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THERMODYNAMIC PROPERTIES OF MULTICOMPONENT REFRIGERANTS

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1. INTRODUCTION

Improved correlations of thermodynamic properties are needed in order to evaluate the potential efficiency improvement of vapor-compression refrigeration systems using non-azeotropic refrigerant mixtures. Such potential has been proclaimed because of the concentration difference between the vapor and liquid phases in equilibrium at overall compositions other than zero or one. The concentration difference results in a temperature difference between the dew-point and bubble-point curves, allowing non-isothermal condensation and evaporation, which can be used advantageously to reduce irreversibilities in the heat exchangers and, therefore, to increase the system performance. Furthermore, by varying the overall composition, it is possible to vary the density of the circulating fluid and control the capacity of the system.

To utilize the potential benefit non-azeotropic mixtures offer it is important to choose the right fluids. The mixture must meet all single-fluid requirements and, in addition, closely match the temperature profiles of the heat-sink and heat-source fluids. Experimental investigations have been made with a number of mixtures in vapor compression installations but without the knowledge of the exact mixture properties.

Since refrigerant mixtures generally do not behave like ideal fluids, experimental equilibrium data have to be taken. The experimental determination of the fluid properties is required to enable an equation of state to account for the fluids irregularities, i.e. non-ideal behavior. These investigations have focused mostly on binary solutions to achieve the non-isothermal phase change, although all the fluid properties will change by using only two components. To compensate for specific undesirable changes, e.g. in density or pressure, another fluid with suitable properties may be added.

In order to describe multicomponent fluids theoretically over a wide range of operating conditions, a correlation is needed for the thermodynamic properties. Spline functions are commonly used to correlate experimental data to represent the liquid volume of a pure fluid. However, spline functions should not be applied to mixtures, since the mixture composition may vary. Averaging the liquid volumes of the pure components could lead to large errors, due to a) non-ideal behavior or b) operating conditions of the mixture above the critical point of one constituent. Thus, an equation of state suitable to predict both vapor and liquid volumes at equilibrium and mixing rules for the appropriate coefficients should be used for multi-component mixtures.

2. MIXING OF FLUIDS

A desired working fluid property may be obtained by mixing two or more pure substances together. An ideal binary solution will show a proportional relationship of the fluid properties to the molar concentration of the mixture. For instance, the vapor pressure of each component in an ideal liquid solution, called the partial pressure, is proportional to the molar mixture concentration (Raoult's law). If the total pressure is not very high, Dalton's law is also obeyed and the total pressure will equal the sum of the partial pressures, as demonstrated in Figure 1 for the liquid phase at a given vapor pressure. In general, however, when the liquid and the vapor phases of the mixture are in equilibrium, the vapor phase will contain a higher concentration of the more volatile component than the liquid phase, due to the preferential evaporation of the low-boiling point component.

Deviations from the ideal behavior occur when the molecules of one component affect the forces existing between the molecules of the other component. If the attraction between one type of molecules is strong compared to the other type, then the component with the weak attraction is forced out of the liquid into the vapor state. Therefore, the total vapor pressure will be higher than calculated using ideal mixing rules. If this effect is very strong, the total vapor pressure of the mixture may be higher than the vapor pressure of either pure component, thus the vapor pressure curve exhibits a maximum over the concentration range. At the concentration where the maximum occurs the dew-point and bubble-point curves must touch each other tangentially according to the theorem of Gibbs-Konovalov, and the vapor and liquid phases have the same composition, resulting in an isothermal phase change. Because of this effect, the blend at this concentration is called an "azeotropic" mixture.

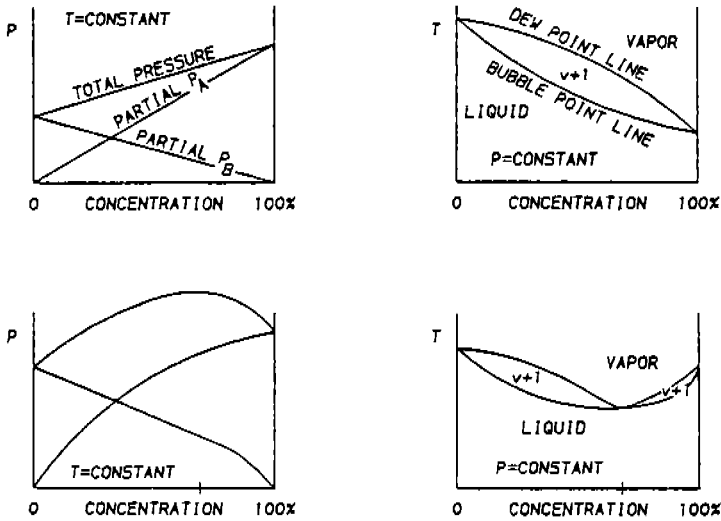


Fig. 1 - Equilibrium curves for an ideal solution and a minimum boiling-point azeotrope //

An azeotropic composition also exists if the total pressure of the mixture is lower than either vapor pressure of the pure constituents. In general, an extremum is more likely to occur as the difference of the pure vapor pressures is reduced. By adding another component to the binary azeotropic mixture, the resulting ternary mixture will now have a concentration difference between the liquid and the vapor phases. Even though the liquid equilibrium curve for a constant concentration of the added component still exhibits an extremum, it will no longer be an azeotropic mixture. The locus of extrema (with increasing concentration of the added component) need not lie on a straight line connecting the binary azeotropic point with the pure-added-component point; rather it may describe a curve, which most likely terminates before the pure-added-fluid point is reached. This fact is in accordance with the phase rules, which limits an azeotropic mixture to only one composition regardless of the number of independent constituents.

However, if the vapor-pressure curve for a binary solution does not pass through a maximum or minimum, the mixture is non-azeotropic, but may still have a strong non-ideal behavior. A simulation of such behavior, using the available equations of state, requires experimental vapor-liquid-equilibrium data points to account for the non-ideal behavior.

3. EQUATION OF STATE

Equations of state used today are improvements of the equation developed by Boyle/Mariotte and Gay/Lussac

$$\frac{p v}{R T} = 1 \quad (1)$$

known as the ideal gas law. To account for non-ideal behavior, an empirical real gas or compressibility factor "Z" was introduced, which Kammerlingh/Onnes expressed as the "virial" equation:

$$\frac{p v}{R T} = Z = 1 + \frac{B}{v} + \frac{C}{v^2} + \dots \quad (2)$$

of which the second coefficient "B" was determined for several refrigerant mixtures by Bougard /2/.

The widest use of the virial type equation is probably found in the Benedict-Webb-Rubin (BWR) equation of state with eight constants and an exponential function (introduced in 1951 /3/). It is capable of representing dense fluids and has been applied in a modified form to refrigerant mixtures in the Soviet Union /4/ and Japan /5,6,7/. Lee and Kesler /8/ developed another well known BWR modification based on a three parameter correlation of the compressibility factor by Pitzer /9/, consisting of a term for spherical molecules (0) and a correction term (1).

$$Z = Z^{(0)} + \left(\frac{\omega}{\omega(R)} \right) (Z^{(R)} - Z^{(0)}) \quad (3)$$

They represented the correction term with a reference fluid using a total of 25 universal constants. Ploecker /10/ developed mixing rules for this equation (LKP), which was applied to refrigerant mixtures by Kuever /11/ and Knapp /12/. The other well known empirical equation of state by Martin and Hou /13/, utilizing 12 individual constants, has been successfully applied to pure refrigerants (see e.g. ASHRAE /14/), but gets too complicated if mixing rules for the coefficients are involved /15/, although /16,17,18/ used it anyway.

The tendency today is to develop an equation of state based on physical meanings allowing a reduced number of coefficients and meaningful mixing rules for them. The development of those types of equations is based on the approach taken by Van-der-Waals in 1873:

$$\frac{p v}{R T} = \frac{v}{v-b} - \frac{a}{v R T} \quad (4)$$

He divided the "real gas" term into repulsion and attraction terms and introduced two coefficients "a" and "b", where "a" is the "Van-der-Waals" attraction force" representing the long range intermolecular electromagnetic attraction, and "b" is the "excluded volume" in which the molecules can not move due to their physical volume. A considerable improvement of the Van-der-Waals equation was achieved by Redlich and Kwong /19/, who modified the attraction term.

$$\frac{p v}{R T} = \frac{v}{v-b} - \frac{a T^{0.5}}{(v+b)RT} \quad (5)$$

where

$$a = A R_c^2 T_c^{2.5} / p_c ; \quad A = 0.42748$$

$$b = B R T_c / p_c ; \quad B = 0.08664$$

Since then, many modifications on the RK equation of state (at least one hundred) have been made. For refrigerant mixture application, the constants "A" and "B" were correlated by Jadot /20/ to

$$A = 0.42137 e^{(0.27868 \omega)} ; B = 0.0855 e^{(0.29161 \omega)}$$

who applied it to several common refrigerants, and Chueh /21/ to

$$A = (R T_c / (v_c - b) - p_c) p_c v_c (v_c + b) / (R T_c)^2$$

$$B = 0.0867 - 0.0125 \omega + 0.011 \omega^2$$

who's correlation was chosen by Stein /22/ and Proust /23/ for R23/R13 and R14/R23/R13, respectively. Kraus and Vollmer /24/ generated a list of "A" and "B" coefficients for a selected number of refrigerants and suggested a temperature exponent in the RK attraction term of 1.0, whereas Soave /25/ eliminated this temperature totally by introducing a temperature-dependent attraction coefficient "a(T)" which he adjusted in 1979 to its final form /26/.

$$\frac{p}{RT} = \frac{v}{v-b} - \frac{a(T)}{(v+b)RT} \quad (6)$$

where

$$a(T) = a(T_c) a(T_r)$$

$$a(T_c) = 0.42748 R^2 T_c^2 / p_c$$

$$a(T_r) = 1. + (1 - T_r)(m + n/T_r)$$

m, n = adjustable parameters

$$b = 0.08664 R T_c / p_c$$

Although this RKS equation of state is very popular (it's being used by DuPont /27/ and Asselineau /28/ for non-azeotropic refrigerant mixtures), an earlier RK modification with a redefined attraction term by Peng and Robinson /29/

$$\frac{p}{RT} = \frac{v}{v-b} - \frac{a(T)}{RT((v+b) + (v-b)b/v)} \quad (7)$$

and a similar approach to Soave's coefficients "a" and "b",

$$a(T) = a(T_c) a(T_r)$$

$$a(T_c) = 0.45724 R^2 T_c^2 / p_c$$

$$a(T_r) = 1. + S(1 - T_r^{0.5})^2$$

$$S = 0.37464 + 1.54226 \omega - 0.26992 \omega^2$$

$$b = 0.0778 R T_c / p_c$$

is being used by Kubic /30/ and Meskel-Lesavre /31/ to correlate their investigated mixtures of R14/13 and R22/11.

The above mentioned Van-der-Waals type equations of state focused on the attraction term, being very important for calculating the vapor volume, but didn't pay sufficient attention to the short-distance repulsion forces, thus they can not represent dense fluids (i.e. liquid volumes) with the desired accuracy. Carnahan and Starling /32/ approximated the virial equation for a rigid-sphere fluid to describe repulsion forces of a real fluid. Taking into account this repulsion term and the exact RKS attraction term did not, however, result into the desired accuracy /33/. Satisfactory results were obtained for pure refrigerants and their mixtures by introducing temperature dependent parameters "a" and "b" into the RKS attraction term /34/, as first suggested by DeSantis /35/.

$$\frac{p}{RT} = \frac{1 + Y + Y^2 - Y^3}{(1 - Y)^3} - \frac{a(T)}{RT(v+b(T))} \quad (8)$$

where

$$Y = b(T) / (4 v)$$

a(T), b(T) = adjustable polynomial

TABLE I

Experimentally investigated thermodynamic properties of refrigerant mixtures

mixture	temp. range	conc. range	data points	investigator
R14-R23	-130 to 10 C	0 to 100	87	Piacentini /18/
	-34 to 95 C	0 to 100	136	Lange /17/
-R23-R13	-73 C @ 3.5 & 6.9 bar		35	Proust /23/
-R13	-35 to 23 C	10 to 90	9	Chaikovski /38/
	-40 to -20 C	14 to 85	15	Zakharov /39/
	-73 to 16 C	0 to 100	65	Kubic /30/
-R22	-138 to -6 C	0 to 100	28	Lavrenchenco /40/
R23-R13	-60 to 0 C	0 to 100	4	Bougard /41/
	27 C	25 / 75	2	Bougard /2/
	-73 to 0 C	0 to 100	73	Stein /22/
-R22	27 C	25 / 75	2	Bougard /2/
-R12	-180 to 0 C	0 to 100	54	Geller /42/
	27 C	25/50/75	3	Bougard /2/
-R11	29 C	25 / 75	2	Bougard /2/
R13-R22	27 C	25 / 75	2	Bougard /2/
-R12	-18 to 17 C	0 to 100	21	Mollerup /43/
	-50 to 50 C	6 to 30	118	Agarwal /44/
-R11	-70 to 20 C	0 to 100	130	Kriebel /45/
	-60 to 0 C	0 to 100	4	Bougard /41/
	29 C	25 / 45	2	Bougard /2/
-R113	25 to 100 C	0 to 100	123	Meskel-Lesavre /46/
R13B1-R22	-20 to 30 C		24	Kuznecov /47/
-R12	-18 to 54 C	0 to 100	9	White /48/
-12-152a	-50 to 90 C	20-60-20	9	White /48/
-12-142b	-18 to 54 C	51-11-28	3	DuPont /49/
-R152a	-18 to 54 C	0 to 100	31	Connon /50/
-R142b	-18 to 54 C	10 to 50	9	DuPont /49/
R143a-R12	-70 to 40 C	0 to 100	72	Geller /42/
R22-R115	-58 to 33 C	-	53	Hinrichsen /51/
-R12	4 to 54 C	25 / 75	116	White /52/
	27 C	10 to 85	-	Whipple /53/
	-20 to 70 C	0 to 100	70	Spauschus /54/
	-60 to 70 C	0 to 100	196	Kriebel /55/
	-60 to 0 C	0 to 100	4	Bougard /41/
	27 C	25/45/59	3	Bougard /2/
	37 to 143 C	20	203	Taikaishi /56/
	69 to 143 C	13 to 80 (graph)	164	Taikaishi /7/
-R12-R142b-15	to 0 C	20-10-70	18	Morrison /57/
-R12-R11	-18 to 54 C	53-25-22	5	DuPont /50/
-R12-R114	10 to 60 C	62- 8- 30	6	Morrison /57/
-R142b	-16 to 49 C	50	4	DuPont /50/
-RC318	27 C	15 to 85	6	Whipple /53/
-R114	-30 to 60 C	0 to 100	curvefit	Kraus /58/
	-20 to 60 C	0 to 100	36	Kruse /59/
-R11	20 to 100 C	15 to 85	29	Meskel-Lesavre /31/
R218-R152a	-60 to 40 C	0 to 100	24	Kuznecov /60/
R12-R152a	0 C	5 to 91	17	Pennington /61/
-R142b	30 to 90 C	16 to 86	4	Lavrenchenco /62/
-RC318	-30 to 100 C	0 to 100	56	Kuznecov /63/
	-30 to 97	0 to 100	252	Kuznecov /64/
	27 C	15 to 85	6	Whipple /53/
-R114	20 to 60 C	15 to 85	10	DuPont /27/
	0 to 60 C	46 / 70	39	Kruse /59/
-R11	29 C	25 / 75	2	Bougard /2/
	10 to 87 C	70 / 92	6	Kruse /15/
	-20 to 90 C	0 to 100	66	Loi /65/
-R113	-30 to 60 C	0 to 100	curvefit	Kraus /58/
R152a-R12B1	50 to 65 C	10/25/30	21	Volobuev /66/
R114-R21	-35 to 65 C	-	56	Hinrichsen /50/

For mixtures, the "Van Laar" mixing rules

$$a_m = \sum_i \sum_j x_i x_j a_{ij} \quad \text{and} \quad b_m = \sum_i x_i b_i \quad (9)$$

where

$$a_{ii} = a_i, \quad a_{jj} = a_j, \quad a_{ij} = a_{ji} = (1 - k_{ij})(a_i a_j)^{0.5}$$

have been applied to calculate the attraction force constant "a" and the volume "b". Prausnitz /36/ pointed out the importance of having the "real" value for "b" (instead of a fitting parameter without physical significance) to obtain the desired accuracy for the mixture, especially if the volumes vary greatly. However, for halogenated hydrocarbon refrigerants and their mixtures, equations (8) and (9) were applied with satisfactory results, if the binary interaction parameter k_{ij} was known from experimental data. A complete description of the equation is given by Morrison and McLinden /37/.

TABLE II

COMPARISON OF EQUILIBRIUM DATA (FENNINGTON, 1950) AND CALCULATIONS FOR THE REFRIGERANT 12/ 152a MIXTURE

C	T (F)	X mol-ffrac	P _{exp} kPa	P _{exp} psia	P _{calc} psia	P _{dev} %	Y _{exp} mol.-frac.	Y _{calc} mol.-frac.	Y _{dev} %
0.	(32)	0.0568	293.8	41.60	42.37	1.81	0.0988	0.1092	9.53
0.	(32)	0.1200	315.8	44.50	44.83	-0.70	0.1833	0.2031	9.76
0.	(32)	0.1833	330.9	46.90	46.82	-0.18	0.2584	0.2776	2.40
0.	(32)	0.2648	345.1	49.14	48.86	-0.58	0.3458	0.3543	2.40
0.	(32)	0.3534	355.0	50.80	50.32	-0.96	0.4185	0.4223	0.89
0.	(32)	0.4473	361.97	51.97	51.76	-0.40	0.4987	0.4843	-3.07
0.	(32)	0.5359	363.7	53.63	53.40	-0.06	0.5696	0.5523	-3.13
0.	(32)	0.6184	363.7	55.99	55.99	0.00	0.6306	0.6680	5.97
0.	(32)	0.6949	363.7	59.72	59.72	0.00	0.6007	0.5757	-4.33
0.	(32)	0.7683	363.7	64.72	64.72	0.00	0.6045	0.5923	-2.35
0.	(32)	0.8203	363.7	71.71	71.73	0.00	0.6098	0.5909	-4.61
0.	(32)	0.8326	363.7	76.2	76.2	0.00	0.6147	0.5909	-4.04
0.	(32)	0.8385	363.7	81.90	81.61	-0.31	0.6259	0.6360	1.82
0.	(32)	0.7557	335.0	51.95	52.08	0.23	0.7160	0.6862	-4.35
0.	(32)	0.8307	346.0	50.77	50.89	0.24	0.7751	0.7532	-2.91
0.	(32)	0.9120	332.0	48.74	48.64	-0.21	0.8665	0.8482	-2.15

COMPARISON OF EQUILIBRIUM DATA (CONNOR, 1981) AND CALCULATIONS FOR THE REFRIGERANT 13B1/ 152a MIXTURE

C	T (F)	X mol-ffrac	P _{exp} kPa	P _{exp} psia	P _{calc} psia	P _{dev} %	Y _{calc} mol-ffrac
-17.	B (0)	0.2491	313.0	43.96	43.78	-0.42	0.6177
-17.	B (0)	0.4985	329.8	57.36	57.83	0.49	0.7555
-17.	B (0)	0.7483	448.6	65.43	65.89	0.58	0.8469
-17.	B (0)	0.9277	343.6	47.36	48.74	2.88	0.9750
-17.	B (0)	0.3956	363.7	52.46	52.41	-0.10	0.7118
-17.	B (0)	0.5034	393.9	57.16	57.28	0.21	0.7573
-17.	B (0)	0.6370	423.8	61.95	62.27	0.51	0.8051
-17.	B (0)	0.7974	439.5	66.74	67.23	0.70	0.8681
-17.	B (0)	0.9343	479.0	70.26	70.26	0.00	0.9458
-17.	B (0)	0.9774	486.0	71.05	70.78	-0.39	0.9796
54.	0 (77)	0.2475	1034.3	150.10	147.46	-1.80	0.4826
54.	0 (77)	0.4959	1293.6	189.36	188.72	-0.45	0.6724
54.	0 (77)	0.7465	1481.7	218.36	218.95	0.27	0.8136
54.	4 (130)	0.2440	1991.7	291.40	287.34	-1.41	0.4048
54.	4 (130)	0.4932	2468.7	363.47	362.06	-0.39	0.6164
54.	4 (130)	0.7448	2836.2	416.42	421.38	1.18	0.7890

COMPARISON OF EQUILIBRIUM DATA (WRITE, 1985) AND CALCULATIONS FOR THE REFRIGERANT 13B1/ 12 MIXTURE

C	T (F)	X mol-ffrac	P _{exp} kPa	P _{exp} psia	P _{calc} psia	P _{dev} %	Y _{calc} mol-ffrac
-17.	B (0)	0.25	244.8	35.50	36.02	1.44	0.4848
-17.	B (0)	0.50	328.9	47.70	47.68	-0.04	0.7281
-17.	B (0)	0.75	409.6	59.40	59.18	-0.36	0.8837
54.	0 (77)	0.25	873.6	126.70	126.39	-0.25	0.4068
54.	0 (77)	0.50	1108.0	160.70	160.15	-0.34	0.6664
54.	0 (77)	0.75	1354.1	196.40	196.04	-0.18	0.8527
54.	4 (130)	0.25	1725.1	250.20	250.08	-0.03	0.3619
54.	4 (130)	0.50	2130.5	309.00	309.38	0.12	0.6223
54.	4 (130)	0.75	2584.8	374.90	375.88	0.25	0.8252

4. EXPERIMENTAL PROPERTIES OF MULTI-COMPONENT REFRIGERANTS

The thermodynamic properties of multi-component refrigerants were experimentally determined to support the analysis on refrigeration systems operating with fluid mixtures. The applications range from cryogenic to high-temperature waste-heat recovery systems, which explains the large number of refrigerant combinations analysed, are listed in table I. Although ternary mixtures offer a large potential for matching desired properties, only a few have been analyzed thermodynamically. Write /48/ published data on the ternary mixture R13B1/R12/R152a, which was chosen as the reference mixture for applying the Carnahan-Starling-DeSantes (CTD) equation of state. Table II shows the comparison for the binary mixtures involved and table III shows the comparison of the ternary mixture. The equation is remarkably accurate in predicting both the vapor pressure and the liquid volume of the mixtures, although the deviation in the vapor concentration seems to be large. But, since this value is based on the composition of the individual components, the relative error at small concentrations increases (see the R12/R152a mixture). The liquid volumes of the ternary mixtures are predicted within 1% to 3%, demonstrating the superiority over other Van-der-Waals modifications.

TABLE III

COMPARISON OF EQUILIBRIUM DATA (WRITE, 1985) AND CALCULATIONS FOR THE REFRIGERANT 13B1/ 12/ 152a MIXTURE

T (F)	X mol-frac	kPa	Pexp psia	Pcalc psia	Pdev %	Yexp mol.-frac.	Ycalc	Ydev %
-17.8 (0)	0.4510 0.0881 0.4609	363.4	52.70	53.45	1.41	0.6808 0.0614 0.2578	0.7077 0.0481 0.2442	3.80 -2.49 -5.56
25.0 (77)	0.4456 0.0883 0.4661	1223.8	177.50	178.16	0.37	0.6020 0.0701 0.3209	0.6206 0.0586 0.3209	2.99 -19.70 -2.20
54.4 (130)	0.4502 0.0877 0.4621	2347.7	340.50	345.49	1.44	0.5687 0.0731 0.3582	0.5705 0.0657 0.3638	0.32 -11.31 1.54
-17.8 (0)	0.1436 0.5273 0.3291			35.21	-	0.2769 0.4219 0.2812	0.3023 0.4042 0.2935	1.79 -4.39 4.21
25.0 (77)	0.1411 0.5257 0.3332			128.28	-	0.2366 0.4492 0.3143	0.2361 0.4373 0.3266	-0.20 -2.72 3.72
54.4 (130)	0.1402 0.5281 0.3316			257.89	-	0.2089 0.4657 0.3255	0.2039 0.4608 0.3352	-2.46 -1.06 2.90
-20.0 (-4)	0.1439 0.5317 0.3244	221.3	32.10	32.53	1.33		0.3044 0.4045 0.2891	- - -
10.0 (50)	0.1439 0.5317 0.3244	597.9	86.70	85.32	-1.61		0.2587 0.4291 0.3122	- - -
50.0 (122)	0.1439 0.5317 0.3244	1646.5	238.80	234.45	-1.85		0.2130 0.4590 0.3250	- - -
70.0 (158)	0.1439 0.5317 0.3244	2509.0	363.90	357.03	-1.93		0.1938 0.4754 0.3307	- - -
90.0 (194)	0.1439 0.5317 0.3244	3685.9	534.60	520.28	-2.75		0.1741 0.4956 0.3303	- - -

COMPARISON OF EQUILIBRIUM DATA (WRITE, 1985) AND CALCULATIONS FOR THE REFRIGERANT 13B1/12/152a MIXTURE

T (F)	X1	X2	X3	Pcalc (psia)	Vl exp (l/kg)	Vl calc (cuft/mol)	Vl dev %	Ycalc	Y2 calc	Y3 calc	
-50.0 (-58)	0.1439	0.3317	0.3244	9.52	0.6826	1.1716	1.1887	1.44	0.3744	0.3721	0.2535
-25.0 (-13)	0.1439	0.3317	0.3244	27.08	0.7180	1.2324	1.2510	1.49	0.3163	0.3998	0.2841
0.0 (32)	0.1439	0.3317	0.3244	63.35	0.7686	1.3034	1.3280	1.70	0.2729	0.4214	0.3037
25.0 (77)	0.1439	0.3317	0.3244	128.35	0.8089	1.3884	1.4292	3.26	0.2598	0.4403	0.3199
50.0 (122)	0.1439	0.3317	0.3244	234.43	0.8834	1.5161	1.5748	3.72	0.2130	0.4590	0.3280
70.0 (158)	0.1439	0.3317	0.3244	357.03	0.9548	1.6902	1.7399	3.74	0.1938	0.4754	0.3307
90.0 (194)	0.1439	0.3317	0.3244	520.28	1.1808	2.0262	2.0879	3.96	0.1741	0.4956	0.3303
					Vl exp	Vl calc	Vl dev				
29.8 (85.6)	0.1439	0.3317	0.3244	145.34	21.38	36.6900	32.7168	-12.14	0.2343	0.4438	0.2219
37.0 (125.1)	0.1439	0.3317	0.3244	274.98	10.32	17.7100	18.4758	-7.49	0.2059	0.4647	0.2394
82.4 (188.9)	0.1439	0.3317	0.3244	463.39	4.927	8.4370	8.4666	0.31	0.1805	0.4817	0.3508
92.7 (200.6)	0.1439	0.3317	0.3244	534.89	3.396	3.8290	4.4197	9.20	0.1700	0.5001	0.3299

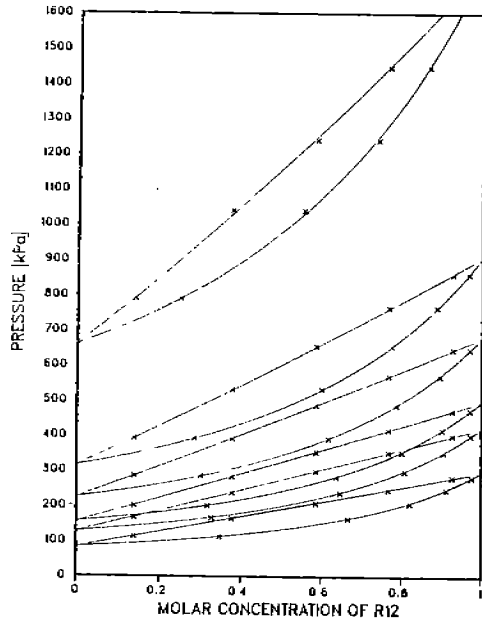
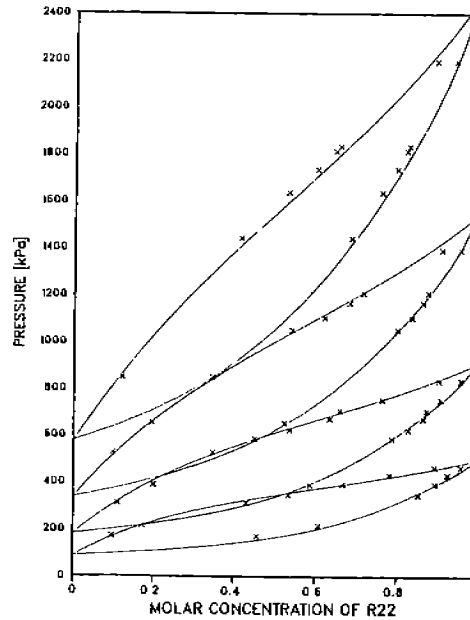
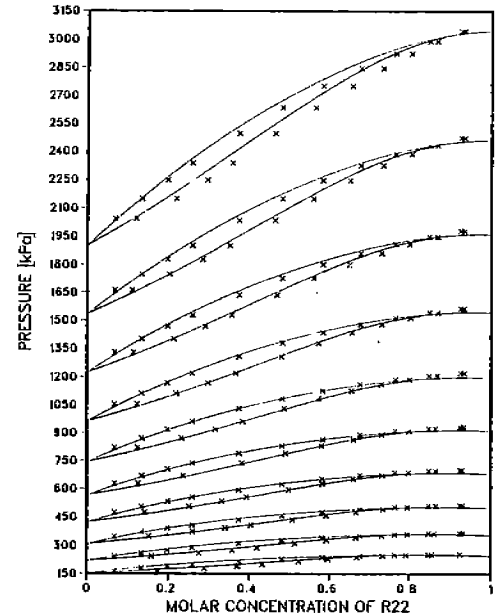
EQUILIBRIUM DIAGRAM FOR THE
R12/R114 MIXTUREEQUILIBRIUM DIAGRAM FOR THE
R22/R114 MIXTUREEQUILIBRIUM DIAGRAM FOR THE
R22/R12 MIXTURE

Fig. 2 - Comparison of vapor-liquid-equilibrium calculations with experimental data.

The individual components, as well as each binary pair of the ternary mixture R114/R12/R22, are of high importance to refrigeration and heat-pump technology. Therefore, the representation of this mixture with the CSD equation of state seems appropriate. The results of the correlation for the binary mixtures is shown in figure 2, where for each pair a pressure-concentration diagram is plotted. For the R12/R22 mixture at high temperatures (70 C), the equilibrium curve shows some deviation from the experimental data. This temperature may not be reached for heat-pump applications. The ternary data, shown in table IV, are limited to about 60 C. As for the R13B1/R12/R152a mixture, the agreement between the measured and calculated data is satisfactory. An attempt to improve the results by adding an other "ternary constant" $f(3)$ to the Van Laar mixing rules, did not succeed.

TABLE IV

COMPARISON OF EQUILIBRIUM DATA AND CALCULATIONS FOR THE REFRIGERANT 114/ 12/ 22 MIXTURE with $f(3)=0$.																
C	T	F	X1	X2	X3	P _{exp}	P _{calc}	P _{dev}	V _{exp}	V _{calc}	V _{dev}	Y _{calc}	Y _{2calc}			
			molar fraction	molar fraction	molar fraction	MPa	MPa	%	ccm/mol	cuft/mol	%	molar fraction	molar fraction			
9.933	49.88	.6536	.0717	.2746	.346	3	30.23	54.15	7.25	101.10	1.6195	1.6508	1.90	0.2598	0.0822	0.6619
34.897	94.81	.6536	.0717	.2746	.678	2	98.36	102.98	4.48	106.63	1.7084	1.7555	2.68	0.3162	0.0842	0.5994
59.877	139.78	.6536	.0717	.2746	1191.6	172.83	178.48	3.17	114.43	1.8330	1.8930	3.17	0.3769	0.0847	0.5982	
9.933	49.88	.5873	.0862	.3265	.394	0	57.14	58.79	2.80	100.49	1.6097	1.6123	0.16	0.2174	0.0929	0.6897
34.897	94.81	.5873	.0862	.3265	.736	7	109.75	111.96	1.98	106.47	1.7055	1.7178	0.72	0.2695	0.0934	0.6391
59.877	139.78	.5873	.0862	.3265	1215.3	190.77	193.94	1.64	113.62	1.8200	1.8579	2.04	0.3236	0.0946	0.5798	

COMPARISON OF EQUILIBRIUM DATA AND CALCULATIONS FOR THE REFRIGERANT 114/ 12/ 22 MIXTURE with $f(3)=-0.0044$																
C	T	F	X1	X2	X3	P _{exp}	P _{calc}	P _{dev}	V _{exp}	V _{calc}	V _{dev}	Y _{calc}	Y _{2calc}			
			molar fraction	molar fraction	molar fraction	MPa	MPa	%	ccm/mol	cuft/mol	%	molar fraction	molar fraction			
9.933	49.88	.6536	.0717	.2746	.346	3	30.23	53.18	5.33	101.10	1.6195	1.6391	2.39	0.2542	0.0822	0.6635
34.897	94.81	.6536	.0717	.2746	.678	2	98.36	101.28	2.88	106.63	1.7084	1.7668	2.30	0.3146	0.0843	0.6010
59.877	139.78	.6536	.0717	.2746	1191.6	172.83	175.74	1.66	114.43	1.8330	1.9096	4.01	0.3753	0.0848	0.5998	
9.933	49.88	.5873	.0862	.3265	.394	0	57.14	57.70	0.96	100.49	1.6097	1.6211	0.70	0.2159	0.0928	0.6913
34.897	94.81	.5873	.0862	.3265	.736	7	109.75	110.06	0.28	106.47	1.7055	1.7298	1.41	0.2678	0.0934	0.6368
59.877	139.78	.5873	.0862	.3265	1215.3	190.77	190.88	0.06	113.62	1.8200	1.8759	2.98	0.3216	0.0946	0.5814	

5. CONCLUSION

Based on the molecular behavior, the existence of azeotropic mixtures has been explained, with the insight that a suitable equation of state is needed to analyze vapor-compression refrigeration systems operating with a mixture of refrigerants. Available equations of state applied to refrigerant mixtures have been cited. Best results are obtained with the Carnahan-Starling-DeSantis equation of state. A list of mixtures, analyzed thermodynamically, is presented, of which two ternary fluids were correlated. The agreement between the calculated and measured data is satisfactory.

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PROPRIÉTÉS THERMODYNAMIQUES DES RÉFRIGÉRANTS DE COMPONENTS MULTIPLES

RÉSUMÉ: Récemment, plus d'attention a concentré sur l'utilisation des mélanges de hydrocarbons haloginées dans des systemes frigorifiques a compression de vapeur, par exemple, les pompes de chaleur. Ce document discute le mélange des fluides et leur caractère non-idéal qui est apprimé par des formules d'état differents. Les types des formules developées dans la siècle passée et appliquées aux fluides frigorifiques et leurs mélanges sont démontrées. Le meilleur formule d'état: la modification De Santis du model "hard-sphere" de Carnahan et Starling est utilisée pour corréler les points équilibres des états liquides et vapeurs pour un nombre des mélanges frigorifiques sélectionnées d'une table de combinaisons des fluides. Enclus est une table des mélanges ternaires basée sur des points d'équilibre binaire, avec une proposition d'incorporer un coefficient ternaire afin de mieux écrire les résultats experimentals.

ABSTRACT

In recent years, increasing attention has been focused on the use of halogenated hydrocarbon mixtures as working fluids in vapor compression refrigeration systems, e.g. heat pumps. This paper discusses phase rules, applied to the equilibrium of the vapor and liquid states of such mixtures. Mixtures of ideal behavior, those that obey Raoult's law, and those with deviations from the law are included. Their behavior may analytically be approximated by different equations of state developed during the past century. An overview on the type of equations is given along with experimental data they approximated. Those equilibrium data are summarized to a table of investigated binary fluid mixtures. A selection of them were correlated with the De Santes equation of state. This equation predicts both the vapor and liquid volumes with satisfactory accuracy up to the vicinity of the critical point. Thermodynamic properties of ternary fluid mixtures, comprised of the correlated binaries, are simulated with the De Santes equation of state and compared with experimental data. Mixing rules are reviewed and suggestions of incorporating a coefficient for the ternary mixture are made to fit the experimental data better.