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# ESTIMATION OF THERMODYNAMIC PROPERTIES OF NON-AZEOTROPIC REFRIGERANT MIXTURES AND APPLICATION TO THE HEAT PUMP SYSTEM

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## ABSTRACT

Thermodynamic properties are estimated for the selected binary non-azeotropic refrigerant mixtures using the Peng-Robinson equation of state and mixing rules. Calculations have been made for eight different mixtures including R13B1/R114, R22/R114, R12/R114, R152a/R114, R13B1/R152a, R13B1/R12, R22/R152a and R22/R142b.

In this study, the binary interaction coefficients of the mixtures have been chosen to calculate thermodynamic properties, such as enthalpy, entropy and the vapor-liquid equilibria. A correlation is proposed to relate the binary interaction coefficient with difference between dipole moments of each pure refrigerant. The calculated values are compared with the existing experimental data and they give reasonably good agreements. Pressure-enthalpy and temperature-entropy diagrams are prepared for a particular composition of each refrigerant mixture.

The simple method of property calculation makes it possible to simulate the performance of a heat pump using non-azeotropic refrigerant mixtures including R22/R114, R22/R152a, R22/R142b, and R13B1/R152a as working fluids.

The simulated results show that the capacity modulation can be obtained by varying the mixture composition in a heat pump with a displacement type compressor. The variation of the coefficient of performance is also studied in a non-azeotropic mixture system.

## NOMENCLATURE

$c_i$  : coefficients  
 $c_p^b$  : constant pressure specific heat at ideal gas state  
 $f^o$  : fugacity  
 $h$  : enthalpy  
 $k_{ij}$  : binary interaction coefficient  
 $P$  : pressure  
 $Q$  : heat transferred  
 $R$  : gas constant  
 $s$  : entropy  
 $T$  : temperature  
 $v$  : specific volume  
 $W$  : compression work  
 $x$  : mole fraction of the liquid phase  
 $y$  : mole fraction of the vapor phase  
 $Z$  : compressibility factor

### Greek letters

$\alpha$  : coefficient related to the equation of state  
 $\mu$  : dipole moment

### Subscript

$b$  : brine  
 $c$  : critical value, condenser  
 $e$  : evaporator  
 $H$  : high temperature side  
 $i$  : inlet,  $i$  component  
 $j$  :  $j$  component  
 $L$  : low temperature side  
 $o$  : standard state, outlet  
 $w$  : water

## 1. INTRODUCTION

It is important to estimate the thermodynamic properties of working fluids for simulation and efficient operation of thermal systems such as refrigerators and heat pumps. The proper working fluid must be chosen for the best performance of the system and the thermodynamic properties of those working fluids should be correctly evaluated.

The research and development have been progressed to achieve the higher performance of heat pumps and refrigerators by utilizing the mixtures of working fluids including non-azeotropic mixtures. The purpose of this study is to estimate thermodynamic properties of binary non-azeotropic refrigerant mixtures to simulate the performance of the systems.

The main advantages of non-azeotropic refrigerant mixtures may be classified into performance enhancement[1] and the capacity control[2]. The former can be achieved by minimizing the mean temperature difference between the working fluid and the heat source or sink by the characteristics of gliding temperature in

the non-azeotropic mixtures. The latter profit of non-azeotropic refrigerants is obtained by changing the mixture ratio during the operation.

In this study, the well-known Peng-Robinson equation of state is chosen to evaluate the thermodynamic properties of the non-azeotropic refrigerant mixtures and the conventional mixing rule is also applied. The calculation of enthalpy and entropy of the mixture makes it possible to analyze the performance of the specified heat pump cycle quantitatively.

The calculation covers the pure components of R13B1, R22, R12, R152a and R114; and the binary mixtures of R13B1/R114, R22/R114, R12/R114, R152a/R114, R13B1/R152a, R13B1/R12, R22/R152a and R22/R142b.

A test rig has been assembled and experiment are in progress to measure performance of a heat pump with various mixtures. In this report, we present only the result of calculation and analysis.

## 2. CALCULATION OF THERMODYNAMIC PROPERTIES

### 2.1 Equation of State

In this study, Peng-Robinson equation of state is chosen for the calculation of the thermodynamic properties of refrigerants since it predicts the properties reasonably well and makes the calculation relatively simple, especially for the case of mixing parameters. The mixing rule is required to evaluate thermodynamic properties of refrigerant mixtures, and the procedure for applying mixing rules will be much complicated when a complex form of equation of state is used.

Peng-Robinson equation of state is well-known in the literature[3]. The working equations are simply repeated here for the completeness of the paper.

$$P = \frac{RT}{v-b} - \frac{a(T)}{v(v+b) + b(v-b)}, \quad (1)$$

$$a(T) = a_c(T_c) \cdot \alpha(T), \quad a_c(T_c) = 0.45724 \frac{R^2 T_c^2}{P_c}, \quad (2)$$

$$b = 0.07780 \frac{R T_c}{P_c}. \quad (3)$$

By using the compressibility factor  $Z$ , the cubic equation of the following form is obtained.

$$Z^3 - (1-B)Z^2 + (A - 3B^2 - 2B)Z - (AB - B^2 - B^3) = 0, \quad (4)$$

where

$$Z = \frac{Pv}{RT}, \quad A = \frac{aP}{R^2 T^2}, \quad B = \frac{bP}{RT}. \quad (5)$$

As usual,  $\alpha(T)$  is expressed as follows.

$$\alpha(T) = 1 + \left(1 - \frac{T}{T_c}\right) \left(m + n \frac{T_c}{T}\right). \quad (6)$$

Two parameters,  $m$  and  $n$  can be determined from the experimental data of the saturated states. In this procedure, the fugacity equality condition is introduced to find  $m$  and  $n$ . Experimental data for vapor pressure are taken from ASHRAE's vapor pressure relation[4] for pure refrigerants.

### 2.2 Mixing Rule and Property Calculation

The equation of state for mixtures can be completed by assigning the proper mixing parameters for the components. The conventional mixing rules are applied in this study[5].

$$a = \sum_i \sum_j x_i x_j a_{ij}, \quad (7)$$

$$b = \sum_i \sum_j x_i x_j b_{ij}, \quad (8)$$

$$a_{ij} = (1 - k_{ij}) \sqrt{a_i a_j}, \quad (9)$$

$$b_{ij} = (1 - \hat{k}_{ij}) \frac{b_i + b_j}{2}. \quad (10)$$

In the present calculation,  $\hat{k}_{ij}$  for the interaction parameter  $b_{ij}$  is treated as zero.

With Peng-Robinson equation of state, the formulae for enthalpy,  $h$ , entropy,  $s$ , and fugacity,  $f$ , are summarized as

$$h = h_o + \frac{1}{2\sqrt{2}b} \left[ a(T) - T \frac{da(T)}{dT} \right] \ln \frac{v - (\sqrt{2} - 1)b}{v + (\sqrt{2} + 1)b} + RT(Z - 1) + \int c_p^o dT, \quad (11)$$

$$s = s_o + R \ln \frac{v - b}{RT} - \frac{1}{2\sqrt{2}b} \frac{da(T)}{dT} \ln \frac{v - (\sqrt{2} - 1)b}{v + (\sqrt{2} + 1)b} + \int \frac{c_p^o}{T} dT, \quad (12)$$

$$\frac{da(T)}{dT} = \frac{1}{2} \sum_{i,j} x_i x_j (1 - k_{ij}) \left( \frac{a_i a_j}{\alpha_i \alpha_j} \right)^{1/2} \left( \frac{d\alpha_i}{dT} \alpha_j + \alpha_i \frac{d\alpha_j}{dT} \right), \quad (13)$$

$$\frac{d\alpha_i}{dT} = - \frac{m_i}{T_c} - n_i \frac{T_c}{T^2}, \quad (14)$$

$$\ln \frac{f_i}{x_i P} = \frac{b_i}{b} (Z - 1) - \ln(Z - B) - \frac{A}{2\sqrt{2}B} \left( \frac{1}{a} - \frac{b_i}{b} \right) \ln \frac{Z + (\sqrt{2} + 1)B}{Z - (\sqrt{2} - 1)B}. \quad (15)$$

In the above equations, data for the specific heat at ideal gas state are taken from ASHRAE[4].

### 2.3 Vapor-Liquid Equilibrium and Binary Interaction Coefficient

Vapor-liquid equilibrium state can be found by phase rule on the condition that the fugacities for liquid and vapor phases are the same. In this study, with given pressure and temperature, composition ratios in vapor and liquid states are found. When either of pressure and temperature data and the composition ratio in one of liquid and vapor phases are given, iterations are performed to find unknowns until the differences of fugacities reach the order of  $10^{-4}$  in eq. (15).

Experimental data for the refrigerant mixtures are taken from various literatures: R13B1/R114[6], R22/R114[7, 8], R12/R114[1], R152a/R114[9], R13B1/R12[10], R13B1/R152a[11], R22/R152a and R22/R142b. The values  $h_o$  and  $s_o$  in eqs. (11) and (12), are adjusted to give the reference values of  $h$  and  $s$  to be 200 kJ/kg and 1 kJ/kgK at saturated liquid state for pure refrigerant and at bubble point for refrigerant mixtures at  $T = 0^\circ\text{C}$ .

### 2.4 Calculated Results of Thermodynamic Properties

Estimated values of  $m$  and  $n$  are shown in Table 1. With these values, vapor pressures of pure refrigerants are calculated and compared with ASHRAE data[14]. Systematic deviations appears but it is acceptable to utilize the data within the range of applications. Enthalpy and entropy of saturated liquid and vapor are also compared with ASHRAE data. The error becomes larger as the temperature reaches close to critical point or lower temperature region.

The binary interaction coefficients are found for each refrigerant mixture from the data of vapor-liquid equilibrium. In this study,  $k_{ij}$  is determined by minimizing the difference between calculated and experimentally measured pressure for a state of given temperature and mole fraction. The calculated values of  $k_{ij}$  are given in Table 2. The average deviation in pressure is within about 1%.  $k_{ij}$  seems to be a weak function of temperature and mole fraction. The calculated binary interaction coefficients from experimental data are plotted in Fig. 1 as a function of differences in dipole moments of the components in mixtures. The following interpolating relation may be used to estimate  $k_{ij}$  when experimental data are not enough for substances such as R22/R142b and R22/R152a.

$$k_{ij} = c_1(\Delta\mu)^2 + c_2|\Delta\mu| + c_3, \quad (16)$$

$$c_1 = 0.0197931, \quad c_2 = 0.0204207, \quad c_3 = 0.0016696. \quad (17)$$

Figure 2 shows some of the vapor-liquid equilibrium relations for pressure, temperature and mole fractions of liquid and vapor phases. Calculated results agree well with the experimental data. In spite of the simple form of Peng-Robinson equation of state, dew point and bubble points are well predicted. Figure 3 indicates the effect of the interaction parameter,  $k_{ij}$ , and shows the results calculated with the aids of Raoult's rule.

Thermodynamic properties of enthalpy and entropy are calculated for refrigerant mixtures. Figures 4 - 7 show pressure-enthalpy and temperature-entropy diagrams at a specific mixture ratio, say, 50/50 mass fraction for R22/R114, R22/R152a, R22/R142b and R13B1/R152a respectively.

Table 1 Calculated values of  $m$  and  $n$  in eq. (6) for several refrigerants

Refrigerant	$m$	$n$
R13B1	0.4380	0.1992
R22	0.4909	0.2212
R12	0.4666	0.1887
R152a	0.6990	0.1212
R142b	0.6789	0.1031
R114	0.5129	0.2424

Table 2 Calculated values of binary interaction coefficient for several mixtures

Mixture	$k_{ij}$	$ \Delta\mu $
R13B1/R114	0.0104	0.15
R22/R114	0.0393	0.92
R12/R114	0.0020	0.01
R152a/R114	0.1047	1.77
R13B1/R152a	0.0802	1.62
R13B1/R12	-0.0009	0.14

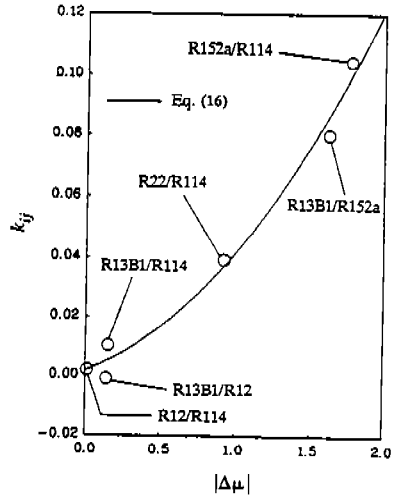
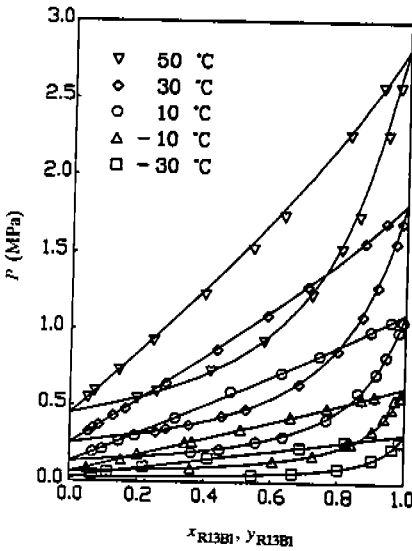
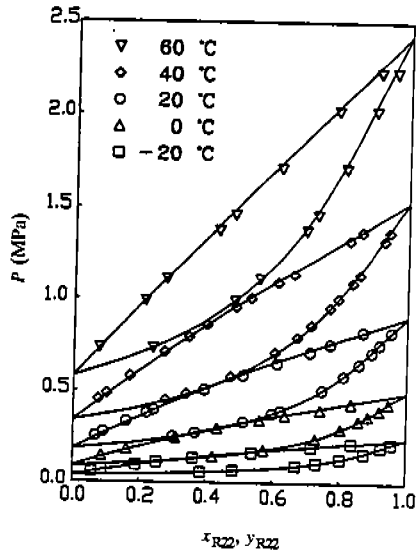


Fig. 1 Relation between  $|\Delta\mu|$  and  $k_{ij}$  ( $|\Delta\mu|$ : difference between dipole moments (Debye),  $k_{ij}$ : binary interaction coefficient)

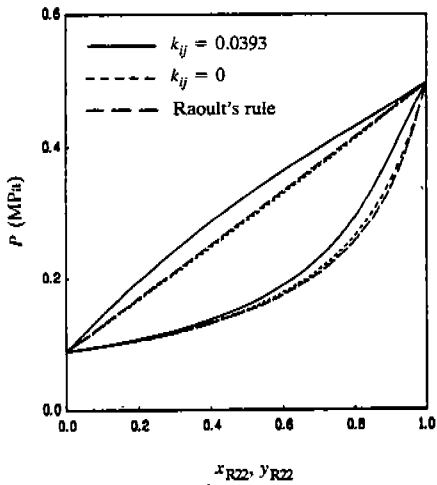


(a) R13B1/R114

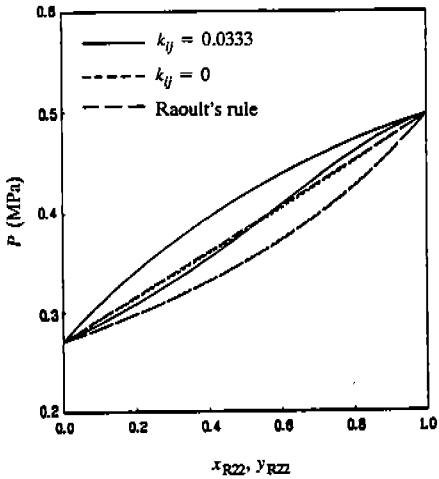


(b) R22/R114

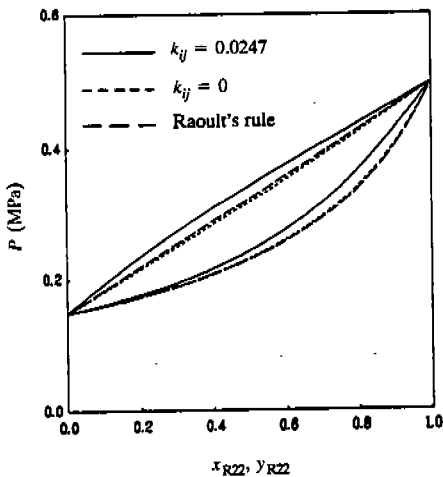
Fig. 2 Vapor-liquid equilibria for the non-azeotropic refrigerant mixtures (Marks represent experimental data.)



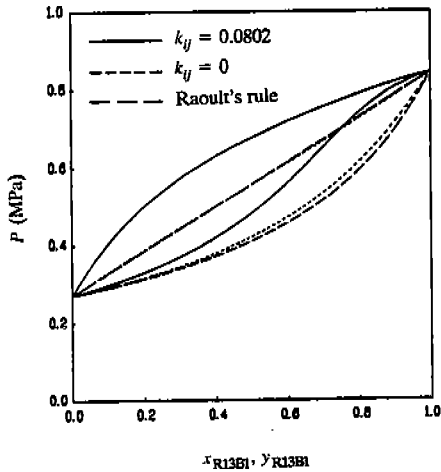
(a) R22/R114



(b) R22/R152a

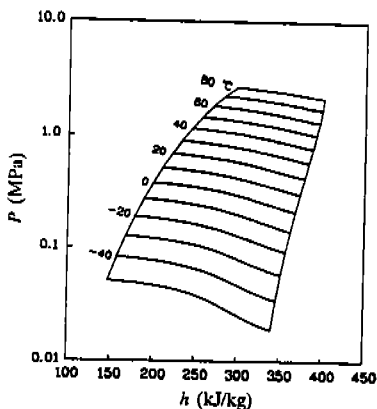


(c) R22/R142b

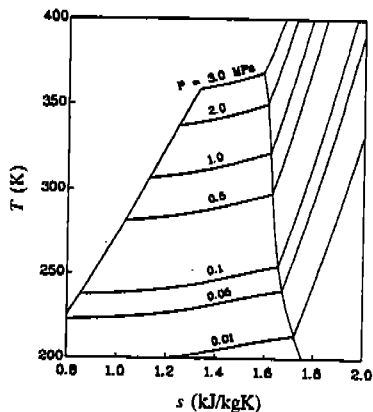


(d) R13B1/R152a

Fig. 3 Comparison of vapor-liquid equilibria with Raoult's rule ( $T = 0^\circ\text{C}$ )

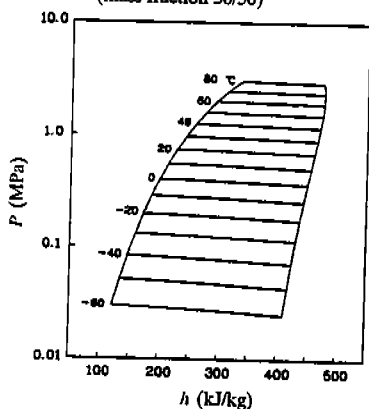


(a) P-h diagram

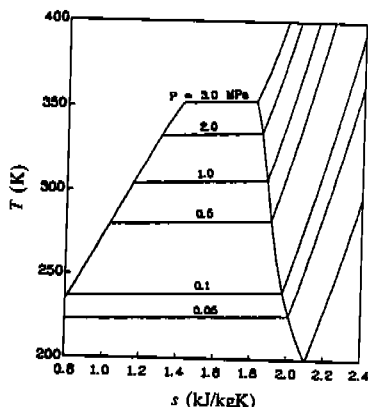


(b) T-s diagram

Fig. 4 Pressure-enthalpy and temperature-entropy diagram for the refrigerant mixture R22/R114 (mass fraction 50/50)

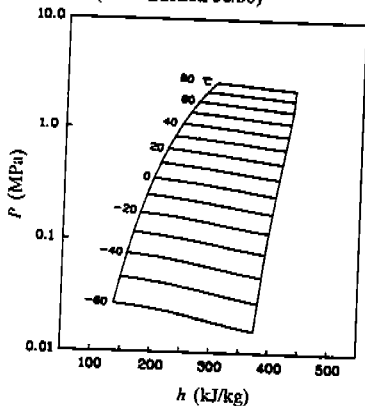


(a) P-h diagram

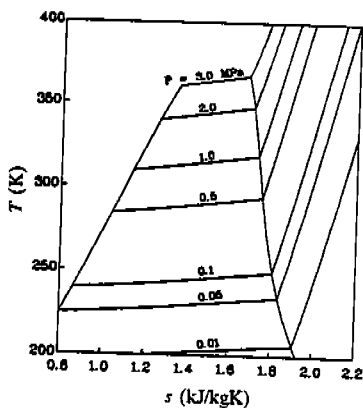


(b) T-s diagram

Fig. 5 Pressure-enthalpy and temperature-entropy diagram for the refrigerant mixture R22/R152a (mass fraction 50/50)



(a) P-h diagram



(b) T-s diagram

Fig. 6 Pressure-enthalpy and temperature-entropy diagram for the refrigerant mixture R22/R142a (mass fraction 50/50)

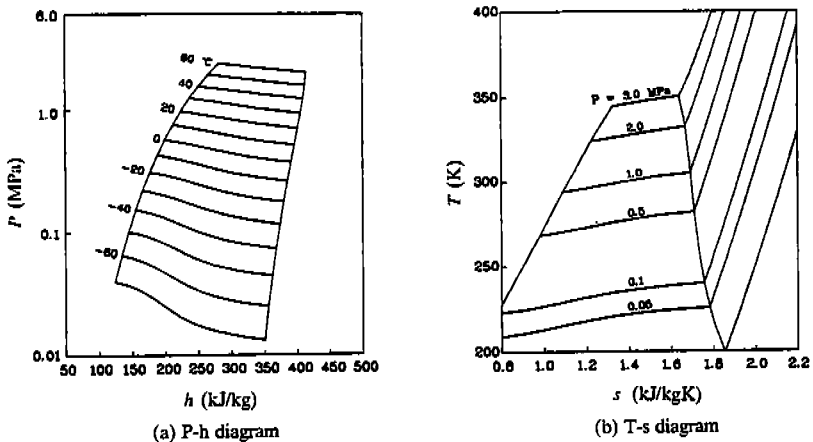


Fig. 7 Pressure-enthalpy and temperature-entropy diagram for the refrigerant mixture R13B1/R152a (mass fraction 50/50)

### 3. ANALYSIS OF HEAT PUMP CYCLES

#### 3.1 Fundamental Assumptions

It is possible to perform the simulation of heat pump cycles by using the thermodynamic properties of refrigerant mixtures. Various combinations are tried to find the characteristics of heat pump operations in modes of constant volumetric flow rate and constant heating capacity. The mixtures includes R22/R114, R22/R152a, R22/R142b and R13B1/R152a. These are the proper combinations to apply to heat pump cycles. It is assumed that the fluid is superheated by 5 °C at the exit of the evaporator and is in saturated liquid state at the exit of the condenser.

Compressor is thought to be reciprocating type with fixed stroke. The efficiency of the compressor is assumed to be a simple function of the the pressure ratio between the outlet and the inlet. In this study, the volumetric efficiency and the compression efficiency of the compressor are regarded as a linear function of pressure ratio[12]. The pressure drops in the flow and the heat transfer except in the condenser and the evaporator are neglected. The heat exchange is assumed to be counterflow type between refrigerant and secondary fluid. The pressure-enthalpy and temperature-entropy diagrams of the cycle are represented schematically in Fig. 8.

#### 3.2 Modulation of Heating Capacity in a Constant Volumetric Flow Rate Cycle

In this section, modulation of heating capacity is dealt with in a heat pump cycle. We assume that the compressor is operated in a mode of constant volume flow rate. The operating and design conditions are given for the temperatures of secondary fluids at inlet and exit of the condenser and the evaporator, overall heat transfer coefficient and volume flow rate of refrigerant as follows:

- water temperature at the condenser inlet ( $T_{wci}$ ) = 25 °C
- water temperature at the condenser outlet ( $T_{wco}$ ) = 40 °C
- brine temperature at the evaporator inlet ( $T_{bei}$ ) = 20 °C
- brine temperature at the evaporator outlet ( $T_{beo}$ ) = 10 °C
- overall heat transfer coefficient in the condenser  $(UA)_c = 0.3 \text{ kW/K}$
- overall heat transfer coefficient in the evaporator  $(UA)_e = 0.3 \text{ kW/K}$
- volume flow rate of the refrigerant ( $\dot{m}$ ) = 0.002 m<sup>3</sup>/s

Iterative method is used to calculate thermodynamic states of refrigerants in the heat pump by using energy balance relations. Calculation is initiated with assuming the temperature of the refrigerant at the condenser exit. The inlet state of evaporator is determined by heat transfer characteristics at the evaporator and then the state at compressor exit is found. Recalculations of states at the condenser are performed with the design condition of  $(UA)_c$ .

Variations of the heating capacity are shown in Fig. 9 as a function of mass fraction of lower boiler in the mixtures. The corresponding coefficients of performance(COP) are drawn in Fig. 10 and defined as follows:

$$\text{COP} = \frac{Q_H}{W} \quad (18)$$



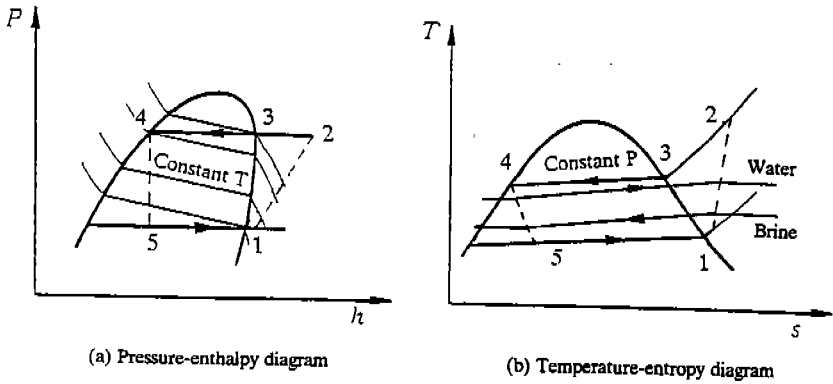


Fig. 8 Schematic diagram of heat pump cycle

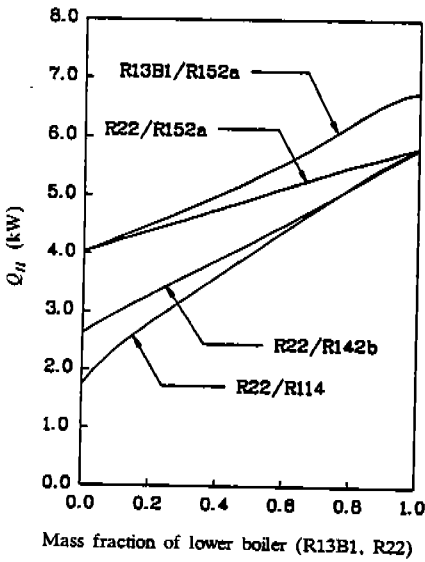


Fig. 9 Variation of heating capacity with respect to the mass fraction of lower boiler in constant volume flow rate cycle

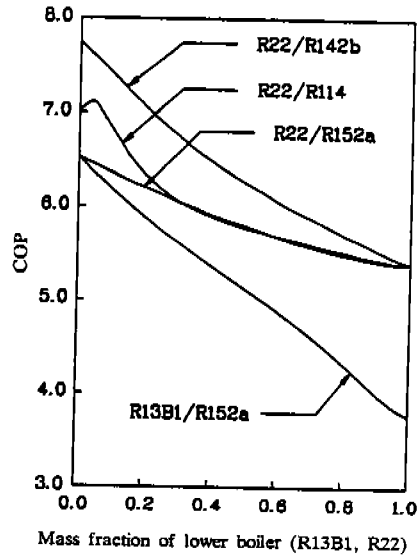


Fig. 10 Variation of COP with respect to the mass fraction of lower boiler in constant volume flow rate cycle

As shown in Figs. 9 and 10, heating capacity,  $Q_h$ , and COP vary nearly monotonically as the components of the mixtures changes. In case of mixtures with R22, heating capacity decreases while COP increases by adding higher boiler to R22. It enables the heat pump to be operated to meet required heating load and higher performance is obtained. Similar result is obtained for the mixture of R13B1/R152a.

### 3.3 Performance Enhancement in a Constant Heating Capacity Cycle

Similar simulations are carried out to find the performance characteristics in a heat pump operated in a mode of a constant heating capacity. A set of operating conditions are chosen to provide a heating capacity of 6 kW. They are as follows:

- water temperature at the condenser inlet ( $T_{wei}$ ) = 25 °C
- water temperature at the condenser outlet ( $T_{wco}$ ) = 45 °C

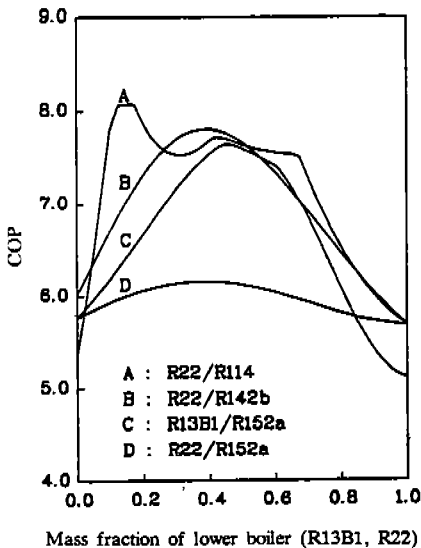


Fig. 11 Variation of COP with respect to the mass fraction of lower boiler in constant heating capacity cycle

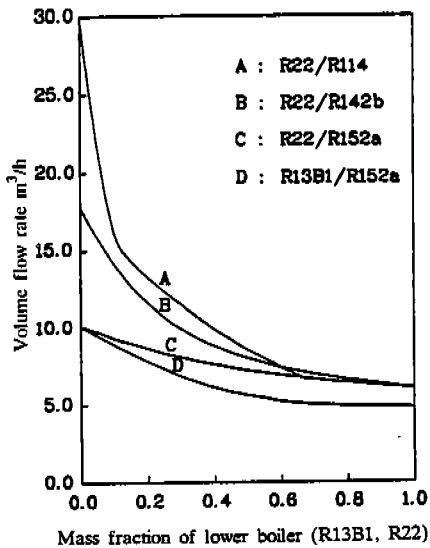


Fig. 12 Variation of volume flow rate with respect to the mass fraction of lower boiler in constant heating capacity cycle

- brine temperature at the evaporator inlet ( $T_{bei}$ ) = 20 °C
- brine temperature at the evaporator outlet ( $T_{beo}$ ) = 5 °C
- heating load ( $Q_H$ ) = 6.0 kW

The calculation procedures are same as the previous case. However, overall heat transfer coefficients,  $U_A$ , in evaporator and condenser are calculated for each mixture to meet the required heating load.

Variations of COP's for four different mixtures are shown in Fig. 11 as a function of mass fraction of lower boiler component. For all cases, the higher value of COP is obtained with the mixtures than with pure components only. The maximum values of COP appear at the mass fraction where the largest temperature difference occurs during phase change. In case of R22/R114 mixture, a plot of calculated COP's has a peculiar shape. The peculiar shape of COP resulted from the fact that the minimum temperature difference was assigned between refrigerant and heat source or heat sink in each end of condenser and evaporator.

The corresponding volume flow rates of the refrigerants at the inlet of compressor are represented in Fig. 12 for four different combinations of mixtures in terms of mass fraction of lower boiler. The flow rate varies monotonically but not linearly.

#### 4. CONCLUDING REMARKS

Peng-Robinson equation of state is used in order to estimate the thermodynamic properties of the refrigerant mixtures. With this equation of state and mixing rules, thermodynamic properties are calculated for the mixtures including R13B1/R114, R22/R114, R12/R114, R152a/R114, R13B1/R152a, R13B1/R12, R22/R152a and R22/R142b.

Necessary binary interaction parameters are found for each mixture to generalize the calculation. A correlation is proposed for the binary interaction coefficients in terms of difference between the dipole moments of each pure refrigerant. Pressure-enthalpy and temperature-entropy diagrams are presented based on the calculation for a certain composition ratio of each refrigerant mixture.

Two types of simulations are carried out to characterize the performance of the heat pump by using non-azeotropic refrigerant mixtures, R22/R152a, R22/R142b, R22/R114 and R13B1/R152a as working fluids. The results show that it is possible to modulate heating capacity in a heat pump with a displacement type compressor and to increase COP in case of a constant heating capacity. These can be achieved by varying composition of a mixture and by choosing proper combinations of pure components.

## ACKNOWLEDGEMENT

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