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Heat Capacity and Thermodynamic Functions of Ferrocenemethanol

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Abstract—The heat capacity ($C_{p,m}$) of ferrocenemethanol (FM) $C_5H_5FeC_5H_4CH_2OH$ have been measured by the low-temperature adiabatic calorimetry method in the range 6–371 K. The triple point temperature, the enthalpy of fusion, and the purity of the substance under consideration have been determined. The ideal gas thermodynamic functions of FM—absolute entropy $S^0_{m(\mathrm{g})}$ and change in the enthalpy $\Delta_0^T H_m$ at 298.15 K—have been derived from the heat capacity data and the known values of the saturation vapor pressure and enthalpy of sublimation. The ideal gas thermodynamic functions $C^0_{p,m}$ and $S^0_{m(\mathrm{g})}$ and the enthalpy of formation of FM have been calculated by the empirical difference method at $T = 298.15$ K. The experimental and calculated values of the thermodynamic functions are consistent within error limits, which proves their reliability.

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Alkyl and aryl derivatives of ferrocene represent a little studied class of metal–organic complexes. They have relatively high thermal stability, high vapor pressure, low toxicity, and high reactivity. Due to a favorable combination of these properties, ferrocene derivatives are widely used in many fields of technology and medicine as components of thermostable polymers, electronic materials, high-octane gasoline additives, and antitumor and hematopoietic drugs. Available data on the thermodynamic functions of ferrocene derivatives are few in number, which impedes the development of scientific foundations of their production and application. For ferrocenemethanol (FM), only the saturation vapor pressures in the range of P 0.1–130 Pa and the enthalpies of vaporization in the solid and liquid states at 298.15 K are known [1]. The present work deals with the complex determination of the thermodynamic properties of FM—the heat capacity; the enthalpy, entropy, and Gibbs energy changes; and the enthalpy of formation—by experimental and calculation methods.

EXPERIMENTAL

Synthesis of ferrocenemethanol. FM was obtained by alkaline hydrolysis of dimethylaminomethylferrocene iodomethylate by the reaction [2]:

$$C_5H_5FeC_5H_4CH_2N^+(CH_3)_3^- + NaOH \longrightarrow C_5H_5FeC_5H_4CH_2OH + N(CH_3)_3. \quad (1)$$

The product was a mixture of two compounds, FM and bis(ferrocenylmethyl) ether (BFE) $(C_5H_5FeC_5H_4CH_2)_2O$, in the ratio 5 : 1, which remained unaltered upon recrystallization of the mixture. The separation of the mixture was carried out by column chromatography on alumina with the use of petroleum ether and diethyl ether for elution of BFE and FM, respectively. The resulting sample of FM was purified by column chromatography and recrystallized from hexane. The absence of impurities was monitored by thin-layer chromatography. According to NMR, the FM sample contained about 2% of impurities (most likely, BFE), which could not be removed by column chromatography. FM was obtained as light yellow needle crystals.

Measurement of heat capacity. The heat capacity of FM was measured on a fully automated setup consisting of an adiabatic calorimeter, an AK-9.02 data acquisition and control system, and a personal computer (PC). The setup and calorimetric procedure were analogous to those described in [3]. A calorimeter cell consisted of a cylindrical titanium container (~1 cm^3) for a sample; a copper sleeve, in which the container was tightly inserted; and an adiabatic shield. The heater of the calorimeter (R ~ 300 Ω) was mounted on the external surface of the sleeve. A miniature rhodium–iron resistance thermometer (R_0 ~ 100 Ω), calibrated against ITS-90, was fixed on the inner surface of the adiabatic shield to decrease the heat capacity of the empty container. Temperatures were measured with an accuracy of $\pm 5 \times 10^{-3}$ K. The difference between the container and adiabatic shield temperatures was mea-

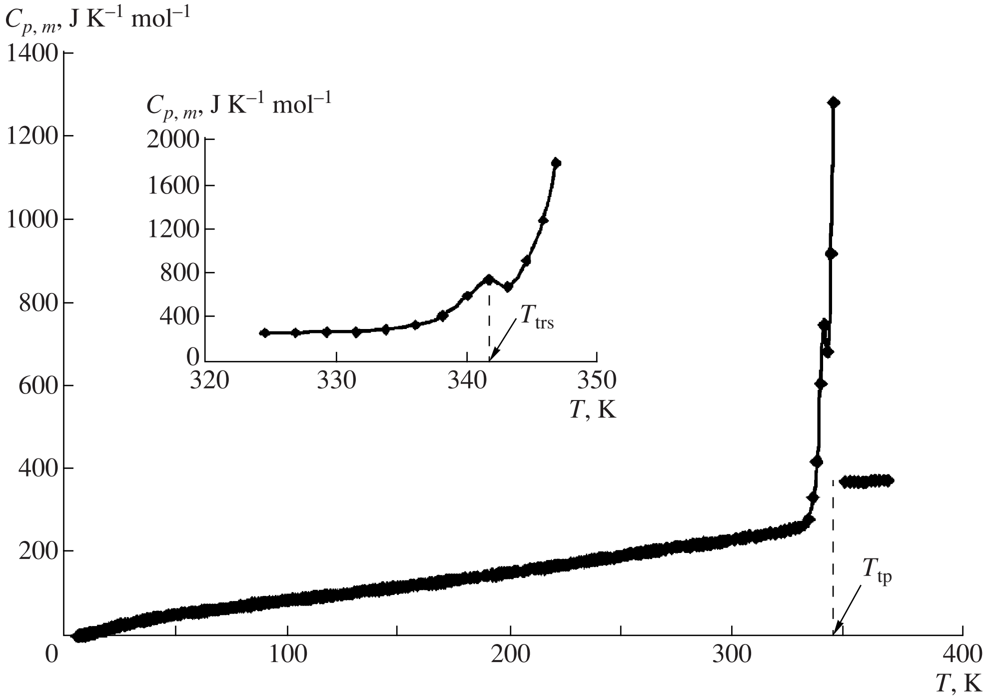

Fig. 1. Heat capacity of FM as a function of temperature. Inset: Anomaly in the range of sample fusion.

sured by a differential thermocouple (Cu + 0.1% Fe)/Chromel. In this work, the sensitivity of the calorimetric system was enhanced by using an 11-junction thermocouple rather than the four-junction one used in [3]. To eliminate temperature gradients on the adiabatic shield, an additional three-junction thermocouple and a heater ($R \sim 133\ \Omega$) were used. This heater was mounted on the upper part of the shield, to which electric wires of the thermometer and main heater ($R \sim 300\ \Omega$) were connected.

The heat capacity was automatically measured by an AK-9.02 system controlled by a PC [3]. The software provided pulsed (stepwise) energy input to the calorimeter and maintained the adiabatic conditions of the experiment. The additional heater on the adiabatic shield compensates for the lack of the second protective shield, which is usually used in high-precision adiabatic calorimeters; however, there is no room to place the second shield in our miniature calorimeter. The modified calorimetric cell is more sensitive than that used in [3]. In particular, the difference between the container and shield temperatures is maintained constant with an accuracy better by an order of magnitude than in [3] (within ±0.5 mK in the entire temperature range).

Due to small dimensions, the cryostat with the calorimeter was placed directly into transport Dewar vessels with refrigerants (liquid helium or nitrogen), which excluded the use of intermediate Dewar flasks and, thus, saved the refrigerants. A high vacuum in the cryostat was maintained by the cryosorption method with the use of an efficient charcoal getter, which excluded the use of a bulky system of roughing and diffusion pumps. The calorimeter was tested by measuring the heat capacity of high-purity copper (99.995 wt %, OSCh 11-4). The $C_{p,m}$ data obtained in the temperature range 5–300 K are consistent with the precision literature data [4], on average, within ~0.2%.

To measure the heat capacity, FM crystals were pressed into a tablet, which was crushed into several pieces. The latter were loaded into the container of the calorimeter. Then, the container was sealed with a brass lid and an indium gasket and filled with helium (the heat exchange gas) up to the pressure $P \approx 24$ kPa.

The heat capacity of FM was measured in the temperature range 6–371 K with the use of liquid helium and nitrogen as refrigerants. The temperature increment in the runs for measuring the heat capacity was 0.1–2.0 K. After an increase in temperature, it took 60–800 s for temperature equilibrium to be achieved depending on the temperature range for measuring the normal (undisturbed) heat capacity in the helium and nitrogen ranges. The heat capacity of the FM sample was 25–40% of the total heat capacity of the calorimeter with the substance. The $C_{p,m}$ values for FM measured in the temperature range 80–85 K with the use of liquid helium and nitrogen are consistent within ±0.5%, which is evidence of the reliability of the procedure of maintaining adiabatic conditions in the modified calorimetric cell. The FM heat capacity curve is shown in Fig. 1. The fusion curve of the substance shows an additional anomaly at $T = 341.75$ K, which is likely related

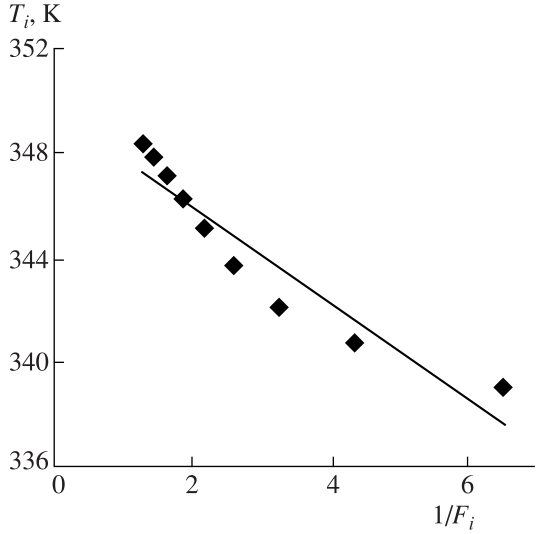

Fig. 2. Equilibrium fusion temperature (T_i) as a function of the reciprocal mole fraction of the melt ($1/F_i$) of FM.

to the presence of an impurity in the FM sample studied. The effect of the impurity on the thermodynamic properties of FM is estimated in the section "Ideal gas thermodynamic functions" for absolute entropy as an example.

Table 1. Equilibrium temperatures T_i as a function of reciprocal mole fraction of the melt $1/F_i$ for FM

T_i, K	q_i, J	$1/F_i$	$T_{i(\text{calc})}$, K
337.091	4.181	13.00	325.871
339.100[a]	4.180	6.50	337.747
340.829[a]	4.181	4.33	341.707
342.206[a]	4.192	3.25	343.690
343.806[a]	4.181	2.60	344.877
345.173[a]	4.181	2.17	345.668
346.293[a]	4.181	1.86	346.233
347.177[a]	4.180	1.62	346.657
347.854[a]	4.180	1.44	346.986
348.370[a]	4.180	1.30	347.250
348.783	4.181	1.18	347.466
349.154	4.180	1.08	347.646
349.584	4.180	1	347.798

Note: [a] The T_i and $1/F_i$ values used in calculation of T_{tp} as recommended in [6].

The purity of the substance (N_2) and the triple point temperature (T_{tp}) were determined calorimetrically by studying the dependence of the equilibrium fusion temperature (T_i) on the reciprocal mole fraction of the molten sample ($1/F_i$) [5]. The results are presented in Fig. 2 and Table 1. The $T_i(1/F_i)$ curves are concave, which can be explained by the formation of the solid solution of BFE in the FM sample under consideration. Least-squares fitting to a linear equation gave the following dependence:

$$T_i = -1.827(1/F_i) + 349.625, \quad R^2 = 0.9008, \quad (2)$$

where T_0 (T_{tp}) = 349.62 K is the fusion temperature of the pure substance, T_1 = 347.80 K is the fusion temperature of the sample at the melt fraction $F = 1$, and $T_1 - T_0 = -1.827$ K is the T_{tp} depression. The mole fraction of impurities (N_2) was determined by the Smith–Aleksandrov method from the experimental data on T_i and $1/F_i$ and based on the equation for calculation of N_2 of a binary system forming a solid solution [7, 8]:

$$T_i = T_0 - \frac{N_2}{A_C}\frac{1-k}{F_i^{1-k}}, \quad (3)$$

where T_i is the equilibrium temperature at the melt fraction F_i, A_C is the cryoscopic constant of the major substance, and k is the coefficient of distribution of impurities between the solid and liquid phases of the system. N_2 was calculated by the formula deduced in [8] by differentiation and taking the logarithm of Eq. (3):

$$\ln\left(-\frac{dT_i}{d(1/F_i)}\right) = \ln\left\{\frac{N_2}{A_C}(1-k)^2\right\} - k\ln(1/F_i), \quad (4)$$

The advantage of Eq. (4) is that the mole fraction of impurities N_2 can be calculated with the use of the coefficient k obtained directly from experimental data on T_i and $1/F_i$. Least-squares processing of experimental data on fractional melting according to Eq. (4) gave the average values $k = -1.3303$ and $\ln\left\{\frac{N_2}{A_C}(1-k)^2\right\} =$ 1.7697. Based on these data and the cryoscopic constant $A_C = \Delta_{\text{fus}}H_m/RT_0^2 = (0.02254 \pm 0.0005)$, obtained by the procedure in [5], we calculated the mole fraction of impurities $N_2 = 0.024$ in the FM sample. The error of calculation of N_2 was ~30% [8].

The enthalpy of fusion of FM was determined calorimetrically based on the total energy absorbed during fusion minus the enthalpies of heating of the normal (undisturbed) crystal, liquid, and empty container in the fusion temperature range. The $\Delta_{\text{fus}}H_m$ values were determined in two runs (Table 2). The thermodynamic properties of FM fusion are summarized in Table 3.

The heat capacity data were approximated by power polynomials using least-squares fitting:

$$C_{p,m} = \Sigma A_i((T - A_k)/B_k)^i, \quad (5)$$

where $(T - A_k)/B_k$ is the normalization coefficient. The heat capacities of the crystalline phase were approximated by three polynomials of degree 7–12, and the

Table 2. Molar enthalpy of fusion ($\Delta_{fus}H_m$) of FM (M = 216.052 g/mol, T_{tp} = 347.80 K)

T_n	T_b	ΔH_1^a	ΔH_2^a	ΔH_3^a	ΔH_4^a	$\Delta_{fus}H_m$
310.146	368.350	9830	7757	44368	84748	22793
308.106	369.779	10326	8300	51854	93502	23021
					Average: 22910 ± 530	

Note: [a] ΔH_4 is the change in the enthalpy on heating of the substance from $T_n < T_b$; ΔH_1 and ΔH_2 are the enthalpies of heating of the substance calculated by integration of the curves of the normal (undisturbed) heat capacity from T_n to T_{tp} and of the heat capacity of the liquid from T_{tp} to T_b, respectively; ΔH_3 is the enthalpy of heating of the empty calorimeter from T_n to T_b.

heat capacity of the liquid was approximated by one third-degree polynomial. The root-mean-square (RMS) deviation of the calculated $C_{p,m}$ values from experimental is 0.6% in the temperature range 10–80 K and 0.2% in the range 80–373 K. Extrapolation of the heat capacity from the initial temperature T = 6.14 K to $T \longrightarrow 0$ K was performed by the equation

$$C_{p,m}/T = \alpha T^2 + \gamma, \quad R^2 = 0.9982, \qquad (6)$$

where $\alpha = 0.005041 \pm 3 \times 10^{-5}$ J K^{-4} mol^{-1} and $\gamma = 0.006 \pm 1 \times 10^{-8}$ J K^{-2} mol^{-1}.

The RMS deviation from the $C_{p,m}$ values calculated by Eq. (6) in the temperature range 6.14–8.70 K (13 experimental data points) is ~2%. Noteworthy is an insignificant value of the constant term γ cause by the presence of the residual entropy of the FM sample, although it contains up to 2.44 mol % of impurities. The characteristic temperature of FM $\Theta = 73.1 \pm 0.2$ K was estimated using the Debye approximation $C_{p,m} = 3RD(\Theta_D/T)$ in the temperature range 6.14–8.70 K. The thermodynamic functions of FM were calculated from the data approximated by Eqs. (5) and (6) and the changes in enthalpy and entropy of fusion. Smoothed heat capacities and thermodynamic functions of solid and liquid FM are presented in Table 4.

Vapor Pressure of Ferrocenemethanol

The molar enthalpies of vaporization and sublimation ($\Delta_{vap}H_m$ and $\Delta_{sub}H_m$, respectively) were obtained [1] from the temperature dependence of the saturated vapor pressure p_{sat}, measured by the dynamic method. The method involves the determination of the mass of a substance transferred in a nitrogen flow followed by calculation of the vapor pressure by the Dalton law for partial vapor pressures of an ideal gas mixture. A sample of the substance (~0.5 g) applied to glass beads 1 mm in diameter was placed into a temperature-controlled (±0.1 K) U-tube, through which a nitrogen flow was passed. The nitrogen flow rate was adjusted to ensure that the vapor and solid phase were in stable equilibrium. The transferred substance condensed in a cooled trap and analyzed chromatographically using the external standard (hydrocarbons). The nitrogen flow rate was controlled by a precision Hoke valve and measured with a bubble gauge. The saturation vapor pressure p_{sat} was calculated by the formula

$$p_{sat} = mRT/VM, \qquad (7)$$

where $V = V(N_2) + V(\text{FM})$; $R = 8.314472$; m and M are the mass and molecular weight of FM, respectively; $V(N_2)$ and $V(\text{FM})$ are the nitrogen and FM volume, respectively, $V(N_2) \gg V(\text{FM})$; and T is the gauge temperature. The $V(N_2)$ value was determined from the flow rate and the measurement time. The method is used for determining small saturated vapor pressures (≤1 kPa). The error of determination of $\Delta_{vap}H_m$ and $\Delta_{sub}H_m$ was 0.5–1.5 kJ mol^{-1} depending on the pressure value and the range of pT measurements.

The saturated vapor pressure was measured in the temperature and pressure ranges 313.30–320.40 K and 0.1–0.25 Pa for crystalline FM and 353.20–393.70 K and 7.88–130.09 Pa for liquid FM [1]. The pT parameters were approximated by the equation

$$R\ln p = a + b/T + \Delta C_{p,m}\ln(T/T_{st}), \qquad (8)$$

where a and b are coefficients, $\Delta C_{p,m} = C_{p,m}(\text{g}) - C_{p,m}(\text{c.p.})$ is the difference between the heat capacities of the vapor and condensed phase, and T_{st} = 2.98.15 K is the standard temperature (arbitrarily chosen). Equation (8) was deduced by integration of the correlation [13]

$$-R[(d\ln p)/d(1/T)] = \Delta_{vap}H_{m,T_{st}} + \Delta C_{p,m}(T - T_{st}), (9)$$

Table 3. Triple point temperature (T_{tp}), enthalpy ($\Delta_{fus}H_m$) and entropy ($\Delta_{fus}S_m$) of fusion, purity (N_1), and cryoscopic constants A_C and B_C

T_{tp}, K	347.80 ± 1.0^a
$\Delta_{fus}H_m$, kJ mol^{-1}	22.91 ± 0.53^b
$\Delta_{fus}S_m$, J K^{-1} mol^{-1}	65.87 ± 1.52
N_1, mol %	97.56 ± 0.80
A_C, K^{-1}	$0.02254 \pm 5 \times 10^{-4}$
B_C, K^{-1}	$0.0008373 \pm 2 \times 10^{-5}$

Note: [a] The literature data on T_{tp} obtained in syntheses of FM: 347–349 K [9], 354–355 K [10], 353–354 K [11], and 351–352 K [12]; [b] $\Delta_{fus}H_m$ (average of the two runs).

Table 4. Smoothed heat capacities and thermodynamic functions of FM ($M = 216.052$ g/mol, $R = 8.31447$ J K^{-1} mol^{-1})

T, K	$C_{p,m}$, J K^{-1} mol^{-1}	$H^0_m(T) - H^0_m(0)$, kJ mol^{-1}	$S^0_m(T)$, J K^{-1} mol^{-1}	$-\{G^0_m(T) - H^0_m(0)\}$, kJ mol^{-1}
Crystal				
2	0.1536	0.000140	0.1050	–
3	0.2818	0.000360	0.1903	0.000210
4	0.4715	0.000740	0.2962	0.000450
5	0.7434	0.001350	0.4295	0.000798
10	4.687	0.01295	1.879	0.005835
15	11.63	0.05321	5.048	0.02251
20	18.89	0.1297	9.396	0.05822
25	25.81	0.2415	14.36	0.1175
30	32.53	0.3875	19.66	0.2024
35	38.90	0.5662	25.16	0.3145
40	44.52	0.7751	30.73	0.4542
45	49.51	1.010	36.27	0.6218
50	53.69	1.269	41.71	0.8165
55	57.26	1.546	47.00	1.039
60	60.87	1.842	52.14	1.286
65	64.05	2.154	57.14	1.560
70	66.46	2.483	61.98	1.855
75	69.40	2.819	66.65	2.180
80	73.69	3.177	71.27	2.524
90	81.73	3.954	80.40	3.282
100	88.12	4.803	89.35	4.132
110	94.19	5.715	98.03	5.069
120	100.3	6.688	103.5	5.731
130	106.7	7.723	114.8	7.197
140	113.2	8.822	122.9	8.387
150	119.9	9.987	131.0	9.656
160	126.7	11.22	138.9	11.01
170	133.8	12.52	146.8	12.44
180	141.1	13.90	154.7	13.94
190	148.6	15.34	162.5	15.53
200	156.2	16.87	170.3	17.19
210	163.9	18.47	178.1	18.93
220	171.8	20.15	185.9	20.75
230	179.8	21.90	193.7	22.66
240	188.1	23.74	201.6	24.63
250	196.5	25.67	209.4	26.68
260	205.0	27.67	217.3	28.82
270	213.1	29.77	225.2	31.02
280	220.6	31.93	233.1	33.32
290	227.7	34.18	240.9	35.68
298.15	233.4 ± 4.7	36.05 ± 0.79	247.3 ± 5.2	37.68 ± 1.17
300	234.8	36.49	248.8	38.14
310	243.2	38.87	256.6	40.67
320	253.6	41.36	264.5	43.27
330	263.6	43.95	272.4	45.95
340	273.5	46.63	280.4	48.72
347.80	281.2	48.79	286.7	50.93
Liquid				
347.80	375.3	71.70	352.6	50.93
350	375.8	72.53	355.0	51.71
360	377.9	76.30	365.6	55.31
370	379.7	80.09	376.0	59.02

Table 5. Coefficients of equations (8) and (12) and entropies of vaporization and sublimation of FM at $T = 298.15$ K. The $C_{p,\,m(g)}$ values of FM at 298.15 K were calculated by the additive method [14]

Parameter	Crystal	Liquid
a	339.7	359.5
b	−111826.0	−115237.0
$C_{p,\,m(g)}$, J K^{-1} mol^{-1}	209.5	229.1
$\Delta_{vap}H_m$, kJ mol^{-1}	–	87.0 ± 0.8
$\Delta_{sub}H_m$, kJ mol^{-1}	100.5 ± 0.5	–
$\Delta_{vap}S_m(T)$, J K^{-1} mol^{-1}	−337.2 ± 0.6	291.7 ± 2.3
$\Delta_{sub}S_m(T)$, J K^{-1} mol^{-1}	−337.2 ± 0.6	–

Table 6. Ideal gas thermodynamic functions of FM at $T = 298.15$ K

$R\ln\{p$(cryst)(298.15)/101.325 kPa$\}$, J K^{-1} mol^{-1}	−131.2
$S^0_m(T)_{(g)}$, J K^{-1} mol^{-1}	453.3 ± 8.6
$(H^0_m(T) - H^0_m(0))_{(g)}$, kJ mol^{-1}	136.6 ± 2.3
$\Delta_f S^0_m(T)_{(g)}$, J K^{-1} mol^{-1}	−522.9 ± 12.5
$\Delta_f G^0_m(T)_{(g)}$, kJ mol^{-1}	207.9 ± 7.9

Note: $\Delta_f S^0_m(T)_{(g)}$ is the entropy of formation of FM.

Table 7. Ideal gas absolute entropy and heat capacity of FM at 298.15 K

Reaction	S^0_{298}	C^0_{p298}
	J K^{-1} mol^{-1}	
$Fe(C_5H_5)(C_5H_4–CH_2–OH) + C_2H_6 = Fe(C_5H_5)_2 + C_3H_7–OH$	460.3	195.7
$Fe(C_5H_5)(C_5H_4–CH_2–OH) + C_3H_8 = Fe(C_5H_5)(C_5H_4–C_2H_5) + C_2H_5–OH$	452.0	201.6
Average	456.2 ± 5.0	198.7 ± 10.0

based on a known thermodynamic equation and derivative

$$R[(d\ln p)/d(1/T)] = \Delta_{vap}H_m, \qquad (10)$$

$$d(\Delta_{vap}H_m)/dT = C_{p,\,m}. \qquad (11)$$

The enthalpy of vaporization was calculated by the formula

$$\Delta_{vap}H_m(\Delta_{sub}H_m) = -b + \Delta C_{p,\,m}T, \qquad (12)$$

obtained by differentiation of Eq. (8) with respect to $1/T$.

The results of approximation of the pT data for FM are presented in Table 5.

Ideal Gas Thermodynamic Functions

The ideal gas thermodynamic functions of FM at 298.15 K—the changes in enthalpy and entropy—were calculated from the corresponding functions for the condensed state (Table 4), the enthalpy and entropy of sublimation (Table 5), and the entropy of an ideal gas undergoing compression from p(298.15 K) to 101.325 kPa, $R\ln(p(298.15\text{ K})/101.325\text{ kPa})$. The ideal gas thermodynamic functions are listed in Table 6.

The effect of the BFE impurity in the FM sample under consideration was estimated by Benson's group additivity method for the gaseous state at 298.15 K. The molar entropy $S_{m(g)BFE} = 692.9$ J K^{-1} mol^{-1} was calculated from the values of $S_{m(g)FM} = 453.3$ J K^{-1} mol^{-1} (Table 6) and the group contributions ΔS[O–(H)(C)] = 121. 50 J K^{-1} mol^{-1} and $\Delta S[O–(C)_2] = 29.33$ J K^{-1} mol^{-1} [15]. The error in determination of the entropy $S_{m(g)FM}$ caused by the impurity of 0.024 mole fraction of BFE was estimated by the difference

$$0.024S_{m(g)BFE} - 0.024S_{m(g)FM} = 5.85 \text{ J K}^{-1}\text{ mol}^{-1},$$

which constitutes 1.3% of $S^0_{m(g)}$ and $C_{p,\,m}$ of FM. The errors of measurement of the heat capacity and related characteristics were calculated by the random error accumulation law with inclusion of all possible sources of error, including the error 1.3% caused by the impurity of BFE in FM.

The entropy of formation of FM $\Delta_f S^0_m(T)_{(g)}$ (Table 7) was calculated as the difference between the absolute entropies of the products and initial reagents [9] of the reaction

$$11C_{(graphite)} + 6H_{2(g)} + 0.5O_{2(g)} + Fe_{(cryst)} =$$
$$= C_5H_5FeC_5H_4–CH_2OH_{(g)}.$$

The ideal gas absolute entropy and heat capacity of FM at 298.15 K were also calculated by the empirical difference method [17]. The use of additive methods is known to be justified for calculation of the so-called characteristic entropy $S^0_{int,\,298} = S^0_{298} + R\ln(\sigma/n)$ (where σ is the symmetry number, and n is the number of optical isomers) [18]. Unfortunately, the molecular symmetry cannot always be correctly determined and this increases the error of the estimated entropy value. The

Table 8. Standard enthalpy of formation of FM at 298.15 K

Reaction	$\Delta_f H^0_{298}$, kJ mol^{-1}
$Fe(C_5H_5)(C_5H_4–CH_2–OH) + C_6H_6 = Fe(C_5H_5)_2 + C_6H_5–CH_2–OH$	48.0
$Fe(C_5H_5)(C_5H_4–CH_2–OH) + C_2H_6 = Fe(C_5H_5)_2 + C_3H_7–OH$	59.7
$Fe(C_5H_5)(C_5H_4–CH_2–OH) + C_3H_8 = Fe(C_5H_5)(C_5H_4–C_2H_5) + C_2H_5–OH$	47.5
Average	52 ± 5

difference method is based on the group additivity principles and is applicable to molecules with unknown group contributions. The reliability of the method as applied to ferrocene derivatives has been proved by the consistency of the $S^0_{m(g)}$ and $C^0_{p,\,m(g)}$ values of ferrocene derivatives with the corresponding data obtained by independent methods [19]. The absolute entropy and heat capacity of FM were calculated based on two hypothetic reactions both parts of which contain structurally related compounds and in which the reagents, except the compound under consideration, have reliably determined thermodynamic functions (Table 8). The $S^0_{m(g)}$ (298.15 K) values of FM obtained by the calorimetric (453.3 ± 8.6 J K^{-1} mol^{-1}) and difference (456.2 ± 5.0 J K^{-1} mol $^{-1}$) methods are consistent within the error limits, which is evidence of the reliability of these values. The calorimetric and calculated $S^0_{m(g)}$ values for FM are consistent, within the error limits, with the absolute entropy of ferrocenyl methyl ether $S^0_{m(g)} = 451.1$ J K^{-1} mol^{-1}, which has the same empirical formula as FM. The consistency of these values confirms the adequacy of applying additive methods to calculations of extensive properties of ferrocene derivatives.

The ideal gas enthalpy of formation of FM at 298.15 K was calculated by the difference method (Table 8). The Gibbs energy of formation of FM $\Delta_f G^0_{m(g)} = 207.9 \pm 10.0$ kJ/mol was calculated from the $\Delta_f H^0_{m(g)}$ and $\Delta_f S^0_{m(g)}$ values in Table 6 and 8. The experimental and calculated data on the thermodynamic functions of FM were reported for the first time.

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