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C. C. VAN NUYS

LIQUEFACTION OF GASES

Filed March 19, 1921

2 Sheets-Sheet 1

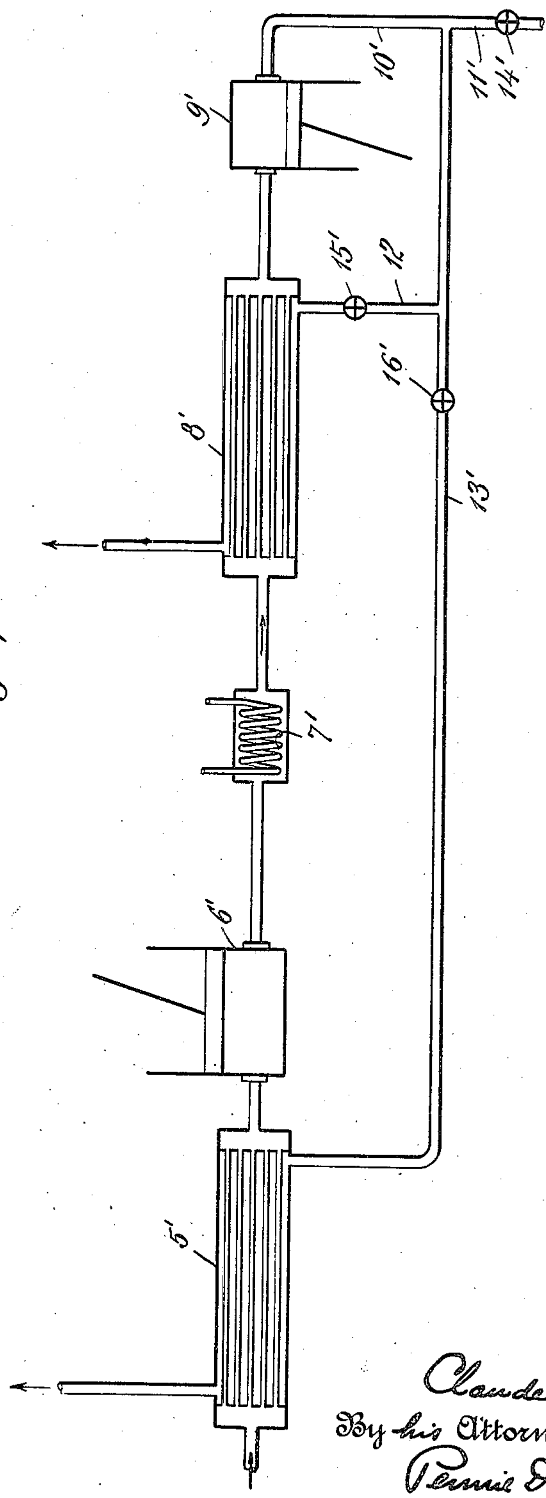

Fig. 1.

Inventor

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By his Attorneys

Pennie Davis Marvin & Edmonds

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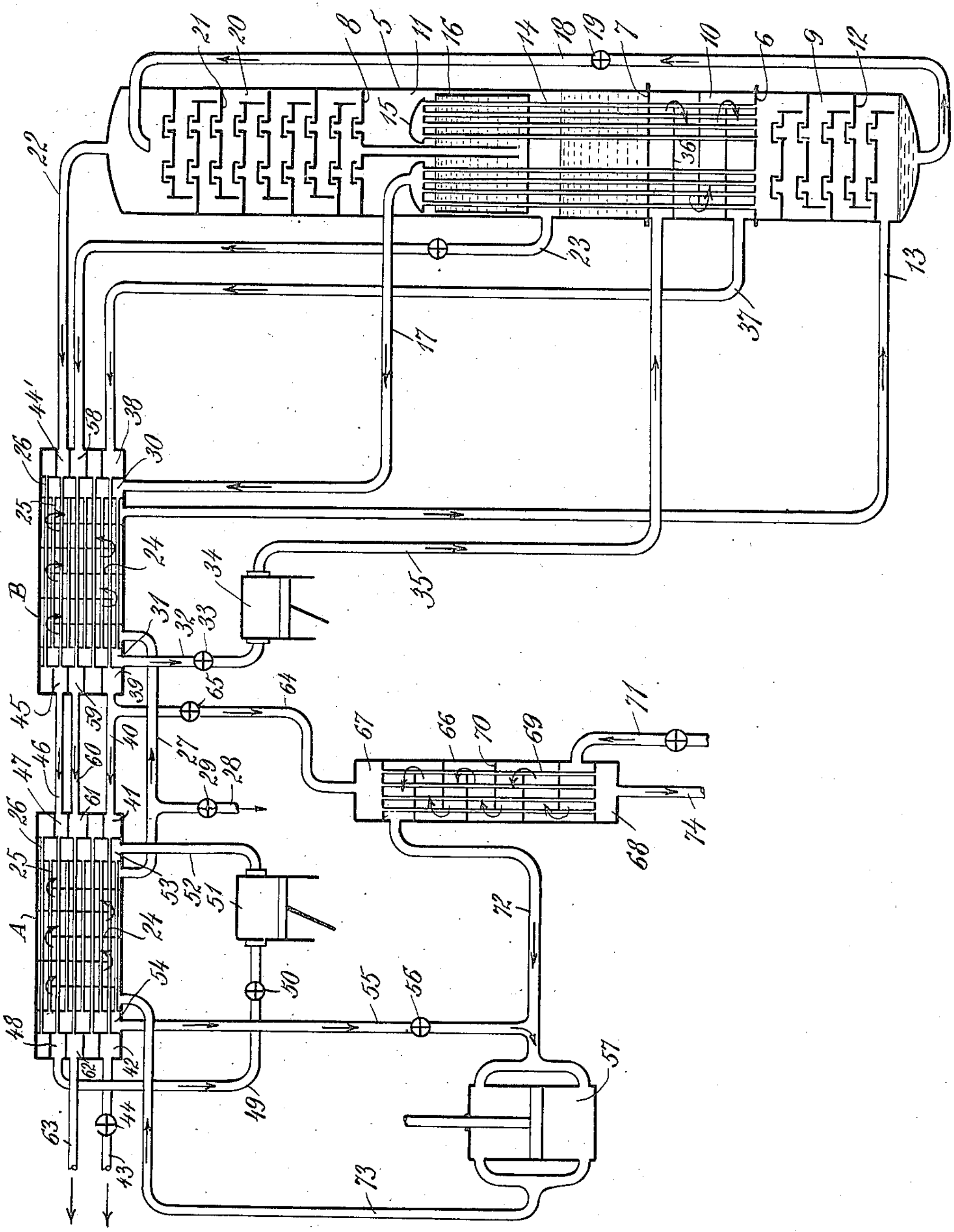

Fig. 2.

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UNITED STATES PATENT OFFICE.

CLAUDE C. VAN NUYS, OF CRANFORD, NEW JERSEY, ASSIGNOR TO AIR REDUCTION COMPANY, INCORPORATED, A CORPORATION OF NEW YORK.

LIQUEFACTION OF GASES.

Application filed March 19, 1921. Serial No. 453,577.

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 the Liquefaction of Gases; 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 gaseous mixtures and the separation of the constituents thereof for the purpose of recovering such constituents in a theoretically and commercially economical manner. The commercial recovery of the elements of gaseous mixtures, particularly of air, has attained considerable importance in the arts, but the practice heretofore has been relatively wasteful from a thermodynamic standpoint, and the utilization of liquefaction methods has doubtless been greatly retarded by the lack of knowledge of fundamental principles and of the best methods of procedure to accomplish the desired result.

All liquefaction methods have depended more or less for refrigeration on the so-called Joule-Thompson effect, resulting from the throttling of a gas or liquid under pressure. The introduction of expansion engines and expansion with external work resulted in some improvement, but even this advance was not accompanied by marked increase in efficiency.

The object of this invention is the accomplishment of a material economy in the liquefaction operation through a reduction of the work required for initial compression of gases and the recovery of work from the products of the operation.

A further object of the invention is the provision of a method for quickly and positively regulating in an economical manner the refrigerative effect of a liquefaction cycle, avoiding as far as possible all thermodynamic irreversible operations therein, such as "throttling" of high pressure fluid.

Another object of the invention is the provision of a method of and apparatus for initially cooling the incoming gas before compression thereof to relatively low temperatures.

Further objects and advantages of the invention will be apparent as it is better understood by reference to the following specification and accompanying drawing. In the drawing:

Fig. 1 is a diagram intended to facilitate the explanation of the principle involved, and

Fig. 2 is a diagrammatic illustration of an apparatus adapted for use in practicing the invention.

In methods of liquefaction as heretofore practiced, it has been customary to subject the gas to compression in one or more stages, and to subsequently extract the heat of compression by suitable cooling devices. In such methods, the incoming gas enters the compressors at substantially atmospheric temperature and the attempt is made to perform the compression as nearly isothermally as possible. But, on account of difficulty of cooling the gas in the cylinder during the compression stroke, a substantial rise of temperature in the gas during the stroke is always experienced, requiring the expenditure of substantial amounts of energy in excess of that necessary for an isothermal compression. Substantially all of the energy expended in compressing the gas appears as heat, which is manifested by a rise in temperature, and this compression heat is subsequently removed from the high pressure gas by means of circulating water in suitable inter- and after-coolers. It is plain that any rise of temperature in the gas during the compression stroke is particularly bad from the standpoint of economy of operation, since this rise of temperature causes the pressure of the gas to be higher. Thus the energy necessarily expended in compressing between given initial and final volumes is increased and this excess of energy applied tends in turn to still further raise the temperature. Any method which tends to cause the energy applied in compression to be more nearly equal that of an isothermal compression for the same volume ratio will thus reduce the amount of heat necessarily eliminated in the inter- and after-coolers.

In any refrigeration cycle, the heat eliminated in the inter- and after-coolers includes not only that due to mechanical imperfections in the system, but also the in-leakage of external heat to the cycle and the heat equivalent of the work necessary to be done in order to absorb this in-leakage of heat at the relatively low temperatures prevailing therein, and to reject it at the relatively high temperature of the atmosphere. This will be more clearly apparent from a consideration of Fig. 1 of the drawing.

In Fig. 1, 5′ is a counter current temperature interchanger through which the gas passes on its way to the compressor 6′. An after-cooler 7′ is connected to the discharge side of the compressor. The compression heat is removed therein by circulating water. A high pressure temperature interchanger 8′ receives the high pressure gases leaving the aftercooler 7′ on their way to an expansion engine 9′. A pipe 10′ is connected to the engine 9′ and is provided with outlet 11′ and branches 12′ and 13′ connected respectively to the interchangers 8′ and 5′. Valves 14′, 15′ and 16′, which may be opened or closed as desired, control the flow of gas.

Let us assume that compressor 6′ and expansion engine 9′ are mechanically perfect and that valves 15′ and 16′ are closed, valve 14′ open, water cooler 7′ shut off, and that the whole system is perfectly insulated. Under these conditions, the compression in compressor 6′ is perfectly adiabatic, and the gas enters engine 9′ at the temperature at which it left compressor 6′. Then the energy expended in compressor 6′ is exactly recovered in expansion engine 9′ and the gas leaving through the valve 14′ is at the same temperature and pressure as that entering interchanger 5′.

Next, assume that water cooler 7′ is placed in operation and that it surrounds the compressor 6′ and is effective during the compression stroke so that the compression in compressor 6′ is perfectly isothermal. Under these conditions, the gas enters expansion engine 9′ at the temperature of the surrounding atmosphere, and the work W_2 recovered therein is less than the work W_1 expended in compressor 6′, the difference $W_1—W_2$ being exactly equal to the work necessary to reversibly cool the exhaust of engine 9′ below the temperature of the atmosphere down to the final temperature attained therein.

Now, close valve 14′ and open valve 15′. The gas then entering expansion engine 9′ has a temperature below that of the surrounding atmosphere, and the work recovered in engine 9′ begins to progressively decrease, i. e., $W_1—W_2$, which is the net expenditure of work in the cycle, increases, always being equal to the work of reversibly lowering the temperature of the exhaust of engine 9′ to the value attained therein, neglecting the small effect of possible irreversible heat transfer in interchanger 8′, due to variation of the specific heat of the fluid at the lower pressure of the engine exhaust. Working with an actual gas and assuming that the system is perfectly insulated, the temperature will be lowered until a portion of the high pressure gas will become liquefied in interchanger 8′.

In any actual liquefaction cycle, the only refrigerative effect necessary after the initial cooling period, is that required to absorb the in-leakage of external heat at the low temperatures at which it is received and reject it at the relatively high temperatures of the surrounding medium, i. e., the atmosphere, and in addition, an amount of refrigerative effect sufficient to perform the necessary work of separation of the constituent gases.

When the amount of liquid obtained is sufficient for the requirements of the subsequent separation by rectification of the constituents of the liquid, any excess refrigerative effect results in an accumulation of liquid which will not be evaporated by the incoming high pressure fluid. When this condition prevails, the refrigerative effect must be reduced in order to avoid an undesirable accumulation of liquid in the liquid reservoirs of the cycle.

Under starting conditions, there must be available enough refrigerative effect in the cycle to initially cool down the apparatus employed as well as the circulating fluid, and, in order to make this starting period reasonably short, the excess refrigerative effect necessary during that period must be considerable, i. e., the quantity $W_1—W_2$ must be relatively large. This result is generally attained by making the initial pressure high enough to supply the necessary available energy and thus ensure the final equilibrium condition in a reasonably short time. As soon as this condition is reached, that is, when the cycle has become sufficiently cooled down, the available work $W_1—W_2$ must then be decreased to a value such that the equivalent refrigerative effect is just sufficient to overcome the in-leakage of external heat and perform the necessary work of separation.

Logically, the proper method to accomplish this reduction of available energy present would be to decrease the pressure at which the cycle operates, i. e., to decrease the work W_1 supplied, but, on account of the difficulty of thus regulating the refrigerative effect in the cycle in a sufficiently rapid and positive manner, it is necessary in methods of liquefaction as heretofore practiced, to resort also to another expedient. The desired result is generally accomplished by throttling, to lower pressure, considerable amounts of the high pressure fluid before it enters the expansion engine. This results in the dissipation of considerable amounts of available energy contained in the high pressure fluid and accounts for a serious loss of efficiency in such systems.

Again referring to Fig. 1, let us assume that the refrigerative effect $W_1—W_2$ is sufficiently large so that the initial cooling of the system has been accomplished in a reasonably short time, and that we then wish to reduce the refrigerative effect without lowering appreciably the pressure attained in compressor 6′. Consider the effect of partially closing valve 15′ and partially opening valve 16′. Under this condition, all of the low pressure exhaust of engine 9′ no longer flows through interchanger 8′. A portion of it circulates in interchanger 5′ coming into indirect contact therein with the incoming low pressure gas before it enters compressor 6′. The high pressure fluid entering engine 9′ will thus be higher in temperature than it would be if all of the low temperature exhaust of engine 9′ were allowed to transverse exchanger 8′, and the exhaust of engine 9′ will also be at a higher temperature. At the same time, the effect of the low temperature exhaust traversing exchanger 5′ is to substantially reduce the temperature of the fluid entering compressor 6′ below that of the surrounding atmosphere, and thus to reduce the amount of compression heat necessarily eliminated in water cooler 7′.

It is clear that under these conditions the actual operation of compressor 6′ will be more nearly equivalent to that of an isothermal compression and thus the thermodynamic efficiency of compressor 6′ will be substantially increased. It is also evident that the amount of fluid entering compressor 6′ per stroke will be increased and thus the amount of fluid circulating in the system, so that engine 9′ must operate at a higher speed. This method of regulating the refrigerative effect also has the advantage of making it possible, in systems for treating atmospheric air, to remove substantial amounts of moisture from the incoming fluid previous to its compression because of the cooling effect of that portion of the engine exhaust circulating in interchanger 5′. While it is true that there will be considerable irreversible heat transfer in interchangers 5′ and 8′ between the incoming fluid and the exhaust of engine 5′ because of the fact that this heat transfer in either interchanger is from all the incoming fluid to only a portion of the outgoing exhaust of engine 9′, still the improved performance of compressor 6′, as well as the advantage for an air system of the possible elimination of a portion of the moisture contained in exchanger 5′, will offset the dissipation of available energy resulting from the irreversible heat transfer. By manipulating valves 15′ and 16′, a rapid and positive method is provided for regulating the refrigerative effect in the system according to the needs thereof and to enable the operator to closely follow the variations therein due to variable operating conditions.

The application of the invention will be more readily understood by reference to Fig. 2 of the drawing, in which 5 indicates a column divided by partitions 6, 7 and 8 into compartments 9, 10 and 11. In the compartment 9, a plurality of trays 12 are arranged for the purpose of permitting partial rectification of liquid descending through the compartment by direct contact with the incoming gaseous mixture delivered through the pipe 13 to the compartment 9. From this compartment, the gaseous mixture travels upwardly through a plurality of tubes 14 which pass successively through the compartments 10 and 11 to a head 15, in which the tubes terminate. In thus passing through the tubes, the gaseous mixture comes first into indirect contact with cold gaseous products of the liquefaction operation in the compartment 10 and cold liquid products of the liquefaction operation in the compartment 11 and the receptacle 16 disposed therein. This liquid is maintained at a pressure lower than that of the gaseous mixture in the tubes, so that the latter is cooled and partially liquefied by evaporation of the liquid surrounding the tubes. The liquid product in the tubes descends therein and is progressively enriched under the principle of "backward return" until it reaches the trays 12 in the compartment 9, where it is subject to partial rectification with further enrichment in the less vaporizable constituent, while the more vaporizable constituent is carried along by the gaseous mixture. In this manner, it is possible to obtain a liquid having upward to 47% of oxygen, for example, if the mixture treated is atmospheric air, and the balance of the gaseous mixture is delivered from the head 15 through a pipe 17.

The liquid accumulating in the compartment 9 is delivered through a pipe 18, having a pressure reducing valve 19 to the top of a rectifier 20 which forms an extension of the column above the partition 8. The rectifier is provided with the usual trays 21 over which the liquid descends in contact with vapors rising from the compartment 11 for the purpose of separating the more volatile constituent from the liquid with progressive enrichment thereof in the less volatile constituent which descends into the compartment 11.

The arrangement described insures the production of a liquid for delivery to the chamber 11, which substantially consists of the less volatile constituent, while the effluent escaping through the pipe 22 has a composition substantially of the original mixture if the invention is applied to the separation of the binary gaseous mixture. If more than two constituents are present in the gaseous mixture, as for example, in atmospheric air containing argon with other and rarer gases, the operation may be so regulated that the argon will follow the liquid into the compartment 11, while the remaining rare gases will be delivered with the nitrogen as an effluent. Vapor released in the compartment 11 is withdrawn through a pipe 23, and consists substantially of pure oxygen in the case assumed.

Since the products of the operation, for example, the residual gas escaping through the pipe 17, the effluent escaping through the pipe 22, and a portion of the product of evaporation in the compartment 11 which escapes through the pipe 23, are relatively cold, it is essential to provide means for transferring this cold to the incoming gaseous mixture, in order that the energy required to produce the cold may be conserved. A suitable exchanger is therefore provided, which preferably consists of a plurality of sections A and B, each having a plurality of baffles 24 about which the incoming gaseous mixture circulates in contact with a plurality of tubes 25 and 26. The sections are connected by a pipe 27 having a purge 28 for the withdrawal of moisture separated in the exchanger, with a valve 29, controlling the escape of condensed moisture. The residual gas is delivered by the pipe 17 to a chamber 30 at the end of the section B of the exchanger and passes thence through tubes 25 to a chamber 31 at the opposite end of the section. The partially warmed gas which is still at the initial pressure of the mixture is delivered by a pipe 32 through a valve 33 to an engine 34 where it is expanded and thereby cooled. The cold gas then passes through a pipe 35 to the chamber 10 of the column and circulates therein about the baffles 36 and around the tubes 14. It escapes through a pipe 37 to a chamber 38 at the end of the section B of the exchanger. The gas travels through tubes 26 to a chamber 39 at the opposite end of the section. A pipe 40 delivers the gas to a chamber 41 in the section A of the exchanger, whence it passes through tubes 26 to a chamber 42 at the opposite end of the section. A pipe 43, controlled by a valve 44, permits withdrawal of the residual gas for any desired purpose.

The effluent is delivered by the pipe 22 to a chamber 44′ at the end of the section B of the exchanger and travels thence through tubes 26, chamber 45, pipe 46, chamber 47, tubes 26 in the section A to a chamber 48, whence it is delivered through a pipe 49, controlled by a valve 50, to an engine 51, where it is expanded with the recovery of work and consequent cooling. The cold product is delivered through a pipe 52 to the chamber 53 in the section A of the exchanger and travels through the tubes 25 therein to the chamber 54, whence it escapes through the pipe 55, controlled by a valve 56, after giving up its cold to the incoming gaseous mixture traveling through the section A, and is mixed with the air entering the compressor 57 for return to the cycle.

The vapor escaping through the pipe 23 is delivered to a chamber 58 at the end of the section B of the exchanger, and passes thence through tubes 26 to a chamber 59, thence through a pipe 60 to a chamber 61 in the section A of the exchanger. The vapor then passes through the tubes 26 to a chamber 62 and is delivered through a pipe 63.

The primary purpose of the present invention is the provision of suitable regulation of the operation of a liquefaction system by distribution of the surplus cold to permit the best utilization thereof and increase the efficiency of the operation, incidentally preventing all unnecessary throttling of high pressure fluid and reducing the amount of energy required to be introduced to the system to a minimum. In carrying out the invention, the surplus cold as hereinbefore indicated, is carried with a portion of the residual gas from the pipe 40 through pipe 64, controlled by a valve 65 to an exchanger 66 which may comprise a casing with chambers 67 and 68 at its opposite ends and tubes 69 enclosed within the shell to permit the passage of the gas in the tubes 69 through the exchanger in indirect contact with the incoming gaseous mixture circulating about the baffles 70. The gaseous mixture enters through a pipe 71, circulates about the tubes 69 and is discharged through a pipe 72 to a compressor 57, where the mixture is mixed with the effluent from the pipe 55 and raised to the desired pressure necessary for the accomplishment of the purpose intended. Thence the gas travels through a pipe 73 to the section A of the primary exchanger. The products traveling through the exchanger 66 are delivered through a pipe 74 and may be conveyed to suitable storage receptacles where the gas may be maintained under pressure or otherwise until used.

As will be readily understood from the preceding explanation, the surplus cold carried by the gas in the pipe 64 is transferred to the incoming gaseous mixture and to the extent that this gas is cooled and therefore reduced in volume, the energy necessary for compression is correspondingly reduced, it being possible to compress a larger volume of gas measured at atmospheric temperature and pressure and to raise this gas to the desired pressure with less expenditure of energy than would be otherwise required. The proportion of cold thus transferred to the incoming gas before compression is readily controlled by manipulating the valve 65. Thus, in starting the apparatus, valve 65 is closed because all of the surplus cold is required to bring the temperature of the apparatus and of the gases therein to the desired low temperature to insure liquefaction. When the system has been established and is properly functioning, the cold accumulated exceeds that required to maintain the low temperature, and, by adjusting the valve 65, this cold is transferred to the incoming gaseous mixture before compression thereof and with the advantages hereinbefore enumerated. The required adjustment will vary from time to time and the simple regulation of the operation through manipulation of the valve constitutes one of the particularly desirable features of the invention. It will be noted, moreover, that the effluent is returned to the cycle for further separation so that there are no losses due to the compression of large volumes of gas which are compressed and thereafter discharged without separation as is usual in systems of liquefaction and separation as heretofore practiced.

In addition to the desirable regulation and reduction of the energy required, which is accomplished through the operation of the invention hereinbefore decribed, it is to be noted that the expansion engines are each adapted for the recovery of a considerable proportion of the initial energy expended in compressing the gaseous mixture and that the energy thus recovered may be utilized in compressing further quantities of the gaseous mixture. It is possible to thus recover and utilize sufficient energy so that only such additional energy need be added to the system as is required by mechanical loss, heat leakage and the energy actually expended in separating the constituents of the gaseous mixture.

From the foregoing, it will be clearly apparent that a method and apparatus have been devised, wherein several desirable results are accomplished in a liquefaction system, and that it is possible through the application of the invention to separate the constituents of gaseous mixtures in a more economical manner than has been possible heretofore. It is to be understood that the apparatus is not illustrated so far as its details will be clearly apparent to those skilled in the art and that such details as well as changes in the method may be introduced so far as such changes are within the scope of the accompanying claims without departing from the invention or sacrificing the advantages enumerated herein.

I claim:

1. In the liquefaction and separation of constituents of gaseous mixtures, a method which comprises subjecting the mixture to compression and subsequently to a liquefaction operation, thereby separating the mixture into a plurality of fractions containing the desired constituents and regulating said operation by utilizing a variable portion of a cold fraction to cool the gaseous mixture prior to compression.

2. In the liquefaction and separation of constituents of gaseous mixtures, a method which comprises subjecting the mixture to compression and subsequently to a liquefaction operation, thereby separating the mixture into a plurality of fractions containing the desired constituents expanding one of the fractions and regulating said operation by utilizing a variable portion of the cold fraction after expansion to cool the gaseous mixture prior to compression.

3. In the liquefaction and separation of constituents of gaseous mixtures, a method which comprises subjecting the mixture to compression and subsequently to a liquefaction operation, thereby separating the mixture into a plurality of fractions containing the desired constituents, utilizing a portion of one of the fractions to cool the mixture after compression, thereby maintaining the low temperature necessary for the operation and regulating said operation by utilizing the balance of the cold fraction to cool the gaseous mixture prior to compression.

4. In the liquefaction and separation of constituents of gaseous mixtures, a method which comprises subjecting the mixture to compression and subsequently to a liquefaction operation, thereby separating the mixture into a plurality of fractions containing the desired constituents, expanding one of the fractions, utilizing a portion of the cold expanded fraction to cool the mixture after compression, thereby maintaining the low temperature necessary for the operation, and regulating said operation by utilizing the remaining portion of the cold expanded fraction to cool the gaseous mixture prior to compression.

5. In the liquefaction and separation of the constituents of gaseous mixtures, a method which comprises subjecting the mixture to compression and subsequently to a liquefaction operation, thereby separating the mixture into a plurality of fractions containing the desired constituents, utilizing the cold fractions to cool the mixture after compression thereof, expanding the fractions to recover energy therefrom, and uti-

lizing a portion of the expanded product to cool the mixture after compression, and regulating the operation by utilizing the balance of the expanded product to cool the mixture before compression.

6. In the liquefaction and separation of constituents of gaseous mixtures, a method which comprises subjecting the mixture to compression and subsequently to a liquefaction operation, thereby separating the mixture into a plurality of fractions containing the desired constituents, utilizing the cold fractions simultaneously to cool the mixture after compression, and regulating the operation by cooling the mixture before compression with a variable portion of one of the cold fractions.

7. In the liquefaction and separation of constituents of gaseous mixtures, a method which comprises subjecting the mixture to compression and to a liquefaction operation, thereby separating the mixture into a plurality of fractions containing the desired constituents and regulating the latter operation by utilizing cold fractions to cool the gaseous mixture after compression during the initial stages, and thereafter diverting a variable portion of the cold products to cool the gaseous mixture before compression.

8. In an apparatus for the liquefaction and separation of the constituents of gaseous mixtures, the combination of a compressor, means for liquefying and separating the mixture into fractions, means permitting transfer of cold from the fractions to the mixture after compression, and means for diverting a variable portion of the cold of the fractions to cool the mixture before compression thereof.

9. In an apparatus for the liquefaction and separation of the constituents of gaseous mixtures, the combination of a compressor, means for liquefying and separating the mixture into fractions, means for expanding the fractions, means permitting transfer of cold from the fractions to the mixture after compression, and means for diverting a variable portion of the cold of the fraction to cool the mixture before compression.

10. In an apparatus for the liquefaction and separation of the constituents of gaseous mixtures, the combination of a compressor, means for liquefying and separating the mixture into fractions, and means for maintaining and regulating the operation by selectively applying the cold of the fractions to the mixture before and after compression.

11. In an apparatus for the liquefaction and separation of the constituents of gaseous mixtures, the combination of a compressor, means for liquefying and separating the mixture into fractions, means for expanding the fractions to recover energy therefrom, and means for maintaining and regulating the operation by selectively applying the cold of the fractions to the mixture before and after compression.

12. In an apparatus for the liquefaction and separation of the constituents of gaseous mixtures, the combination of a compressor, means for liquefying and rectifying a portion of the mixture to separate the constituents thereof, means for recovering energy from the gaseous products, and means for maintaining and regulating the operation by selectively applying the cold of the separated constituents to the mixture before and after compression.

In testimony whereof I affix my signature.

CLAUDE C. VAN NUYS.