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Cytryn

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[54] CRYOGENIC ABSORPTION CYCLES

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[21] Appl. No.: **152,332**

[52] **U.S. Cl.**............................ **62/101,** 60/36, 62/9, 62/112, 62/335, 62/467, 62/476, 203/DIG. 17
[51] **Int. Cl.**.. **F25b 15/00**
[58] **Field of Search**....... 62/46, 101, 102, 112, 467, 62/476; 60/36

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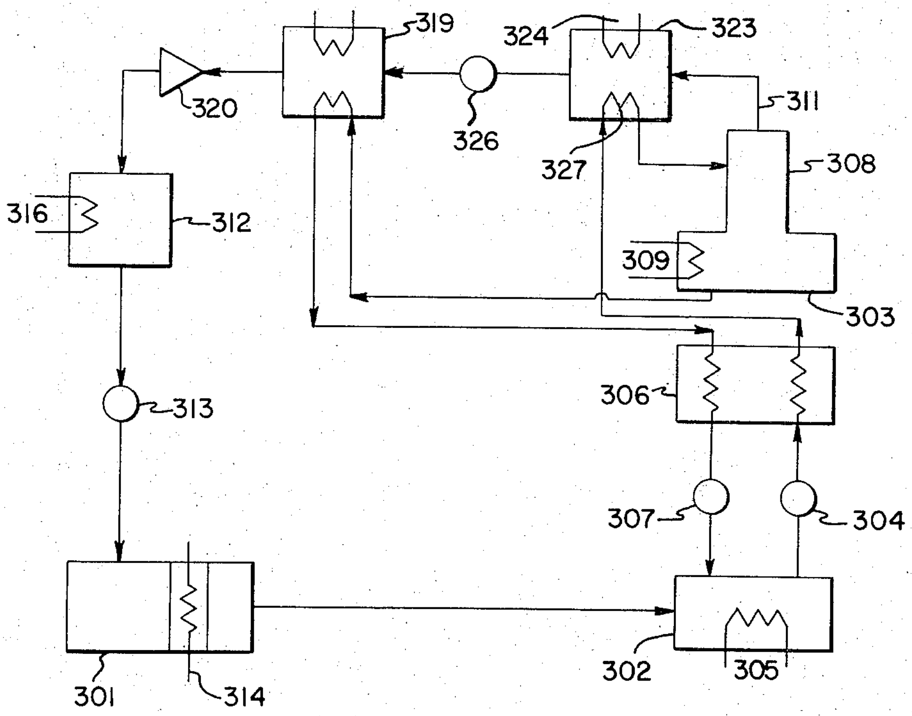
Assistant Examiner—Peter D. Ferguson
Attorney, Agent, or Firm—Millen, Raptes & White

[57] ABSTRACT

For the development of power and/or the production of cryogenic fluids, e.g., oxygen, absorption refrigeration cycles are employed. For example, one process comprises the steps of absorbing a refrigerant vapor in a liquid absorbent, increasing the pressure on resultant mixture of said refrigerant and said absorbent, distilling and rectifying the mixture into substantially pure refrigerant vapor and pure absorbent, reducing the pressure on resultant pure liquid absorbent and returning the latter to the absorbing step, cooling and condensing the refrigerant vapor to the liquid state, reducing the pressure upon the liquid refrigerant to below the triple point of the refrigerant to produce solid refrigerant, sublimating the solid refrigerant to the vapor state, and passing resultant refrigerant vapor to the absorbing step at a rate that maintains the pressure below the triple point.

10 Claims, 17 Drawing Figures



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SHEET 1 OF 8

FIG. I

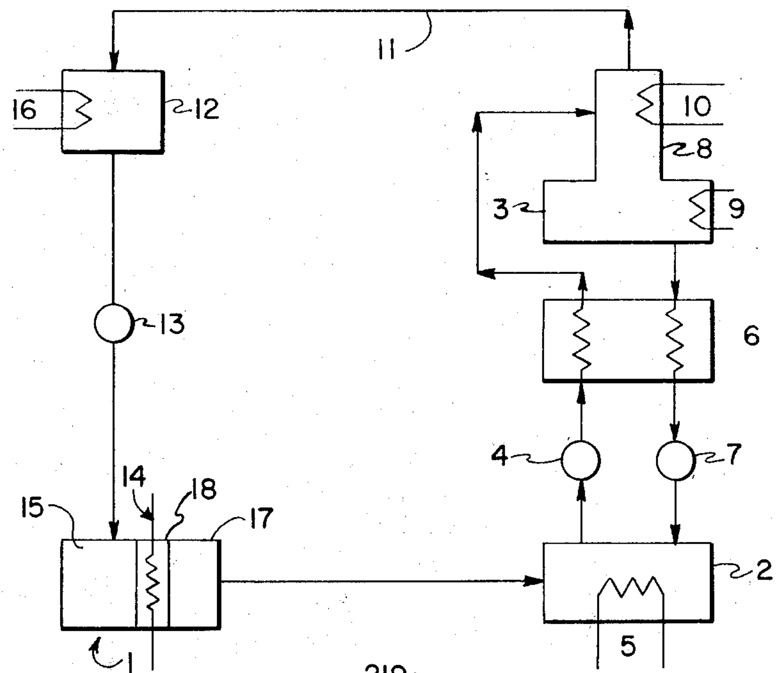
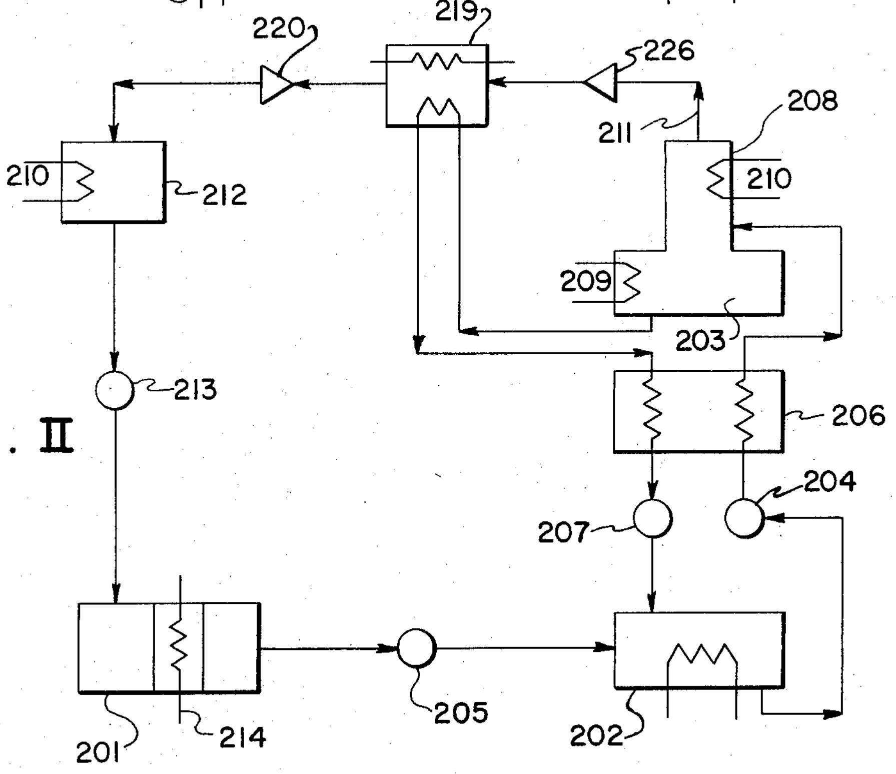


FIG. II



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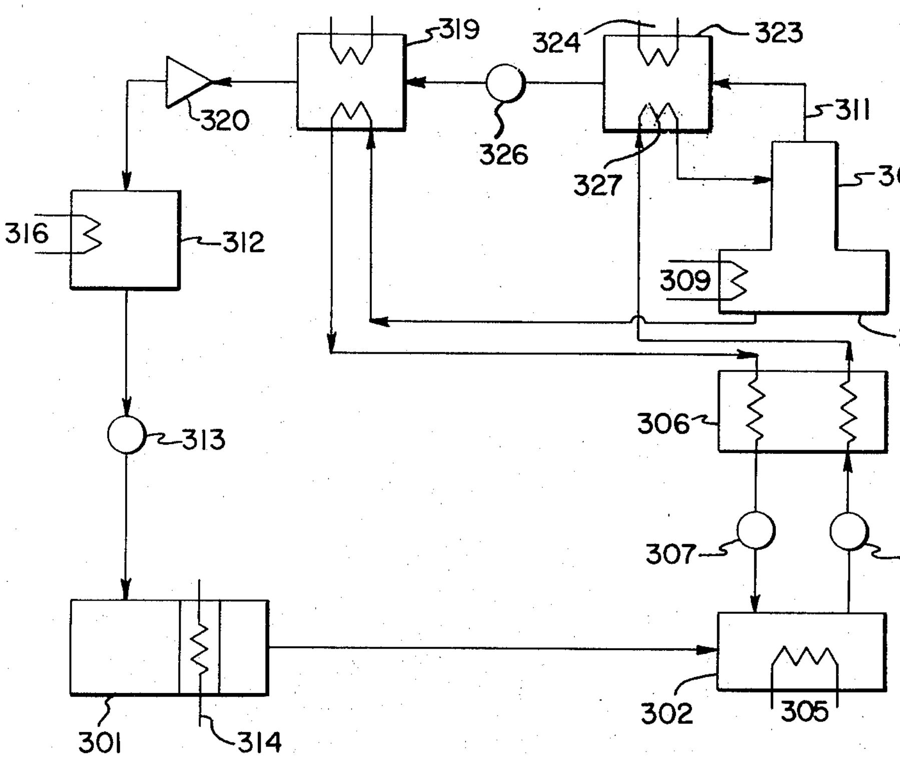

FIG. III

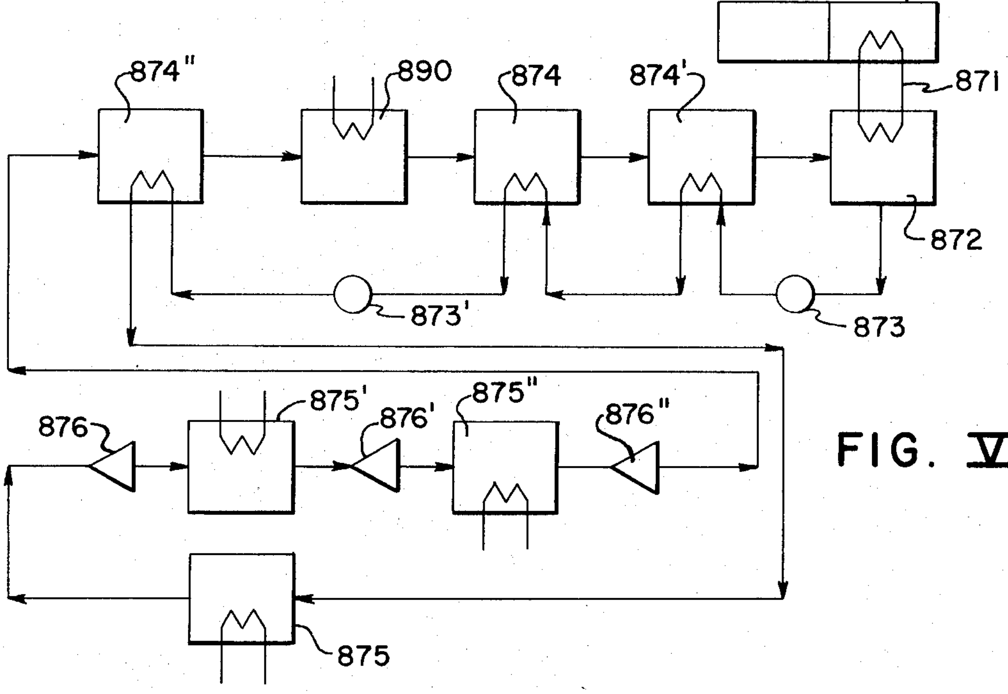

FIG. VIII

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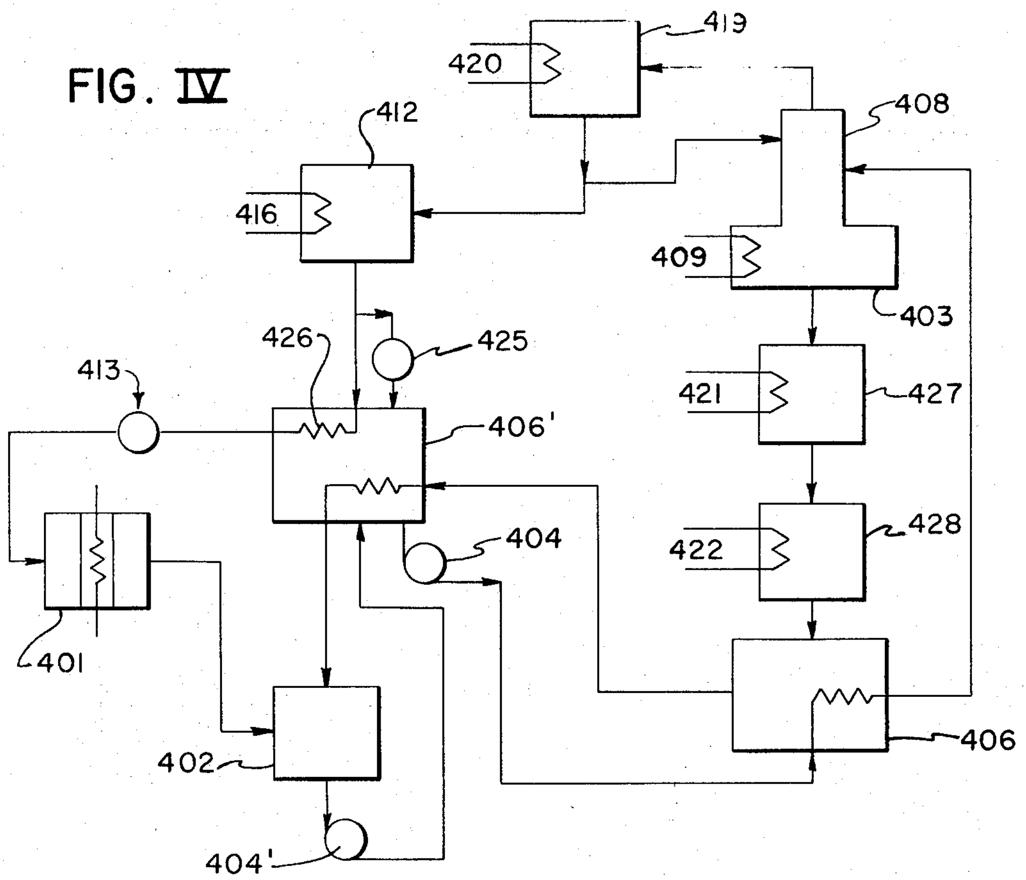
FIG. IV



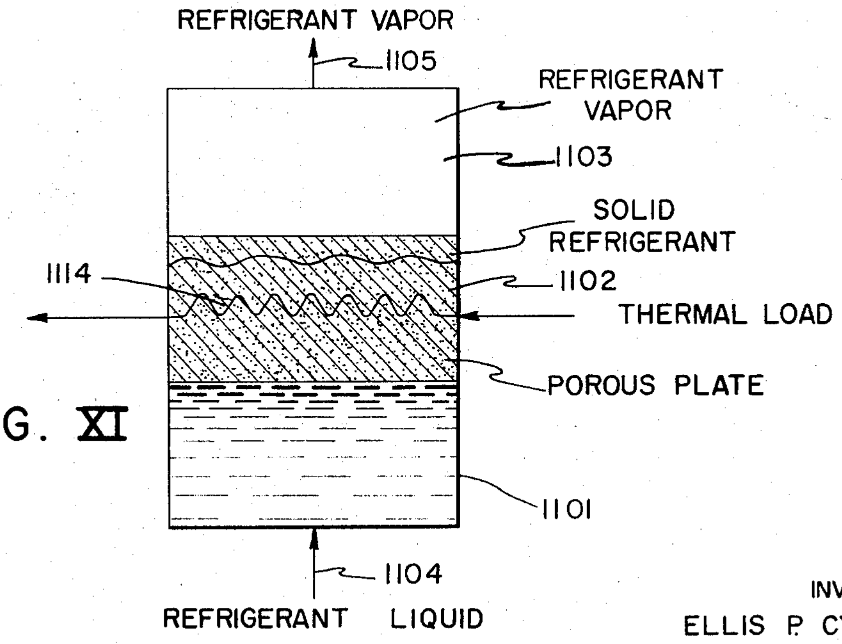


FIG. XI

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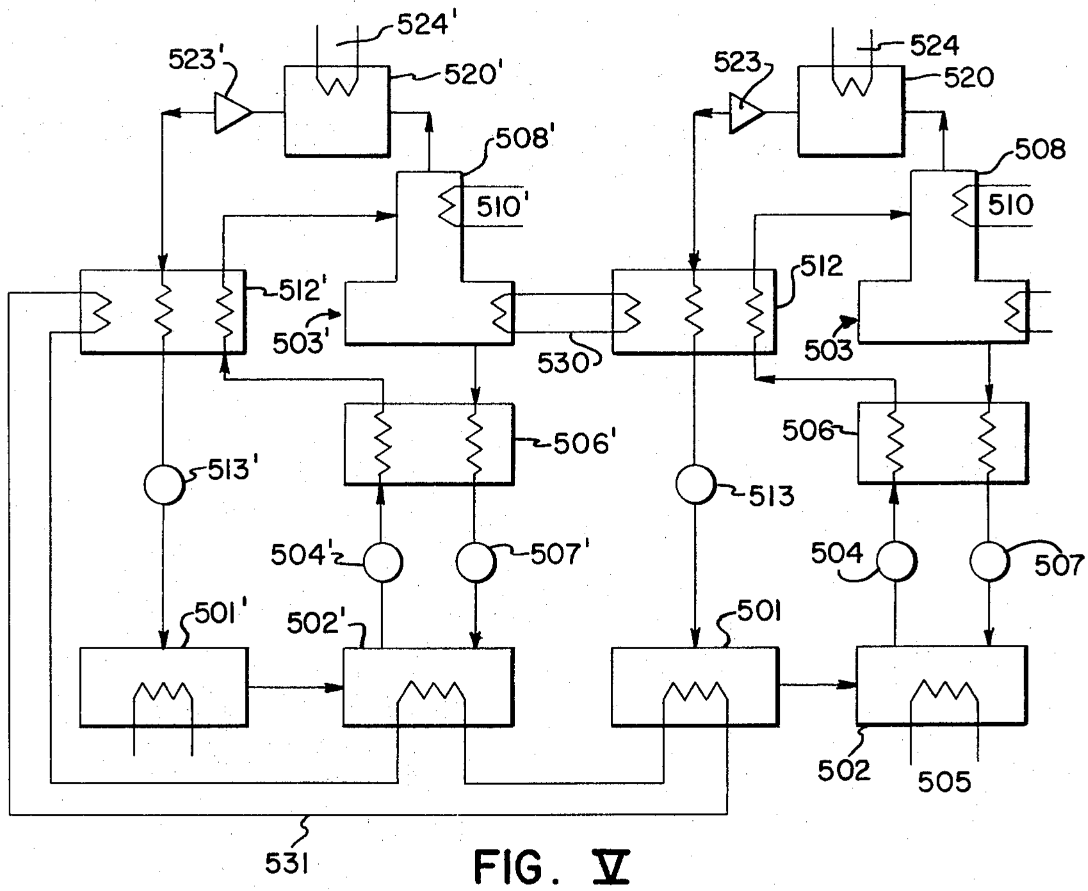

FIG. V

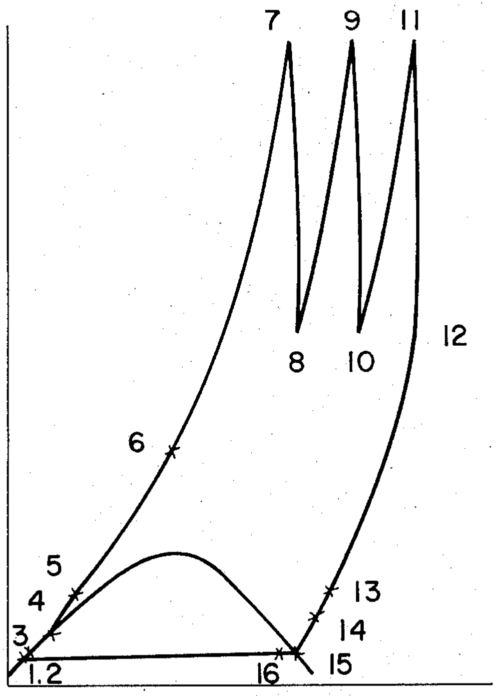

FIG. XIV

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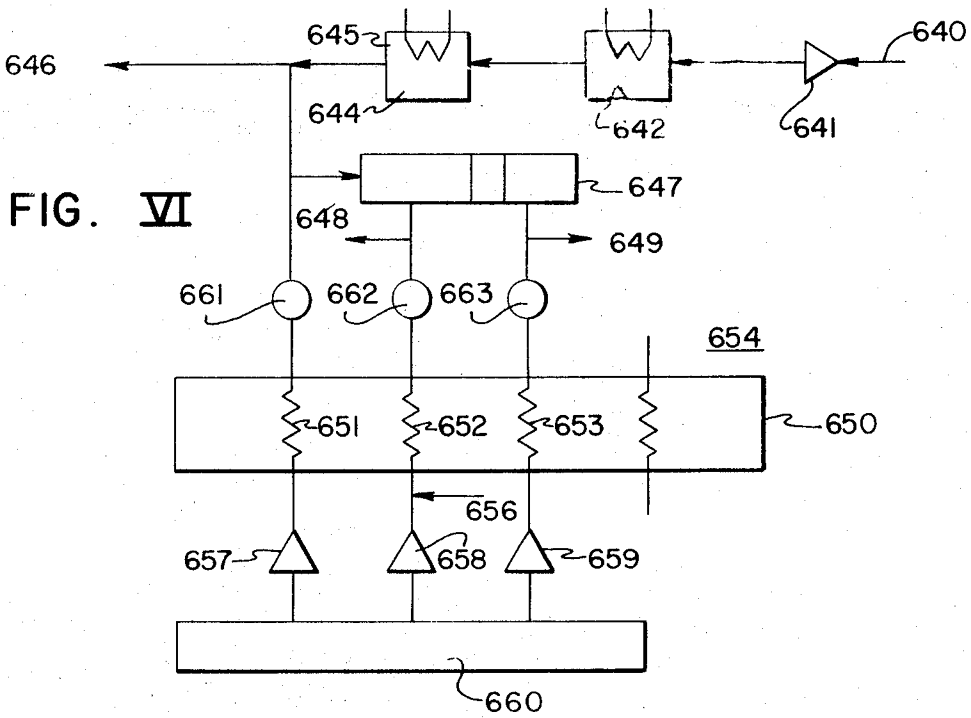

FIG. VI

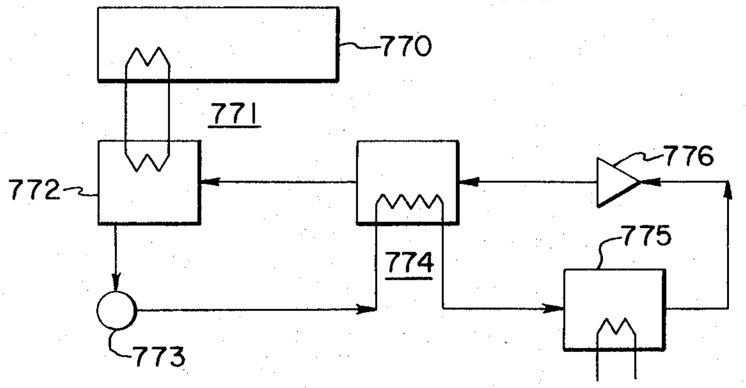

FIG. VII

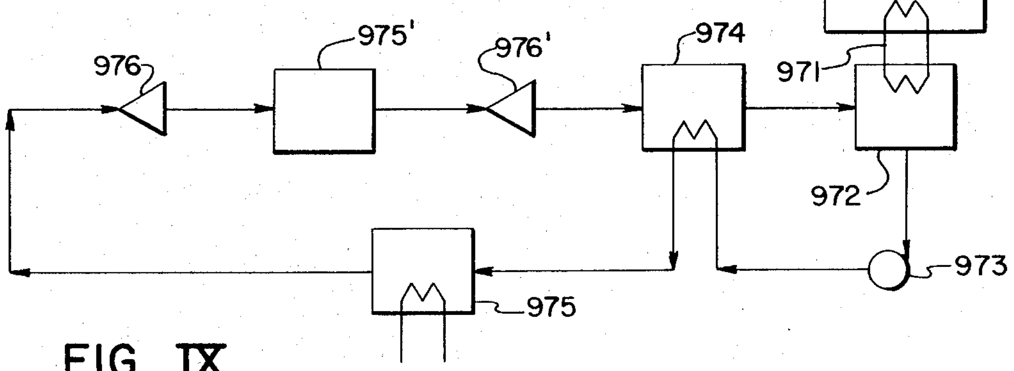

FIG. IX

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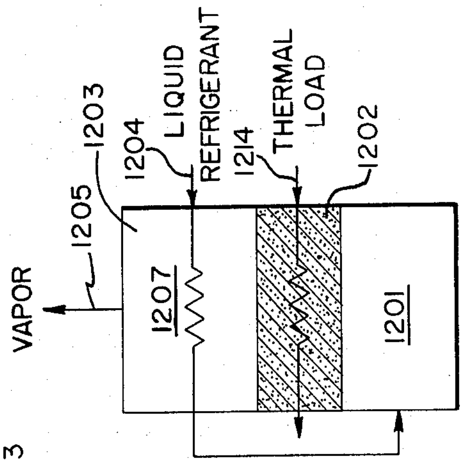

FIG. XII

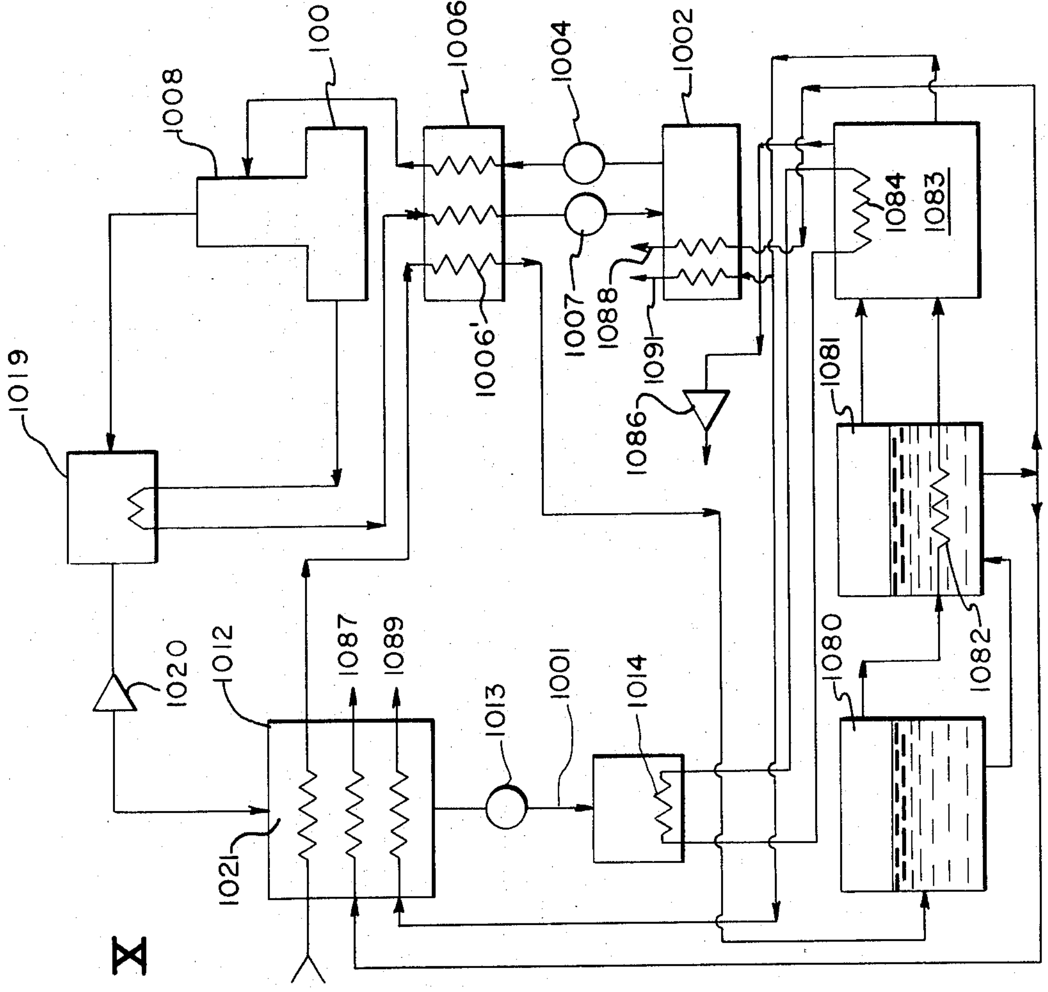

FIG. X

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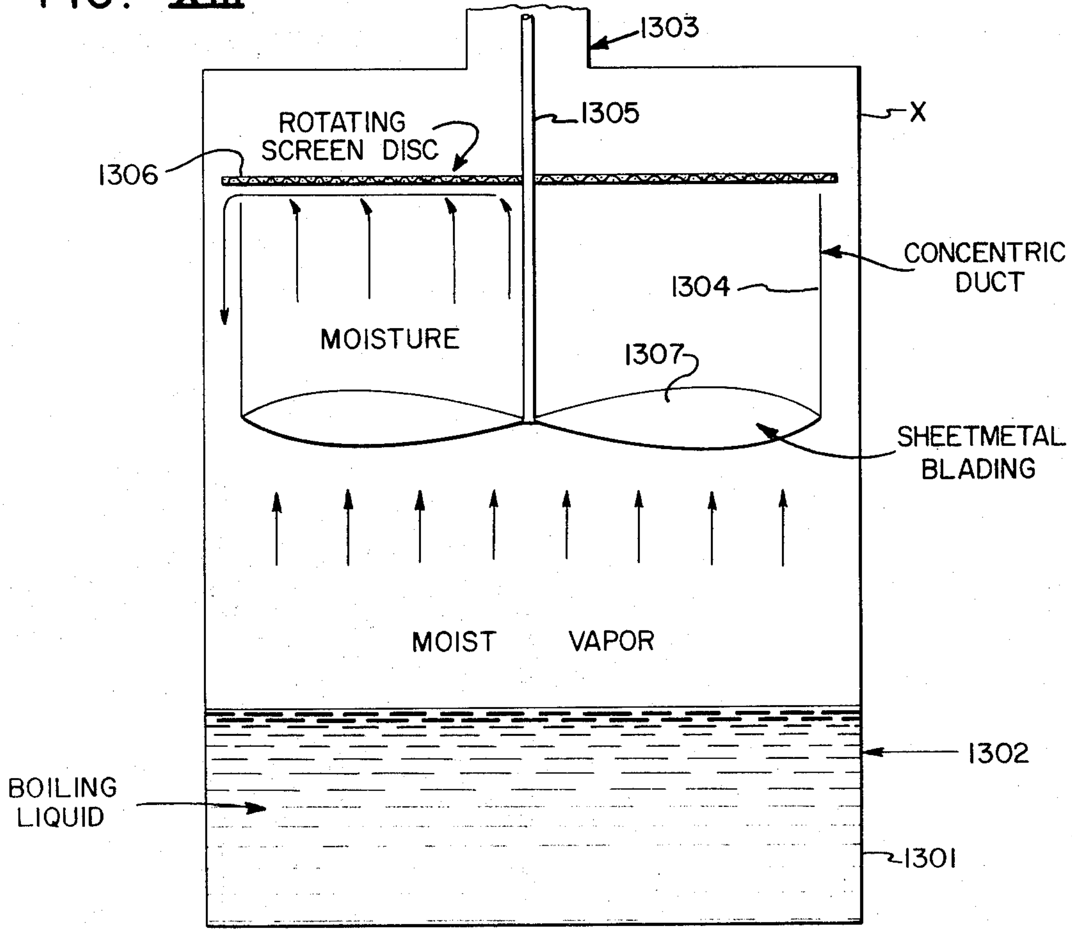
FIG. XIII



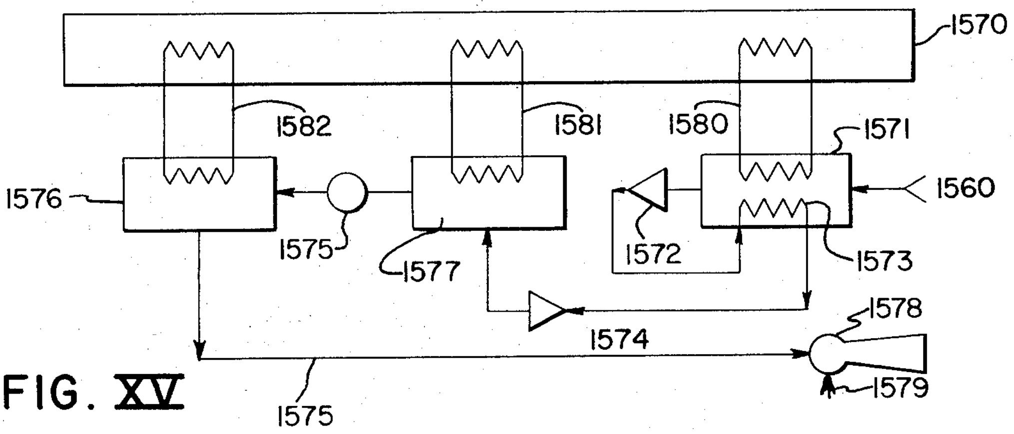
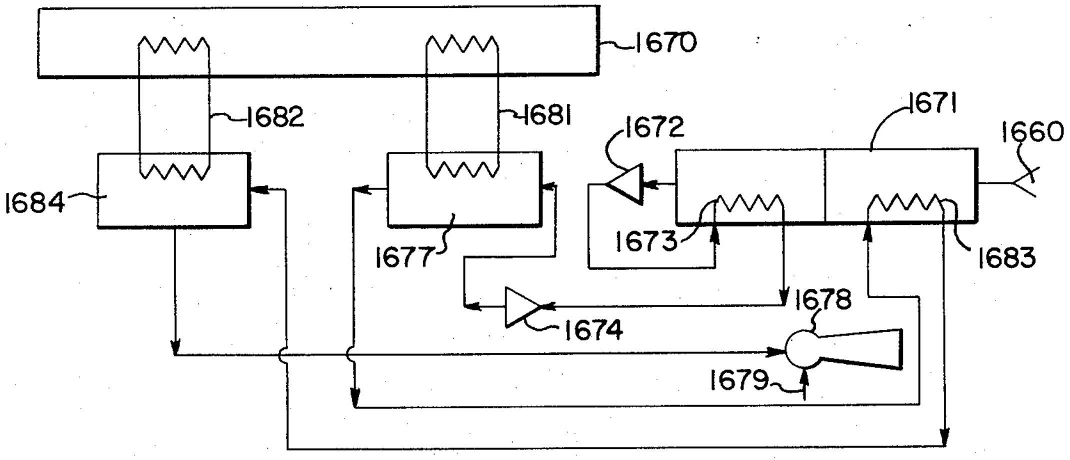


FIG. XV

FIG. XVI



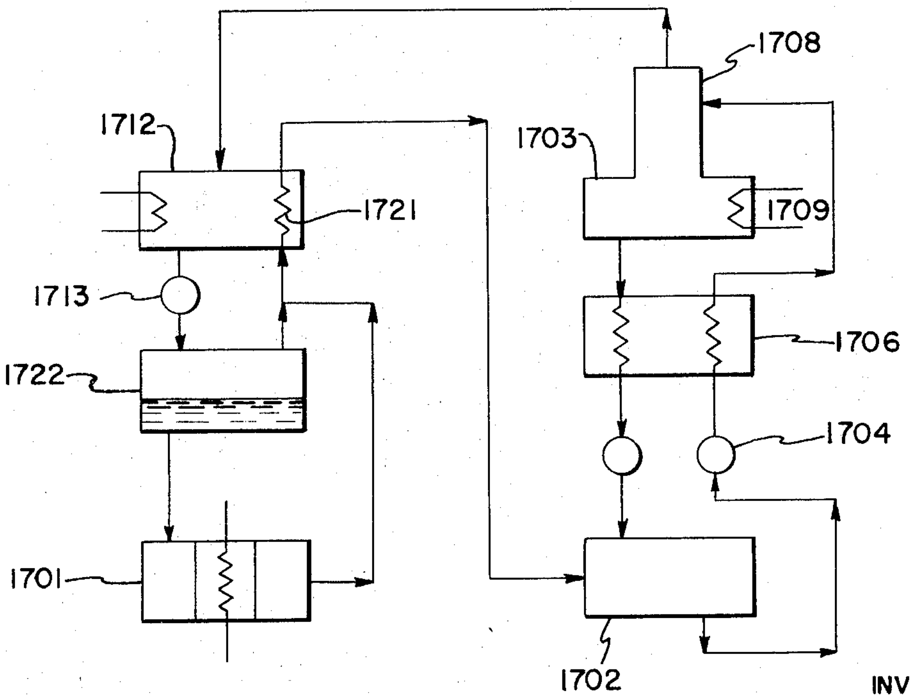


FIG. XVII

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CRYOGENIC ABSORPTION CYCLES

This invention relates to improvements in industrial processes for the development of power and the production of useful industrial products, such as liquid air, liquid oxygen, liquid nitrogen and the development of cryogenic temperatures and is based upon new arrangements and cycles of absorption refrigeration.

BACKGROUND OF THE INVENTION

Since the development of the steam engine in the Seventeenth Century, the common source of energy for man's use has been the combustion of fossils fuels at high temperatures. This burning of fossils fuel in either a furnace or in an internal combustion engine has resulted in the pollution of the atmosphere with both the products of combustion and with heat, and the removal of heat in the development of power has resulted in the thermal pollution of large bodies of water. In a high temperature energy system, such as the steam turbine, the working fluid water is first evaporated at high pressure and then expanded in the turbine and finally condensed to liquid at temperatures above the ambient temperature. The heat rejected is usually discharged into a river or lake. The use of water as the working fluid introduces the exceedingly high heat of vaporization of water. This heat of vaporization is energy of which a large part is lost in the system. Because the prior processes can utilize only a small fraction of the heat supplied by the burning of fuel, the net result is that our environment is subjected to a serious thermal pollution.

SUMMARY OF THE INVENTION

The present invention offers techniques which permit the reduction of polluting effect of the prior process for converting heat into power, as these techniques utilize heat which has been wasted. One embodiment of the present invention begins with air at ambient temperature and pressure and liquifies the air at subatmospheric pressure and temperature and recovers the energy from the air. As a feature of this process the air can be heated during the process by what is now considered to be waste heat, and the energy of this waste heat recovered. The present invention teaches the recovery of useful work from waste heat and from solar energy.

This invention is based upon the employment of one or more absorption refrigeration cycles, so arranged that energy may be recovered from the cycle and allows the production of cryogenic temperatures and the production of useful products. This invention is directed to utilization primarily of cycles in which the refrigerant is highly or completely soluble in the absorbent, such as, but not limited to the use of a hydrocarbon, such as methane, in solution of a higher boiling hydrocarbon, such as ethane or propane. Other combinations such as ethane in solution in propane or propane in butane are illustrative. Further examples of useful combinations are solutions of nitrogen in methane, or ethane, or hydrogen in methane. Any hydrocarbon whose saturation pressure and temperature relationships are between that of methane and butane is acceptable. It is apparent that substituted hydrocarbons such as the halogenated hydrocarbons can be used. In order to secure the maximum differences in temperatures, this invention contemplates the employment of a cascade operation having a series of absorption refrigeration cycles using different refrigerants, such as the use of ethane or propane in the first cycle, ethane or methane in the second cycle, and methane or nitrogen in final cycle. If even lower temperatures are desired, additional cycles using neon, hydrogen or helium as the refrigerants may be employed in lower temperature cycles.

It is thus an object of this invention to provide a system in which very low cryogenic temperatures can be obtained with the energy for the system being derived from waste heat.

It is a further object of the invention to recover the latent energy from low temperature heat sources such as waste heat from power plants or from solar energy.

It is a further object of this invention to recover pure gases from air using low grade heat as the source of the energy needed to separate the pure gas from air.

It is a further object of this invention to recover pure water from saline and impure waters using an absorption refrigeration cycle to supply the energy to separate the pure water from the brine.

It is a further object of this invention to recover energy from fluids which are being liquified.

It is a further object of this invention to produce a low temperature process in which the refrigerant is sublimed.

It is still a further object of this invention to provide an evaporator-sublimator which has a porous partition.

It is a further object of the invention to provide a power system which can be utilized for the propulsion of vehicles in which the amount of heat discharged is substantially reduced and in which the efficiency is materially increased.

Further objects and advantages of the present invention will become apparent upon further study of the specification and claims.

BRIEF DESCRIPTION OF THE DRAWINGS

The more specific objects and advantages of this invention will be more readily apparent from the ensuing description wherein reference is made to the accompanying drawings illustrating the preferred embodiments of the invention.

In the drawings,

FIGS. I to X and XV to XVII are schematic flow sheets illustrating the principal features of the various embodiments.

FIG. I shows the basic absorption refrigeration cycle in a simplified form in which an evaporator-sublimator is used.

FIG. II shows an embodiment of the absorption refrigeration cycle of the basic system in which energy is recovered by the cycle.

FIG. III shows another embodiment of the basic system in which energy is recovered.

FIG. IV is another embodiment of the absorption refrigeration cycle which permits the recovery of thermal energy from the system.

FIG. V shows an embodiment of the invention in which two absorption refrigeration cycles are connected in a cascade manner and in which mechanical energy is recovered in each cycle.

FIG. VI shows an embodiment of the invention in which air is liquified and energy is recovered.

FIG. VII shows a further embodiment in which a gas is liquified and in which energy is recovered.

FIG. VIII shows a system for recovering energy from low temperature source by the use of air as a pressure medium.

FIG. IX shows a system similar to FIG. VII in which two turbines are employed.

FIG. X illustrates an embodiment of the invention in which the refrigeration cycle is combined with a saline water distillation system.

FIG. XI is cross-sectional view through an evaporator-sublimator of this invention.

FIG. XII is a cross-sectional view of another embodiment of an evaporator-sublimator of this invention.

FIG. XIII is a chart showing the conditions during a power recovery cycle of this invention.

FIG. XIV is a cross-sectional view of flash distillation vessel of this invention.

FIGS. XV and XVI are illustrations of this invention in which the power generated is used as a propulsive force.

FIG. XVII shows the invention as applied to liquefaction of gases.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

FIG. 1 illustrates the basic refrigeration cycle employed by this invention. In this Figure and throughout the description of this specification only the basic elements of the system are described. Auxiliary equipment common to refrigeration systems is omitted from the drawing and from the description to facilitate the understanding of the principles of the invention.

The present invention employs a basic absorption system which includes the step of evaporating the refrigerant in a heat sink by the removal of heat from another body, followed by the absorption of the refrigerant in an absorbent to form a liquid solution. The solution is transferred to another place and heated to separate the refrigerant from the absorbent followed by the condensation and return of the refrigerant to the evaporator. The system preferably is operated with the separator and condenser at a higher pressure than the absorber. While it is possible to introduce a third fluid to the refrigerant and absorbent solution to produce transfer of the fluids by diffusion without the requirements for mechanical energy inputs, this invention contemplates a continuous system in which mechanical energy is used to transfer the solution of refrigerant in absorbent from the zones of lower pressure to the zones of higher pressure. This energy can be recovered, at least in part from the absorbent and the refrigerant as they move from the zones of higher pressure to the zones of lower pressure. In order that substantial refrigerating effects are obtained and that there be available substantial recovery of energy, it is contemplated to have substantial difference in pressure between these zones.

In FIG. I, the evaporator-sublimator **1** is connected by a conduit with the absorber **2.** This conduit may be provided with means to produce a lower pressure in the evaporator-sublimator 1 than in the absorber **2.** The provision of such means is particularly desirable when the refrigerant is present as a solid in the evaporator-sublimator and the pressure is below the triple point, and when it is desirable to increase the solubility of the refrigerant in the absorbent.

The absorber **2** receives the vapor from the evaporator-sublimator and also receives absorbent from the regenerator **3.** The absorber **2** can be provided with known means for effecting contact between the vapor and the liquid. The pressure in the absorber will be maintained below the saturation pressure for the refrigerant in the absorbent. The solution which is a mixture of the refrigerant and absorbent is transferred by the pump **4** to the regenerator **3.**

As the refrigerant and absorbent used in the preferred embodiments of this invention may have close boiling points, it is generally necessary to have a distillation process embodying a rectification system to separate the substantially pure refrigerant from the relatively pure absorbent. While it is generally contemplated to employ a rectification column, there are some combinations of refrigerant and absorbent which can be separated by simple distillation.

The regenerator or separator **3** includes a rectification column **8** having a cooling coil **10** to provide the necessary reflux for separation. This column can be of any well-known construction and can be either a plate column or a packed column. The regenerator will also be provided with a heating coil **9.** This coil will ordinarily supply the major part of the heat used in the process and will generally reach the highest temperature in the cycle.

In accordance with good distillation practice, the solution of refrigerant and absorbent will be introduced into the column at an optimized point. The composition of the mixture introduced at the point will approximate the composition of the mixture in the column at the point of introduction. The preferred mode of heating the mixture of the refrigerant and absorbent before it is introduced into the column will be described later.

The column **8** will produce a vapor stream of substantially separated refrigerant at the top of the column and a stream of liquid absorbent relatively free from refrigerant from the bottom of the regenerator **3.** The absorbent which is hot and under high pressure is returned to the absorber prior to which it must be reduced in temperature and pressure to substantially the temperature and pressure in the absorber. The pressure may be reduced by passing the liquid through the turbine **7** which will recover part of the energy imparted by the pump **4.** The liquid absorbent may be cooled, at least in part, by heat exchange with the solution which is being fed to the column **8.** The heat exchanger **6** is shown provided with coils or the like for effecting this exchange of heat. When the amount of heat in the liquid absorbent is greater than that which can be absorbed by the solution, the absorbent can be cooled by other means.

The substantially pure vapor discharged from the top of the column is passed through the line **11** to the condenser **12.** As the vapor in condenser **12** is under substantially higher pressure than exists in the evaporator, it can be condensed to a liquid at a higher temperature than exists in the evaporator-sublimator **1** or the absorber **2.** The condenser **12** will cool the refrigerant to a temperature below its condensation point at the pressure existing in the condenser. This will discharge a portion of the heat from the system.

The condensed refrigerant is passed as a liquid through the pressure reducing means **13.** This can be a simple pressure reducing valve or orifice. However, it is preferred to use a device which will recover at least some of the energy available upon the release of pressure. This device will normally take the form of a turbine of known construction, but any other form of device which will recover the energy can be used. It is to be understood that whenever the term "turbine" is used to described a means for recovering energy by pressure reduction, any similar expansion engine is included.

The evaporator-sublimator **1** is provided with a heat exchange means **14**, which supplies the heat necessary to vaporize the refrigerant and is cooled to approach the lowest point in the cycle. The evaporator-sublimator **1** is preferably of the construction shown in more detail in FIGS. XI and XII, and will be described later. This evaporator-sublimator is designed to permit the conversion of the refrigerant to vapors by either sublimation or evaporation. The liquid refrigerant from the pressure reduction means **13** is fed into the first compartment **15** of the evaporator-sublimator **1.** This compartment is separated from the vapor section **17** by a porous plate **18** through which passes the heat exchange means **14.** The liquid in compartment **15** is at a slightly higher pressure than exists in the vapor section **17**, and thereby oozes through the porous partition.

When the pressure in the compartment **17** is below the triple point, the refrigerant will freeze as it is passed through the porous partition. The frozen refrigerant will thus block the pores in the plate and prevent further flow. The heat exchange means **14** will then supply the heat necessary to sublime the refrigerant. At this stage the heat exchanger **14** constitutes the heat sink of the process. This manner of operation requires that the pressure in the vapor section be below the triple point for the refrigerant. To maintain this pressure may require the positive removal of vapor from the section **17** by mechanical means.

If the pressure of the refrigerant in the section **17** is not below the triple point of the refrigerant, the liquid refrigerant will ooze through the porous plate and be evaporated by the heat from the heat exchange **14.**

The evaporator-sublimator **1**, the absorber **2**, the regenerator **3**, the column **8**, and the condenser **12**, are provided with suitable heat exchange means **14, 5, 9, 10** and **16**, respectively. The heat exchanger **14** will supply the heat necessary to vaporize the liquid refrigerant and will cool the fluid circulating therein to the lowest temperature in the system. The heat exchangers **5, 10** and **16** will abstract heat from the system.

As this invention prefers the use of refrigerants of the class of methane, ethane, nitrogen, neon, hydrogen and helium with absorbents selected from the lower boiling hydrocarbons and lower boiling point inorganic fluids, the heat of solution in absorber **2** will be relatively small and the amount of heat removed by heat exchanger **5** will be a minimum and in some instances the heat exchanger **5** may be omitted.

Since the refrigerants employed in the present invention have relatively low boiling points, the highest temperature necessary in the regenerator **3** can be relatively low and can be supplied with waste heat or by solar heat. The temperature of condensation selected in the highest temperature cycle can be selected according to the needs of the process and the cooling medium available. In some instances, water at ambient temperature can be used, and in others the heat can be rejected through a suitable heat exchanger directly to the ambient atmosphere.

FIG. II shows another embodiment of the cycle shown in FIG. I which permits the conversion of some of the thermal energy within the absorption refrigeration system to mechanical energy. In this modification, the gaseous refrigerant discharging from the column **208** of the regenerator **203**, is first compressed then heated and expanded to recover part of the energy. The gas leaving the column **208** is fed to a compressor **226** through the conduit **211** of a suitable type. The compressed vapor is passed through the heat exchanger **219** where the vapors are heated. All or part of this heat may be supplied by passing the relatively pure absorbent from the regenerator **203** through the heat exchange elements of the exchanger **219.** The exchanger may also supply heat from external sources.

The heated and compressed gaseous refrigerant is then expanded through the turbine **220** to convert the thermal energy to mechanical energy. The cooled refrigerant at lower pressure is then passed to the condenser **212** where it is cooled to condensation point. The liquid is then passed through the pressure reduction means **213** and fed into the evaporator-sublimator **201.** The vapors from the evaporator-sublimator **201** are passed by mechanical inducement in pump **205** to the absorber **202** and mixed with absorbent which has passed through the heat exchangers **219** and **206** and turbine **207.** The solution from the absorber **202** is pumped by pump means **204** through the heat exchanger **206** to the column **208.**

Referring to the embodiment illustrated in FIG. III, the pure absorbent from the regenerator **303** is passed through the heat exchange means **319** and supplies part of the heat to the refrigerant which has been compressed by pump **326.** The partially cooled absorbent then is passed to the heat exchanger **306** and then through the turbine **307** to the absorber **302.** As the absorbent has been partially cooled before arriving at the heat exchanger **306**, it supplies only a part of the heat necessary for conditioning the mixture or solution of refrigerant and absorbent to be fed into the column. Additional heat can be supplied to the mixture by cooling the vapors in the heat exchange means **327.**

The heat for the separation of the mixture is supplied by the heat exchange means **309**, and the refrigerant is vaporized by the heat supplied in the evaporator-sublimator **301** by the heat exchange means **314.** Heat is removed from the condenser by the heat exchange means **316**, and the absorber by heat exchange means **305.** It is to be understood that the area of heat exchange surfaces in the regenerator **303**, the condenser **312**, the heater **306**, the cooler **323**, the absorber **302**, and the heater **319**, will be selected to give the transfer appropriate to steady operation.

The features which are specifically shown in FIGS. I, II and III can be combined or modified by the features of each other and can be used in connection with auxiliary equipment as is well-known in the art.

FIG. IV illustrates a cycle which is an embodiment of the basic cycle and which is designed to produce very low temperatures in single cycle. This arrangement materially reduces the amount of energy required to generate a given refrigerating effect. In this example the values are given for a cycle using methane as the refrigerant and propane as the absorbent.

In a specific operation of FIG. IV, the evaporator-sublimator **401** is supplied with about 0.45 pounds of methane per second at a temperature of about 163° R. and discharges the vapors at about 135° R. at a pressure of 0.1354 psia. The vapors are passed to the absorber **402** and are mixed with about 1.1 pounds per second of propane having a temperature of about 154.5° R. The pressure in the absorber **402** is about 0.0967 psia. The solution of methane in propane is discharged from the absorber at the rate of about 1.6 pounds per second and at a temperature of about 153° R. The solution passes to a heat exchanger corresponding to the heat exchanger **6** of FIG. I. In FIG. IV this heat exchanger has two sections **406** and **406'**. The solution enters the section **406'** and is heated by indirect heat exchanges with two separate sources of heat. One source of heat is the stream of propane returning from the regenerator **403** to the absorber. This stream is supplied at the rate of about 1.14 pounds per second at a temperature of about 159° R. The other source of heat is the condensed methane from condenser **412** which has a temperature of about 229° R. and is passed through the heat exchanger at the rate of 0.45 pounds per second. Simultaneously, a minor stream of the condensed methane from condenser **412** is introduced into the solution of methane and propane in the heat exchanger section **406'** by turbine **425.** This stream is supplied at the rate of 0.19 pounds per second. The solution is discharged from the heat exchanger **406'** at the rate of 1.79 pounds per second at a temperature of 155° R. The solution is then heated in heat exchanger section **406** to about 374° R, by the stream of propane returning to the absorber. The solution is pressurized by the pumps **404** and **404'** to a pressure of about 600 psia and is introduced into column **408** of the regenerator or separator **403.** The regenerator **403** is heated by the coil **409** which received a heating medium at 658° R. The separated propane leaves the regenerator at a weight of 1.144 pounds per second at a temperature of 653° R. Before entering the heat exchanger **406,** the stream of propane is cooled by passing through heat exchangers **427** and **428.** The stream of propane is cooled by fluid passing through coils **421** and **422** to a temperature of about 449° R. The methane leaves the top of the column **408** at the rate of about 5.47 pounds per second and is transferred to heat exchanger **419** where the methane is cooled by fluid in the coil **420.** The methane leaving the column **408** is at about 340° R. and is cooled to 336° R. in the heat exchanger **419.** A major amount of the methane amounting to about 4.82 pounds per second is returned to the column **408** where it serves as reflux. The minor portion of the methane amounting to about 0.64 pounds per second is transferred to the condenser **412.** In condenser **412,** the methane is cooled and liquified to a temperature about 229° R. and the stream is passed to the heat exchanger **406'**. The major portion of the condensate amounting to 0.45 pounds per second passes through the coil **426** and is passed through the pressure reducing means **413** into the absorber **401.** A minor portion of the condensed methane is passed through turbine **425** into contact with the solution in the heat exchanger **406'** and mixed therewith.

The mode of operation as described for FIG. IV presents a specific manner in which the present invention may be applied. While relative quantities and temperatures given are considered as merely illustrative of a

single operation, it should be noted that this operation requires only the addition of mechanical energy to operate the pumps **404** and **404'**. In this example, the heat supplied was at 658° R. or 199° F. which would be normally considered as waste heat. In this example, the heat supplied is such that $Q=$ about 229 in the regenerator and the heat supplied to the evaporator is such that $Q=100$. Also in the example, the heat is removed in the exchangers **427** and **428** amounts to such that $Q=164$ and the amount removed by exchanger **419** amounts to such that $Q=$ about 50 and the heat removed in the condenser is such that $Q=124$. From these values, it will be appreciated that in the cycle a cooling effect of about one half of the heat supplied is obtained at a temperature of 135° R. or −324° F. with the use of waste heat and minor amount of mechanical energy.

The quantities of refrigerant, absorbent and temperatures may be varied to suit specific problems without departing from the invention.

FIG. V illustrated one manner in which it contemplated to arrange two absorption refrigerating cycles of this invention, in a cascade manner so as to utilize maximum percentage of the energy supplied to the system. The Figure also illustrates how energy can be recovered in a cascade system. In each of the cycles shown in this Figure, the vapors of refrigerant are passed from the respective evaporator-sublimators **501** and **501'** to the corresponding absorbers **502** and **502'** and are there mixed with the returning absorbent. The separate solutions of refrigerant and absorbent are pumped by pumps **504** and **504'** through the respective heat exchangers **506** and **506'**. In each of the cycles of this Figure a further refinement of the utilization of energy is shown in that, instead of passing directly from the heat exchangers **506** and **506'** to the midpoints of the columns **508** and **508'** of the regenerators **503** and **503'**, the solutions are passed through the heat exchange coils in condensers **512** and **512'** and then lead into the columns **508** and **508'**. The vapors from the columns **508** and **508'** are passed through their respective heat exchangers **520** and **520'**. The vapors are heated in these exchangers by heating fluid supplied to coils **524** and **524'**. While the connection is not shown on the drawing for passing the returning absorbent from the regenerators **503** and **503'**to the heat exchangers **520** and **520'**, it is to be understood that a portion, at least of the heat supplied to the vapors, may be derived from these sources as shown in FIG. III. The separate streams of vapors heated in exchangers **520** and **520'** are expanded by passing them through the corresponding turbines **523** and **523'**. The vapors from the turbines are then fed to the condensers **512** and **512'** respectively and the energy in the liquid refrigerant recovered in the pressure reducing means **513** and **513'** and the liquids passed to the evaporator-sublimators **501** and **501'**.

In FIG. V the two cycles are shown as being in heat exchange relation by having a heat transfer means **530** removing heat from condenser **512** and supplying the same heat to the regenerator **503'**. Another heat transfer means **531** is shown for removing heat from the condenser **512'** and absorber **502'** and supplying this heat to the evaporator **501.**

The turbines **507** and **507'** perform the same functions as the corresponding parts in FIG. I, as do the heat exchangers **505, 509, 510** and **510'**.

While the cascade arrangement is illustrated with only two cycles, three, four or more cycles can be constructed and connected in the manner shown. The first cycle of a series could employ ethane as the refrigerant, the second could use methane, and subsequent cycles could employ nitrogen, neon, hydrogen and helium as refrigerants. The number of cycles and the refrigerant will be selected according to the needs of the system.

As shown by the several Figures of the drawing, the available heat in one portion of the system can be transferred to another location in the same cycle where the difference in temperature is sufficient to effect a worthwhile heat exchange. The area of the heat exchange surfaces will be selected to give the desired transfer of heat. The individual features may be combined whenever a significant saving of heat or energy will be effected.

FIG. VI illustrates a generic arrangement for the liquification of a gas such as air, using the heat sink of an individual cycle or a plurality of cycles to remove the heat from the air. In this Figure, the details of the refrigeration cycles have been omitted and are indicated merely by the cooling coils in the heat exchangers **642** and **644.**

Atmospheric air enters through a conduit **640** and is passed through the turbine **641** into a region of lower pressure and is passed through the heat exhangers **642** and **644** of the absorption refrigeration cycle. The cooling of the air is provided by substantially isentropic expansion in the turbine and by heat exchange with the heat sinks of the refrigeration evaporators in the heat exchangers **642** and **644,** where the air is condensed to liquid. The system may be provided with known means to remove water vapor and carbon dioxide, to avoid fouling of the heat exchanger surfaces.

The liquid air is discharged from the heat exchanger **644** into conduit **645** and may be drawn off as a product by conduit **646.** Alternatively, the liquid air may be fed to separator **647,** which may be of known construction, e.g., a rectification column which will separate the liquid air into its components. Frequently, only nitrogen and oxygen will be separated, but the invention contemplates the recovery of the minor constituent gases of the atmosphere, e.g., argon, neon, helium, krypton, hydrogen xenon, ozone and radon, if desirable. The carbon dioxide in the air may also be recovered in the process.

The oxygen and nitrogen may be drawn off at **648** and **649,** if desired, to use the separated element as such and may be supplied to other processes. The liquid air from conduit **645** may be passed to pump **661** where the fluid is pressurized and then passed to coil **651.** Similarly, the oxygen passes to pump **662** and coil **652,** and the nitrogen to pump **663** and coil **653** of heat exchanger **650.** The respective streams can then be passed, if desired, to turbines **657, 658** or **659** respectively. The product may be recovered by vessel **660.** In the event that oxygen is being passed through the turbine **658,** it may be desirable to mix the oxygen with a fuel which is introduced through conduit **656** and to ignite the mixture before the combustion gas is passed through the turbine **658.**

This Figure illustrates the many ways in which the absorption refrigeration system can be used commercially to recover energy and to supply liquid, air, oxygen, nitrogen, or the rare gases to industrial processes. Since the process of refrigeration as described in this specification does not require the consumption of large amounts of energy, it provides these materials in an economical manner.

In FIG. VI, the heat exchanger **650** may also serve to transfer heat between two or more of the streams. As for instance the coil **651** which receives liquid air may serve to further cool other streams, or may be further cooled by the other streams. The coil **654** is indicated as a separate heat exchange means for an independent heat transfer medium to supply heat to or to remove heat from the exchanger **650,** and may serve to transfer heat between the liquid air, the nitrogen or oxygen and the absorption refrigeration cycle. There may be a plurality of these means as desired. The vessel **660** into which the gases are individually collected may serve as a heat sink for the absorption refrigeration system or as an independent cooling means.

FIG. VII illustrates the basic system for recovering energy using a low temperature in the cycle with air as the energy transfer medium with liquifaction of the air. In this cycle the lowest temperature will be substantially the temperature of liquid air, and the highest temperature normally contemplated is that available from waste heat. While it is preferred to use waste heat as the source of the highest temperature in the cycle, it is clear that if the conditions are feasible the air can be heated to a higher temperature by the combustion of fuel. In the preferred form the cascade absorption refrigeration system is used to produce the low temperatures in the cycle. A cascade refrigeration system as illustrated in FIG. V is indicated by the block **770** in the drawing. This system is provided with heat transfer means **771** to remove heat from the energy producing system. While only a single means **771** is indicated in the drawing it is to be understood that this means may be composed of a plurality of separate connections for transferring heat at different temperatures between the systems.

The heat exchanger, which is shown diagrammatically, is supplied with a gas, usually air, which is condensed by the cooling effect of the transfer means to a liquid. While air is usually the gas employed, nitrogen or other gases can be used to avoid the risk of combustion and oxidation. The liquid air from the heat exchanger **772** is passed to the pump **773** which increases the pressure on the liquid. The change in pressure is usual quite significant. The liquid at the higher pressure is circulated through the heat exchangers **774** and **775** and converted to gas at high pressure and temperature and then is expanded through the turbine **776.** The air leaving the turbine is cooled in heat exchanger **774** by heat exchange with the liquid air from the pump **773.** The cooled air is then fed to the condenser or heat exchanger **772** completing the cycle.

This Figure shows a simplified energy recovery system, in which energy in the form of heat is supplied to the system by the heat exchanger **775,** which roughly corresponds to the boiler of a conventional steam power system, and which converts the liquid air to hot gas at high pressure. The hot compressed air is expanded through the turbine and cooled by the liquid air from the condenser, which corresponds to the condenser of a steam system. The pump **773** corresponds to the injector on a steam boiler system. Since the lowest temperature in the proposed system is near absolute zero the efficiency of the system is high. The maximum efficiency of a steam system is low since the temperature of condensation is high. As pointed out above, while the invention contemplates the use of waste heat, the air may be heated in heater **775** by heat from any source.

FIG. VIII illustrates a more developed system for recovering energy. This Figure employs the basic energy system set forth in FIG. VII. In this Figure, the absorption refrigeration system is indicated by the block **870**. This absorption refrigeration system can be like the one shown in FIG. V but the details of the system have been omitted for the purpose of clarity. The refrigeration system is shown as removing heat from the energy recovery system by the heat transfer means **871** associated with the condenser or heat exchanger **872**. The liquid gas which will be, hence forth referred for convenience as liquid air, is passed from the condenser **872** to the first pump **873** which increases the pressure of liquid air to about 50 psia. The pressurized liquid air is passed through the heat exchangers **874** and **874'** and is heated by the air leaving the turbines. The liquid air is then pressurized by the pump **873'** to a very high pressure such as 3500 psia., and is fed to the heat exchanger **874''**. In this heater, the liquid air is vaporized and converted into gas at high pressure and much higher temperature. The hot gas is further heated in heat exchanger **875** and introduced into the turbine **876**. The air as discharged from turbine **876** is reheated to about the original high temperature by the reheater **875'** and is expanded through a second turbine **876'**. The gas at lower pressure and temperature is reheated to about the original high temperature in reheater **875''** and is expanded through the third turbine **876''**. The air is then passed through the heat exchanger **874''** and to the condenser **872** after passing through the cooler **890** and the heat exchangers **874** and **874'**.

As an example, this system can be arranged to circulate air at the rate of one pound per second through the cycle. If the pressure in the condenser is maintained at atmospheric pressure, the temperature in the condenser will be about 142° R. The liquid air is pressurized to about 50 psia. and passed through heat exchangers **874'** and **874** and the temperature raised to about 165° R. The pump **873** raises the pressure to about 3,500 psia. and the temperature is raised to about 202° R. The liquid air is passed through the heaters **874** and **875** and is converted to gas at 700° R. (240° F.). The hot air is cooled in passing through the turbine **876** to 437° R. and the pressure is reduced to about 565 psia. In the heater **875'**, the air is returned to the temperature of 700° R. In turbine **876'**, the temperature is dropped to 473° R. and the pressure to about 91 psia. In the heater **875'**, the air is reheated to about 700° R. The expansion in turbine **876''** drops the temperature of the air to 473° R. and the pressure to atmospheric. The air is cooled in the heat exchangers **890**, **874**, **874'** and **874''** before being condensed to liquid at 142° R.

The values set forth in this cycle are illustrated by the chart shown in FIG. XIV. The points on the diagram are identified as follows: **1**, indicates the condition of the liquid air leaving the condenser **872**; **2**, the condition of the liquid air leaving the pump **873**; **3**, **4** and **5**, the condition of the liquid air leaving the heat exchanger **874**, **874'** and **875'**; **6**, the condition of the air leaving the pump **873'**; **7**, the condition of the air leaving the heater **875** and entering the turbine **876**; **8**, the condition of the air discharged from the first turbine **876**; **9**, the condition of the air leaving the reheater **875'** and entering the second turbine **876'**; **10**, the condition of the gas as discharged from the second turbine; **11**, the condition of the air leaving the second reheater **875''** and entering the third turbine **876''**; **12**, the condition of the air as discharged from the third turbine; **13**, **14**, **15** and **16**, the condition of the air as it is cooled and returned to the condenser at point **1**.

The liquid air flowing from the condenser **872** is pressurized by the pump **873** (point **2** on the chart) and is returned in indirect heat exchange in heater **874** to absorb part of the latent heat of the condensing air. This transfer of energy is possible with air, as air is essentially a binary mixture of oxygen and nitrogen, and the dew point temperature is approximately 5.5° F. higher than its bubble point. The heat exchanger **874** warms the liquid air to slightly below its saturation point (point **4** on the chart). The liquid is pressurized by pump **873'** to the pressure at turbine inlet (point **8** on the chart). The liquid at high pressure is vaporized in the heat exchanger **875**. In this heat exchanger, the highest temperature in the cycle is reached. The temperature shown can readily be reached by employing low quality thermal energy, such as waste heat. Nothing in this disclosure should be construed as preventing the use of higher temperatures which can be obtained from other heat sources.

The system shown, when supplied with air at the rate of one pound per second, would produce about two hundred horsepower in excess of that required to operate the pumps **873** and **873'**, subject to the limitation of the efficiencies of the turbines and losses in the system.

FIG. IX illustrates another embodiment of the invention for the recovery of energy, preferably using the absorption refrigeration system as a means for establishing the necessary temperature differential. In this Figure **970** indicates an absorption refrigeration system and **971** indicates a heat transfer means for transfering heat from the power recovery system to the heat sink of the refrigeration cycle. This system includes a condenser **972** for liquifying a gas such as air. The liquid air is pressurized by the pump **973** and is heated by the heat exchanger **974**. The heating medium is the air being cooled and condensed. The pressurized and heated liquid air is vaporized in the heat exchanger **975** and is introduced into the turbine **976** and then reheated in reheater **975'** and passed into turbine **976'**. This turbine discharges the air at the pressure of the condenser.

This Figure shows an arrangement generally corresponding to the system of FIG. VIII, but in which the construction has been simplified. This Figure shows an arrangement which will allow a substantial recovery of power with a lower plant investment. The actual selection of the number of turbines and the number of reheaters will depend upon an economic balance between the cost of equipment and the value of the power drived.

FIG. X illustrates the recovery of pure water by the use of a low grade heat source. In the production of water from saline water or impure water, one of the major problems has been the cost of the power required to vaporize the water. Another problem has been the scaling of the water in the heating vessels. The utilization of the absorption refrigeration systems of this invention will overcome some of these previous difficulties.

In FIG. X the evaporator of the absorption refrigeration system is indicated as **1001**, the refrigerant absorber as **1002**, the pump for the solution of refrigerant and absorbent as **1004**, the regenerator as **1003** and the column as **1008**. The vapors of the refrigerant are passed to the heater **1019** and are heated by indirect heat exchange with the absorbent from the regenerator **1003**. The heated vapors are then expanded through the turbine **1020**, to recover energy and to cool the vapors. The vapors are condensed in condenser **1012** and the liquid refrigerant is passed through the pressure reduction means **1013** to the evaporator **1001**. The refrigeration system thus far disclosed is similar to that shown in FIG. IV.

The condenser **1012** includes a heat exchanger element **1021** through which is passed the water to be distilled. The refrigerant and the pressure of condensation are selected so that the heat of the condensing vapors heats the water to be distilled. The warmed water is then passed to the heat exchange element **1006'** in the heat exchanger **1006**, and the water is further heated by the absorbent returning to the absorber **1002** from the regenerator **1003**.

The hot water is then fed into the distillation system. The distillation system comprises a series of flash chambers which utilize the latent heat in the water to vaporize a portion of the water. The hot water is introduced in the first flash chamber **1080**, and a portion of the water flashed into steam. The steam is fed through the heat exchange means **1082** in the second flash chamber **1081** and is condensed. The water from the first flash chamber is fed to the second chamber **1081** which is at a lower pressure. A second quantity of water flashes into steam. While only two flash chambers are shown, it is to be understood that the number of flash chambers may be selected according to the design criteria of such distillation systems.

The vapors from the final flash chamber and the condensate from the heat exchanger **1082** are fed into the condensing chamber **1083**. This chamber is cooled by heat exchange element **1084** through which is circulated a heat exchanger medium which also is passed through the element **1014** of the evaporator **1001**. The non-condensible gases in the saline water are removed from the distillation system by the ejector **1086**. The evaporator **1001** which is heated by the condensing water vapor in the condenser **1083**, will maintain a minimum pressure and temperature in the water vapor condenser. The unevaporated water or waste brine from the final distillation stage is discharged through the heat exchange means **1087** in the refrigerant condenser **1012** or through the heat exchange means **1088** in the refrigerant absorber **1002**, to remove the heat of these elements. In a like manner, the distilled water is passed through the heat exchanger means **1089** in the refrigerant condenser **1012** or through the heat exchange means **1091** in the absorber **1002** or through both.

FIG. X demonstrates the application of absorption refrigeration system of this invention using a low temperature heat source to produce energy and to perform useful chemical engineering unit process operations. While this example shows the application of the process of this invention to the distillation of water, it is apparent that other liquids could be distilled in a similar manner. Furthermore, the temperature differential available from the absorption refrigeration cycles of this invention can be used in other unit processes requiring temperature changes. For example, water could be purified by freezing rather than by distillation. The invention could also be used to dehydrate materials as by freeze drying since the invention can produce both low temperature and low pressure.

FIG. XI shows the construction of a preferred form of the evaporator-sublimator of this invention. The figure is a cross section through the vessel constituting the evaporator-sublimator. The vessel is normally provided with insulation about the walls. The interior of the vessel is divided into a liquid receiving section **1101** and a vapor section **1103** with a porous plate **1102** separating the section from each other. The liquid to be vaporized is introduced into the section **1101** by the pipe **1104**. The vapor is removed from section **1103** by the pipe **1105**. This pipe is designed to maintain the pressure in the section **1103** at a desired level. The pipe **1105** may include a fan, if necessary, to maintain the desired pressure.

The porous plate **1102** which serves as a partition, is formed of an open cell material such as porous brick or stone or metal which will permit the slow passage of the liquid through the partition. The partition includes a heat exchange means **1114** which will supply the heat necessary to vaporize the liquid. This heat exchange means serves as the heat sink in the refrigeration cycle.

The evaporator-sublimator is operated as a sublimating means by establishing a pressure in the section **1103** which is below the triple point of the refrigerant. Under these conditions, the refrigerant, as it passes through the partition **1102**, will freeze in the passages and block further flow of liquid. The heat exchange means **1114** will supply heat to sublimate the refrigerant. As the refrigerant is evaporated, more liquid refrigerants will pass into the plate and be frozen. Thus, the passage for the liquid is automatically limited to the rate at which the frozen material is sublimed by the heat.

When the pressure in the chamber is above the triple point of refrigerant, the liquid will ooze through the plate and be heated by the heat exchange means and will evaporate into the chamber **1102**. This will occur before the system has reached the triple point pressure at the time the system is being started up or the system can be operated under these conditions as desired.

FIG. XII is another embodiment of the evaporator-sublimator. In this Figure, the liquid chamber is designated as **1201**, the vapor chamber as **1203** and the porous plate as **1202**. The liquid is supplied by pipe **1204** and the vapor removed by pipe **1205**. This embodiment differs from that shown in FIG. XI by having the feed pipe **1204** pass through the vapor section **1203**. This pipe includes the heat exchange means **1207** in the vapor section. This permits the liquid refrigerant to be further cooled before entering the chamber **1201**. This construction assures a rapid stabilization of conditions to enable the operation of the evaporator-sublimator as a sublimator. The heat sink is designated by the heat exchange means **1214**.

FIG. XIII shows a vapor separator particularly adapted to be used in the flash distillation chambers of the system shown in FIG. X. While particularly adapted for this type of system, the separator can be used in any distillation system benefitted by little or no entrainment of the distilland in the vapor. In this Figure, **1301** indicates the vessel for receiving the liquid to be distilled through the pipe **1302** and discharging the vapor through the pipe **1303**. In the vessel above the level of the boiling liquid is a baffle means **1304**. This baffle means includes a shaft **1305** which is mounted for rotation about an axis. A series of turbine blades **1307** are secured in an inclined position to the shaft so that the passage of vapor towards the outlet pipe **1303** cause the shaft to rotate. A perforate plate **1306** secured to the shaft above the turbine blades rotates with the shaft. The plate, preferably in the form of a fine mesh screen, engages any droplets of liquid and centrifugally throws them outwardly away from the outlet. While it is preferred to have the vapors rotate the screen, it would be possible to use other means for the purpose.

FIGS. XV and XVI illustrate a more specific embodiment of the cycles shown in FIG. VI. In these Figures, the energy recovery system is used to provide motive power for a vehicle. The vehicle may be any vehicle requiring energy for propulsion, such as aircraft, boats, air-cushioned vehicles as Hovercraft and trains, railroad cars, road vehicles or tube cars. The power derived can be used directly as in the thrust of a jet or indirectly by the use of a driven turbine.

In FIG. XV, the heat sink of an absorption refrigeration system is indicated by the block **1570**. The power generating system receives air from the atmosphere at **1560**. The entrance may be in the form of a scoop, taking advantage of the vehicles forward motion to increase the flow of air. The entering air is passed to the precooler **1571** and is conveyed from there to the turbocompressor **1572**. The compressed air passes through the heat exchange means **1573** in the precooler. The compressed air is fed to the turbine **1574** and there expanded. The cooled air is then passed into the condenser **1577**, in which it is further cooled by supplying heat to the refrigeration cycle, and is condensed to a liquid. The liquid air is pressurized by the pump **1575** and passed to the heat exchanger **1576** in the refrigeration cycle. This exchanger heats the air to vaporize it. The hot pressurized air is fed to the nozzle of the thrust means **1578**. Fuel may also be supplied to the thrust nozzle through line **1579** and burnt with the air to supply reaction forces to the vehicle.

Heat exchange connection **1580**, **1581** and **1582** transfer heat from the refrigeration cycle to the precooler, to the condenser, and to the heater. The precooler will use well-known techniques to free the air from ice, carbon dioxide and the like and to remove the ice from the precooler.

The thrust means **1578** may be a jet engine or a rocket nozzle or a turbojet engine. While it is desirable, in many instances, to use fuel in the engine, wherever the added heat of combustion or the polluting effect of combustion is to be avoided, the engine may be powered solely by the expanding gas.

FIG. XVI illustrates another embodiment of the invention as used for the propulsion of a vehicle. In this Figure, the air enters the system at **1660** and is passed to the precooler **1671**. The dried cooled air is fed to the compressor **1672**. The compresser gas then is passed to the heat exchanger **1673** in the precooler and then fed to the turbine **1674** and is there expanded. The air is condensed in condenser **1677**. The liquid air is passed through the heat exchange means **1683** in the precooler and is further heated in the heat exchanger **1684** before being introduced into the propulsion means **1678**. The heat exchangers **1681** and **1682** transfer heat to the refrigeration cycle.

In this example the precooler is not connected with the refrigeration cycle as shown in the previous figure.

FIG. XVII shows an embodiment of the invention as applied to the use of gases such as nitrogen, hydrogen, neon and helium as refrigerants.

FIG. XVII illustrates one absorption refrigeration cycle of a cascade system. In this Figure, the absorber **1702** feeds the solution of a gas such as hydrogen in a liquid hydrocarbon to the pump **1704** and hence to the heat exchanger **1706** and to the column **1708** of the regenerator or separator **1703**. The heat necessary to separate the gas from the absorbent is preferably supplied by the condenser of another cycle in the cascade arrangement by means **1709**. The gas is then supplied to a heat exchanger **1712**. This exchanger is arranged to remove heat from the gas and supply this heat to an evaporator of another cycle in the cascade system. This heat exchanger also includes another heat exchange element **1721**. The cooled gas from the heat exchanger **1712** is passed through the expansion means **1713** into the chamber **1722**. This chamber is at lower pressure than **1712** and a portion of the gas is liquified and is passed into the evaporator-sublimator **1701**. The vapors from the evaporator-sublimator **1701** and the vapors from the chamber **1722** are combined and are passed through the heat exchanger element **1721** in the chamber **1712** and then passed to the absorber **1702**.

The vapors separated from the liquid and the vapors from the evaporator-sublimator thus serve to cool the gas in the chamber **1712**.

When hydrogen is the refrigerant, the heat exchanger **1712** may be cooled by the heat sink of an evaporator-sublimator of another cycle of the cascade to 94° R. The hydrogen is further cooled by the heat exchange element **1721** by the hydrogen from the evaporator and the chamber **1722**. The hydrogen is cooled to the liquefaction by passage through the expansion means **1713**. The liquid hydrogen from chamber **1722** may be passed to the evaporator **1701** in which it may serve as the heat sink in connection with a cooler cycle for liquifying helium. If liquid hydrogen is desired as a product, it is withdrawn from the chamber **1722** and make up hydrogen is supplied to the absorber **1702**.

The same cycle is employed to liquify helium with the exception that liquid hydrogen is employed as the cooling fluid in the element of the heat exchanger **1712**.

A neon cycle can be substantially the same as for hydrogen, and will include the expansion of neon in the means **1713**. It is desirable to include a cycle in the cascade system, and then the neon heat sink will be used to cool the hydrogen before liquefaction.

The several figures of the drawing illustrates preferred embodiments of the invention. The several embodiments show numerous ways in which it is contemplated to apply the invention to recover energy from low temperature heat sources, and to perform chemical processes and recover valuable products.

From the foregoing description, one skilled in the art can easily ascertain the essential characteristics of this invention, and can without department from the spirit and scope thereof, make various changes and modifications of the invention to adapt it to various usages and conditions.

What is claimed is:

1. A refrigeration process comprising the steps of:

absorbing a refrigerant vapor in a liquid absorbent;

increasing the pressure on resultant mixture of said refrigerant and said absorbent;

distilling and rectifying the mixture into substantially pure refrigerant vapor and pure absorbent;

reducing the pressure on resultant pure liquid absorbent and returning the latter to the absorbing step;

cooling and condensing the refrigerant vapor to the liquid state;

reducing the pressure upon the liquid refrigerant to below the triple point of the refrigerant to produce solid refrigerant;

sublimating the solid refrigerant to the vapor state; and

passing resultant refrigerant vapor to the absorbing step at a rate that maintains the pressure below the triple point.

2. A process according to claim **1** wherein prior to the sublimating step the liquid refrigerant is passed through a porous plate and solid refrigerant is formed in said plate.

3. A process according to claim **2** wherein the porous plate is heated to sublimate the refrigerant.

4. A process according to claim **1** wherein the passage of the refrigerant from the sublimation step to the absorbing step is induced by mechanical means.

5. A process according to claim **1** in which the pressure on the liquid absorbent is reduced by passing said liquid absorbent through a turbine, thereby recovering energy therefrom.

6. A process according to claim **1** in which the refrigerant is selected from the group consisting of nitrogen, hydrogen, neon, helium and hydrocarbon having a saturation pressure between that of butane and methane; and the absorbent is a liquid having a freezing point below the temperature of the process and selected from the group consisting of a hydrocarbon liquid and an inorganic liquid.

7. A process according to claim **1** wherein the refrigerant is methane and the absorbent is selected from ethane and propane.

8. A process according to claim **1** wherein the cooling and condensing of the refrigerant is conducted in heat exchange with a separate absorbent refrigeration cycle.

9. A process according to claim **1** wherein the heat for distilling and rectifying the mixture is supplied by heat exchange with a separate absorbent refrigeration cycle.

10. A process for the recovery of energy and refrigeration comprising the steps of:

absorbing a refrigerant vapor in a liquid absorbent;

increasing the pressure on the resultant mixture of refrigerant and absorbent;

distilling and rectifying the mixture into substantially pure refrigerant vapor and pure absorbent;

heating the refrigerant vapor from the distillation step by indirect heat exchange with absorbent from the distillation step, to simultaneously increase the temperature of the vapor refrigerant and reduce the temperature and pressure of the liquid absorbent;

recovering energy from the refrigerant vapor by reducing its temperature and pressure;

condensing the vaporous refrigerant to the liquid state;

recovering the energy of the liquid refrigerant by reducing its pressure and temperature;

evaporating the liquid refrigerant under reduced pressure; and

returning the absorbent and the refrigerant to the absorbing step.

* * * * *