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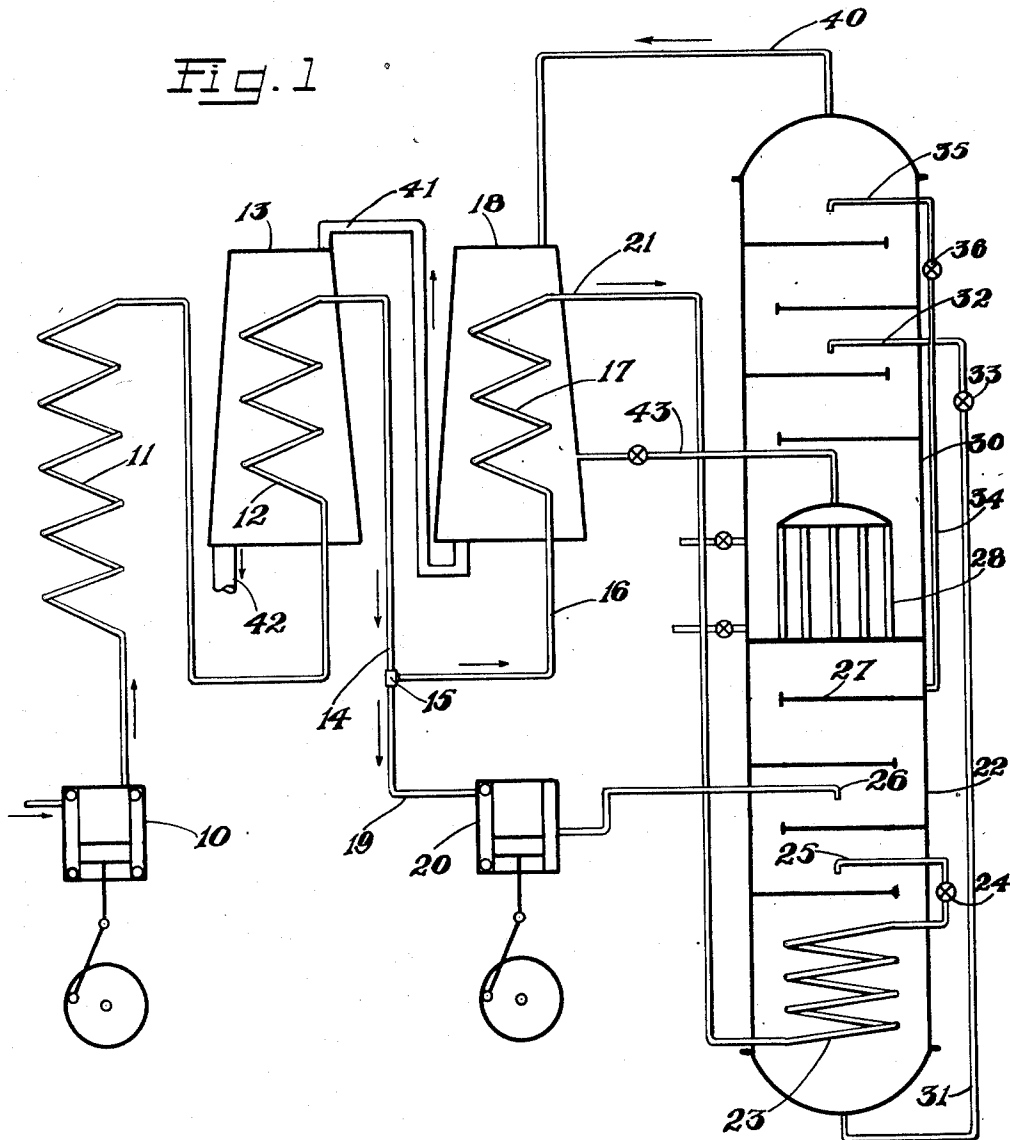
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METHOD AND APPARATUS FOR LIQUEFYING AND SEPARATING GASEOUS MIXTURES

Filed Sept. 10, 1932

3 Sheets-Sheet 1



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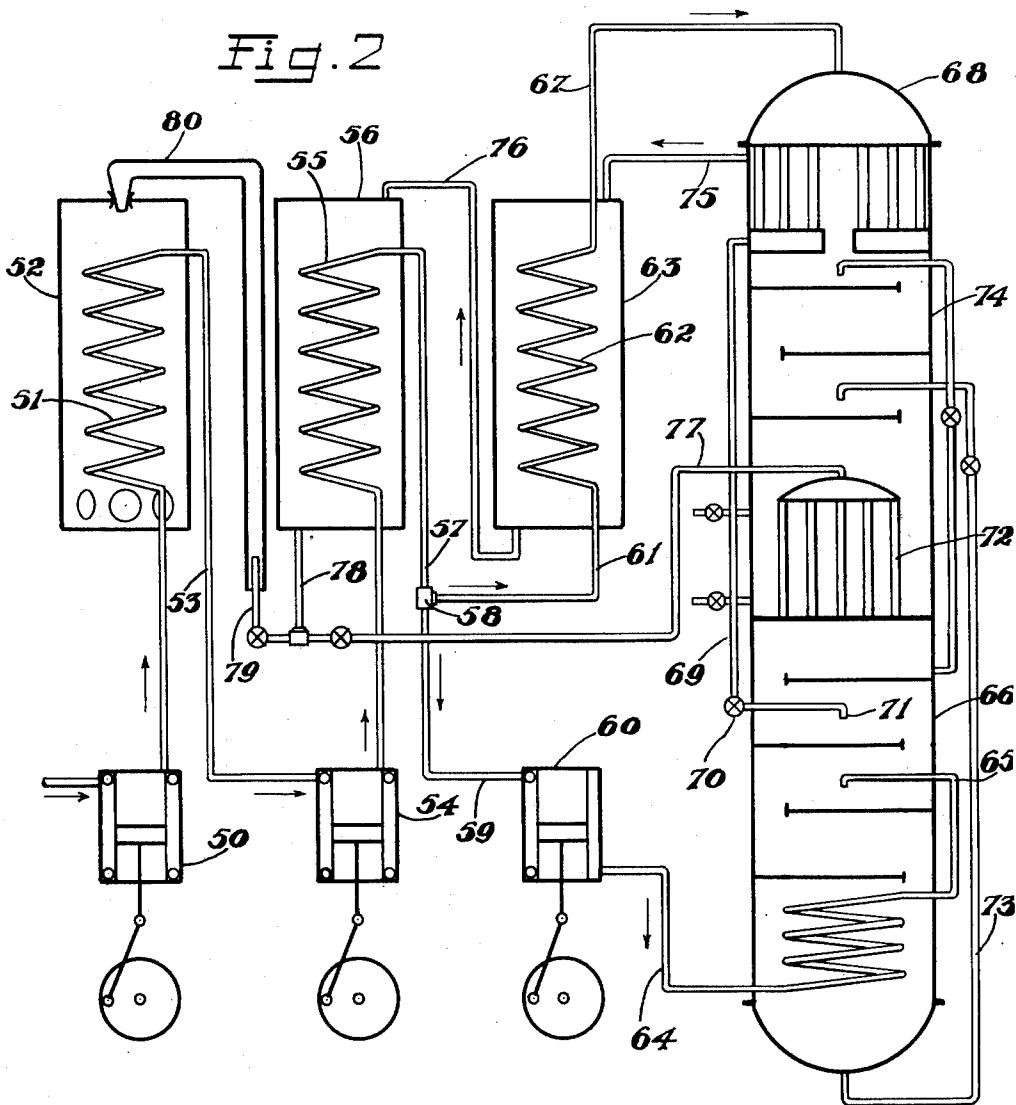
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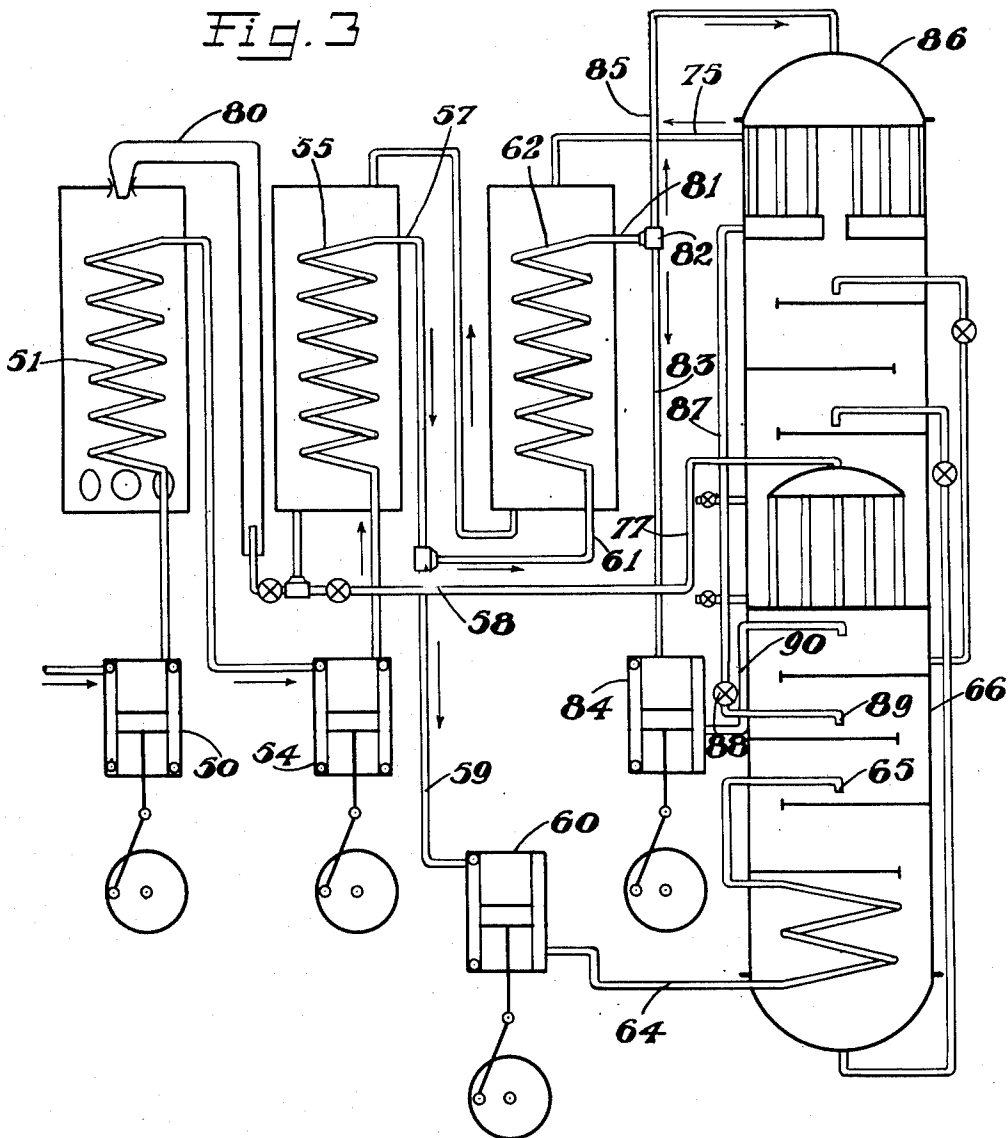
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METHOD AND APPARATUS FOR LIQUEFY-
ING AND SEPARATING GASEOUS MIX-
TURESWilliam W. Fraser, New York, N. Y., assignor to
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6 Claims. (Cl. 62—175.5)

This invention relates to a method and apparatus for liquefying and separating gaseous mixtures into their constituents. More particularly, it relates to a method and apparatus for liquefying air and separating it into constituents in a manner which yields oxygen of relatively high degrees of purity.

The invention has for its object generally to provide an improved method for liquefying gases and separating the same into constituents together with suitable apparatus for carrying out the same, whereby separated gas products of relatively high degrees of purity are obtained with a relatively small expenditure of energy.

More specifically, it is an object to provide an improved heat cycle for the operation of gas liquefying and rectifying apparatus, which permits starting of the apparatus and obtaining the desired gas products in substantial quantities in relatively short periods of time, in a manner having relatively high overall thermal efficiencies.

It is also an object to provide a heat cycle for liquefying and rectifying apparatus which utilizes substantially all the refrigerating effect of the waste products from the rectifying apparatus employed to produce liquefaction and separation of gases.

Other objects of the invention will in part be obvious and will in part appear hereinafter.

The invention accordingly comprises the several steps and the relation of one or more of such steps with respect to each of the others, and the apparatus embodying features of construction, combinations of elements and arrangement of parts which are adapted to effect such steps, all as exemplified in the following detailed disclosure, and the scope of the application of which will be indicated in the claims.

For a fuller understanding of the nature and objects of the invention, reference should be had to the following detailed description taken in connection with the accompanying drawings, in which:

Fig. 1 is a diagrammatic view of apparatus, mainly illustrated in section, which exemplifies suitable apparatus and means for carrying out a process in accordance with the invention;

Fig. 2 and Fig. 3 are similar views showing modified forms of apparatus adapted for the practice of the invention, but in which the principle thereof is carried out with greater degrees of refinement than in the apparatus of Fig. 1.

The method and apparatus herein provided incorporate the principles of liquefaction of gases devised by Linde and employ the expansion of

a gaseous mixture through an expansion valve into a suitable separating chamber, for example the receiving chamber of a rectifying column whereby there is obtained liquefaction of the gaseous mixture together with simultaneous separation of the same into constituents. It is also proposed to utilize the refrigerating effect produced by expanding the gaseous mixture in such a manner as to cause the same to do external work. This is commonly achieved by means of an expansion engine. In the method and apparatus of the present invention these two principles of refrigeration and liquefaction are advantageously combined, portions of the gaseous mixture to be treated being cooled simultaneously by the two expansion principles, after which they are introduced together into the rectifying column.

Heretofore, it has been proposed to utilize more or less of the refrigerating effect of waste products from the rectifying apparatus in order to conserve the energy input in the heat cycle doing the work of liquefying and separating into constituents the gas mixture.

In the practice of the present invention, it is proposed to utilize not only a combination of the two principles of expansion in obtaining liquefaction, but to practice rectification in such a manner as to attain any desired degree of separation of the gaseous constituents together with substantially complete utilization of the refrigerating effect of the waste products from the rectifying apparatus. Hence, substantially all the energy input is conserved within the heat cycle through which the portions of the gaseous mixture being treated pass.

In effecting utilization of the refrigerating effect of the waste products from gas-liquefying or rectifying apparatus, it is customary to pass the cold waste products through heat exchangers which have heated portions of the gas mixture to be treated passing in countercurrent fashion in heat exchanging relation with the waste products. The heat exchangers commonly employed comprise a chamber generally provided with baffles through which are passed tubes carrying the cooling medium, the product to be cooled passing about the baffles and over the tubes in countercurrents; the relation in the exchangers, however, of the hot and cold mediums may be reversed. In order to utilize the refrigerating effect of such cooling medium efficiently, it is essential that the temperature difference between the cooling medium and the medium to be cooled shall be uniform. In the practice of the present in-

vention, uniformity is insured by effecting heat exchange in a plurality of stages which not only achieves uniform distribution of the temperature gradient, but also insures a uniform distribution of the pressure drop, whereby uniform activity at all points in the passage of the heat exchanging mediums is attained and the cooling effect of the cooling medium substantially completely utilized. It is hence important that where the cooling medium is initially under pressure, that the same shall be properly expanded during its passage in order to utilize the cooling effect made possible by the remnant energy of the waste products initially under pressure. It is here contemplated, though not necessary, that all waste products from the liquefying and rectifying apparatus shall be utilized in this manner.

Referring now to the drawings and particularly to Fig. 1, 10 denotes a compressor which compresses the gaseous mixture to be treated to a relatively high pressure. Where air is the gaseous mixture being treated, this initial pressure may be, for example, one hundred atmospheres; the air to be compressed is preferably initially purified and dehumidified by suitable means not here shown in the interests of clearness in the drawings, but are well known in the art. The compressed gas is passed from the compressor 10 to a suitable cooling means 11, for example a coil or radiator exposed for cooling by the atmosphere. After traversing this coil, the mixture is passed to the inner conduit or coil 12 of a heat exchanger 13. Conduit 14 here provides the exit from coil 12, and leads to a branch point 15, where the now cooled compressed medium is separated into two portions; one portion being led by way of the conduit 16 to an inner conduit or coil 17 of heat exchanger 18; the other portion being led by way of conduit 19 to an expansion engine 20. The cooled portion of the compressed medium which leaves the heat exchanger 18 passes by way of the exit conduit 21 to a receiving chamber 22 of the high pressure column of a multi-column rectifying apparatus. The conduit 21 is here indicated as including additional cooling means, in the form of a coil 23 disposed in the base of the column, by which the compressed medium is brought to the temperature not greatly different from that of liquefaction prior to its introduction and expansion into the receiving chamber 22. The discharge from the coil 23 is through an expansion valve 24 and a distributing nozzle 25 disposed within the chamber.

The portion of the compressed medium which has been caused to expand in the expansion engine 20, when properly cooled, is also introduced into the receiving chamber 22 by means of a suitable distributing nozzle here shown at 26. In the arrangement shown, it is seen that the gas portions discharging into the chamber 22 from the nozzles 25 and 26 become converted into liquid and vapor, the liquid gravitating to the lower portion of the column where a pool of condensate collects and may submerge the coil 23. This column is also shown as provided with suitable dephlegmating means, for example perforated partitions 27. The column terminates in a condenser 28 which insures the backward return of condensate by the recondensation of vapors arising in the column. In this manner, there is insured the countercurrent washing by the returned condensate of the vapors arising by distillation from the bottom of the column. These vapors, it will be seen, are those of the more

volatile fraction or constituent of lowest boiling point in the gas mixture liquefied in the chamber 22, so that the liquid which collects in the bottom of the column becomes gradually enriched in the less volatile constituent, the degree of enrichment being determined by the rate at which liquid is withdrawn from the column. In the practical operation of a column where air is liquefied in the chamber 22, the liquid which collects in the bottom of the column may attain a composition containing 40% or more of liquid oxygen.

The liquid withdrawn from the high pressure column is passed to the receiving chamber 30 of the low pressure column superposed above the high pressure column. This is here achieved by providing a conduit 31 leading from the bottom of chamber 22 to a distributing nozzle 32 in the chamber 30. The exit of fluid from the nozzle 32 is controlled by means of an expansion valve 33. Where liquid condensate of the less volatile constituent collects in the chamber 22, for example as shown on the top dephlegmating tray of the group at 27, this may be likewise passed into the low pressure column by means of a conduit 34 having a distributing nozzle 35 in the chamber 30, and provided with a controlling valve 36. This latter rectifying column subjects the gaseous mixture liquefied therein to further distillation and counter-current washing, whereby a gas product of still greater purity than had in the first column separates out. The purified liquid product may be withdrawn from the lower end of chamber 30. Thus it will be seen that where air is being treated, a liquid containing a very high percentage of oxygen collects about the condenser 28, which latter supplies the heat for distilling off a gas fraction, representing mainly nitrogen, from the low pressure column. Substantially pure gaseous oxygen collects in the lower part of chamber 30 above the liquid and may be withdrawn from a point in suitable proximity to the pool of liquid that collects therein.

The cold uncondensed vapors are withdrawn from the top of the chamber 30 by way of the discharge conduit 40. This conduit is arranged to supply the cooling medium to the exchanger 18, the entrance of the cooling medium being arranged to pass in countercurrent fashion over the coil 17 in the exchanger 18. From the other end of the exchanger 18, the cooled products which have now been partially warmed, are passed by means of a conduit 41 into the exchanger 13, where they are passed in similar countercurrent fashion over the coil 12. In both these exchangers the passage of the cooling medium is preferably arranged to take place accompanied by expansion. This is accomplished by providing increasing volume accompanying the passage of the medium, and is here indicated by the taper shown on the exchangers 13 and 18. The passage of the cooling medium is thus arranged to enter progressively a larger and larger space until the medium discharges at a pressure relatively close to atmospheric through a discharge passage 42.

In the operation of the apparatus above described, it is seen that the compressor 10 accomplishes the step of compressing the gaseous mixture to the required pressure, after which cooling steps are practiced which reduce the compressed mixture to substantially atmospheric temperature. It is then separated into parts, one of which is conveyed to the expansion engine 20, where the step of expansion by doing external work is performed on the portion prior to its

introduction in a cooled state in the receiving chamber 22. The other portion of the compressed mixture which is led from the conduit 14 by the conduit 16 is further cooled in the heat exchanger 18, where it is brought into heat exchanging relation with the waste product led from the top of the rectifying column by conduit 40. This step of cooling a portion of the compressed mixture to a relatively low temperature is accomplished in such a manner as to utilize the greater portion of the refrigerating effect of the waste products. The final cooling of this portion of mixture by its passage through coil 23 and expansion valve 24 is such as to bring it substantially to the temperature of liquefaction for the pressure obtaining in the chamber 22.

In the high pressure column of the rectifying apparatus, it is seen that the vapors and liquid introduced into the pressure chamber are subject to fractional distillation and countercurrent washing, whereby the more volatile constituents rise and are removed as vapors from the top of the chamber while the less volatile constituent is carried down and collects as a liquid in the bottom of the chamber. While the liquid which collects in the bottom of chamber 22 will have the amount of the less volatile constituent continually increased by the practice of fractional distillation, it is seen that withdrawals from this chamber determine a certain maximum content thereof, the rate of withdrawal being here regulated by the valve 33, which also serves as an expansion valve for the introduction of fluid into the chamber 30 of the low pressure column. The liquid thus passed from the high pressure column to the low pressure column is subject to further fractional distillation and countercurrent washing until a gas product of the desired purity is attained. The rate of distillation in the low pressure column is dependent upon the temperature difference between the liquid in chamber 30 and the condenser 28, which difference is determined by the respective pressure conditions in the chambers 22 and 30. The conditions in the former may be controlled in part by the rate at which the more volatile constituent is withdrawn from the interior of condenser 28, since this constituent comprises the fraction from which heat is extracted with greatest difficulty. Means are accordingly provided to control such withdrawal. In the arrangement shown, this means comprises a conduit 43 leading from the condenser dome and arranged to discharge into the exchanger 18 at a point which is substantially at the temperature of this last withdrawn product and passes in countercurrent fashion about the coil 17. The passage of this cold medium is thus parallel with that introduced by the conduit 43. The refrigerating effect of this last withdrawn waste product is thus also utilized in the practice of the method of the present invention.

In the form of apparatus shown in Fig. 2, the compression is accomplished in a plurality of stages which are correlated with the stages of cooling arranged to utilize to the fullest practical extent the refrigerating effect of the waste products from the rectifying apparatus here employed. A compressor 50 is shown as accomplishing the first stage of compression, from which it discharges into an inner conduit or coil 51 of an exchanger 52 and then discharges into a conduit 53 leading to a second stage compressor 54, from which it passes into an inner conduit or coil 55 of an exchanger 56. From this second

exchanger, a conduit 57 leads to a point 58 where the compressed medium is divided, one part passing by way of the conduit 59 to an expansion engine 60, the other part passing by way of conduit 61 to an inner conduit or coil 62 of a heat exchanger 63. The portion of the medium which is expanded by doing external work in the expansion engine 60 is passed by way of conduit 64 to a nozzle 65 arranged to discharge in a receiving chamber 66 of the high pressure column of a multi-column rectifying apparatus. The other portion is passed from the coil 62 by way of conduit 67 into the precooling means 68, which may be in the form of a heat exchanger in the top of the rectifying apparatus. From this exchanger, the conduit 69 leads by way of an expansion valve 70 to a distributing nozzle 71 in the chamber 66. This chamber has a condenser 72 at its upper end and is arranged to collect condensate at its lower end. The liquid collected is arranged to be withdrawn by means of a conduit 73 leading from the bottom of chamber 66 and passing into receiving chamber 74 of a low pressure column superposed above the high pressure column in the rectifying apparatus.

A conduit 75 is arranged to withdraw the waste products from the upper end of the rectifying apparatus, these products having first passed through the exchanger 68, are then introduced into the exchanger 63, where they pass in countercurrent fashion over the coil 62 and have exit by way of conduit 76. This latter conduit passes these products on to exchanger 56 where they pass in countercurrent fashion over the coil 55. A conduit 77 is arranged to withdraw undensified products from the dome of the condenser 72. This conduit is arranged to join with a conduit 78, which provides for the exit of the waste products from the heat exchanger 56. The commingled waste products from the conduits 77 and 78 are then passed preferably by means of an injector or other expansion device 79 into the enlarged conduit 80, which further cools the waste products by releasing the energy remaining in them. The expanded products are then passed in heat exchanging relation over the coil 51 of the initial exchanger 52. This exchanger is substantially at atmospheric pressure and the waste products passing from the conduit 80 produce a cooling draft which effects the cooling performed intermediate the low pressure and the high pressure stages of compression practiced in this form of the invention.

The operation of this species is seen to be substantially the same as that shown in Fig. 1, except that the initial compression is here effected in two stages and there are an equal number of stages of cooling associated with the stages of compression, the initial cooling stage utilizing that portion of the refrigerating effect which is most difficult to utilize, namely that of the waste products when at a very low pressure and at relatively high temperature, it having been previously heated in the other exchangers to a point not greatly different from that represented by the initial heat input of the compression machines. Thus, it is seen that by the practice of the cooling of the compressed mixture to a temperature in the neighborhood of that of the atmosphere, in a plurality of stages, a heat cycle is accomplished whereby the necessary initial cooling is accomplished at very little cost and a very efficient heat cycle results.

In the arrangement shown in Fig. 3, the compression is not only accomplished in a plurality

of stages which are correlated with the cooling stages, but the expansion is also accomplished in a plurality of stages. Here, compressors 50 and 54 accomplish compression by stages, the same as shown in Fig. 2, these compressors discharging respectively into coils 51 and 55. The compressed mixture, in consequence, travels successively through these coils, emerging from the second coil by way of conduit 57, which leads to a branch point 58 where it is divided into parts, one of which is led by conduit 59 to expansion engine 60; the second being led by conduit 61 to coil 62 of a third heat exchanger.

The first portion, expanded by the engine 60, is passed by conduit 64 to a distributing nozzle 65 into a receiving chamber 66 of the high pressure column of the rectifying apparatus, the same as shown in Fig. 2. The other portion emerging from coil 62 is treated differently in this form of device from that shown in Fig. 2. Here, the exit conduit 81 of the coil 62 leads to another branch point 82, from which a conduit 83 leads a portion to a second expansion engine 84, while a conduit 85 leads the other portion to a pre-cooling means 86; this latter may be in the form of a heat exchanger that supplies cooled medium by way of conduit 87 to expansion valve 88 and distributing nozzle 89 in the chamber 66. The portion from the expansion engine 84 is preferably introduced in the chamber 66 by means of a distributing nozzle 90. It is contemplated, however, that such further expanded medium may be introduced at other points of the rectifying column, since this portion is mainly used to accelerate the initial obtaining of liquid in the rectifying apparatus.

In this latter form of device, the waste products are withdrawn from the rectifying apparatus through conduits 75 and 77, as shown in Fig. 2 and a final cooling effect produced by expansion in the conduit 80, which supplies a cooling medium for the initial heat exchanger.

While the rectifying apparatus here employed is shown in the form of a two-column apparatus which is a thoroughly practical form of device for the liquefaction and separation of air into constituents, and from which an oxygen product may be obtained from the low pressure column, which is of 98% or higher purity, it is evident that, by the use of three or more columns, substantially any desired degree of purity may be attained in the product desired. It will also be seen that by the use of such multi-column apparatus, the initial pressure at which the waste products having the refrigerating effect supplied to the exchangers is reduced. By the step of cooling in a plurality of stages, as here proposed, it is seen, moreover, that the low pressure waste products may be utilized to the fullest practical extent and thereby obtain the benefit of substantially their full refrigerating effect.

Since certain changes in carrying out the above process and in the constructions set forth, which embody the invention, may be made without departing from its scope, it is intended that all matter contained in the above description or shown in the accompanying drawings shall be interpreted as illustrative and not in a limiting sense.

Having described my invention, what I claim as new and desire to secure by Letters Patent, is:

1. In apparatus for separating gaseous mixtures, the combination with a multi-column rectifying apparatus having different pressures in the columns arranged for the distilling off of gas fractions, of a multi-stage compressing means arranged to compress the whole of the gas mixture

to be separated in successive stages to a relatively high degree of compression, a plurality of interchangers arranged to receive and cool the compressed gas mixture as it passes from stage to stage whereby a succession of cooling stages is provided, conduit means for receiving said highly compressed gas mixture and dividing the same into two parts, an expansion engine for receiving and expanding one of said parts and passing the same to a high pressure column of said rectifying apparatus, an additional interchanger for receiving and cooling said second part of the highly compressed gas mixture, valved expansion means for discharging said second part into a column of said rectifying apparatus, conduit means for withdrawing a cold waste product from another column of said rectifying apparatus and passing the same through said interchangers, and means for further cooling said waste product by causing the same to expand progressively and do internal work and utilizing said cooling effect in at least one of said interchangers.

2. In apparatus for separating gaseous mixtures the combination with a rectifying apparatus having a high pressure column and a low pressure column for the distilling off of gas fractions, of a two-stage compressor arranged to compress the whole of the gas mixture to be prepared successively to a relatively high degree of compression, cooling means arranged to effect inter-stage cooling of said compressed gas mixture as it passes from stage to stage whereby a progressive cooling effect correlated with said compression stages is provided, conduit means for receiving all of said highly compressed gaseous mixture and dividing the same into two parts, an expansion engine for expanding one of said parts and passing the same to said high pressure column, additional cooling means for receiving and cooling said second part, valved expansion means for discharging said second cooled part into said high pressure column, conduit means for withdrawing a cold waste product from at least one column of said rectifying apparatus and passing the same to at least one stage of said cooling means, means for further cooling said withdrawn waste product by causing the same to expand progressively and do internal work, and means for utilizing said cooling effect in at least one of said cooling means.

3. The method of separating gaseous mixtures into constituents by liquefaction and rectification which comprises compressing the mixture to a relatively high pressure, cooling the compressed mixture to successively lower temperatures in a plurality of stages, dividing said mixture at a point intermediate said cooling stages into a plurality of portions, expanding, collecting and liquefying said portions, conjointly rectifying said liquefied portions successively in stages at high and low pressures, separating and withdrawing relatively uncondensable fractions from each of said high and low pressure rectifying stages, immediately thereafter effecting throttling expansion of the fraction separated from said high pressure stage to enhance the cooling effect, passing the fraction separated from the low pressure rectifying stage in heat exchanging relation with the compressed mixture in one of said cooling stages, admixing the throttled fraction with said low pressure fraction, and passing the resulting mixture in heat exchanging relation with the compressed mixture in another of said stages.

4. The method of separating gaseous mixtures into constituents by liquefaction and rectification which comprises compressing the mixture suc-

- cessively in stages to a relatively high pressure, initially cooling the compressed mixture in stages located between desired compression stages, dividing said mixture at the terminus of said initial
- 5 cooling stages into a plurality of portions, finally cooling one of said portions in at least one additional cooling stage and then expanding the same by throttling expansion, engine expanding the remaining portion, collecting and liquefying said
- 10 portions, conjointly rectifying said liquefied portions successively in stages at high and low pressures, separating and withdrawing relatively uncondensable fractions from each of said high and low pressure rectifying stages, immediately there-
- 15 after effecting throttling expansion of the fraction separated from said high pressure stage to enhance the cooling effect, passing the fraction separated from the low pressure rectifying stage with progressive expansion in countercurrent heat
- 20 exchanging relation with the compressed mixture in said initial and final cooling stages, and applying directly the cooling effect of said throttled fraction to a predetermined initial cooling stage by admixing the same with said low pressure
- 25 fraction, whereby said fractions jointly cool said compressed mixture and conserve the refrigeration thereof.
5. In apparatus for separating gaseous mixtures into constituents, the combination with a
- 30 two-column rectifying apparatus having columns operated respectively at high and low pressures and yielding gas fractions, of means for compressing the mixture to a desired high pressure, a plurality of interchangers, each having a passage for
- 35 compressed mixture and a passage for cooling medium arranged to pass and cool the compressed mixture successively, means for expanding the cooled mixture and supplying the same to the high pressure column of said apparatus, conduits for
- 40 separating and withdrawing relatively uncondensable fractions respectively from each of said high and low pressure columns, throttling expansion means located in the gas fraction withdrawal conduit of said high pressure column for expanding the separated fraction immediately
- upon withdrawal, conduit means for supplying the fraction withdrawn from said low pressure column to the cooling medium passage of each of said interchangers successively in countercurrent relation to the passage of said compressed mixture, and additional conduit means for supplying the throttled fraction to said cooling passages of certain of said interchangers at a point nearer the outlet of the cooling passages of said series than where said low pressure fraction is admitted.
6. The method of separating gaseous mixtures into constituents by liquefaction and rectification which comprises compressing the input gaseous mixture to a relatively high pressure, cooling such compressed mixture to successively lower temperatures in a plurality of stages, expanding, collecting and liquefying said cooled mixture, rectifying said liquefied mixture successively in stages at high and low pressures, separating and withdrawing relatively uncondensable fractions from each of said rectifying stages, immediately thereafter reducing the temperature and pressure of the fraction separated from the high pressure stage by throttling expansion, applying the low pressure fraction to accomplish at least a part of the cooling of the input compressed mixture, admixing said expanded fraction with said low pressure fraction at a point later in the outgoing direction than where said low pressure fraction is admitted to said cooling operation and where its temperature on expansion corresponds substantially with that of said low pressure fraction, and immediately using the resultant mixture in heat exchanging relation to accomplish a further part of said cooling of the input compressed mixture.
- WILLIAM W. FRASER.

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