

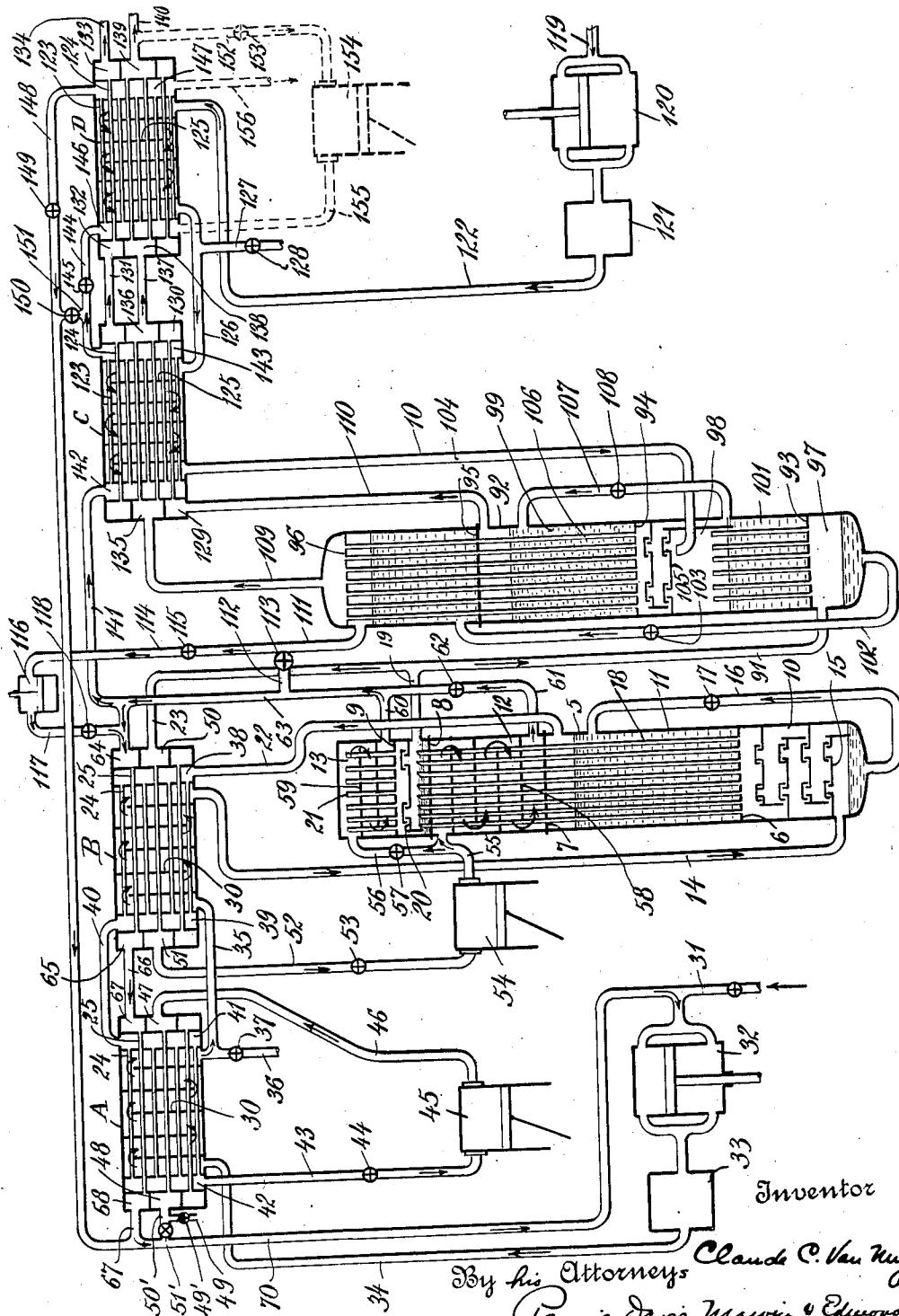
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SEPARATION OF THE CONSTITUENTS OF GASEOUS MIXTURES

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SEPARATION OF THE CONSTITUENTS OF GASEOUS MIXTURES.

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This invention relates to the separation from a gaseous mixture having two or more components of one of these components, the critical temperature of which is lower than any temperature employed in carrying out the method of partial liquefaction whereby the desired result is accomplished. While the method hereinafter described is particularly adaptable for the separation of hydrogen from water-gas or producer-gas, it may be applied with like advantage to the separation of a component of any gaseous mixture, the constituents of which have boiling points differing from one another and which constituents may, with one exception, be liquefied under the conditions hereinafter described.

It has been proposed heretofore to separate hydrogen from water-gas or producer-gas by liquefaction methods involving compressing and cooling the mixture, liquefying as completely as possible the condensable constituents therein by indirect contact with preceding liquefied portions, evaporating at a lower pressure, and expanding the uncondensable residue in an expansion engine or motor for the purpose of producing the refrigerative effect which is essential to the continuation of the method.

Such a method has the disadvantage that the quantity of hydrogen available for expansion with external work is generally insufficient to maintain the necessary refrigeration. It is, moreover, extremely difficult to design an expansion engine or motor to operate satisfactorily upon hydrogen as a working fluid. The tendency of the hydrogen to leak around the piston and through the valves of the engine makes the operation of the expansion engine exceedingly inefficient and the presence of small percentages of carbon monoxide in the unliquefiable hydrogen residue makes such leakage dangerous to operators. In fact, it has been found generally necessary in the operation of the method described, to recompress the separated hydrogen in an auxiliary compressor and to return it to the expansion engine for a second expansion in order to maintain the necessary refrigerative effect, thus introducing additional expense with no compensating advantage.

The operation of this method has also the disadvantage that the lowest temperature

maintained in the cycle during the liquefaction of the incoming gaseous mixture is obtained in the low pressure hydrogen exhaust from the expansion engine and the liquefaction of the last portions of carbon monoxide or other condensable gases are obtained by indirect contact with this gaseous engine exhaust. It is always difficult to maintain constant the lowest temperature in a liquefaction cycle by means of a cold gas. In a method employing a cold gas to maintain the lowest temperature of the cycle if, under variable operating conditions, a change of temperature is produced in the gaseous refrigerant, the effect is almost immediately to cause a variation of the condensable constituents liquefied and thus a variation in the purity of the uncondensable effluent. It is preferable to stabilize the lowest temperature necessary to the operation of the method by maintaining it through evaporation of a body of cold liquid, since under such conditions the effect of any variations of refrigerative effect is only to increase or decrease the mass of cold liquid present, the evaporating temperature being necessarily fixed at any given pressure. With the method hereinbefore described, it is impossible to attain this desirable object, and for this and other reasons enumerated, the method cannot be efficiently operated and consequently has found no broad application in the art.

It is the object of the present invention to overcome the difficulties referred to and to provide a method of efficiently separating an uncondensable residue from a gaseous mixture for the purpose of recovering the constituents forming the residue in a relatively pure condition.

A further object of the invention is the provision of a method of and apparatus for treating gaseous mixtures by liquefaction to separate a desired constituent thereof in an economical and commercially applicable manner.

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 which an apparatus adapted to the accomplishment of the desired object is illustrated. No attempt has been made to illustrate those details of the apparatus which persons

skilled in the art may readily supply. Thus the drawing will serve to assist in the disclosure of the invention without confusing it with the non-essential features which form a part of every liquefaction system.

Let us assume for the purpose of clearly describing the method which is the subject of the present invention that the mixture to be treated is ordinary "blue" water-gas from which the moisture and carbon-dioxide has been completely removed by suitable means so that the mixture to be treated in the liquefaction cycle contains substantially 50% of hydrogen, 1 to 3% of nitrogen and 47 to 49% of carbon monoxide.

A distinguishing feature of the present invention is the fact that instead of expanding the unliquefiable gaseous residue in an engine or motor in order to produce the necessary refrigeration to maintain a continuous cycle, an auxiliary external refrigeration cycle is employed with a working fluid which may be either atmospheric air or a mixture containing substantially greater proportions of nitrogen than is present in atmospheric air.

According to the method herein disclosed, the major portion of the refrigerative effect required in the water-gas cycle is obtained by circulating substantial quantities of pure nitrogen at atmospheric pressure and at a sufficiently low temperature previously obtained by expanding the nitrogen with external work in a suitable engine or turbine in indirect contact and counter-current with the incoming water-gas. The nitrogen thus employed is obtained from the separation of the oxygen-nitrogen mixture which constitutes the working fluid of the auxiliary refrigeration cycle hereinbefore mentioned. The maintenance of the constancy of the lowest temperature employed in the water-gas cycle is not accomplished by means of this cold nitrogen exhaust. For that purpose, pure liquid nitrogen is employed at a pressure of one atmosphere, or, if desirable, at a reduced pressure, this liquid nitrogen also being obtained in the manner hereinafter described from the auxiliary nitrogen-oxygen cycle.

The incoming water-gas mixture, after the major portion of the carbon monoxide has been liquefied and thus separated by indirect contact with preceding portions of liquid carbon monoxide at a pressure of substantially one atmosphere, comes into indirect contact with the cold liquid nitrogen and the last portions of carbon monoxide and the nitrogen remaining in the mixture are thereby removed by liquefaction in the tubes of a selective condenser employing the principle of "backward return". The result of this final selective liquefaction of the gaseous mixture is to produce an uncondensable vapor residue consisting sub-

stantially of hydrogen and containing not more than 1 to 2% of carbon monoxide and a small fraction of a percent of nitrogen. The uncondensable residue and also the carbon monoxide-nitrogen obtained from the vaporization of the liquid produced in the water-gas condenser are brought into indirect contact by means of suitable heat interchangers with the incoming water-gas to assist in the refrigeration thereof as hereinafter described. The pure nitrogen employed as above described to assist the separated water-gas products in cooling the incoming water-gas together with the evaporated liquid nitrogen employed to produce the final condensation of the water-gas cycle and also the remainder of the separated nitrogen employed in the auxiliary cycle, all at a pressure of substantially one atmosphere, are ultimately returned to the main compressor of the auxiliary cycle while the oxygen mixture separated as hereinafter described in that cycle is rejected. Thus, ultimately the result is to attain a working fluid for the auxiliary cycle composed of substantially greater percentages of nitrogen than is contained in atmospheric air. For reasons hereinafter pointed out, the upper limit of this nitrogen content which can possibly be attained is around 93%. Accordingly, it is possible to obtain without rectification a working fluid in the auxiliary cycle, the major portion of which circulates in a closed cycle and from which it is unnecessary to initially remove moisture or carbon dioxide. To this cycled nitrogen sufficient atmospheric air is added to compensate for the oxygen mixture rejected as hereinafter described.

In the auxiliary cycle, the gaseous mixture after compression in the main auxiliary compressor is cooled in a suitable after-cooler and then enters the auxiliary interchangers where it is further cooled by indirect contact with the separated products obtained in that cycle and enters the bottom of a selective tubular condenser consisting of a plurality of vertical tubes and provided at the bottom with several rectification trays of the usual form to assist in obtaining the maximum possible degree of oxygen enrichment in the liquid delivered from the condenser. This maximum possible enrichment is obtained when the liquid condensed at the bottom has a composition necessary for phase equilibrium with the vapor mixture entering the condenser. The uncondensed gaseous residue leaving the top of the auxiliary condenser and consisting substantially of pure nitrogen at the original pressure of the auxiliary compressor, is divided into two parts, the greater of which is expanded with external work in a suitable engine or turbine in order to reduce its temperature to a point permitting its employment to

assist in refrigerating both the water-gas and auxiliary cycles. The second portion of the uncondensed residue leaving the top of the auxiliary condenser is conducted to the bottom of the water-gas condenser where it enters a plurality of closed tubes around which the liquid carbon monoxide which is condensed in the water-gas condenser collects. In vaporizing this liquid carbon monoxide, the nitrogen is liquefied and thereafter the liquid is conducted to the top section of the water-gas condenser where it serves to liquefy the last portions of carbon monoxide and nitrogen in the water-gas. The exhaust leaving the nitrogen expansion engine is divided into two portions. One portion is employed to refrigerate the water-gas cycle as already described, and the other assists in the refrigeration of the auxiliary cycle.

The oxygen-enriched liquid produced at the bottom of the auxiliary condenser is led through a pipe carrying a pressure reducing valve and is delivered to the bottom portion of the space surrounding the tubes of the auxiliary condenser where it is vaporized by condensing the gaseous mixture ascending in these tubes. The vapor thus formed is conducted through the auxiliary interchangers in indirect contact with the incoming fluid therein. The temperature of the product of the oxygen-containing liquid is thus restored to substantially that of the atmosphere, and it is then expanded with external work in a suitable engine or motor in order to lower its temperature to a point permitting its employment to assist in the refrigeration of the warm end of the auxiliary cycle. After such use in which the temperature of the gas is restored to that of the atmosphere, it is rejected. This oxygen-containing product is the only mixture leaving the auxiliary cycle, and it is apparent that its composition must ultimately become identical with that of the air which enters the cycle. Similarly, the composition of the liquid produced at the bottom of the auxiliary condenser must also attain the same composition. This liquid will have a composition such that it is in phase equilibrium with the incoming vapor mixture circulating in the auxiliary cycle and it follows that the composition of the auxiliary working fluid which is compressed in the auxiliary compressor will be that of a vapor having phase equilibrium with liquid air, i. e., substantially 7% oxygen and 93% nitrogen.

In describing the apparatus illustrated in the drawing, attention will first be given to the air or refrigerating cycle which is employed for the purpose of insuring the necessary refrigeration for the water-gas cycle. Referring to the drawing, 5 indicates a column comprising a casing divided by parti-

tions 6, 7, 8 and 9 into a plurality of compartments 10, 11, 12 and 13, the several functions of which will hereinafter appear. The cold compressed gaseous mixture, which, in starting the apparatus, is preferably air is delivered to the chamber 10 through a pipe 14 and passes in the chamber through a plurality of rectification trays 15 of the usual type which support layers of liquid resulting from the selective liquefaction of the incoming gaseous mixture. The trays serve to partially rectify this liquid, reducing the proportion of the more volatile constituent therein and the liquid thus partially rectified is accumulated in the bottom of the chamber 10.

The accumulated liquid is delivered through a pipe 16 and a pressure reducing valve 17 to the chamber 11 where it surrounds a plurality of tubes 18 extending through the partitions 6, 7 and 8 and communicating with the chamber 10. Thus the gaseous mixture entering the chamber 10 is subjected to indirect contact with a surrounding liquid, which, being at a lower pressure, serves to cool and liquefy portions of the gaseous mixture in the tubes. The liquid thus formed flows downwardly in the tubes in direct contact with the incoming gaseous mixture and is enriched in the less volatile constituent under the "backward return" principle. The liquid flowing down the tubes is that which accumulates in the bottom of the chamber 10 and is subsequently delivered to the chamber 11 where it in turn serves as a refrigerating medium.

Continuing through the tubes 18, the gaseous mixture is subjected in the chamber 12 to indirect contact with a cold gaseous medium supplied as hereinafter described to the chamber. The residual gas which leaves the tubes at their upper ends escapes through a pipe 19. A portion of this gas may, however, pass upwardly through a rectification tray 20 which supports a layer of liquid and thence into closed tubes 21 extending into the chamber 13 and surrounded therein by a portion of the cold gaseous medium which is supplied to the chamber 12. The tubes 21 serve to produce a liquid which is delivered onto the tray 20 and thence onto the partition 8 where it surrounds the upper ends of the tubes 18. It will be noted that the ends of the tubes 18 extend slightly above the partition in order to permit the accumulation of a layer of liquid, and the surplus liquid overflows into the pipe 19, and is finally delivered to the water gas column as hereinafter described. This arrangement insures sufficient liquid for the final treatment of the water gas mixture under certain conditions which may prevent the formation of the required amount of liquid in the water gas column. The vapor produced in the chamber 11

by the transfer of cold to the gaseous mixture in the tubes 18 is delivered from the chamber through a pipe 22. Since this gas is very cold, it is employed directly in reducing the temperature of the incoming gaseous mixture before it enters the column 5. For this purpose a portion of the gas escaping through the pipe 19 is also utilized, being withdrawn through a pipe 23. An exchanger is employed for the purpose of effecting the transfer of heat from the incoming mixture to the outgoing gases. This exchanger preferably comprises sections A and B, each consisting of a casing enclosing a plurality of tubes 24 and 25 about which the incoming gaseous mixture is caused to circulate by baffles 30 arranged in each section. Thus the gaseous mixture entering through a pipe 31 is compressed in a compressor 32 cooled in an aftercooler 33 which may be supplied with cooling water, for example, and is delivered through a pipe 34 to the section A of the exchanger. After traveling therethrough in the manner indicated by the arrows, the partially cooled gas is delivered from the section A through a pipe 35 to the section B of the exchanger, and similarly traveling therethrough is delivered by the pipe 14 to the chamber 10 in the column 5. A purge 36 controlled by a valve 37 permits the withdrawal of moisture accumulating in the section A of the exchanger.

The gas escaping from the chamber 11 through the pipe 22 is delivered thereby to a chamber 38 at one end of the section B of the exchanger and travels through the tubes 24 to a chamber 39 at the opposite end of the section B. Thence it is delivered through a pipe 40 to a chamber 41 at the end of the section A of the exchanger. After traveling through the tubes 24, it arrives at a chamber 42 at the end of the section A of the exchanger. When a sufficient volume of the gas is obtained at a suitable pressure, as will occur under certain conditions of operation, the gas is withdrawn from the chamber 42 through a pipe 43 controlled by a valve 44 and is delivered to an expansion engine or turbine 45 where it is expanded with external work and thereby cooled. The cold gas at substantially atmospheric pressure is delivered through a pipe 46 to a chamber 47 at the end of the section A of the exchanger and thence travels through tubes 25 to a chamber 48 at the opposite end of the section A of the exchanger. The gas is thence discharged through a pipe 49 controlled by a valve 49' having given up its cold to the incoming mixture, and being, therefore, of no further utility in the operation. When the composition of the gas is approximately that of air, it may be returned with advan-

tage to the cycle to replace the "make-up" air which is otherwise introduced. This obviates the necessity of "scrubbing" the air entering the cycle. A suitable connection 50' controlled by a valve 51' is provided for this purpose.

That portion of the gaseous effluent from the column 5 which is withdrawn through the pipe 23 is delivered thereby to a chamber 50 at one end of the section B of the exchanger and travels thence through tubes 25 to a chamber 51 at the opposite end of the section B of the exchanger. The gas thus warmed by indirect contact with the incoming gaseous mixture is delivered by a pipe 52 controlled by a valve 53 to an expansion engine or turbine 54, where it is expanded with external work and thereby cooled. The cold gas is delivered through a pipe 55 and a branch 56 thereof controlled by a valve 57 to the chambers 12 and 13 of the column 5, and is caused to circulate therein about the tubes 18 and 21 by baffles 58 and 59 arranged within the chambers. The gas escapes through a pipe 60 and a pipe 61 controlled by a valve 62, and a portion thereof is delivered by a pipe 63 communicating therewith to a chamber 64 at the end of the section B of the exchanger. Thus the gas travels through tubes 25 to a chamber 65 at the opposite end of the section B of the exchanger. A pipe 66 connects the chamber 65 with a chamber 67 at one end of the section A of the exchanger and the gas travels thence through tubes 25 to a chamber 68 at the opposite end of the section A, and is delivered through a pipe 69 to a pipe 70 whereby it is returned to the inlet of the compressor 32. Thus this gas which constitutes the working fluid of the air column is returned to the cycle and may be employed repeatedly without further purification for the removal of moisture and carbon dioxide, thereby saving the expense of this purification. As already pointed out this gas will eventually approximate a composition having 93% nitrogen and 7% oxygen.

A portion of the gas escaping from the column 5 through the pipe 19 is delivered by a pipe 91 to the lower portion of the water-gas column 92, which comprises a shell divided by partitions 93, 94, 95 and 96 into a plurality of chambers 97, 98, 99 and 100. The gas entering the chamber 97 from pipe 91 passes upwardly in closed tubes 101 which are surrounded by a body of liquid accumulating as a result of the selective liquefaction of the gaseous mixture therein. In the specific application of the method under consideration, the gas entering the tubes 101 is substantially pure nitrogen, and the liquid surrounding the tubes is carbon-monoxide and nitrogen derived from the water-gas

which is under treatment. The nitrogen liquefied in the tubes 101 accumulates in the bottom of the chamber 97 and is delivered therefrom together with liquid nitrogen supplied from the column 5 through a pipe 102 having a pressure reducing valve 103 to the chamber 100 at the top of the column 92.

The water-gas after compression and cooling as hereinafter described, is delivered through a pipe 104 to the chamber 98 above the liquid surrounding the tubes 101. It passes upwardly through trays 105 of the usual form, carrying layers of liquid which are produced by the selective liquefaction of the gas in tubes 106, extending through the partitions 94, 95 and 96. In the tubes 106, the gas is subjected first to indirect contact with liquid accumulating in the chamber 98 and delivered to the chamber 99 through a pipe 107 having a pressure reducing valve 108. Thus, the liquid in the chamber 99 is maintained at a pressure somewhat lower than the pressure of the gaseous mixture entering the chamber 98, with the result that heat is transferred thereto from the gaseous mixture in the tubes. The liquid formed in the tubes flows downwardly therein with enrichment in the less volatile constituent under the principle of "backward return", and this liquid which accumulates in the chamber 98 is in turn delivered to the chamber 99. Continuing through the tubes 106, the gaseous mixture is subjected to the low temperature of the body of liquid which is delivered to the chamber 100 through the pipe 102, and substantially all of the constituents of the gaseous mixture with the exception of the hydrogen are liquefied in the tubes 106 and returned therethrough to the chamber 98, while the residual gas escapes through a pipe 109 from the column.

The vapor produced in the chamber 92 by the liquefaction of the gaseous mixture in the tubes 106 escapes through a pipe 110 and the vapor similarly produced in the chamber 100 escapes through a pipe 111. This gas, being substantially nitrogen which is the working fluid of the air cycle, may be delivered through a pipe 112 controlled by a valve 113 to the pipe 63, and thence returned to the compressor 32. Under some conditions, it may be desirable to maintain a reduced pressure in the chamber 100, and consequently a pipe 114 controlled by a valve 115 communicates with the pipe 111 and with a vacuum pump 116. From the vacuum pump the gas is delivered through a pipe 117 controlled by a valve 118 to the pipe 63 and is thence returned to the compressor 32, giving up its cold to the incoming gaseous mixture in the sections A and B of the exchanger.

The products escaping from the column 92 through the pipes 109 and 110 are very cold, and it is desirable, therefore, to transfer the cold to the incoming water-gas mixture. An

exchanger consisting of sections C and D, is therefore employed and the water-gas entering through a pipe 119 is compressed by a compressor 120, cooled in an aftercooler 121 which may be supplied with cooling water, and delivered through a pipe 122 to the section D of the exchanger. The exchanger is provided with tubes 123 and 124, and baffles 125 causing the water-gas to circulate about the tubes. A pipe 126 connects the sections C and D of the exchanger so that the gas traveling therethrough is finally delivered to the pipe 104 previously referred to. A purge 127 provided with a valve 128 permits the withdrawal of liquids condensed in the section D of the exchanger.

The gas escaping from the column 92 through the pipe 110 is delivered thereby to a chamber 129 at one end of the section C of the exchanger and travels through tubes 124 to a chamber 130 at the opposite end of the exchanger. A pipe 131 connects the chamber 130 with a chamber 132 at the end of the section D of the exchanger, and thence the gas travels through tubes 124 to a chamber 133 at the opposite end of the section D from which the gas escapes through a pipe 134. The gas may be delivered thereby to a suitable storage receptacle, and used, for example, in superheating the steam which is utilized in the production of water gas.

The gas, for example hydrogen, escaping from the column 92 through the pipe 109 is delivered thereby to a chamber 135 at the end of the section C of the exchanger and travels through tubes 124 to a chamber 136 at the opposite end of the section C of the exchanger. A pipe 137 connects the chamber 136 to a chamber 138 at the end of the section D of the exchanger and the gas travels thence through tubes 124 to a chamber 139 at the opposite end of the section D of the exchanger. A pipe 140 delivers the gas from the chamber 139 to a suitable storage receptacle.

In the event that sufficient refrigeration is not maintained by the operation of the column 92 as hereinbefore described, a portion of the cold nitrogen from the pipe 63 may be withdrawn through a pipe 141 and delivered to a chamber 142 at one end of the section C of the exchanger. Traveling thence through tubes 123, the gas is delivered to a chamber 143 of the section C of the exchanger. A pipe 144, controlled by a valve 145 connects the chamber 143 to a chamber 146 at one end of the section D of the exchanger, and the gas travels thence through tubes 123 to a chamber 147 at the opposite end of the section D of the exchanger. The gas is withdrawn therefrom through a pipe 148 controlled by a valve 149 and is delivered to the pipe 70 and thereby returned to the inlet of the compressor 32.

Under certain conditions, hydrogen escaping through the pipe 140 may be still at considerable pressure and in order to utilize this pressure advantageously, a by-pass 150 controlled by a valve 151 is adapted to deliver the cooling nitrogen from the pipe 144 directly to the pipe 148. The valves 145 and 149 being closed, the hydrogen may be withdrawn from the pipe 140 and delivered through a pipe 152 controlled by a valve 153 to an engine or motor 154 where it is expanded with external work and thereby cooled. The cold hydrogen is delivered from a pipe 155 to the chamber 146 at the end of the section D of the exchanger and travels through tubes 123 to the chamber 147, from which it is withdrawn through a pipe 156 and delivered to a suitable storage receptacle.

From the foregoing description, it will be observed that, as pointed out heretofore, the gaseous mixture to be separated is finally subjected to a liquid cooling medium, designed to prevent variations in temperature which affect the operation of refrigerating systems employing a gaseous cooling agent for the final cooling of the mixture. The liquid cooling agent is produced in an economical manner avoiding all losses which might result from the extensive rectification and recovering and utilizing the refrigerating effect to the fullest extent. It is possible in producing the refrigerating liquid to recover a considerable proportion of the energy originally expended in compressing the circulating medium, and provision is made for such recovery in the engines or motors hereinbefore described. Since the working fluid of the air cycle circulates continuously, it need not be purified for the removal of moisture or carbon dioxide except as additions of air to the cycle are required from time to time, and furthermore, since the working fluid finally approaches a definite composition and consists primarily of nitrogen, the losses due to energy expended in separating the constituents are almost entirely obviated.

In the separation of water-gas and similar gaseous mixtures in the manner hereinbefore described, a corresponding efficiency is accomplished through the elimination of rectification, the separation being almost entirely accomplished by selective liquefaction with "backward return" of the liquid constituents. A large proportion of the energy originally employed in compressing the gaseous mixture is recovered, particularly if the hydrogen is expanded in the manner hereinbefore described. It is possible, therefore, to produce hydrogen, for example, from gaseous mixtures containing it, such as water gas, in an economical manner; and since water gas is available at relatively slight expense, hydrogen may be pro-

duced at a correspondingly low cost and in a satisfactory condition with respect to purity for numerous uses to which it is adapted.

The invention herein described is particularly adapted to employment in the recovery of hydrogen from water gas, but it is equally advantageous in separating helium, for example, from natural gas, and, in fact, for the separation of any constituent of a gaseous mixture which is not readily liquefiable under conditions which ensure the liquefaction of other constituents. The claims are not, therefore, limited to the treatment of water gas, it being the intention to embrace all uses to which the invention may be applied.

Various changes may be made in the details of operation and in the apparatus hereinbefore described without departing from the invention or sacrificing any of the advantages thereof.

I claim:

1. A method of separating a constituent which is not readily liquefiable from a gaseous mixture, comprising subjecting the mixture to selective backward return condensation with previously liquefied portions thereof evaporating at a lower pressure, and thereafter with an extraneous liquid evaporating at a lower temperature to selectively liquefy substantially all but the desired constituent of the mixture.

2. A method of separating a constituent which is not readily liquefiable from a gaseous mixture, comprising subjecting the mixture to indirect contact with previously liquefied portions thereof evaporating at a lower pressure, then to indirect contact with an extraneous liquid evaporating at a lower pressure, and returning the selectively formed liquid in direct contact with the mixture undergoing liquefaction.

3. A method of separating a constituent which is not readily liquefiable from a gaseous mixture, comprising subjecting the mixture to selective backward return condensation with successively colder media, the final medium being an extraneous evaporating liquid.

4. A method of separating a constituent which is not readily liquefiable from a gaseous mixture, comprising subjecting the mixture to selective liquefaction by indirect contact with successively colder media, the final medium being an extraneous evaporating liquid, and returning the selectively formed liquid in direct contact with the mixture undergoing liquefaction.

5. A method of separating a constituent which is not readily liquefiable from a gaseous mixture, comprising subjecting the mixture to selective liquefaction in successive stages, first by indirect contact with liquefied portions of the mixture, and then

by indirect contact with a colder liquid, and employing the liquid resulting from the selective liquefaction to produce the colder liquid by indirect contact of an extraneous gaseous medium therewith.

6. A method of separating a constituent which is not readily liquefiable from a gaseous mixture, comprising subjecting the mixture to selective backward return condensation in successive stages, first by indirect contact with liquefied portions of the mixture, and then by indirect contact with a colder liquid evaporating at a pressure below atmospheric.

7. A method of separating a constituent which is not readily liquefiable from a gaseous mixture, comprising subjecting the mixture to selective liquefaction by indirect contact with successively colder media, the final medium being an extraneous liquid produced by indirect contact of a gaseous medium with liquefied portions of the mixture.

8. A method of separating a constituent which is not readily liquefiable from a gaseous mixture, comprising subjecting the mixture to selective liquefaction by indirect contact with successively colder media, the final medium being an extraneous liquid produced by indirect contact of a cold gaseous medium with liquefied portions of the mixture, and supplying cold to make up for heat leakage in the system by heat interchange of the mixture with other portions of the cold gaseous medium.

9. A method of separating a constituent which is not readily liquefiable from a gaseous mixture, comprising subjecting the mixture to selective liquefaction by indirect contact with successively colder media, the final medium being an extraneous liquid produced by indirect contact of a cold gaseous medium with liquefied portions of the mixture, and maintaining a separate liquefaction cycle to produce the cold gaseous medium.

10. A method of separating a constituent which is not readily liquefiable from a gaseous mixture, comprising subjecting the mixture to selective backward return condensation with successively colder media, the final medium being an extraneous liquid produced from a cold gaseous medium, and maintaining a separate liquefaction cycle to supply the cold gaseous medium.

11. A method of separating a constituent which is not readily liquefiable from a gaseous mixture, comprising subjecting the mixture to selective backward return condensation with successively colder media, the final medium being an extraneous liquid, maintaining a separate liquefaction cycle to supply the extraneous liquid, and returning the vapor from this liquid to the separate liquefaction cycle.

12. A method of separating a constituent which is not readily liquefiable from a gaseous mixture, comprising subjecting the mixture to selective liquefaction by indirect contact with successively colder media, the final medium being a liquid produced from an extraneous gaseous medium, maintaining a separate liquefaction cycle to supply the gaseous medium, and supplying the necessary refrigeration for the separate liquefaction cycle by expansion of the products thereof with external work.

13. A method of separating a constituent which is not readily liquefiable from a gaseous mixture, comprising subjecting the mixture to selective liquefaction by indirect contact with successively colder media, the final medium being an extraneous liquid produced by indirect contact of a cold gaseous medium with liquefied portions of the mixture, withdrawing the vapor from the extraneous liquid, and returning it as the gaseous medium to produce additional quantities of the extraneous liquid.

14. A method of separating a constituent which is not readily liquefiable from a gaseous mixture, comprising subjecting the mixture to selective liquefaction by indirect contact with successively colder media, the final medium being an extraneous liquid produced by indirect contact of a cold gaseous medium with liquefied portions of the mixture, withdrawing the vapor from the extraneous liquid, recompressing the vapor, and returning it as the gaseous medium to produce additional quantities of the extraneous liquid.

15. A method of separating a constituent which is not readily liquefiable from a gaseous mixture, comprising subjecting the mixture to selective liquefaction by indirect contact with successively colder media, the final medium being an extraneous liquid, expanding the unliquefiable residue of the gaseous mixture, and utilizing the cold thereof to refrigerate the incoming gaseous mixture.

16. A method of separating a constituent which is not readily liquefiable from a gaseous mixture, comprising subjecting the mixture to selective liquefaction by indirect contact with successively colder media, the final medium being an extraneous liquid, maintaining a separate liquefaction cycle to supply gas for producing the extraneous liquid, and utilizing a portion of the gas as a refrigerating agent for the incoming gaseous mixture.

17. A method of separating a constituent which is not readily liquefiable from a gaseous mixture, comprising subjecting the mixture to selective liquefaction by indirect contact with successively colder media, the final medium being an extraneous liquid produced by indirect contact of a gaseous medium with liquefied portions of the mixture, maintaining a separate liquefaction cycle to provide

the gaseous medium, and utilizing a portion of the gaseous medium to refrigerate the incoming gaseous mixture.

18. A method of separating a constituent which is not readily liquefiable from a gaseous mixture, comprising subjecting the mixture to selective backward return condensation with successively colder media, the final medium being an extraneous liquid, maintaining a separate liquefaction cycle to supply gas for the extraneous liquid, and returning the vapor from the extraneous liquid and substantially all of the product of the separate liquefaction cycle for recirculation in the cycle.

19. An apparatus for separating a constituent which is not readily liquefiable from a gaseous mixture, comprising a column having a plurality of chambers disposed one above the other each adapted to receive a liquid, means extending continuously through the chambers and adapted to convey the gaseous mixture in indirect contact with the liquids therein, means for supplying liquid produced by selective liquefaction of the gaseous mixture to one of the chambers, and means for supplying an extraneous liquid to another of the chambers.

20. An apparatus for separating a constituent which is not readily liquefiable from a gaseous mixture, comprising a column having a plurality of chambers each adapted to receive a liquid, means extending through the chambers and adapted to convey the gaseous mixture in indirect contact with the liquids therein, means for supplying liquid produced by selective liquefaction of the gaseous mixture to one of the chambers, and means for supplying an extraneous liquid to another of the chambers, including means for liquefying a gaseous medium by indirect contact with the liquid produced by selective liquefaction of the gaseous mixture.

21. An apparatus for separating a constituent which is not readily liquefiable from a gaseous mixture, comprising a column having a plurality of chambers disposed one above the other each adapted to receive a liquid, means extending continuously through the chambers and adapted to convey the gaseous mixture in indirect contact with the liquids therein, means for supplying liquid produced by selective liquefaction of the gaseous mixture to one of the chambers, means for supplying an extraneous liquid to another of the chambers, and means for withdrawing vapor at a pressure below atmospheric from the chamber containing the extraneous liquid.

22. An apparatus for separating a con-

stituent which is not readily liquefiable from a gaseous mixture, comprising a column having a plurality of chambers each adapted to receive a liquid, means extending through the chambers and adapted to convey the gaseous mixture in indirect contact with the liquids therein, means for supplying liquid produced by selective liquefaction of the gaseous mixture to one of the chambers, and means for supplying an extraneous liquid to another of the chambers, including means for liquefying a gaseous medium by indirect contact with the liquid produced by selective liquefaction of the gaseous mixture and an auxiliary liquefaction cycle maintained for the purpose of supplying the gaseous medium.

23. An apparatus for separating a constituent which is not readily liquefiable from a gaseous mixture, comprising a column having a plurality of chambers each adapted to receive a liquid, means extending through the chambers and adapted to convey the gaseous mixture in indirect contact with the liquids therein, means for supplying liquid produced by selective liquefaction of the gaseous mixture to one of the chambers, means for supplying an extraneous liquid to another of the chambers, including means for liquefying a gaseous medium by indirect contact with the liquid produced by selective liquefaction of the gaseous mixture and an auxiliary liquefaction cycle maintained for the purpose of supplying the gaseous medium, and means for expanding the products of the auxiliary cycle and to utilize the refrigerating effect thus developed.

24. An apparatus for separating a constituent which is not readily liquefiable from a gaseous mixture, comprising a column having a plurality of chambers each adapted to receive a liquid, means extending through the chambers and adapted to convey the gaseous mixture in indirect contact with the liquids therein, means for supplying liquid produced by selective liquefaction of the gaseous mixture to one of the chambers, means for supplying an extraneous liquid to another of the chambers, including means for liquefying a gaseous medium by indirect contact with the liquid produced by selective liquefaction of the gaseous mixture and an auxiliary liquefaction cycle maintained for the purpose of supplying the gaseous medium, and means for returning the gaseous medium to the auxiliary cycle for recirculation therein.

In testimony whereof I affix my signature.

CLAUDE C. VAN NUYS.