Dec. 13, 1960 L. E. MILLS 2,963,875

HEAT PUMP

Filed May 18, 1953 3 Sheets-Sheet 1

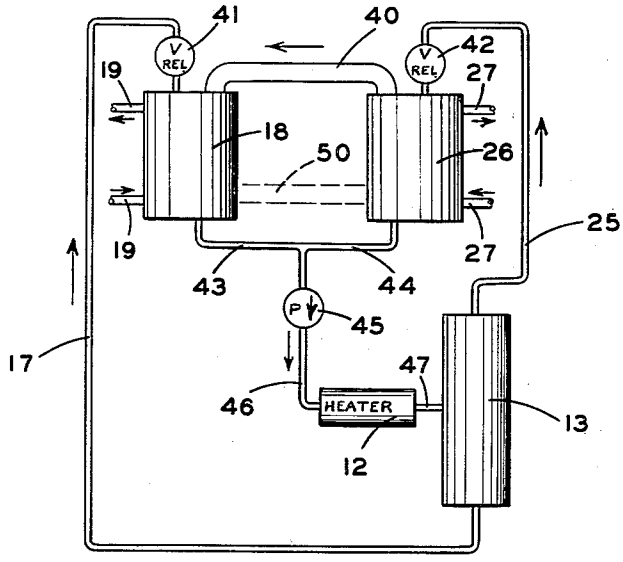


Fig. 1

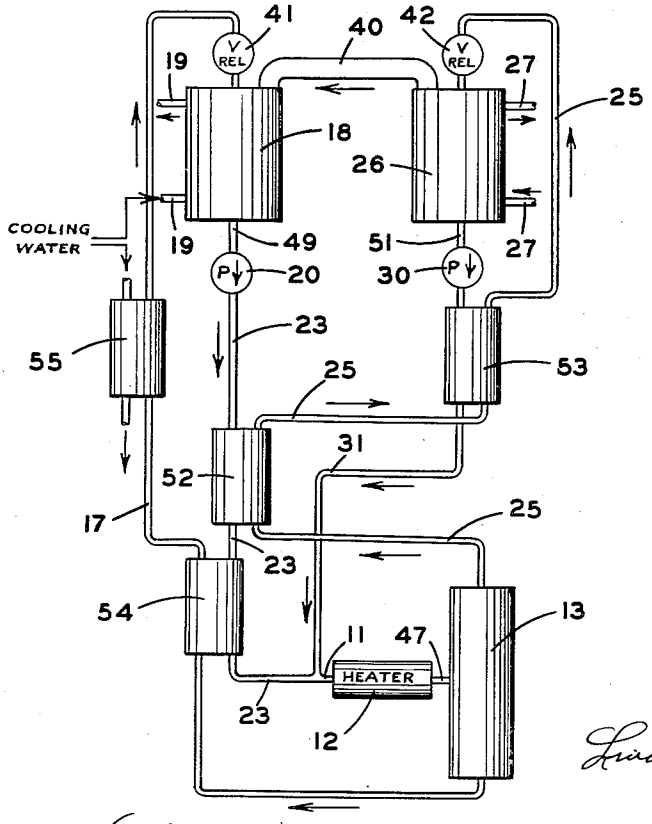


Fig. 3

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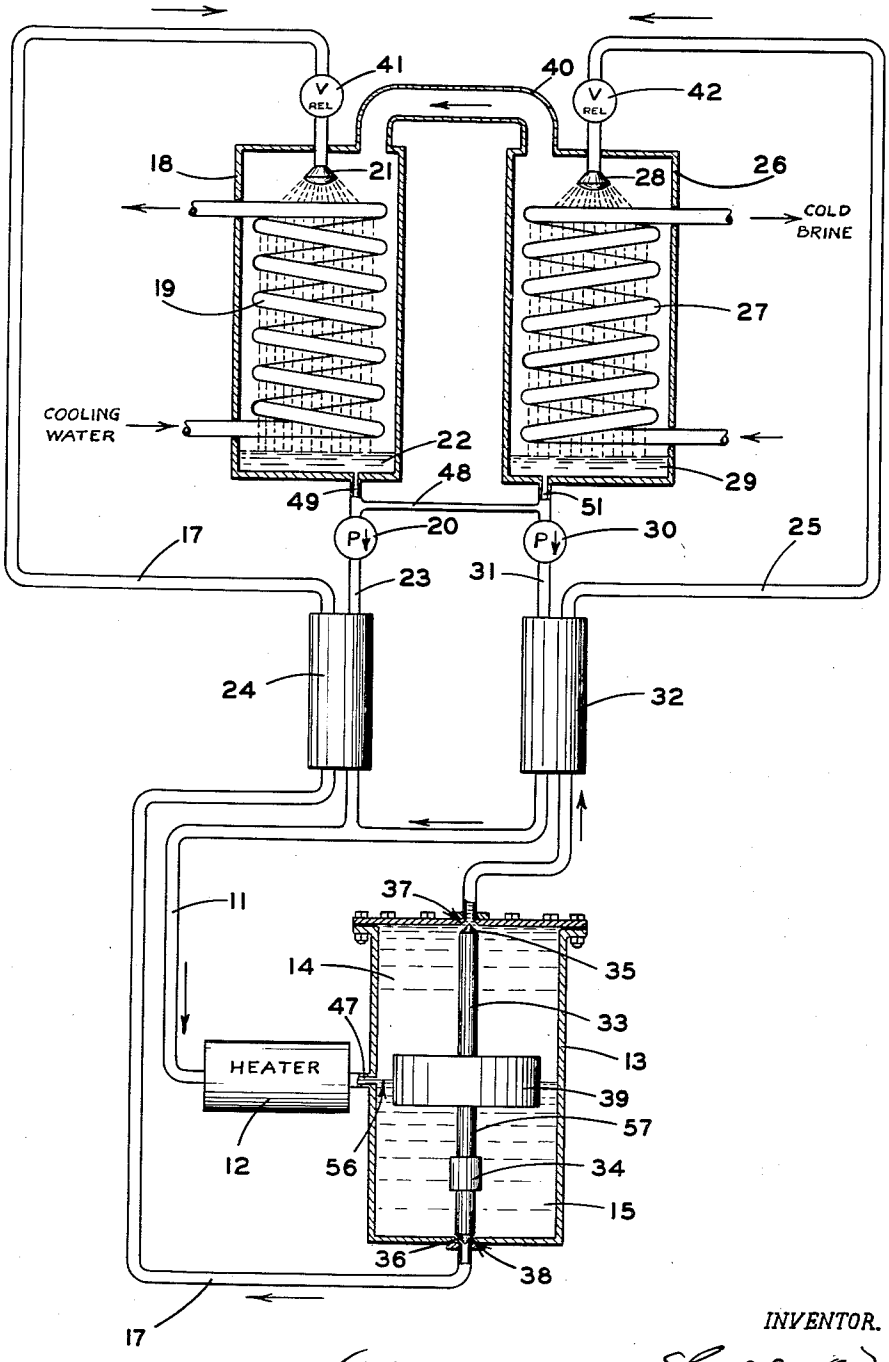


Fig. 2

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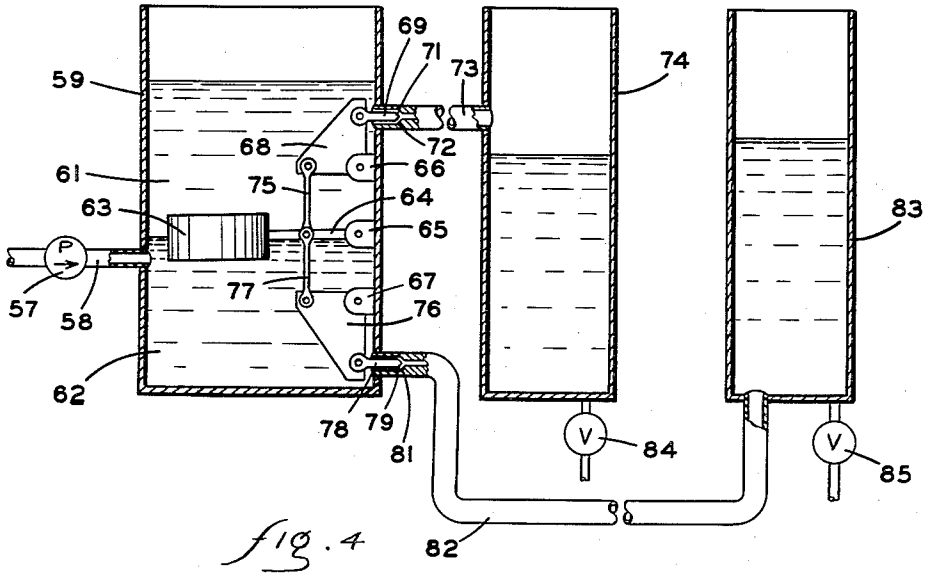


fig. 4

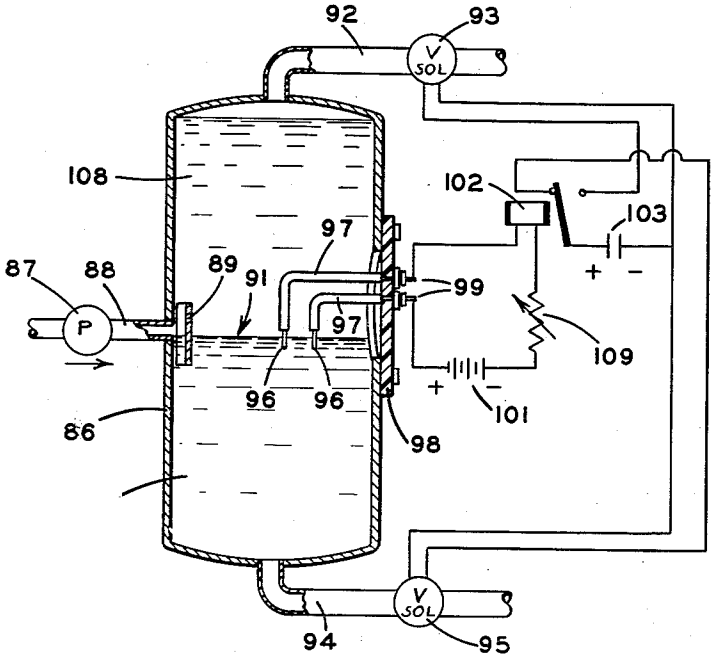


fig. 5

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United States Patent Office 2,963,875 Patented Dec. 13, 1960

2,963,875

HEAT PUMP

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Filed May 18, 1953, Ser. No. 355,750

29 Claims. (Cl. 62—112)

This invention relates to the transfer of heat, particularly to a novel method and to apparatus and compositions useful for transferring heat from a region of lower temperature to a region of higher temperature. This application is a continuation in part of co-pending application Serial No. 75,079, filed February 7, 1949 and now Patent No. 2,638,760.

The transfer of heat from a region at one temperature to a region at a higher temperature is necessary in many processes, including such extensively practiced processes as refrigeration, air conditioning and cooling operations in general. In such processes, heat is extracted from one region, thereby reducing its temperature to a desired degree, and discharged to another region, thereby increasing its temperature. In refrigeration or cooling practice the discharged heat is generally dissipated by cooling water or air, or in some other convenient way. The apparatus and systems of substances used in transfering heat from one region to a region of higher temperature is generally referred to as a "heat pump."

Of increasing importance is the use of this type of process primarily for the purpose of heating by utilizing the transferred heat liberated in the region of higher temperature for useful purposes, the heat extracted from the region of lower temperature being in this instance replenished from any convenient low cost source, such as the atmosphere, water, and the like. Buildings have been heated satisfactorily in this manner by extracting heat from the air or water out of doors, or even from the soil, and discharging it inside the building.

The transfer of heat from a region of lower temperature to a region of higher temperature has heretofore practically always been effected by one of two processes. In one of these processes, referred to as the "compression" process or method, a liquid of suitable boiling point is caused to evaporate in a vaporizer in the region being cooled thus absorbing heat from the region. The vapor is removed continuously from the vaporizer by a pump and compressed. The compressed vapor is then cooled in a condenser, e.g. with air or cooling water, to convert it to liquid form, after which it is reintroduced into the vaporizer to effect further cooling. A number of low-boiling substances have been used, or proposed for use, in this process including ammonia, sulfur dioxide, carbon dioxide, dichlorodifluoromethane, methyl chloride, propane and many others including even water. In the case of water the vapor is generally discarded and fresh water introduced into the vaporizer. A refrigerant having a high latent heat of vaporization and a suitably low boiling point is desirable for use in this process to reduce the weight of material cycled per unit of refrigeration effected and to avoid the necessity for using a highly evacuated vaporizer. This method involves the use of costly compressing machinery and of a source of relatively costly energy to operate the compressor.

The other generally utilized method for effecting refrigeration, referred to as the "absorption" method, involves the boiling of substantially anhydrous ammonia in a vaporizer to cool the latter and the absorption of the vapors in relatively dilute ammonia in an absorber. The heat which is evolved in the absorber is dissipated with air or cooling water. The effluent from the absorber, which is relatively rich in ammonia, is then transferred to a still, or generator, operating under a higher pressure than that prevailing in the absorber and vaporizer, and fitted with a fractionating column. In this apparatus a portion of the ammonia is distilled and led to a condenser where it is cooled and collected in as nearly anhydrous form as possible. The collected liquid ammonia is then reintroduced into the vaporizer and the weak ammonia liquor remaining in the still is reintroduced into the absorber. This process is less economical in the expenditure of energy to produce a given unit of refrigeration than is the compression system, but the energy can be supplied in the form of a fairly low grade heat source so that the system or process finds extensive use in situations where a large amount of refrigeration is desired and a relatively inexpensive source of heat at a sufficiently high temperature, e.g. at about 3 to about 50 lb./sq. in. gauge, is available in large quantities. The equipment to operate the process is, however, costly to install, even though no gas compressor is required, because of the necessity of carrying out the fractional distillation of the strong ammonia liquor under considerable pressure. In practice, only a small proportion of the ammonia is distilled from the strong liquor during each cycle. This requires the circulation in the apparatus of a very large proportion of the ammonia in the form of relatively dilute liquor without its ever being used to effect refrigeration.

In both of the conventional methods for effecting cooling just described, the principal cost of operation usually arises from the necessity of expending energy to restore the refrigerant evaporated in the vaporizer to a liquid condition wherein it can be reintroduced into the vaporizer and used again. The same is true when either method is used for heating purposes rather than for refrigeration, the principal difference being that the desired effect is obtained by utilizing the heat discharged to the absorber or condenser, respectively. It is apparent that the present status of the refrigeration art leaves much to be desired both in the way of simplicity and cost of apparatus and in the cost of operation, and that any improvements in either respect would be of great value.

In the co-pending application referred to there is described a new and novel method or cycle for effecting refrigeration which avoids both the gas compression step and equipment of the conventional compression method and the fractional distillation step and equipment of the conventional absorption method. There are also described certain apparatus and certain systems of substances whereby the method can be carried out. The present application is concerned with valuable and novel variations of and improvements in the method claimed in the parent application and with apparatus and systems of substances whereby the new method and the variations thereof can be carried out easily and economically.

The method for effecting refrigeration described in the parent application utilizes a system of substances comprising a low-boiling component and a high-boiling component chosen so that the coefficient of solubility with respect to temperature of the low-boiling component in the high-boiling component is negative when both substances are in liquid form. Under such circumstances, the solubility of the low-boiling component in the high-boiling component decreases as the temperature of the mixture is raised and, provided the substances are present in proper proportions, two liquid phases are present in the heated mixture, one of which is rich in the low-boiling component and the other of which is rich in the high-

boiling component. Such liquid phases which are in equilibrium with one another are known as "conjugate solutions."

It frequently happens in such systems that at some low temperature, depending upon the particular system involved, the liquid phases merge and the system becomes homogeneous. The temperature at which this occurs is known as a "lower consolute temperature" or a "lower critical solution temperature." Such a system, whether or not it has a lower consolute temperature, is herein sometimes referred to as a "negative conjugate system" to distinguish it from the better kown "positive conjugate systems" wherein the coefficients of solubility with respect to temperature of the components in one another are positive. Such latter systems may have an "upper consolute temperature" or "upper critical solution temperature" above which the conjugate solutions merge to give a homogeneous mixture.

In the method described in the parent application a negative conjugate system is heated in a closed vessel under pressure, herein referred to as a "separation pressure," sufficiently high to maintain it substantially in liquid form, i.e. under at least its substantial total vapor pressure, at a temperature herein referred to as a "separation temperature," sufficiently high to cause formation in the system of high-boiling and low-boiling conjugate solutions, the low-boiling solution being enriched with respect to the low-boiling component of the system and the high-boiling solution being impoverished with respect thereto. The conjugate solutions are then separated from one another at the separating temperature without substantial vaporization of the components thereof. The low-boiling and the high-boiling solutions are then placed in liquid form in separate containers connected by a vapor conduit, e.g. in a vaporizer and in an absorber, respectively, of a conventional absorption type refrigeration apparatus, and the high-boiling solution is cooled by any appropriate means, e.g. by cooling water or air. Under such conditions, vapor of the low-boiling component distills from the low-boiling solution, which is thereby impoverished with respect to the low-boiling component and cooled and is thus available for refrigerating purposes, and is absorbed or dissolved in the high-boiling solution, which is thereby enriched with respect to the low-boiling component, the heat of absorption being dissipated by the cooling means. This process continues until interrupted or until the temperature of the low-boiling solution and the concentrations of the low-boiling component in the high-boiling and in the low-boiling solutions have attained values such that the partial vapor pressure of the low-boiling component in each solution at the respective temperatures is the same. The impoverished low-boiling solution remaining in the vaporizer and the enriched low-boiling solution remaining in the absorber are subsequently combined to furnish the original negative conjugate system which is then heated as in the step first described.

A complete refrigeration cycle is thus effected wherein the gaseous refrigerant is restored to its liquid state ready for re-use without the expenditure and the subsequent dissipation of energy corresponding to the energy of liquefaction described previously. Furthermore, since only liquids are concerned in the heating and separation steps and in the return of the conjugate solutions to the absorber and vaporizer, respectively, heat interchangers can be employed advantageously to carry out the first stages of the heating step using the hot separated high-boiling and low-boiling conjugate solutions and the latter thereby cooled before being introduced into the absorber and vaporizer, respectively. In practice, the cycle is preferably carried out in continuous fashion, the conjugate solutions being separated and conveyed to the absorber and vaporizer, respectively, and the enriched and impoverished solutions being withdrawn therefrom and heated, all in continuous manner. In this way substantially constant conditions of temperature and pressure can be maintained in any particular part of the cycle.

In the present application there are described apparatus in which the new cycle can be carried out, systems of substances which can be employed in carrying out the cycle and variations in the cycle itself which are of value in effecting the transfer of heat from a region of lower temperature to a region of higher temperature. These features and their advantages will be apparent as the description proceeds.

The invention can be readily understood by reference to the accompanying drawing wherein, in the interest of clarity, certain features are shown on a somewhat exaggerated scale and wherein:

Figure 1 is a schematic representation of apparatus useful in carrying out the method or cycle of the invention.

Figure 2 is a schematic representation of a modification of the apparatus of Figure 1 showing certain features more in detail.

Figure 3 is a schematic representation of a further modification of the apparatus of Figure 1.

Figure 4 is a schematic representation of a modification of a part of the apparatus of Figure 1 illustrating its general applicability in other processes.

Figure 5 is a schematic representation of a modification of the apparatus of Figure 4.

In the operation of the new method or cycle utilizing a negative conjugate system, as illustrated by reference to Figure 1, the system is heated under a separation pressure greater than its vapor pressure to maintain the components in substantially liquid form in any conventional heater **12** to a separation temperature at which a desired degree of separation of the components into conjugate solutions is effected, one of which is rich in the low-boiling component and the other of which is rich in the high-boiling component. The solutions are then separated mechanically from one another in liquid form, as in a separator **13**, which will be described later, without substantial decrease in the pressure and temperature below the separation temperature and pressure. The low-boiling solution, i.e. the conjugate solution rich in the low-boiling component, is then conveyed as by way of a conduit **25** and a pressure relief valve **42** into a conventional vaporizer **26** and the high-boiling solution, i.e. the conjugate solution rich in the high-boiling component, is conveyed as by way of a conduit **17** and a pressure relief valve **41** into an absorber **18** and cooled therein to an absorbing temperature, e.g. by cooling water flowing through a coil **19** or by air. The vaporizer **26** and the absorber **18** are connected by a vapor conduit **40** to permit free flow of vapor between them. Due to the effect of the cooling water on the high-boiling solution in the absorber **18** and to the relatively low proportion of low-boiling component therein, its vapor pressure is reduced greatly and vapor of the low-boiling component flows from the vaporizer **26** into the absorber **18** and is absorbed in the high-boiling solution therein.

This process continues until the temperature of the low-boiling solution in the vaporizer **26** is reduced to an evaporation temperature such that its vapor pressure is equal to the vapor pressure of the high-boiling solution at the absorbing temperature prevailing in the absorber **18**. Because of the relatively low vapor pressures of the components other than the low-boiling component, the total vapor pressures of the solutions correspond closely to the partial vapor pressures of the low-boiling component in the two solutions. Due to the fact that the concentration of the low-boiling component in the low-boiling solution introduced into the vaporizer **26** is very much greater than it is in the high-boiling solution introduced into the absorber **18** and due, further, to the fact that the solubility of the low-boiling component in the high-boiling component is greater at the absorption temperature than at the separation temperature, the low-boiling solution in the vaporizer **26** is cooled to a temperature many degrees below the temperature prevailing in the absorber **18**. This fall in temperature in the vaporizer can thus be utilized for

cooling or refrigeration purposes, e.g. by circulating brine through a coil 27 in the vaporizer 26 or in any other convenient manner.

The product from the absorber 18, consisting of the high-boiling conjugate solution which has been enriched with low-boiling component, and any liquid residue remaining in the vaporizer 26, consisting of the low-boiling solution impoverished with respect to the low-boiling component, are conveyed, as by conduits 43, 44 and 46 and pump 45 to the heater 12, and the cycle repeated. As generally practiced, the method is carried out continuously, the system of substances being circulated continuously after the fashion just described.

It is to be noted that in the operation of the process the pressures prevailing in the absorber 18 and in the vaporizer 26 are at all times equal to one another and that the pressures prevailing in the heater 12 and the separator 13, and in the conduits communicating therewith between the pump 45 and the relief valves 41 and 42, are also at all times substantially equal to one another, but that this latter pressure is higher than that prevailing in the absorber and vaporizer. This latter condition follows from the fact that the vapor pressure of the system of substances in the heater and separator at the separation temperature, which pressure is at least equaled by the pressure developed by the pump 45, is greater than either the vapor pressure of the high-boiling solution at the absorber temperature or the vapor pressure of the low-boiling solution at the evaporation temperature. In the modification shown, the relief valves 41 and 42 are set to open at a pressure higher than the vapor pressure of the system prevailing in the heater and absorber, but less than the maximum pressure at which the pump 45 is capable of forwarding the system through the heater and separater. In this way a constant flow of liquid substantially free from vapor can be maintained through the heater and separator, and a proper pressure differential can be maintained automatically between the absorber and vaporizer on the one hand and the heater and separator on the other hand.

It is, of course, understood that the entire apparatus is, prior to its operation, purged of air and that during operation any air which is allowed to enter the apparatus inadvertently should be purged therefrom for best operation of the process. In many instances the low-boiling component at least, e.g. ammonia, will have a boiling point sufficiently low that the entire apparatus is at all times under greater than atmospheric pressure during normal operation of the process. Under such conditions any leakage which may occur will be outward and will not result in the introduction of air into the apparatus.

The apparatus which can be used in carrying out the process and the flow of substances in the process is subject to considerable variation without departing from the spirit of the invention. Thus, in Figure 2, certain features of which will be described in more detail later, there is shown one modification wherein the enriched high-boiling solution from the absorber 18 and the impoverished low-boiling solution from the vaporizer 26 are forwarded by separate pumps 20 and 30, respectively, to the heater 12. The use of separate pumps in this fashion to develop pressure on the two solutions before they are combined is sometimes advisable, particularly when there is a tendency for heat to be developed upon mixing the two effluents. In such an instance the vapor pressure of the warm mixture may be greater than that prevailing in the absorber 18 and vaporizer 26 and there is thus a tendency for the mixture to back up into the vaporizer or the absorber or both. When two pumps are employed they are generally synchronized so as to forward the respective solutions at approximately the respective rates which will result in maximum efficiency of operation of the cycle. When separate pumps are provided as shown in Figure 2, it is sometimes advisable to provide a cross connection, such as a conduit 48, between the conduit 49, extending between the absorber 18 and the pump 20, and the conduit 51, extending between the vaporizer 26 and the pump 30. By providing the conduit 48, which is generally of smaller diameter than the conduits 49 and 51, any variation on the part of the pumps 20 and 30 in removing the solutions from the absorber 18 and the condenser 26 at the precise rate at which they collect therein is compensated for by flow of a small amount of one of the solutions through the conduit 48 so that it mixes with the other solution. Such mixing of a small proportion of one of the solutions with the entire amount of the other solution does not generally produce any significant temperature rise in the mixture. The conduit 48, can, of course, extend between the vaporizer 26 and the absorber 18 either below or slightly above the normal level of the liquids therein and the same result be accomplished.

Heat exchangers can also be employed, if desired, to promote the efficiency of the process and to reduce the amount of heat necessary to be supplied prior to the separation. In Figure 2, for example, there is indicated at 32 a heat exchanger of any conventional type by means of which heat is exchanged between the hot low-boiling conjugate solution flowing in the conduit 25 from the separator 13 and the impoverished low-boiling solution from the vaporizer 26 which is being forwarded by the pump 30 through the conduits 31 and 11 to the heater. In this manner the temperature of the low-boiling conjugate solution entering the vaporizer 26 is lowered, thus reducing the amount of vaporization which must occur from the solution to lower its temperature to the temperature being maintained in the vaporizer, and at the same time the temperature of the impoverished low-boiling solution to the heater 12 flowing in the conduits 31 and 11 is raised, thus reducing the amount of heat which must be supplied to the system in the heater 12. In the same manner, heat can be exchanged, as in an exchanger indicated at 24, between the enriched high-boiling solution flowing from the absorber in the conduits 23 and 11 to the heater, and the high-boiling conjugate solution flowing in the conduit 17 from the separator 13 to the absorber 18. In this manner, the amount of heat necessary to add to the system in the heater 12 is further reduced and the amount of cooling water necessary to be circulated in the conduit 19 is reduced.

Certain other arrangements of heat exchangers are also of value in certain instances. Thus, in the arrangement shown in Figure 3 the low-boiling conjugate solution flowing from the separator 13 to the vaporizer 26 through the conduit 25 can be first forwarded through a heat exchanger 52 where it exchanges heat with the relatively cool enriched high-boiling solution from the absorber, which is being forwarded by the pump 20 through the conduits 23 and 11 to the heater, and then through a heat exchanger 53 where it exchanges further heat with the colder impoverished low-boiling solution from the vaporizer 26, which is being forwarded by the pump 30 through conduits 31 and 11 to the heater. This arrangement is sometimes particularly advantageous because the amount of impoverished low-boiling solution flowing from the vaporizer 26 is considerably less than the amount of low-boiling conjugate solution entering the vaporizer 26 by way of the conduit 25. On the other hand, the amount of enriched high-boiling solution flowing in the conduit 23 is considerably greater than the amount of high-boiling conjugate solution flowing in the conduit 17. By first pre-cooling the low-boiling conjugate solution in the heat exchanger 52 and then forwarding it through the heat exchanger 53, its final temperature as it enters the vaporizer 26 is lower than if it were caused to exchange heat only with the impoverished low-boiling solution from the vaporizer as in the modification of Figure 2. The high-boiling conjugate solution, flowing from the separator 13 through the conduit 17

to the absorber 18, can, with advantage, be forwarded through a heat exchanger 54 wherein it is caused to exchange heat with the enriched high-boiling solution from the absorber 18 after the latter has exchanged heat with the low-boiling conjugate solution. In this manner the enriched high-boiling solution is warmed still further and at the same time the high-boiling conjugate solution flowing in the conduit 17 is cooled to a considerable degree. In addition, the high-boiling conjugate solution flowing in the conduit 17 can, before it enters the absorber 18, be conveyed through another heat exchanger or pre-cooler 55 wherein it is cooled by cooling water to substantially the same temperature as that prevailing in the absorber 18.

Other appropriate arrangements of heat exchangers whereby the ratio of heat extracted from the cooling medium circulating in the conduit 27 in the vaporizer 26 to the amount of heat supplied to the heater 12 can be increased will be apparent as the description proceeds. The particular arrangement of heat exchangers and the number thereof employed in any particular instance will, of course, depend upon a number of factors including the particular system of substances used, the degree of cooling or refrigeration desired, the arrangement of the other units of the apparatus, and upon other factors.

The absorber 18 and the vaporizer 26 can, in most instances be of any suitable and conventional construction, it being only desirable that as good heat exchange between the solutions therein and the cooling medium, e.g. cooling water flowing in the conduit 19, on the one hand and the refrigerating medium, e.g. brine flowing in the conduit 27, on the other hand be provided for. In one suitable modification, shown somewhat in detail in Figure 2, the absorber 18 consists of a closed vessel of suitable dimensions containing a coil 19 through which cooling water is circulated. The high-boiling conjugate solution is distributed over the coil by a spray head 21 as it enters the vessel in such a manner that it trickles downward over the turns of the coil. During its travel downward over the coil, it is continuously cooled and presents a large surface to the atmosphere of vapor entering the absorber from the vaporizer 26 through the vapor conduit 40. The vapor conduit 40 should be of sufficiently large internal diameter to avoid substantial restriction to the flow of vapor through it. Enriched high-boiling solution dropping from the coil 19 collects in the bottom of the absorber 18 as a liquid layer 22 and is subsequently removed by the pump 20.

In similar manner brine which is to be cooled to serve as a refrigerating medium circulates in a coil 27 in the vaporizer vessel 26. The low-boiling conjugate solution enters the vaporizer through a spray head 28 and trickles down over the turns of the coil 27 during which time low-boiling component evaporates from it and flows out of the vaporizer through the vapor conduit 40. The brine flowing in the coil 27 is thus chilled to the desired temperature and is then available for cooling and refrigerating purposes. The unevaporated impoverished low-boiling solution collects as a liquid layer 29 in the bottom of the vaporizer 26 and is subsequently removed by the pump 30.

The separation of the conjugate solutions from one another at the separating temperature can be carried out in any convenient manner using any convenient apparatus. Generally speaking, when the process is used for cooling or refrigeration purposes, the low-boiling component has a boiling point considerably below atmospheric temperature at atmospheric pressure and the separation must be carried out under superatmospheric pressure to maintain the system of substances substantially in the liquid form. One particularly convenient apparatus for separating the conjugate solutions from one another is shown somewhat in schematic form in Figure 2. The separator comprises the vessel 13 of suitable construction to withstand the necessary internal pressure. The heated system of substances comprising both high-boiling and low-boiling components enter the separator by way of a conduit 47 and in the separator form two distinct liquid layers 14 and 15 of the conjugate solutions. In the modification shown, the low-boiling conjugate solution 14, which is rich in the low-boiling component, has a density less than that of the high-boiling conjugate solution 15, which is poor in the low-boiling component. The low-boiling conjugate solution 14 collects in the upper part of the vessel 13 from where it is conducted by way of conduit 25 to the vaporizer 26 as described previously. The heavier high-boiling conjugate solution 15 collects in the lower part of the vessel 13 and is subsequently conveyed to the absorber 18 by way of the conduit 17 as described previously. The conjugate solutions have a common interface 56. In certain instances it is advantageous to combine the heating and separating means in the same piece of equipment rather than to perform these operations separately.

To provide for automatic regulation of the discharge of the two conjugate solutions 14 and 15 from the separator, a float 39 is provided inside the vessel 13 which, together with the members attached thereto to be described, has an average density intermediate the densities of the conjugate solutions 14 and 15. The float, therefore, seeks and assumes a position in the vessel 13 such that it floats on the interface 56 between the two conjugate solutions. The float 39 rises and falls as the interface 56 rises and falls with changing ratios of the amounts of conjugate solutions 14 and 15 in the vessel 13. The float is provided with suitable top and bottom valve rods or projections 33 and 57, respectively. The rod 33 is shaped at its upper end to form a valve face 35 adapted to fit into a valve seat 37 formed in the upper end, e.g. in the cover or in an insert therein, of the vessel 13 and communicating with the conduit 25. In similar fashion the lower rod 57 is shaped at its lower end to form a valve face 36 adapted to fit into valve seat 38 formed in the bottom wall, or in an insert therein, of the vessel 13 and communicating with the conduit 17. A suitable adjustment 34 is provided integral with the rod 57 so that the distance of the valve faces 35 and 36 from one another can be adjusted. This latter distance is adjusted so that, when either of the valve faces 35 or 36 is seated in its respective valve seat 37 or 38, the other valve face is removed from its valve seat by a suitable distance and thus provides a means for fluid to flow out of the separator 13.

In operation, with either a steady or an intermittent flow of fluid into the separator through the conduit 47, one or the other of the valves 35 or 36 will be open at all times. In certain instances both valves will be at least partially open. When more than a normal amount of the heavier high-boiling conjugate solution 15 is in the vessel, the float 39 rises and closes the valve 35 at the same time opening the valve 36 thus preventing flow of the lighter low-boiling conjugate solution 14 from the vessel 13, but permitting flow of the heavier high-boiling conjugate solution 15 from the vessel 13. When the vessel 13 contains an excess of the lighter low-boiling conjugate solution 14 the float 39 falls slightly opening the valve 35 and closing the valve 36, thus permitting a part of the low-boiling conjugate solution 14 to flow from the vessel, but preventing the high-boiling conjugate solution 15 from flowing from the vessel. In steady operation of the apparatus it is generally found that the float 39 maintains an intermediate position so long as the feed to the separator is substantially constant and the relief valves 41 and 42 are set to open at the same pressure. Under such conditions the conjugate solutions 14 and 15 both flow continuously from the separator in the same ratio in which they enter the vessel through the conduit 47.

It is to be noted that the separating apparatus as described operates with the vessel 13 entirely full of liquid and free from any vapor space. Any vapor which may accumulate in the apparatus through accident or inadvertence escapes immediately through the upper valve 35. It is to be noted, further, that in the modification de-

scribed wherein the pressure in the separator is greater than the vapor pressure of the system of substances therein, the pressure is maintained by the operation of the pumps **20** and **30** working against the setting of the relief valves **41** and **42** and that the operation of the separator is independent of the setting of the relief valves. Should the relief valves **41** and **42** be set to open at different pressures, the inequality is compensated for by the operation of the separator. Each conjugate solution is permitted to flow through the respective relief valve only in proportion to the rate at which it enters the separator. The hydrostatic pressure maintained in the separator vessel **13** by the pumps, although it may vary somewhat depending upon any inequality of setting of the relief valves **41** and **42**, will at all times be sufficient to force fluid through the particular relief valve to which fluid is being supplied. When the overall composition of the system of substances being used and the temperature of the system attained in the heater **12** are adjusted to optimum conditions, the entire apparatus operates with maximum efficiency attainable with the temperature of the cooling water employed.

The operation of the apparatus shown in Figures 1, 2 and 3 when using a particular system of substances can be controlled in a number of ways. Thus the pump **45** of Figure 1, or the pumps **20** and **30** of Figures 2 and 3, can be operated intermittently or at a variable speed and the amount of low-boiling conjugate solution which is introduced into the vaporizer **26** can be controlled to provide for periods of high and low refrigeration demand. When two pumps are employed, e.g. pumps **20** and **30** of Figures 2 and 3, the rate of flow of the impoverished low-boiling solution and of the enriched high-boiling solution can be regulated to some extent independently of one another to provide for optimum efficiency at different vaporizer temperature levels if this appears desirable. The operation of the pumps can be controlled automatically either in response to the pressure prevailing in the vaporizer and absorber or in response to the temperature of the cold brine leaving the vaporizer through the conduit **27** or in response to the temperature of any other control point desired. The operation of the apparatus and the amount of cooling produced can also be controlled to some extent by regulating the temperature to which the system of substances is heated in its passage through the heater **12**. Regulation in this manner may alter to some extent the efficiency of operation of the entire apparatus because of its effect on the degree of segregation of the low-boiling and high-boiling components into the low-boiling and high-boiling conjugate solutions, respectively, in the separator.

Although the separator just described, together with certain modifications thereof, is preferred in the operation of the process as usually carried out for refrigerating or cooling purposes, any other convenient separating apparatus can be employed. The separator described can, however, be employed for the continuous separation of any immiscible liquids used in applications other than in the heat pump with which the present application is concerned. In Figure 4, for example, there is shown an adaption of the separator to the separation of immiscible liquids under atmospheric pressure wherein open vessels can be used. In this modification the mixture which is to be separated is fed by gravity or by a suitable pump **57** through a conduit **58** into the open tank **59** where it separates by gravity into a lighter liquid phase **61** and a heavier liquid phase **62**. A float **63** is mounted on a float arm **64** which is pivotally mounted to pivot in a vertical plane on a bracket **65** secured to a wall of the tank. Brackets **66** and **67** are also secured to the wall of the tank one being above and one being below the bracket **65**. A rotary member **68**, conveniently a triangular plate, is pivotally mounted on the bracket **66** so that it is free to pivot vertically. A valve rod **69** is pivoted at one of its ends to an upper corner of the plate **68** so as to travel horizontally as the member **68** pivots at **66**. The rod **69** is formed at its other end with a valve surface **71** contoured to fit a valve seat **72** which is in communication with a conduit **73** which in turn leads to a storage tank **74**. A lifter rod **75** is pivotally mounted at one of its ends on the third corner of the plate **68** and at its other end on the float **63** or the float rod **64**. In similar manner, another triangular plate **76** is pivotally mounted so as to pivot in a vertical plane on the bracket **67** and is connected with the float **63** or the float rod **64** by the pivotally mounted rod **77**. A valve rod **78** is pivotally mounted at the lower corner of the plate **76** and is formed at its free end with a valve surface **79** adapted to engage and close a valve seat **81** which is in turn in communication with a conduit **82** leading to a second storage tank **83**. Drawoff valves **85** and **85** may be provided to permit removal of the separated immiscible liquid phases from storage tanks **74** and **83** as desired.

The modification just described operates in a manner similar to the modification described previously. The float **63** has a density intermediate the two liquid phases and floats at the interface between them. When an excess of the heavier immiscible phase **62** enters the tank **59** the float **63** rises and the rotatable members **68** and **76** rotate clockwise. The valve surface **79** moves away from the valve seat **81** thus opening the valve wider and permitting more of the liquid **62** to flow by gravity into the storage tank **83**. At the same time the valve surface **71** approaches the valve seat **72** and reduces the rate of flow of the liquid phase **61** from the tank. When an excess of the lighter liquid **61** enters the tank **59**, the float **63** is lowered and the rotatable members **68** and **76** rotate counterclockwise, the operation of the valves is reversed permitting more of the lighter liquid **61** to flow into the storage tank **74** while decreasing the rate or stopping the flow of the heavier liquid **62** into the storage tank **83**. It is apparent that, in the operation of this modification wherein the flow of fluid is largely by gravity, the tanks **59**, **74** and **83** should be located with due regard to their relative elevations.

Although the utilization of a float arrangement for operating the outlet valves from the separator, such as those shown in Figures 2 and 4, is generally satisfactory and preferred it frequently happens that the actual differences in specific gravities of the liquid phases being separated is very small and that the utilization of a float to operate the valves becomes unwieldy because of the large size of the float which is needed. In such an instance it is sometimes convenient to operate the valves by other means. One such arrangement is shown in Figure 5 wherein the difference in electrical conductivity of the two liquid phases is utilized to accomplish this purpose. The mixture to be separated is supplied to the separator vessel **86** by way of a pump **87** and a conduit **88**. The mixture separates in the vessel **86** into a lighter upper layer **108**, which, for example, is assumed to be a poor conductor, and into a heavier lower layer **107**, which here is assumed to be a good conductor. A baffle plate **89** can be secured inside the vessel opposite the conduit **88** to prevent undue turbulence at the liquid interface **91**. The vessel **86** is equipped at its top with a drawoff conduit **92** and a solenoid valve **93**, normally in a closed position. It is also equipped at the bottom with another drawoff conduit **94** and another solenoid valve **95**, also normally in closed position. Although the valves **93** and **95** are, in the modification shown, operated by solenoids, they can be motor operated or operated automatically in any other convenient manner.

A pair of electrodes **96** is positioned within the tank **86** at the level near which it is desired to maintain the liquid interface **91**. The electrodes are connected by insulated leads **97** through an insulating plate **98** in the wall of the vessel to terminals **99** outside the tank. These

terminals are in turn connected by appropriate lead wires in series with a battery **101** and a relay **102** in such fashion that the relay is energized when current flows between the electrodes **96**. A variable resistance **109** can be inserted in the relay circuit to prevent the flow of enough current between the electrodes **96** when they are immersed in the liquid phase **108**, which is the least conductive of the two phases, to activate the relay **102**, but to allow activation of the relay when the electrodes protrude into the more conductive of the liquid phases **107**. The relay controls the flow of current from a source of E.M.F. **103** to the valve **95**, when the electrodes **96** project into the lower conductive liquid layer **107** and the relay is activated, and to the valve **93** when the electrodes **96** are surrounded entirely by the poorly conductive liquid layer **108** and the relay is not activated. In this way, when the interface **91** rises, the relay **102** is activated, the valve **93** remains closed, the valve **95** opens and some of the liquid phase **107** flows from the separator. When the interface **91** falls, the relay **102** is no longer activated, the valve **95** closes, the valve **93** opens and some of the lighter liquid layer flows from the separator.

Still another modification of the separator utilizes the difference in light absorptive properties of the phases together with suitable photoelectric cells and electronic controls to operate the valves controlling the flow of the liquid phases from the apparatus. The separator described can be used advantageously for separating any immiscible liquids regardless of the pressure under which the operation is carried out so long as they differ from one another sufficiently in one property to enable automatic control to be effected. Mixtures which may be separated include mineral oils and water, vegetable oils and water, mineral oils and aqueous alcohol, aniline and water, sulfuric acid and mineral oil, liquid sulfur dioxide and mineral oil, alcohol and strong soda ash solution, and many others.

The pumping means **45** of Figure 1 and **20** and **30** of Figures 2 and 3, employed in operating the heat pump with which the present application is concerned can comprise any suitable means for forwarding the respective liquids under the required conditions. It is advantageous to provide pumping means which is free of packing glands, stuffing boxes and other parts which are prone to leak after long usage. At the same time the pump must, depending upon the circumstances, be capable of handling such liquids as aqueous ammonia, aqueous sulfur dioxide, aqueous weak acids, aromatic hydrocarbons, ammoniacal copper salt solutions and the like without undue corrosion.

Because the new method is a species of absorption method it may at times be advisable to include a certain amount of a gas of low density, e.g. hydrogen or helium, with the substances charged into the apparatus to assist in the circulation of vapors of the low-boiling component from the vaporizer to the absorber as is practiced in well known manner in one modification of the conventional ammonia absorption system. When such a low density gas is used, it should, of course, be as little soluble in the liquid components of the system as possible.

In addition, provision should be made in the apparatus for continuous recycling of the gas between the vaporizer and absorber and back again. This is conveniently accomplished by providing a second vapor conduit, shown in dotted outline at **50** in Figure 1, between the vaporizer and absorber and located below the vapor conduit **40**, preferably just above the maximum level of liquid collecting in either the vaporizer **26** or the absorber **18**.

It should be pointed out that the method of the invention can be considered as comprising the circulation of a high-boiling component first through the separator **13**, referring to Figure 1, then through the absorber **18** and then back to the separator while simultaneously forwarding a low-boiling component through the separator **13**, thence through the vaporizer **26** and back to the separator, the conditions in the separator **13** being maintained so that the solubility of the low-boiling component in the high-boiling component when both are in liquid form is less than it is under the conditions maintained in the absorber **18**.

Because of the unsaturation of the high-boiling component in the absorber **18** with respect to the low-boiling component in the vaporizer **26** and the consequent non-equilibrium existing between the two liquids in the vaporizer and absorber, vaporization of a part of the low-boiling component and absorption thereof in the high-boiling component occurs, as described previously.

It thus becomes more clear that the rates of circulation of the high-boiling and low-boiling components can be varied independently of one another, e.g. by dual pump **20** and **30** of Figure 2, over rather wide limits without at the same time changing the amount of either of the components contained in the apparatus. It is apparent that an optimum value for this ratio, as well as for the total amount of each component circulated, will exist in each particular instance, depending upon the ratio of the actual amounts of the respective components making up the system and the performance expected.

Inasmuch as a portion of the high-boiling component circulates with the low-boiling component, because of the incomplete separation of the substances in the separator, the two portions of high-boiling component, i.e. that which circulates through the absorber **18** and that which circulates through the vaporizer **26** can be thought of separately. The operation of the system can then be thought of as comprising the cycling of a first portion of the high-boiling component first through a separator **13** and then through an absorber **18** and back to the absorber while simultaneously cycling a second portion of the high-boiling component through the separator **13**, thence through a vaporizer **26** and back to the separator **13**, the conditions in the separator **13** being maintained such that the second portion of the high-boiling component is enriched therein with the low-boiling component at the expense of the first portion and the conditions in the absorber **18** being maintained such that the first portion of the high-boiling component is enriched therein with the low-boiling component at the expense of the second portion, i.e. by vaporization of low-boiling component from the latter. When regarded in this manner it is seen that the first and second portions of the high-boiling component can be cycled at rates independent of one another within wide limits and that an optimum ratio of such rates can be found for each particular set of circumstances.

A further modification involves the replacing of either of the portions of high-boiling component with a second high-boiling component, immiscible with the first high-boiling component, and circulating the two high-boiling components with the accompanying low-boiling component. Here again, the rates of circulation of the two high-boiling components can be effected at an optimum ratio. Thus, the second portion of high-boiling component, referred to in the preceding paragraph, can be replaced with a suitable water-immiscible substance, e.g. an aromatic hydrocarbon, such as meta-xylene, to form the system composed of ammonia, meta-xylene and water which is referred to later.

In carrying out the process using this system, the water is forwarded through the separator **13**, then through the absorber **18** and back to the separator while the meta-xylene is forwarded through the separator, then through the vaporizer **26** and back to the separator to complete the cycle for each high-boiling component. By maintaining the separator **13** at a temperature and pressure higher than those prevailing in the vaporizer **18**, the meta-xylene is enriched with ammonia in the separator at the expense of the water while in the absorber the water is enriched with ammonia at the expense of the

meta-xylene in the vaporizer, the latter being cooled by the vaporization of ammonia therefrom.

For most efficient operation of the process, the segregation of the low-boiling component under the conditions prevailing in the separator into the low-boiling solution and its concentration therein should both be as great as possible while the solubility of the low-boiling component in the high-boiling component in the absorber under the conditions prevailing therein and the vapor pressure of the resulting solution should be as low as possible. Thus, when a two-component system is employed, the mutual solubility of the components under the conditions prevailing in the separator should be as low as possible but, under the conditions prevailing in the absorber should be as high as possible. The system composed of triethyl amine and water meets these requirements well. When such a system is heated under pressure to about 70 degrees C., low-boiling and high-boiling conjugate solutions are formed, the former containing 96 percent triethyl amine and the latter containing 1.6 percent triethyl amine, the balance in each solution being water. With an absorber temperature of about 18 degrees C., the lower consolute temperature of the system, or lower, the water and triethyl amine are miscible in all proportions.

In the case of a system of more than two components wherein the first of the high-boiling components is circulated through the absorber and the separator and the second is circulated through the vaporizer and separator, best operation of the process is obtained when the components are chosen and the apparatus operated so that the second high-boiling component is enriched with the low-boiling component as much as possible in the separator at the expense of the first high-boiling component and the latter is enriched with the low-boiling component as much as possible in the absorber at the expense of second high-boiling component in the vaporizer. These conditions are well realized using a system composed of water, ammonia and meta-xylene with a separator temperature of about 80 degrees to 150 degrees C. and an absorber temperature of about 15 degrees to 30 degrees C. Under such conditions the meta-xylene is enriched strongly in the separator at the expense of the water and the water is enriched strongly in the absorber at the expense of the meta-xylene in the vaporizer.

Another example of a three-component negative conjugate system which can be used advantageously in the process is that composed of water, sodium hydroxide and ammonia in the ratios of about 15 to 55, 5 to 60 and 20 to 80 parts by weight, respectively. Using such a system and a separator at a temperature of about 60 degrees C., or higher, a low-boiling conjugate solution rich in ammonia and a high-boiling solution impoverished with respect to ammonia are obtained. When these solutions are introduced into the vaporizer and absorber, respectively, and the latter cooled, the high-boiling solution therein becomes enriched with ammonia at the expense of the low-boiling solution in the vaporizer.

Systems useful in practicing the process are not limited to two- and three-component systems, but may include systems of four and more components. The system composed of water, sodium hydroxide, and ammonia, in the proportions given in the last paragraph, and meta-xylene is but one example of a useful four-component system. This can, with advantage, be converted to a five-component system by the addition of sodium or potassium chloride either in place of or in addition to the sodium hydroxide. It is to be noted that it is usually advisable that a component added to a negative conjugate system to promote further segregation of the low-boiling component in the low-boiling solution be chosen so that it is soluble at the separation temperature in one of the components but of only limited solubility in the other, preferably substantially insoluble therein. Such a relationship usually converts the negative conjugate system to another negative conjugate system wherein a more nearly complete enrichment of the low-boiling solution with the low-boiling component occurs in the separator.

In the case of the system consisting of ammonia and water, substances soluble in water but substantially insoluble in ammonia which can be added include many inorganic compounds, such as the alkali metal hydroxides and halides, compounds which in aqueous solution form complexes or salts with ammonia which are unstable at higher temperatures including cupric sulfate, cadmium chloride, zinc nitrate, acetic acid, monoammonium tartrate and many others. Organic compounds soluble in water which can be added include certain of the mono- and poly-hydroxy alcohols, polyglycols and many others. Substances soluble in liquid ammonia at the separation temperature but substantially insoluble in water include many organic compounds, such as certain organic amines, certain halohydrocarbons, aromatic hydrocarbons, and many others. Mixtures of either group or mixtures of members from each group can be added with advantage in many instances.

Of particular interest and advantage is the addition of an aromatic hydrocarbon to a system comprising ammonia and water. The aromatic hydrocarbons form positive conjugate systems with ammonia. The system composed of meta-xylene and ammonia has an upper consolute temperature of 15 degrees C. Consequently, meta-xylene is miscible in all proportions with ammonia at the separation temperature which is, of course, generally about 15 degrees C. Meta-xylene is substantially insoluble in water. However, when the conjugate solution from the separator is introduced into the vaporizer and the temperature thereof lowered by vaporization of ammonia to below 15 degrees C., the solution separates in the absorber into two other conjugate solutions, the compositions of which depend upon the degree to which the temperature in the vaporizer falls during normal operation of the cycle. When the temperature falls, for example, to −10 degrees C., the two phases contain approximately 8 percent and 88.5 percent, respectively, of ammonia, the partial vapor pressure of ammonia in the latter phase being considerably higher than its partial pressure would be if the entire contents of the vaporizer were homogeneous. There is thus a greater utilization for cooling of the ammonia introduced into the vaporizer. It is even sometimes desirable to cool the low-boiling solution of ammonia and meta-xylene from the separator in a separate step to about the temperature of the vaporizer and to separate the ammonia-rich and xylene-rich conjugate solutions which form. The ammonia-rich solution is then forwarded to the vaporizer and the xylene-rich solution is returned to the separator.

The method of the invention is not limited with respect to the particular negative conjugate system employed. Such systems are generally characterized by the formation at a lower temperature of a compound or molecular association between the components which becomes unstable and reverts to the individual components at a higher temperature. Low-boiling components of such systems useful in the present method include ammonia, the low-boiling aliphatic amines, i.e., aliphatic amines boiling below about 90 degrees C., sulfur dioxide, carbon dioxide, dimethyl ether, and others. Appropriate high-boiling components when using the low-boiling components mentioned may be selected from among water, mono- and poly-hydroxy alcohols, polyglycols, certain amines, and others as well as mixtures thereof and certain inorganic salts including those mentioned. The nature of certain substances with respect to the low- and high-boiling components which can be added to such systems with advantage has been discussed previously.

Certain modifications of the invention contemplate systems, and their use, wherein a component of the high-boiling solution reacts chemically with the low-

boiling component to form a definite compound stable at the temperature prevailing in the absorber, but sufficiently unstable at the separation temperature to regenerate the low-boiling component in free form.

In the case of an ammonia-water system, for instance, cupric sulfate can be dissolved in the water. The soluble complex tetramminecopper (II) sulfate formed by absorption of ammonia in aqueous cupric sulfate in the absorber decomposes when the mixture is heated to reform cupric sulfate and ammonia. Other substances which absorb ammonia in aqueous admixture at conventional absorber temperatures and from which ammonia is again released at elevated temperatures and which thus can, under proper conditions, be included advantageously in a lower conjugate system for use in the present refrigeration cycle include ammonium acid tartrate, ammonium molybdate, ammonium ferricyanide, diammonium citrate, ammonium dichromate, acetic acid and others. Often mixtures of such substances can be included to advantage.

Referring again to the ammonia-water system, it is often advantageous to include a component which is miscible with liquid ammonia but not with water at the separation temperature. Such substances include dialkyl ethers, such as diethyl ether, dimethyl ether, methyl propyl ether, the low molecular weight alkyl amines, such as mono-, di- and trimethyl and ethyl amines, hexyl amine and the like, amides, such as acetamides and benzamide and heterocyclic nitrogen compounds, such as pyridine, quinoline and pyrrole. The inclusion in the system of certain aromatic hydrocarbons, such as benzene, toluene, xylene, cumene, ethyl benzene, p-cymene and others, and the advantages accruing thereto, have been discussed previously.

It is generally true that inclusion in the system of a third component, in addition to the high-boiling and low-boiling components, which is much more soluble in one of the latter than in the other, either increases the degree of segregation of the high-boiling and low-boiling components into the respective high-boiling and low-boiling conjugate solutions at a particular temperature over the segregation obtained without the addition of the third component or leads to a particular degree of separation at a lower temperature than would be the case without the inclusion of the third component. Two-component systems which are homogeneous over a particular range of temperatures are often converted, by the addition of a third component which is more soluble in one component than in the other, to a system having a lower consolute temperature within the same particular temperature range and which when heated to a temperature higher than the lower consolute temperature, but still within the particular temperature range, separates into conjugate solutions.

The following cyclic operation using a negative conjugate system consisting of substantially equal parts by weight of triethyl amine and water illustrates, but does not limit, the method of the invention. The mixture is heated in a closed container to a temperature of about 70 degrees C., at which temperature it has a vapor pressure of about 450 millimeters of mercury, and the liquid layers which form are separated from one another without cooling and without substantial vaporization thereof. One of the layers contains about 1.6 percent of triethyl amine and the other contains about 96 percent of triethyl amine, the balance in each case being water. The layers have specific gravities of approximately 0.98 and 0.71, respectively. The layer containing 1.6 of triethyl amine is introduced into an absorber and cooled with cooling water at about 15 degrees C., at which temperature it has a vapor pressure of about 21 millimeters of mercury, and the layer containing about 96 percent of triethyl amine is introduced into a vaporizer having a vapor conduit connecting it with the absorber. Triethyl amine distills from the vaporizer and the temperature of the liquid remaining therein falls to 0 degrees C. or slightly above, its vapor pressure at 0 degrees C. being substantially equal to the vapor pressure of the fresh cooled 1.6 percent solution in the absorber. The triethyl amine vapors are absorbed by the liquid in the absorber are subsequently drawn off and pumped into sorber are subsequentially drawn off and pumped into the heating vessel and heated as first described.

In another illustrative cyclic operation of the process 317 parts by weight of a mixture containing 41.2 percent sodium hydroxide, 40.9 percent water, 16.9 percent ammonia and a total of 1.0 percent sodium chloride and sodium chlorate as impurities in the sodium hydroxide is heated in a closed vessel at 60 degrees C. under a pressure of about 450 lb./sq. in. and the conjugate solutions which form as layers separated at the same temperature and pressure. The conjugate solution rich in ammonia consisting of 60 parts of a solution containing 9.7 percent sodium hydroxide, 37.7 percent water, 47.7 percent ammonia and 4.9 percent combined sodium chloride and sodium chlorate is placed in a vaporizer connected by a vapor conduit with an absorber. The other conjugate solution consisting of 257 parts by weight of a solution containing 48.7 percent sodium hydroxide, 41.6 percent water, 9.7 percent ammonia and traces of sodium chloride and sodium chlorate is placed in the vaporizer and cooled to about 25 degrees C. Ammonia vaporizes in the vaporizer and is absorbed in the solution in the absorber, the fluid remaining in the vaporizer being cooled to a low temperature. The liquids remaining in the vaporizer and absorber are then removed and placed in the closed vessel and heated to form the original conjugate solutions.

In yet another illustrative operation of the process about equal parts of 40 percent aqueous ammonia and of meta-xylene are placed in a closed vessel and heated to about 100 degrees C. and the conjugate solutions separated at the same temperature. The ammonia-rich meta-xylene layer is placed in a vaporizer and the aqeuous layer is placed in an absorber connected with the vaporizer by a vapor conduit. The solution in the absorber is cooled to about 25 degrees C. whereupon the solution in the vaporizer boils vigorously and ammonia distills and is absorbed in the solution in the absorber, the solution remaining in the vaporizer being cooled to a low temperautre. The solutions remaining in the absorber and in the vaporizer are returned to the closed vessel and heated to about 100 degrees C. whereupon the original conjugate solutions are formed.

Although the method of the invention has been described with particular reference to cooling or refrigeration wherein a desirably low temperature is maintained in the vaporizer, it is pointed out that the method is also capable, using appropriate systems of substances, of serving for the production of useful heat in the absorber. Thus, by using appropriate systems of substances, heat may be extracted from the atmosphere, from stream or ocean water, or even from soil, by the vaporizer and discharged in the absorber at a temperature sufficiently high so that water or other fluid circulated through the "cooling coil" in the absorber is heated to a temperature at which it can be employed directly as hot water or for heating buildings or for other useful purposes. It is obvious that the particular degree of refrigeration or cooling desired, on the one hand, and the particular degree of heating desired, on the other hand, will govern to a large extent the particular system of substances employed in operating the method as well as the particular operating conditions used.

I claim:

1. The method which includes: heating a negative conjugate system comprising a high-boiling component and a low-boiling component under a separation pressure greater than the total vapor pressure of the heated system to a separation temperature at which the system comprises

a high-boiling conjugate solution impoverished with respect to the low-boiling component and a low-boiling conjugate solution enriched with respect to the low-boiling component; separating the conjugate solutions from one another at the separation temperature and pressure; decreasing the pressure on the separated conjugate solutions to a pressure below the separation pressure; cooling the impoverished high-boiling conjugate solution in vapor contact with the enriched low-boiling conjugate solution to cause vaporization of the low-boiling component from the low-boiling conjugate solution and leave a low-boiling solution impoverished with respect to the low-boiling component and at a temperature below the temperature of the high-boiling conjugate solution and to cause enrichment of the high-boiling conjugate solution with respect to the low-boiling component by absorption of the vapor of the latter therein; increasing the pressure on the enriched high-boiling solution and on the impoverished low-boiling solution and combining them to form the original negative conjugate system; and exchanging heat between the separated low-boiling conjugate solution prior to decreasing the pressure thereon and the impoverished low-boiling solution subsequent to increasing the pressure thereon and prior to combining it with the enriched high-boiling solution.

2. The method which includes: heating a negative conjugate system comprising a high-boiling component and a low-boiling component under a separation pressure greater than the total vapor pressure of the heated system to a separation temperature at which the system comprises a high-boiling conjugate solution impoverished with respect to the low-boiling component and a low-boiling conjugate solution enriched with respect to the low-boiling component; separating the conjugate solutions from one another at the separation temperature and pressure; decreasing the pressure on the separated conjugate solutions to a pressure below the separation pressure; cooling the impoverished high-boiling conjugate solution in vapor contact with the enriched low-boiling conjugate solution to cause vaporization of the low-boiling component from the low-boiling conjugate solution and leave a low-boiling solution impoverished with respect to the low-boiling component and at a temperature below the temperature of the high-boiling conjugate solution and to cause enrichment of the high-boiling conjugate solution with respect to the low-boiling component by absorption of the vapor of the latter therein; increasing the pressure on the enriched high-boiling solution and on the impoverished low-boiling solution and combining them to form the original negative conjugate system; and exchanging heat between the separated high-boiling conjugate solution prior to decreasing the pressure thereon and the enriched high-boiling solution subsequent to increasing the pressure thereon and prior to combining it with the impoverished low-boiling solution.

3. The method which includes: heating a negative conjugate system comprising a high-boiling component and a low-boiling component under a separation pressure greater than the total vapor pressure of the heated system to a separation temperature at which the system comprises a high-boiling conjugate solution impoverished with respect to the low-boiling component and a low-boiling conjugate solution enriched with respect to the low-boiling component; separating the conjugate solutions from one another at the separation temperature and pressure; decreasing the pressure on the separated conjugate solutions to a pressure below the separation pressure; cooling the impoverished high-boiling conjugate solution in vapor contact with the enriched low-boiling conjugate solution to cause vaporization of the low-boiling component from the low-boiling conjugate solution and leave a low-boiling solution impoverished with respect to the low-boiling component and at a temperature below the temperature of the high-boiling conjugate solution and to cause enrichment of the high-boiling conjugate solution with respect to the low-boiling component by absorption of the vapor of the latter therein; increasing the pressure on the enriched high-boiling solution and on the impoverished low-boiling solution and combining them to form the original negative conjugate system; and exchanging heat between the separated enriched low-boiling conjugate solution prior to decreasing the pressure thereon first with the enriched high-boiling solution subsequent to increasing the pressure thereon and then with the impoverished low-boiling solution subsequent to increasing the pressure thereon.

4. The method which includes: heating a negative conjugate system comprising a high-boiling component and a low-boiling component under a separation pressure greater than the total vapor pressure of the heated system to a separation temperature at which the system comprises a high-boiling conjugate solution impoverished with respect to the low-boiling component and a low-boiling conjugate solution enriched with respect to the low-boiling component; separating the conjugate solutions from one another at the separation temperature and pressure; decreasing the pressure on the separated conjugate solutions to a pressure below the separation pressure; cooling the impoverished high-boiling conjugate solution in vapor contact with the enriched low-boiling conjugate solution to cause vaporization of the low-boiling component from the low-boiling conjugate solution and leave a low-boiling solution impoverished with respect to the low-boiling component and at a temperature below the temperature of the high-boiling conjugate solution and to cause enrichment of the high-boiling conjugate solution with respect to the low-boiling component by absorption of the vapor of the latter therein; increasing the pressure on the enriched high-boiling solution and on the impoverished low-boiling solution and combining them to form the original negative conjugate system; exchanging heat between the separated, enriched low-boiling conjugate solution prior to decreasing the pressure thereon first with the enriched high-boiling solution subsequent to increasing the pressure thereon and then with the impoverished low-boiling solution subsequent to increasing the pressure thereon; and exchanging heat between the impoverished high-boiling conjugate solution and the enriched high-boiling solution subsequent to the exchange of heat between the latter and the enriched low-boiling solution.

5. The method which includes: heating a negative conjugate system comprising a high-boiling component selected from the group consisting of water and the mono- and poly-hydroxy alcohols, a low-boiling component selected from the group consisting of ammonia, the aliphatic amines boiling below about 90 degrees C., sulfur dioxide, carbon dioxide and dimethyl ether, and a substance other than the low-boiling component soluble in the high-boiling component but of limited solubility in the low-boiling component under a pressure greater than the vapor pressure of the heated system to form a high-boiling conjugate solution and a low-boiling conjugate solution therein, the low-boiling solution being rich in the low-boiling component; separating the conjugate solutions from one another without substantial cooling or vaporization thereof; and cooling the high-boiling solution in vapor contact with the low-boiling solution to cause vaporization of the low-boiling component therefrom and cooling thereof to a temperature below that of the high-boiling solution.

6. The method which includes: heating a negative conjugate system comprising water as a high-boiling component, ammonia as a low-boiling component and a compound selected from the group consisting of the alkali metal hydroxides and chlorides under a pressure greater than the total vapor pressure of the heated system to form a high-boiling conjugate solution and a low-boiling conjugate solution therein, the low-boiling conjugate solution being rich in ammonia; separating the conjugate

solutions from one another without substantial cooling or vaporization thereof; and cooling the high-boiling conjugate solution in vapor contact with the low-boiling conjugate solution to cause vaporization of ammonia from the low-boiling conjugate solution and cooling of the low-boiling solution to a temperature below that of the high-boiling solution.

7. The method which includes: heating a negative conjugate system comprising water as a high-boiling component, ammonia as a low-boiling component and sodium hydroxide under a pressure greater than the total vapor pressure of the heated system to form a high-boiling conjugate solution and a low-boiling conjugate solution therein, the low-boiling conjugate solution being rich in ammonia; separating the conjugate solutions from one another without substantial cooling or vaporization thereof; and cooling the high-boiling conjugate solution in vapor contact with the low-boiling conjugate solution to cause vaporization of ammonia from the low-boiling conjugate solution and cooling of the low-boiling solution to a temperature below that of the high-boiling solution.

8. The method which includes: heating a neagtive conjugate system comprising from about 15 to about 55 parts by weight of water as a high-boiling component, from about 20 to about 80 parts of ammonia as a low-boiling component and from about 5 to about 60 parts of sodium hydroxide under a pressure greater than the total vapor pressure of the heated system to form a high-boiling conjugate solution and a low-boiling conjugate solution therein, the low-boiling conjugate solution being rich in ammonia; separating the conjugate solutions from one another without substantial cooling or vaporization thereof; and cooling the high-boiling conjugate solution in vapor contact with the low-boiling conjugate solution to cause vaporization of ammonia from the low-boiling conjugate solution and cooling of the low-boiling solution to a temperature below that of the high-boiling solution.

9. The method which includes: heating a negative conjugate system comprising water as a high-boiling component, ammonia as a low-boiling component and sodium chloride under a pressure greater than the total vapor pressure of the heated system to form a high-boiling conjugate solution and a low-boiling conjugate solution therein, the low-boiling conjugate solution being rich in ammonia; separating the conjugate solutions from one another without substantial cooling or vaporization thereof; and cooling the high-boiling conjugate solution in vapor contact with the low-boiling conjugate solution to cause vaporization of ammonia from the low-boiling conjugate solution and cooling of the low-boiling solution to a temperature below that of the high-boiling solution.

10. The method which includes: heating a negative conjugate system comprising a high-boiling component selected from the group consisting of water, the mono- and poly-hydroxy alcohols and the polyglycols, a low-boiling component selected from the group consisting of ammonia, the low-boiling aliphatic amines, sulfur dioxide, carbon dioxide and dimethyl ether and a substance other than the high-boiling component soluble in the low-boiling component but of limited solubility in the high-boiling component under a pressure greater than the vapor pressures of the heated system to form a high-boiling conjugate solution and a low-boiling conjugate solution therein, the low-boiling solution being rich in the low-boiling component; separating the conjugate solutions from one another without substantial cooling or vaporization thereof; and cooling the high-boiling solution in vapor contact with the low-boiling solution to cause vaporization of the low-boiling component therefrom and cooling thereof to a temperature below that of the high-boiling solution.

11. The method of claim 10 wherein the high-boiling component is water, the low-boiling component is ammonia and the substance soluble in the low-boiling component is an organic compound non-reactive with water and ammonia.

12. The method of claim 10 wherein the high-boiling component is water, the low-boiling component is ammonia and the substance soluble in the low-boiling component is a liquid aromatic hydrocarbon.

13. The method of of claim 10 wherein the high-boiling component is water, the low-boiling component is ammonia and the substance soluble in the low-boiling component is meta-xylene.

14. The method of claim 10 wherein the high-boiling component is water, the low-boiling component is ammonia and the substance soluble in the low-boiling component is meta-xylene, the ammonia and meta-xylene being in a ratio forming a pair of conjugate solutions at a temperature below about 15 degrees C.

15. The method which includes: heating a negative conjugate system comprising a high-boiling component selected from the group consisting of water, the mono- and poly-hydroxy alcohols and the polyglycols, a low-boiling component selected from the group consisting of ammonia, the low-boiling aliphatic amines, sulfur dioxide, carbon dioxide and dimethyl ether, a substance other than the low-boiling component soluble in the high-boiling component but of limited solubility in the low-boiling component and a substance other than the high-boiling component soluble in the low-boiling component but of limited solubility in the high-boiling component under a pressure greater than the vapor pressure of the heated system to form a high-boiling conjugate solution and a low-boiling conjugate solution therein, the low-boiling solution being rich in the low-boiling component; separating the conjugate solutions from one another without substantial cooling or vaporization thereof; and cooling the high-boiling solution in vapor contact with the low-boiling solution to cause vaporization of the low-boiling component therefrom and cooling thereof to a temperature below that of the high-boiling solution.

16. The method of claim 15 wherein the high-boiling component is water, the substance soluble in the high-boiling component is selected from the group consisting of the alkali metal hydroxides and chlorides, the low-boiling component is ammonia and the substance soluble in the low-boiling component is an aromatic hydrocarbon.

17. The method of claim 15 wherein the high-boiling component is water, the substance soluble in the high-boiling component is sodium hydroxide, the low-boiling component is ammonia and the substance soluble in the low-boiling component is meta-xylene.

18. The method of claim 15 wherein the high-boiling component is water, the substance soluble in the high-boiling component is sodium hydroxide, the low-boiling component is ammonia and the substance soluble in the low-boiling component is meta-xylene, the water, sodium hydroxide and ammonia being in the ratios of 15 to 55, 5 to 60 and 20 to 80 parts by weight, respectively.

19. The method of claim 15 wherein the high-boiling component is water, the substance soluble in the high-boiling component is sodium hydroxide, the low-boiling component is ammonia and the substance soluble in the low-boiling component is meta-xylene, the water, sodium hydroxide and ammonia being in the ratios of 15 to 55, 5 to 60 and 20 to 80 parts by weight, respectively, and the ammonia and meta-xylene being in a ratio forming conjugate solutions at a temperature below about 15 degrees C.

20. A liquid, multiphase composition of matter comprising ammonia, water and meta-xylene, the amounts of ammonia and of meta-xylene in the composition being in a ratio which, in a two-component system consisting only of ammonia and meta-xylene in the same ratio, causes conjugate solutions to form at a temperature below an upper consulate temperature of the two-component system.

21. A liquid, multiphase composition of matter com-

prising ammonia, water and cumene, the amounts of ammonia and of cumene in the composition being in a ratio which, in a two-component system consisting only of ammonia and cumene in the same ratio, causes conjugate solutions to form at a temperature below an upper consulate temperature of the two-component system.

22. A liquid, multiphase composition of matter comprising ammonia, water and toluene, the amounts of ammonia and of toluene in the composition being in a ratio which, in a two-component system consisting only of ammonia and toluene in the same ratio, causes conjugate solutions to form at a temperature below an upper consulate temperature of the two-component system.

23. A liquid, multiphase composition of matter comprising ammonia, water, a liquid aromatic hydrocarbon and a substance soluble in water but sparingly soluble in ammonia and the aromatic hydrocarbon.

24. A composition as claimed in claim 23 wherein the substance soluble in water is selected from the group consisting of the alkali metal hydroxides and chlorides, the ammonia and aromatic hydrocarbon being present in a ratio forming conjugate solutions at a temperature below the upper consolute temperature of the system consisting of ammonia and the aromatic hydrocarbon.

25. A liquid, multiphase composition of matter comprising water, sodium hydroxide, ammonia and meta-xylene, the water, sodium hydroxide and ammonia being in the ratio of 15 to 55, 5 to 60 and 20 to 80 parts by weight, respectively, and the ammonia and meta-xylene being in a ratio forming conjugate solutions at a temperature below about 15 degrees C.

26. In apparatus for effecting transfer of heat from a region of lower temperature to a region of higher temperature using conjugate solutions, the combination including: a separator for separating a high-boiling and a low-boiling conjugate solution from one another at a separating temperature and under a separating pressure greater than the total vapor pressure of the solutions at the separating temperature; a vaporizer; means to convey a low-boiling conjugate solution from the separator into the vaporizer and to reduce the pressure thereon; an absorber; means to convey a high-boiling conjugate solution from the separator into the absorber and to reduce the pressure thereon, the vaporizer and absorber communicating with one another by way of a vapor conduit; means to cool the absorber to cause vaporization of a low-boiling component from a low-boiling solution in the vaporizer and absorption of the vapor in a high-boiling solution in the absorber thereby to cool the vaporizer and impoverish the low-boiling solution and to enrich the high-boiling solution with respect to the low-boiling component; a first pump means to convey an impoverished low-boiling solution from the vaporizer under the separating pressure into the separator; a second pump means to convey an enriched high-boiling solution from the absorber under the separating pressure into the separator; means to heat the solutions prior to the separation step; and a heat interchanger adapted to exchange heat between a low-boiling conjugate solution being conveyed from the separator at the separation pressure and an impoverished low-boiling solution being conveyed from the vaporizer at the separation pressure.

27. In apparatus for effecting transfer of heat from a region of lower temperature to a region of higher temperature using conjugate solutions, the combination including: a separator for separating a high-boiling and a low-boiling conjugate solution from one another at a separating temperature and under a separating pressure greater than the total vapor pressure of the solutions at the separating temperature; a vaporizer; means to convey a low-boiling conjugate solution from the separator into the vaporizer and to reduce the pressure thereon; an absorber; means to convey a high-boiling conjugate solution from the separator into the absorber and to reduce the pressure thereon, the vaporizer and absorber communicating with one another by way of a vapor conduit; means to cool the absorber to cause vaporization of a low-boiling component from a low boiling solution in the vaporizer and absorption of the vapor in a high-boiling solution in the absorber thereby to cool the vaporizer and impoverish the low boiling solution and to enrich the high-boiling solution with respect to the low-boiling components; a first pump means to convey an impoverished low-boiling solution from the vaporizer under the separating pressure into the separator; a second pump means to convey an enriched high-boiling solution from the absorber under the separating pressure into the separator; means to heat the solutions prior to the separation step; and a heat interchanger adapted to exchange heat between a high-boiling conjugate solution being conveyed from the separator under the separation pressure and an enriched high-boiling solution being conveyed from the absorber under the separation pressure.

28. In apparatus for effecting transfer of heat from a region of lower temperature to a region of higher temperature using conjugate solutions, the combination including: a separator for separating a high-boiling and a low-boiling conjugate solution from one another at a separating temperature and under a separating pressure greater than the total vapor pressure of the solutions at the separating temperature; a vaporizer; means to convey a low-boiling conjugate solution from the separator into the vaporizer and to reduce the pressure thereon; an absorber; means to convey a high-boiling conjugate solution from the separator into the absorber and to reduce the pressure thereon, the vaporizer and absorber communicating with one another by way of a vapor conduit; means to cool the absorber to cause vaporization of a low-boiling component from a low-boiling solution in the vaporizer and absorption of the vapor in a high-boiling solution in the absorber thereby to cool the vaporizer and impoverish the low-boiling solution and to enrich the high-boiling solution with respect to the low-boiling component; a first pump means to convey an impoverished low-boiling solution from the vaporizer under the separating pressure into the separator; a second pump means to convey an enriched high-boiling solution from the absorber under the separating pressure into the separator; means to heat the solutions prior to the separation step; and heat interchangers adapted to exchange heat between a low-boiling conjugate solution being conveyed from the absorber under the separation pressure and, first, an enriched high-boiling solution being conveyed from the basorber under the separation pressure and, second, an impoverished low-boiling solution being conveyed from the vaporizer under the separation pressure.

29. In apparatus for effecting transfer of heat from a region of lower temperature to a region of higher temperature using conjugate solutions, the combination including: a separator for separating a high-boiling and a low-boiling conjugate solution from one another at a separating temperature and under a separating pressure greater than the total vapor pressure of the solutions at the separating temperature; a vaporizer; means to convey a low-boiling conjugate solution from the separator into the vaporizer and to reduce the pressure thereon; an absorber; means to convey a high-boiling conjugate soultion from the separator into the absorber and to reduce the pressure thereon, the vaporizer and absorber communicating with one another by way of a vapor conduit; means to cool the absorber to cause vaporization of a low-boiling component from a low-boiling solution in the vaporizer and absorption of the vapor in a high-boiling solution in the absorber thereby to cool the vaporizer and impoverish the low-boiling solution and to enrich the high-boiling solution with respect to the low-boiling component; a first pump means to convey an impoverished low-boiling solution from the vaporizer under the separating pressure into the separator; a sec-

ond pump means to convey an enriched high-boiling solution from the absorber under the separating pressure into the separator; means to heat the solutions prior to the separation step; a heat interchanger adapted to exchange heat between a low-boiling conjugate solution being conveyed from the separator under the separation pressure and, first, an enriched high-boiling solution being conveyed from the absorber under the separation pressure and, second, an impoverished low-boiling solution being conveyed from the vaporizer under the separation pressure; and a heat interchanger adapted to exchange heat between a high-boiling conjugate solution being conveyed from the separator under the separation pressure and an enriched high-boiling solution being conveyed from the absorber under the separation pressure subsequent to the exchange of heat between the enriched high-boiling solution and the low-boiling conjugate solution.

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UNITED STATES PATENT OFFICE

CERTIFICATION OF CORRECTION

Patent No. 2,963,875 December 13, 1960

Lindley E. Mills

It is hereby certified that error appears in the above numbered patent requiring correction and that the said Letters Patent should read as corrected below.

Column 22, line 7, for "components" read -- component --; line 47, for "absorber" read -- separator --; same column 22, line 49, for "basorber" read -- absorber --.

Signed and sealed this 6th day of June 1961.

(SEAL)
Attest:

ERNEST W. SWIDER
Attesting Officer

DAVID L. LADD
Commissioner of Patents