

# Heat Pump Cycles with Nonazeotropic Refrigerant Mixtures in Thermodynamic Diagrams

R. Radermacher, Ph.D.

## ABSTRACT

Various thermodynamic diagrams that are well known in absorption heat pump design and distillation techniques are introduced in this paper for nonazeotropic halogenated hydrocarbon mixtures. As an example, a typical compressor heat pump cycle for refrigerant mixtures is displayed and the cycle itself discussed using these diagrams.

It is shown that virtually all the necessary thermodynamic design information can be obtained from the enthalpy-composition diagram. It offers the possibility of determining the enthalpies, pressures, temperatures, and compositions involved by simple geometric constructions, even when the refrigerant flow rate varies in certain components.

Furthermore, it is shown by an example that thermodynamic diagrams provide a basic understanding of the influence of refrigerant properties on the heat pump cycle.

## INTRODUCTION

Most vapor-compression-type heat pumps as well as most power generation devices currently built employ single-component working fluids. This is, in principal, also true for compressor heat pumps, although they may employ azeotropic mixtures, because these mixtures behave as a single-component working fluid. The thermodynamic cycle commonly used in vapor-compression-type heat pumps is a reversed and slightly modified Rankine cycle.

The application of this type of heat pump is limited by the thermodynamic properties of the single-component working fluid. These limitations are due to the dependence of the vapor pressure on temperature, the mismatching of temperature profiles in the evaporator and condenser, and the poor ability to control capacity.

The use of nonazeotropic refrigerant mixtures has been widely suggested as a way to overcome these restrictions.

From a thermodynamic point of view, changing to a two-component mixture adds a degree of freedom to the system by introducing a new variable, the composition, which is defined as:

$$x = \frac{\text{weight of one component [kg]}}{\text{weights of all components [kg]}} \quad (1)$$

If the pressure were chosen as the independent variable, either the temperature or the composition could be chosen as the second independent variable, while the other one is then fixed by the first two (which is not a possibility when the composition is already fixed by using only one component or an azeotropic mixture).

Dr. Reinhard Radermacher, Visiting Scientist, National Bureau of Standards, Washington, D.C., now Assistant Professor at the University of Maryland, Mechanical Engineering Department, College Park, MD.

It should be noted that the new degree of freedom for a certain mixture is somewhat limited. For a given pressure the boiling temperature can be changed by adjusting the composition in a range between the boiling temperatures of the two pure components only.

This new degree of freedom of a two-component mixture offers certain advantages in heat pump operation, especially when separated streams are employed, as in subcooling, two-stage evaporation, or two-stage condensation. In order to make these advantages more apparent and to provide the means to better understand the influence of mixture properties on heat pump design and performance, a basic heat pump process with separated streams will be described and explained using various thermodynamic diagrams. These diagrams are generally employed for nonazeotropic mixtures in other applications of mixtures, such as distillation processes or absorption heat pumps. For example, a study of a heat pump process with a refrigerant mixture of fixed composition and no separation of streams is given in Kraus and Vollmer (1979), while Dvorak (1980) displays a heat pump process in an enthalpy-composition diagram without any comment concerning the use of the diagram.

The variables that would interest a designer of a vapor compression heat pump are: pressure, temperature, composition, enthalpy, specific volume, entropy, and transport properties. In order to display all these variables, a multidimensional diagram should be generated, which, of course, is not practical. Several two-dimensional diagrams are in use showing any two variables on their axis and displaying projections of some of the other variables as sets of curves of constant properties like isobars, isotherms, etc. If a mixture is considered, the composition is an additionally important variable, which must be displayed in the diagrams, especially when separation of streams or changes in composition are to be considered. In order to do so, two types of diagrams are possible: (1) diagrams generated for a single component that were extended for mixtures and (2) diagrams that show the composition as a variable on one of their axes.

This paper will consider mixtures of two components only. Although a mixture with more components can be employed, the diagrams would become too complicated for cycle analysis.

In general, the same advantages that the employment of nonazeotropic working fluid mixtures offer in heat pumps can be obtained in power generation devices as well. This scheme is pursued, for example, in connection with the use of geothermal energy (Kestin 1980). Therefore, considerations discussed here are similar to those necessary when a Rankine cycle with nonazeotropic working fluid mixtures is considered.

#### A BASIC HEAT PUMP PROCESS

Various heat pump processes employing nonazeotropic refrigerant mixtures have been suggested in the literature.\* For this paper, only one basic design with separation of fluid streams has been chosen to demonstrate the use of thermodynamic diagrams. The heat pump cycle is shown schematically in figure 1. The superheated vapor (0) leaving the compressor will be desuperheated (1) and partially condensed in the condenser (2). All the liquid formed up to point (2) in the condenser is drained, expanded (8), evaporated in the subcooler (9), and fed into the compressor suction lines. The main stream of refrigerant, which has been completely condensed (3), becomes, therefore, significantly subcooled (4) by acting as a heat source for the evaporation of the bypassed stream. The main stream is then expanded (5), vaporized in the evaporator (6), and fed into the compressor suction line, where it is merged with the evaporated bypass stream before entering the compressor (7).

The enthalpies delivered or absorbed in each component can be worked out by considering mass and energy balances for each component of the heat pump. The subscripts refer to states indicated in figure 1, and the expressions are based on one unit of mass of superheated vapor leaving the compressor.

Then the amount of heat delivered in the condenser,  $q_c$ , is:

$$q_c = h_0 - h_3 - y(h_2 - h_3) \quad (2)$$

\*A good literature review is given in W. F. Stoecker, "Energy Characteristics of a Two Evaporator Refrigerator Using a Refrigerant Mixture," ORNL/Sub/81-7762/2081.

where

$$y = \frac{x_0 - x_3}{x_2 - x_3} \quad (3)$$

The fraction of liquid drawn from the condenser at (2). The amount of heat absorbed in the evaporator,  $q_{ev}$ , is:

$$q_{ev} = (1 - y)(h_6 - h_5) \quad (4)$$

while the amount of heat exchanged in the subcooler,  $q_s$ , is:

$$q_s = (1 - y)(h_3 - h_4) = y(h_9 - h_8) = q_{sy} \quad (5)$$

and the work,  $w$ , supplied by the compressor is:

$$w = (h_0 - h_7) \quad (6)$$

where

$$h_7 = yh_9 + (1 - y)h_6 \quad (7)$$

For simplicity, it has been assumed that the fluids leaving the condenser and the evaporator are saturated.

## THE HEAT PUMP CYCLE DISPLAYED IN THE DIAGRAMS

### The Temperature-Entropy Diagram

The temperature-entropy diagram is well known for single components. One of its attributes is that areas in the diagram represent energies and thus provide an overview about energies involved in a certain process. A second attribute is that irreversibilities can be easily determined. In literature, temperature-entropy diagrams can be found for mixtures of two (Kouremenos 1971) and three (Eber 1967) components.

In order to retain the usual shape of the diagram, the entropy values of the two pure components should be chosen in a way so that the two-phase region of both pure components overlap. Figure 2 displays the phase boundary lines for the components A and B. The position of the two-phase regions can be chosen, since only differences of the entropy are known and of interest. In between the phase boundary lines of the two pure components A and B are located the phase boundary lines of the mixtures.

Each dome has its own set of isobars in the region of the liquid phase as well as in the region of the vapor phase and the two-phase region. The isobars in the first two regions do not deviate from the principal shape of the isobars of the pure components. But in the two-phase region, the isobars of the mixtures are curves with a positive slope and are not necessarily straight lines. At a given pressure, the lines b and d represent boiling and dew-point lines, respectively. They are isobars, too, and they indicate the saturation temperature for a given composition.

Figure 2 also illustrates the heat pump process of figure 1. All numbers correspond to those defined in figure 1. In this and the following diagrams, it is distinguished between two types of points of state. The first type, shown in figure 2 and the following figures as full dots, represents saturated working fluid with a quality equal to 0 or 1, which means all fluid present at this point is in one phase. Expressed in another way, since all isopleths are given for saturation conditions, these points represent correct values in relation to the axes of diagrams, as well as in relation to all isopleths.

The second type is correct in relation to the axes only. They represent all other fluid conditions not covered by the first type of points, i.e., subcooled or superheated fluids or fluids with a quality different from 0 or 1. In this case, the isopleths are meaningless. These points are indicated by a circled dot. For example, point 8 represents the entropy of the mixture and its temperature after the expansion process correctly. But the mixture is in the two-phase region and the composition of the liquid is certainly not what can be found by interpolation at point 8. This is not apparent because of the position of point 8 alone.

The temperature-entropy diagram can be used to determine the amount of entropy produced in a process and to trace irreversibilities. For example, in this diagram, the irreversibilities, i.e., the increase in entropy caused by expansion (4-→5, 2-→8) and compression (7-→0), are obvious. Areas within the T-S diagram still represent energies, but they have to be weighted with the fraction of fluid flowing in a particular component. A shortcoming is that the set of isobars can hardly be displayed because the complexity of the diagram would be greatly increased.

### The Pressure-Enthalpy Diagram

The  $p$ - $h$  diagram is the most common one used in the design of compression heat pumps. Usually the  $p$ - $h$  diagram of a single component provides information about pressure, temperature, enthalpy, entropy, and specific volume in at least some regions of the diagram. Since for mixtures the composition needs to be taken into account, other information needs to be omitted.

As the T-S diagram, the  $p$ - $h$  diagram can be set up so that the two-phase regions of the two components A and B overlap as shown in figure 3 (Schwind 1962). That is possible since only enthalpy differences are known. The phase boundary lines of the mixtures typically fall between those of the pure components.

Each dome has its own set of isotherms in the liquid region as well as in the vapor and the two-phase region. In the liquid and the vapor region, the principal shape of these lines is the same for the pure components and the mixtures. But in the two-phase region, the isotherms of the mixtures show a negative slope. The lines b and d again represent the boiling and the dew-point line, respectively, at a fixed pressure.

Figure 3 shows the heat pump cycle in a  $p$ - $h$  diagram for mixtures. The significant advantage of this diagram compared with that discussed earlier is that the enthalpies exchanged during each process can be determined from the diagram with some further calculation; that is, the enthalpy differences indicated by the diagram are valid for a unit mass of working fluid. However, it must be remembered that in the various components where the streams are separated, these enthalpy values have to be evaluated according to equations 2 through 7. For any changes of conditions that causes changes in flow rates or composition, these calculations have to be repeated.

This repetition of calculations for each operating condition and the fact that the temperatures involved cannot be obtained simply, due to the multiplicity of sets of isotherms, represent two shortcomings of this diagram.

### The Enthalpy-Composition Diagram

The enthalpy-composition diagram originally introduced by Mollier and Bosnjakovic (1965) found a wide application in the design of absorption heat pumps (Niebergall 1959) and distillation techniques (McCabe and Smith 1976). It provides considerable information about enthalpies absorbed or delivered in individual components of a heat pump while the changes occurring in composition temperature and pressure can be easily displayed. By applying certain rules, the enthalpies for all processes within the heat pump can be found by simple geometric construction (Bosnjakovic and Blackshear 1965).

The enthalpy-composition diagram, figure 4, shows (like the other diagrams discussed) three different regions. Region 1 is the all-liquid region with its isobars and isotherms. There is only one set of isotherms and one set of isobars necessary in the liquid region. The only approximation involved is that the enthalpy of the liquid phase is independent of the pressure, which is usually quite minor. Therefore, enthalpies and temperatures of subcooled liquids can be determined quite easily, which is not the case for the diagrams discussed above. Region 2 represents the two-phase region, where the isotherms are straight lines and where each pair of isobars gets its own set of isotherms. Section 3 is the superheated vapor area. In this area the isotherms are usually almost-straight lines, since the heat of mixing of gases is negligible, and again, each isobar has its own set of isotherms as in the previous diagrams. Lines b and d represent the boiling point and the dew-point lines.

The major advantage of the  $h$ , $x$  diagram compared with those discussed above is the following:

As equations 2 through 7 show, all heat and amounts of work applied to the heat pump cycle are dependent on the enthalpy differences and differences in compositions. Both of these

values can be found on the axis of the diagram and, when applying the lever rule, the heat exchanged in single components can be displayed as lines that have the same relative lengths as the amounts of heat they represent. In particular, the equations have been written per unit mass of superheated vapor leaving the compressor; therefore, all heat derived from the diagram is correct for the given fraction of the flow rate when the lever rule is applied.

Further, any change in composition, pressure, temperature, or enthalpy and its effect on the other variables can also be studied without further calculations by just repeating the geometric construction, as explained below.

Figure 4 shows the heat pump process in a  $h,x$  diagram.

First, one must find the amount of heat rejected in the condenser,  $q_c$ , which is given in equation 2. However,  $q_c$  can also be written as:

$$q_c = h_0 - h_c \quad (8)$$

where

$$h_c = h_3 + y(h_2 - h_3) \quad (9)$$

Using  $y$  as given in equation 3, equation 9 can be changed to:

$$\frac{h_c - h_3}{h_2 - h_3} = \frac{y}{1} = \frac{x_0 - x_3}{x_2 - x_3} \quad (10)$$

The values  $(x_2 - x_3)$  and  $(x_0 - x_3)$  are represented by line  $k$  and  $(h_2 - h_3)$  by line  $l$  in figure 4. Then,  $h_c$  is found on line  $i$  (which coincides here almost with the isobar) and  $q_c$  is determined by noting the single difference, equation 8, as shown in figure 4. A graphical outline of this procedure may be stated as follows: Connect points 2 and 3 by a straight line; where it intersects with the line of constant composition,  $x_0$ , the value of  $h_c$  is found. Since in this methodology, one considers only enthalpies and compositions and no other values, the rule is truly independent of the state of the fluids. Similar procedures can be applied for the evaluation of any other heat exchanges within the heat pump, as shown below.

For the evaporator, equation 4 may be rearranged to obtain:

$$\frac{q_{ev}}{h_6 - h_5} = \frac{x_2 - x_0}{x_2 - x_3} \quad (11)$$

Again, the distances  $(x_2 - x_0)$  and  $(x_2 - x_3)$  are represented in figure 4 (line  $m$ ). Also, the enthalpy difference  $(h_6 - h_5)$  can be found (line  $n$ ), and according to the lever rule  $q_{ev}$  is determined as indicated.

The amount of work necessary to compress the vapor from state (7) to state (0) is given by equation 6 where  $h_7$  can be found according to equation 7.

By rearranging equation 7 one obtains:

$$\frac{h_7 - h_6}{h_9 - h_6} = \frac{x_0 - x_3}{x_2 - x_3} \quad (12)$$

Line  $s$  represents the differences in composition  $(x_0 - x_3)$  and  $(x_2 - x_3)$  and line  $t$  the difference in enthalpies  $(h_9 - h_6)$ . By applying the lever rule as shown in figure,  $h_7$  is then found.

The amount of heat exchanged in the subcooler can be determined accordingly. The rearranged equations are:

$$\frac{q_{sy}}{h_9 - h_8} = \frac{x_0 - x_3}{x_2 - x_3} \quad (13)$$

and

$$\frac{q_s}{h_3 - h_4} = \frac{x_2 - x_0}{x_2 - x_3} \quad (14)$$

The application of the lever rules for these equations has been omitted from figure 4 for the sake of clarity; however, no new method or thought is involved.

For the particular heat pump process shown here, this diagram provides further information about the effect of subcooling. As can be seen from equations 2 and 4 the heat of condensation and of evaporation is hardly affected by the draining of  $y$  of liquid phase from the condenser. This is because the term  $y(h_2 - h_3)$  in equation 2 represents only the sensible heat of the bypassed stream, which is a minor contribution to the heat of condensation. (In principle its heat could be supplied to the condenser cooling fluid in a separate heat exchanger, increasing  $q_c$  and  $q_{gy}$ .) As a consequence, according to the energy balance for the entire heat pump, the work of compression is also almost constant. But, as can be seen from isotherms  $T_1$  and  $T_2$  in figure 4, the lowest temperature achieved in the evaporator is decreased by subcooling the mainstream, while the pressures remain unchanged. This consideration is true as long as the flow rate,  $y$ , is small compared to the overall flow rates, which means the amount of cooling provided by the bypass stream in the subcooler is not larger than the amount of sensible heat that can be supplied by the mainstream under given conditions. But, draining a bypass stream from the condenser increases the composition of the more volatile component in the liquid, leaving the condenser at point 3. As a consequence, the lower limit of the temperature interval for condensation is decreased by a small amount.

### CONCLUSIONS

The plotting of the various thermodynamic properties of mixtures has led to graphical solution techniques of great value in the fields of distillation-column analysis and absorption heat pumps. These geometric techniques are of great value when analyzing the performance of a system, particularly when seeking innovative designs or to perform quantitative evaluation of the designs. Since nonazeotropic mixtures operating in vapor compression heat pumps follow the same thermodynamic principles of these other mixtures, these techniques are equally applicable for their analysis, as has been demonstrated.

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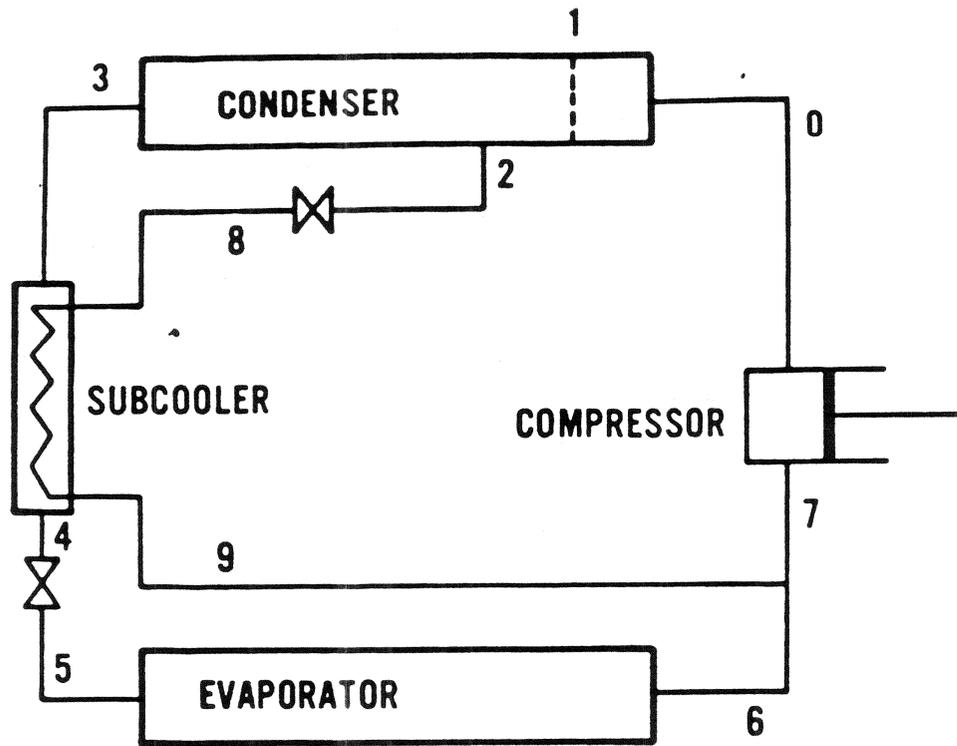


Figure 1. Scheme of the basic heat pump cycle

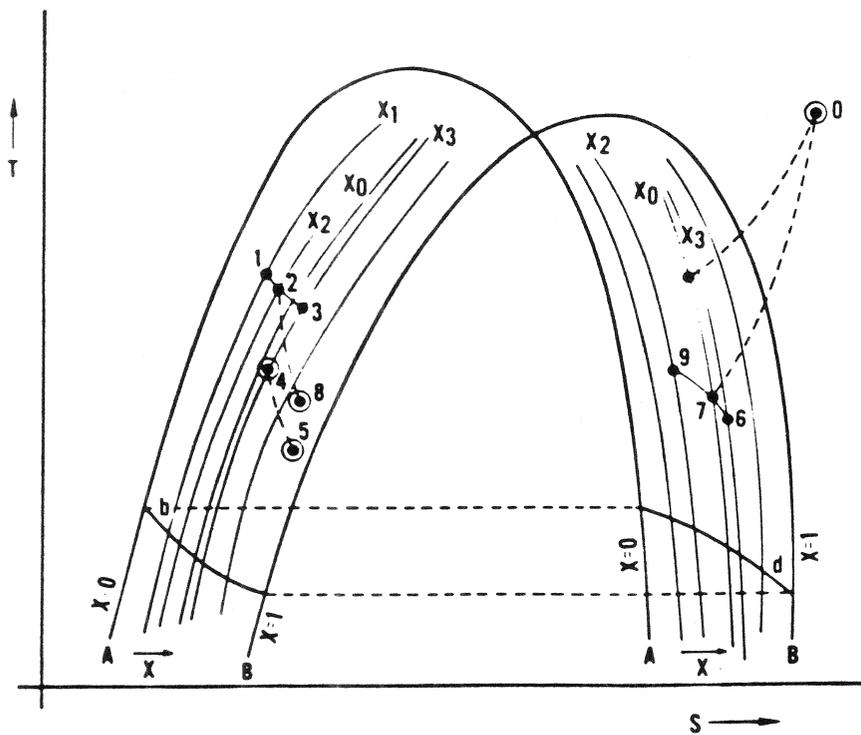


Figure 2. Temperature-entropy diagram for a mixture

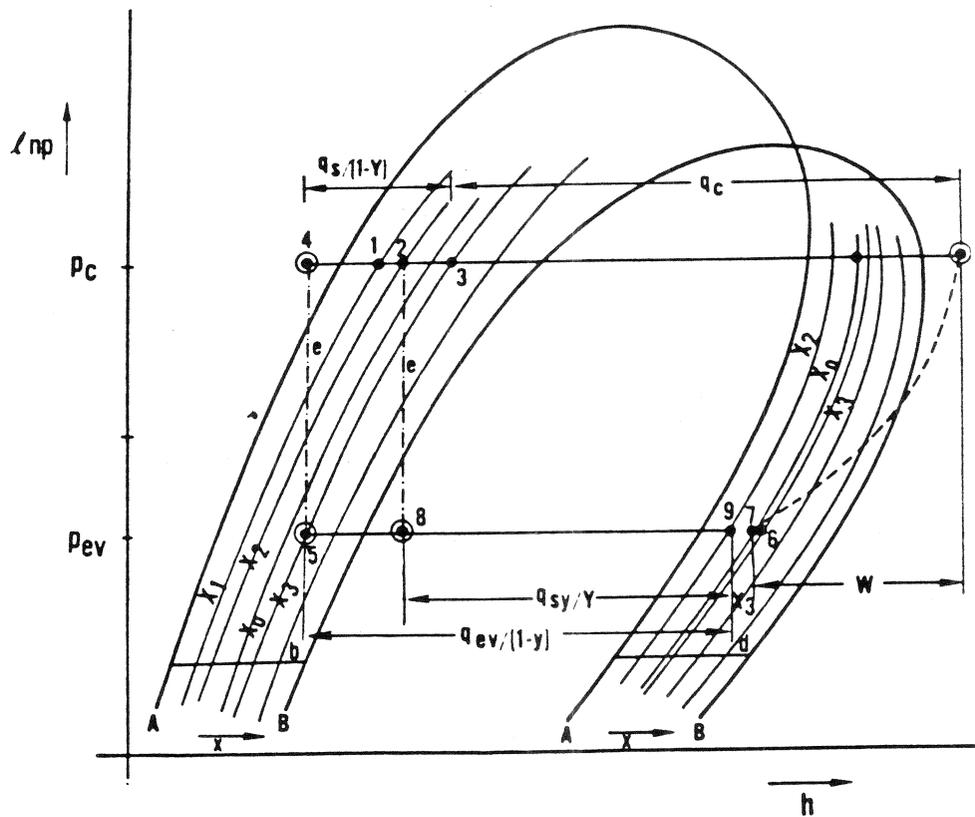


Figure 3. Pressure-enthalpy diagram for a mixture

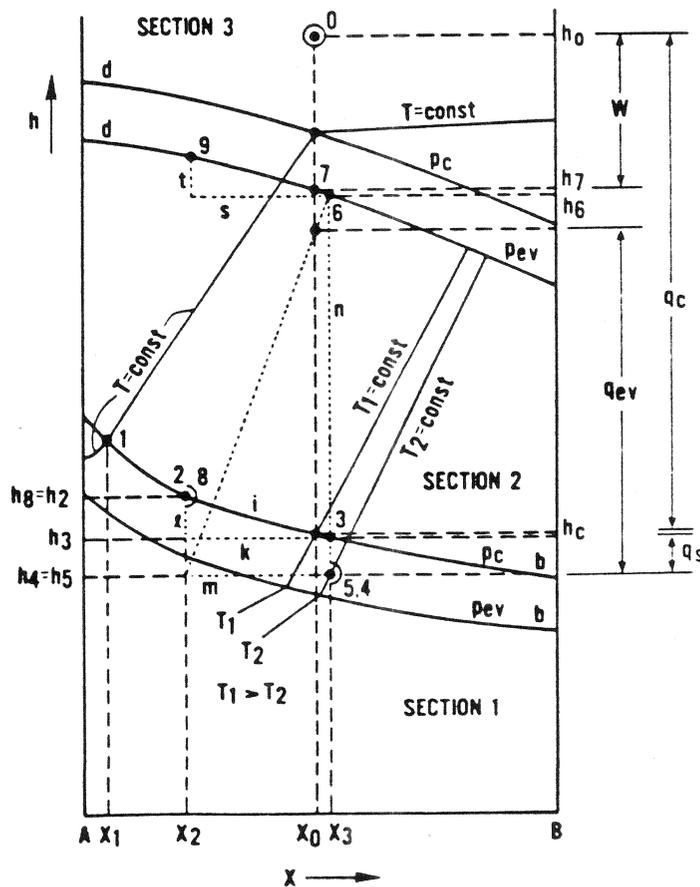


Figure 4. Enthalpy-composition diagram