

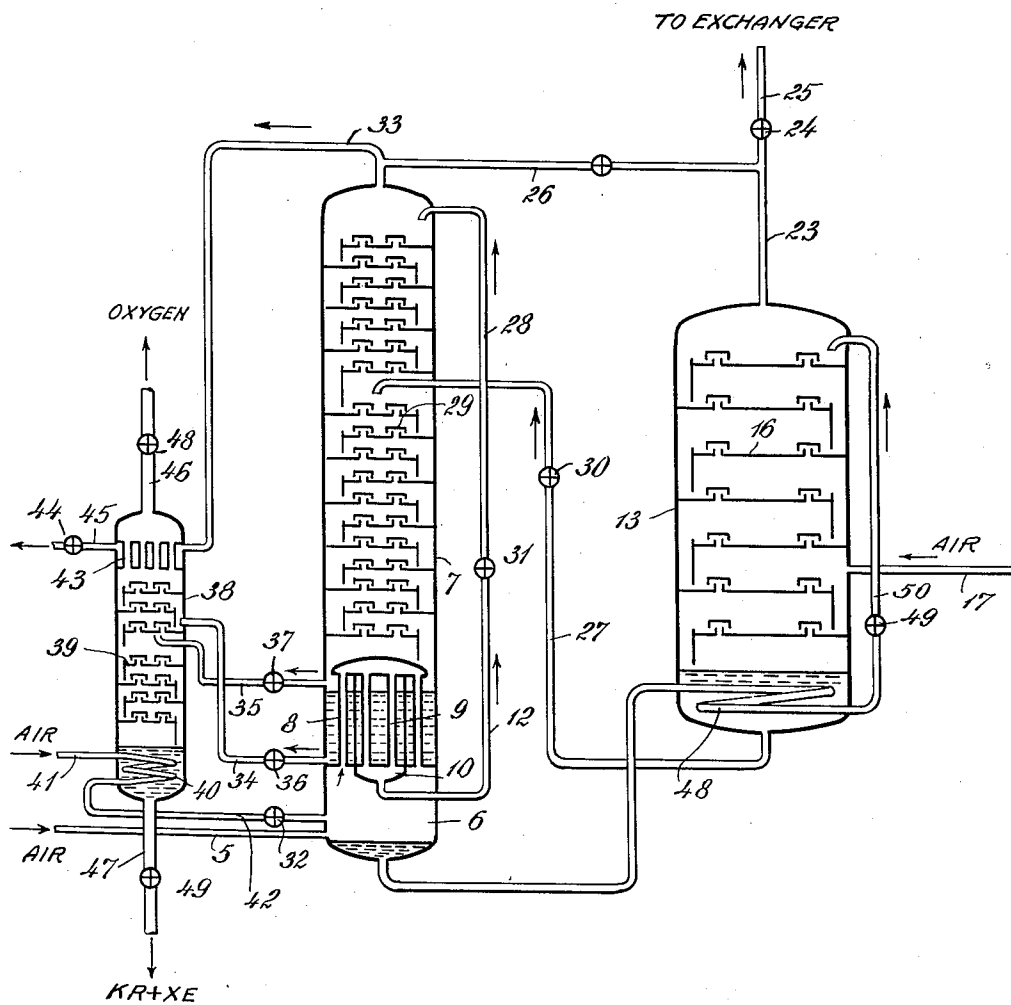
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RECOVERY OF KRYPTON AND XENON

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RECOVERY OF KRYPTON AND XENON

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This invention relates to the separation of the rare gases krypton and xenon from the atmosphere and the recovery of these gases in quantities such as to permit commercial applications thereof.

Air contains only minute proportions of krypton and xenon, and the ordinary methods of separating air for the recovery of nitrogen, oxygen and argon take no account of the rarer gases. No practicable commercial method of recovering these gases has been available heretofore.

It is the object of the present invention to provide a simple, practical and effective method of separating and recovering krypton and xenon from the atmosphere.

A further object of the invention is the provision of a method of treating relatively large volumes of air at low cost to permit the recovery of krypton and xenon therefrom. These gases are thus made available for various commercial and industrial uses.

In carrying out the present invention, no attempt is made to recover all of the nitrogen, oxygen and argon as separate gases of substantial purity, since the primary function of the method is the recovery of the rarer gases krypton and xenon. The constituents of the atmosphere are subjected to primary separation to afford a liquid fraction which is utilized for the purpose of concentrating krypton and xenon from additional quantities of air. The subsequent rectification of the liquid enriched in krypton and xenon with other liquids and vapors produced affords a liquid further enriched in krypton and xenon. This liquid is subjected then to a further rectification to effect separation of oxygen, leaving a liquid concentrate rich in krypton and xenon which can be withdrawn and utilized. A portion of the oxygen and also of the nitrogen is also recoverable, but the major portion of all of the air treated is returned to the atmosphere as a gaseous mixture from which only the krypton and xenon have been removed.

The method as thus generally outlined will be better understood by reference to the following specification and the accompanying diagrammatic drawing, illustrating an apparatus which is adapted for use in the practice of the method. It will be understood that details of the apparatus well known in the art are not illustrated or described, the purpose being to present simply and clearly the essentials of the invention as hereinafter claimed.

Referring to the drawing, a portion of the air

to be treated, after initial compression to a suitable pressure and cooling in the usual exchangers (not shown) is introduced through a pipe 5 to the bottom compartment 6 of a column 7. The air passes upwardly through tubes 8 immersed in a liquid product accumulated as hereinafter described, and thence downwardly through tubes 9 into a collector 10. In passing through the tubes 8, the air is subjected to selective liquefaction with the resulting formation of a liquid more or less closely in phase equilibrium with the composition of the air, that is to say, a liquid containing approximately from 21 to 45% of oxygen, the balance being nitrogen with some of the argon and a considerable portion of the krypton and xenon of the air treated. The liquid flows backwardly and accumulates in the compartment 6. The unliquefied residue, consisting largely of nitrogen, in passing downwardly through the tubes 9 is also liquefied and accumulates in the collector 10. This liquid also may contain some krypton and xenon as well as a portion of the argon.

In the usual method of treating air to separate oxygen and nitrogen, these two liquids are immediately delivered at different levels to a rectifier 7 to effect a separation of the constituents. In the method forming the subject matter of the present application, however, one or the other of these liquids, for example, the one condensed in tubes 8 and collected in compartment 6 instead of being immediately delivered to rectifier 7, is conducted while still under pressure to coil 48 surrounded by liquid enriched in oxygen as well as krypton and xenon located in the base of a column 13. The liquid in the coil 48 is subcooled by evaporating a portion of the liquid surrounding the coil and is then delivered by means of valve 49 and pipe 50 to a rectifier 13 provided with the usual trays 16. The liquid in flowing downwardly over trays 16 comes into contact with a relatively large volume of air under low pressure introduced into the middle of rectifier 13 by means of pipe 17. The effect will be to wash from the large volume of entering air, by means of the liquid introduced through the pipe 50, substantially all of the krypton and xenon together with some of the oxygen while the effluent leaving rectifier 13 through pipe 23 will consist of a gaseous mixture, principally nitrogen but containing oxygen and argon. The effluent may be sent to an exchanger through a valve 24 and pipe 25.

The liquid, enriched in krypton and xenon, which accumulates in the bottom of the rectifier

13 is withdrawn through pipe 27, controlled by valve 30 and is delivered to an intermediate level of the column 7 in which the usual rectification trays 29 are disposed. The liquid and any residual vapor from the collector 10 is delivered through a pipe 12, valve 31 and pipe 28 to the top of the rectifier 7 and flows downwardly over the trays 29 therein to effect a further washing of the vapors arising from the lower portion of the rectifier. If the liquid from the collector 10 is delivered to the coil 48, the liquid from the compartment 6 will be delivered to the top of the rectifier 7. As previously indicated, either of the liquids accumulating in the compartment 6 and collector 10 can be used as a wash liquid for the large volume of air in the rectifier 13.

In flowing downwardly over the trays 29, the two liquids introduced to the column 7 are subjected to rectification with vapors arising from the body of liquid surrounding tubes 8 and 9. This liquid is vaporized in the initial condensation of the entering air, and the resulting vapors, together with those formed during the rectification, pass upwardly through the column 7 and escape as an effluent consisting principally of nitrogen with some or all of the argon present in the liquid, through a pipe 33. The liquid flowing downwardly through the column finally accumulates about the tubes 8 and 9 and consists principally of oxygen and substantially all of the krypton and xenon which has been separated from the air entering through the pipes 5 and 17.

A portion of the liquid, together with vapors from the lower part of the column 7, is delivered through pipes 34 and 35 controlled by valves 36 and 37 to intermediate levels of an auxiliary rectifier 38 containing the usual trays 39 and having at the bottom a coil 40 which is supplied with air, previously compressed and cooled, through a pipe 41. In traveling through the coil, the air causes vaporization of the liquid surrounding the coil and is itself liquefied, and, it may be, somewhat subcooled. The liquid travels through the pipe 42 and valve 32 to the compartment 6, thus joining the liquid accumulating in that compartment. The vapor passes upwardly through the trays in contact with the downwardly flowing liquid and passes finally through tubes 43 of a condenser which is cooled by the effluent escaping from the column 7 through the pipe 33. A valve 44 controls the flow of the effluent which escapes finally through a pipe 45 to an exchanger. By utilizing the pipe 26 a portion of the effluent from the rectifier 13 may be similarly utilized. The condenser 43 separates from the vapors a liquid which becomes much concentrated in krypton and xenon when it reaches the bottom of rectifier 38. The effluent from this rectifier escapes through a pipe 46 controlled by a valve 48 and consists of substantially pure oxygen which may be delivered through an exchanger to a suitable collector in which the oxygen may be accumulated for use. The liquid at the bottom of the rectifier may be withdrawn through a pipe 47 controlled by a valve 49. It consists of a concentrate of krypton and xenon and is the principal product of the method as described. It may be utilized after further purification for any desired purpose.

From the foregoing description it is very evident that the method forming the subject matter of this application is an efficient and practicable method of extracting the krypton and xenon from large quantities of atmospheric air while at the same time an air separation apparatus for

the production of high purity oxygen is operated in connection therewith. The relation between the separation of the several constituents of air and the procedure by which krypton and xenon are extracted from a large quantity of air not otherwise treated is such that an important advantage and economy in the air separation method itself is secured. This arises from the fact that one of the two liquids into which the air entering the rectifier 7 is converted is enriched in oxygen by reason of its passage through the krypton-xenon rectifier 13. That is to say, the liquid entering the krypton-xenon rectifier through pipe 50 and re-entering the rectifier 7 through pipe 27 carries a substantially higher percentage of oxygen after leaving the krypton-xenon rectifier than when it enters. This is due in part to the lower pressure prevailing in rectifier 13 compared to that in the tubes 8 and in part due to the coil 48 located at the base of rectifier 13. The method, as will be evident, affords the possibility of treating large quantities of air and the recovery therefrom in a simple and satisfactory manner of the krypton and xenon content of the air, together with a separate portion consisting of oxygen in substantial purity. Thus, krypton and xenon in quantities enabling the use of these products for various commercial purposes are made available.

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

I claim:

1. The method of recovering krypton and xenon from the atmosphere which comprises subjecting compressed and cooled air to selective liquefaction to separate two liquid fractions, utilizing one of the fractions to wash krypton and xenon from a relatively large volume of gaseous air and rectifying the resulting liquid rich in krypton and xenon with the other liquid fraction produced by selective liquefaction and vapors resulting from partial evaporation of the liquid product.

2. The method of recovering krypton and xenon from the atmosphere which comprises subjecting compressed and cooled air to selective liquefaction to separate two liquid fractions, utilizing one of the fractions to wash krypton and xenon from a relatively large volume of gaseous air, rectifying the resulting liquid rich in krypton and xenon with the other liquid fraction produced by selective liquefaction and vapors resulting from partial evaporation of the liquid product, and subjecting the liquid product to an auxiliary rectification to produce a liquid concentrate containing the major portion of the krypton and xenon in the air treated and an effluent consisting of oxygen exceeding in quantity the amount thereof in the air subjected to initial selective liquefaction.

3. The method of recovering krypton and xenon from the atmosphere which comprises subjecting compressed and cooled air to selective liquefaction to separate two liquid fractions, subcooling and utilizing one of the fractions to wash krypton and xenon from a relatively large volume of gaseous air and rectifying the resulting liquid rich in krypton and xenon with the other liquid fraction produced by selective liquefaction and vapors resulting from partial evaporation of the liquid product.

4. The method of recovering krypton and xenon from the atmosphere which comprises sub-

jecting compressed and cooled air to selective liquefaction to separate two liquid fractions, sub-cooling and utilizing one of the fractions to wash krypton and xenon from a relatively large volume of gaseous air, rectifying the resulting liquid rich in krypton and xenon with the other liquid fraction produced by selective liquefaction and vapors resulting from partial evaporation of the liquid product, and subjecting the liquid product to an auxiliary rectification to produce a liquid concentrate containing the major portion of the krypton and xenon in the air treated and an effluent consisting of oxygen exceeding in quantity the amount thereof in the air subjected to initial selective liquefaction.

5. The method of recovering krypton and xenon from the atmosphere which comprises subjecting compressed and cooled air to selective liquefaction to separate two liquid fractions, utilizing one of the fractions to wash krypton and xenon from a relatively large volume of gaseous air, rectifying the resulting liquid rich in krypton and xenon with the other liquid fraction produced by selective liquefaction and vapors resulting from partial evaporation of the liquid product, subjecting the liquid product to an auxiliary rectification to produce a liquid concentrate containing the major portion of the krypton and xenon in the air treated and an effluent consisting of oxygen exceeding in quantity the amount thereof in the air subjected to initial selective liquefaction, and condensing a portion of the effluent from the auxiliary rectification to wash

krypton and xenon from the vapors produced therein.

6. The method of recovering krypton and xenon from the atmosphere which comprises subjecting compressed and cooled air to selective liquefaction to separate two liquid fractions, sub-cooling and utilizing one of the fractions to wash krypton and xenon from a relatively large volume of gaseous air, rectifying the resulting liquid rich in krypton and xenon with the other liquid fraction produced by selective liquefaction and vapors resulting from partial evaporation of the liquid product, subjecting the liquid product to an auxiliary rectification to produce a liquid concentrate containing the major portion of the krypton and xenon in the air treated and an effluent consisting of oxygen exceeding in quantity the amount thereof in the air subjected to initial selective liquefaction, and condensing a portion of the effluent from the auxiliary rectification to wash krypton and xenon from the vapors produced therein.

7. The method of recovering krypton and xenon from the atmosphere which comprises initially separating the air by cooling and liquefaction into at least two separate liquid fractions, utilizing one of the fractions to wash krypton and xenon from a relatively large volume of gaseous air and rectifying the resulting liquid rich in krypton and xenon with other liquids and vapors produced in the initial separation and subsequent rectification.

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