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Vapor Pressure and Heat Capacities of Perfluoro-*N*-(4-methylcyclohexyl)piperidine

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Abstract—Heat capacities of perfluoro-*N*-(4-methylcyclohexyl)piperidine (PMCP) have been measured by low-temperature adiabatic calorimetry. The purity of the compound, its triple-point temperature, and its enthalpy and entropy of fusion have been determined. The saturated vapor pressure was determined by comparative ebulliometry as a function of temperature in the 6.2–101.6 kPa pressure range and 374.2–460.9 K temperature range. The calorimetric enthalpy of vaporization at T = 298.15 K has been measured. The following thermodynamic properties were calculated for PMCP: normal boiling temperature, enthalpy of vaporization $\Delta_{vap}H_m^0(T)$ as a function of temperature, and critical parameters. The enthalpies of vaporization at 298.15 K obtained experimentally and by calculation methods match within their error limits, which validates their adequacy and the adequacy of the $\Delta_{vap}H_m^0 = f(T)$ equation as an extrapolation.

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Perfluorinated organic compounds (PFO) have high chemical and thermal stability, absolute biological inertness, and express weak intermolecular interactions. The combination of these properties can be assigned to the high C–F bond strength and the shielding of the carbon framework by fluorine atoms. The weakness of intermolecular interactions is responsible for the inability of perfluorocarbons to dissolve and transfer considerable amounts of gases, in particular, oxygen and carbon dioxide. On account of these properties, perfluorocarbons have found wide application in biology and medicine as efficient gas-transfer media (blood substitutes). The saturated vapor pressure of PFO at the human body temperature (310 K), p_s^{310}, is one of the key properties of a blood substitute. p_s^{310}, which ranges from 0.16 to 2.66 kPa, determines the stability of an aqueous emulsion of fluorocarbon and its delivery rate from the body. Medicine uses PFO compositions with high or low vapor pressures. Perfluoro-N-(4-methylcyclohexyl)piperidine, which has low p_s^{310}, is a component of Ftorosan (Russia) blood substitute [1] in mixture with perfluorodecaline.

The PMCP sample to used in this work was synthesized at the Institute of Organoelement Compounds, Russian Academy of Sciences, by perfluorination of 4-methylcyclohexylpiperidine with cobalt trifluoride [2]. A sample of the as-synthesized compound was purified by fractional distillation; its purity (99.99 wt %) was determined by gas–liquid chromatography on a Perkin-Elmer F-22 chromatograph equipped with a flame-ionization detector using a glass capillary column (l = 50 m, d = 0.3 mm, OV-101 stationary phase). The PMCP sample was a mixture of chair (60%) and boat (40%) conformers, as analyzed by ^{19}F NMR spectra (Perkin-Elmer R-32 spectrometer, CF_3COOH external reference). The chromatographic separation of conformers was impossible because of the similarity of their physicochemical properties.

LOW-TEMPERATURE HEAT CAPACITY

PMCP heat capacities were measured on a automated vacuum adiabatic calorimeter interfaced with an Aksamit data acquisition and control system (AK-6.25). The setup design and determination procedure are described in [3]. The heat capacity measurement error was 1.0–2.0% for 6–20 K, 0.5–1.0% for 20–85 K, and 0.2–0.3% for temperatures above 85 K. Heat capacities $C_{s,m}$ were measured at 10.3–347.5 K at the saturated vapor pressure. Liquid helium or nitrogen was the cooling agent. Crystallization occurred while a test sample was cooled from room temperature to 77.4 K for 12 h (in the absence of heat lift to the adiabatic shell, which slows down crystallization). The heat capacity versus temperature plot (Fig. 1) shows a thermal anomaly associated with fusion of the sample. The heat capacity difference

$$C_{p,m} - C_{s,m} = T(\partial V/\partial T)_p(\partial P/\partial T)_s,$$

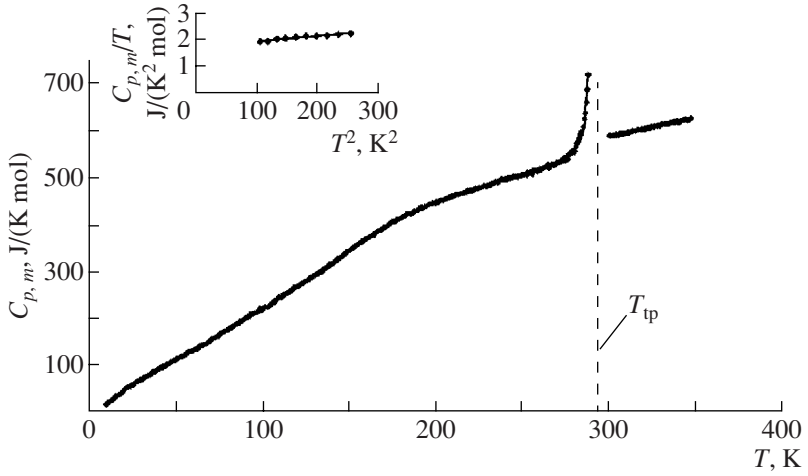

Fig. 1. Heat capacity vs. temperature for PMCP.

which was estimated for a liquid at 298.15 K, was within the $C_{s,m}$ error limits; therefore, we ignored it over the entire range of the temperatures studied.

The purity and triple-point temperature (T_{tp}) of the test compound were determined calorimetrically by studying the equilibrium fusion temperature (T_i) as a function of the inverse molten fraction of the sample ($1/F_i$) [4]. The results of two experiments are illustrated by Fig. 2 and, in part, Table 1. The $T_i(1/F_i)$ plots for both experiments are concave curves, which can be interpreted by mixed-crystal formation as a result of rapid crystallization. The least-squares fits give

$$T_i = -0.466(1/F_i) + T_0, \quad R^2 = 0.9359, \qquad (1)$$

where $T_0(T_{tp}) = 293.26$ K is the fusion temperature of the pure compound, $T_1 = 292.80$ K is the fusion temperature of the sample with the molten fraction equal to $F = 1$, and $T_1 - T_0 = -0.46$ K is the T_{tp} depression. The impurity mole fraction N_2 was determined by the Smith and Aleksandrov method using $T_i = f(1/F_i)$ experimental data and the equation for N_2 in a binary system with solid solution formation [6, 7]:

$$T_i = T_0 - \frac{N_2}{A_K}\frac{1-k}{F_i^{1-k}}, \qquad (2)$$

Here, T_i is the equilibrium temperature for the molten fraction F_i, A_K is the cryoscopic constant for the major substance, and k is the partition coefficient of impurities between the solid and liquid. The weakness of this equation for calculating N_2 consists in the need to determine K by an independent method. In [7], Eq. (2) was transformed, by differentiating and taking logarithm, to

$$\ln\left(-\frac{dT_i}{d(1/F_i)}\right) = \ln\left\{\frac{N_2}{A_K}(1-k)^2\right\} - k\ln(1/F_i). \qquad (3)$$

Equation (3) can determine k directly from $T_i = f(1/F_i)$ experimental data and calculate the impurity mole fraction (N_2). The least-squares fits of two fractional fusion data sets gave mean values:

$$k = 1.241 \text{ and } \ln\left\{\frac{N_2}{A_K}(1-k)^2\right\} = 0.41.$$

These data and the cryoscopic constant $A_K = \Delta_{fus}H_m^0/RT_0^2 = 0.011635 \pm 0.00002$, which was obtained as in [4], were used to calculate the impurity mole fraction in the PMCP test sample: $N_2 = 0.0034$. The N_2 error was ~30%.

The enthalpy of fusion for PMCP was determined calorimetrically with the continuous supply of energy, required for the phase transition in the test compound, followed by $\Delta_{fus}H_m$ (J/mol) calculations from

$$\Delta_{fus}H_m = \Delta H - \Delta H_1 - \Delta H_2 - \Delta H_3, \qquad (4)$$

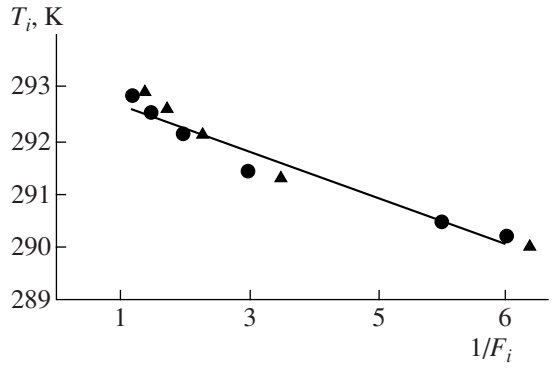

Fig. 2. Equilibrium fusion temperatures (T_i) vs. reciprocal melt mole fraction ($1/F_i$) for PMCP.

Table 1. Equilibrium temperature T_i as a function of reciprocal melt mole fraction, $1/F_i$, for PMCP

T_i, K	q_i, J	$1/F_i$	$T_{i(\mathrm{calc})}$, K
290.232[a]	4.900	7.0287[a]	290.077
291.334[a]	4.900	3.5144[a]	291.724
292.154[a]	5.042	2.3205[a]	292.283
292.649[a]	4.900	1.7446[a]	292.553
292.961[a]	4.900	1.3977[a]	292.715
293.191[a]	4.900	1.1659[a]	292.824
293.459	4.900	1.0000	292.901
–	–	0.0000	293.370

Note: [a] T_i and $1/F_i$ used to calculate T_{tp}, as recommended in [5].

Here, ΔH is the enthalpy increment upon heating of the compound from $T_{\mathrm{in}} < T_{\mathrm{tp}}$, a temperature at which it has a normal heat capacity, to $T_{\mathrm{f}} > T_{\mathrm{tp}}$; ΔH_1 and ΔH_2 are the enthalpies of heating for the test compound, which were calculated by integrating the normal heat capacity curves from T_{in} to T_{tp} and the heat capacities of the liquid from T_{tp} to T_{f}, respectively; and ΔH_3 is the enthalpy of heating of an empty calorimeter from T_{in} to T_{f}. Five calorimetric experiments were carried out to determine $\Delta_{\mathrm{fus}}H_m$ (Table 2). Table 3 lists the thermodynamic parameters of fusion for PMCP obtained by adiabatic calorimetry and differential scanning calorimetry. The purity of the test sample (N_1), triple-point temperature, and enthalpy of fusion obtained by the two independent methods match within their error limits, which validates their adequacy.

Experimental heat capacity versus temperature data were fitted to polynomials as in [3]. Calculated $C_{p,m}$ values match measured ones within the error limits: the mean-square deviation is 0.25%. Extrapolation of the heat capacity from 10.27 K to $T \longrightarrow 0$ was carried out using

$$C_{p,m}/T = \alpha T^2 + \gamma, \quad (5)$$

where $\alpha = 0.00202 \pm 0.0002$ kJ/(K^4 mol) and $\gamma = 0.724 \pm 0.04$ J/(K^2 mol) are the factors of a linear dependence calculated from $C_{p,m}$ experimental data in the 10.27–15.96 K range. The mean-square deviation of the $C_{p,m}$ calculated by Eq. (5) from those found experimentally is ±2.8%. The constant term in Eq. (5) equals the residual entropy of the test sample, which is a mixture of two conformers: $S_m^0(0) = 1.72$ J/(K mol).

The thermodynamic functions of PMCP were calculated by integrating the $C_{p,m} = f(T)$ polynomial functions for a crystal and liquid and summing-up the enthalpies and entropies of fusion of the test compound. The function values below 10.27 K were found by integrating Eq. (5) and $C_{p,m} = \alpha T^3 + \gamma T$. Table 4 lists smoothed $C_{p,m}(T)$, $S_m^0(T) - S_m^0(0)$, $H_m^0(T) - H_m^0(0)$, and $-\{G_m^0(T) - H_m^0(0)\}$ functions in the condensed state for the range of the temperatures studied.

VAPOR PRESSURE AS A FUNCTION OF TEMPERATURE

The saturated vapor pressure of PMCP at various temperatures was determined by a comparative dynamic method on a setup built of a differential ebulliometer (for measuring boiling (T_{b}) and condensation (T_{cond}) temperatures) and a pressure gage system (for automated pressure regulation and determination in the ebulliometer) [8, 9]. The pressure gage system, whose hart was a mercury contact pressure gage, operated in the manostat mode. T_{b} and T_{cond} were measured by mercury resistance thermometers ($R_0 \sim 100\ \Omega$) at the pressures automatically maintained by the pressure-gage system at the gage-contact levels. To adjust a fixed pressure equal to the saturated vapor pressure of the test

Table 2. Molar enthalpy of fusion $\Delta_{\mathrm{fus}}H_m$ for PMCP (M = 595.103 g/mol, m_{vac} = 1.80945 g, T_{tp} = 293.26 K)

T_{in}	T_{f}	ΔH_1^{a}	ΔH_2^{a}	ΔH_3^{a}	ΔH_4^{a}	$\Delta_{\mathrm{fus}}H_m^{\mathrm{a}}$
255.636	306.488	54793	20052	8042	18359	8340
255.558	305.944	54314	20092	7720	18185	8317
255.633	305.547	53860	20054	7485	18012	8309
259.019	308.583	53855	18320	9287	17943	8305
258.394	308.042	53881	18642	8965	17964	8310
						Average: 8316 ± 17

Note: [a] Physical meaning of ΔH_i (J/mol) is disclosed in the text after Eq. (4).

Table 3. Thermodynamic properties of fusion[a] for PMCP as measured by adiabatic calorimetry (AC) and differential scanning calorimetry (DSC)

Property	AC	DSC
T_{tp}, K	293.26 ± 0.2	293.7 ± 0.4
$\Delta_{fus}H_m$, kJ/mol	8.316 ± 0.017	8.60 ± 0.1
$\Delta_{fus}S_m$, J/(K mol)	28.35 ± 0.06	–
N_1, %	99.66 ± 0.1	99.57 ± 0.1
A_K, K^{-1}	$0.01164 \pm 2 \times 10^{-5}$	–

Note: [a] T_i and $1/F_i$ used to calculate T_{tp}, as recommended in [5].

compound, argon gas was fed into the ebulliometric system. The pressures at the gage contacts were determined by precalibration against references, water (bidistillate) and *n*-decane (chromatographically pure), for which precision saturated vapor pressure versus temperature data are known [10, 11]. T_b and T_{cond} were measured automatically on the AK-6.25 system, which was used for heat capacity measurements. Instrumental errors in pressures and temperatures were as follows: $S_p \le \pm 26$ Pa, and $S_T \le \pm 0.01$ K. The volume of the test-liquid required for T_b and T_{cond} measurements was 6.5 and ~9 cm^3, respectively.

The set of ebulliometric experiments was started with the determination of the ebulliometric purity of the test compound as $\Delta T_{eb} = T_b - T_{cond}$ on the ebulliometric scale [12]. Some liquid (~0.5 cm^3) was first distilled off the ebulliometer to entrain volatile impurities and trace water in an azeotrope. The saturated vapor pressure of *p*-perfluoro-*N*-(4-methylcyclohexyl)piperidine was determined as a function of temperature for the 374–461 K temperature range and the 6.2–101.6 kPa pressure range. Table 5 lists the boiling and condensation temperatures and saturated vapor pressures of PMCP. The difference $\Delta T = T_b - T_{cond}$ corresponds to degree III on the five-point ebulliometric purity scale [12], which is due to 0.34 mol % impurities in the test compound (Table 3). The difference between the T_b values measured at the beginning of an experiment and at the end falls within the instrumental error limits (S_T), proving that the test sample remained unchanged during ebulliometric measurements.

The boiling temperature and saturated vapor pressure data were fitted, as in [8, 9], to the four-parameter equation

$$-RT\ln p = f(T),$$

which was derived from the Clausius–Clapeyron equation in the approximation for $\Delta Cp, m = C^0_{p,m}(\text{gas}) = C^0_{p,m}(\text{liq})$ as a linear function of *T*. Least-squares fits with orthogonal functions were used. In the concise form, the final equations for the saturated vapor pressure and the enthalpies of vaporization are as follows:

$$\ln(p/\text{kPa}) = A + B(\text{K}/T) + C\ln(T/\text{K}) + D(T/\text{K}), \quad (6)$$

$$\Delta_{vap}H_m/\text{J mol}^{-1} = R\{-B - C(T/\text{K}) + D(T/\text{K})^2\} \times \Delta Z \pm \{\sigma(\Delta_{vap}H^0_m) + s(\Delta Z)\Delta_{vap}H_m\}, \quad (7)$$

Here, ΔZ is the difference between the compressibility factors for gas and liquid; *A*, *B*, and *C* are linear combinations of orthogonal parameters; *D* is an independent coefficient, equal to the minimum orthogonal parameter; $\sigma(\Delta_{vap}H^0_m)$ is the error in the enthalpies of vaporization due to *pT* errors; and $s(\Delta Z)$ is the ΔZ uncertainty from Eq. (8) estimated at ~1% [8, 9]. ΔZ, which accounts for the vapor nonideality and phase volume increments upon vaporization, was calculated from

$$\Delta Z = \{P/(RT)\}\{V(\text{gas}) - V(\text{liq})\}, \quad (8)$$

where *V*(gas) and *V*(liq) are, respectively, the volumes of the gas and liquid calculated from the density of the liquid and *pT* parameters, as in [8, 9]. The PMCP density obtained in [13] for the range 293–343°C with ±0.01% precision is fitted to

$$\text{c/g cm}^{-3} = 1.9782 - 1.998 \times 10^{-3}t/°\text{C} - 1.42 \times 10^{-6}(t/°\text{C})^{-2}. \quad (9)$$

Statistical analysis of Eqs. (6) and (7) on the basis of the inequality

$$F_{calc} = D^2/S^2(D) \ge F_{0.05}(1, f), \quad (10)$$

as in [8, 9], showed a significant nonzero value of *D*, which has the highest error: $F_{calc}(527.4) > F_{0.05}(4.60)$. Here, $F_{0.01}(1, f)$ and F_{calc} are, respectively, the tabulated [14] and calculated values of the Fischer criterion and *f* is the number of the degrees of freedom.

Processing of *pT* data for PMCP gave the following values for the factors in Eqs. (6) and (7): *A* = 210.05772, –*B* = 13 500.83, –*C* = 30.83011, and $D \times 10^{-3}$ = 28.0834. The mean-square deviation of calculated *P* from experimentally found values was within the error limits (S_p = 5 Pa). The number of significant digits was chosen such that the mean square deviation did not exceed the vapor pressure and temperature determination errors.

The enthalpy of vaporization at 298.15 K was determined by a balance method in an adiabatic calorimeter using the nitrogen carrier gas for enhancing vaporization. The substance weight required for a set of six to eight experiments was 0.5–1.0 g. The setup used and the details of measurements are found in [8, 9]. The errors in the enthalpies of vaporization are 0.2–0.5%.

Table 6 displays the normal boiling temperature for PMCP, the calorimetric enthalpies of vaporization, and those calculated from Eq. (6). The match, within the

Table 4. Smoothed thermodynamic functions for PMCP

T, K	$C_{p,m}$, J/(K mol)	$H_m^0(T) - H_m^0(0)$, kJ/mol	$S_m^0(T) - S_m^0(0)$, J/(K mol)	$-\{G_m^0(T) - H_m^0(0)\}$, kJ/mol
		Crystal		
5	8.873	0.02186	8.704	0.02166
10	19.26	0.09125	17.913	0.08788
15	32.64	0.2199	28.161	0.2025
20	48.27	0.4223	39.696	0.3716
25	60.86	0.6968	51.897	0.6006
30	71.11	1.0269	63.904	0.8902
35	82.05	1.4093	75.673	1.239
40	93.41	1.8481	87.375	1.647
45	104.0	2.3419	98.995	2.113
50	113.9	2.8867	110.46	2.636
55	123.9	3.4813	121.79	3.217
60	133.5	4.1251	132.99	3.854
65	142.8	4.8154	144.04	4.547
70	154.5	5.5579	155.04	5.295
75	166.1	6.3600	166.09	6.097
80	177.6	7.2190	177.18	6.955
85	188.9	8.1354	188.29	7.869
90	200.2	9.1083	199.41	8.839
95	211.4	10.137	210.53	9.863
100	222.6	11.222	221.66	10.94
110	245.3	13.562	243.94	13.27
120	268.4	16.130	266.27	15.82
130	292.4	18.933	288.70	18.60
140	317.5	21.982	311.28	21.60
150	345.2	25.293	334.11	24.82
160	370.6	28.873	357.21	28.28
170	394.0	32.698	380.39	31.97
180	415.0	36.745	403.52	35.89
190	432.5	40.986	426.45	40.04
200	447.8	45.390	449.03	44.42
210	460.8	49.934	471.20	49.02
220	473.2	54.604	492.92	53.84
230	485.1	59.396	514.22	58.87
240	496.4	64.304	535.11	64.12
250	506.9	69.321	555.59	69.58
260	518.0	74.444	575.68	75.23
270	532.8	79.692	595.48	81.09
280	549.0	85.101	615.15	87.14
290	565.3	90.673	634.70	93.39
293.26	570.7	92.524	641.05	95.47
		Liquid		
293.26	582.2	100.84	669.40	95.47
298.15	586.3 ± 1.2	103.70 ± 0.34	679.06 ± 2.1	98.76 ± 0.71
300	587.8	104.78	682.69	100.0
310	596.0	110.70	702.10	107.0
320	604.2	116.70	721.15	114.1
330	612.2	122.78	739.87	121.4
340	620.1	128.95	758.26	128.9
350	627.8	135.19	776.35	136.5

Table 5. Boiling temperatures (T_b) and saturated vapor pressure (p_{exp}) for PMCP

p_{exp}, kPa	T_b, K
6.202	374.186
	374.178[a]
	374.138[b]
8.391	381.556
10.764	387.917
13.404	393.739
16.807	400.006
20.844	406.215
25.038	411.700
30.883	418.211
37.224	424.240
45.775	431.187
56.065	438.270
67.440	444.987
81.509	452.148
93.084	457.346
95.219	458.241
97.343	459.122
99.494	459.999
101.616	460.854

Notes: [a] T_b remeasured after the entire pT curve was recorded. [b] Condensation temperature, T_{cond}.

Table 6. Normal boiling temperature ($T^a_{n.b}$) and standard enthalpy of vaporization ($\Delta_{vap}H^0_m$) at 298.15 K and $T_{n.b}$ for PMCP

$T_{n.b}$, K	460.74 ± 0.01
$\Delta_{vap}H^0_m$ (298.15 K), kJ/mol	56.56 ± 0.24 (cal)[b]
	56.58 ± 0.88 (p–T)[c]
$\Delta_{vap}H^0_m$ ($T_{n.b}$), kJ/mol	40.68 ± 0.44 (p–T)[c]

Notes: [a] Calculated from (6). [b] Obtained calorimetrically. [c] Calculated from (7).

Table 7. Thermodynamic functions of PMCP in an ideal gas state at T = 298.15 K and residual entropy S^0_m at 0 K

$C^0_{p,m}(T)$[a], J/(K mol)	423.2
$p_s(T)$, Pa	81.37
$\Delta_{vap}H^0_m$ (T), kJ/mol	56.56 ± 0.24
$\Delta_{vap}S^0_m$ (T), J/(K mol)	189.70 ± 0.8
$R\ln\{p_s(T)/101325\ \text{Pa}\}$, J/(K mol)	–59.26
$\{S^0_m(T) - S^0_m(0)\}$ (g), J/(K mol)	809.5 ± 3
$\{H^0_m(T) - H^0_m(0)\}$ (g), kJ/mol	160.26 ± 0.5
$\{G^0_m(T) - G^0_m(0)\}$ (g), kJ/mol	–81.09 ± 0.8
$S^0_m(0)$, J/(K mol)	1.72 ± 0.05

Note: [a] Calculated from additivity [17]; $p_s(T)$, saturation vapor pressure; $\Delta_{vap}H^0_m$ and $\Delta_{vap}S^0_m$, the enthalpy and entropy of vaporization, respectively; $R\ln\{p_s(T)/101325\ \text{Pa}\}$, the entropy of compression of an ideal gas from p = 101325 Pa to $p_s(T)$; $\{S^0_m(T) - S^0_m(0)$, $H^0_m(T) - H^0_m(0)$, and $G^0_m(T) - G^0_m(0)\}$, the entropy, enthalpy, and Gibbs free energy increments, respectively.

error limits, between the enthalpies of vaporization determined by the two independent methods validates their adequacy and the adequacy of Eq. (6) as an extrapolation equation in the range ΔT = 76 K.

The saturated vapor pressure and density data were used to calculate the critical parameters of PMCP proceeding from the corresponding states law, which was developed in [15]. Calculations by the algorithm described in [16] gave the following parameters: T_c = 600 K, V_c = 950 cm^3/mol, and P_c = 1.25 MPa; the thermodynamic similarity criterion was A_{cr} = 0.474. The calculation errors estimated for several references [16] were ±1, 2, 3–5, and 2%, respectively.

Table 7 lists the major thermodynamic functions in the ideal-gas state at 298.15 K calculated from the data displayed in Table 4, calorimetric $\Delta_{vap}H^0_m$ (298.15 K), and the entropy of compression of an ideal gas from p = 101.325 kPa to p_s (298.15 K), which was estimated from Eq. (6). The PMCP vapor pressure at the human body temperature, p_s^{310} = 157 Pa, is 0.16–2.66 kPa, a range permissible for use of PFO as blood substitute.

Figure 3 presents the critical temperatures, enthalpies of vaporization, and oxygen capacities (φ_{O_2}) for *cis*- and *trans*-perfluorobicyclo(4,3,0)nonanes (I and II), *cis*- and *trans*-perfluorobicyclo(4,4,0)decanes (III and IV; components of Ftorosan blood substitute); PMCP (V); and some of their hydrocarbon analogues (VI–IX), respectively. φ_{O_2} (cm^3/100 mL), which is the oxygen volume in 100 mL of a liquid, was calculated by an empirical method developed in [18, 19] based on regular solutions theory. φ_{O_2} is a function of intermolecular

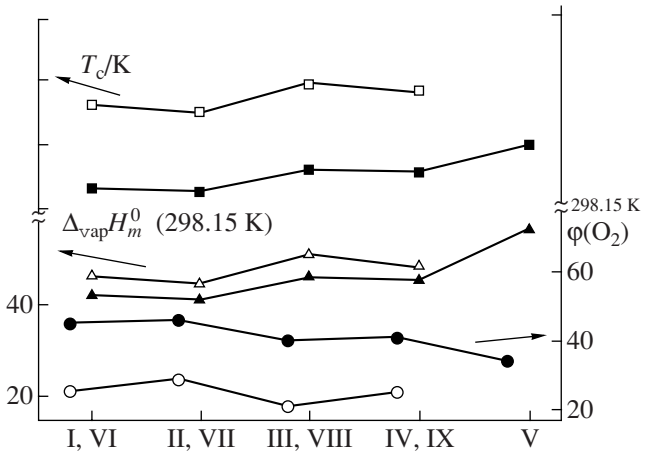

Fig. 3. Critical temperatures (T_c, K), enthalpies of vaporization (298.15 K, J/mol), and oxygen capacities (φ_{O_2}, cm^3/100 mL) for (*1–3*) perfluorinated compounds I–V and (*1'–3'*) their hydrocarbon analogues (VI–IX).

interaction energy. The critic temperatures and enthalpies of vaporization of perfluorinated organic compounds are lower than for their hydrocarbon analogues, whereas their oxygen capacities are higher, which can be explained by the smaller intermolecular interaction energies of PFO.

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