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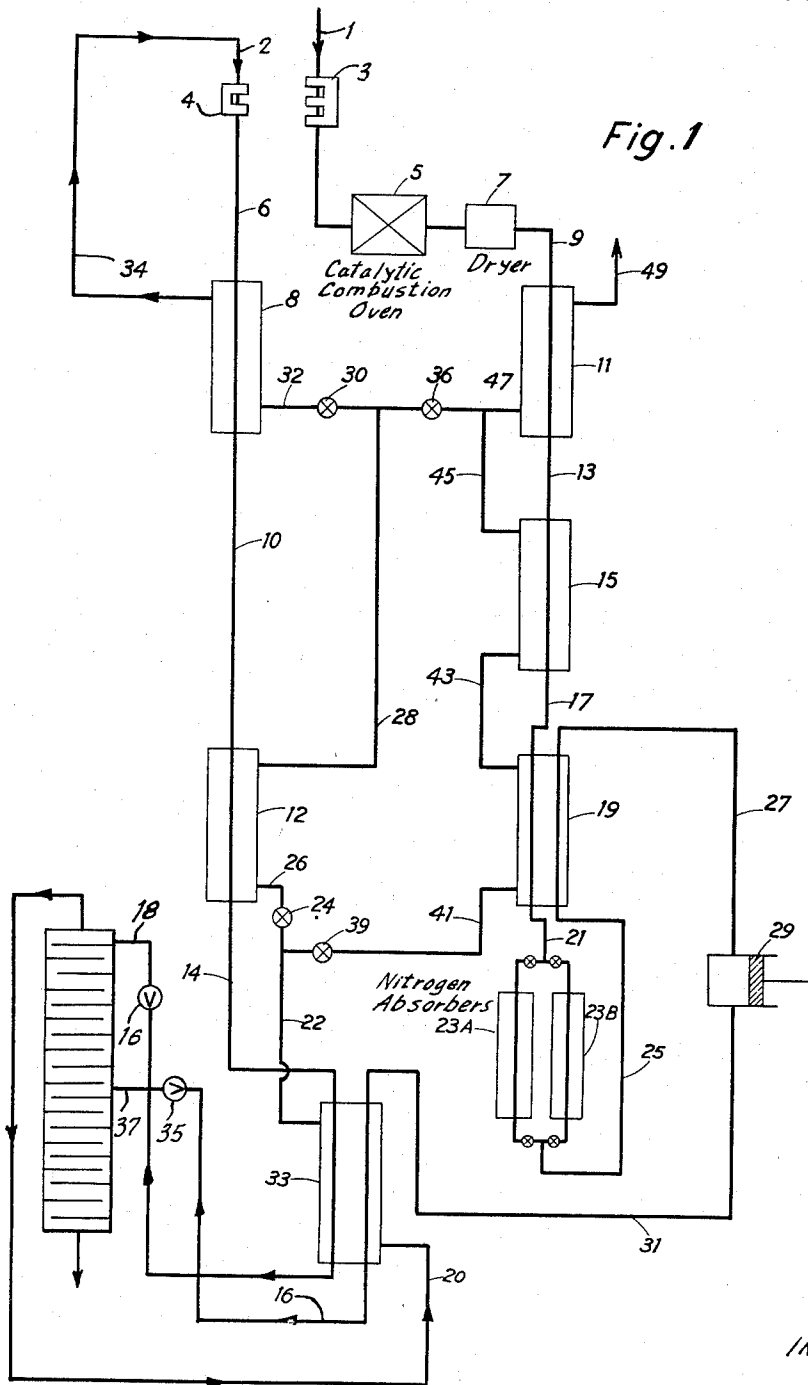
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GAS LIQUEFACTION PROCESS

Filed Aug. 12, 1957

2 Sheets-Sheet 1



INVENTOR

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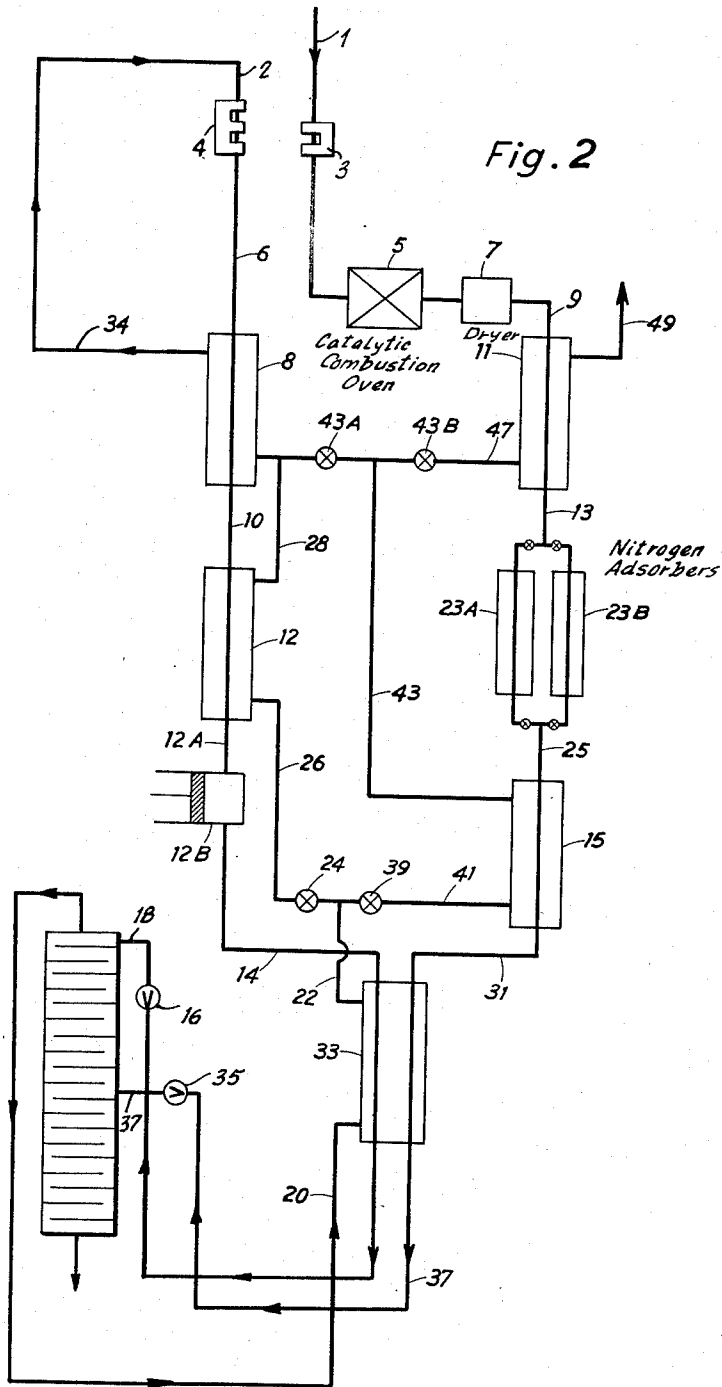
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GAS LIQUEFACTION PROCESS

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9 Claims. (Cl. 62—11)

The present invention relates to a process for liquefying a gas non liquefiable by expansion without external work, from the normal temperature, in which the gas to be treated comprises two fractions, the first one of which is expanded with external work and the second one of which is cooled by a heat exchange with the expanded gas of the first fraction, then subjected to a free expansion and partly liquefied.

The gases which are not liquefiable by free expansion, to which the process applies, have an inversion point for the Joule-Thomson effect, lower than the room temperature; a free expansion, starting from that temperature causes no cooling but a heating; it is thus impossible to liquefy them by a free expansion, without having them undergo a preliminary and important refrigeration bringing them to a temperature level lower than the inversion temperature for the Joule-Thomson effect. Amongst these gases, hydrogen and helium may be mentioned.

Amongst the known processes for liquefying these gases, some comprise an expansion with external work, starting from an initial temperature and with such an expansion ratio that the expanded gas is partly liquefied. This is a disadvantage, since the efficiency in cold production of an expansion with external work is good only if the expanded gas is substantially above its dew point and, on the other hand, it is difficult to have an expansion machine operate satisfactorily when liquid appears in it.

According to another process, the two fractions of the gas to be liquefied, after compression, are cooled by a heat exchange with a bath of liquefied gas such as liquid nitrogen, then separated; the first one is expanded with external work with no production of liquid, and ensures, by heat exchange, the cooling of the second one, which then undergoes a free expansion with a partial liquefaction; the non liquefied expanded gas ensures the cooling of the second fraction, then of the whole of the gas to be liquefied. The efficiency of the expansion with external work is better than in the previous case, but recourse must be had to an outside cold source for obtaining the liquid of the preliminary cooling bath.

The process according to the invention makes it possible to avoid the above mentioned drawbacks. It is characterized in that the compressed gas of the second fraction is cooled in a temperature interval above the temperature of the gas of the first fraction, previous to its expansion with external work, by means of a flow of expanded gas greater than its own flow.

The fact of cooling the gas of the second fraction by means of a larger gas flow makes it possible to lower its temperature in a more important manner before the free expansion and, consequently, to increase to a very large extent, the cold production efficiency of that expansion and consequently the amount of liquid produced, without having recourse to a cold source outside the apparatus.

Although the two fractions of the gas to be liquefied may be raised to the same pressure, it is preferable to raise the first fraction to a higher pressure than the second

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one. There is obtained, by expansion with external work of that high initial pressure to a relatively low pressure, the important production of cold necessary for obtaining gas in a liquid condition; a portion of the cold thus produced is transmitted by heat exchange to the second fraction, the free expansion of which then causes the partial liquefaction.

A particularly important application of this process relates to the case when it is desired to separate by rectification of the gas to be liquefied, another gas having a volatility little different, for instance when desiring to separate by rectification a light isotope from a heavy isotope of that gas. The expanded gas of the two fractions, a portion of which is liquefied, is then sent to a rectification apparatus. The more volatile gas obtained in a gaseous condition and possibly the less volatile gas are sent into heat exchange with the gas of the two fractions, the gas from the rectification, however, being sent for heat exchange with the gas of the second fraction in a greater amount than with the gas of the first fraction in a temperature interval above the temperature of the gas of the first fraction before its expansion with external work; the ratio of these quantities is controlled, of course, by usual means, as a function of the cold supply required by the rectification apparatus, and of the initial pressures of the two gas fractions.

The process according to the invention lends itself, in particular to the liquefaction of hydrogen, with a view to its separation into pure hydrogen and deuterium, but it can also be used for the liquefaction of other gases more difficult to liquefy than air, with a view to separating their isotopes or some of these gases from one another.

The process according to the invention will be described in greater detail hereinafter, in its application to the liquefaction of hydrogen before its separation by rectification, into pure hydrogen and deuterium, with reference to the appended drawing, which represents two diagrams of installations for its application.

Figure 1 represents an apparatus for the liquefaction of pure hydrogen free of deuterium, and of impure hydrogen, to be separated, obtained by electrolysis for instance, the expansion with external work taking place on the impure electrolytic hydrogen circuit.

Figure 2 shows a similar apparatus, but in which the expansion with outside work takes place on the pure hydrogen circuit.

In the installation represented in Figure 1, the electrolytic hydrogen which contains, in general, besides deuterium, as main impurities, oxygen (0.2% in volume, approximately) and nitrogen (about 0.1% in volume) is brought to the installation through the conduit 1 and compressed by compressor 3 to about 120 kg./cm.². It then enters a catalytic combustion oven 5, for instance of the platinum or palladium type, operating at about 200° C., and in which the oxygen it contains is transformed into water.

After cooling of the hydrogen into a cooler of the usual type, not shown, the water produced is stopped by a drying device 7, for instance of the alumina gel type, placed near the combustion oven.

The hydrogen, freed of oxygen is then sent back to a first heat exchanger 11 where it is cooled to about -100° C. by a substantially equal flow of pure hydrogen from the rectification apparatus, already partly warmed up as will be described hereinafter. The partly purified hydrogen is then sent through a conduit 13 to a heat exchanger 15 where it is cooled to -175° C. approximately by a lower and adjustable flow of pure hydrogen from the rectification apparatus.

The compressed hydrogen then goes through a con-

duit 17 to a new heat exchanger 19 where it is cooled again:

(a) by pure hydrogen, with a lower and adjustable rate of flow;

(b) by a return in counter-current to itself at the cold end of the exchanger, after elimination of the nitrogen in the adsorption apparatus which will be described hereinafter. The exchanger 19 makes it possible to lower temporarily the temperature of the hydrogen to be treated to about -230°C ., a temperature favorable for the subsequent elimination of nitrogen by adsorption. This temperature, however, is too low for allowing later an expansion with external work with a good efficiency; this is the reason why the hydrogen freed of nitrogen is then brought back to a temperature close to its temperature at the hot end of the exchanger by return in counter-current to itself.

The hydrogen, thus refrigerated to -230°C . is brought, through the conduit 21 to the nitrogen purifier, which comprises a pair of adsorption units 23A—23B; these are fitted with an adsorbing substance, which is not a catalyst for the reaction of transformation of ortho-hydrogen into para-hydrogen, and is selected, for instance, amongst certain silica-gels or charcoals; the hydrogen flows through one of these two units, which adsorbs the nitrogen it contains, while the other one is being regenerated by one of the usual methods (desorption in a vacuum, by heating, or by sweeping at a high temperature by a dry gas at a low pressure); these units are interchanged at fixed time intervals by a set of valves.

Upon issuing from the nitrogen purifier, the purified hydrogen goes, through the conduit 25, to the heat exchanger 19, already mentioned, where it is warmed up from -230°C . to about -175°C . It is then sent through the conduit 27 to the expansion machine 29 where it expands with external work, from 120 kg./cm.² to about 3 kg./cm.² while cooling down to about -235°C . Then it goes, through the conduit 31, to the heat exchanger 33 where it circulates in the same direction as the pure hydrogen under pressure of the free expansion circuit and in opposite direction to the pure hydrogen at low pressure from the rectification apparatus and is cooled down to about -250°C . It is then expanded through the valve 35 and introduced through the conduit 37 into the rectification apparatus, in a partly liquefied condition.

The pure hydrogen for ensuring the reflux in the rectification apparatus, is brought to the liquefaction installation through conduit 2; it is compressed, in the first place by the compressor 4 to about 25 kg./cm.²; then it goes, through conduit 6 to the heat exchanger 8 where it is refrigerated to about -100°C . by a substantially equal flow of pure hydrogen at low pressure, already partly warmed up. It then passes, through conduit 10 to the heat exchanger 12 where it is cooled down to about -230°C ., by a larger and adjustable flow of pure hydrogen at low pressure introduced in counter-current in the exchanger.

From the exchanger 12, the pure hydrogen under pressure goes, through the conduit 14, to exchanger 33 already mentioned, where it is cooled down to about -245°C . by the entirety of the low pressure pure hydrogen from the rectification column. It is then expanded through the valve 16 and liquefied for the most part, then introduced into the rectification apparatus through the conduit 18.

The pure, gaseous hydrogen at low pressure, from the rectification apparatus, at its boiling temperature (about -252°C .) goes, through the conduit 20 to the exchanger 33, mentioned above, where it cools the compressed hydrogen of the two circuits; it issues therefrom through the conduit 22 then is divided into two portions controlled by valves 24 and 39.

The first portion, the rate of flow of which is controlled by the valve 24 so as to be substantially larger

than that of the compressed pure hydrogen in the free expansion circuit, is sent through the conduit 26 to the exchanger 12 in counter-current to this same compressed pure hydrogen which makes it possible to refrigerate to a very important extent, then is evacuated therefrom through the conduit 28 and is divided again into two portions. One of these, in proportions controlled by the valve 30 in such a manner that its rate of flow be substantially equal to the rate of flow of pure hydrogen under pressure, is sent through conduit 32 to the exchanger 8 where it circulates in counter-current to the pure hydrogen under pressure and issues approximately at room temperature through the conduit 34. It may then be sent back to the compressor for pure hydrogen. The other one is added at an adjustable rate, through the valve 36 to the low pressure pure hydrogen used for cooling the electrolytic hydrogen circuit so as to restore substantially the equality of the rates of flow of gases circulating in opposite directions.

The second portion of the low pressure pure hydrogen issuing from the conduit 22 is sent at a controlled rate of flow through the valve 39 into the conduit 41 then to the exchanger 19 already mentioned where it heats up to about -175°C . It goes, through the conduit 43 to the exchanger 15 where it heats up to about -100°C ., then, after the addition of hydrogen, already mentioned, through the valve 36, through the conduit 47 to the exchanger 11 where it circulates in counter-current to a substantially equal flow of electrolytic hydrogen and issues at a temperature close to room temperature through the conduit 49.

It should be realized, of course, that the flows through the valves 24, 39, 30 and 36, and the initial pressures of the two circuits of electrolytic hydrogen and pure hydrogen, as well as the pressure at the outlet from the expansion machine with external work 29 cannot be adjusted independently and should be controlled in correlation, according to the necessary contribution in cold for the operation of the rectification apparatus.

In the installation for the liquefaction of hydrogen, represented in Figure 2, the various elements are similar, but the expansion machine with external work 12B is located in the pure hydrogen circuit, with an initial compression of about 120 kg./cm.², and there is sent, through the valve 39 and conduit 41 to the heat exchanger 15 a flow of low pressure pure hydrogen larger than the flow of hydrogen compressed to about 25 kg./cm.² circulating in this same exchanger. The equality of the rates of flow of cooled and heated gases in the two circuits is restored by adjustment of the valve 43A and 43B.

The choice of one or the other of the two arrangements described above cannot be determined according to a general rule, one and the other both offering certain advantages. Thus the first arrangement—expansion machine with external work on the electrolytic hydrogen circuit—offers a greater flexibility of operation. On the other hand, the second arrangement makes it possible to operate the purification devices—catalytic combustion oven and adsorption type purifier—under a lower pressure and to avoid the repercussion of jolts in the operation of the expansion machine on the adsorption type purifier.

What I claim is:

1. A process for liquefying hydrogen and separating it by rectification under a low pressure into deuterium-enriched hydrogen and deuterium-depleted hydrogen, comprising the steps of: compressing a stream of said hydrogen to a high pressure, cooling it to a temperature above -175°C . by heat exchange with an equal mass flow rate of a low pressure hydrogen stream issued from said rectification, further cooling it to about -175°C . by heat exchange with a smaller mass flow rate of a low-pressure hydrogen stream issued from said rectification, expanding it with external work and rectifying it, compressing a stream of warmed up deuterium-depleted hy-

drogen issued from said rectification to an intermediate pressure, cooling it to a temperature above -175°C . by heat exchange with an equal mass flow rate of a low-pressure hydrogen stream issued from said rectification, further cooling it to a temperature under -175°C . by heat exchange with a larger mass flow rate of a low pressure hydrogen stream issued from said rectification, subjecting it to a free expansion and feeding it to said rectification as a wash liquid.

2. A process according to claim 1, wherein the high-pressure hydrogen stream at about -175°C . is further cooled to about -230°C ., purified by adsorption at the same temperature and warmed up again to about -175°C ., before being expanded with external work.

3. A process for liquefying hydrogen and separating it by rectification under a low pressure into deuterium-enriched hydrogen and deuterium-depleted hydrogen, comprising the steps of: compressing a stream of warmed up deuterium-depleted hydrogen issued from said rectification to a high pressure, cooling it to a temperature above -175°C . by heat exchange with an equal mass flow rate of a low-pressure hydrogen stream issued from said rectification, further cooling it to about -175°C . by heat exchange with a smaller mass flow rate of a low pressure hydrogen stream issued from said rectification, expanding it with external work and feeding it to said rectification as a wash liquid, compressing a stream of hydrogen to be separated to an intermediate pressure, cooling it to a temperature above -175°C . by heat exchange with an equal mass flow rate of a low-pressure hydrogen stream issued from said rectification, further cooling it to a temperature under -175°C . by heat exchange with a larger mass flow rate of a low-pressure hydrogen stream issued from said rectification, subjecting it to a free expansion and rectifying it.

4. A process according to claim 3, wherein the intermediate pressure hydrogen stream cooled to a temperature above -175°C . is purified by adsorption at said temperature, before being cooled to a temperature under -175°C .

5. A process for liquefying hydrogen and separating it by rectification under a low pressure into deuterium-enriched hydrogen and deuterium-depleted hydrogen, comprising the steps of: compressing a first stream of hydrogen to a high pressure, cooling it to a temperature above -175°C . by heat exchange with an equal mass flow rate of a low pressure hydrogen stream issued from said rectification, cooling it to about -175°C . by heat exchange with a smaller mass flow rate of a low pressure hydrogen stream issued from said rectification, expanding it with external work and feeding it into the rectification zone, compressing a second hydrogen stream to an intermediate pressure, cooling it to a temperature above -175°C . by heat exchange with an equal mass flow rate of a low pressure hydrogen stream issued from said rectification, cooling it to under -175°C . by heat exchange with a larger mass flow rate of a low pressure hydrogen stream issued from said rectification, subjecting it to a free expansion and introducing it into the rectification zone, warming up a low pressure deuterium-depleted hydrogen stream issued from said rectification and recycling it as one of said first and second hydrogen streams.

6. A process for liquefying hydrogen and separating it by rectification under a low pressure into deuterium-enriched hydrogen and deuterium-depleted hydrogen, comprising the steps of: compressing a first stream of hydrogen to a high pressure, cooling it in a first temperature interval by heat exchange with an equal mass flow rate of a low pressure hydrogen stream issued from said rectification, further cooling it by heat exchange with a smaller mass flow rate of a low pressure hydrogen stream issued from said rectification, expanding it with external

work and feeding it into the rectification zone, compressing a second hydrogen stream to an intermediate pressure, cooling it by heat exchange with an equal mass flow rate of a low pressure hydrogen stream issued from said rectification to a temperature above that of said first stream before its expansion with external work, further cooling it by heat exchange with a larger mass flow rate of a low pressure hydrogen stream issued from said rectification to a temperature under the Joule-Thomson effect inversion point and under that of said first stream before its expansion with external work, subjecting it to a free expansion, introducing it into the rectification zone, warming up a low pressure deuterium depleted hydrogen stream issued from said rectification and recycling it as one of said first and second streams.

7. A process for liquefying hydrogen and separating it by rectification under a low pressure into deuterium-enriched hydrogen and deuterium-depleted hydrogen, comprising the steps of: compressing a first stream of hydrogen, cooling it by heat exchange with an equal mass flow rate of a low pressure hydrogen stream issued from said rectification, further cooling it by heat exchange with a smaller mass flow rate of a low pressure hydrogen stream issued from said rectification, expanding it with external work, introducing it into the rectification zone, compressing a second hydrogen stream, cooling it by heat exchange with an equal mass flow rate of a low pressure hydrogen stream issued from said rectification to a temperature above that of said first stream before its expansion with external work, further cooling it by heat exchange with a larger mass flow rate of a low pressure hydrogen stream issued from said rectification to a temperature under the Joule-Thomson effect inversion point and under that of said first stream before its expansion with external work, subjecting it to a free expansion and introducing it into the rectification zone, warming up a low pressure deuterium-depleted hydrogen stream issued from said rectification and recycling it as one of said first and second streams.

8. A process for liquefying a gas the Joule-Thomson effect inversion point of which is under room temperature, and separating it by low pressure rectification into component gases, comprising the steps of: compressing a first gas stream, cooling it by heat exchange with an equal mass flow rate of a low pressure gas stream issued from said rectification, further cooling it by heat exchange with a smaller mass flow rate of a low pressure component gas stream issued from said rectification, expanding it with external work and introducing it into the rectification zone, compressing a second gas stream, cooling it by heat exchange with an equal mass flow rate of a low pressure component gas stream issued from said rectification to a temperature above that of said first stream before its expansion with external work, further cooling it by heat exchange with a larger mass flow rate of a component gas stream issued from said rectification to a temperature under said Joule-Thomson effect inversion point and under that of said first stream before its expansion with external work, subjecting it to a free expansion and introducing it into the rectification zone, warming up a low pressure component gas stream issued from said rectification and recycling it as one of said first and second streams.

9. A process according to claim 8, wherein the gas of the first stream is compressed to a higher pressure than that of the gas of the second stream.

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