Equation-of-State-Based Thermodynamic Charts for Nonazeotropic Refrigerant Mixtures

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ABSTRACT

Application of a nonazeotropic mixture to a refrigeration machine offers a new degree of freedom in controling machine performance by control of circulating mixture composition. Presenting possible thermodynamic cycles of such a machine operating with different mixture compositions requires developing appropriate thermodynamic charts with refrigerant mixture composition as a variable.

This paper presents thermodynamic charts developed for a nonazeotropic mixture, R13B1/R152a. The developed charts (pressure—enthalpy, temperature—entropy, and enthalpy—composition), though for sake of clarity showing limited data, offer important insight for understanding vapor compression cycles for different compositions. An equation of state capable of describing both the liquid and vapor phases, property algorithms and iteration schemes used in determination of the nonazeotropic mixture thermodynamic properties have been explained.

INTRODUCTION

The use of nonazeotropic refrigerant mixtures in machinery that operate on the vapor compression cycle has been under intensive research during the past several years. Several major thermodynamic advantages have been hypothesized (Vakil 1983a, 1983b) and, in some cases, measured in the laboratory (Cooper and Borchardt 1979). At the present time, the National Bureau of Standards (NBS) and the Electric Power Research Institute (EPRI) are developing a rather comprehensive computer simulation model of the vapor compression cycle operating on a binary mixture so that equipment manufacturers will be able to evaluate specific designs prior to embarking on an expensive program of hardware development. An essential part of this model is the equation of state and the algorithms associated with it for determining all the necessary thermodynamic state properties. This package is useful in itself, and when linked with canned computer graphics routines, it is possible to generate refrigerant charts. How this might be carried out is the subject of this paper.

EQUATION OF STATE

It has been shown by Morrison et al. (n.d.) that it is now possible to describe both the liquid and the vapor properties, including those under the vapor dome, of refrigerants as well as refrigerant mixtures, with a single equation of state. He also has shown that when this approach is applied to mixtures, it has a significant advantage over the traditional methods of using a vapor equation of state and a library of liquid properties. The advantage is that it will accurately predict property values in regions near or above the critical point of either of the binary components (Morrison 1985). This is possible when the equation of state has a repulsive term that can adequately characterize the molecular forces in the liquid phase, as does Morrison's equation:

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$$\frac{pv}{RT} = \frac{1 + y + y^2 - y^3}{(1 - y)^3} - \frac{a}{RT(v + b)} \qquad (1)$$

where $y = \frac{b}{4v}$

In spite of the complexity of both the repulsive term (first term on the left side) and the attractive term, they are only functions of state properties and a molecular attractive parameter (a) and a molecular size parameter (b). These parameters, in turn, are functions of temperature when dealing with single-component refrigerants and functions of temperature and composition when mixtures are being described. For single-component refrigerants, a second degree polynomial is adequate for determining them:

$$a = a(0) + a(1)T + a(2)T^2 \qquad (1a)$$

$$b = b(0) + b(1)T + b(2)T^2 \qquad (1b)$$

where $a(0)$, $a(1)$, $a(2)$, $b(0)$, $b(1)$, and $b(2)$ are constants based on empirical data for a given refrigerant. For binary mixtures, these parameters may be determined by:

$$a = w_I^2 a_I + 2w_I w_{II} a_{I,II} + w_{II}^2 a_{II}$$

$$b = w_I^2 b_I + 2w_I w_{II} b_{I,II} + w_{II}^2 b_{II}$$

Parameters a_I, a_{II}, b_I, and b_{II} are for pure refrigerants and are obtained by Equations 1a and 1b.

where

$$a_{I,II} = (1 - f_{I,II})(a_I a_{II})^{1/2}$$

$$b_{I,II} = [(b_I^{1/3} + b_{II}^{1/3})/2]^3$$

$$f_{I,II} = d - cT$$

$w_I, w_{II} = $ molar compositions of the mixture, fraction of I and II component, respectively.

Note that measurements on the mixture are required but only enough to ensure accurate values of the constants c and d, which allow for compensation of the interactions of the different molecular species. The other constants are known from single-component data or the known molar fraction of the mixture, where $w_I + w_{II} = 1$.

In addition to Equation 1, written once for the vapor phase and once for the liquid phase, to account for compositional differences, only the specific heat for the perfect gas mixture is required to determine all the thermodynamic properties of a binary mixture in either digital or graphical form. A scheme for doing this follows.

PROPERTY ALGORITHMS

When working with the vapor compression cycle, it is usually desirable to know temperature, pressure, enthalpy, and entropy in both the saturated and superheated states. In addition, it is desirable to know quality in the saturated states and specific volume in the superheated states. The most important states, of course, are those outlining the vapor dome. For mixtures, the additional variable of composition is interjected, complicating the calculative procedure considerably. This new dimension requires an accounting for properties of each component in each phase, since, when dealing with nonazeotropic mixtures, the components are more or less volatile, relative to one another, by definition.

For pure component (single refrigerant) analysis, it is first necessary to determine saturation pressure for a given temperature. Since Equation 1 also contains specific volume, an iterative process is mandatory for both the liquid and vapor phases. The criteria for verifying that the saturation pressure and specific volume "guesses" are correct is the equality of the Gibbs free energy and pressure of the two phases. The logic of this procedure is illustrated in the flow diagram in Figure 1.

The first properties needed for mixtures are composition, pressure, and bubble point temperature. Composition and usually pressure are known, and bubble point temperature is found by iteration using the criteria that the liquid composition (XL) resulting from the guess is equal to known input composition (XW). The solution logic is illustrated in the flow diagram of Figure 2, where the parameters are graphed in the phase diagram of Figure 3. After the composition and pressure values are entered and the first guess of bubble temperature is initiated, the saturation pressure of each of the components is calculated by the same procedures as outlined in Figure 1. These pressures are used as criteria for ensuring that the guessed bubble point temperature is at least within the limits of possibility, i.e., within the saturation temperature limits of the pure components, as shown in Figure 3. The next step is one of zeroing in on the unique bubble temperature value for the given pressure and liquid composition values by determining if the phases are in equilibrium. This determination usually requires the procedure similar to that outlined in Figure 1, where a test for chemical potential in lieu of Gibbs free energy is required. This is a rather lengthy procedure, and it is not practical to use such an algorithm in a larger vapor compression cycle simulation program, where property values are requested on the order of hundreds of thousands of times because of iterative routines in the cycle construction. The equation of state can be used, along with the criteria that the equilibrium between liquid and vapor phases must exist at the lowest Gibbs free energy state, to generate sufficient data to create polynomial curve fits. For this case, pressure and liquid composition are entered and a bubble temperature is systematically guessed until the resultant liquid composition agrees with the entered value. Figure 3 illustrates this procedure schematically, where the iterative temperature guesses and their resultant bubble and dew-line points are slid up and down the constant (input) pressure two-phase envelope until XL = XW. The entire process is then repeated to determine dew-line temperature.

For known temperature, all other properties may be determined explicitly (Morrison n.d.). Of additional interest for chart construction are enthalpy and entropy. The molar enthalpy may be determined by:

$$h_m = h^{pg} + \frac{a'bT - ab'T - ab}{b^2} \ln \frac{v+b}{v} + \frac{ab'T - ab}{b(v+b)} + \frac{8RTv(8v-b)}{(4v-b)^3}(b - b'T) \qquad (2)$$

where prime denotes a temperature derivative.

The molar enthalpy of a perfect gas of a mixture, h^{pg}, is the integral of a linear weighting of the heat capacities of the component perfect gases:

$$h^{pg} = \int_{T_{ref}}^{T} c_p dT = \int_{-40°F}^{T} \left[w_I c_{p,I} + w_{II} c_{p,II} \right] dt \qquad (2a)$$

where $c_{p,I}$ and $c_{p,II}$ are the component heat capacities that are functions of temperature, whose coefficients are determined empirically.

$$c_{p,I} = c_{p,I}(0) + c_{p,I}(1)T + c_{p,I}(2)T^2 \qquad (2b)$$

$$c_{p,II} = c_{p,II}(0) + c_{p,II}(1)T + c_{p,II}(2)T^2$$

The rest of the terms in Equation 2 are a result of complication of the mixture's enthalpy zero reference state, which is necessarily different from the conventional assumption of -40 F (-40°C) for the pure components. These terms have been algebraically rearranged so they are expressed entirely as functions of the same variables in the equation of state.

Molar entropy may be expressed in a similar form:

$$S_m = w_I \left[\int_{-40}^{T} \frac{c_{v,I}}{T} dT + R \ln \frac{v}{w_I \cdot v_I^*} - \Delta S_I^{pg}(v_I^*, -40 \, F) \right] \qquad (3)$$

$$+ \; w_{II} \left[\int_{40}^{T} \frac{c_{v,II}}{T} \, dT + R \ln \frac{v}{w_{II} \cdot v_{II}^{*}} - \Delta S_{II}^{pg} \; (v_{II}^{*}, \; -40 \; F) \right]$$

$$+ \; \Delta S_{m}^{pg}(v,T)$$

where v_{I}^{*} and v_{II}^{*} are reference state (−40 F, −40°C) molar volumes of liquid for either of the pure components; ΔS_{I}^{pg} and ΔS_{II}^{pg} are the differences of entropy between perfect and real gas having molar volume of saturated pure component liquid I and II, respectively, at the reference temperature (−40 F, −40°C); and ΔS_{m}^{pg} is the difference of entropy between perfect and real mixture of actual molar volume v and at actual mixture temperature, T.

In either case, ΔS^{pg} can be evaluated by Equation 3a with v put to v_{I}^{*} or v_{II}^{*}, if pure components are considered.

$$\Delta S^{pg} = \frac{a'b - ab'}{b^{2}} \ln \frac{v + b}{v} + \frac{ab'}{b(v + b)} - \frac{Rb(16v - 3b)}{(4v - b)^{2}} - \frac{8RTb'v(8v - b)}{(4v - b)^{3}} \tag{3a}$$

The definition of quality for mixtures is similar to that of single-component fluids, except that it is convenient to use composition of saturated liquid and vapor being in equilibrium at a given temperature and pressure as the weighting parameters. The equations have the same form as single-components:

$$x = \frac{m_{v}}{m_{L} + m_{v}} \tag{4}$$

where m_{L} = mass of fluid in the liquid phase

m_{v} = mass of fluid in the vapor phase

x = quality

from which comes:

$$x = \frac{XL - XW}{XL - XV} \tag{5}$$

For mixtures, the evaluation of the saturated state compositions is made for a specific pressure and temperature. Coupling these results (XL, XV) with initial mixture composition allows for the use of Equation 5 to determine quality, as illustrated in Figure 3. The saturation state compositions of the two phases are taken along the isotherm at the bubble and dew line intersections, respectively, since each phase has a different composition. The determination of this quality value for this specific isotherm and pressure envelope uniquely locates it under any vapor dome, since temperature and pressure are independent properties in the two-phase region for mixtures.

THERMODYNAMIC CHARTS

Two major issues exist at this time in constructing thermodynamic charts for nonazeotropic refrigerant mixtures. The first is what coordinates should be selected for purposes of expediant analysis. It seems reasonable to assume that the traditional diagrams of temperature/entropy and pressure/enthalpy for single-component vapor compression refrigerant analysis would be of interest. Also, it has been shown by Radermacher (1984) that the enthalpy/composition diagram, which employs mixtures and has proved so valuable in absorption refrigeration analysis, offers some unique insight for nonazeotropic analysis. The second issue, the complexity of so many families of curves, may not really have a solution. Because of the number of variables that need to be represented and because only two-dimensional graphs are available for quantitative representation, it would appear that only selective portions of all the variables can be illustrated. For this paper, the effect of changing composition was mostly limited to vapor dome variations, while the superheat properties are shown for only one composition.

There exists a myriad of "canned" computer graphics software packages, which are adequate for creating these charts. Usually all that is needed as input is an identifiable list of desired paired-properties values and a scale definition for the coordinate axes. Thus, for the figures illustrated in this paper, the output or results of the calculations discussed in the previous section were generated on a uniform incremental basis, each for a sufficient number of data points that the graphics program could get a smooth curve over the range of interest.

The temperature/entropy graph of Figure 4, which illustrates the constant pressure process under the vapor dome, is not identical with a constant temperature process in nonazeotropic mixtures. Turning this around, it can be inferred that a constant pressure condensing or evaporating process will result in a variable temperature phase change, which is to be expected since the entering phase will continually be changing in composition. This diagram also illustrates variation of the specific latent heat (i.e., width of vapor dome) with composition. As the initial liquid weight fraction of the more volatile component (R 13B1) is decreased, the vapor dome width is increased, indicating a potential increase in refrigerant capacity per unit of material. As with single-component analysis, this diagram has academic interest; but, except for second law (exergy) analysis, it is not of as much practical value as the charts of Figures 5 and 6.

Figure 5, the pressure/enthalpy diagram, illustrates more explictly the temperature gradient a given evaporation or condensation process may undergo. With this information, it is possible to design counterflow heat exchangers to minimize heat transfer irreversibilities with the source and sink media. It may also be helpful for refrigerant circuit design to convert a traditional cross-flow heat exchanger into a quasi-counterflow one. Figure 5 also illustrates that the temperature gradient will vary, depending on composition (note the $-30°$ line for each vapor dome). Assuming that the vapor compression system operates so that the evaporator exit condition is near or slightly above the saturation state, a series of pressure/enthalpy charts would make it possible to obtain the density value for each operating condition so as to estimate the mass rate of refrigerant flow variation. In evaluating the effect of composition on capacity potential, the graphs can, however, be misleading. Since the coordinates are sometimes extrinsic properties made intrinsic by dividing by the mass of refrigerant (and in the case of mixtures, this mass will change with composition) the mass flow can be inversely proportional to capacity (enthalpy difference) per unit mass. This is the case for R 13B1/R 152a. As the percentage of R 13B1 is increased, the Δh available under the vapor dome is diminished; but this molecule is considerably heavier than the R 152a, and the increase of mass flow rate (assuming compressor is a constant volume machine) is more than enough to offset a decrease in absolute capacity, ΔH.

Figure 6 may ultimately prove to be the most useful. If the use of mixtures is intended for capacity modulation purposes (Vakil 1983b), then a criteria for selection will be that the initial liquid composition have the maximum temperature/quality (dT/dx) gradient possible. This can be visualized on one enthalpy/composition chart by noting the slopes of the constant temperature lines through the two-phase region. For the case of R 152a/R 13B1, the maximum gradient occurs at approximately XW = 0.5. Much additional information may be obtained from this sort of chart directly for the purposes of estimating the input and output energy flows of a given operating system by simply reading the differences in enthalpies between the state points, once they are located on the graph, in a similar manner as is done in absorption systems. In this manner, the effects of such concepts as liquid line subcooler may be quantified by noting the changes in work input, condenser heat, and evaporator heat required (Radermacher 1984).

SUMMARY

The determination of thermodynamic properties using an equation of state capable of describing both the liquid and vapor phases has advantages in both simplicity and accuracy. That is, fewer empirically based data are necessary to define the fundamental equation and resultant mixture property values in the entire range of interest, including the fact that the area near and above the critical point of either component will be determined without loss in precision. Once the equation of state and the perfect gas heat capacity for constant pressure are empirically determined for each component, all other mixture properties may be determined for either phase as well as the two-phase region. The method for doing this, however, is not always straightforward; iterative procedures are required for saturation line pressure, given temperature (or visa versa); phase-weighting procedures for determining quality component molecular interactions to be accounted for by mixing rules, etc. The results of these calcula—

tions can be tabulated in a format suitable for an independent computer graphics program, so that the traditional (T-s and p-h) and innovative charts can be generated.

Even in this day of dominant automated digital data formatting, an analog representation of data (i.e., charts) has its role. At the very early or most creative stage of design, they can represent a first level quantitative background for determining the effects of cycle or system alterations. This performance approximation procedure would appear even more critical when using mixtures, because the introduction of a new independent variable (composition) into the refrigerating cycle analysis adds considerable complexity to understanding how the system is operating. Exactly which combination of properties needs to be plotted will depend, in part, on the directions in which the nonazeotropic mixture vapor compression cycle evolves. Thus the cycle and the refrigerant charts will tend to evolve together. The enthalpy/composition diagram, borrowed from the absorption refrigeration field, has obvious usefulness. However, all the charts can quickly become so complex due to the number of variables that selection of which families of curves to include and which to omit remains a continuing challenge. Ultimately, a linkage between the equation of state software and graphics software could be developed so that any desired chart of any input composition could be generated directly.

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APPENDIX

Morrison's equation of state has been empirically evaluated for two nonazeotropic refrigerant mixtures, R 13B1/R 152a and R 114/R 22. It is felt, however, that it is probably valid for any pair in the halogen family. For the sake of completeness of the example in this paper, the following empirical data are given:

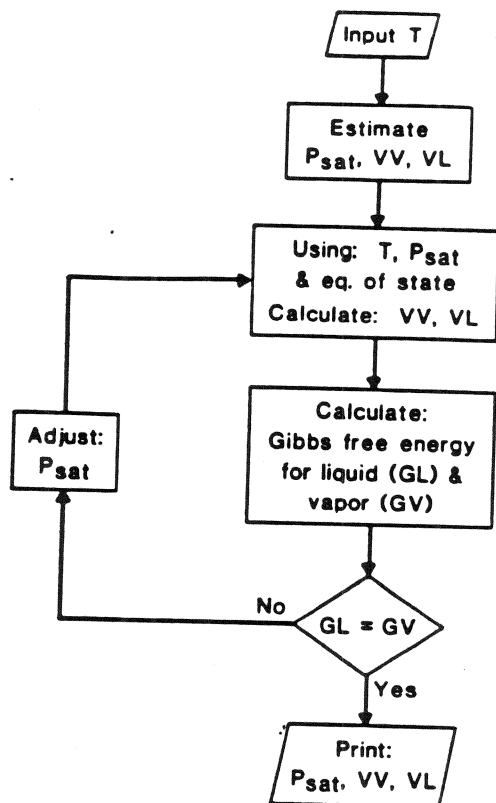### Pure Components Constants

R 13B1	R 152a
$a_I(0) = 25.4145$	$a_{II}(0) = 27.39273$
$a_I(1) = -0.063368$	$a_{II}(1) = -0.0594212$
$a_I(2) = 4.140051 \cdot 10^{-5}$	$a_{II}(2) = 3.317696\ E\text{-}5$
$b_I(0) = 0.1353977$	$b_{II}(0) = 0.1239878$
$b_I(1) = -1.50409 \cdot 10^{-4}$	$b_{II}(1) = -1.445514\ E\text{-}4$
$b_I(2) = -1.354434 \cdot 10^{-7}$	$b_{II}(2) = -1.902238\ E\text{-}8$
$c_{p,I}(0) = 0.0199537$	$c_{p,II}(0) = 0.02228$
$c_{p,I}(1) = 2.16394 \cdot 10^{-4}$	$c_{p,II}(1) = 1.54009 \cdot 10^{-4}$
$c_{p,I}(2) = 1.7024 \cdot 10^{-7}$	$c_{p,II}(2) = 3.06670 \cdot 10^{-9}$

R 13B1/R 152a Mixture Constants

$$d = 0.1466$$
$$c = -2.241 \cdot 10^{-4}$$

Figure 1. Flow chart for calculating single
component properties

GL – Gibbs free energy of liquid
FV – Gibbs free energy of vapor
VL – Spec. volume of liquid
VV – Spec. volume of vapor
P_{sat} – Sat. pressure
T – temperature

Figure 2. Flow chart for calculating bubble
line temperature of mixture
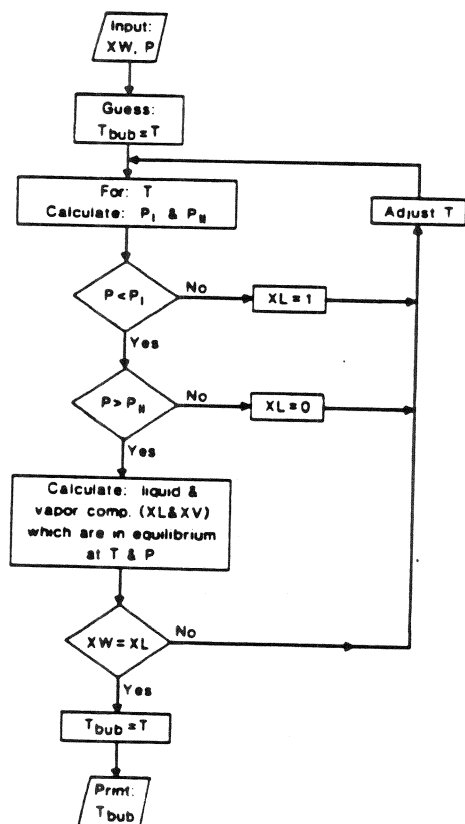
P_I – Sat. pressure of more volatile
component at temperature T
P_{II} – Sat. pressure of less volatile
component at temperature T
XL – Composition of liquid being
in equilibrium with vapor at
temperature T and pressure P
XV – Composition of vapor being
in equilibrium with liquid at
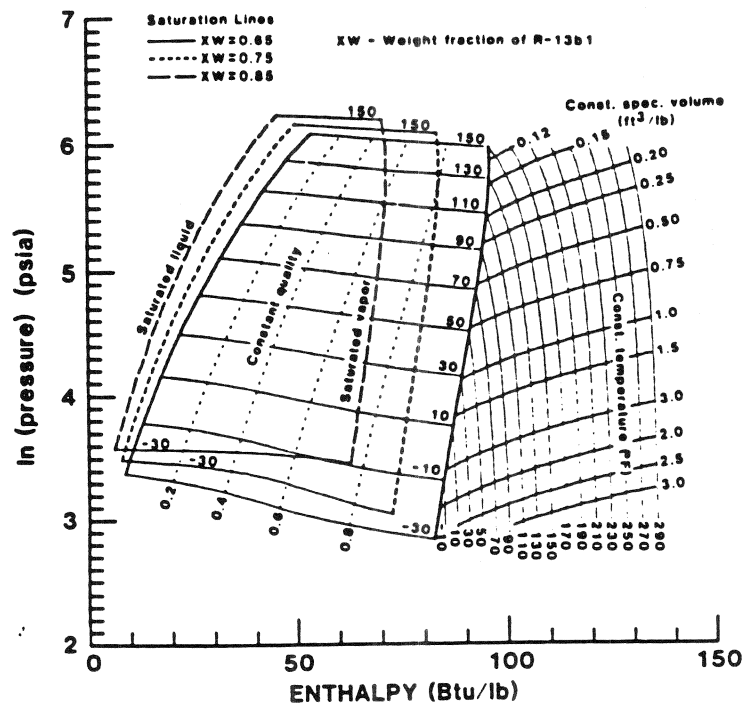temperature T and pressure P
XW – Mixture composition

Figure 5. *Pressure-enthalpy diagram for R 13B1/R 152a mixture (constant pressure lines, constant quality lines, and constant specific volume lines given for XW - 0.65)*
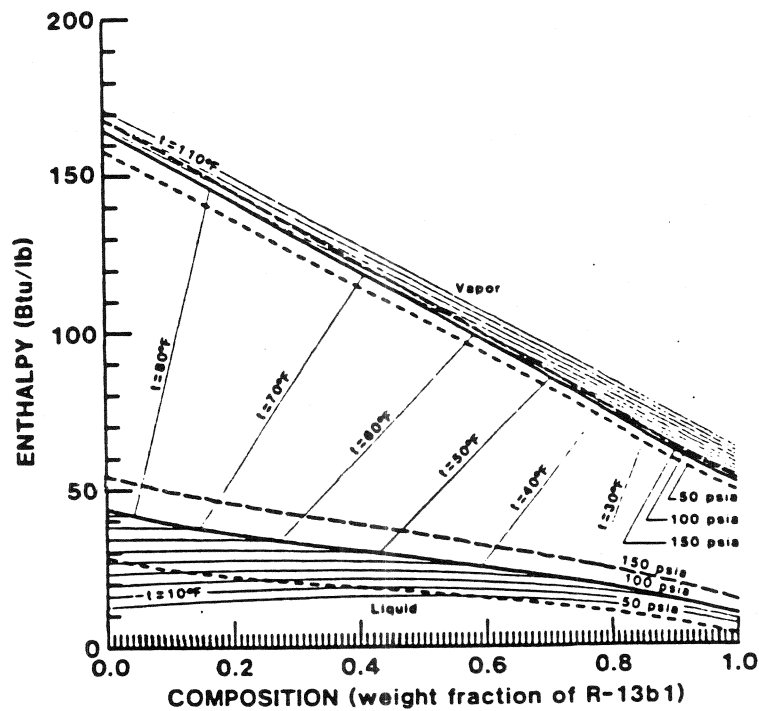

Figure 6. *Enthalpy-composition diagram for R 13B1/R 152a mixture (constant temperature lines given for pressure 100 psia)*