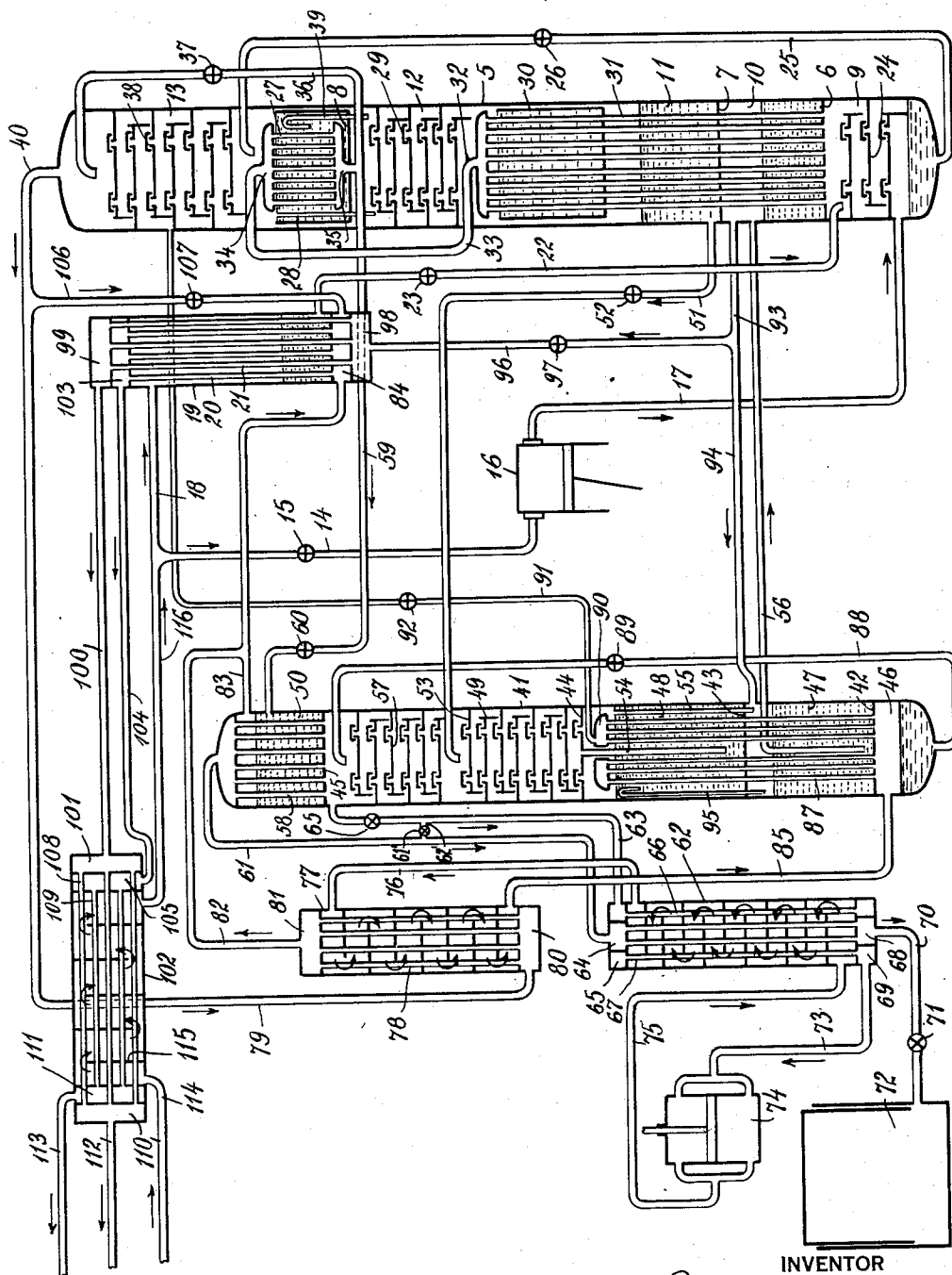
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SEPARATION OF THE CONSTITUENTS OF GASEOUS MIXTURES

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SEPARATION OF THE CONSTITUENTS OF GASEOUS MIXTURES.

Application filed May 24, 1923. Serial No. 641,035.

To all whom it may concern:

Be it known that I, CLAUDE C. VAN NUYS, a citizen of the United States, residing at Cranford, in the county of Union, State of New Jersey, have invented certain new and useful Improvements in Separation of the Constituents of Gaseous Mixtures; and I do hereby declare the following to be a full, clear, and exact description of the invention, such as will enable others skilled in the art to which it appertains to make and use the same.

This invention relates to the liquefaction 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, which, for the purpose of this disclosure, is considered to be composed of oxygen, nitrogen and argon, thereby disregarding the minute quantities of rare gases present. It may be applied for a like purpose to other ternary mixtures, the constituents of which have different boiling points.

It has been proposed heretofore to separate the constituents of a ternary gaseous mixture such as air by liquefaction and subsequent rectification. The methods used have, however, relatively low efficiency when compared with the theoretical possibilities.

It is the object of this invention to eliminate many of the sources of energy loss and to otherwise improve the methods of separating the constituents of ternary gaseous mixtures as heretofore practiced by avoiding as far as possible all thermodynamically irreversible operations in connection with the production and utilization of the refrigerative effect required in the liquefaction cycle.

A further object of the 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 the 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 portions 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.

In common with the method disclosed in my copending application, Serial No. 615,036, filed January 26, 1923, the separation of the three constituents is accomplished 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%. The nitrogen fraction which is available at a pressure of from four to six atmospheres is liquefied, and a portion of the liquid is utilized in the second step. The balance of the liquid nitrogen is utilized in the third step as hereinafter described.

The second step of the operation 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, and in a manner similar to that described in said co-pending application is delivered to an intermediate point of the 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 state and an argon product containing a small amount of oxygen and only a very minute quantity, if any, of nitrogen. A small amount of substantially pure nitrogen is also separated in this step as a residual uncondensed gas, which is returned at a suitable level to the primary rectification column by means of which the second separation is accomplished.

In common with said co-pending application, 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. Also, as in said co-pending application, the method which forms the subject of the present disclosure provides for efficiently applying a sufficient amount of refrigerative effect directly to the auxiliary liquefaction cycle to overcome the effects of heat leakage therein, 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. The present method differs from that described in said co-pending application in that part of the refrigerative effect applied to the auxiliary cycle is produced in a somewhat different manner whereby the amount of the working fluid necessary to be compressed and "cycled" through the auxiliary apparatus is very much reduced, and thus an important economy in the cost of operation of the apparatus is accomplished.

In the co-pending application, I have pointed out that the amount of residual uncondensed nitrogen obtainable at the top of the tubular system constituting the primary "backward return" vaporizer, wherein the initial selective condensation is accomplished, is considerably in excess of that necessary, after liquefaction thereof, for subsequent use as "reflux" liquid nitrogen in the primary cycle. This excess residual nitrogen is utilized, after being brought into indirect contact with succeeding portions of the incoming air, as a working fluid in an expansion engine or turbine, whereby it attains an extremely low temperature, and becomes a suitable refrigerant for use at a suitable point in the system.

In the operation of that method, however, it is difficult, particularly in an apparatus of the size in commercial use to-day, to attain a high efficiency in the expansion of

the residual nitrogen passing through said expansion engine or turbine on account of the relatively small amount thereof available for that purpose. Moreover, when the expansion machine is of the reciprocating type, it is difficult, on account of the pulsations induced by the machine in the tubes of the primary vaporizer, to maintain a sufficiently high purity of the residual uncondensed nitrogen so that, after liquefaction of the portion necessary for that purpose, it is suitable for use as "reflux" in the primary column.

I have discovered that that portion of the residual nitrogen not necessary for "reflux" needs may be utilized in a much more efficient manner to reduce the cost of operating the system, with the further advantage that no expansion machine is required. In the operation of the method forming the subject of this disclosure all the residual uncondensed nitrogen available at the top of the primary vaporizer is liquefied in the "reflux" condenser of the primary column; but only as much of the liquid thus produced as is necessary as "reflux" in the primary column is utilized for that purpose. The remaining portion of the liquid nitrogen is delivered to the space surrounding the tubes of a condenser located at the top of the auxiliary rectifier. All or a portion of the vapors ascending in the auxiliary rectifier pass through the tubes of this condenser and is subjected to selective liquefaction therein.

Experiments as well as calculations show that about twice as much residual nitrogen is available at the top of the primary vaporizer as is necessary for "reflux" needs in the primary cycle and that the portion of this residual nitrogen which is not needed as primary "reflux" will, if it is applied as liquid nitrogen in the auxiliary condenser, reduce the amount of liquid necessary to be cycled in the auxiliary cycle by approximately one half in producing a given composition of argon product and high purity oxygen liquid.

Another advantage of thus utilizing the liquid nitrogen is that it assists in overcoming the effects of heat leakage in the auxiliary cycle. In my co-pending application I have pointed out the effects of heat leakage in the auxiliary cycle and the advantage of overcoming said effects by the use of an auxiliary "liquefier." This advantage consists in the fact that by the application of refrigerative effect directly to the auxiliary liquefaction cycle, the liquid oxygen returned to the primary from the auxiliary column is somewhat greater than the amount necessary to constitute the total oxygen product of the separation. Since any refrigerative effect, however, applied to the auxiliary cycle, will product the same result, it is apparent that the present inven-

tion secures the advantage just pointed out in a somewhat different manner than by the method disclosed in said co-pending application.

5 Another advantage of the use of the auxiliary liquefier as described in said co-pending application is that the liquefaction accomplished in that liquefier is produced by the cold outgoing products of the primary
10 apparatus before they pass through the primary liquefier, and for this reason any liquefaction accomplished in the auxiliary liquefier reduces by an equivalent amount the liquefaction necessary to be accomplished
15 in the primary liquefier. In the operation of the method forming the subject of the present disclosure, the liquid nitrogen delivered to the auxiliary cycle is produced in the primary cycle, and hence the refrigerative effect thereof in the auxiliary cycle
20 will not reduce the amount of liquefaction necessary to be accomplished in the primary liquefier. Therefore, in common with the method disclosed in said co-pending application, provision is made, in the method forming
25 the subject of the present disclosure, for an auxiliary liquefier. The amount of liquefaction necessary in this liquefier is, however, somewhat reduced, being only that
30 necessary to compensate for heat leakage in the auxiliary cycle. This heat leakage has been much reduced on account of the fact that the amount of working fluid cycled in the auxiliary apparatus is, by the operation
35 of the present method, much reduced. The effect is therefore cumulative.

For convenience the invention will be described in more detail with reference to the drawing, the primary and auxiliary columns
40 being considered separately. The primary column 5 comprises a shell divided by partitions 6, 7 and 8 into a lower rectifying compartment 9, vaporizing compartments 10 and 11, and upper rectifying compartments
45 12 and 13. The gas to be treated, after compression and cooling, is preferably divided into two portions, and one portion is delivered through a pipe 14 controlled by a valve 15 to an expansion engine 16 wherein
50 it is expanded with external work and thereby cooled. The cold expanded gas passes through a pipe 17 to the compartment 9 of the column. The balance of the cold compressed gas is delivered by a pipe 18 to a
55 liquefier 19 wherein it is cooled by cold gaseous products of the column passing through tubes 20 and 21 as hereinafter described. The cold compressed gas is thus liquefied, and the liquid is delivered through
60 a pipe 22 controlled by a valve 23 to the compartment 9 of the column near the upper end thereof. This liquid flows downwardly over trays 24 of the usual kind employed in rectifying columns and is thereby sub-
65 jected to the rectifying action of the ex-

panded gas which enters through the pipe 17. An initial rectification of this liquid together with other liquid formed by selective liquefaction of the rising gas occurs and a liquid product gathers in the bottom
70 of the compartment which approximates a composition which is in phase equilibrium with the gas entering through the pipe 17.

The liquid accumulating in the bottom of the compartment 9 is delivered by a pipe
75 25 through a pressure-reducing valve 26 to the rectifying compartment 13 of the column and accumulates about a condenser comprising a number of tubes 27. The liquid overflows through a tube 28 and passes thence
80 downwardly over trays 29 of the usual type employed in rectification columns and is subjected to vapors rising through the column. The rectification of the liquid is thus ac-
85 complished, and as it escapes it becomes more and more impoverished in the least condensible constituent. The liquid accumulates in a container 30 within the column and overflows into the compartment 11.

The entering gas with the vapors rising
90 from the compartment 9 passes through a plurality of tubes 31 which are surrounded by liquid accumulated as described in the container 30 and compartment 11 and by
95 liquid which is supplied to the compartment 10 as hereinafter described. The refrigerative effect of this liquid causes selective liquefaction of the entering gases and results in the separation of the liquid which flows
100 backwardly into the compartment 9 from an unliquefied residue which continues through the tubes 31 to a header 32 with which the tubes communicate. This unliquefied residue escapes through a pipe 33 and is delivered to a header 34 communicating with
105 the tubes 27 of the condenser. These tubes are surrounded by liquid, and during the passage of the gas through the tubes it is liquefied and descends into a header 35. A pipe 36 communicating with this header and
110 provided with a valve 37 permits the diversion of a portion of the liquid to the upper part of the rectification compartment 13. This liquid is the "reflux" which flows
115 downwardly over trays 38 of the type usually employed in rectification columns and by contact with the rising vapors is impoverished in the least condensible constituent. The vapors from the compartment 12 enter the compartment 13 through
120 a pipe 39 and thence pass upwardly through the trays 38.

As the result of the operation as described, a liquid and an unliquefied residue are first
125 produced. In the treatment of air the liquid contains substantially all of the oxygen and argon and some of the nitrogen of the air. The unliquefied residue is substantially pure nitrogen. This nitrogen is liquefied and a portion of the liquid is employed as a
130

reflux in the second or rectification step of the process which results in the separation of liquid produced by selective liquefaction into a gaseous effluent which is also substantially pure nitrogen and a liquid containing a large proportion of oxygen, e. g., 93%, or more, and substantially all of the argon originally present in the air. The effluent escapes through a pipe 40 and after utilization as a refrigerant as hereinafter described it may be employed as desired or rejected.

To accomplish the separation of the rich oxygen liquid containing argon into its constituents, an auxiliary column 41 is employed. This column comprises a shell divided by partitions 42, 43, 44 and 45 into a lower compartment 46, a liquid oxygen compartment 47, a vaporizer compartment 48, a rectifying compartment 49 and a condenser compartment 50. That portion of the liquid in the compartment 11 of the primary column which is not vaporized therein is delivered by a pipe 51 controlled by a valve 52 to an intermediate point of the rectifying compartment 49 and flows downwardly therein over trays 53 of the kind usually employed in rectification columns wherein it is subjected to the rectifying action of the vapors rising through the column. The downwardly flowing liquid passes through a pipe 54 into the compartment 48 and overflows through a pipe 55 into the compartment 47. During its passage the liquid is freed from the more readily vaporizable constituents, for example, nitrogen and argon, and the liquid accumulating in the compartment 47 is substantially pure oxygen. This liquid is returned through a pipe 56 to the compartment 10 of the primary column where it is vaporized by the passage of gas through the tubes 31.

The vapors rising through the rectifying compartment 49 are subjected in the upper portion thereof to liquid supplied as hereinafter described and flowing downwardly over trays 57 of the usual kind employed in rectification columns. The vapors which contain a high percentage of argon with some oxygen and nitrogen pass upwardly through tubes 58 which extend through the condenser compartment 50. This compartment is filled with liquid nitrogen delivered through a pipe 59 controlled by a valve 60 from the header 35 of the primary column. The liquid thus supplied is the portion of the liquid which is not employed as "reflux" in the primary column. The liquid in the condenser 50 is vaporized and the vapors passing through the tubes 58 are concurrently subjected to selective liquefaction resulting in the separation of the more readily condensible constituent, oxygen, for example, which returns through the tubes into the compartment 49. The remaining va-

pors escape through a pipe 61 to an exchanger 62. A portion of the vapors from the column 41 may be diverted through a pipe 63 without passing through the tubes 58 of the condenser and likewise delivered to the exchanger 62. The pipe 61 communicates with a compartment 64 at the end of the exchanger and the pipe 63 likewise communicates with a compartment 65. Tubes 66 and 67 connect these compartments to corresponding compartments 68 and 69 at the opposite end of the exchanger. A pipe 70 controlled by a valve 71 delivers the gas entering the compartment 68 to a gasometer 72 in which it is stored, this gas being one of the products of the operation, for example, argon. The gas entering the compartment 69 passes through a pipe 73 to a compressor 74 where it is recompressed and cooled by the usual intercoolers. From the compressor the gas passes through a pipe 75 to the exchanger 62 wherein it circulates about the tubes 66 and 67, being cooled by the gases passing through these tubes. By means of a by-pass 61' and valves 62' and 63' the operator may cause all of the vapors from the column 41 to pass through the tubes 58 and thence to the compressor 74, or all of the vapors may be directed through the tubes 58 to the gasometer 72. Thus when the valves 63' and 73 are closed and the valve 62' is open all of the vapors will be recompressed. If the valves 62' and 63' are closed and the valve 71 is open, all of the vapors will pass to the gasometer. Normally the valve 62' is closed and the valves 63' and 71 are open to permit operation as hereinbefore described.

From the exchanger 62 the cooled gas is delivered by a pipe 76 to an auxiliary liquefier 77 and passes therein about a plurality of tubes 78 through which a cooling agent such as the effluent from the primary column is caused to travel. For this purpose a pipe 79 connects the pipe 40 with a compartment 80 at the end of the liquefier 77. After passing through the pipe 78 the gas is delivered through a compartment 81 and pipe 82. The gas joins the vapor formed in the condenser 50 which escapes through a pipe 83, and the combined gases are delivered to a compartment 84 at the end of the liquefier 19.

The gas which is cooled by its passage through the auxiliary liquefier 77 and partially or wholly liquefied is delivered through a pipe 85 to the lower compartment 46 of the auxiliary column. It passes thence upwardly through tubes 87 which are surrounded by the bodies of liquid in the compartments 47 and 48. Selective liquefaction of the gas in the tubes results, and the liquid flows backwardly into the compartment 46 and is thence delivered through a pipe 88 and pressure-reducing valve 89 to the upper

part of the rectification compartment 49 as hereinbefore described. This liquid is substantially free from the most volatile constituent, for example, nitrogen, which passes in an unliquefied state through the tubes 87 to a header 90 and thence through a pipe 91 controlled by a valve 92 to the upper part of the rectification compartment 13 of the primary column.

Oxygen vapors formed in the compartment 10 of the primary column are delivered through a pipe 93, and a portion thereof may be returned through a pipe 94 to the compartment 47 of the auxiliary column. These vapors, together with the vapors formed in the compartment, pass upwardly through a pipe 95 and mingle with the vapors formed in the compartment 48. The vapors rise through the descending liquid to accomplish rectification thereof. The result of the operation as described is the gradual enrichment of the gas circulating in the auxiliary cycle until it includes a high proportion of argon and is suitable for withdrawal as a product of the operation. This withdrawal is preferably accomplished after the gas has passed through the condenser 50 and is thus freed from some or all of the oxygen which may still be included therein. It is possible in this manner to obtain argon substantially free from nitrogen and containing a very low proportion of oxygen and at the same time to materially reduce the amount of work necessary in the auxiliary cycle by limiting the amount of gas which is recompressed therein. The other product of the auxiliary column is substantially pure oxygen which is returned to the primary column in liquid form as hereinbefore described to be vaporized therein.

This oxygen vapor is withdrawn through a pipe 96 controlled by a valve 97 and is delivered to a compartment 98 at one end of the liquefier 19. It passes through the tubes 21 of the liquefier to a compartment 99 at the opposite end and thence through a pipe 100 to a compartment 101 of an exchanger 102. The gas delivered to the compartment 84 of the liquefier passes through tubes 20 therein to a compartment 103 at the opposite end of the liquefier and thence through a pipe 104 to a compartment 105. A by-pass 106 controlled by a valve 107 permits delivery of the effluent from the primary column to the compartment 84 of the liquefier. This is particularly useful in starting the apparatus or in operating it independently of the auxiliary column.

The exchanger 102 comprises a shell with a plurality of tubes 108 and 109 through which gas passes from the compartments 101 and 105 to corresponding compartments 110 and 111 at the opposite end of the exchanger. From these compartments the

gases escape through pipes 112 and 113 which may communicate with storage receptacles or may deliver the gas to the atmosphere, depending upon whether it is to be used or rejected.

The gas entering the system is introduced through a pipe 114 to the exchanger 102 and passes about baffles 115 in contact with the tubes 108 and 109. The gas is thus cooled and is delivered through a pipe 116 with which pipes 14 and 18 communicate. It is understood that prior to its introduction to the exchanger 102 the gas entering the system has been compressed and cooled in the usual manner.

The purpose of the invention has been discussed heretofore but attention is particularly directed to the utilization of the liquid produced in the tubes 27 for cooling the tubes 58 of the condenser and to the advantages of this mode of operation as hereinbefore enumerated. It is to be observed that details as to the amount of gas passing through this condenser or circulated independently thereof may be varied and that this utilization of the liquid from the primary column for refrigeration purposes may be carried out in connection with various modifications of the system which are described herein for illustrative purposes and without departing from the invention as herein set forth and claimed.

I claim:—

1. A method of separating the constituents of gaseous mixtures, which comprises subjecting the compressed and cooled mixture to selective liquefaction to separate a liquid enriched in the less volatile constituents and a residual gas, liquefying the residual gas, rectifying the liquid enriched in the less volatile constituents with a portion of the liquefied residual gas, subjecting the liquid product of the rectification to an auxiliary rectification, and cooling the gaseous product of the auxiliary rectification by heat exchange with the balance of the liquefied residual gas to separate the least volatile constituent therefrom.

2. A method of separating the constituents of gaseous mixtures, which comprises subjecting the compressed and cooled mixture to selective liquefaction to separate a liquid enriched in the less volatile constituents and a residual gas, liquefying the residual gas by heat exchange with the liquid enriched in the less volatile constituents, rectifying the liquid enriched in the less volatile constituents with a portion of the liquefied residual gas, subjecting the liquid product of the rectification to an auxiliary rectification and cooling the gaseous product of the auxiliary rectification by heat exchange with the balance of the liquefied residual gas to separate the least volatile constituent therefrom.

3. A method of separating the constituents of gaseous mixtures, which comprises subjecting the compressed and cooled mixture to selective liquefaction to separate a liquid enriched in the less volatile constituents and a residual gas, liquefying the residual gas, rectifying the liquid enriched in the less volatile constituents with a portion of the liquefied residual gas, subjecting the liquid product of the rectification to an auxiliary rectification, and cooling a portion of the gaseous product of the auxiliary rectification by heat exchange with the balance of the liquefied residual gas to separate the least volatile constituent therefrom.
4. A method of separating the constituents of gaseous mixtures, which comprises subjecting the compressed and cooled mixture to selective liquefaction to separate a liquid enriched in the less volatile constituents and a residual gas, liquefying the residual gas, rectifying the liquid enriched in the less volatile constituents with a portion of the liquefied residual gas, subjecting the liquid product of the rectification to an auxiliary rectification, cooling a portion of the gaseous product of the auxiliary rectification by heat exchange with the balance of the liquefied residual gas to separate the least volatile constituent therefrom, reliquefying the remainder of the gaseous product of the auxiliary rectification and returning it for further rectification.
5. A method of separating the constituents of gaseous mixtures, which comprises subjecting the compressed and cooled mixture to selective liquefaction to separate a liquid enriched in the less volatile constituents and a residual gas, liquefying the residual gas, rectifying the liquid enriched in the less volatile constituents with a portion of the liquefied residual gas, subjecting the liquid product of the rectification to an auxiliary rectification, cooling a portion of the gaseous product of the auxiliary rectification by heat exchange with the balance of the liquefied residual gas to separate the least volatile constituent therefrom, recompressing and reliquefying the remainder of the gaseous product of the auxiliary rectification and returning it for further rectification.
6. A method of separating the constituents of gaseous mixtures, which comprises subjecting the compressed and cooled mixture to selective liquefaction to separate a liquid enriched in the less volatile constituents and a residual gas, liquefying the residual gas, rectifying the liquid enriched in the less volatile constituent with a portion of the liquefied residual gas and utilizing the remainder of the liquefied residual gas as a refrigerant in the further separation of the constituents of the liquid produced by the first rectification.
7. A method of separating the constituents of gaseous mixtures, which comprises subjecting the compressed and cooled mixture to selective liquefaction to separate a liquid enriched in the less volatile constituents and a residual gas, liquefying the residual gas by heat exchange with the liquid enriched in the less volatile constituents, rectifying the liquid enriched in the less volatile constituent with a portion of the liquefied residual gas and utilizing the remainder of the liquefied residual gas as a refrigerant in the further separation of the constituents of the liquid produced by the first rectification.
8. A method of separating the constituents of gaseous mixtures, which comprises subjecting the compressed and cooled mixture to selective liquefaction to separate a liquid enriched in the less volatile constituents and a residual gas, liquefying the residual gas, rectifying the liquid enriched in the less volatile constituent with a portion of the liquefied residual gas, and utilizing the remainder of the liquefied residual gas as a refrigerant in the further separation of the constituents of the liquid produced by the first rectification after the latter has been subjected to a second rectification.
9. A method of separating the constituents of gaseous mixtures, which comprises subjecting the liquid and vapors containing said constituents to rectification, compressing a portion of the gaseous effluent of the rectification, cooling it to separate one of the constituents from the liquid which is thereby impoverished in that constituent, utilizing the impoverished liquid as a rectifying agent in said rectification, subjecting the remainder of the effluent to cooling to liquefy and separate the least volatile constituent and withdrawing the portion of the effluent thus purified.
10. A method of separating the constituents of gaseous mixtures, which comprises subjecting the liquid and vapors containing said constituents to rectification, compressing a portion of the gaseous effluent of the rectification, cooling it to separate one of the constituents from the liquid which is thereby impoverished in that constituent, utilizing the impoverished liquid as a rectifying agent in said rectification, subjecting the remainder of the effluent to cooling by heat exchange with an evaporating liquid to liquefy and separate the least volatile constituent and withdrawing the portion of the effluent thus purified.
11. A method of separating the constituents of gaseous mixtures, which comprises subjecting the liquid and vapors containing said constituents to rectification, compressing a portion of the gaseous effluent of the rectification, cooling it to separate one of the constituents from the liquid which is

thereby impoverished in that constituent, utilizing the impoverished liquid as a rectifying agent in said rectification, subjecting the remainder of the effluent to cooling by heat exchange with an evaporating liquid to liquefy and separate the least volatile constituent, withdrawing the portion of the effluent thus purified and supplying the liquid employed in cooling the effluent from a separate liquefaction cycle in which the liquid and vapors which are subjected to rectification are likewise produced.

12. A method of separating the constituents of ternary gaseous mixtures, which comprises subjecting a liquid and its vapors produced from said mixture and containing chiefly the least volatile constituent to rectification by means of a liquid containing another and more volatile constituent, withdrawing the gaseous effluent of this rectification, separating a portion of the most volatile constituent from said gaseous effluent by liquefying the remaining gas, utilizing this liquid in the rectification and when the effluent has been sufficiently enriched in the constituent of intermediate volatility subjecting a portion thereof to cooling to separate the least volatile constituent therefrom.

13. A method of separating the constituents of ternary gaseous mixtures, which comprises subjecting a liquid and its vapors produced from said mixture and containing chiefly the least volatile constituent to rectification by means of a liquid containing another and more volatile constituent, withdrawing the gaseous effluent of this rectification, separating a portion of the most volatile constituent from said gaseous effluent by liquefying the remaining gas, utilizing this liquid in the rectification and when the effluent has been sufficiently enriched in the constituent of intermediate volatility subjecting a portion thereof to cooling by heat interchange with a liquid to separate the least volatile constituent therefrom.

14. A method of recovering argon from air, which comprises subjecting a liquid and vapors containing oxygen, nitrogen and argon to continuing rectification, compressing the gaseous effluent, cooling it to separate a liquid containing chiefly argon and oxygen and a gaseous residue containing practically all of the nitrogen, using the last-named liquid in said rectification and when the effluent has been sufficiently enriched in argon subjecting a portion thereof to cooling to separate oxygen therefrom.

15. A method of recovering argon from air, which comprises subjecting a liquid and vapors containing oxygen, nitrogen and argon to continuing rectification, compressing the gaseous effluent, cooling it to separate a liquid containing chiefly argon and

oxygen and a gaseous residue containing practically all of the nitrogen, using the last-named liquid in said rectification and when the effluent has been sufficiently enriched in argon subjecting a portion thereof to cooling by heat exchange with liquid nitrogen to separate oxygen therefrom.

16. A method of separating the constituents of gaseous mixtures, which comprises subjecting the compressed and cooled mixture to selective liquefaction to separate a liquid enriched in the less volatile constituents and a residual gas, liquefying the residual gas, rectifying the liquid enriched in the less volatile constituents with a portion of the liquefied residual gas, subjecting the liquid product of the rectification to an auxiliary rectification, cooling the gaseous product of the auxiliary rectification by heat interchange with the balance of the liquefied residual gas to separate the least volatile constituent therefrom, recompressing the remainder of the gaseous product of the auxiliary rectification, subjecting it to a partial liquefaction to separate the most volatile constituent therefrom and utilizing the liquid thus obtained in the auxiliary rectification.

17. A method of recovering argon from air, which comprises subjecting a liquid and vapors containing oxygen, nitrogen and argon to continuing rectification, cooling the gaseous effluent by heat interchange with a liquid, compressing the gaseous effluent, subjecting the compressed effluent to a liquefaction operation to separate a liquid containing chiefly argon and oxygen and a gaseous residue containing practically all of the nitrogen, and using the last named liquid in said rectification.

18. A method of separating the constituents of ternary gaseous mixtures, which comprises subjecting a liquid and its vapors produced from said mixture and containing chiefly the least volatile constituent to rectification by means of a liquid containing another and more volatile constituent, subjecting the gaseous effluent of this rectification to heat-interchange with a liquid, thereby separating additional quantities of the least volatile constituent, compressing the remainder of the effluent, subjecting it to a liquefaction operation to separate a liquid containing the two less volatile constituents and a residual gas consisting of the most volatile constituent and utilizing this liquid in said rectification.

19. In an apparatus for separating the constituents of gaseous mixtures, the combination of means for rectifying a liquid and vapors containing said constituents, means for recompressing and cooling a portion of the gaseous effluent from the rectification to separate one of the constituents

as a gaseous residue and to produce a liquid for use in said rectification, and separate means for subjecting the remainder of the effluent to cooling to liquefy another constituent.

20. In an apparatus for separating the constituents of gaseous mixtures, the combination of means for rectifying a liquid and vapors containing said constituents, means for recompressing and cooling a portion of the gaseous effluent from the rectification to separate one of the constituents as a gaseous residue and to produce a liquid for use in said rectification, and a backward-return condenser above the rectifying means to cool the remainder of the ef-

fluent by heat-exchange with a liquid whereby another constituent is liquefied.

21. In an apparatus for separating the constituents of gaseous mixtures, the combination of means for rectifying a liquid and vapors containing said constituents, means for subjecting the effluent from the rectification to heat-interchange with a liquid, and separate means for recompressing and cooling the effluent to separate one of the constituents as a gaseous residue and to produce a liquid for use in said rectification.

In testimony whereof I affix my signature.

CLAUDE C. VAN NUYS.