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Heat Capacities and Thermodynamic Functions of Propanoylferrocene and Propylferrocene[†]

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The heat capacities of propanoylferrocene (POF), $C_5H_5FeC_5H_4COC_2H_5$, and propylferrocene (PF), $C_5H_5FeC_5H_4C_3H_7$-*n*, were measured by vacuum adiabatic calorimetry in the temperature ranges from (10 and 7) K to 372 K. The temperatures and enthalpies of the phase transitions and the purity of the samples have been determined. The solid phase transition of PF was studied by single-crystal crystallography in the temperature range from (150 to 200) K. The thermodynamic functions (absolute entropies, changes of the enthalpy, and Gibbs energy) of POF and PF were calculated for the solid and liquid phases of the temperature intervals studied. The ideal gas thermodynamic functions were derived at $T = 298.15$ K using the data on saturated vapor pressure and the enthalpies and entropies of vaporization. A reliability of the ideal gas thermodynamic functions was corroborated by the additive calculation method. A mutual congruence of the absolute entropies of alkylferrocenes and acylferrocenes studied in this work and available in the literature were critically analyzed.

Introduction

The cyclopentadienyl of iron (ferrocene) and its derivatives are the sandwich-type organometallic compounds discovered in the 50th years of the 20th century. Due to an auspicious combination of the chemical and physical properties (high thermal stability, high saturation vapor pressures, and low toxicity), these compounds are used in many fields of technology and medicine. They have found wide application as heat resistant polymers, metallic and oxide coverings, electronic materials, high octane additives to the motor fuels, and anticancer and blood creating drugs, etc.[1] Ferrocene is the most investigated member of this class of organometallic compounds,[2] but the data on the physicochemical properties of the numerous ferrocene derivatives (FD) are very scarce. The standard enthalpies of formation, the heat capacities, the saturation vapor pressures, and the main thermodynamic functions (changes of the entropy, enthalpy, and Gibbs energy) were studied for 12 aliphatic and aryl derivatives of ferrocene.[3−6] Dorofeeva and Varushchenko[7] reported critical analysis of some of these data using density functional theory (DFT) and the empirical calculation method of group equations (EMGE). Our determinations of the low-temperature heat capacities and main thermodynamic functions of benzoylferrocene, benzylferrocene, and ferrocenemethanol were reported in refs 8 and 9. For many other ferrocene derivatives, these values are still lacking. The thermodynamic properties of the propanoylferrocene and propylferrocene were determined in this work for the first time. The critical analysis of absolute entropies, $S^0_m(g)$, of alkylferrocenes and acylferrocenes allows us to verify the reliability and mutual congruence of $S^0_m(g)$ values and all thermodynamic data used for their calculation.

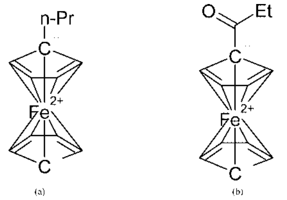

Figure 1. (a) Ferrocene, propyl-; Propylferrocene; CASRN 1273-92-3 and (b) Ferrocene, (1-oxopropyl)-; Propanoylferrocene; CASRN 1271-79-0.

Experimental Section

Preparation of the Compounds. Propanoylferrocene (POF) (Figure 1) was prepared by acylation of ferrocene with propionyl chloride, C_2H_5COCl, in a dry solution of methylene chloride, CH_2Cl_2. The reaction proceeded in the presence of aluminum chloride, $AlCl_3$, as a catalyst.[10] The reagents were taken in equimolar quantities that allowed us to minimize the impurities of ferrocene and 1,1′-dipropionyl-ferrocene in the final products. Propanoylferrocene was isolated from the reaction mixture by the column chromatography method (CCM) on silica gel. The residues of ferrocene and propanoylferrocene were eluted with petroleum ether and diethyl ether, respectively. After distillation of the latter, the POF sample was dried on air, repeatedly purified by CCM on silica gel, and then recrystallized in diethyl ether. Propanoylferrocene was a fusible powder with dark orange lamellar crystals. The mole fraction of POF determined by a calorimetric melting study and DSC was 0.9924 and 0.9912, respectively.

Propylferrocene (PF) (Figure 1) was synthesized by the Clemmensen reaction of reducing propanoylferrocene with amalgam (Zn/Hg) in the presence of hydrochloric acid, HCl.[10] Propylferrocene was extracted from the reaction mixture by diethyl ether. The raw product underwent column chromatography on silica gel, and then PF was eluated with petroleum ether. After distillation of the solvent, the sample was twice rectified in a vacuum. Propylferrocene was a dark liquid with

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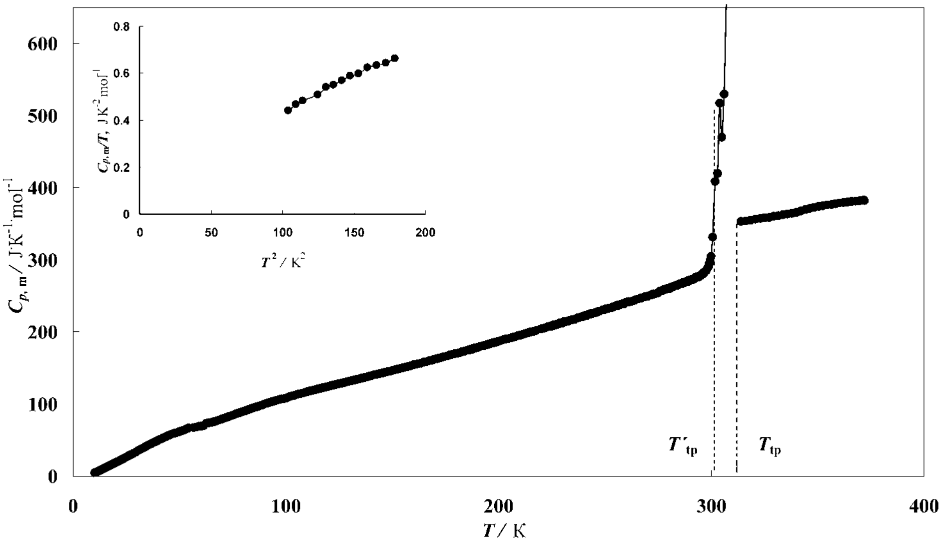

Figure 2. Molar heat capacity, $C_{p,\mathrm{m}}$, of propanoylferrocene as a function of temperature, T, where T_{tp} and T'_{tp} denote the triple point and temperature of an additional peak $T'_{\mathrm{tp}} = (304.0 \pm 0.5)$ K, respectively. In the inset, a dependence of $C_{p,\mathrm{m}}/T$ on T^2 is given for the helium range of the temperatures.

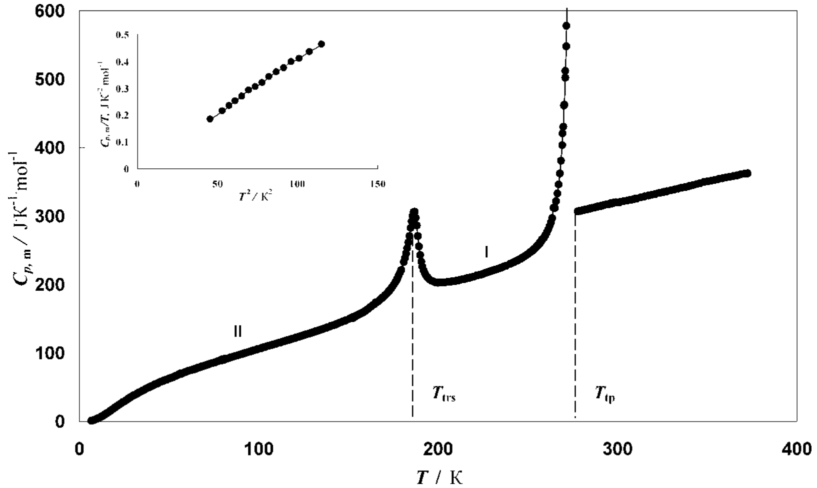

Figure 3. Molar heat capacity, $C_{p,\mathrm{m}}$, of propylferrocene as a function of temperature, T, where T_{tp} and T_{trs} denote the triple point and temperature of a λ-like transition. In the inset, a dependence of $C_{p,\mathrm{m}}/T$ on T^2 is given for the helium range of the temperatures.

an unpleasant smell. The mole fraction of PF determined by the calorimetric melting study and DSC was 0.9893 and 0.9895, respectively.

Heat Capacity and X-Ray Crystallography Measurements. The low-temperature heat capacities of propanoylferrocene and propylferrocene were measured in a fully automated setup consisting of a vacuum adiabatic calorimeter, a data acquisition and control system, AK-9.02, and a personal computer, PC. The construction of the calorimeter and the procedure was described in refs 8 and 11. The uncertainty of the heat capacity measurements is about 6 % between temperatures (6 and 30) K, (0.5 to 1) % from (30 to 80) K, and (0.3 to 0.2) % above 80 K.[8] The low-temperature heat capacity measurements were carried out using liquid helium and nitrogen as the refrigerants. The solid sample of POF was cooled from room temperature to helium temperature at the rate (5 to 7)·10^{-3} K·s^{-1}. The sample of PF reveals a tendency to form a metastable phase in cooling. The stable crystal phase of PF was prepared by melting (30 to 35) % of the sample during ≤ 20 h followed by slow cooling and quenching at T = 77.4 K. The heat capacity curve of POF exhibits a fusion (Figure 2) and that of PF a gradual solid-to-solid transition and their fusion (Figure 3). The fusion curve of POF has an additional peak at T = (304.0 ± 0.5) K. We do not rule out the possible effect of the impurities (~0.01 mol fraction) on the additional anomaly in the fusion curve of POF.

Table 1. Thermodynamic Properties of Propylferrocene in the Gradual Solid-to-Solid Transition

properties	crystal II→I
$T_{\mathrm{trs}}{}^{a}$/K	186.70 ± 0.30
$\Delta_{\mathrm{trs}}T^{b}$/K	156.1 – 204.0
$\Delta_{\mathrm{trs}}H_{\mathrm{m}}{}^{c}$/(kJ·mol^{-1})	1.23 ± 0.01
$\Delta_{\mathrm{trs}}S_{\mathrm{m}}{}^{c}$/(J·K^{-1}·mol^{-1})	6.59 ± 0.06

[a] T_{trs} is the temperature of the solid-to-solid transition. [b] $\Delta_{\mathrm{trs}}T$ denotes the temperature interval of the transition. [c] $\Delta_{\mathrm{trs}}H_{\mathrm{m}}$ and $\Delta_{\mathrm{trs}}S_{\mathrm{m}}$ are the enthalpy and entropy of the transition.

The temperature of the gradual transition of crystal II to crystal I of PF (Table 1) was ascribed to that of the maximum $C_{p,\mathrm{m}}$ value in the heat capacity peak. The changes of enthalpy, $\Delta_{\mathrm{trs}}H_{\mathrm{m}}$, and entropy, $\Delta_{\mathrm{trs}}S_{\mathrm{m}}$, of the thermal anomaly were evaluated by summing up these values in each experimental $C_{p,\mathrm{m}}$ point with subtracting appropriate functions of the empty calorimeter and those for the hypothetic normal parts of the $C_{p,\mathrm{m}}$ curve. Small $\Delta_{\mathrm{trs}}H_{\mathrm{m}}$ and $\Delta_{\mathrm{trs}}S_{\mathrm{m}}$ values of the thermal anomaly could be interpreted as the "order—disorder" transition. The nature of this transition was studied by X-ray crystallography.

Table 2. Crystallographic Data[a] of Propylferrocene Crystal at the Temperatures (150 and 200) K

T/K	symmetry, space group	$10^{-10}a$/m	$10^{-10}b$/m	$10^{-10}c$/m	β^0	$10^{-30}V$/m^3	Z	R_1	wR_2
150	monoclinic, $P2_1/c$	13.738(4)	7.541(1)	10.660(2)	99.76(3)	1088.4(4)	4	0.061	0.112
200	monoclinic, $P2_1/c$	13.977(4)	7.621(1)	10.521(2)	96.87(3)	1112.6(4)	4	0.064	0.136

[a] a, b, c, β, and V are parameters of the crystal lattice; Z denotes the number of molecules in the unit cell; and R_1 and wR_2 are the factors of the crystal structure quality.

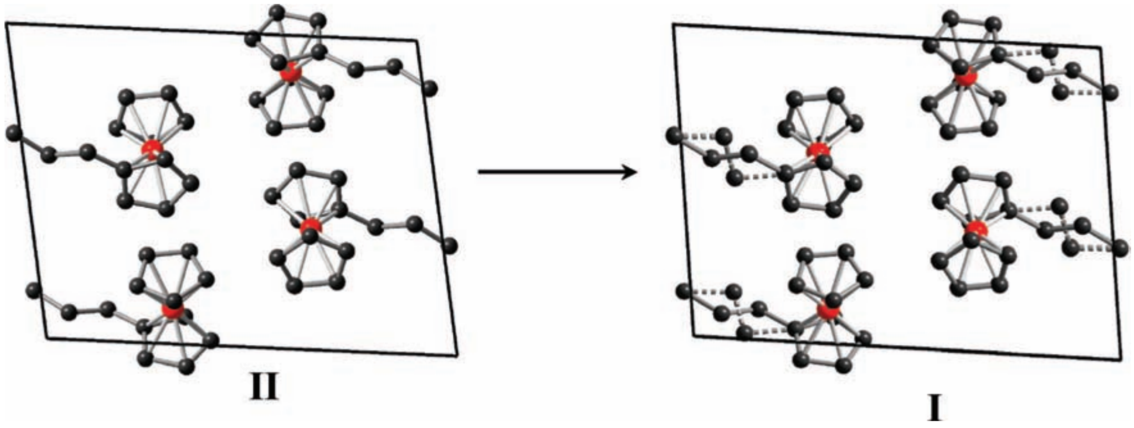

Figure 4. Structure of the propylferrocene crystal refined with SHELXL97 at the temperatures 150 K (II) and 200 K (I).

For X-ray study of PF, the crystals were grown in a glass capillary by cooling it to temperatures (40 to 50) K below the melting point. This resulted in the formation of a fine powder sample. The latter was then heated to a temperature at which some part of the crystals remained in the melt. Subsequent slow cooling of the sample at a rate of 0.003 K·s^{-1} produced the intergrowth of several crystals in the capillary. The part of the capillary containing two to three crystals was then chosen for the data collection. The crystallographic data were collected on an image plate of a diffractometer (IPDS, Stoe) using Mo Kα radiation ($\lambda = 0.71073 \cdot 10^{-10}$ m) at $T = (150$ and $200)$ K before and after transition, respectively. Crystal structures were solved by the use of SHELXS[12] and refined with SHELXL.[13] Table 2 lists crystallographic data of propylferrocene. The structure of PF at 200 K contains a propyl group disordered between two positions (in ca. 2:1 ratio) obviously due to thermal motion (Figure 4). The transition of the crystal II ($T = 150$ K) to the crystal I ($T = 200$ K) was accompanied by significant changes of the lattice parameters: basis vectors a, b, and c, angle β, and volume V. While both a and b parameters became larger, the c parameter and β angle slightly decreased (Table 2). Structure solution revealed that lower temperature modification of the propylferrocene contained the molecule with only one orientation of the propyl group. Apparently, the transitions in reverse order occurred when heating the crystals from (150 to 200) K. Thus, the solid-state anomaly of PF is caused by the onset of the internal rotation of propyl groups in the molecules, also accompanied by a small shift of the pentadienyl cycles around the axes passed through their centers. These variations led to the orientation disorder of the crystal phase II (Figure 3).

The enthalpies of fusion, $\Delta_{\text{fus}}H_{\text{m}}$, of POF and PF were determined by the calorimetric method on the basis of the total enthalpy adsorbed during fusion with subtraction of the enthalpy changes when heating the hypothetic normal crystal and the liquid and the empty calorimeter in the temperature interval of the fusion (Table 3).

Table 3. Molar Enthalpy of Fusion, $\Delta_{\text{fus}}H_{\text{m}}$, of Propanoylferrocene and Propylferrocene Calculated from the Equation $\Delta_{\text{fus}}H_{\text{m}} = \Delta H_{\text{tot}} - \Delta H_1 - \Delta H_2 - \Delta H_{\text{emp}}$ (1)[a]

K		J·mol^{-1}				
T_{in}[b]	T_{f}[b]	ΔH_1[b]	ΔH_2[b]	ΔH_{emp}[b]	ΔH_{tot}[b]	$\Delta_{\text{fus}}H_{\text{m}}$
			POF			
294.311	325.470	4806	5050	65098	93992	19038
292.656	330.460	5262	6839	59882	91262	19279
					mean	19159 ± 120
			PF			
256.315	296.040	5341	6247	10875	34905	12442
253.371	296.773	6085	6481	11867	37195	12762
252.928	292.478	6196	5117	10786	35118	13019
					mean	12741 ± 167

[a] m(POF) = 242.095 g·mol^{-1}; m(PF) = 228.111 g·mol^{-1}. [b] T_{in} and T_{f} are the initial and final temperatures of the calorimeter; ΔH_{tot} is the enthalpy increment in heating the calorimeter with the substances from T_{in} to T_{f}; ΔH_{emp} denotes the enthalpy increment needed for heating the empty container from T_{in} to T_{f}; ΔH_1 and ΔH_2 are the heating enthalpies calculated from the normal heat capacities of the crystal and liquid phases in the temperature intervals from T_{in} to T_{tp} and from T_{tp} to T_{f}, respectively.

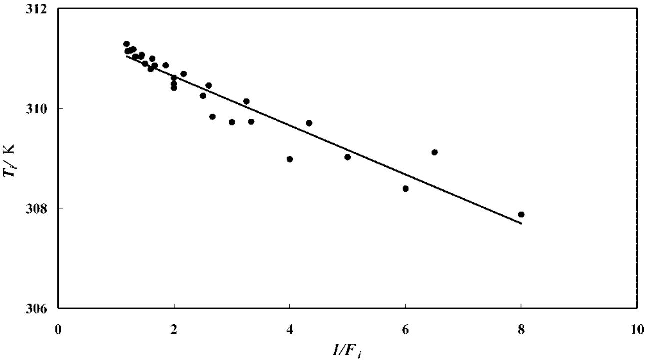

Figure 5. Equilibrium fusion temperatures, T_{i}, as a function of the fraction melted, $1/F_{\text{i}}$, of propanoylferrocene for four experiments. The straight line was drawn using eq 2.

The triple point temperatures, T_{tp}, and the purities of POF and PF were determined by calorimetric study of the reciprocal fraction of the samples melted, $1/F_{\text{i}}$, in dependence on the equilibrium fusion temperatures, T_{i}.[14] Four by four experiments were made for determination of the $T_{\text{i}} = f(1/F_{\text{i}})$ dependences (Figures 5 and 6). Examples of one by one experiments are given in Table 4. All curves of the $T_{\text{i}}(1/F_{\text{i}})$ dependences have concave forms that can be explained by formation of the solid

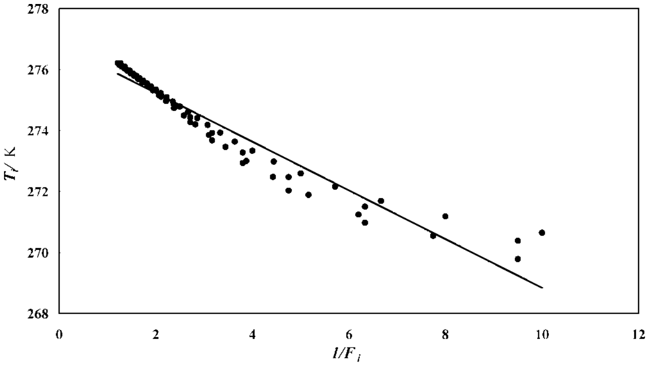

Figure 6. Equilibrium fusion temperatures, T_i, as a function of the fraction melted, $1/F_i$, of propylferrocene for four experiments. The straight line was drawn using eq 2.

Table 4. Equilibrium Melting Temperatures, T_i, Reciprocal of the Sample Fraction Melted, $1/F_i^a$, $T_{i(calcd)}$ Values Calculated from the Linear Dependence of T_i on $1/F_i$, (Equation 2) for Propanoylferrocene (POF) and Propylferrocene (PF)

T_i^a/K	q_i^b/J	$(1/F_i)$	$T_{i(calcd)}$/K
		POF	
308.37	2.895	13.00	306.34
309.12[a]	2.895	6.50[a]	308.96
309.70[a]	2.895	4.34[a]	309.84
310.14[a]	2.895	3.25[a]	310.28
310.46[a]	2.895	2.60[a]	310.54
310.69[a]	2.895	2.17[a]	310.72
310.86[a]	2.895	1.86[a]	310.84
310.99[a]	2.895	1.63[a]	310.94
311.07[a]	2.903	1.44[a]	311.01
311.18[a]	2.895	1.30[a]	311.07
311.29	2.895	1.18	311.12
311.39	2.895	1.08	311.15
311.52	2.895	1	311.19
		0	311.56
		PF	
347.93[a]	4.177	9.00[a]	347.93
348.74[a]	4.177	4.50[a]	348.74
349.02[a]	4.178	3.00[a]	349.01
349.15[a]	4.177	2.25[a]	349.14
349.23[a]	4.177	1.80[a]	349.23
349.28[a]	4.177	1.50[a]	349.28
349.32[a]	4.177	1.29[a]	349.32
349.35	4.178	1.13	349.35
350.31	4.177	1	349.37
		0	349.55

[a] The T_i and $1/F_i$ values were used for calculation of x_2, T_{tp}, A_{cr}, and B_{cr} in the range of $1/F_i$ from 1.20 to ≤ 10 according to ref 15. [b] q_i denotes a quantity of energy used for melting of the F_i substance fraction.

solutions. The data on T_i and $1/F_i$ values were fitted by the least-squares method (LSM) with equation[14]

$$T_i = d + f\cdot(1/F_i) \qquad (2)$$

where $d = T_0(T_{tp})$ is the triple point temperature of the pure compound; $f = (T_1 - T_0)$ denotes a depression of the T_0 value caused by impurities; T_1 is the triple point temperature of the completely melted substance under study ($F_i = 1$). The f values are equal to (0.49 and 0.80) K for POF and PF, respectively. The triple point temperatures and cryoscopic constants (Table 5) were determined according to the Rossini method.[14] The mole fraction of impurities, x_2, in the POF and PF samples were determined by the Smit−Aleksandrov method[19,20] using the equation for the equilibrium fusion temperature of the binary system with solid solution[20]

$$\ln\left(-\frac{dT_i}{d(1/F_i)}\right) = \ln\left\{\frac{x_2}{A_{cr}}(1-k)^2\right\} - k\cdot\ln(1/F_i) \qquad (3)$$

where A_{cr} is a cryoscopic constant of the compound under study and k denotes a coefficient of the impurity distribution between the solid and liquid phases of the system. Equation 3 makes it possible to determine k directly from the experimental dependences $T_i = f(1/F_i)$ and then to calculate the x_2 value. The data on $\ln(-dT_i/d(1/F_i))$ and $1/F_i$ were fitted by a linear equation using the LSM method. The k and $\ln\{(x_2/A_{cr})(1-k)^2\}$ values are equal to −1.0187 and 0.2594 for POF and −0.9437 and 0.7153 for PF, respectively. They were used for estimation of the mole fraction of impurity x_2 and that of the main substances, x_1 (Table 5).

The molar heat capacities of POF and PF were divided into several intervals and were fitted by polynomials

$$C_{p,m} = \sum_{i=0}^{n} A_i\cdot\{[(T/\mathrm{K}) - A_k]/B_k\}^i \qquad (4)$$

where $[(T/\mathrm{K}) - A_k]/B_k$ is the normalizing term; A_k and B_k are the scale factors; and i is the degree of polynomial. The values of the A_i polynomial were calculated by using the degrees of polynomials from 4 to 9. Extrapolation of the heat capacities to $T \to 0$ K was carried out by Debye approximation[21]

$$C_{p,m} = n\cdot R\cdot D\left(\frac{\Theta_D}{T}\right) \qquad (5)$$

where $R = 8.31447\ \mathrm{J\cdot K^{-1}\cdot mol^{-1}}$; D is the Debye function; $n = 3$; and Θ_D is a characteristic temperature. The values $\Theta_D(\mathrm{POF}) = (71.0 \pm 0.9)$ K and $\Theta_D(\mathrm{PF}) = (76.9 \pm 0.7)$ K were evaluated in the temperature ranges from (10.2 to 13.4) K and from (6.75 to 10.7) K, respectively. The least-squares deviations (LSD) of the calculated heat capacities from the experimental ones are equal to 7 % and 10 % for POF and PF, respectively.

Thermodynamic functions of the ferrocene derivatives were calculated by integration of eqs 4 and 5 and summing up the values of the enthalpy and entropy changes in the ranges of the phase transitions. The values of $C_{p,m}(T)$, $\{H^0_m(T) - H^0_m(0)\}$, $S^0_m(T)$, and $\{G^0_m(T) - H^0_m(0)\}$ over the temperature ranges studied are listed in Tables 6 and 7. The smoothed $C_{p,m}$ values of POF and PF are in agreement with experimental data within relative error limits from 0.8 % for the temperature range from

Table 5. Thermodynamic Properties of Fusion and Mole Fraction of Propanoylferrocene (POF) and Propylferrocene (PF) Determined by Adiabatic Calorimetry (AC) and DSC

	POF		PF	
properties	AC	DSC	AC	DSC
$T_{tp}(T_{fus})^a$/K	311.62 ± 0.51[a]	311.62	276.83 ± 0.50	278.20
$\Delta_{fus}H_m{}^b$/ (kJ·mol^{-1})	19.16 ± 0.12	19.69	12.74 ± 0.17	14.67
$\Delta_{fus}S_m{}^b$/ (J·K^{-1}·mol^{-1})	61.58 ± 0.39	–	46.15 ± 0.61	–
$x_1{}^c$/mole fractions	0.9924 ± 6·10^{-3}	0.9912	0.9893 ± 1·10^{-2}	0.9895
$A_{cr}{}^d$/K^{-1}	(237.3 ± 1.4)·10^{-4}	–	(199.9 ± 2.6)·10^{-4}	–
$B_{cr}{}^d$/K^{-1}	(184.4 ± 1.5)·10^{-5}	–	(289.6 ± 4.3)·10^{-5}	–

[a] T_{tp} and T_{fus} are the triple point and fusion temperatures; literature data on T_{fus} of POF are (311.1 to 312.1) K in refs 16−18. [b] $\Delta_{fus}H_m$ and $\Delta_{fus}S_m$ denote the enthalpy and entropy of fusion. [c] x_1 is the mole fraction of the substances under study. [d] A_{cr} and B_{cr} are the cryoscopic constants calculated according to ref 14.

Table 6. Smoothed Molar Thermodynamic Properties of Propanoylferrocene, $C_{13}H_{14}OFe$[a]

T	$C_{p,m}$	$\{H^0_m(T) - H^0_m(0)\}$	$S^0_m(T)$	$-\{G^0_m(T) - H^0_m(0)\}$
K	$J \cdot K^{-1} \cdot mol^{-1}$	$kJ \cdot mol^{-1}$	$J \cdot K^{-1} \cdot mol^{-1}$	$kJ \cdot mol^{-1}$
		Crystal		
10	4.607	0.01261	1.703	0.00442
15	11.25	0.05079	4.709	0.01984
20	18.61	0.1253	8.946	0.05362
25	26.27	0.2374	13.92	0.1106
30	34.16	0.3884	19.40	0.1936
35	42.07	0.5790	25.27	0.3054
40	49.63	0.8085	31.38	0.4467
45	56.35	1.074	37.63	0.6194
50	61.76	1.370	43.86	0.8230
55	66.08	1.690	49.95	1.057
60	70.11	2.030	55.87	1.322
65	74.36	2.391	61.65	1.616
70	79.11	2.775	67.33	1.938
75	84.35	3.183	72.97	2.290
80	89.80	3.618	78.59	2.669
90	99.79	4.567	89.75	3.510
100	108.7	5.610	100.8	4.470
110	116.7	6.737	111.5	5.528
120	124.2	7.942	122.0	6.698
130	131.6	9.222	132.2	7.964
140	138.9	10.58	142.2	9.328
150	146.4	12.00	152.1	10.82
160	154.0	13.50	161.8	12.39
170	161.9	15.08	171.3	14.04
180	170.0	16.74	180.8	15.80
190	178.3	18.48	190.2	17.66
200	186.8	20.31	199.6	19.61
210	195.4	22.22	208.9	21.65
220	204.1	24.22	218.2	23.78
230	212.9	26.30	227.5	26.03
240	221.9	28.47	236.7	28.34
250	231.0	30.74	246.0	30.76
260	240.3	33.09	255.2	33.26
270	250.1	35.55	264.4	35.84
280	260.5	38.10	273.7	38.54
290	271.7	40.76	283.1	41.34
298.15	280.7 ± 0.56	43.01 ± 0.16	290.7 ± 1.2	43.66 ± 0.38
300	282.7	43.53	292.5	44.22
310	293.8	46.41	301.9	47.18
311.13	295.0	46.75	303.0	47.52
		Liquid		
311.13	347.6	65.91	364.6	47.52
320	353.3	69.01	374.4	50.80
330	359.7	72.58	385.4	54.60
340	365.7	76.21	396.2	58.50
350	372.9	79.90	406.9	62.52
360	378.5	83.66	417.5	66.64
370	381.9	87.46	427.9	70.86

[a] $m = 242.095$ $g \cdot mol^{-1}$; m is the molar mass.

(13 to 46) K, (0.3 to 0.6) % between temperatures (46 and 85) K, and from (0.1 to 0.2) % above $T = 85$ K.

Vapor Pressure of the Ferrocene Derivatives. The molar enthalpies of vaporization, $\Delta_{vap}H_m$, and sublimation, $\Delta_{sub}H_m$, of the POF and PF have been determined from the temperature dependences of the saturated vapor pressure, p_{sat}, measured by Emel'yanenko, Verevkin, Krol et al.[22] using a transpiration method.[23] The method is based on the determination of the amount of the compound transported by a nitrogen stream followed by calculation of the vapor pressure using Dalton's law for the ideal gas mixture. The temperature dependences of the saturated vapor pressures were determined in the temperature and pressure intervals from (315.6 to 380.5) K and (0.32 to 43.26) Pa for POF and (298.4 to 358.1) K and (1.13 to 102.6) Pa for PF, respectively. The pT parameters were fitted with the equation[23]

$$R \ln(p_{sat,i}/p^0) = a' + \frac{b'}{(T_i/K)} + \{\Delta C_{p,m}/(J \cdot K^{-1} \cdot mol^{-1})\} \cdot \ln\left(\frac{T_i}{T_{ref}}\right) \quad (6)$$

where $p^0 = 101325$ Pa; a' and b' are the coefficients; $\Delta C_{p,m} = C_{p,m}(g) - C_{p,m}(l)$ is the difference between the molar heat capacities of the gas and liquid; and T_{ref} denotes the reference temperature, 298.15 K.

The enthalpy of the vaporization was calculated from the formula

Table 7. Smoothed Molar Thermodynamic Properties of Propylferrocene, $C_{13}H_{16}Fe$[a]

T	$C_{p,m}$	$\{H^0_m(T) - H^0_m(0)\}$	$S^0_m(T)$	$-\{G^0_m(T) - H^0_m(0)\}$
K	$J \cdot K^{-1} \cdot mol^{-1}$	$kJ \cdot mol^{-1}$	$J \cdot K^{-1} \cdot mol^{-1}$	$kJ \cdot mol^{-1}$
		Crystal II		
5	0.5339	0.000668	0.1780	0.000222
10	3.806	0.009802	1.368	0.003878
15	11.48	0.04748	4.322	0.01735
20	20.55	0.1273	8.853	0.04976
25	29.50	0.2527	14.41	0.1076
30	37.60	0.4209	20.52	0.1947
35	44.82	0.6272	26.87	0.3132
40	51.46	0.8683	33.30	0.4637
45	57.41	1.140	39.71	0.6470
50	62.94	1.441	46.05	0.8615
55	68.11	1.769	52.29	1.107
60	72.96	2.122	58.43	1.384
65	77.55	2.498	64.45	1.691
70	81.91	2.897	70.36	2.028
75	86.11	3.317	76.16	2.395
80	89.89	3.758	81.84	2.789
90	98.25	4.699	92.91	3.663
100	106.2	5.721	103.7	4.649
110	114.1	6.823	114.2	5.739
120	122.0	8.003	124.4	6.925
130	130.2	9.263	134.5	8.222
140	139.3	10.61	144.5	9.620
150	149.6	12.05	154.5	11.12
160	161.7	13.61	164.5	12.71
170	173.8	15.29	174.7	14.41
180	185.9	17.08	184.9	16.20
186.70	194.0	18.36	191.9	17.47
		Crystal I		
186.70	191.3	19.59	198.5	17.47
190	193.3	20.22	201.9	18.14
200	199.5	22.19	211.9	20.19
210	205.6	24.21	221.8	22.37
220	212.1	26.30	231.5	24.63
230	220.2	28.46	241.1	26.99
240	230.2	30.71	250.7	29.46
250	244.6	33.08	260.4	32.02
260	274.7	35.65	270.4	34.65
270	324.0	38.64	281.7	37.42
276.03	286.8	40.00	286.6	39.10
		Liquid		
276.03	305.9	52.74	332.7	39.10
280	308.4	53.96	337.2	40.46
290	314.9	57.08	348.1	43.87
298.15	319.5 ± 0.6	59.67 ± 0.18	356.9 ± 0.9	46.74 ± 0.32
300	320.5	60.26	358.9	47.41
310	325.8	63.49	369.5	51.06
320	331.8	66.78	380.0	54.82
330	338.2	70.13	390.3	58.67
340	344.4	73.54	400.5	62.63
350	350.7	77.02	410.5	66.66
360	356.6	80.55	420.5	70.83
370	361.5	84.14	430.3	75.07

[a] $m = 228.111$ $g \cdot mol^{-1}$; m is the molar mass.

$$\Delta_{\mathrm{vap}}H_{\mathrm{m}}(\Delta_{\mathrm{sub}}H_{\mathrm{m}}) = -b' + \{\Delta C_{p,\mathrm{m}}/(\mathrm{J\cdot K^{-1}\cdot mol^{-1}})\}\cdot(T_{\mathrm{i}}/K) \tag{7}$$

that was derived by differentiation of eq 6 upon $1/T$. The ideal gas heat capacities of POF and PF required for the $\Delta C_{p,\mathrm{m}}$ calculation were obtained by the additive Chickos and Acree method.[24] The thermodynamic values calculated from eqs 6 and 7 are listed in Table 8. The uncertainties of the vaporization (sublimation) functions were estimated from (1 to 1.5) % depending on the temperature interval of the pT parameters extending to $T = 298.15$ K.

Calculation and Discussion of the Ideal Gas Thermodynamic Functions. The changes of the enthalpy, entropy, and Gibbs energy of POF and PF in the ideal gas state at $T = 298.15$ K (Table 9) were calculated on the basis of the appropriate functions in the condensed state (Tables 6 and 7), enthalpies and entropies of sublimation and vaporization (Table 8), and entropies of the ideal gas compression from $p(298.15\ \mathrm{K})$ to $(p/\mathrm{kPa}) = 101.325$ (Table 9). There are no vapor pressure data over the crystal phase of POF. Therefore, the following values were used for calculation of the thermodynamic functions of POF: the enthalpy of vaporization and the entropy of compression estimated from the vapor pressure data over the liquid in spite of the different slopes of pT curves for solid and liquid phases.

The standard enthalpies of formation (Tables 10 and 11), absolute entropies, and heat capacities of POF and PF at $T = 298.15$ K have been calculated by the empirical method of the group equations,[33] which is equivalent to the rules of group additively. The results of this method were shown to be in good agreement with those obtained by using isodesmic reactions for benzoyl and benzyl derivatives of ferrocene.[8] The ideal gas absolute entropies of propyl and propanoylferrocenes were compared with those for other members of the series of alkylferrocenes (ALF) and acylferrocenes (ACF) studied in refs 3 and 4 (Table 12). An agreement between $S^0_{\mathrm{m}}(\mathrm{g})(\mathrm{calor})$ and $S^0_{\mathrm{m}}(\mathrm{g})(\mathrm{calcd})$ values within the limits of their uncertainties confirms the reliability of these values, as well as all the thermodynamic properties used for their calculation (the heat capacities, saturated vapor pressures, entropies of sublimation, etc.).

Table 8. Coefficients of Equations 6 and 7, $C^0_{p,\mathrm{m}}(g)$ Values at $T = 298.15$ K Calculated Analogously to Ref 24, the Enthalpies and Entropies of Vaporization, $\Delta_{\mathrm{vap}}H_{\mathrm{m}}(T)$ and $\Delta_{\mathrm{vap}}S_{\mathrm{m}}(T)$, and Those of Sublimation, $\Delta_{\mathrm{sub}}H_{\mathrm{m}}(T)$ and $\Delta_{\mathrm{sub}}S_{\mathrm{m}}(T)$, at $T = 298.15$ K for Propanoylferrocene (POF) and Propylferrocene (PF)

properties	POF	PF
a'	253.5	231.4
b'	−111513.9	−97325.7
$T_{\mathrm{i}}^{a22}/\mathrm{K}$	315.6	298.4
$T_{\mathrm{f}}^{a22}/\mathrm{K}$	380.5	358.1
$\Delta C_{p,\mathrm{m}}(T)/(\mathrm{J\cdot K^{-1}\cdot mol^{-1}})$	−103.5	−93.7
$C^0_{p,\mathrm{m}}(g)(T)/(\mathrm{J\cdot K^{-1}\cdot mol^{-1}})$	253.8	225.9
$\Delta_{\mathrm{vap}}H_{\mathrm{m}}(T)/(\mathrm{kJ\cdot mol^{-1}})$	80.67 ± 0.80	69.40 ± 0.70
$\Delta_{\mathrm{vap}}S_{\mathrm{m}}(T)/(\mathrm{J\cdot K^{-1}\cdot mol^{-1}})$	270.6 ± 2.7	232.8 ± 2.3
$\Delta_{\mathrm{sub}}H_{\mathrm{m}}(T)/(\mathrm{kJ\cdot mol^{-1}})$	99.04 ± 1.50	−
$\Delta_{\mathrm{sub}}S_{\mathrm{m}}(T)/(\mathrm{J\cdot K^{-1}\cdot mol^{-1}})$	332.2 ± 5.0	−

[a] T_{i} and T_{f} are the initial and final temperatures of the vapor pressure data, respectively.

Table 9. Ideal Gas Thermodynamic Functions of Propanoylferrocene (POF) and Propylferrocene (PF) Calculated from Calorimetric Data on the Heat Capacities and Enthalpies of Sublimation and Vaporization and Ideal Gas Entropy of Compression at $T = 298.15$ K

properties	POF	PF
$R\ \ln\{p(T)/101.325\ \mathrm{kPa}\}/(\mathrm{J\cdot K^{-1}\cdot mol^{-1}})$	−120.5	−95.1
$\{H^0_{\mathrm{m}}(T) - H^0_{\mathrm{m}}(0)\}^a/(\mathrm{kJ\cdot mol^{-1}})$	142.1 ± 1.5	129.1 ± 1.4[b]
$S^0_{\mathrm{m}}(\mathrm{g})^a/(\mathrm{J\cdot K^{-1}\cdot mol^{-1}})$	502.7 ± 5.1	494.3 ± 5.0[b]
$\{G^0_{\mathrm{m}}(T) - H^0_{\mathrm{m}}(0)\}(\mathrm{g})^a/(\mathrm{kJ\cdot mol^{-1}})$	−7.8 ± 2.1	−18.3 ± 2.0

[a] The changes of the enthalpy, entropy, and Gibbs energy, respectively. [b] The uncertainties of $\{H^0_{\mathrm{m}}(T) - H^0_{\mathrm{m}}(0)\}$ and $S^0_{\mathrm{m}}(\mathrm{g})$ values of PF were doubled as the enthalpy and entropy of sublimation and compression entropy of this compound were calculated from the vapor pressure data over the liquid phase due to lack of appropriate data for the crystal phase.

Table 10. Calculation of the Thermodynamic Properties of Propanoylferrocene by the Empirical Method of Group Equations[a]

reaction	$\Delta_{\mathrm{f}}H^0_{\mathrm{m},298}$ kJ·mol⁻¹	$S^0_{\mathrm{m},298}$ J·K⁻¹·mol⁻¹	$C^0_{p,\mathrm{m},298}$ J·K⁻¹·mol⁻¹
$\mathrm{F{-}CO{-}C_2H_5 + C_6H_6 = F + C_6H_5{-}CO{-}C_2H_5}$	39.7		
$\mathrm{F{-}CO{-}C_2H_5 + C_2H_6 = F + C_2H_5{-}CO{-}C_2H_5}$	56.9	513.6	
$\mathrm{F{-}CO{-}C_2H_5 + C_3H_8 = F + C_3H_7{-}CO{-}C_2H_5}$	58.1		
$\mathrm{F{-}CO{-}C_2H_5 + C_6H_6 = F{-}CO{-}H + C_6H_5{-}C_2H_5}$	52.4		
$\mathrm{F{-}CO{-}C_2H_5 + C_6H_5{-}CH_3 = F{-}CO{-}C_6H_5 + C_3H_8}$	44.8		
$\mathrm{F{-}CO{-}C_2H_5 + C_6H_5{-}C_2H_5 = F{-}CO{-}C_6H_5 + C_4H_{10}}$	44.3		
$\mathrm{F{-}CO{-}C_2H_5 + C_2H_6 = F{-}C_2H_5 + CH_3{-}CO{-}CH_3}$	44.7	512.4	232.5
$\mathrm{F{-}CO{-}C_2H_5 + C_4H_{10} = F{-}C_2H_5 + C_2H_5{-}CO{-}C_2H_5}$	45.8		
$\mathrm{F{-}CO{-}C_2H_5 + C_6H_6 = F{-}C_2H_5 + C_6H_5{-}CO{-}H}$	58.7		
average:	**50 ± 6**[b]	**513 ± 10**[c]	**232 ± 4.6**[c]

[a] $\mathrm{F = Fe(C_5H_5)_2}$, $\mathrm{F{-} = Fe(C_5H_5)(C_5H_4{-})}$. The enthalpies of formation for reference species were taken from ref 25 (organic compounds) and ref 7 (ferrocene and its derivatives). The entropy and heat capacity values were taken from ref 26 ($\mathrm{C_2H_6}$), ref 27 ($\mathrm{C_2H_5{-}CO{-}C_2H_5}$), ref 28 ($\mathrm{CH_3{-}CO{-}CH_3}$), and ref 7 ($\mathrm{F{-}C_2H_5}$). Values of $S^0_{\mathrm{m},298}$ (362.6 J·K⁻¹·mol⁻¹) and $C^0_{p,\mathrm{m},298}$ (162.6 J·K⁻¹·mol⁻¹) for F were calculated in this work from B3LYP/6-31G(d,p) molecular parameters. [b] Uncertainty of $\Delta_{\mathrm{f}}H^0_{\mathrm{m},298}$ is a mean square value. [c] The errors of $S^0_{\mathrm{m},298}$ and $C^0_{p,\mathrm{m},298}$ values were evaluated in 2 %.

Table 11. Calculation of the Thermodynamic Properties of Propylferrocene by the Empirical Method of Group Equations[a]

reaction	$\Delta_{\mathrm{f}}H^0_{\mathrm{m},298}$ kJ·mol⁻¹	$S^0_{\mathrm{m},298}$ J·K⁻¹·mol⁻¹	$C^0_{p,\mathrm{m},298}$ J·K⁻¹·mol⁻¹
$\mathrm{F{-}C_3H_7 + C_6H_6 = F + C_6H_5{-}C_3H_7}$	156.3	489.8	
$\mathrm{F{-}C_3H_7 + C_6H_5{-}CH_3 = F + C_6H_5{-}C_4H_9}$	168.7		
$\mathrm{F{-}C_3H_7 + C_2H_6 = F + C_5H_{12}}$	167.9		
$\mathrm{F{-}C_3H_7 + C_3H_8 = F + C_6H_{14}}$	168.8		
$\mathrm{F{-}C_3H_7 + C_2H_6 = F{-}C_2H_5 + C_3H_8}$	157.1	485.0	231.1
$\mathrm{F{-}C_3H_7 + C_6H_5{-}CH_3 = F{-}C_2H_5 + C_6H_5{-}C_2H_5}$	157.5	492.7	233.7
average:	**163 ± 6**[b]	**489 ± 10**[c]	**232 ± 4.6**[c]

[a] $\mathrm{F = Fe(C_5H_5)_2}$, $\mathrm{F{-} = Fe(C_5H_5)(C_5H_4{-})}$. The enthalpies of formation for reference species were taken from ref 25 (organic compounds) and ref 7 (ferrocene and its derivatives). The entropy and heat capacity values were taken from ref 29 ($\mathrm{C_6H_6}$, $\mathrm{C_6H_5{-}C_2H_5}$), ref 26 ($\mathrm{C_2H_6}$), ref 30 ($\mathrm{C_3H_8}$), ref 31 ($\mathrm{C_6H_5{-}CH_3}$), ref 32 ($\mathrm{C_6H_5{-}C_3H_7}$), and ref 7 ($\mathrm{F{-}C_2H_5}$); values of $S^0_{\mathrm{m},298}$ (362.6 J·K⁻¹·mol⁻¹) and $C^0_{p,\mathrm{m},298}$ (162.6 J·K⁻¹·mol⁻¹) for F were calculated in this work from B3LYP/6-31G(d,p) molecular parameters. [b] Uncertainty of $\Delta_{\mathrm{f}}H^0_{\mathrm{m},298}$ is a mean square value. [c] The errors of $S^0_{\mathrm{m},298}$ and $C^0_{p,\mathrm{m},298}$ values were evaluated in 2 %.

A mutual congruence of the entropies in each series was analyzed depending on the molar mass of the substances, m,

Table 12. Absolute Entropies of Ferrocene (F) and Some Alkyl- and Acylferrocenes, viz., Ethyl-F (EF), Propyl-F (PF), Butyl-F (BF), Formil-F (FF), Acetyl-F (AF), and Propanoyl-F (POF) in the Ideal Gas and Condensed States at T = 298.15 K

compound	ref	S^0_m(cond) (calor) J·K^{-1}·mol^{-1}	S^0_m(g) (calor) J·K^{-1}·mol^{-1}	S^0_m(g) (calcd) J·K^{-1}·mol^{-1}	S^0_m(g)^a J·K^{-1}·mol^{-1}
F	34, 35	211.85 ± 1.1^b	361.0 ± 3.6^{b,c}	362.6 ± 10^d	362 ± 7
EF	4, 7	(354.1 ± 1.1)^f	(525.3 ± 2.9)^f	453 ± 10^d	453 ± 9
PF	this work	356.6 ± 0.9	494.3 ± 5.0	489 ± 10^e	492 ± 8
BF	4	398.1 ± 1.2	(586.3 ± 3.4)^f	527 ± 10^e	527 ± 10
FF	4, 7	241.3 ± 0.7	(398.1 ± 2.8)^f	435 ± 10^d	435 ± 10
AF	3	264.6 ± 0.8	478.3 ± 2.9	–	478 ± 3
POF	this work	291.0 ± 1.2	502.7 ± 5.1	513 ± 10^e	508 ± 8

[a] Recommended S^0_m(g) values. [b] The errors of S^0_m(cond)(calor) and S^0_m(g)(calor) values were evaluated in this work. [c] The ideal gas entropy of ferrocene was calculated using the S^0_m(cond)(calor) value and summary correction ΔS_m = 149.1 J·K^{-1}·mol^{-1} for the entropy of sublimation and the entropy of the ideal gas compression (evaluated from the literature entropy data for ferrocene listed in ref 35). [d] Calculation by ST and DFT methods on the level B3LYP/6-31G(d, p). [e] Calculation by empirical difference method.[36] [f] Unreliable values.

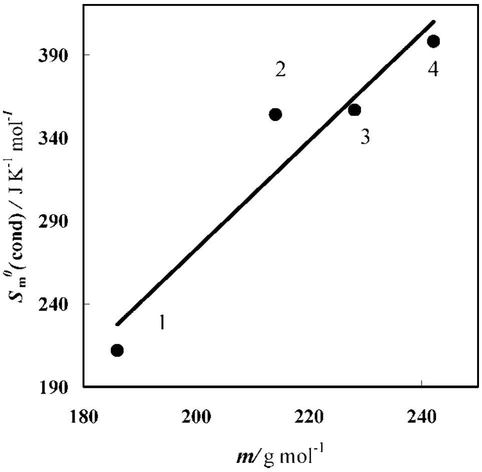

Figure 7. Change of the absolute entropies for condensed states in the series of alkylferrocenes: ferrocene[34,35] (1), ethylferrocene[4] (2), propylferrocene (3), butylferrocene[4] (4) at T = 298.15 K. The straight line was computed from eq 8; m is the molar mass of the compounds.

the linear change of the S^0_m values in homologous series being assumed. Figure 7 shows a distribution of the calorimetric S^0_m(cond)(calor) values for the series of alkylferrocenes in condensed states relative to a straight line correlation obtained by LSM fitting these data (Table 12)

$$S^0_m(\text{cond})(\text{ALF})/(\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}) = 3.250\cdot(m/\text{g}\cdot\text{mol}^{-1}) - 377.1 \quad (8)$$

The LSD deviation of the calculated entropies from those obtained on the basis of experimental C_p data accounts for σ_s = 29.1 J·K^{-1}·mol^{-1}. The entropy of ethylferrocene deviates by the value of 10.5 % from the linear dependence of the other homologues. This deviation and σ_s value are several times larger than the uncertainty of S^0_m(cond) and can be explained by errors in calorimetric heat capacity data.[4] An availability of error in calorimetric value of EF entropy was confirmed by changing σ_s from (29.1 to 4.0) J·K^{-1}·mol^{-1} after excluding this value from the considered series (Figure 8).

The ideal gas entropies of alkylferrocenes in dependence on m were fitted by the equation

$$S^0_m(\text{g})(\text{ALF})/(\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}) = 3.840\cdot(m/\text{g}\cdot\text{mol}^{-1}) - 361.8 \quad (9)$$

that was obtained by the LSM method using the ideal gas calorimetric entropies of F, NPF, and NBF and the S^0_m(g)(calcd) value of EF calculated by statistical thermodynamic (ST) and DFT methods[7] (Table 12). The LSD deviation for eq 9, σ_s = 29.1 J·K^{-1}·mol^{-1}, is large enough. At the same time, the S^0_m(g)(calor) values of NPF and NBF deviate from the smoothed straight line of eq 9 (Figure 8) by 3.9 % and 3.2 %, respectively, that can be explained by a too large entropy of NBF. After replacing the latter by the S^0_m(g)(calcd) value (Table 12), a more accurate correlation with σ_s = 6.2 J·K^{-1}·mol^{-1} was obtained

$$S^0_m(\text{g})(\text{ALF})/(\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}) = 2.994\cdot(m/\text{g}\cdot\text{mol}^{-1}) - 192.7 \quad (10)$$

The appropriate deviations of the S^0_m(g) value for NPF and NBF from the new correlation did not exceed ~ 1 %.

A comparison of the absolute entropies of acylferrocenes in condensed and ideal gas states is shown in the Figure 9, where the straight line correlations were computed from the equations obtained by LSM approximation of the calorimetric entropies of Table 12

$$S^0_m(\text{cond})(\text{ACF})/(\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}) = 1.392\cdot(m/\text{g}\cdot\text{mol}^{-1}) - 50.68 \quad (11)$$

$$S^0_m(\text{g})(\text{ACF})/(\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}) = 2.664\cdot(m/\text{g}\cdot\text{mol}^{-1}) - 144.6 \quad (12)$$

The σ_s value for eq 11 equals 6.1 J·K^{-1}·mol^{-1}, which accounts for ≤ 2.5 % of the S^0_m(cond) (ACF) values. An appropriate deviation of eq 12 is large enough, σ_s = 23.4 J·K^{-1}·mol^{-1}. At the same time, the calorimetric S^0_m(g)(calor) value of formylferrocene deviates from the linear dependence of the other members by 6.7 % that can be explained by errors in vapor pressures and/or the entropy of sublimation used for calculation of S^0_m(g)(calor). After excluding the latter value from the series

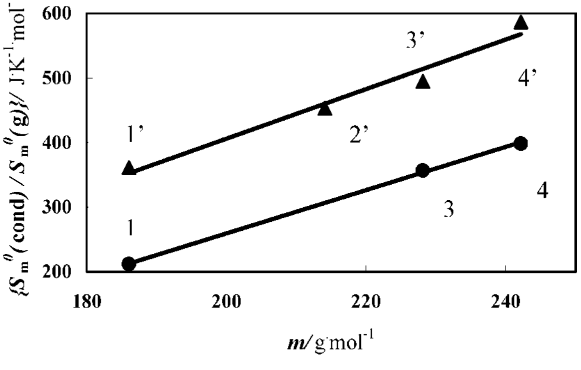

Figure 8. Changes of the absolute entropies of alkylferrocenes in condensed (1, 3, 4) and ideal gas (1′, 2′, 3′, 4′) states in dependence on the molar mass, m, at T = 298.15 K. The signs of the compounds are analogous to Figure 7.

and replacing it with the S^0_m(g)(calcd) value estimated by ST and DFT methods (Table 12), a more accurate, straight line correlation with $\sigma_s = 6.1\ \mathrm{J \cdot K^{-1} \cdot mol^{-1}}$ was obtained

$$S^0_m(\mathrm{g})(\mathrm{ACF})/(\mathrm{J \cdot K^{-1} \cdot mol^{-1}}) = 2.589 \cdot (m/\mathrm{g \cdot mol^{-1}}) - 118.9 \quad (13)$$

The deviations of the ideal gas entropies of ACF from the new correlation reduced to ≤ 1.4 % which was near the error limits of the F, AF, and POF entropies.

The critical analysis of the experimental and calculated values of the absolute entropies of the alkyl and acyl derivatives of ferrocene allowed to conclude that S^0_m(cond)(calor) and S^0_m(g)(calor) values of acetyl,[3] propyl, and propanoylferrocenes (Table 12) are reliable within their uncertainties. The entropy values of ethylferrocene[4] in the condensed state and the entropies of butyl[4] and formyl[4] ferrocenes in the ideal gas states are unreliable due to experimental errors of EF heat capacity and those of the vapor pressures and the enthalpies of vaporization of NBF and FF (Table 12). The uncertainties of these literature values[4] were considerably understated.

Table 13 lists values of $\Delta_f H^0_m$(g), $\Delta_f S^0_m$(g), and $\Delta_f G^0_m$(g) for POF and PF. The $\Delta_f S^0_m$(g) values were calculated according to the reactions

$$13\mathrm{C}_{(\mathrm{cr.,graphite})} + 7\mathrm{H}_{2(\mathrm{g})} + 1/2\mathrm{O}_{2(\mathrm{g})} + \mathrm{Fe}_{(\mathrm{cr.III,cub})} = \mathrm{C_5H_5FeC_5H_4{-}COC_2H_{5(g)}} \quad (14)$$

$$13\mathrm{C}_{(\mathrm{cr.,graphite})} + 8\mathrm{H}_{2(\mathrm{g})} + \mathrm{Fe}_{(\mathrm{cr.III,cub})} = \mathrm{C_5H_5FeC_5H_4{-}C_3H_{7(g)}} \quad (15)$$

using recommended S^0_m(g) values of POF and PF (Table 12) and the absolute entropies of $\mathrm{C}_{(\mathrm{cr.,graphite})}$, $\mathrm{H}_{2(\mathrm{g})}$, $\mathrm{O}_{2(\mathrm{g})}$, and $\mathrm{Fe}_{(\mathrm{cr.III,cub})}$ at $T = 298.15$ K taken from refs 37 and 38.

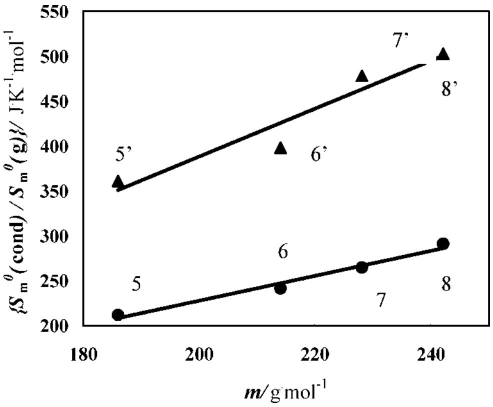

Figure 9. Change of the absolute entropies in the series of acylferrocenes: ferrocene[34,35](5), formylferrocene[4] (6), acetylferrocene[3] (7), and propanoylferrocene (8) in condensed (5−8) and ideal gas (5′−8′) states at $T = 298.15$ K. The straight lines were computed from eqs 11 and 12; *m* is the molar mass of the compounds.

Table 13. Ideal Gas Thermodynamic Functions of Propanoylferrocene (POF) and Propylferrocene (PF) at $T = 298.15$ K Calculated from the Empirical Method of Group Equations and Calorimetric Data

	$\Delta_f H^0_m(\mathrm{g})^a$ / $\mathrm{kJ \cdot mol^{-1}}$	$\Delta_f S^0_m(\mathrm{g})^a$ / $\mathrm{J \cdot K^{-1} \cdot mol^{-1}}$	$\Delta_f G^0_m(\mathrm{g})^a$ / $\mathrm{kJ \cdot mol^{-1}}$
POF	50 ± 6	−610 ± 8	232 ± 6.5
PF	163 ± 6	−654 ± 8	358 ± 6.5

[a] $\Delta_f H^0_m$(g), $\Delta_f S^0_m$(g), and $\Delta_f G^0_m$(g) are the standard enthalpy, entropy, and Gibb's free energy of formation.

Conclusions

The paper deals with the thermodynamic investigation of the phase equilibriums of propanoylferrocene (POF) and propylferrocene (PF) which are members of the large class of ferrocene derivatives, and thermodynamic data for many of them are still lacking.

The heat capacities, phase transitions, and purity of the substances were determined by vacuum adiabatic calorimetry in the temperature intervals from (10 and 7) K to 372 K. The heat capacity curve of POF reveals a fusion, and that of PF exhibits a solid-to-solid transition and the fusion. The X-ray crystallographic study of PF showed that solid-phase transition was caused by the onset of the internal rotation of the propyl groups in the molecules of PF. Thermodynamic properties of the transition and fusions (the temperatures and the changes of the enthalpies and entropies) have been determined. The heat capacities of POF and PF were fitted by polynomials. Extrapolation of the heat capacities to $T \rightarrow 0$ K was carried out by using the Debye function. The main thermodynamic functions (absolute entropies, changes of the enthalpy, and Gibbs energy) of POF and PF were calculated for the solid and liquid phases of the temperature intervals studied. The ideal gas thermodynamic functions were derived at $T = 298.15$ K using the enthalpies of vaporization and sublimation calculated from the saturated vapor pressures of the work.[22]

A critical analysis of the absolute entropies, S^0_m(g), of the alkylferrocenes and acylferrocenes obtained in this work and available in the literature allowed us to verify the reliability and mutual congruence of the thermodynamic data used for calculation of S^0_m(g) values. The standard enthalpies of formation, $\Delta_f H^0_m$, of POF and PF were calculated by the empirical method of the group equation.[33] The $\Delta_f H^0_m$ and S^0_m(g) values were used for calculation of the enthalpies, entropies, and Gibbs energy of formation of POF and PF at $T = 298.15$ K.

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