

Simulation of Isothermal and Adiabatic Leak Processes of Zeotropic Refrigerant Mixtures

M.S. Kim, Ph.D.

Associate Member ASHRAE

D.A. Didion, D.Eng., P.E.

Fellow ASHRAE

Nonflammable zeotropic mixtures of flammable and nonflammable refrigerants are possible alternative refrigerants for use in domestic heat pumps and air conditioners. Refrigerant leakage from such a system is of paramount concern since it is possible that a mixture composition will shift to a flammable range.

This paper presents simulations of leak processes of zeotropic refrigerant mixtures. Idealized cases of isothermal and adiabatic leak processes are considered in this study as representations of slow and fast leaks, respectively. Results of simulations are presented for a selected composition of binary and ternary refrigerant mixtures; R-32/134a and R-32/125/134a. Mass fraction changes of the mixtures are presented with respect to the percentage leak of the original charge. In the isothermal leak process, the fraction of the more volatile refrigerant in both vapor and liquid phases decreases for either a vapor or a liquid leak. The mass fraction changes at a low initial temperature are greater than those at a high initial temperature. During the adiabatic leak process, the vapor mass fraction of the more volatile component increases, while the liquid mass fraction of that component decreases for both vapor and liquid leak processes.

INTRODUCTION

Researchers have found only a limited number of alternative refrigerants to CFCs and HCFCs which meet the essential characteristics for heat pump and air conditioning applications. They have concentrated on developing safe, chlorine-free, single component fluids with similar vapor pressures to those of the refrigerants which are to be replaced. Successful examples of their research are the development of HFC-134a as an alternative to CFC-12 and HCFC-123 as an alternative to CFC-11. However, the search for an alternative refrigerant to HCFC-22 and R-502 has been far more difficult. No safe (e.g. non-flammable), single component fluid is known to have adequately close performance characteristics to be adopted as a substitute. Therefore, manufacturers are considering mixtures of two or more refrigerants to obtain adequately close properties, thereby avoiding having to alter component sizes of their product lines to adjust to refrigerants with different properties.

When mixing fluids it occasionally happens that azeotropes form. These mixtures remain at a constant temperature and composition throughout boiling or condensation; consequently, they are not different from single component refrigerants for all practical purposes. The more common occurrence is the formation of zeotropic (or non-azeotropic) mixtures that have temperature and composition changes during evaporation or condensation processes. There are potential advantages to using zeotropes, such as increased cycle performance, capacity control, and a wide choice of desired properties. However, there are also possible disadvantages to using zeotropic mixtures, including system design changes, difficulty in charging and servicing, and composition changes during a leak (Didion 1990).

Min Soo Kim is an assistant professor at the Department of Mechanical Engineering, Seoul National University, Korea. Dr. Kim was a visiting researcher and **David A. Didion** is the leader of the Thermal Machinery Group, Building Environment Division of the Building and Fire Research Laboratory at the National Institute of Standards and Technology, Gaithersburg, Maryland.

There is an ever dwindling pool of available fluids due to environmental restrictions, giving new incentives for refrigerant mixture development. Hydrocarbons and flammable hydrofluorocarbons (HFC's), which had previously been discounted for safety reasons, now offer an expansion of the candidate list if they are mixed with nonflammable HFC's. It is, therefore, important to be able to predict the composition change of zeotropic mixtures under all leak conditions, even uncontrolled leak conditions. Recent studies relating to the leak process of refrigerant mixtures have been done with an industrial heat pump (Blaise 1988) and an automotive air conditioning system (Kruse 1988). Also, leak experiments of specific mixtures have been compared with computer simulations by Shiflett et al. (1992), and Kruse and Rinne (1992), but a generic model as discussed herein is not known to have been presented in the open literature.

In this paper, leak scenarios related with zeotropic mixtures are discussed. The scope of this study includes a prediction of the composition changes of the zeotropic mixtures in both isothermal and adiabatic leak processes for both vapor and liquid leak cases. The isothermal leak process represents an ideal case of a very slow leak, and the adiabatic leak process represents an ideal case of a very fast leak from a heat pump system or a refrigerant storage cylinder. Two refrigerant mixtures proposed as alternatives to R-22, namely, R-32/134a (30/70) and R-32/125/134a (30/10/60) have been chosen for presentation of sample calculations in this study (Domanski 1993). (Numbers in parentheses refer to composition in mass percentage as presented in ASHRAE Standard 34 (ASHRAE 1992)).

MODELING & SIMULATION

Schematic diagram of the modeled system is shown in Figure 1(a) for a vapor leak, and (b) for a liquid leak. The system is composed of a constant volume cylinder with a small hole through which the refrigerant charge escapes as either a vapor or liquid. The zeotropic refrigerant mixture inside the cylinder is assumed to be in a state of vapor-liquid equilibrium, thus the vapor composition is different from the liquid composition. The leak process is also assumed to be either isothermal or adiabatic, which represents a very slow or fast leak process, respectively. In the isothermal leak process, the temperature of the system is kept constant and heat transfer through the walls supplies the energy required for the vaporization process. In the adiabatic leak process, the system is assumed to be insulated, so that no heat is transferred through the walls. Therefore, the

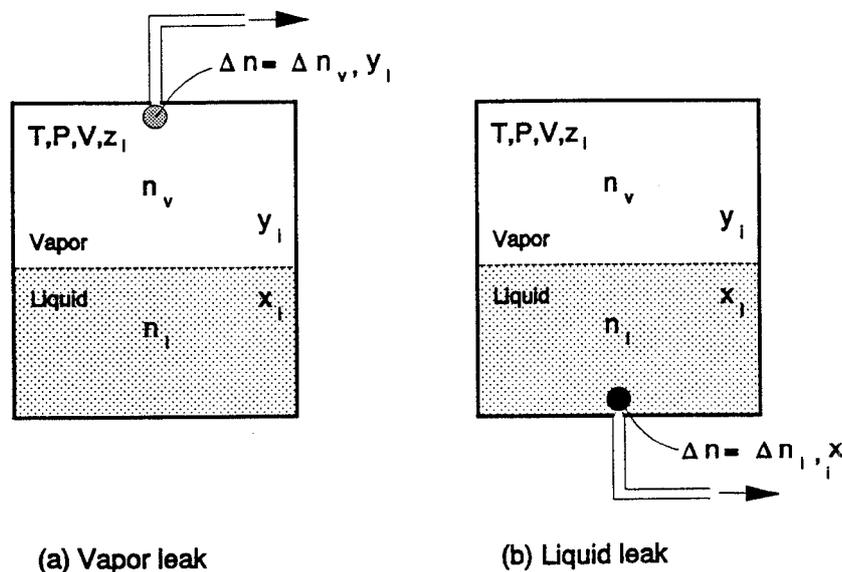


Figure 1. Schematic diagram of vapor and liquid leak models.

interior fluid temperature decreases because the energy needed for the vaporization process is taken from the refrigerant remaining in the cylinder. An additional assumption is that the escaping vapor has the same composition as the vapor inside the cylinder during the vapor leak. Similarly, for the liquid leak process, the composition of escaping liquid is assumed to have the same composition as that of the liquid inside the cylinder. The simulation of the leak processes proceeds as a quasi-steady state process with finite time increments. During alternate steps, the simulation proceeds with (1) the mass escaping and, (2) readjustment of the internal fluid to thermodynamic equilibrium accounting for the previous loss of mass. When performing the simulations, the properties of refrigerants and refrigerant mixtures are calculated using the REFPROP program (Gallagher 1991).

Analysis of leakage phenomena is more conveniently done if all specific properties are defined on a molar basis. The overall molar quality, \mathcal{Q} , is defined by the molar fraction in the vapor phase with respect to the total number of moles in the system, and is irrespective of any particular component. By definition, \mathcal{Q} is equal to 0 when the system is full of saturated liquid, and \mathcal{Q} is equal to 1 when the system is filled only with saturated vapor. The overall mole fraction of the i -th component in the cylinder, z_i , is the sum of the mole fraction of the component i in both liquid and vapor phases.

$$z_i = \frac{n_l + n_v}{n} \quad (1)$$

$$= x_i(1 - \mathcal{Q}) + y_i\mathcal{Q} \quad (2)$$

where x_i is the mole fraction of the i -th component in the liquid phase and y_i is the mole fraction of the i -th component in vapor phase. Subscripts l and v refer to the liquid and vapor phases.

Consider first a vapor leak where a small amount of vapor, Δn_v of mole fraction y_i , escapes from the cylinder. Since only vapor is leaking, $\Delta n_v = \Delta n$, the total number of moles released. The new quasi-steady state of the remaining fluid has an overall mole fraction of the i -th component, z'_i (prime refers to the property after a leak);

$$z'_i = \frac{x_i n_l + y_i (n_v - \Delta n_v)}{n - \Delta n} \quad (3)$$

By defining a parameter ε as a fraction of the escaping moles with respect to the total, and using the overall molar quality, Equation (3) can be rearranged as

$$z'_i = \frac{x_i(1 - \mathcal{Q}) + y_i\mathcal{Q}\left(1 - \frac{\varepsilon}{\mathcal{Q}}\right)}{1 - \varepsilon} \quad (4)$$

Similarly the molar volume after a leak is expressed as

$$v' = \frac{V}{n - \Delta n} = \frac{v}{1 - \varepsilon} \quad (5)$$

Finally the change of the overall mole fraction of the i -th component after a vapor leak is determined by subtracting Equation (2) from (4):

$$\Delta z_i = z'_i - z_i = -\varepsilon(1 - \mathcal{Q})(y_i - x_i) \quad (6)$$

For the case of a liquid leak, a small amount of liquid, Δn_l of component i , escapes and because this is the only phase leaking from the system, $\Delta n_l = \Delta n$. The overall mole fraction of the i -th component in the system after a liquid leak is represented by the following Equation:

$$z'_i = \frac{x_i(n_l - \Delta n_l) + y_i n_v}{n - \Delta n} \quad (7)$$

By introducing the parameter ε , and the overall molar quality Q , Equation (7) can be rearranged as

$$z'_i = \frac{x_i(1 - Q) \left(1 - \frac{\varepsilon}{1 - Q} \right) + y_i Q}{1 - \varepsilon} \quad (8)$$

The molar volume after a liquid leak in this case is represented as in Equation (5). The change of the overall mole fraction of component i after a small liquid leak is derived by subtracting Equation (2) from (8), which is shown in Equation (9).

$$\Delta z_i = \varepsilon Q (y_i - x_i) \quad (9)$$

In addition to calculating the overall mole fraction change and the molar volume change in the vapor or liquid leak processes as above described, the pressure inside the cylinder during the leak process should also be determined. In the isothermal leak process, the temperature inside the cylinder remains constant throughout the process. Unlike the isothermal case, the temperature decreases during the adiabatic leak process because the energy required for the vaporization is taken from the refrigerant inside the cylinder. The internal energy in the cylinder after a leak in the adiabatic leak process can be determined from the first law of thermodynamics.

$$u' = \frac{u - \varepsilon h_e}{1 - \varepsilon} \quad (10)$$

In Equation (10), u is the internal energy in the system and u' refers to the internal energy after a leak; h_e represents the enthalpy of the escaping refrigerant. It is assumed that no heat or work are transferred through the system boundary and both potential and kinetic energy are negligible.

The calculation procedure in the isothermal leak process is as follows: The molar volumes of vapor and liquid phases in the saturation state are first calculated with given initial conditions. The overall mole fraction and the molar volume in the system after a small vapor or liquid leak are calculated with Equations (4) and (5) for a vapor leak, or (8) and (5) for a liquid leak at a given temperature. The system pressure at given overall mole fraction should be determined so that the calculated molar volume at a new equilibrium state is equal to that given by Equation (5). During the adiabatic leak process, the temperature decreases and the internal energy in the system after a leak must satisfy Equation (10). Generally, internal energy is a function of temperature, pressure and overall mole fraction, therefore, at the new overall mole fraction given by Equation (4) or (8), both the temperature and the pressure should be changed to correspond to the new internal energy after a leak to satisfy Equation (10). At the same time, calculated molar volume should satisfy Equation (5). As an initial state, a saturated liquid state with a quality of zero is selected for either isothermal or adiabatic processes of a vapor or liquid

leak, because the case with an initial quality greater than zero undergoes less change during the leak. The final state in the isothermal leak process is chosen as the saturated vapor state. In the adiabatic leak process, the simulation is stopped when the pressure inside the cylinder is equal to the atmospheric pressure for a vapor leak. For an adiabatic liquid leak, the leak simulation stops when all the liquid has escaped.

A schematic diagram of pressure and composition changes during the isothermal vapor leak process is shown in Figure 2. At the initial state, the cylinder is assumed full of the saturated liquid of mole fraction x_i , thus $x_i = z_i$, the overall mole fraction. As shown in Figure 2, pressure, and both liquid and vapor mole fractions are interrelated during the isothermal leak process. Therefore, once temperature and pressure are given, liquid and vapor mole fractions are determined from the equation of state. As the vapor leak progresses, the system pressure decreases and the overall mole fraction of the i -th component in the system changes according to Equation (4). The liquid and vapor mole fractions also vary along the bubble and the dew-point curves respectively, as shown in Figure 2. At the final state, all the liquid is evaporated and the system is full of saturated vapor, therefore the overall mole fraction z_f in the system is equal to y_f . Continued leakage from this point would result in pressure decrease and no further composition shift.

The diagram of the adiabatic vapor leak process is schematically shown in Figure 3. In the adiabatic leak process, the temperature decreases as the leak continues, therefore the vapor-liquid equilibrium at the decreased temperature should be used to describe the adiabatic leak process. Originally, the cylinder is filled with the saturated liquid of composition x_i at initial temperature and pressure. As the adiabatic vapor leak continues, both the system temperature and pressure decrease and satisfy Equations (5) and (10) at the overall mole fraction of the i -th component given by Equation (4). The overall mole fraction of the more volatile component, z_i , is slightly higher than x_i throughout the leak process. The liquid and vapor mole fractions in the cylinder change along the bubble and the dew-point curves at the decreased temperature and pressure determined above. The final compositions in the liquid and the vapor phases are marked as x_f and y_f in Figure 3.

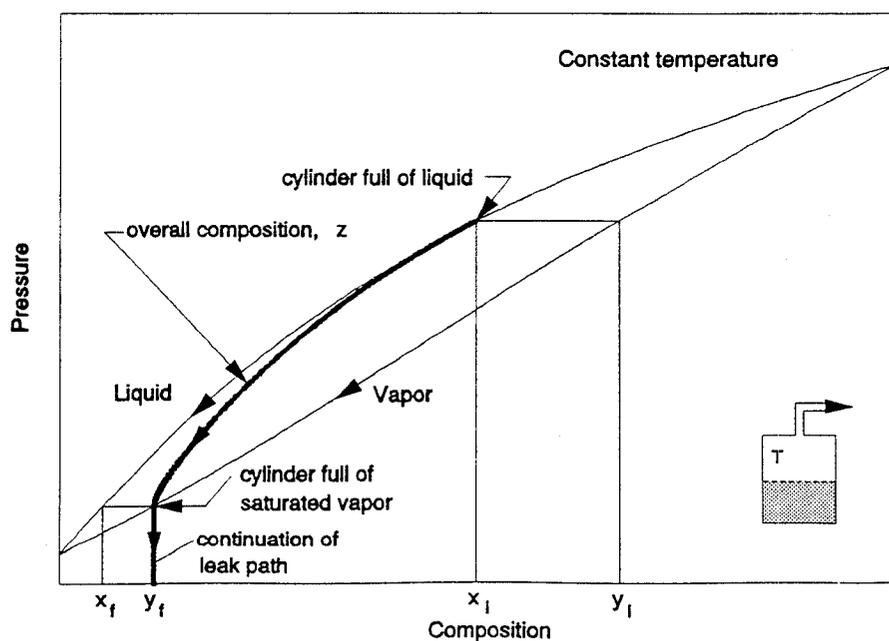


Figure 2. Schematic diagram of pressure and composition changes during an isothermal vapor leak process

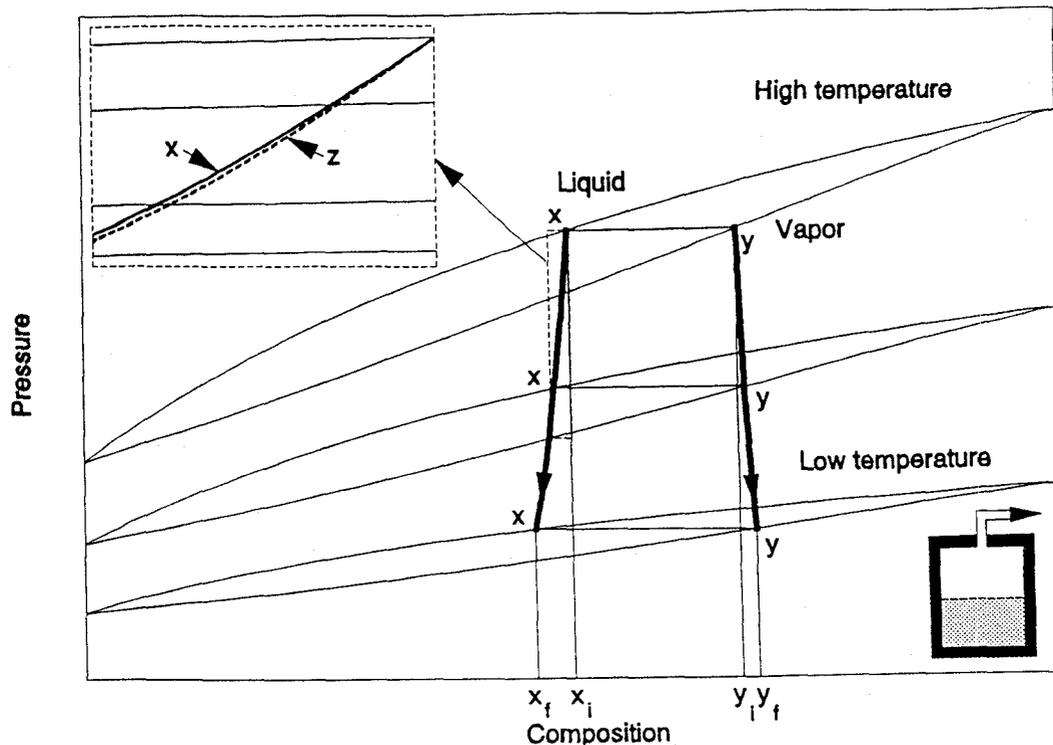


Figure 3. Schematic diagram of pressure and composition changes during an adiabatic vapor leak process

SIMULATION RESULTS OF THE ISOTHERMAL LEAK PROCESS

Isothermal Leak of R-32/134a (30/70) Mixture

The mass fraction change during the isothermal vapor leak process for the R-32/134a mixture is shown in Figure 4 as a function of mass percentage of the refrigerant leaked out of the system. The liquid, vapor, and overall mole fractions, x , y , and z , obtained by the simulation are converted to mass fractions X , Y , and Z , and shown in this figure. The vapor, liquid, and overall mass fractions of the more volatile component (R-32 in this case) decrease during the isothermal vapor leak because the mass fraction of R-32 in the leaking vapor phase is greater than that in the liquid phase. Simultaneously, the mass fractions of the less volatile component (R-134a) in both vapor and liquid phases increase during the isothermal vapor leak. Since R-32 is the flammable component in this zeotropic refrigerant mixture (Richard 1992), it is important that the leaking vapor and the remaining refrigerant mixture in the system maintain a nonflammable composition during the vapor leak. It should be noted that the initial vapor during the isothermal vapor leak has the highest percentage of R-32. The simulation is stopped when the final overall mass fraction in the cylinder, Z_i , is that of the saturated vapor phase, Y_i . The vertical line in Figure 4 represents the final state with only saturated vapor in the cylinder.

In the isothermal leak process of the liquid phase for the R-32/134a mixture, the mass fraction changes are shown in Figure 5. Both the vapor and liquid mass fractions of the more volatile component (Y_{R-32} and X_{R-32}) decrease in this process because their compositions in the vapor-liquid equilibrium state decrease as the pressure decreases. However, the overall mole fraction (z_i) of the more volatile refrigerant increases during the isothermal liquid leak according to Equation (9) because the liquid mole fraction (x_i) of this component is less than the vapor mole fraction (y_i).

The pressure and the overall mass fraction changes during the isothermal vapor and liquid leaks of the R-32/134a mixture are shown in Figure 6. The bubble and dew point

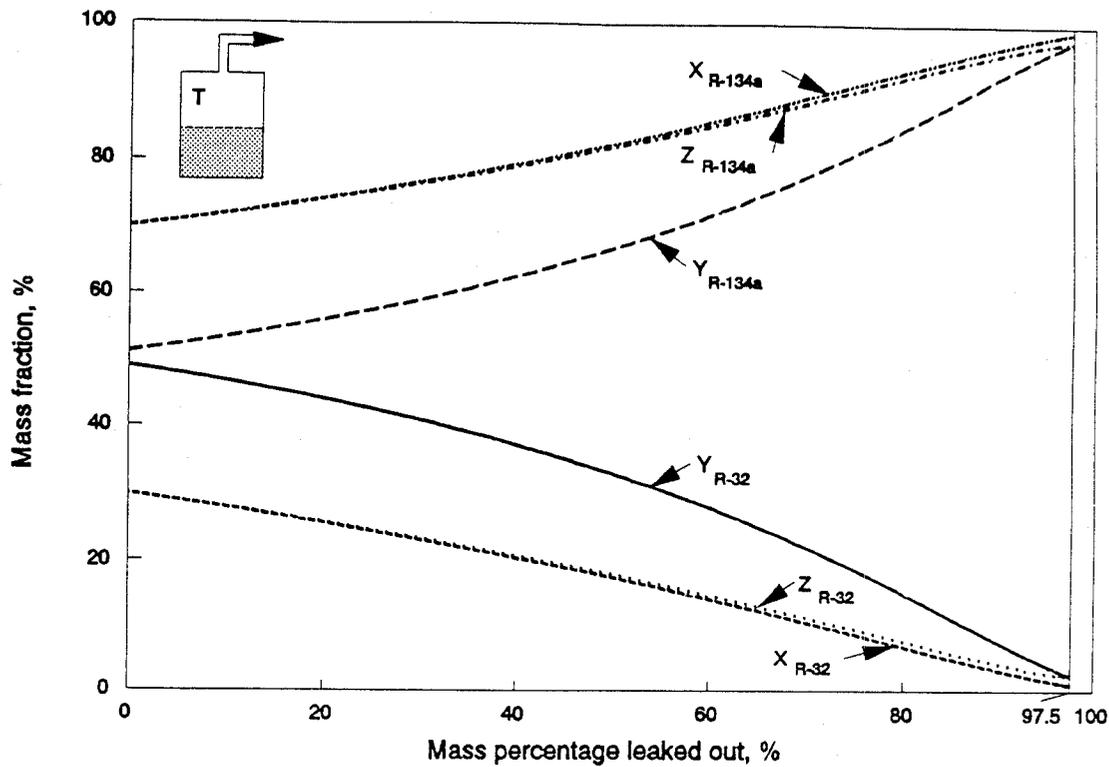


Figure 4. Mass fraction change during the isothermal vapor leak of the R-32/134a mixture as a function of mass percentage leaked out

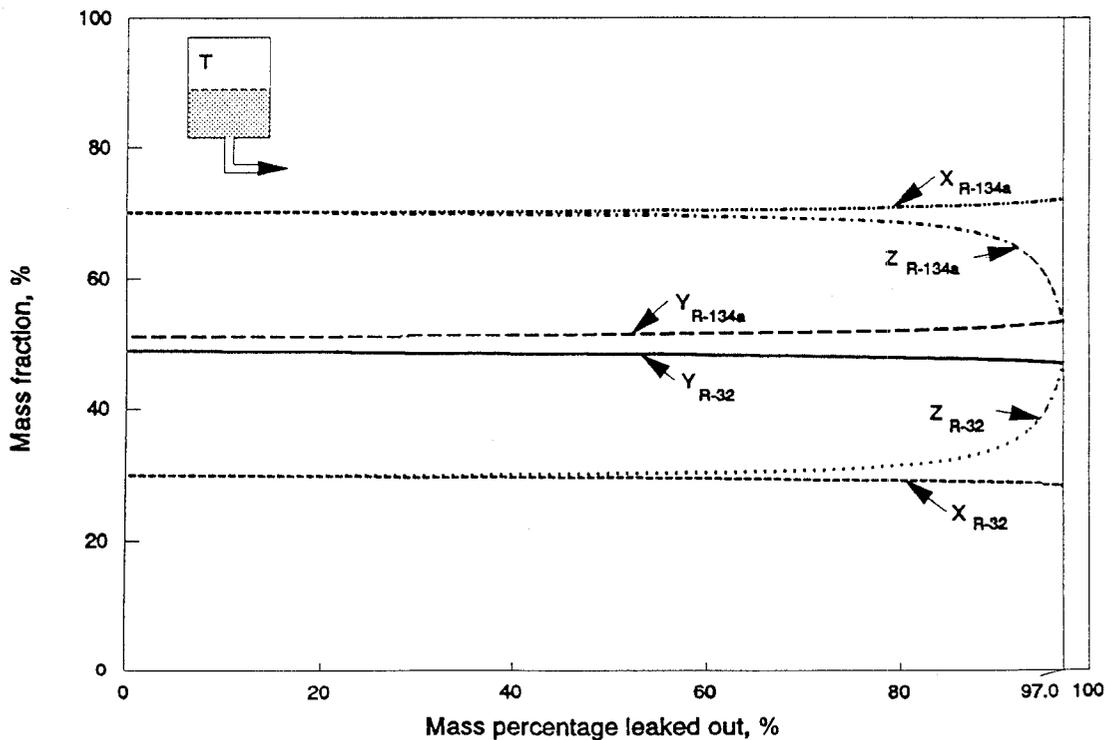


Figure 5. Mass fraction change during the isothermal liquid leak of the R-32/134a mixture as a function of mass percentage leaked out

curves at different temperatures are also shown. In Figure 6, V and L represent the overall mass fraction changes during the vapor and liquid leaks, and i and f indicate initial and final states of the leak process, respectively. As the vapor or liquid leak continues isothermally, the system pressure decreases and the vapor and liquid mass fraction of the more volatile component, R-32, decrease. However, the overall mass fraction of the more volatile component in the system decreases during the vapor leak (curve V in Figure 6) and increases during the liquid leak (curve L in Figure 6). As the leak occurs at a lower temperature, the overall mass fraction change is greater than that at a higher temperature. For the case of vapor leak, the escaping vapor from the cylinder must first be evaporated from the liquid phase. Therefore, the composition change is greater due to the preferential evaporation of the more volatile component from the liquid phase. Accordingly, during a liquid leak, only a small fraction of liquid must be vaporized to replace the volume of the escaping liquid and there is no drastic change in the system. Therefore, the pressure decreases slightly and the mass fraction changes in both vapor and liquid phases are also small. Note that even though the overall mass fraction of the flammable component, R-32, in the cylinder increases, the mass fraction of R-32 in the leaking liquid decreases, that is, the escaping liquid contains a lower percentage of R-32 than the initial refrigerant mixture as the liquid phase leaks (see also Figure 5).

The composition change described by Equations (4) and (8) for either a vapor or liquid leak is affected by the selection of the size of ϵ . It is found that the affect of the choice on the calculations for the final pressure and mass fractions is small for choices below 0.01. In this study results are presented for a choice of 0.001 for both the vapor and liquid leak processes, which is a reasonable compromise between computer run time and precision of the results.

Isothermal Leak of R-32/125/134a (30/10/60) Mixture

For the R-32/125/134a mixture, the mass fraction change during the isothermal vapor leak is shown in Figure 7 with respect to the leaked mass percentage of the original charge. The vapor and liquid mass fractions of the most volatile refrigerant (R-32) decrease during the vapor leak. This is because the vapor and liquid mass fractions of the most volatile component in the vapor-liquid equilibrium state decrease as the pressure lowers. Consequently, the mass fractions of the least volatile component (R-134a) in both vapor and liquid phases increase during the vapor leak. In general, the mass fraction of a component of intermediate volatility in a ternary mixture can be increased or decreased as the pressure itself decreases due to the leak, and depending on the thermodynamic vapor-liquid equilibrium state of the mixture. For the intermediate volatile component (R-125), the mass fractions in both vapor and liquid phases decrease as the leak continues. Considering that R-32 is flammable, and that neither R-125 nor R-134a are flammable (Richard 1992), it is desirable that the refrigerant mixture in the system remains in a nonflammable region as the vapor leaks out. The overall mass fraction of R-32 in the cylinder decreases because that of the leaking vapor is greater than the mass fraction of R-32 in the cylinder. Initially the overall mass fraction of each component is chosen to be equal to the liquid mass fraction, and the leak process is simulated until the final composition is equal to that of the vapor phase, when the cylinder is filled only with saturated vapor (no liquid droplets). The mass fraction changes during the isothermal vapor leak of the R-32/125/134a mixture at different temperatures are shown in Figure 8. In this figure, the points marked with v_i and v_f represent the initial and the final mass fractions of the vapor phase, respectively; l_i and l_f indicate those of the liquid phase. The overall mass fraction change is also shown in this figure, as the marked curve connecting the point l_i to v_f . As the temperature is lowered, the vapor, liquid, and overall mass fraction changes are greater.

The mass fraction change during the liquid leak of the R-32/125/134a mixture is shown in Figure 9 as a function of mass percentage leaked out. The vapor and liquid

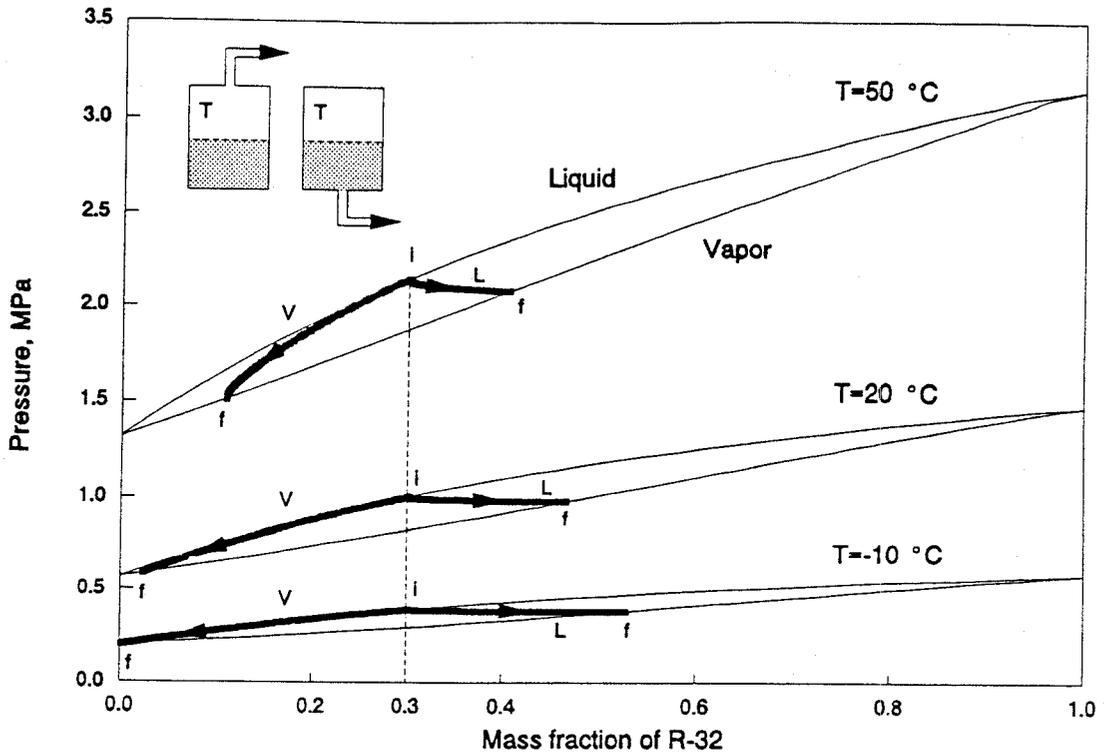


Figure 6. Pressure and overall mass fraction changes during the isothermal vapor and liquid leaks of the R-32/134a mixture at different temperatures (V and L represent vapor and liquid leak processes, and i and f represent initial and final states.)

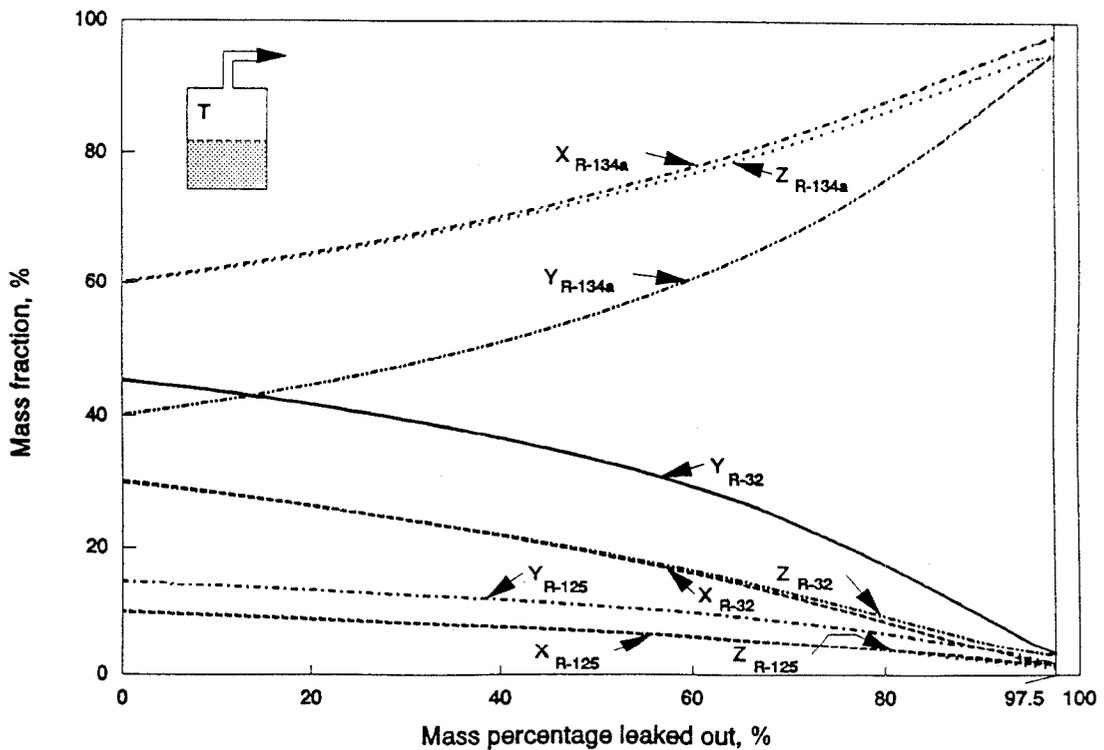


Figure 7. Mass fraction change during the isothermal vapor leak of the R-32/125/134a mixture as a function of mass percentage leaked out

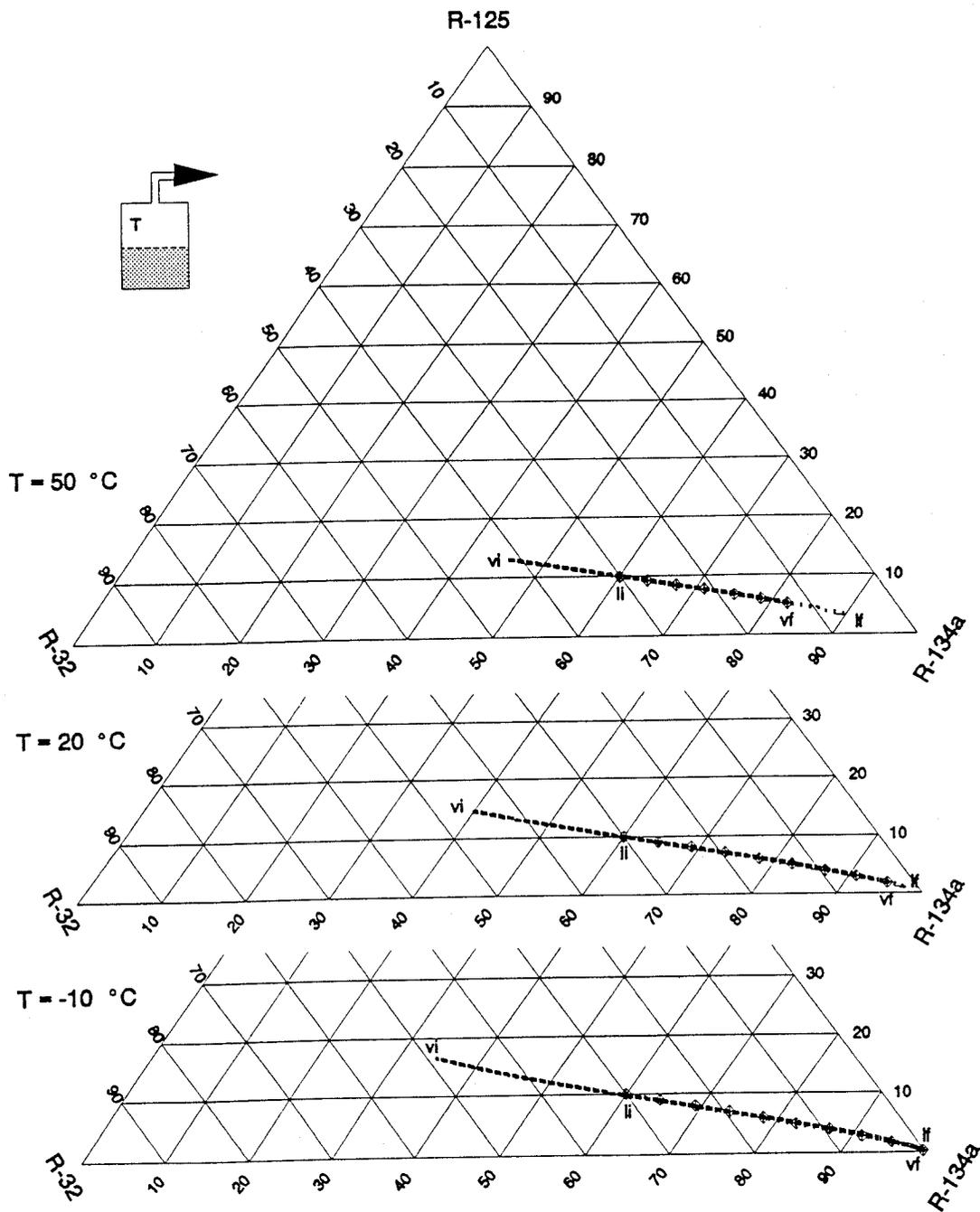


Figure 8. Mass fraction change during the isothermal vapor leak of the R-32/125/134a mixture at several temperatures

(*v* and *l* represent vapor and liquid phases, and *i* and *f* represent initial and final states.)

mass fractions of the most volatile refrigerant in the cylinder decrease slightly because of the pressure decrease caused by the leak. The mass fractions in the leaking liquid are represented by X_i . The overall mass fraction of the most volatile refrigerant (Z_{R-32}) increases because the mass fraction of this component in the escaping liquid is less than that in the vapor phase. As the liquid leak progresses, there is a higher percentage of R-32 in the remaining refrigerant mixture compared to the initial mixture.

The mass fraction change during the liquid leak of the R-32/125/134a mixture is shown in Figure 10 on a triangular composition diagram. The mass fraction change in the vapor phase (curve from v_i to v_f) and that in the liquid phase (curve from l_i to l_f) are also marked in this figure. As the liquid phase leaks from the cylinder, the pressure decreases, and the vapor and liquid mass fractions of the most volatile refrigerant (R-32) decrease. However, the overall mass fraction of the most volatile component in the sys-

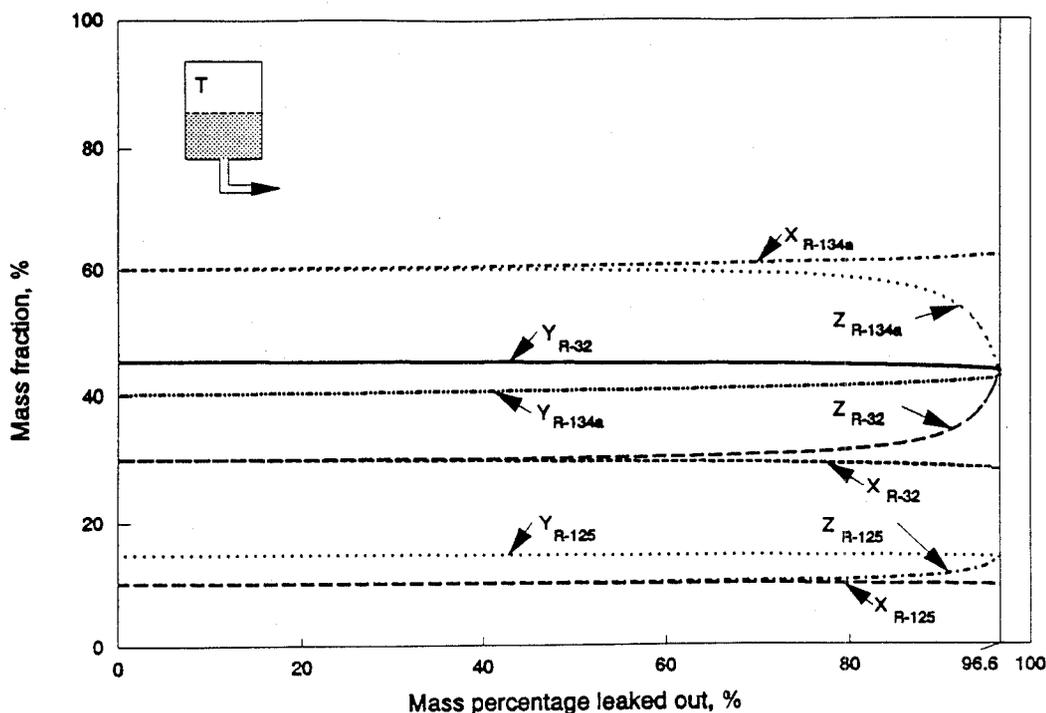


Figure 9. Mass fraction change during the isothermal liquid leak of the R-32/125/134a mixture as a function of mass percentage leaked out

tem increases during the liquid leak, as displayed by the marked curve connecting the points from l_i (initial overall mass fraction) to v_f (final overall mass fraction) in Figure 10. When the leak occurs at a lower temperature, the overall mass fraction changes and changes in the vapor and liquid phases are greater.

SIMULATION RESULTS OF THE ADIABATIC LEAK PROCESS

Adiabatic Leak of R-32/134a (30/70) Mixture

The mass fraction changes of each component in the vapor and liquid phases and the overall mass fraction change are shown in Figure 11 as a function of the leaked mass percentage during the adiabatic vapor leak process of the R-32/134a mixture. The liquid mass fraction of the more volatile component (R-32) decreases while the vapor mass fraction of this component increases. The overall mass fraction of R-32, Z_{R-32} , lies nearly on top of X_{R-32} and Z_{R-134a} is slightly lower than X_{R-134a} . The adiabatic vapor leak path is shown on the pressure and mass fraction diagram in Figure 12. This figure shows the changes in vapor and liquid phases, and the overall mass fraction change in the cylinder. Bubble and dew-point curves at four different temperatures are shown in order to indicate the mass fractions in the vapor and liquid phases, at those temperatures. As the vapor leaks adiabatically, the system pressure and temperature decrease, and it is noteworthy that the vapor mass fraction of the flammable component (R-32) increases. Figure 11 shows how the leak stops at 26.7% mass loss, because the system pressure decreases to the atmospheric pressure at the temperature of -41.1°C , as indicated in Figure 12.

During the adiabatic liquid leak process, the vapor, liquid, and overall mass fraction changes are shown in Figure 13. The vapor mass fraction of the more volatile component (R-32) increases in this process while the liquid mass fraction of this component experiences a negligible decrease. The overall mass fraction of the more volatile component increases according to Equation (9) because the liquid mole fraction of R-32 is less than the vapor mole fraction. The liquid leaks out until the leaked mass percentage

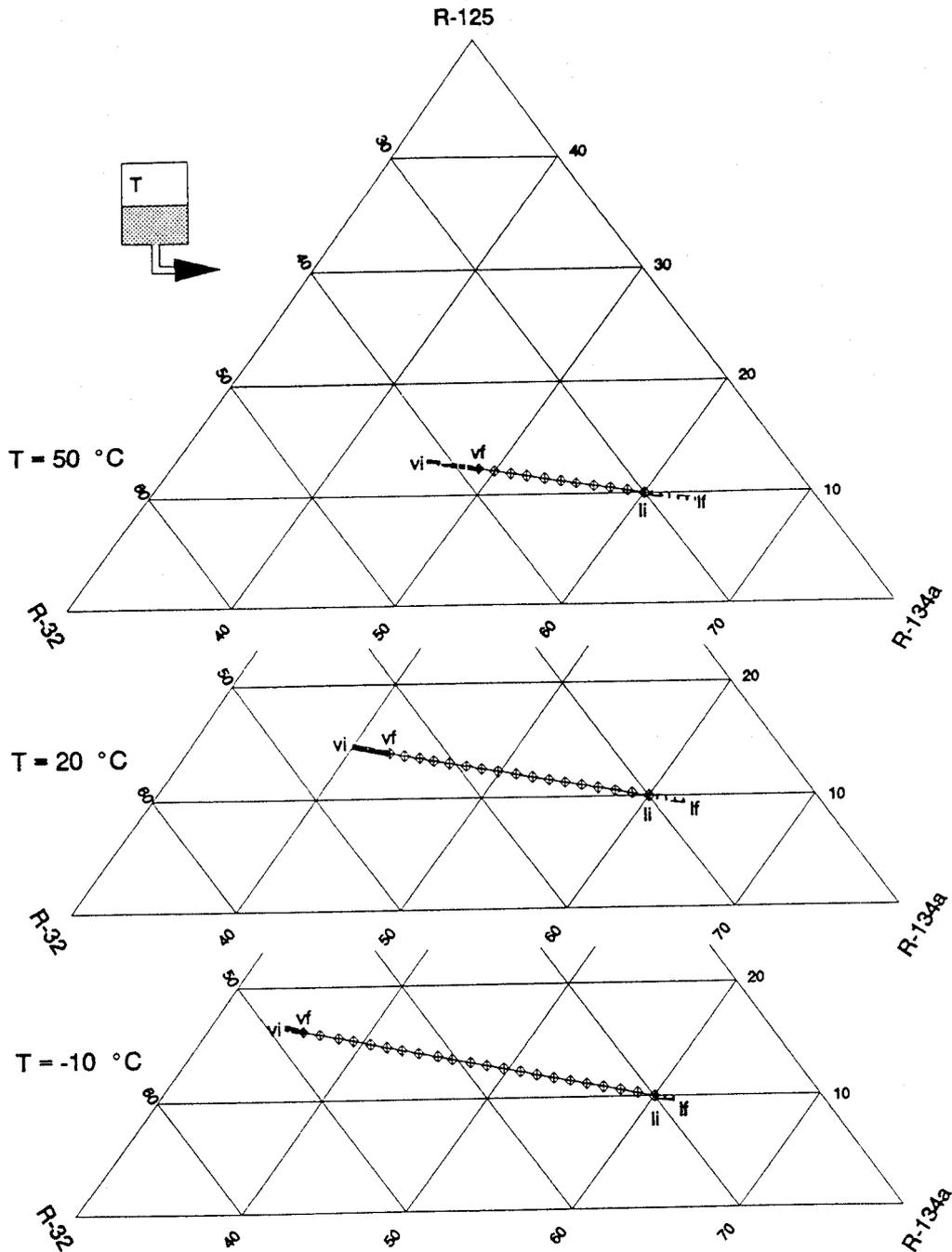


Figure 10. Mass fraction change during the isothermal liquid leak of the R-32/125/134a mixture at several temperatures

(*v* and *l* represent vapor and liquid phases, and *i* and *f* represent initial and final states.)

reaches 97.8% where the temperature drops from 20°C to 9.7°C at the pressure higher than the ambient pressure (see Figure 14). In this adiabatic liquid leak, the pressure and the mass fraction changes are shown in Figure 14. The bubble and dew-point curves at 3 different temperatures are shown and the vapor, liquid, and overall mass fraction (*Y*, *X*, and *Z*) changes are also displayed. As the liquid leaks adiabatically from the cylinder, the system pressure and temperature decrease and the vapor mass fraction of the more volatile component (R-32) increases slightly.

The pressure decreases and the temperature changes in the adiabatic vapor and liquid leaks are shown in Figure 15. For a vapor leak, the temperature in the cylinder decreases drastically because the evaporation energy is taken from the liquid phase.

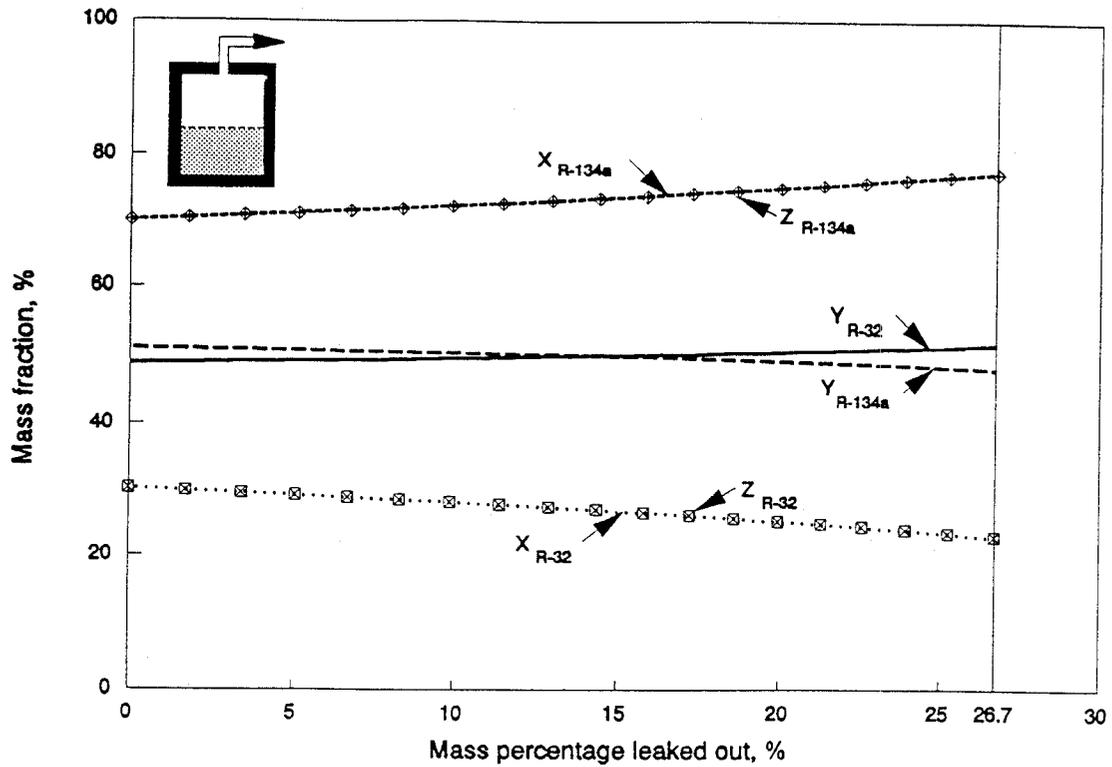


Figure 11. Mass fraction change during the adiabatic vapor leak of the R-32/134a mixture as a function of mass percentage leaked out

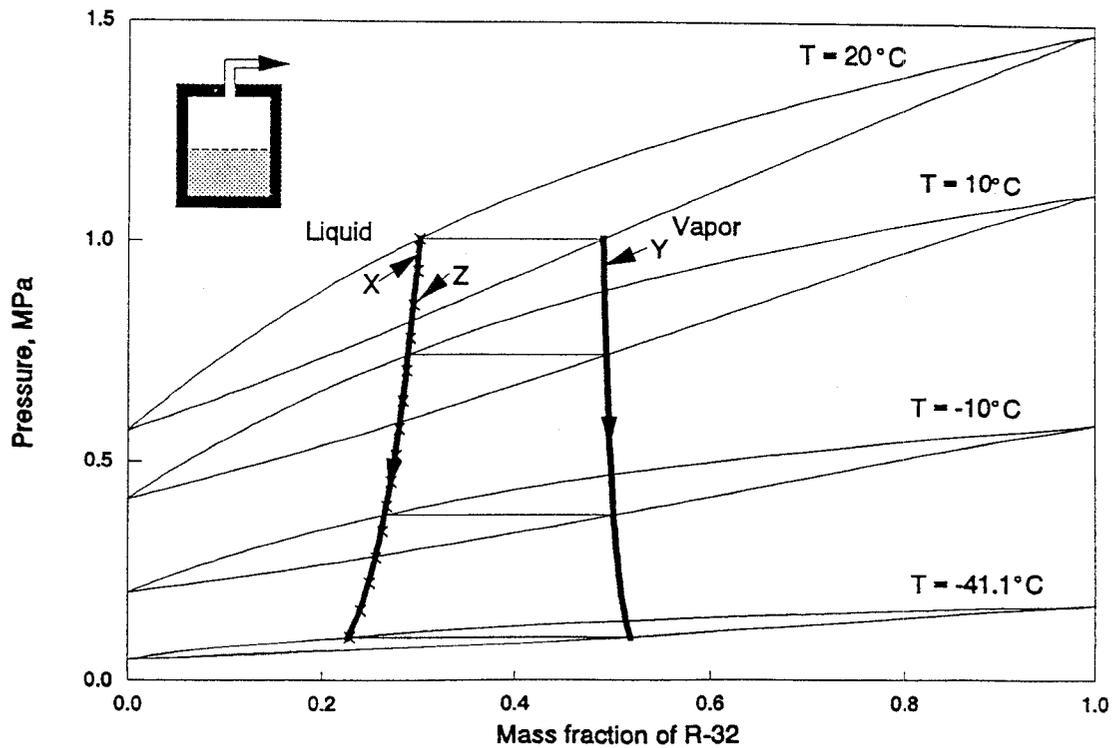


Figure 12. Pressure and mass fraction changes during the adiabatic vapor leak of the R-32/134a mixture

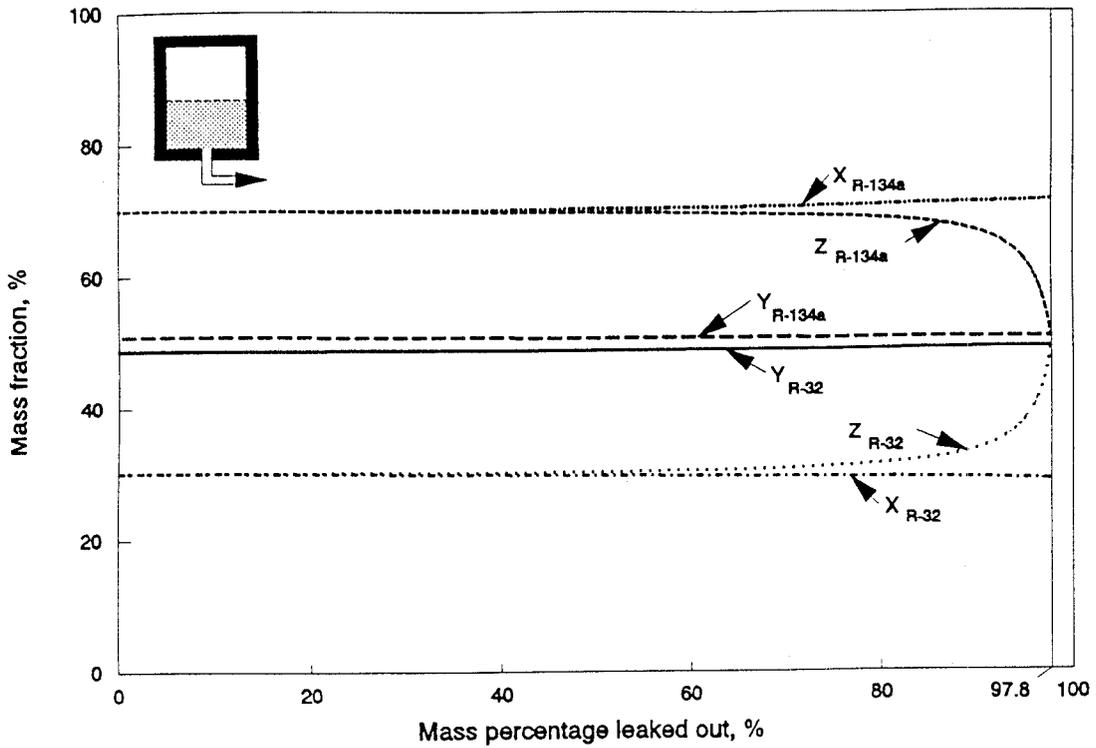


Figure 13. Mass fraction change during the adiabatic liquid leak of the R-32/134a mixture as a function of mass percentage leaked out

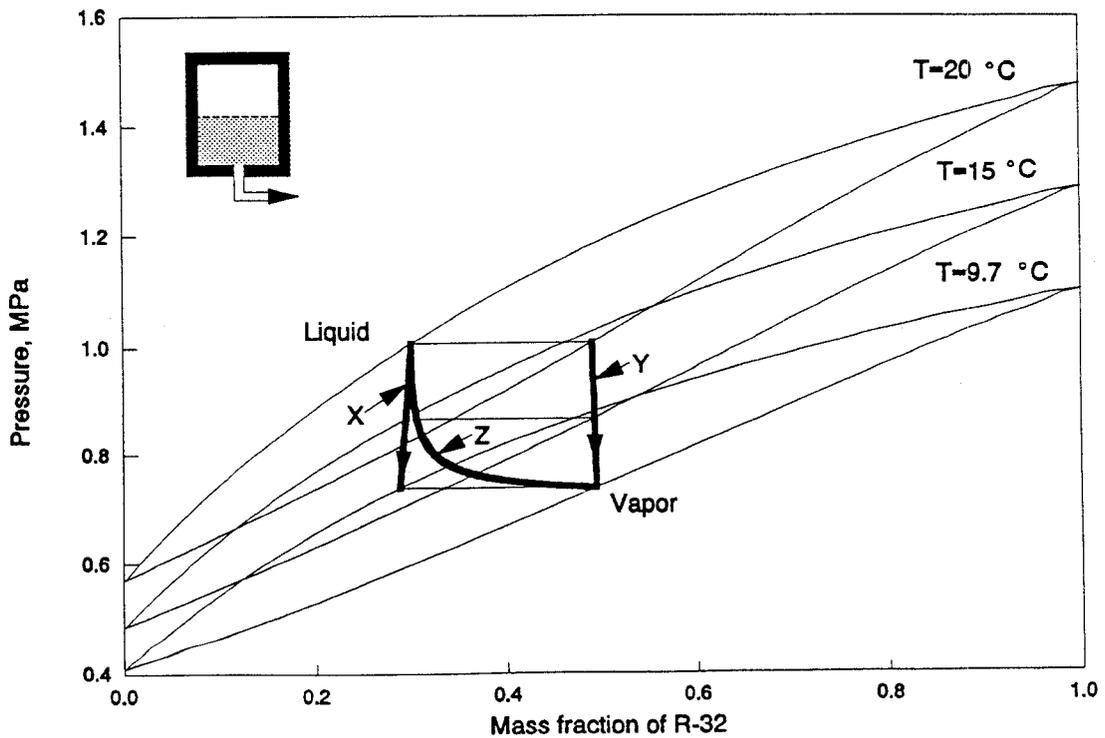


Figure 14. Pressure and mass fraction changes during the adiabatic liquid leak of the R-32/134a mixture

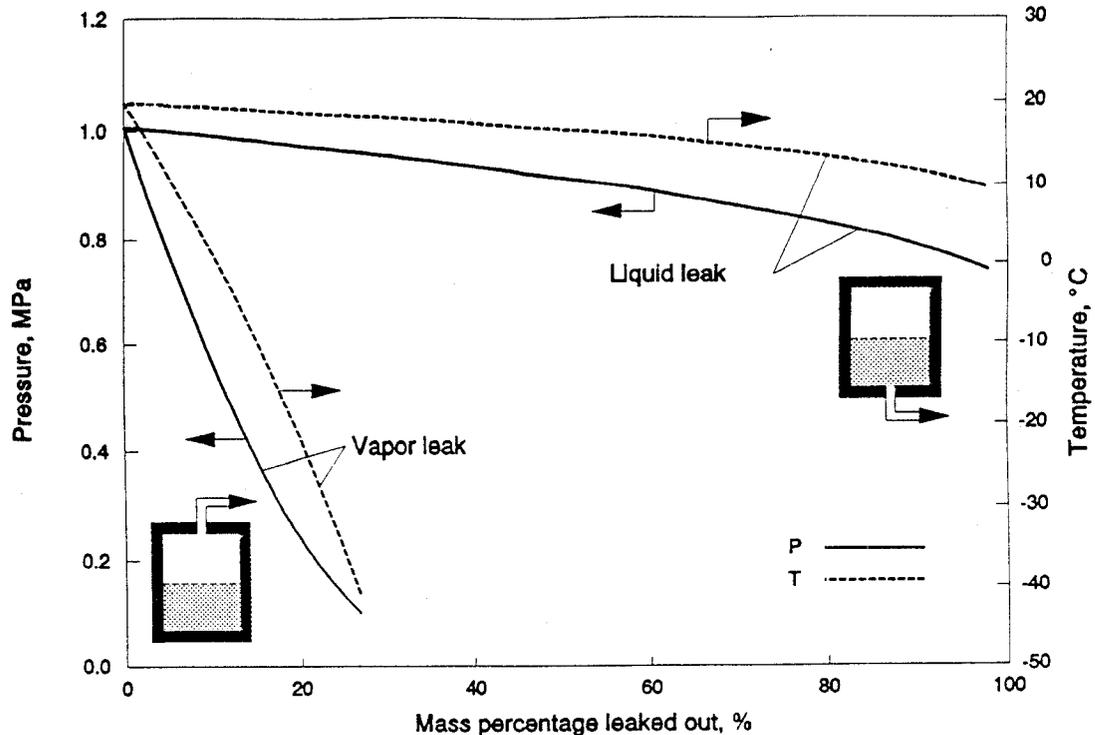


Figure 15. Pressure and temperature changes during the adiabatic vapor and liquid leaks of the R-32/134a mixture

The internal energy changes by Equation (10), and the corresponding saturation pressure decreases. Therefore, the evaporation is suppressed due to the temperature drop for the adiabatic vapor leak process, and the pressure decreases to the atmospheric pressure at which no further leak occurs. However, for a liquid leak, because very little liquid evaporates, due to the large volume difference between liquid and vapor phases, the temperature drops slightly and the pressure decreases until all the liquid escapes from the cylinder.

Adiabatic Leak of R-32/125/134a (30/10/60) Mixture

The mass fraction change during the adiabatic vapor leak of the R-32/125/134a mixture is shown in Figure 16 with respect to the mass percentage leaked out. The mass fractions of the most volatile refrigerant (R-32) and of the intermediate volatile component (R-125) in the vapor phase increase, while the vapor mass fraction of the least volatile component (R-134a) decreases during the vapor leak. However, the mass fractions of R-32 and R-125 in the liquid phase decrease and consequently the liquid mass fraction of R-134a increases. The mass fraction changes in both vapor and liquid phases depend on the vapor-liquid equilibrium state of the refrigerant mixture at a given pressure and temperature. It is important to note that the mass fraction of the flammable component in the leaking vapor, Y_{R-32} , increases slightly during the vapor leak. Initially the overall mass fraction, Z_i , is equal to the liquid mass fraction (cylinder full of liquid), X_i . During the whole leak process, the overall mass fraction shows negligible difference from the liquid mass fraction. This means most molecules in the cylinder exist in the liquid phase mainly because the evaporation is suppressed due to the temperature drop. The simulation is terminated when the pressure inside the cylinder is equal to the ambient pressure, at which point the leaked mass percentage is marked with a vertical line at 28.8% mass leak, as shown in Figure 16.

The mass fraction changes in the vapor and liquid phases in the adiabatic liquid leak of the R-32/125/134a mixture are shown in Figure 17 with respect to the mass percentage leaked out. The changes in liquid and vapor mass fractions of all components are negligible. For a liquid leak, because of the large volume difference between liquid and

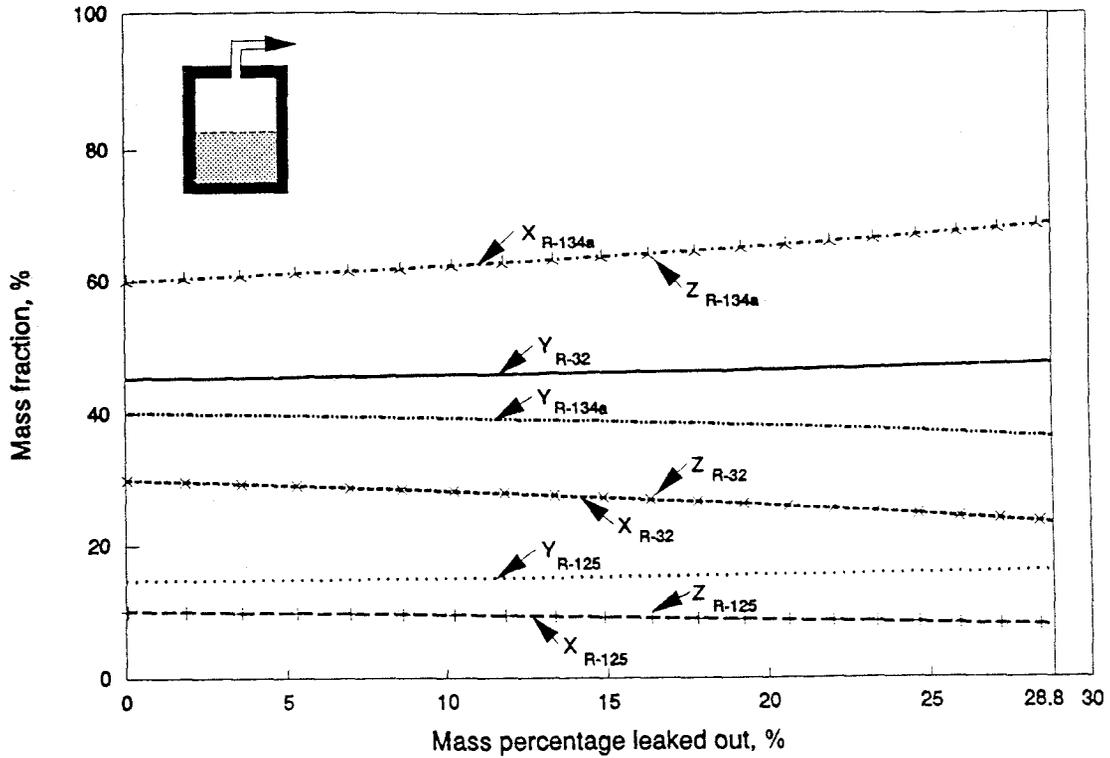


Figure 16. Mass fraction change during the adiabatic vapor leak of the R-32/125/134a mixture as a function of mass percentage leaked out

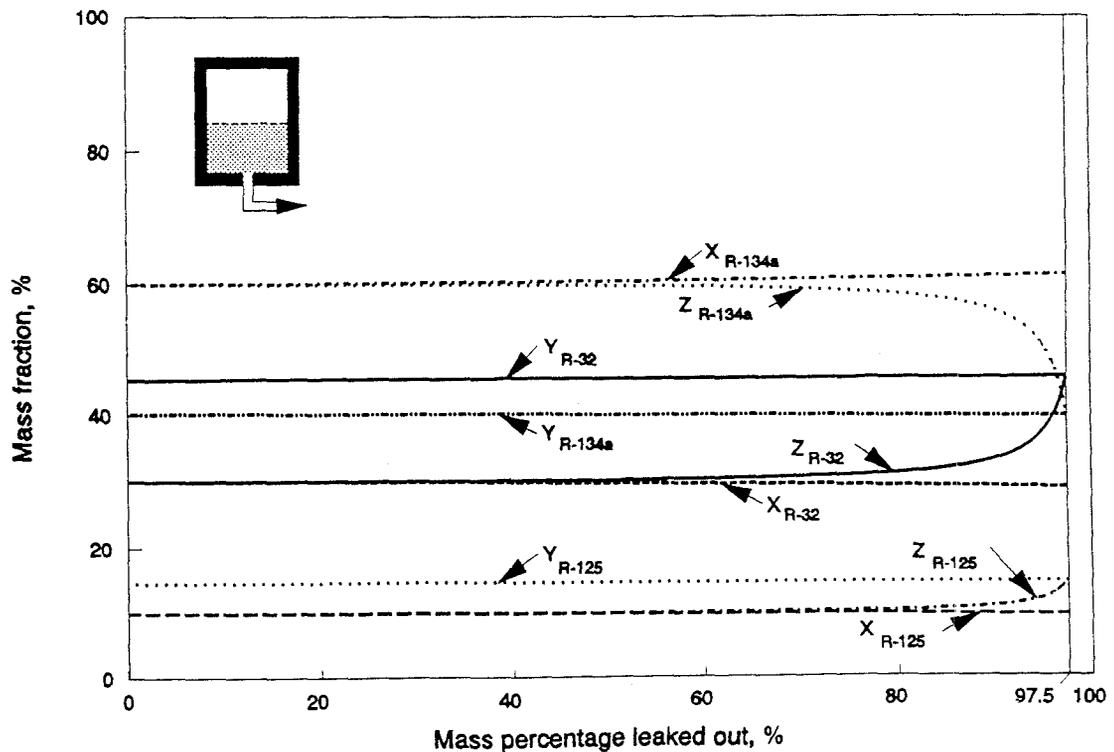


Figure 17. Mass fraction change during the adiabatic liquid leak of the R-32/125/134a mixture as a function of mass percentage leaked out

vapor phases, very little liquid evaporates to occupy the volume of the escaped liquid. The pressure inside the cylinder decreases until all the liquid escapes from the cylinder.

CONCLUDING REMARKS

In this study, the isothermal and the adiabatic leak processes are formulated for both vapor and liquid leak cases. This formulation is based upon a simple leak model, and idealized isothermal and adiabatic leak processes represent a slow and a fast leak, respectively. Simulations are carried out for selected mass fractions of binary and ternary refrigerant mixtures; R-32/134a (30/70) and R-32/125/134a (30/10/60). The mass fraction change in the system is presented as a function of the mass percentage leaked out of the system. In the isothermal leak process, both vapor and liquid mass fractions of the most volatile component decrease during the vapor and liquid leaks, and the overall mass fractions of this component decreases during the vapor leak, but increases during the liquid leak. As the temperature is lowered, the overall mass fraction change becomes greater. In the adiabatic leak process, the liquid mass fraction of the most volatile component decreases while the vapor mass fraction of this component increases. The temperature and pressure inside the cylinder decrease drastically for the adiabatic vapor leak and drop slightly for the adiabatic liquid leak. The results of this study show that the refrigerant mixture left in the system remains in a nonflammable region during the isothermal vapor leak for both cases of binary and ternary mixtures. The highest fraction of the flammable component, R-32, in the mixture is obtained in the vapor phase at the initial state. In the adiabatic leak process, the highest fraction of R-32 is obtained in the vapor phase at the final state of the leak process.

Since the simulation in this study is based on REFPROP 4.0, which uses the Carnahan-Starling-DeSantis equation of state, its precision can be no better than this equation represents the vapor-liquid equilibrium data. Experience so far has indicated two possible problem areas. For pure components, predicted values above a reduced temperature of about 0.95 (i.e. within about 15 – 20°C of the critical temperature) may be suspect, particularly for derived data (for example, enthalpy or entropy). Mixtures, too, have this problem since the predicted mixture data is based on individual component data. Thus one must be careful that the mixture data is not within 5% of the critical point for any component. In addition, the mixing coefficients, when predicted, may be suspect. REFPROP states when they are predicted and when they have been measured. Examples in this paper specifically avoided the above problem areas.

In reality, a refrigerant charging process is close to the adiabatic leak process. If the system is charged with a liquid refrigerant from the bottom of a charging cylinder, the mass fraction change for a zeotropic mixture is negligible. One of the problems associated with a leak is how to measure the amount of refrigerant leaked out of the system. If the initial pressure, amount of charge, and the composition of the zeotropic refrigerant mixture are known, the amount leaked out of the system can be estimated by measuring the pressure of the system and applying the Equations described in this paper.

ACKNOWLEDGMENTS

The authors thank Mr. Terry G. Statt, Project Manager at Electric Power Research Institute (EPRI), and John Ryan of the U.S. Department of Energy for their sponsorship, and the Korea Science and Engineering Foundation (KOSEF) for its financial support of M.S. Kim's stay at NIST. The authors recognize the invaluable contributions of Dr. Graham Morrison of the Thermophysics Division at NIST. He passed away in August, 1993 and his support and guidance will be greatly missed. Finally, the authors appreciate the collaboration with Dr. Donald B. Bivens and Dr. A. Yokozeki of Du Pont for suggestions made in the early stages of the model's development.

NOMENCLATURE

h_e	enthalpy of escaping refrigerant, kJ/kmol	Y	vapor mass fraction
N	total number of components	y	vapor mole fraction, $y_i = \frac{n_{v_i}}{\sum_{j=1}^N n_{v_j}} = \frac{n_{v_i}}{n_v}$
n	total number of moles, kmol	Z	overall mass fraction
n_l	number of moles in the liquid phase, kmol	z	overall mole fraction
n_v	number of moles in the vapor phase, kmol	ϵ	escaping fraction of the total moles, $\epsilon = \Delta n/n$
P	pressure, MPa		
Q	molar quality, $Q = n_v/n$		
T	temperature, °C		
u	internal energy, kJ/kmol		
V	system volume, m ³		
v	molar volume, m ³ /kmol, $v = V/n$		
X	liquid mass fraction		
x	liquid mole fraction, $x_i = \frac{n_{l_i}}{\sum_{j=1}^N n_{l_j}} = \frac{n_{l_i}}{n_l}$		
			Subscripts and Superscript
		i	initial state, i -th component
		f	final state
		l	liquid phase
		v	vapor phase
		'	property at the next step after a leak

REFERENCES

- ASHRAE. 1992. *ANSI/ASHRAE Standard 34-1992, Number designation and safety classification of refrigerants*. Atlanta: ASHRAE.
- Blaise, J.C., T. Dutto, and J.L. Ambrosino. 1988. First industrial application of non-azeotropic mixture. *Int. J. Refrig.* 11: 255-258.
- Didion, D.A., and D.B. Bivens. 1990. Role of refrigerant mixtures as alternatives to CFCs. *Int. J. Refrig.* 13: 163-175.
- Domanski, P.A., and D.A. Didion. 1993. Theoretical evaluation of R-22 and R-502 alternatives. Gaithersburg, Maryland: National Institute of Standards and Technology (NIST).
- Gallagher, J., M. McLinden, G. Morrison, M. Huber, and J. Ely. 1991. NIST Thermodynamic properties of refrigerants and refrigerant mixtures database (REFPROP). Ver. 3.03. *NIST Standard Reference Database 23*. Gaithersburg, Maryland: NIST.
- Kruse, H., and U. Hesse. 1988. Possible substitutes for fully halogenated chlorofluorocarbons using fluids already marketed. *Int. J. Refrig.* 11: 276-283.
- Kruse, H., and F. Rinne. 1992. Performance and leakage investigations of refrigeration and air-conditioning systems using refrigerant mixtures as working fluids. In *Proceedings of 1992 International Refrigeration Conference at Purdue*, vol. 2: 621-630.
- Richard, R.G., and I.R. Shankland. 1992. Flammability of alternative refrigerants. *ASHRAE Journal* 34(4): 20-24.
- Shiflett, M.B., A. Yokozeki, and P.R. Reed. 1992. Property and performance evaluation of 'SUVA' HP refrigerants as R-502 alternatives. In *Proceedings of 1992 International Refrigeration Conference at Purdue*, vol. 1: 15-22.