

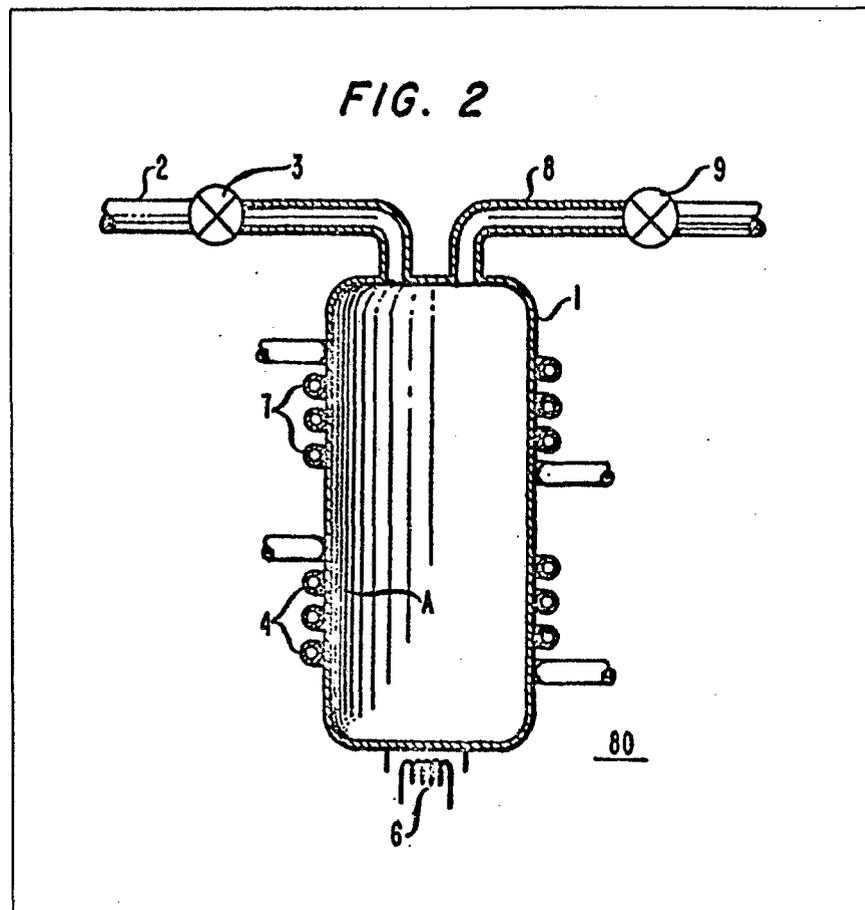
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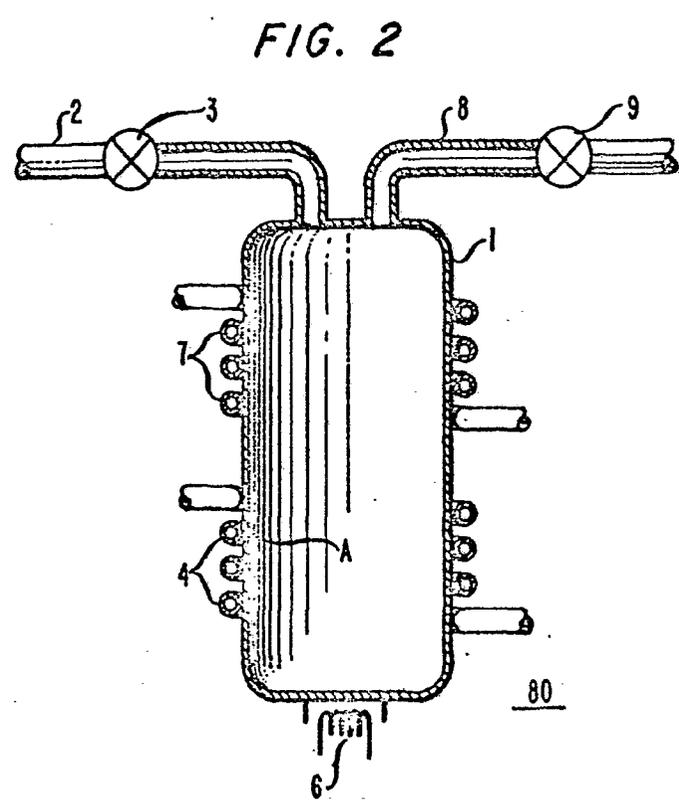
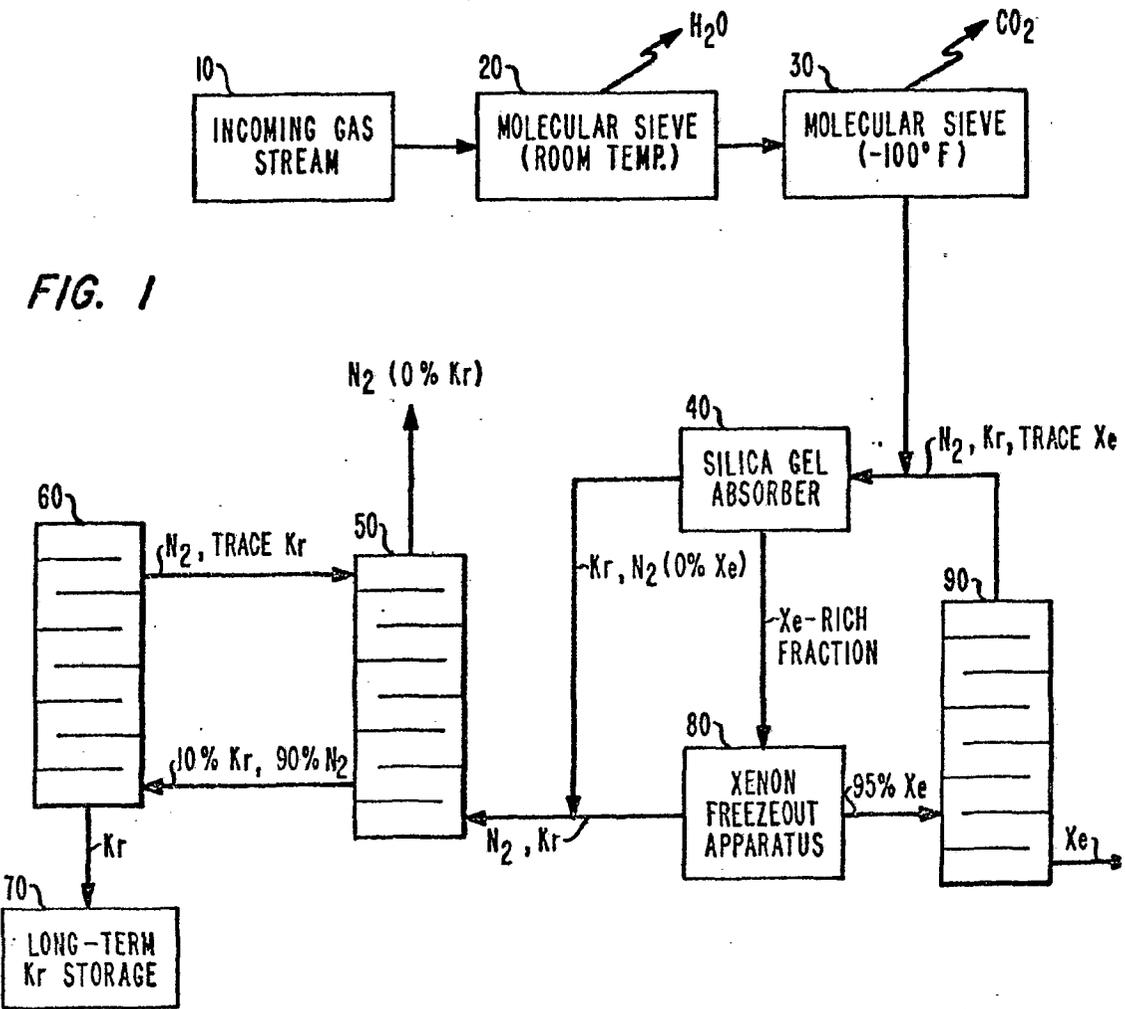
(54) Method of gas separation

(57) In order to separate a mixture of gases having widely different partial pressures at a given temperature, a chamber 1 is employed. A batch of gas mixture is passed into the chamber 1. The walls of the chamber 1 are cooled refrigerant which passes through coils 4 and 7 in heat exchange relationship with said walls.

By this means the temperature of the chamber is cooled to a temperature (and held at such temperature until equilibrium is reached) at which all the components of the gas mixture have changed state, at least one being solidified and at least one liquefied. The liquid constituents are removed first. Then the chamber is warmed to facilitate removal of the previously solidified constituents.



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SPECIFICATION

Gas separation process

The present invention relates generally to the field of gas separation and substantially differ from one another at a particular temperature.

- 5 It is well known that in nuclear fuel reprocessing plants a certain amount of radioactive krypton gas is released during chemical processes which are used to dissolve spent nuclear fuel rods.
- 10 Rather than allow such radioactive gas to contaminate the atmosphere, environmental standards generally require that such krypton be recovered and stored for a period of about 100 years. As the half-life of krypton is approximately
- 15 10 years, storage for 100 years will reduce the radioactivity of the krypton to virtually insignificant levels, at which time it will be comparatively safe to use or release the gas to atmosphere. Storage of a large quantity of gas for
- 20 a period of 100 years obviously poses substantial problems and cost with respect to such storage, even if only in terms of the space required. Therefore, it has been an objective of the art to develop an efficient process for separation of
- 25 these radioactive gases so that the least amount possible of the particular gas need be stored. Hence, there is and has been a need for an efficient method of separating radioactive krypton from other gases.
- 30 In one common type of nuclear fuel reprocessing plant the krypton arrives at the separation point mixed with argon, xenon and nitrogen; other gaseous products of the fuel dissolution process such as oxygen and
- 35 hydrocarbons having been removed by catalytic combustion or adsorption methods. However, it is difficult to remove xenon from nitrogen by distillation methods as the pressures and temperatures typically used are such that any
- 40 xenon present tends to freeze and clog columns, etc. By comparison, Kr and Xe can be separated from oxygen with relative ease, although there are some freezing problems with this process as well. Hence, the art has recognised that a need exists
- 45 for a highly efficient and inexpensive process for separation of the gases krypton and xenon from nitrogen. In particular, a method is needed for the efficient separation of xenon, as the krypton can then be distilled from the nitrogen.
- 50 Another approach to the problem of nuclear fuel reprocessing plants involves a similar process to that already described except that the krypton and xenon come mixed together with helium gas which, of course, is also inert. A process for the
- 55 separation of the krypton and xenon from helium is described in US patent no. 4 080 429. The described process is carried out in sealed containers and the retorts and reaction vessels utilised are continually flushed with helium. The
- 60 krypton and xenon are separated from the helium by passing the mixture into a large container having surfaces cooled by liquid nitrogen. As the freezing point of the krypton and xenon are above the liquefaction temperature of nitrogen, while

- 65 that of helium is below such nitrogen and xenon freeze out on to the walls of the container while the helium flows therethrough. However, the fact that the krypton has a significant partial pressure—1.7 mm Hg at liquid nitrogen
- 70 temperatures means that some of the krypton will be entrained in and necessarily escape with the helium gas streams; therefore, the helium must be further precessed, in order to ensure that virtually all of the krypton has been removed therefrom.
- 75 Moreover, the xenon and krypton remaining in the container are subsequently separated from each other in order to avoid storing xenon for unnecessarily long periods of time. This approach, while not unworkable, is not especially efficient and, in particular, is not well suited to the
- 80 separation of nitrogen from krypton and xenon because much more nitrogen is used in the nitrogen-based approach than is helium in the other method discussed above. Thus, even more
- 85 krypton and xenon will tend to become entrained with the nitrogen than with the helium. Consequently, it is an object of the invention to provide an efficient, simple and workable method for separating one or more gases from a feed gas
- 90 stream.

- According to the present invention there is provided a method for separating a gas mixture, comprising the steps of: (a) admitting a batch of said mixture into a chamber; (b) cooling at least
- 95 part of the walls (or other surfaces) of said chamber to a temperature at least as low as the lowest boiling point of the gases of said mixture; (c) maintaining the said temperature for a time such that essentially equilibrium conditions are
- 100 reached, such that at least one of the components of the gas mixture is solidified and at least one other component remains as liquid in said chamber; (d) removing the liquid component(s)
- 105 from said chamber; and (e) thereafter warming the chamber and removing the previously solidified component(s).

The invention will now be described by way of example with reference to the accompanying drawing in which:

- 110 Figure 1 is a diagrammatic view of a process for separating one gas from another; and

Figure 2 is a schematic cross-sectional view of a freeze-out exchanger device suitable for the practice of the process depicted in Figure 1.

- 115 It is to be understood throughout this specification that the method according to the invention is generally applicable to the separation of gases from one another. However, the primary application of the process is expected to be the
- 120 separation of krypton and xenon from nitrogen and for purposes of illustration, the invention will be described in those terms. In the ensuing description all percentages are by volume.

- 125 Referring first to Figure 1, the incoming gas stream, consisting essentially of nitrogen, argon, water vapour, carbon dioxide and very small quantities of krypton and xenon, is shown arriving at 10. In all the processes described herein, argon behaves similarly to the nitrogen and

argon/nitrogen mixtures will therefore sometimes be referred to simply as nitrogen. The incoming gas stream is passed first through a conventional molecular sieve 20, typically operated at room temperature for removing water, and a second molecular sieve 30, generally operated at about -100°F (-73°C) for removing carbon dioxide.

5 The gas stream, now consisting essentially of 98% nitrogen, 2% argon, and krypton and xenon in quantities of hundreds of parts per million, is passed through adsorber 40, which may be comprised of a bed of silica gel, which removes essentially all the xenon from the stream, along with considerable nitrogen and a small quantity of krypton. Typically, two such beds are arranged in parallel, with appropriate controls, so that one can be regenerated by eg. heating and flushing with nitrogen, while the other is adsorbing the xenon-rich fraction of the stream. Essentially all the xenon can be removed from the stream by this step. However, the xenon-rich fraction is only approximately 30% xenon, the balance being roughly 67% N_2 and 3% krypton, so that the xenon-rich fraction is generally further purified before it can be used or released to the atmosphere. The process typically practised to refine further the xenon-rich fraction, which will be described more fully hereinafter, embodies the process and apparatus according to the invention.

10 After removal of substantially all the xenon from the gas stream in absorber 40, the krypton can be separated by fractional distillation methods in columns or stills 50 and 60 without danger of xenon freeze-up and clogging. A first krypton-rich steam (up to approximately 10% krypton) is produced by still 50, which may be arranged to vent krypton-free N_2 to the atmosphere; this stream may be further refined in still 60 to yield a product of approximately 90% or greater krypton, which is then held in long term storage 70 as described above until its radioactivity has diminished to acceptably low levels to permit its release or use.

15 The significant improvement made by the present invention lies in the method used to separate xenon from nitrogen and krypton after the xenon-rich fraction of the gas stream has been removed by adsorber 40.

20 Referring now to Figure 2, a large metallic container 1 is illustrated which is encircled by tubular coils 7 and 4 and which preferably is fitted with an electric heater 6 at its base. In operation, a batch of a mixture of nitrogen, xenon and krypton gas is introduced into chamber 1 through line 2 and valve 3. Either prior to or after the introduction of the fixed quantity of the gas mixture into container 1, liquefied nitrogen is caused to flow through coil 4 so that the wall of container 1 reaches the temperature of the liquid nitrogen, approximately -320°F (77K). At this temperature, all three components of the mixture will first liquefy and thereafter the krypton and xenon will tend to freeze out; being denser than the nitrogen, they will tend to collect on the walls and bottom of the container 1. After a suitable time has been

spent in this condition, the coil 7 may also be filled with liquid nitrogen so that the entire interior wall of the container eventually reaches -320°F (77K). At this point, valve 9 may be opened permitting the escape of gaseous nitrogen through tube 8. Preferably a slight vacuum is applied to reduce the pressure in the vessel to a point below that in the tubes 4 and 7; alternatively the LN_2 in tubes 4 and 7 can be slightly pressurised.

70 Additionally, heater 6 may be energised in order to speed the evaporation of nitrogen. So long as the liquid nitrogen is present in tubes 4 and 7, the walls will stay at -320°F (77K) despite the introduction of a small quantity of heat at 6 and therefore most of the krypton and substantially all of the xenon will remain frozen solidly to the walls of the container. When all the nitrogen has been exhausted from container 1, the heater may be further energised and liquid nitrogen is removed from coils 4 and 7. The krypton and xenon will then liquefy to be drained, or will be gasified and removed via tube 8 and valve 9, depending on the precise temperature and pressure conditions existing within container 1. Preferably the container 1 is warmed from the top down so as to avoid large, sudden changes in pressure caused by any liquid xenon vaporising on the heated surface near the heater 6.

80 At 77°K the approximate vapour pressures of N_2 are 758 torr, of krypton 1.8 torr and of xenon 2.0 millitorr. The great difference between the vapour pressures of nitrogen and that of the other gases means that the separation can be made very efficient; to be more exact, the fraction of the xenon that is evaporated with the nitrogen is:

$$\frac{\text{vapour pressure of xenon}}{\text{vapour pressure of } \text{N}_2} = \frac{2 \times 10^{-3}}{7.58 \times 10^2} \quad \text{or} \quad \frac{2.0}{758} \quad \text{or} \quad \frac{2.0}{758}$$

approximately 2.64×10^{-6} . The krypton fraction lost is considerably more:

$$\frac{\text{vapour pressure of krypton}}{\text{vapour pressure of } \text{N}_2} = \frac{1.8}{758} \quad \text{or} \quad \frac{1.8}{758} \quad \text{or} \quad \frac{1.8}{758}$$

105 This fraction of krypton separated from xenon with the nitrogen is rather high to be released to the atmosphere and therefore it and the nitrogen with which it is mixed are returned to an earlier stage in the krypton recovery process (Figure 1) for re-refining.

110 If the nitrogen is removed by simply warming it and venting the chamber 1, the xenon which remains is mixed with approximately 7% N_2 and 1% krypton. This efficiency can be further improved by evacuation of container 1; in this way the nitrogen level can be brought below about 2%. the xenon may be further refined in a conventional still or column 90 (Figure 1).

120 As indicated above, the process according to the invention is a batch rather than a continuous process. That is, that only a given quantity of the gas mixture is introduced into container 1 at any

time and it remains there until equilibrium conditions have been approached. In continuous processes, difficulties arise due to the inability to predict conditions and unavoidable variations from equilibrium will result in losses of separation efficiency and, potentially, loss to atmosphere of radioactive materials such as Kr—85.

It will be appreciated by those skilled in the art that various improvements and refinements can be made to the method of the invention which will further improve its efficiency. For example, improvements can be realised by reducing the temperature of the container walls by subcooling nitrogen in tubes 4 and 7, thereby reducing wall temperature below 77°K. In fact, when the process is so practiced, the difference of several degrees in the temperature of the wall results in a reduced krypton vapour pressure thereby allowing more complete retention of the krypton with the xenon. If the vessel is thereafter rewarmed to 77°K then application of a suitable vacuum will preferentially sublime the krypton from the xenon.

It will be understood by those skilled in the art that the process according to the invention is aided in its remarkable efficiency by the fact that krypton and xenon exhibit low partial pressures at the temperature of liquid nitrogen (77°K). Although xenon is soluble in liquid nitrogen and evaporation of liquid nitrogen causes the solubility limit of xenon is evaporated due to its low partial pressure at this temperature. This, in addition to xenon freezing out on the walls, etc of container 1, solid xenon that was dissolved in liquid nitrogen will remain in the container upon evaporation of liquid nitrogen. Consequently a thorough separation of xenon and nitrogen is achieved. It will be realised that distillation columns will not be effective to perform such a separation as the necessity of operation at approximately liquid nitrogen temperatures (77°K) due to use of liquid nitrogen as reflux will cause xenon to freeze and clog the column. Such freezing precludes the column from operating under equilibrium conditions and therefore, efficient and thorough separation of xenon and nitrogen is precluded.

Finally, it will be appreciated that the scope of the invention is far broader than the specific embodiment discussed above.

CLAIMS

1. A method for separating a mixture of gases having widely differing vapour pressures at a given temperature into its constituent parts comprising the steps of (a) admitting a fixed

quantity of such gas mixture to a chamber the walls of which are cooled to a temperature such that all the components of the gas mixture are either liquefied or solidified; (b) holding the chamber and its contents at said temperature for a time such that essentially equilibrium conditions are reached, so that at least one component of the mixture remains liquid and one or more of the other components of the mixture are in the solid state; (c) removing the liquid component(s); (d) thereafter allowing the chamber to warm up, thereby liquifying the solidified components, and (e) removing the previously solidified component(s) from said chamber.

2. A method for separating a gas mixture comprising the steps of (a) admitting a batch of said mixture into a chamber; (b) cooling at least part of the walls (or other surfaces) of said chamber to a temperature at least as low as the lowest boiling point of the gases of said mixture; (c) maintaining the said temperature for a time such that essentially equilibrium conditions are reached, such that at least one of the components of the gas mixture is solidified and at least one other component remains as liquid in said chamber; (d) removing the liquid component(s) from said chamber; and (e) thereafter warming the chamber and removing the previously solidified component(s).

3. A method as claimed in claim 1 or 2 wherein the liquid component(s) are removed by applying a vacuum to the chamber.

4. A method as claimed in claim 1 or claim 2 wherein heat is applied to the liquid component(s) to speed removal thereof.

5. A method as claimed in claim 1 or claim 2 wherein the chamber is cooled by exposing part of its exterior wall surface to a quantity of a liquid refrigerant, and wherein, after essentially equilibrium conditions have been reached within the chamber, essentially all the remaining exterior wall surface is similarly cooled.

6. A method as claimed in claim 5, wherein a partial vacuum is applied to said liquid refrigerant, to lower its temperature further.

7. A method as claimed in any one of the preceding claims, in which the gas mixture comprises nitrogen, argon, krypton and xenon, and the walls of the chamber are cooled by liquid nitrogen, the argon and nitrogen being liquefied and the xenon and krypton being solidified.

8. A method for separating a gas mixture substantially as herein described with reference to the accompanying drawing.