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ZEOTROPIC MIXTURE SEPARATIONS ANALYSES

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ABSTRACT

A thermodynamic model to simulate a slow vapor leak of fluorocarbon based refrigerant mixtures has been developed and compared with experimental data. Model calculations are in excellent agreement with the experimental data, and with a vapor leakage model developed by other researchers.

INTRODUCTION

Refrigerant mixtures have become an important approach for replacement of chlorine containing compounds, offering increased freedom of adjusting thermophysical properties to achieve goals of system capacity and energy efficiency. However, additional considerations are required when using zeotropic refrigerant mixtures. Among these are the potential composition changes due to vapor leakage from a storage container or application system. In some cases these changes can lead to unsatisfactory system performance. Proper application of refrigerant mixtures requires an understanding of vapor leak behavior and composition changes, and a description of a simulation model for slow vapor leaks is presented in this paper. Another simulation model has been developed by Kim and Didion (1), and comparisons will be made with their model calculations.

MODEL DESCRIPTION

Begin with a mental image of a closed container of liquid and vapor, the inside vapor pressure being higher than the outside pressure at a given temperature. A small hole exists in the vapor space of the container, with the vapor leaking out so slowly that vapor-liquid equilibrium (VLE) is maintained at a constant temperature. When the liquid in question is either a pure compound or an azeotropic mixture, the inside vapor pressure and compositions will be invariant during the leak process. In the case of zeotropic mixtures, vapor leakage will result in pressure reduction and the composition in the container being continuously changed.

Let R represent a molar flow rate of escaping vapor, and L a molar liquid left in the container. During the leak, the overall mass balance states:

$$dL/dt = -R \tag{1}$$

A mass balance for the individual components are given by:

$$x_i(dL/dt) + L(dx_i/dt) = -Ry_i, \quad i = 1, \dots, N \tag{2}$$

where x_i and y_i are the liquid and vapor mole fractions, respectively, of i -th compound of an N -component mixture. Combining equations (1) and (2) yields:

$$dx_i/dt = (dL/dt)/L(y_i - x_i), \quad i = 1, \dots, N \tag{3}$$

A new time variable, s , is defined instead of t : $s = \log(L_0/L)$, where L_0 is the initial liquid molar amount and L is the liquid molar amount at time t after the start of the leak. With this time variable, equation (3) becomes:

$$dx_i/ds = x_i - y_i, \quad i = 1, \dots, N \quad (4)$$

The integration by s is more convenient than the time t integral, since it is explicitly related to the amount of the material loss (L/L_0). During the integration it is assumed that the vapor leak is slow enough that system temperature remains constant and the VLE condition is satisfied. At each small time step, the following set of VLE equations must be solved simultaneously for x_i , y_i , and the system pressure P at a given temperature T .

$$P\phi_i^l x_i = P\phi_i^v y_i \quad i = 1, \dots, N \quad (5)$$

$$\sum_{i=1}^N x_i = \sum_{i=1}^N y_i = 1$$

where ϕ is the fugacity coefficient for liquid or vapor. Any proper equation of state (EOS) may be applied for equation (5). We have used a modified Redlich-Kwong EOS (2) for this purpose.

In practice we are interested in the leak behavior as a function of the weight percent of the material loss versus the initial amount of refrigerant. This requires the relationship between the time variable of s and the weight loss percent, w . To do this, we must know the liquid and vapor mole fractions in the container during the integration by s . At time s , the liquid (L) and vapor (G) moles in the container are:

$$L = L_0 e^{-s} \quad (6)$$

$$G = (V_0 - Lv_l)/v_g \quad (7)$$

where V_0 is the total volume of the container, and v_l and v_g are liquid and vapor molar volumes, respectively. If we assume that the container is initially filled with liquid, then $V_0 = L_0 v_l(0)$ where $v_l(0)$ is the initial liquid molar volume. Without loss of generality, L_0 can be set to be unity: $V_0 = v_l(0)$. The initial total weight is $L_0 M_0 = M_0$ where M_0 is the average molecular weight of the initial liquid. Then the weight loss percent, w , at time s is given by:

$$w = 100(1 - M_l L/M_0) = 100(1 - M_l e^{-s}/M_0) \quad (8)$$

where M_l is the average molecular weight of liquid in the container at time s .

$$M_l = \sum_{i=1}^N m_i x_i \quad (9)$$

with i -th molecular weight of m_i .

Using equation (8), we can identify how much material has been lost during the leak period of s . In equation (7), v_g is calculated by the equation of state, while v_l is obtained from an accurate correlation, as the cubic equation of state we used is not sufficiently accurate for the liquid molar volume. Finally the integration of the differential equations ends when the next time step reaches the condition that the amount of liquid vaporized is equal to or larger than the remaining liquid in the container.

COMPARISON WITH EXPERIMENTAL DATA

The validity of the vapor leak model has been demonstrated for several refrigerant mixtures. Model calculations were compared with experimental data for R407C (R32/R125/R134a), R404A (R125/R143a/R134a), 45/55 weight % R125/R143a, and R401A (R22/R152a/R124). The comparisons are shown in Figures 1 - 8 for liquid and vapor compositions. The solid lines represent the model calculations and the open circles are the measured data points. The calculated data are in excellent agreement with the experimental data, most comparisons being within two weight percent. The largest deviation was three weight percent for the concentration of R134a in the vapor phase of R407C. Based on data from this work and other related studies, we know that the model calculations are within one weight percent, and the experimental data are within 2 - 3 weight percent.

Although vapor leak experiments are conceptually simple, much care is required in actual practice. Many hours are required for the sufficiently slow leak to prevent liquid droplet carryover with the vapor, and system temperature must be kept constant. Sampling and gas chromatography procedures require careful attention to maintain accuracy and reproducibility within 1%. For the experimental data reported here, 1800 gm of mixture was placed in a steel cylinder. A needle valve was attached to the cylinder valve, which was connected to plastic tubing attached to a flow meter. The needle valve was adjusted for an initial flow of about 2.5 gm/min. Weight loss was determined by balance readings. A gas syringe was used to pierce the plastic tubing and take vapor samples. Liquid samples were taken by inverting the cylinder and flashing the liquid refrigerant mixture through the needle valve into the plastic tubing, which was connected to a bubbler. The resulting vapor sample represented the liquid composition. Duplicate samples were taken and analyzed by gas chromatography. If the results were not within 0.5% for each component in the mixture, additional samples were taken and analyzed until this requirement was met.

COMPARISON WITH ANOTHER VAPOR LEAK MODEL

A different vapor leak model has been developed by Kim and Didion (1) which has been termed REFLEAK. Their vapor leakage model is based on a series of repeating flash calculations, while the present model is based on integration of differential equations representing composition changes. Kim and Didion used the Carnahan-Starling-DeSantis equation of state in their calculations, while the present model uses a modified Redlich-Kwong equation of state. In spite of these differences, the vapor leakage models are in good agreement when accurate binary interaction parameters are used.

In Figure 9 we have plotted vapor compositions during vapor leakage of the R32/R125/R134a mixture (R407C) calculated by the two models. The solid lines represent the present model calculations, and the symbols (*) represent REFLEAK calculations. There is essentially no difference in the numbers calculated by the two models. This implies that the model representations of the vapor leakage process are consistent, and the VLE correlations by the two equations of state are in agreement. In Figure 10 we have plotted vapor compositions of the R22/R152a/R124 mixture (R401A), showing differences for the R22 and R124 concentrations. At 90 weight percent loss, the two model calculations are different by 6

weight percent for R22 and R124. These differences are due to the binary interaction parameters used for this ternary mixture in the Carnahan-Starling-DeSantis equation of state, as two of the three interaction parameters were estimated rather than being measured; while in the present model, all interaction parameters were measured. This has been confirmed by adjusting the REFLEAK interaction parameters for the R22/R152/R124 mixture to match with the present model.

SUMMARY

The vapor leakage model described in this paper has been verified with several well-defined sets of experimental data, and is in good agreement with a different vapor leakage model developed by other researchers. The model calculations are sufficiently accurate that time-consuming laboratory experiments may be replaced by model calculations.

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- (2) Shiflett, M.B. and A. Yokozeki. 1993. Near Azeotropic Refrigerants as Alternatives for R502. *ASHRAE Journal* 35(2):24-28.

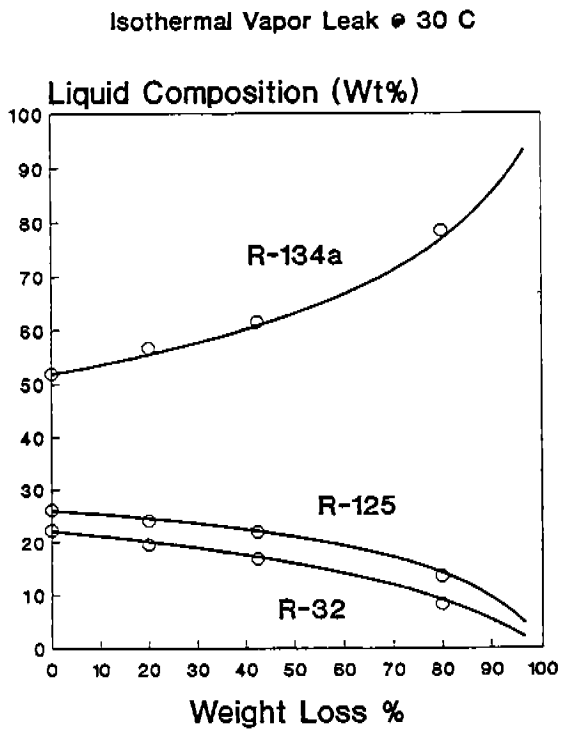


Figure 1

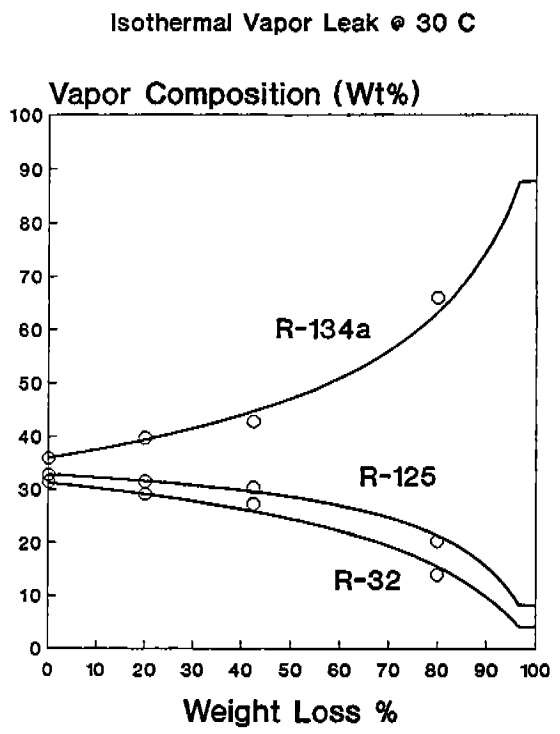


Figure 2

Isothermal Vapor Leak @ 23 C

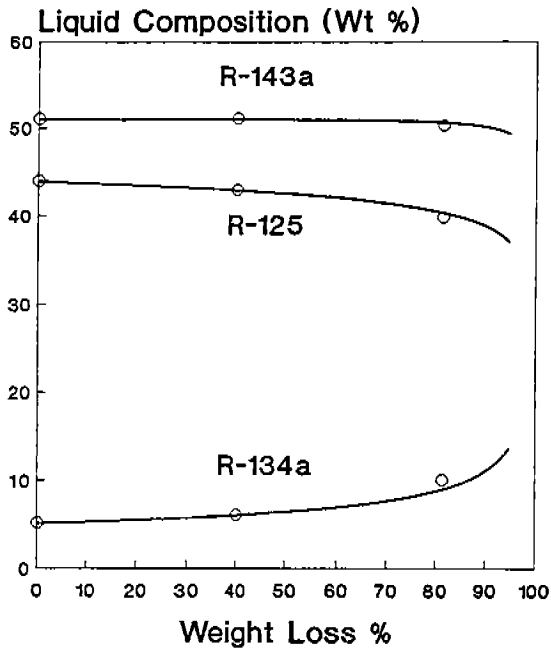


Figure 3

Isothermal Vapor Leak @ 23 C

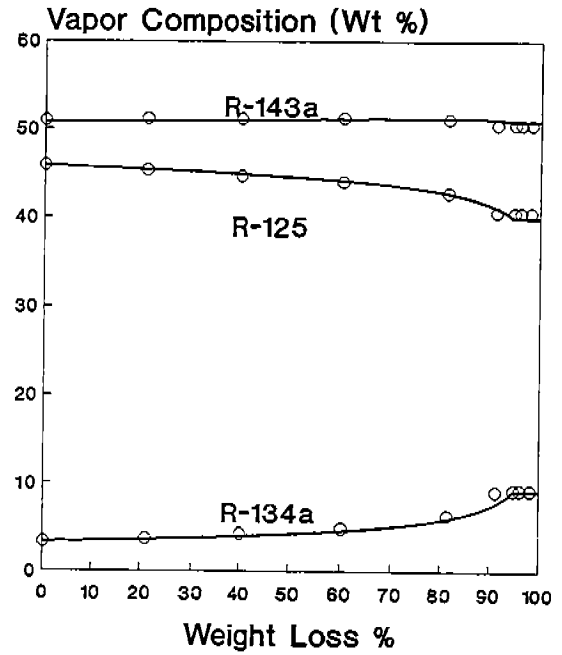


Figure 4

Isothermal Vapor Leak @ 24 C

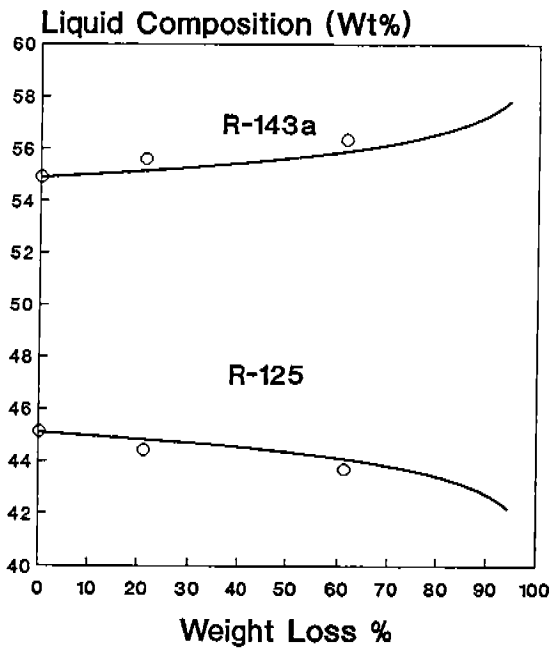


Figure 5

Isothermal Vapor Leak @ 24 C

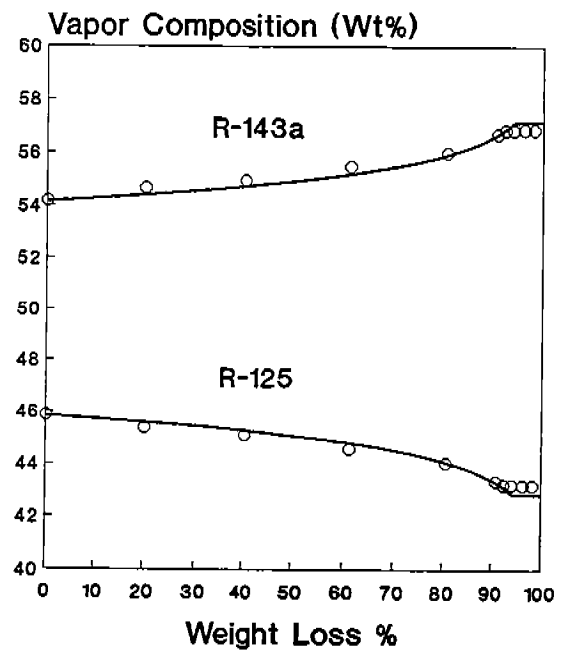


Figure 6

Isothermal Vapor Leak @ 21 C

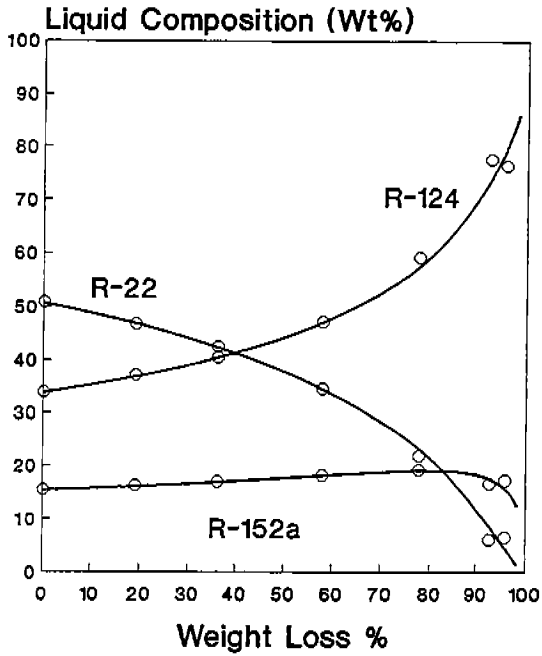


Figure 7

Isothermal Vapor Leak @ 21 C

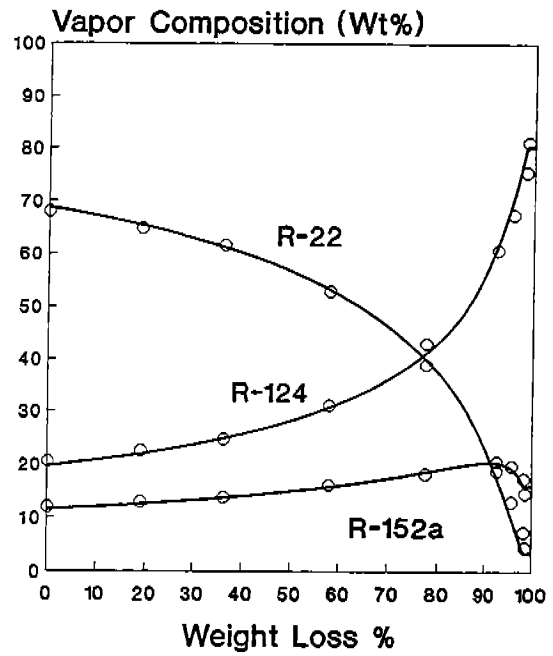


Figure 8

Isothermal Vapor Leak @ 30 C

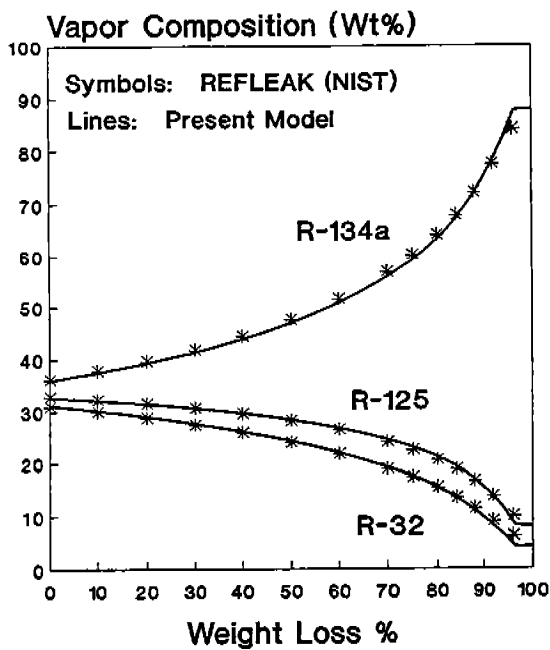


Figure 9

Isothermal Vapor Leak @ 21 C

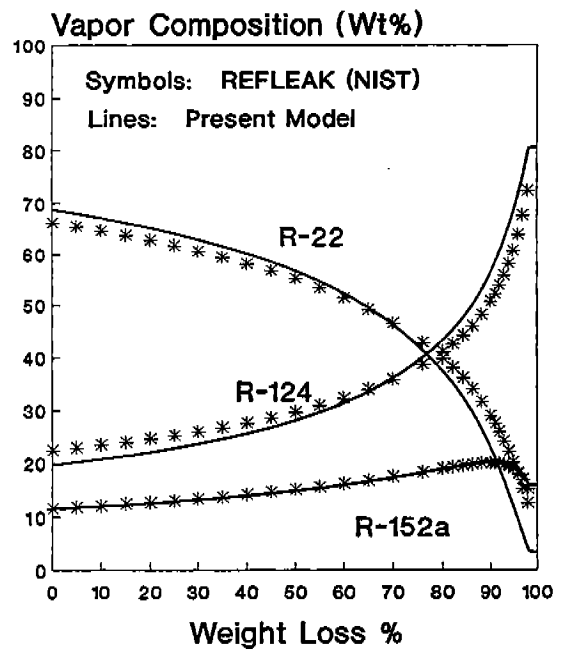


Figure 10