

THERMODYNAMIC PROPERTIES OF THE FC218-HFC134a REFRIGERANT MIXTURE

V. N. Anisimov, V. P. Zheleznyi,
Yu. V. Semenyuk, and Yu. A. Chernyak

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Phase equilibria and thermal properties of the FC218-HFC134a mixture have been experimentally studied. A cubic equation of state describing the experimental data obtained is given. Tables of thermodynamic parameters of the mixture in the state of liquid-vapor phase equilibrium are calculated.

Replacement of ozone-destructive substances by alternatives is a complicated problem due to contradictory requirements imposed on working media of refrigeration plants and heat pumps from the viewpoint of ecology (allowance for possible global warming and destruction of the ozone layer), energy efficiency, heat-transfer intensity, fire safety, compatibility of structural materials, solubility in oils, and so on. Under these conditions it is expedient to use mixtures consisting of ozone-safe refrigerants with purposeful combination of the favorable properties of their components. In this respect, the use of azeotropic mixtures as working media, whose energy efficiency is, as a rule, higher than that of pure components, is most promising [1]. Moreover, refrigeration plants operating on azeotropic mixtures are easier to service, and the energy characteristics of those plants are distinguished by higher stability than those that use zeotropic compositions.

With the aim of searching for new ecologically pure and energy-efficient working media we have investigated the phase-equilibrium parameters of the FC218-HFC134a mixture. For this, an experimental setup was used that realized the variable-volume piezometer method. The design of the setup and the measurement procedure are similar to those described in [2].

The pressure in the piezometer was measured by MP-60 and MP-6 dead-weight pressure-gauge testers, class 0.05. As a medium for pressure transfer, we used mercury, whose level in the measuring cell was determined by a KM-8 cathetometer. The calibration error for the piezometer volume did not exceed 0.06%. Temperature was measured by a PTS-10 standard platinum resistance thermometer complete with an R348 potentiometer, class 0.002, and an R321 standard wire resistor class 0.01, using a compensation scheme with an error of 0.015 K. The purities of the mixture components were 99.8% for the FC218 and 99.9% for the HFC134a.

We measured p, v, T of the FC218-HFC134a mixture in the state of the liquid-vapor equilibrium for 14 compositions at temperatures of from 270 to 332 K over the entire concentration range. The unexcluded remainders of the systematic error did not exceed 0.15% for pressure, 0.2% for liquid and vapor density, and $0.3 \cdot 10^{-4}$ mole/mole for mixture concentration.

To describe the experimental data, we used the following equation of state:

$$p = RT \left(\frac{1}{v-b} - \frac{a}{v(v+c)} \right), \quad (1)$$

where $a, b,$ and c are coefficients determined by the following combination rules:

$$a = X_1^2 a_1 + 2X_1 X_2 k_a (a_1 a_2)^{0.5} + X_2^2 a_2, \quad b = X_1^2 b_1 + 2X_1 X_2 k_b (b_1 b_2)^{0.5} + X_2^2 b_2,$$

$$c = X_1^2 c_1 + 2X_1 X_2 k_c (c_1 c_2)^{0.5} + X_2^2 c_2,$$

TABLE 1. The Coefficients of Eqs. (2), (3), and (4) and Critical Parameters of the Mixture Components

Composition	Value										
	g_0	g_1	g_2	g_3	α_R	A	B	β	T_{cr}, K	p_{cr}, MPa	$\rho_{cr}, kg/m^3$
FC218	0.045	0.06336	0.2392	0.72	7.4446	6.8456	1.6623	0.3297	345.05	2.6707	628
HFC314a	0.027	0.045	0.355	0.534	7.4029	6.2822	1.7198	0.3282	374.25	4.06	509

where $a_1, b_1, c_1, a_2, b_2,$ and c_2 are the coefficients of the equations of state of type (1) for the mixture components; X_1 and X_2 are the molar compositions of the components.

The experimental data were adequately described by the following temperature dependences of the parameters of binary interaction:

$$k_a = 0.8325 + 0.2 ((290 - T)/300)^2 + \omega_1 (X_2 - 0.38),$$

$$\omega_1 = 0.113 + 0.01 (310 - T)/30 \quad \text{at } X_2 \leq 0.38,$$

$$\omega_1 = 0.05 + 0.003 (310 - T)/30 \quad \text{at } X_2 > 0.38;$$

$$k_b = 0.951 + \omega_2 (X_2 - 0.38),$$

$$\omega_2 = 0.12 \quad \text{at } X_2 \leq 0.38;$$

$$\omega_2 = 0.054 - 0.6 ((315 - T)/300)^2 \quad \text{at } X_2 > 0.38.$$

The expression for the temperature dependence of the coefficients b_i is of the form:

$$b = g_0 + g_1 \left(\frac{T_{cr}}{T} - 1 \right)^{g_2} \exp \left(-g_3 \left(\frac{T_{cr}}{T} - 1 \right) \right), \quad (2)$$

where g_i are coefficients determined by processing the published data [3, 4] on the saturated-vapor pressure and density on the boiling and condensation lines.

The coefficients a_i and c_i were determined for each temperature from the phase-equilibrium conditions using data on the saturated-vapor pressure p_s , density of boiling liquid ρ' , and coefficient b calculated by Eq. (2). Values of p_s and ρ' were calculated with the aid of the following equations [5]

$$\ln (p_{cr}/p_s) = \alpha_R t + A t^{2.64}, \quad (3)$$

$$\ln (\rho'/\rho_{cr}) = B t \left(1 - 1.113 \frac{t}{\ln t} \right)^{0.4}, \quad (4)$$

where $t = \ln (T_{cr}/T)$; $\alpha_R, A, B,$ and β are coefficients obtained by approximating the data of [3, 4]. It should be noted that B and β coincide in their meaning with the critical amplitude and index, respectively, and Eq. (4) describes ρ' adequately in the range from the triple to the critical point.

The coefficients of Eqs. (2)-(4) and critical parameters of the components are given in Table 1.

Deviations of the pressures and densities of the mixture on the line of the liquid-vapor phase equilibrium calculated by Eq. (1) from experimental data are shown in Fig. 1.

To calculate the enthalpy and entropy of the mixture, we used the relations

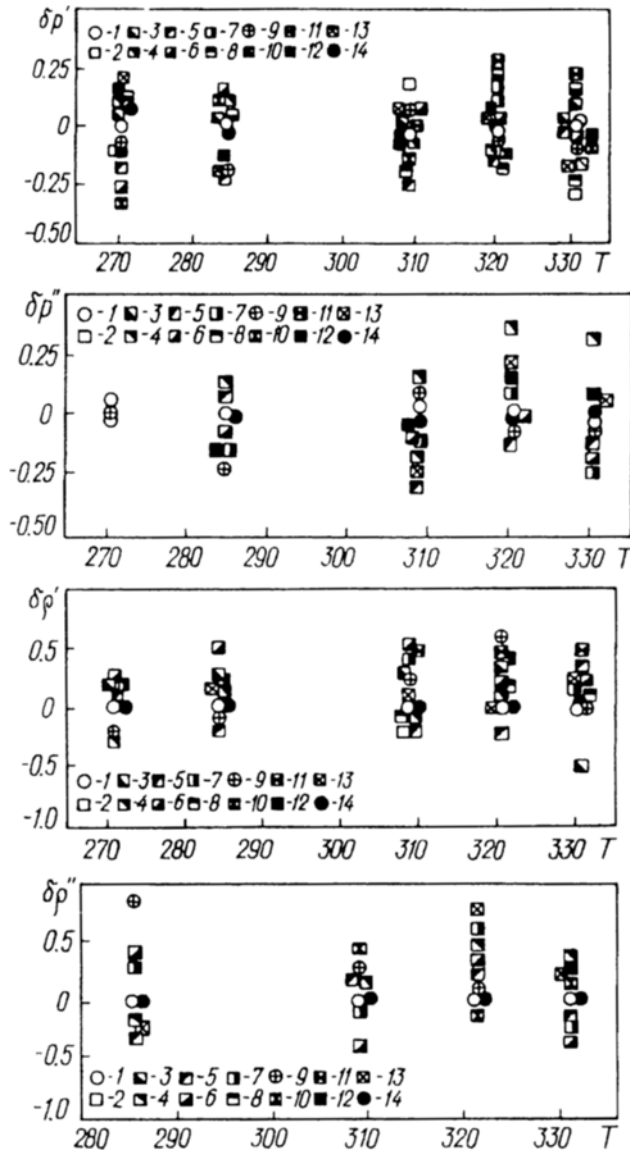


Fig. 1. Deviations of values calculated by Eq. (1) from experimental data: 1) $X = 0$ (FC218); 2) 0.1164; 3) 0.2571; 4) 0.2661; 5) 0.3523; 6) 0.3580; 7) 0.3661; 8) 0.3752; 9) 0.4050; 10) 0.4194; 11) 0.5382; 12) 0.6601; 13) 0.7513; 14) 1.0 (HFC134a).

$$h = \sum_{i=1}^2 X_i h_i^0 + RT \left(\frac{b}{v-b} + \frac{a}{v+c} + \frac{T}{c} \frac{da}{dT} \ln \left(1 + \frac{c}{v} \right) \right),$$

$$s = \sum_{i=1}^2 X_i (s_i^0 - R \ln (X_i RT)) + R \left(\ln (v-b) + \frac{1}{c} \left(a + T \frac{da}{dT} \right) \ln \left(1 + \frac{c}{v} \right) \right),$$

where h^0 , s^0 are the ideal gas functions determined by the method described in [6].

The derivative da/dT was determined by the expression

$$\frac{da}{dT} = X_1^2 \frac{da_1}{dT} + 2X_1 X_2 \sqrt{\left(\frac{da_1}{dT} \frac{da_2}{dT} \right)} + X_2^2 \frac{da_2}{dT}.$$

TABLE 2. Thermodynamic Properties of the FC218-HFC134a Mixture in the State of Phase Equilibrium

X_1 , mole/mole	p' , MPa	ρ' , kg/m ³	h' , kJ/(kg·K)	s' , kJ/(kg·K)	p'' , MPa	ρ'' , kg/m ³	h'' , kJ/(kg·K)	s'' , kJ/(kg·K)
T = 220 K								
0.2	0.0529	1654.5	344.5	3.771	0.0507	4.89	466.7	4.322
0.4	0.0543	1615.9	353.7	3.788	0.0527	4.56	482.8	4.386
0.6	0.0513	1581.8	353.3	3.783	0.0383	2.92	503.3	4.489
0.8	0.0455	1533.1	345.0	3.760	0.0302	2.00	529.5	4.615
T = 240 K								
0.2	0.1392	1572.7	367.5	3.860	0.1336	12.16	480.3	4.335
0.4	0.1427	1539.3	374.5	3.879	0.1419	11.59	496.2	4.392
0.6	0.1365	1506.8	374.9	3.877	0.1112	7.94	516.8	4.484
0.8	0.1227	1461.9	369.0	3.861	0.0885	5.47	543.0	4.601
T = 260 K								
0.2	0.3068	1484.4	390.6	3.956	0.2957	25.45	493.8	4.354
0.4	0.3147	1455.6	396.3	3.967	0.3144	24.77	509.5	4.406
0.6	0.3033	1425.5	397.7	3.969	0.2651	18.16	530.1	4.488
0.8	0.2742	1385.9	393.9	3.960	0.2140	12.61	556.4	4.596
T = 280 K								
0.2	0.5944	1386.6	414.0	4.041	0.5759	50.23	507.0	4.374
0.4	0.6099	1361.8	419.3	4.053	0.6100	47.67	522.5	4.422
0.6	0.5907	1335.6	421.8	4.058	0.5436	36.72	543.0	4.496
0.8	0.5359	1303.5	420.0	4.055	0.4479	25.77	569.4	4.597
T = 300 K								
0.2	1.0469	1274.7	438.2	4.123	1.0210	91.89	519.3	4.394
0.4	1.0751	1252.2	443.8	4.136	1.0752	86.54	534.5	4.439
0.6	1.0441	1232.6	447.3	4.146	0.9936	68.54	554.8	4.506
0.8	0.9498	1211.7	447.3	4.148	0.8383	48.53	581.4	4.601
T = 320 K								
0.2	1.7202	1138.4	463.8	4.204	1.6906	168.22	529.2	4.399
0.4	1.7671	1112.9	470.5	4.221	1.7671	156.43	544.2	4.437
0.6	1.7181	1106.6	474.9	4.234	1.6693	123.89	564.8	4.509
0.8	1.5658	1105.3	476.2	4.240	1.4408	87.33	591.6	4.601
T = 340 K								
0.2	2.6928	945.1	493.5	4.292	2.6727	359.08	529.9	4.399
0.4	2.7704	887.8	503.6	4.319	2.7703	326.49	544.0	4.437
0.6	2.6896	922.7	507.7	4.330	2.6515	243.56	568.8	4.509
0.8	2.4515	969.4	508.4	4.336	2.3284	157.95	598.5	4.601

Since the temperature dependence of the coefficients a_i was not available in analytical form, the derivatives da_i/dT were calculated by a formula obtained for the enthalpy difference $h'' - h'$ that was derived with the aid of the equation of state of type (1):

$$\frac{da_i}{dT} = \frac{c}{T \ln \left(\frac{1 - c/v^*}{1 + c/v'} \right)} \times \left(\frac{T(v^* - v') (dp_s/dT)}{RT} - \frac{b}{v^* - b} + \frac{a}{v^* + c} + \frac{b}{v' - b} - \frac{a}{v' + c} \right).$$

The suggested three-constant equation of state of the mixture (1) and the described procedure for determination of its coefficients make it possible to describe experimental data with a higher accuracy than the van der Waals equations, which are widely used for this purpose. Moreover, our method used to calculate h and s ensures thermodynamic consistency of thermal and caloric quantities.

The conducted experimental and theoretical studies of the FC218-HFC134a mixture have produced reliable values of its thermodynamic properties in the state of the liquid-vapor phase equilibrium (Table 2). An azeotropic composition equal to 0.405 molar fractions of the HFC134a is determined. It is established that this composition does not change, in fact, in the range of $220 \text{ K} < T < T_{cr}$.

The above information can be used as a basis for further scientific and engineering developments aimed at incorporating the FC218-HFC134a mixture as a working medium for certain refrigeration plants and heat pumps.

NOTATION

p , pressure, MPa; T , temperature, K; v , molar volume, m^3/kmole ; R , gas constant, $\text{kJ}/(\text{kg}\cdot\text{K})$; a , b , c , coefficients of the equation of state; X , mixture composition, mole/mole; k_a , k_b , parameters of binary interaction; p_s , saturated-vapors pressure; ρ' , liquid density on saturation line; h , enthalpy; s , entropy; p' , v' , h' , s' , parameters on boiling line; p'' , v'' , h'' , s'' , parameters on condensation line; T_{cr} , P_{cr} , ρ_{cr} , critical parameters.

REFERENCES

1. G. Morrison, M. Q. McLinden, Azeotropy in refrigerant mixtures, *Int. J. Ref.*, 16, No. 2, 129-138 (1993).
2. Yu. M. Aften'ev, in: *Thermophysical Properties of Substances and Materials [in Russian]*, Collected Works, Issue 15 (1980), pp. 115-123.
3. A. V. Dobrokhotov, V. P. Zheleznyi, A. V. Maslennikov, Yu. V. Semenyuk, and E. E. Ustyuzhanin, *Kholod. Tekh.*, No. 7, 12-16 (1991).
4. Octafluoropropan (Refrigerant R218), *Thermodynamic Properties at Temperatures from 190 to 430 K and Pressures from 0.01 to 50 MPa. Tables of Standard Reference Data [in Russian]*, Moscow (1990).
5. V. P. Zheleznyi, D. A. Vladimirov, O. P. Ponomareva, et al., in: *Abstracts of the All-Union Scientific-Technical Conference "Cold in the Service of the National Economy," Leningrad (1991)*, pp. 5
6. I. I. Perel'shtein and E. V. Parushin, *Thermodynamic Properties of the Working Media of Refrigeration Plants and Heat Pumps [in Russian]*, Moscow (1984).