June 2, 1942. H. KAHLE 2,284,662

PROCESS FOR THE PRODUCTION OF KRYPTON AND XENON

Filed March 12, 1937 2 Sheets-Sheet 1

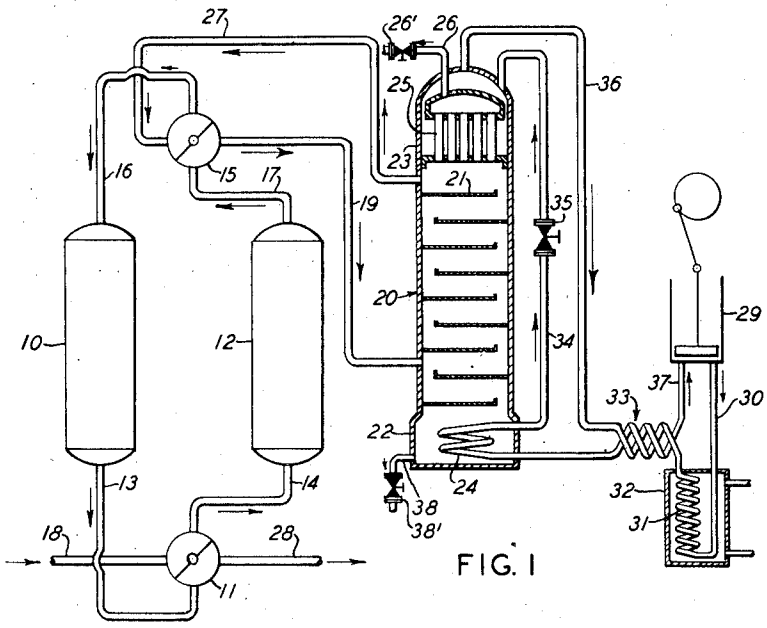


FIG. 1

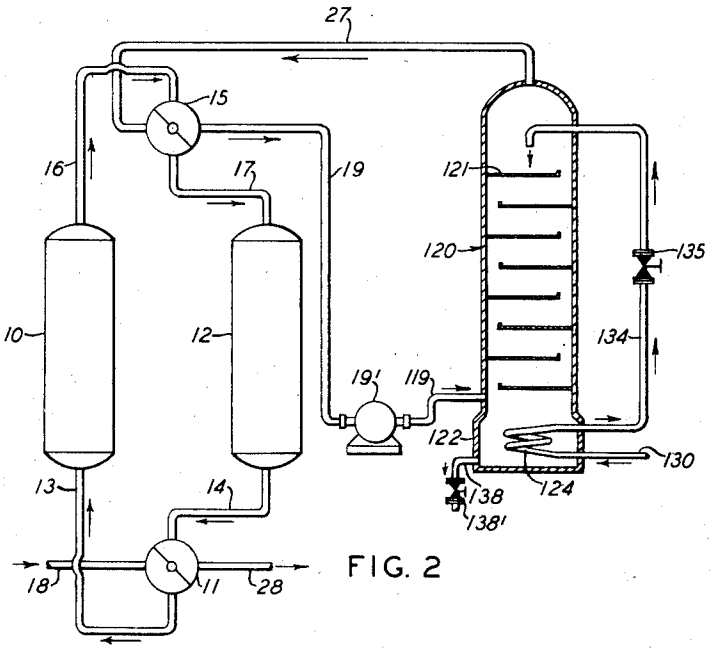


FIG. 2

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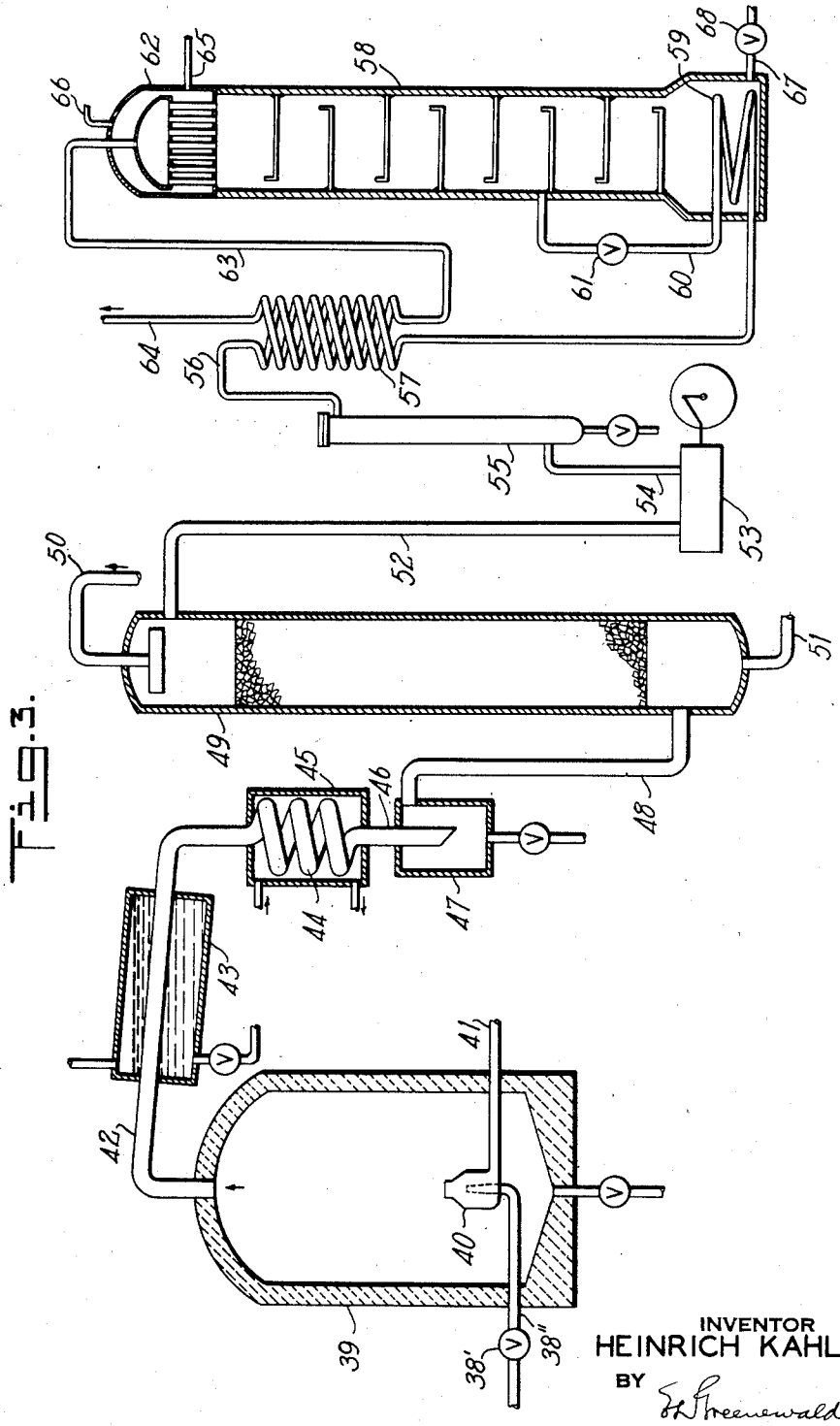


Fig. 3.

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PROCESS FOR THE PRODUCTION OF KRYPTON AND XENON

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3 Claims. (Cl. 23—209)

This invention relates to a process for the production of krypton and xenon, and particularly to the recovery of krypton and xenon from gas mixtures containing hydrocarbons.

Various processes have been proposed for recovering the rare gases krypton and xenon, in particular from the air through enrichment in an oxygen-containing atmosphere. However, due to the fact that hydrocarbon concentrations occur simultaneously with the rare gases, the processing of the crude concentrate is made extraordinarily difficult and expensive. Particularly when the concentrate is to be directly processed to recover the pure rare gases, the most careful removal of even the slightest traces of hydrocarbons, which are present in small percentages in a large volume of gas, is necessary due to the high degree of enrichment effected. Despite all precautionary measures having been taken, this method of operation has nevertheless resulted in some accidents.

Therefore the principal object of the present invention is to provide a method for recovering krypton and xenon by which the above difficulties are fundamentally eliminated.

Other objects of the present invention are: to provide a method for recovering krypton and xenon by enrichment in an atmosphere free of oxygen; for recovering krypton and xenon from oxygen-free gas mixtures; for separating krypton from a gas mixture by washing with a liquefied gas having a higher boiling point than krypton and in which krypton is soluble.

These and other objects of the invention and the novel features thereof which achieve these objects will become evident from the following description taken in connection with the accompanying drawings, in which:

Fig. 1 is a diagrammatic view partly in section of an apparatus for practicing the method of the present invention; and

Fig. 2 is a similar view of another form of the apparatus.

Fig. 3 is a diagrammatic view partly in section of an apparatus for the further treatment of a rare gas concentrate obtained by means of a preliminary rectifying apparatus such as shown in Fig. 1.

In accordance with the invention the enrichment of the rare gaes, krypton and xenon is effected in a reducing, i. e., oxygen-free atmosphere. For this purpose there is used for the production of krypton and zenon either an oxygen-free byproduct gas or if, as in air separation, the preliminary enrichment of these rare gases in an oxygen-containing atmosphere cannot be prevented, the presence of oxygen is excluded during the processing of the raw mixture.

The new process is best more fully explained in connection with various preferred examples. In the specification and claims, it is to be understood that the word krypton is intended to include both the rare gases krypton and xenon collectively unless otherwise set forth.

If nitrogen is utilized in a process for ammonia synthesis, which nitrogen has been produced from air by the chemical elimination of the oxygen, or if the hydrogen for the synthesis is produced by the gasification of fuels with oxygen, then the synthesis gases contain krypton and xenon which become enriched in these gases by recycling through the process. Even though such enrichment can proceed to the point where the krypton content is greater than that in the air, no attempt has heretofore been made to use such gas mixtures for the production of krypton, due to the fact that their separation as compared to air separation is exceedingly more difficult due to their complicated composition.

According to the present invention, gas mixtures of the type such as the residual gases resulting from the synthesis of ammonia are used for the production of krypton in order to be able to carry out the enrichment of the krypton in an oxygen-free atmosphere.

This method of recovering krypton and xenon will be more fully explained by reference to Fig. 1, in which periodically reversible cold accumulators 10 and 12 of known variety have their warn ends connected to a reversing valve 11 by conduits 13 and 14 and their cold ends connected to reversing valve 15 by conduits 16 and 17. The gas mixture to be treated is conducted to valve 11 by a conduit 18 and flows through one or the other of the accumulators to reversing valve 15 from which it is conducted by conduit 19 to the lower portion of a separating column 20 where it is washed by countercurrent contact with a reflux liquid passing downward through the column. The column is provided with rectifying trays 21 to improve the contact. The lower portion or kettle 22 of the column is provided with a heating coil 24 and the upper portion is provided with a condenser 25 which is surrounded by a cooling jacket 23. The condenser may be provided with a dome vent conduit 26 having a stop valve 26'.

The treated gas passes out of the column at its upper portion through a conduit 27 which connects to the reversing valve 15. The treated

mixture after passing through the accumulators where it gives up its refrigeration, passes to valve 11 and is conducted away from the valve by conduit 28. Any desired means for heating the coil 24 and cooling the condenser 25 may be employed, for example, an external closed nitrogen cycle as shown in the figure. Nitrogen is compressed by the compressor 29 whose outlet conduit 30 connects to a cooling coil 31 submerged in cooling water in jacket 32. From cooling coil 31 the nitrogen is conducted through one pass of the heat exchanger 33 and then to the heating coil 24 where the nitrogen liquefies and heats the liquid in kettle 22. The liquid nitrogen is conducted through conduit 34 to the jacket 23 being expanded through the expansion valve 35 interposed in conduit 34. The liquid nitrogen in jacket 23 vaporizes due to the absorption of heat from the gases entering the condenser 25 and the vapors produced are drawn off by conduit 36 which conducts them to the other pass of heat exchanger 33. Here the vapors are heated by absorbing heat from the compressed nitrogen flowing in the opposite direction. The suction conduit 37 of the compressor conducts the warmed vapors out of the heat exchanger 33 so that the compressor may recompress them and recycle the nitrogen. The amount of heat delivered to the coil 24 may be regulated by providing a suitable controllable bypass around the heat exchanger 33. The temperature of the condenser 25 may be controlled by regulating the pressure under which the nitrogen evaporates in the jacket 23. The rare gas containing concentrate that collects in kettle 22 is withdrawn through a conduit 38 controlled by valve 38'.

The residual gases from the synthesis of ammonia for example, are cooled in the periodically alternated cold accumulators 10 or 12 in countercurrent heat exchange with the krypton-freed gas and then introduced into the rectification column 20. A portion of the gas mixture passing up the column is liquefied in condenser 25, trickles downward in column 20 in countercurrent relation to the rising gas and thereby washes out the krypton which collects in the liquid in kettle 22 at the bottom of the column. The kettle 22 is heated by means of an auxiliary gas, e. g. nitrogen which is liquefied under pressure in the coil 24 and thereupon after expansion through valve 35 is evaporated by cooling condenser 25. The auxiliary gas is preferably conducted in cyclic fashion, i. e., after its evaporation in jacket 23 it is heated in countercurrent relation with itself in exchanger 33 and after compression in the compressor 29 and cooling is again employed for heating the column 20.

The recovery of the krypton from the gas mixture can now be effected by two different methods. The one method of operation according to the invention is analogous to the known scrubbing processes in which liquids are utilized whose boiling points are lower than that of krypton. For such a method there is condensed in condenser 25 principally nitrogen and a small quantity of methane to form the reflux liquid. Under these circumstances the gas mixture is separated into nitrogen-containing hydrogen, which is withdrawn through conduit 27, and into a mixture of the hydrocarbons collecting in kettle 22 which contains the krypton. The krypton concentrate is thereupon withdrawn through conduit 38.

Another method of krypton recovery according to the invention is contrary to any process previously employed, in that solvents for krypton are employed as washing media which are less volatile than krypton. It was found that hydrocarbons such as in particular, propane and the like, show a high solvent power and an extensive miscibility with krypton. Use is made of this discovery in a method of operation carried out in a form of apparatus which will be described in connection with Figure 2 where a mixture of hydrocarbons is liquefied at the foot of a separating column and is conducted as washing medium to the head of the column.

In the form of apparatus shown in Fig. 2, the rare gas containing mixture cooled by passage through the cold accumulators 10 or 12 is conducted to an expansion engine 19' wherein the gas mixture is expanded to a lower pressure with the production of external work so as to provide refrigeration to counteract heat losses. The expanded mixture is conducted by conduit 119 from the expander to a column 120 where it passes upward in intimate countercurrent contact with reflux liquid passing down the column. The treated gas passes from the top of the column 120 through the conduit 27 to the valve 15 which in the position shown passes the cold treated gas to accumulator 12 where it deposits its refrigeration. The treated gas flows out of accumulator 12 through conduit 14 to valve 11 which is in the position to pass the treated gas to discharge conduit 28. The incoming rare gas containing mixture in this position of the valves is seen to flow through accumulator 10 to be cooled and to be passed to conduit 19 by valve 15. When the valves 11 and 15 are reversed the flow through the accumulators is in the opposite direction, the treated mixture flowing through accumulator 10 and the incoming mixture flowing through accumulator 12. In this form of apparatus, reflux is provided by supplying a hydrocarbon gas which may preferably be a member of the paraffine series, for example, propane under pressure through a conduit 130 to the heating coil 124 disposed within the lower kettle 122 of the column 120. From the heating coil 124, where the propane is cooled and liquefied by heating the liquid in kettle 122, the propane is conducted as reflux liquid to the upper tray 121 of the column after passage through the expansion valve 135. The cold liquid propane, passing down the column dissolves krypton and carries it down to the kettle 122 becoming more concentrated in krypton as it passes down. The more volatile gases are driven off by the heating of the lower kettle but the solvent power of the propane holds the krypton back and a krypton concentrate may be withdrawn from the lower kettle 122 through the conduit 138 which is controlled by valve 138'.

Other oxygen-free and krypton-containing gases can be used for the safe production of krypton in accordance with the present invention in the same manner as the residual gases from the synthesis of ammonia are treated. To this group belong all gas mixtures which are produced through the gasification of fuels by the utilization of air or oxygen, and which generally contain hydrogen as their principal component, such as for example, the gases used for coal hydrogenation or for syntheses, or the residual gases from the hydrogenation or syntheses.

It has been proposed to recover krypton from gas mixtures such as flue gas which are richer in nitrogen than air. These gases, however, always contain residual oxygen which becomes enriched together with the krypton and the hy-

drocarbons, so that the danger of explosion caused by the simultaneous presence of oxygen and hydrocarbons also exists in these instances. This hazard is eliminated by the method of the present invention.

The embodiment of the invention according to which the preliminary enrichment of the krypton is effected, for example, during the separation of air in an oxygen-containing atmosphere, wherein the presence of oxygen is not excluded until the krypton concentrate is to be treated, this is more fully explained below in connection with a preferred example, as diagrammatically shown in Fig. 3.

In an air separation plant, air is subjected to rectification by washing with liquid air in a rectifying column and the washed liquid at the foot of the column is evaporated to such a degree only that, in addition to the principal component oxygen, it contains approximately 1% krypton and a maximum of 1% hydrocarbon. This mixture or concentrate is withdrawn from the separation plant, evaporated, and in accordance with the present invention, the oxygen content thereof is completely reacted with an excess of hydrogen. The oxygen-free concentrate thus produced is then subjected to further enrichment. Pure hydrogen is not required for this conversion, but it is possible, however, to utilize other hydrogen containing gases such, for example, as conversion hydrogen which contains nitrogen, carbon monoxide or hydrocarbons. Likewise, fractions from the separation treatment of coke-oven gas or of hydrocarbon mixtures can be employed for this purpose.

One form of an apparatus for carrying out this further treatment is illustrated in Figure 3. As shown, the rare gas concentrate containing oxygen, produced by an air separation apparatus or by treatment in an apparatus such as that illustrated in Figure 1 from which it is withdrawn through valve 38', enters the apparatus shown in Figure 3 through conduit 38''. The mixture is introduced as shown, into the chamber of a reactor 39, preferably by means of nozzle 40. A combustible gas, for example hydrogen, is conducted to nozzle 40 through a conduit 41 for admixture with the oxygen-containing mixture. This combustible gas is preferably added in excess of the amount necessary for the complete combustion of the oxygen of the mixture and the products of combustion pass by means of conduit 42 into a condenser 44. Heat evolved by the combustion reaction may be used to generate steam in a boiler 43. Condenser 44 is preferably enclosed by a water jacket 45 to cause the condensible products of combustion such as water, to collect in a liquid separator 47 into which the products pass through a conduit 46. The remaining gas mixture, including gaseous products of combustion, is conducted from separator 47, by means of a conduit 48 into the bottom of an alkaline washing tower 49 where the gases pass upwardly and countercurrently to a descending stream of caustic solution or other medium suitable for removing carbon dioxide. For example, incoming washing liquid may enter through a conduit 50 and after falling through the tower 49, which is preferably packed to increase interfacial surface contact between liquid and gas, the liquid containing carbon dioxide is withdrawn at 51. Such liquid may be treated to remove carbon dioxide after which, if desired, it may be recirculated to the top of the tower 49. The washing step effected in tower 49 obviously, may be omitted if the gas mixture originally contained no hydrocarbons and pure hydrogen is used for the combustion. By means of a conduit 52 the washed gas, comprising in addition to the rare gases and hydrocarbons, the more volatile gases such as hydrogen, nitrogen and carbon monoxide, is conveyed from tower 49 to the inlet of a compressor 53 where it is compressed to a desired pressure. The compressed gas passes through a discharge conduit 54 to an absorber 55 which contains a dehydrating agent such as caustic, whereby the last traces of water are removed.

The dry gas then passes by means of conduit 56, through a heat exchanger 57, whereby it is cooled to a low temperature, and conducted into a rectifying column 58 through a heating coil 59 in the base of the column, wherein the gas is liquefied by heat exchange with liquid in the base of the column. From the coil 59, the substantially liquefied gas passes through a conduit 60 and an expansion valve 61 and enters onto a desired plate of the lower portion of fractionating column 58. The low boiling gaseous constituents pass up the column, and into contact with a reflux condenser 62 which condenses low boiling constituents to provide a sufficient amount of reflux to effect the separation of the rare gas from the gas mixture. The low boiling constituents such as hydrogen and nitrogen passing through reflux condenser 62 are discharged through a conduit 63 to heat exchanger 57 to chill the incoming gas entering through conduit 56 and leave the apparatus by a conduit 64. Reflux condenser 62 may be refrigerated in any suitable manner, for example as indicated in Figure 1 by means of a closed nitrogen circuit, whereby the liquid nitrogen enters through a conduit 65 and upon evaporation the nitrogen leaves through a conduit 66. The concentrated liquefied rare gases collecting at the base of the column are withdrawn therefrom through a conduit 67 by control valve 68.

The scrubbing of the rare gases from the concentrate can be effected in a particularly simple manner by washing the gas mixture either with liquid substances more volatile than krypton, such as relatively more volatile nitrogen or carbon monoxide, or with less volatile substances, such as relatively less volatile propane as previously described. The hereby resulting liquid, which is rich in krypton and xenon, can then be processed to pure krypton.

The advantages of the new process include not only the absolute exclusion of the dangers caused by the hydrocarbons, but rather also that the number of different wash liquids which become available for washing out the krypton is appreciably increased, since, by means of the present process, it is possible for the first time to employ hydrocarbons as washing mediums for the production of krypton.

I claim:

1. Process for producing the rare gases krypton and xenon which comprises collecting a concentrate of said rare gases, treating the said concentrate with liquid propane to dissolve said rare gases, separating said liquid propane containing said rare gases from the remainder of said concentrate, and separating the propane from the krypton and xenon.

2. Process for producing the rare gases krypton and xenon which comprises collecting a concentrate of said rare gases, the proportion of krypton in said concentrate being greater than the proportion of xenon, treating such con-

centrate with a liquid comprising liquefied propane to dissolve said rare gases, separating said liquid containing said rare gases from the remainder of said concentrate, and separating said liquid from the krypton and xenon.

3. Process for the production of krypton and xenon from an oxygen containing starting gas containing said rare gases which comprises forming a rare gas concentrate by chemical conversion of the entire oxygen content of said starting gas, removing the conversion products, further enriching the rare gas content by effecting a chemical conversion of components other than said rare gases, removing the products of said second conversion, treating said concentrate with liquid propane to dissolve said rare gases, separating said liquid propane containing said rare gases from the remainder of said concentrate, and separating said propane from the krypton and xenon.

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