# AN EXPERIMENTAL STUDY OF HEAT CAPACITY OF THE AZEOTROPIC MIXTURE HFC23/FC116[1]

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**ABSTRACT**

The specific heat capacity of azeotropic mixture HFC23/FC116 (64/36 mol.%) were measured by adiabatic calorimeter method along 3 isochores in the temperature range from 175 K to 266 K. Uncertainties of the experimental data did not exceed 0.15 %. The heat capacity of the mixture at the saturation was determined and its temperature dependence was established. Caloric properties on the liquid-vapor coexistence curve were calculated. The paper presents the experimental data on isochoric heat capacity of the mixture HFC23/FC116 (64/36 mol.%), equation of state for liquid phase and functional relations of thermodynamic properties on the saturation line.

KEY WORDS: alternative refrigerants, heat capacity, mixture, thermodynamic properties

## 1. INTRODUCTION

Manufacturing and consumption of ozone-depleting refrigerants R12, R13, R22, R503, etc. is strongly regulated by Montreal Protocol. Hundreds of papers concerning thermodynamic properties of replacements were published for the last several years. However the problem of developing alternative low-temperature refrigerants (normal boiling temperature is in an interval 180-190 K) does not solved yet. Applying environmentally safe R170 (ethane) as a refrigerant is extremely limited due to its flammability. Mixture HFC23/FC116, as a potential alternative for low-temperature applications, were recently under investigation [1-6]. Two new refrigerants introduced by ICI and DuPont are R508A (HFC23/FC116, 39/61 wt.%) and R508B (HFC23/FC116, 46/54 wt.%), respectively.

Study of phase equilibrium and thermodynamic properties of the mixture HFC23/FC116 was started at the Odessa State Academy of Refrigeration in 1990 [1-3] and recently was continued [4, 5]. Obtained results show temperature dependence of azeotropic concentration of the mixture from 39 mol.% (FC116) at 180 K to 33 mol.% at 285 K. However, experimental data on caloric properties of mixture HFC23/FC116 were not available that caused difficulties in developing thermodynamically consistent equation of state in a wide range of thermodynamic parameters.

## 2. EXPERIMENTAL RESULTS AND CALCULATIONS

Study of isochoric heat capacity of the mixture HFC23/FC11 (64/36 mol.%) were carried out by adiabatic calorimeter method with direct heat transference at the commercial experimental apparatus UNTO. Design of the apparatus and experimental technique are described in details in [7]. Design of the present apparatus was improved by using microvalve for loading the measurement cell out of the calorimetric system. Relatively low ratio of heat capacity of the cell and investigated sample, and additional adiabatic conditions

significantly improved the accuracy of the experimental data. The methodology of analysis of the experimental uncertainties considered in [7, 8] were used to estimate the accuracy of our data on heat capacity. The uncertainty of $C_S$ in the present measurements did not exceed 0.15 %. The calibration of the experimental apparatus and its reliability was confirmed by measurements of heat capacity of propane and RC-318 and comparing obtained results with corresponding equation of states [9, 10].

The purity of the components of mixture sample were 99.79 mol.% for HFC23 and 99.80 mol.% for FC116. Before loading the sample was properly degassed.

The measurements of isochoric heat capacity were performed along 3 isotherms $V_1$(293.15 K)=1.3640 $10^{-3}$ $m^3kg^{-1}$ (169≤T≤272.15 K), $V_2$(293.15 K)=1.4257 $10^{-3}$ $m^3kg^{-1}$ (169≤T≤251.15 K) and $V_3$(293.15 K)=1.7948 $10^{-3}$ $m^3kg^{-1}$ (172.80≤T≤253.04 K). Obtained results on heat capacities $C_V^2$ and $C_S$ are given in Table. 1.

For calculations of caloric properties we used data on critical parameters of the mixture HFC23/FC116 (64/36 mol.%) obtained earlier ($T_C$=287.26 K, $P_C$=4.023 MPa $\rho_C$=571.10 kg $m^{-3}$) [1, 5]. For determination of heat capacity $C_S$ at the saturation the correction on quazi-isochoric character of measured data were applied. It required to know thermodynamic properties of the mixture on liquid-vapor coexistence curve. Bubble pressures and saturated liquid densities of HFC23/FC116 [1,5] were fitted by the following equations

$$\ln\left(\frac{P_C}{P_S}\right) = \alpha_R\tau + b\tau^C \qquad (1)$$

$$\ln\left(\frac{p'}{\rho_C}\right) = B\tau^{\beta F_1(\tau)} \tag{2}$$

where $\alpha_R$, $b$, $c$, $B$ and $\beta$ are coefficients ($\alpha_R$=7.0650, $b$=4/9064, $c$=2.64; $B$=1.6865; $\beta$=0.3264), $P_S$ is vapor pressure, $\tau = \ln\left(\frac{T_C}{T}\right)$ and $F_1(\tau)$ is universal crossover function for normal substances, $F_1(\tau) = 1 - 1.113\frac{\tau^{0.4}}{\ln(\tau)}$

Calculated values of heat capacity $C_S$ were fitted by polynomial dependence

$$C_S' = 1108.9506 + 96.4058t^{-2/3} - 557.70687t^{1/2} + 4121.698t \tag{3}$$

where $t$ is reduced temperature, $t = (T_C - T)/T_C$.

Calculations of isobaric heat capacity on the bubble curve were based on semi-empirical equation of state for liquid phase developed at the Department of Engineering Thermophysics , OSAR [11]

$$\frac{P}{RT\rho} = 1 - 1.744\frac{\varepsilon_e}{kT}\left[(b_{oe}\rho)^2 - 0.4654(b_{0l}\rho)^4\right] \tag{4}$$

where $P$ is pressure, $R$ is universal gas constant, $\varepsilon_e/k$ and $b_{ol}$ are functions of temperature expressed as

$$\varepsilon_e/k = 0.795T_C\exp\left[c(1 - T/T_C)\right] \tag{5}$$

$$b_{oe} = 2\pi N\sigma_e^3/3 \tag{6}$$

where $\sigma_e^3$ is function of temperature, $\sigma_e^3 = a - bT$; $a$, $b$ and $c$ are coefficients; and $N$ is Avogadro's number.

Equation of state (4) were developed by modification of cell model of liquid by introducing intermolecular potential (12, 6) with variable parameters. Eq. (4) is thermodynamically consistent. It fits data within experimental uncertainties and can be applied for extrapolation and prediction of thermodynamic properties [11]. Coefficients of the Eq. (4) were determined in [1] and they have the following values: $a$=0.0199040320; $b$=0.002779295; $c$=2.53722059.

Using Eq. (4), the isobaric heat capacity on the bubble curve $C_P'$ was computed

$$C_P' = C_S' + T\left(\frac{\partial V}{\partial T}\right)' \frac{dP_S}{dT} \tag{7}$$

and then was fitted by Eq. (8)

$$C_P' = 94150153 - 33560238\ t + 56669179\ t^{-1},\ \text{J kg}^{-1}\ \text{K}^{-1} \tag{8}$$

where $t$ is reduced temperature, $t = (T_C - T)/T_C$.

Based on developed correlations for specific heat capacity the values of enthalpy and entropy were determined at the saturation

$$H'(T) = \int_{T_0}^{T_S} C_P(T)dT + H_0,\quad S' = \int_{T_0}^{T_S} \frac{C_S'}{T}\,dT + S_0;$$

$$r = \frac{dP}{dT}T(V''-V'),\quad S'' = \frac{dP_S}{dT}(V''-V') + S',\quad H'' = H'+r. \tag{9}$$

Values of enthalpy and entropy at saturation (at $T$=200 K) were taken equal 400 and 4 kJ kg$^{-1}$ K$^{-1}$ respectively.

Thermodynamic data of mixture HFC23/FC116 obtained earlier [1, 5] were used for calculation of caloric properties. Results of these calculations for mixture HFC23/FC116 (64/36 mol. %) are summarized in Table 2.

## 3. CONCLUSION

Caloric properties of alternative mixture HFC23/FC116 were determined. Obtained experimental results on specific heat capacity allow to improve equations for HFC23/FC116 developed earlier [5, 6]. Data on specific heat capacity were used for developing reference thermodynamic data of the refrigerant R508B.

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## REFERENCES


1. Zhelezny, V.P., Semenyuk, Yu.V. and Aftenev, Yu.M. *Kholodilnaya Tekhnika i Tekhnologiya (Refrig. Equip. and Technology)*, (1990), 50: 79-81.
2. Zhelezny, V.P. and Potapov, M.D. *Trans. Techn. Inst. of Refr. Industry, Leningrad, USSR* (1990): 137-140.
3. Zhelezny, V.P.and Potapov, M.D. *Trans. Dagestan Scientific Center RAN, Inst. of Phys., Maxachkala, USSR* (1991): 44-52.
4. Geller, V.Z. and Zhelezny, V.P. *Proc. Int. Refr. Conf., Purdue, IN* (1996): 397-402.
5. Zhelezny, V.P., Semenyuk, Yu.V. and Anisimov, V.N. *Proc. Int. Refr. Conf., Purdue, IN* (1996): 453-458.
6. Bivens, D.B., Yokozeki, A. and Geller, V.Z. *Proc. Int. Refr. Conf., Purdue, IN* (1996): 403-408.
7. Anisimov, M.A., Kovalchuk, B.A., Rabinovitch, V.A. and Smirnov, V.A. *Fizicheskie konstanty i svoistva veschestv (Physical constants and properties of substances) GSSSD* (1974), 8: 237-245.
8. Magee, J.W. *Rev. Int. Froid*. (1992), 15: 372-380.
9. GSSSD P100-84 Freon C318. Specific heat capacity and specific entropy of boiling liquid at temperatures from -38 $^0$C to 65 $^0$C. Tables of recommended reference data (in Russian, Moscow: Standard Publ.).
10. GSSSD P32-82 Propane. Isochoric heat capacity in two-phase region at temperatures 90-350 K. Tables of recommended reference data (in Russian, Moscow: Standard Publ.).
11. Kesselman, P.M. and Onufriev, I.V. *Inzh. Fiz. Zhurn. (J. Eng. Phys.)* (1979), 37(2): 316-323.

12. Kesselman, P.M. and Inshakov, S.A. *Inzh. Fiz. Zhurn. (J. Eng. Phys.)* (1984), 46(6): 959-964

Table 1. Experimental data on specific heat capacity of HFC23/FC116

| $T$, K | $C_V^2$, J kg$^{-1}$ K$^{-1}$ | $C_S'$, J kg$^{-1}$ K$^{-1}$ | $\Delta C_S'$ |
|---|---|---|---|
| 175.327 | 1074.11 | 1075.14 | +0.0133 |
| 186.159 | 1086.89 | 1088.89 | +0.0086 |
| 196.711 | 1102.59 | 1106.19 | -0.0022 |
| 206.944 | 1121.38 | 1127.52 | -0.0169 |
| 216.953 | 1144.03 | 1154.13 | -0.0202 |
| 256.896 | 1308.20 | 1384.48 | -0.0856 |
| 177.529 | 1076.44 | 1077.63 | +0.0119 |
| 188.455 | 1090.03 | 1092.31 | +0.077 |
| 192.488 | 1095.90 | 1098.76 | +0.0034 |
| 195.937 | 1101.31 | 1104.76 | -0.0023 |
| 203.270 | 1114.16 | 1119.24 | -0.0144 |
| 206.689 | 1120.87 | 1126.93 | -0.0160 |
| 210.457 | 1128.80 | 1136.13 | -0.0194 |
| 219.381 | 1150.29 | 1161.67 | -0.0168 |
| 232.443 | 1190.31 | 1211.75 | +0.0213 |
| 245.020 | 1242.03 | 1282.10 | +0.0596 |
| 180.161 | 1079.43 | 1080.83 | +0.0094 |
| 191.466 | 1094.35 | 1097.05 | +0.0029 |
| 194.589 | 1099.16 | 1102.37 | +0.0011 |

Table 1. (Continued)

| $T$, K | $C_V^2$, J kg$^{-1}$ K$^{-1}$ | $C_S'$, J kg$^{-1}$ K$^{-1}$ | $\Delta C_S'$ |
|---|---|---|---|
| 199.412 | 1107.16 | 1111.32 | -0.0076 |
| 208.418 | 1124.44 | 1131.05 | -0.0176 |
| 217.928 | 1146.50 | 1157.10 | -0.0191 |
| 226.333 | 1170.14 | 1186.08 | -0.0016 |
| 238.635 | 1213.85 | 1242.90 | +0.0468 |
| 248.295 | 1258.31 | 1305.81 | +0.0526 |

Table 2. Thermodynamic properties of mixture HFC23/FC116 (64/36 mol. %) on liquid-vapor coexistence curve

| $T$, K | $P$, MPa | ρ', kg m$^{-3}$ | ρ", kg m$^{-3}$ | $r$, kJ kg$^{-1}$ | $C_S$', kJ × kg$^{-1}$K$^{-1}$ | $C_P$', kJ × kg$^{-1}$K$^{-1}$ | $S$', kJ × kg$^{-1}$K$^{-1}$ | $S$", kJ × kg$^{-1}$K$^{-1}$ | $H$', kJ kg$^{-1}$ | $H$", kJ kg$^{-1}$ |
|---|---|---|---|---|---|---|---|---|---|---|
| 180 | 0.07659 | 1562.4 | 5.18 | 158.96 | 1.0797 | 1.0811 | 3.8846 | 4.7677 | 378.04 | 537.00 |
| 185 | 0.10243 | 1541.7 | 6.73 | 158.13 | 1.0870 | 1.0889 | 3.9143 | 4.7691 | 383.46 | 541.59 |
| 190 | 0.13470 | 1520.7 | 8.58 | 157.78 | 1.0950 | 1.0975 | 3.9434 | 4.7738 | 388.93 | 546.71 |
| 195 | 0.17444 | 1499.2 | 10.81 | 157.00 | 1.1037 | 1.1070 | 3.9719 | 4.7770 | 394.44 | 551.44 |
| 200 | 0.222175 | 1477.2 | 13.54 | 155.06 | 1.1133 | 1.1176 | 4.0000 | 4.7753 | 400.00 | 555.06 |
| 205 | 0.28079 | 1554.6 | 16.82 | 152.55 | 1.1239 | 1.1295 | 4.0276 | 4.7771 | 405.62 | 558.17 |
| 210 | 0.34980 | 1431.5 | 20.73 | 149.59 | 1.1357 | 1.1429 | 4.0548 | 4.7671 | 411.30 | 560.89 |
| 215 | 0.43107 | 1407.6 | 25.36 | 146.28 | 1.1489 | 1.1582 | 4.0817 | 4.7621 | 417.05 | 563.33 |
| 220 | 0.52597 | 1383.0 | 30.82 | 142.63 | 1.1637 | 1.1756 | 4.1083 | 4.7566 | 422.89 | 565.52 |
| 225 | 0.63593 | 1357.4 | 37.21 | 138.78 | 1.1806 | 1.1958 | 4.1346 | 4.7514 | 428.81 | 567.59 |
| 230 | 0.76246 | 1330.8 | 44.68 | 134.66 | 1.1999 | 1.2193 | 4.1608 | 4.7463 | 434.85 | 569.51 |
| 235 | 0.90715 | 1303.0 | 53.37 | 130.35 | 1.2222 | 1.2472 | 4.1868 | 4.7414 | 442.01 | 571.36 |
| 240 | 1.07170 | 1273.8 | 63.52 | 125.71 | 1.2485 | 1.2807 | 4.2128 | 4.7365 | 447.33 | 573.04 |
| 245 | 1.25792 | 1242.9 | 75.37 | 120.74 | 1.2799 | 1.3219 | 4.2389 | 4.7317 | 453.83 | 574.57 |
| 250 | 1.46776 | 1210.0 | 89.30 | 115.30 | 1.3182 | 1.3737 | 4.2651 | 4.6119 | 460.56 | 575.86 |