Thermodynamics and molecular dynamics of some ferrocene derivatives

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The heat capacities of acetylferrocene, 1,1′-diacetylferrocene, and 1,1′-diethylferrocene were investigated by low-temperature adiabatic calorimetry in the temperature range from 5 to 300 K and their thermodynamic functions were calculated. The enthalpies of combustion of the substances were determined by calorimetry of combustion, and the thermodynamic functions of their formation were calculated by quantum chemistry methods. Inter- and intramolecular interactions of the ferrocene derivatives were also studied by the methods of molecular mechanics and molecular dynamics.

Key words: ferrocene, acetylferrocene, diacetylferrocene, diethylferrocene, heat capacity, thermodynamic functions, enthalpy of combustion, enthalpy of formation, molecular dynamics.

The discovery of ferrocene initiated a vigorous development of the organometallic chemistry of transition metals. Cyclopentadienyl derivatives of iron and other transition metals are of great significance for fundamental science and widely used in practice, for example, as combustion catalysts, antiknocks, medicines, and in the preparation of various films. Fundamentals of some areas of application of metallocenes have been founded in the works by A. N. Nesmeyanov and his colleagues.[1,2]

Studies of the thermodynamic properties of these compounds allow one to determine the optimum conditions of various chemical reactions and processes. However, despite the urgent character of these studies, standard enthalpies of formation have been studied up to presently only for 67 metallocene derivatives and data on the temperature dependence of the heat capacity have been obtained only for 15 compounds, including mixed compounds. Despite the fact that numerous iron cyclopentadienyl derivatives are known, thermodynamic studies have been performed for ferrocene only.[3–5]

In this work, three iron cyclopentadienyl compounds were investigated: acetylferrocene (AF), 1,1′-diacetylferrocene (DAF), and 1,1′-diethylferrocene (DEF). Their thermodynamic functions were compared with those of ferrocene (Fig. 1, *a*).

Experimental

Acetylferrocene (AF) was obtained by acylation of ferrocene with acetyl chloride in the presence of $AlCl_3$.[6] AF was purified from ferrocene and 1,1′-diacetylferrocene by recrystallization from a cyclohexane—chloroform mixture. After the solvent was removed, orange crystals of AF were obtained in 30—35% yield. Based on the melting point (361.0±0.5 K) and data of elemental and IR spectroscopic analyses, the content of admixtures in the AF sample was <1.0 wt.%.

1,1′-Diacetylferrocene (DAF) was obtained by the previously described procedure,[7] during longer acylation of ferrocene in the presence of a minor excess of Lewis acid with recrystallization from hot chloroform. The red crystals obtained were washed with small portions of chloroform and dried at a reduced pressure (the yield was 50—60%). According to the data of elemental and IR spectroscopic analyses, the content of the main substance in the DAF sample was no less than 99.5 wt.%.

1,1′-Diethylferrocene (DEF) was obtained by the reduction of 1,1′-diacetylferrocene with activated zinc in the presence of conc. HCl [6,7] and purified by fractional distillation at a reduced pressure, taking the medium fraction with b.p. 361 K (0.15 Torr), the yield being 50—70%. The content of admixtures in the DEF sample, according to the results of calorimetric measurements, was 0.36 mol.%.

A vacuum adiabatic calorimeter was used to determine the heat capacity. Adiabatic conditions were maintained by two screens that surrounded a calorimetric platinum 15-cm^3 ampule and had constantan heaters. Pockets for platinum and germanium resistance thermometers were arranged along the axis of the ampule, and an induction-less constantan heater was mounted on the side surface of the ampule. The temperature difference between the ampule and internal screen (as well as between the screens) was monitored by batteries of differential "copper—iron-doped gold" thermocouples. The temperature of the screens was controlled automatically. The heat capacity of crystalline AF was measured in the 5—300 K temperature

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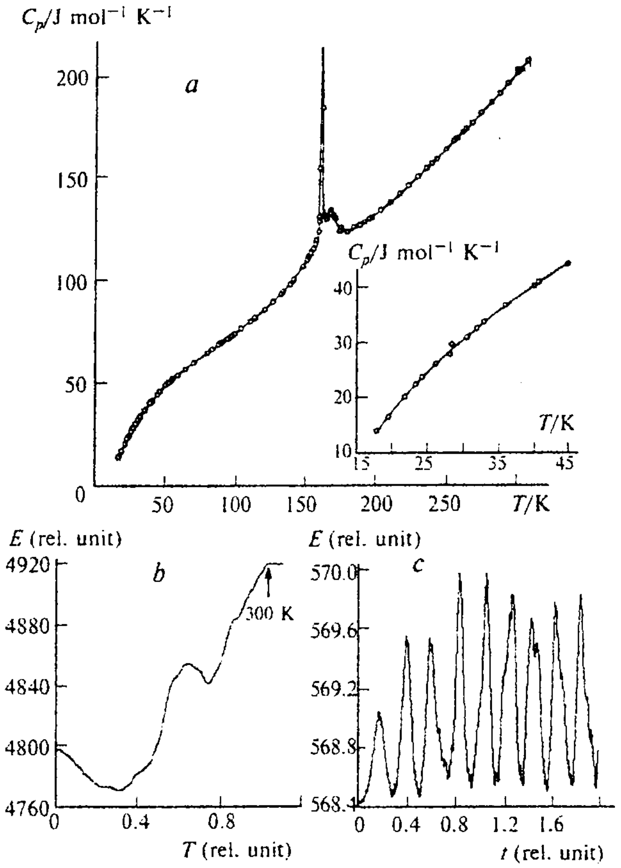

Fig. 1. *a*. Temperature dependence of the heat capacity of crystalline ferrocene in the 0—300 K range (experimental data[5]). *b*, *c*. Temperature dependences of the total energy of ferrocene in the condensed state (*b*) and potential energy of gaseous ferrocene (*c*) obtained by the molecular dynamics method (0—300 K). The experimental temperature dependence of the heat capacity of crystalline ferrocene in the 17—45 K interval is shown in insertion. Here and in Figs. 2—4, the following designations were used: *E* is energy, *T* is temperature, and *t* is time during which the temperature increases linearly.

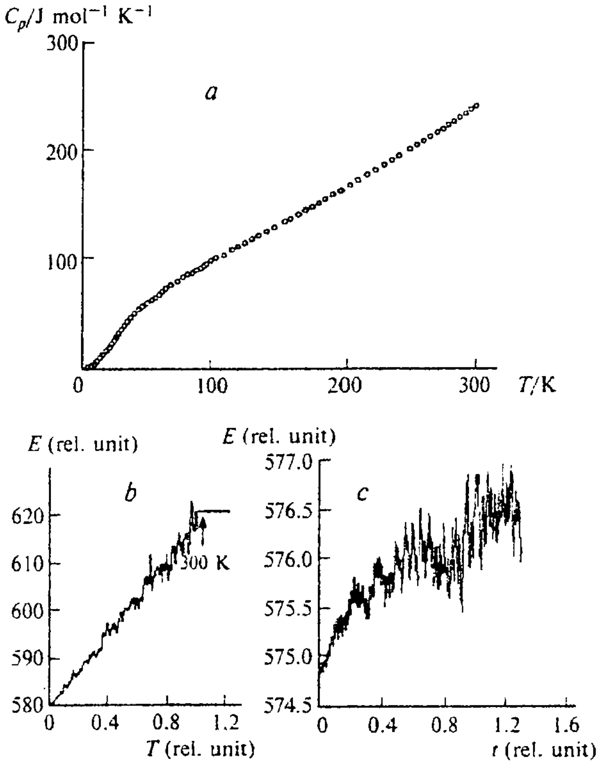

Fig. 2. *a*. Temperature dependence of the heat capacity of crystalline AF in the 0—300 K range (experimental data). *b*, *c*. Temperature dependences of the total energy of AF in the condensed state (*b*) and potential energy of gaseous AF (*c*) obtained by the molecular dynamics method (0—300 K).

range (86 experimental points, Fig. 2, *a*), and the weighed sample of the compound was 4.5139 g ($1.979 \cdot 10^{-2}$ mol). The heat capacity of crystalline DAF was measured in the 5—300 K temperature range (84 experimental points, Fig. 3, *a*), and the weighed sample of the compound was 4.5723 g ($1.693 \cdot 10^{-2}$ mol). For DEF, 120 experimental points were obtained (Fig. 4, *a*), and the weighed sample of DEF was 5.9547 g ($2.459 \cdot 10^{-2}$ mol). The heat capacities of AF, DAF, and DEF were 40—80% of the total heat capacity of the ampule filled with the substance.

Potentiometers (accuracy class 0.005 and 0.002) were used in electric circuits applied for measurements of a voltage drop and a current in the heater of the ampule and thermometers. Measuring thermometers (germanium, for the work in the 4—12 K range, and platinum, for temperatures above 12 K) were produced and calibrated in the Research Institute of Physicotechnical and Radiotechnical Measurements of the Committee of Standards of the Russian Federation. The time of current passing through the heater of the ampule was measured by a printing chronograph with an error of 0.002 s. The energy equivalent of the calorimeter was determined by measuring the heat capacity of the calorimetric ampule filled with helium to a pressure of 40 Torr. Deviations of experimental points from the smoothed curve (both in the determination of the energy equivalent and measurement of the heat capacity of the substances under study) did not exceed 0.2% at temperatures above 60 K and increased gradually to 1% at temperatures <10 K. To verify the procedure with respect to the value of the systematic error, the heat capacity of benzoic acid (K-1 trade mark, D. I. Mendeleev Research Institute of Metrology, St. Petersburg) was measured. The results coincided with the known values of heat capacity of benzoic acid[8] with an error of 2% in the 5—10 K range; 0.8%, in the 10—25 K interval; and -0.2%, at higher temperatures. Taking into account that the thermodynamic functions are calculated by the integration of the curves $C_p = f(T)$ and $C_p = f(\ln T)$ (where C_p is the heat capacity, and T is temperature), we assume that the error of their values (Tables 1 and 2) is the same. A correction for the curvature of the $C_p = f(T)$ function in the calculations of the heat capacity was not applied.[3]

Enthalpies of combustion of substances were determined on a V-08 calorimetric setup with a stationary bomb.[9] The electric energy was dosed during combustion by the discharge of a capacitor battery (capacity 8000 μF, V = 30 V). The temperature rise in experiments was measured by a platinum resistance thermometer (R = 50 Ohm) switched in a Whitestone bridge scheme. The energy equivalent of the calorimeter was established by standard benzoic acid (K-1 trade mark). Prior to

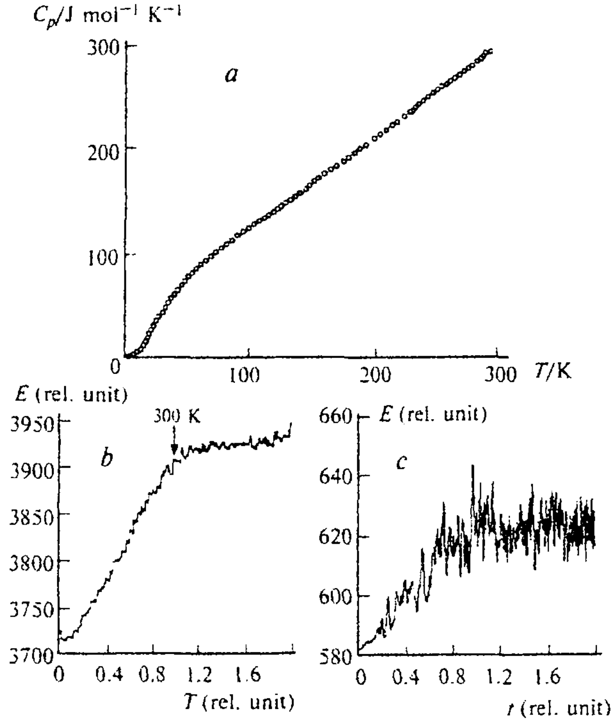

Fig. 3. *a*. Temperature dependence of the heat capacity of crystalline DAF in the 0—300 K range (experimental data). *b*, *c*. Temperature dependences of the total energy of DAF in the condensed state (*b*) and potential energy of gaseous DAF (*c*) obtained by the molecular dynamics method (0—300 K).

experiments. 1 mL of water was introduced into the bomb. Crystalline AF and DAF were burned as three-four pellets of $1 \cdot 10^{-4}$ kg in a thin quartz crucible with several holes in the side walls. To provide a high degree of combustion and the needed temperature rise, a pellet of benzoic acid with the

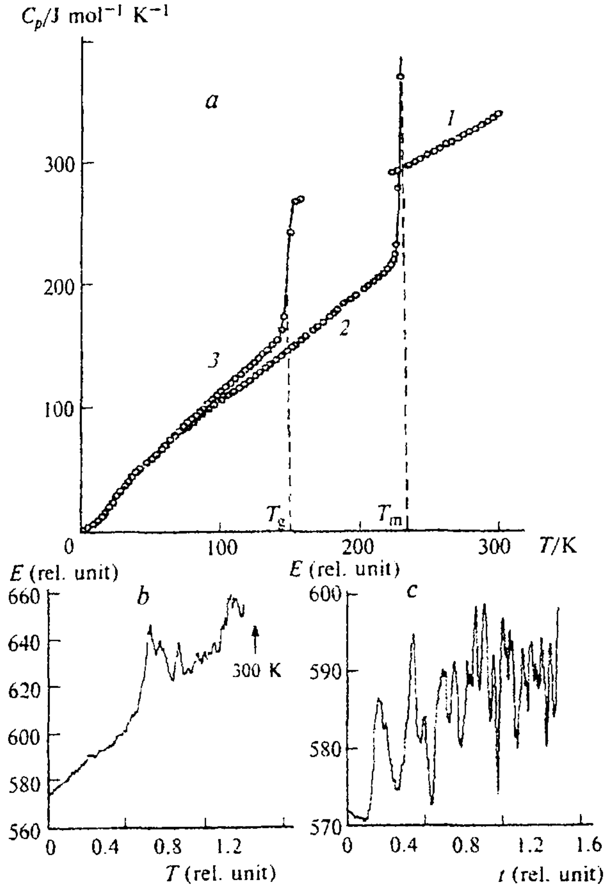

Fig. 4. *a*. Temperature dependence of the heat capacity of liquid (*1*), crystalline (*2*), and glassy (*3*) DEF in the 0—300 K range (experimental data). *b*, *c*. Temperature dependences of the total energy of DEF in the condensed state (*b*) and potential energy of gaseous DEF (*c*) obtained by the molecular dynamics method (0—300 K).

Table 1. Heat capacity (C_p) and thermodynamic functions of crystalline AF and DAF

T/K	C_p /J mol^{-1} K^{-1}	$H(T) - H(0)$ /kJ mol^{-1}	$S(T)$ /J mol^{-1} K^{-1}	$-[G(T) - G(0)]$ /kJ mol^{-1}
		Acetylferrocene		
5	0.463	0.0006	0.157	0.0002
50	58.85	1.299	40.94	0.7479
100	98.80	5.319	95.08	4.189
150	131.3	11.08	141.3	10.12
200	167.2	18.53	183.9	18.26
250	204.6	27.82	225.2	28.50
298.15	244.5	38.62	264.6	40.29
		1,1′-Diacetylferrocene		
5	0.384	0.0009	0.065	0.0006
50	72.84	1.539	47.12	0.8173
100	122.8	6.257	114.3	4.904
150	164.4	13.71	172.0	12.09
200	207.2	23.00	225.2	22.03
250	251.0	34.45	276.1	34.57
298.15	293.9	47.54	324.0	49.02

Table 2. Heat capacity (C_p) and thermodynamic functions of glassy, crystalline, and liquid DEF

T/K	C_p /J mol^{-1} K^{-1}	$H(T) - H(0)$ /kJ mol^{-1}	$S(T)$ /J mol^{-1} K^{-1}	$-[G(T) - G(0)]$ /kJ mol^{-1}
		Glass		
5	1.098	0.00182	0.5551	0.00096
50	66.60	1.532	50.68	1.002
100	116.3	6.162	112.9	5.131
140	162.5	11.62	158.5	10.56
		Crystal		
5	1.098	0.00182	0.5551	0.00096
50	64.30	1.517	50.35	1.001
100	109.7	5.884	109.1	5.029
150	154.5	12.49	162.1	11.82
200	200.8	21.37	212.9	21.21
236.95	235.1	29.43	249.8	29.75
		Liquid		
236.95	309.6	50.46	338.5	29.75
250	317.3	54.55	355.3	34.28
298.15	348.2	70.56	413.8	52.82

corresponding weight was also placed in the crucible. Liquid DEF was burnt in sealed polyethylene ampules. Specially purified oxygen was used for burning (pressure $3 \cdot 10^6$ Pa). In each experiment, gaseous products of combustion were analyzed for the content of carbon dioxide, whose amount was used for the calculation of the weight of the substance taken for the experiment. To determine the composition of solid products of combustion, quantitative X-ray phase analysis was used. In all cases, Fe_3O_4 with an admixture of Fe_2O_3 (on the average, to 10 wt.%)* was formed, which corresponds completely to similar results on combustion of ferrocene.[5]

Results and Discussion

Heat capacity

The heat capacity of crystalline AF increases monotonically in the range from 5 to 300 K without any anomalies. The enthalpy ($H°$) and entropy ($S°$) of AF were calculated from the curves of the dependences of the heat capacity on the temperature and the logarithm of temperature:

$$[H°(T) - H°(0)] = \int_0^T C_p \mathrm{d}T;$$

$$S°(T) = \int_0^T C_p \mathrm{d}\ln T.$$

The Gibbs function ($G°$) at each temperature was calculated from the data on enthalpy and entropy by the Gibbs—Helmholtz equation:

$$[G°(T) - G°(0)] = [H°(T) - H°(0)] - T \cdot S°(T).$$

The results of calculations and the averaged values of heat capacity of AF are presented in Table 1.

The C_p values in the temperature region <5 K, which are necessary for the calculation of the thermodynamic functions of AF and DAF, were obtained by extrapolation of the experimental $C_p = f(T)$ curve to 0 K by the equations $C_p = 4D(88.75/T)$ and $C_p = 10D(128.2/T)$, respectively. The D coefficient and characteristic temperature were found from the heat capacities of AF and DAF in the 5—11 K region. The resulting equation describes the experimental C_p values at 5—11 K with an accuracy of 0.5% and 0.2% for AF and DAF, respectively. It was accepted that this equation describes the heat capacities of AF and DAF at lower temperatures with the same accuracy.

As in the case of AF, the heat capacity of DAF increases monotonically in the range from 5 to 300 K. The enthalpy and absolute entropy of DAF were calculated from the curves of the $C_p = f(T)$ and $C_p = f(\ln T)$ dependences, respectively. The Gibbs function at each temperature was calculated by the Gibbs—Helmholtz equation. The results of calculations are presented in Table 1.

Under conditions of the calorimetric experiment, DEF was crystallized and underwent glass transition (Fig. 4, *a*). The glass transition of liquid DEF on fast cooling (with a rate of 0.3 K s^{-1}) is associated with the fact that the molecular structure of DEF is a nonrigid system in which free rotation of ethylcyclopentadienyl ligands and free rotation of ethyl groups about the C_5H_4—CH_2 bond occurs. The latter very much impedes crystallization, unlike that of ferrocene, and results in a decrease in the melting point. The glass transition temperature (T_g) determined from the break on the plot of the temperature dependence of the entropy of the substance near T_g is equal to 142.5±0.5 K. The heat capacities of the glass and supercooled liquid were mea-

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* In the calculation of the enthalpy of combustion of ferrocene derivatives, the correction for the content of 10 wt.% Fe_2O_3 in Fe_3O_4 was —0.8 kJ mol^{-1} (calculated per iron content in the sample).

sured in the 5—145 K range. The crystal was obtained during crystallization of the devitrified liquid under conditions close to adiabatic. Its heat capacity in the region from 5 K to the melting point was studied. On slow cooling of liquid DEF, a supercooled liquid was obtained, whose heat capacity was measured in the range from 230 K to the melting point of DEF. The heat capacity of liquid DEF was studied in the interval from the melting point to 300 K.

To determine the melting point of DEF, equilibrium melting temperatures (T_F) at different fractions of the melt (F) in the sample under study were measured on a calorimeter. The melting temperatures of the sample under study (T_m) and DEF (100% purity) ($T_m{}^0$) were determined from the $T_F = f(F^{-1})$ plot described by the equation $T_F = T_m{}^0 - F^{-1}(T_m{}^0 - T_m)$, respectively:

$$T_m = 236.87\pm0.01 \text{ K}, \; T_m{}^0 = 236.95\pm0.01 \text{ K}.$$

The enthalpy of melting ($\Delta_m H$) of DEF was measured by the method of continuous energy supply, calculating it from the equation

$$\Delta_m H = \left(\Delta H_1 - \int_{T_0}^{T_m^0} C_p^{cr} dT - \int_{T_m^0}^{T_1} C_p^{liq} dT - \int_{T_0}^{T_1} C_a dT \right) \cdot (M/m),$$

where ΔH_1 is the total amount of the energy supplied during continuous heating of the calorimeter with the substance from the initial $T_0 < T_m{}^0$ to the final temperature $T_1 > T_m{}^0$; $C_p{}^{cr}$ and $C_p{}^{liq}$ are the heat capacity of crystalline and liquid DEF, respectively; C_a is the heat capacity of the calorimetric ampule; m is the weighed sample of the DEF; and M is the weight of 1 mole of DEF. The value $\Delta_m H = 21033\pm25$ J mol^{-1} was found from two experiments.

The total content of admixtures (X_2) that do not form solid solutions with the main substance in the DEF sample was calculated from the equation

$$-\ln(1 - X_2) = \frac{\Delta_m H}{R(T_m^0)^2} \cdot \Delta T,$$

where $\Delta T = 0.08$ K is the depression of the melting temperature of DEF. We found $X_2 = 0.36\pm0.02$ mol.%.

The values of the heat capacity of crystalline DEF for temperatures <5 K were obtained by extrapolating the experimental curve of heat capacity to 0 K by the equation $C_p = 3D(61.4/T)$, in which the D coefficient and the characteristic temperature were found from the experimental values of the heat capacity of crystalline DEF in the 5—18 K temperature range. The equation obtained describes the experimental C_p values of crystalline DEF in this temperature range with an error of 0.25%. It was accepted that this equation describes the heat capacity of crystalline DEF at lower temperatures with the same accuracy. The results of calculation of the thermodynamic functions of crystalline, glassy, and liquid DEF and the averaged heat capacity values are presented in Table 2.

The difference between the zero enthalpies and the zero entropy of glassy DEF were calculated by the data on the $C_p = f(T)$ dependence for glassy and crystalline DEF:

$$[H^\circ{}_g(0) - H^\circ{}_{cr}(0)] = \int_0^{T_m^0} [C_p{}^{cr} - C_p{}^{g}] dT + \Delta_m H = \\ = 11.14\pm0.05 \text{ kJ mol}^{-1},$$

$$S^\circ(0) = \int_0^{T_m^0} [C_p{}^{cr} - C_p{}^{g}] d\ln T + \Delta_m H/T_m{}^0 = \\ = 31.0\pm0.05 \text{ kJ (mol K)}^{-1},$$

where $C_p{}^g$ is the heat capacity of glassy DEF; H_g° and H_{cr}° are the enthalpies of glassy and crystalline DEF, respectively.

The corresponding differences of the Gibbs function in the temperature region from 0 to T_g were calculated from the obtained results:

$$G^\circ{}_g(T) - G^\circ{}_{cr}(T) = [H^\circ{}_g(0) - H^\circ{}_{cr}(0)] - TS^\circ(0),$$

where $[H^0{}_g(0) - H^0{}_{cr}(0)]$ is the difference of enthalpies of glassy and crystalline DEF.

The values obtained at a pressure of 101.325 kPa are presented below:

T/K	0	50	100	140
$G^\circ{}_g(T) - G^\circ{}_{cr}(T)$ /kJ mol^{-1}	11.14	9.59	8.04	6.80

These results are the quantitative estimation of the metastability of glassy DEF relative to its thermodynamically stable crystalline state.

Molecular dynamics

It is of interest to reveal changes in inter- and intramolecular interactions of ferrocene and its derivatives studied in the present work. For this purpose, we studied the temperature profiles of the total, potential, and kinetic energies of ferrocene, AF, DAF, and DEF in the condensed and gaseous states by the molecular dynamics method. As a rule, we chose 300 K. (In some experiments, the value of 500 K was additionally chosen for refinement, as in the case of DAF and DEF.)

The structures of the four derivatives were calculated by the molecular mechanics MM+ and modified semiempirical INDO methods. Ferrocene, cobaltocene, and nickelocene were chosen as the confidence criterion. In these cases, the parametrization was performed in such a way that the calculated enthalpy of formation of the gaseous compound from atoms at 298 K coincided with the experimental value[5] with an accuracy of 4 kJ. For the condensed state of the substances, calculations were performed by the molecular dynamics method with periodical boundary conditions. During the calculation, the influence of the number of molecules in the "potential box" (from 1 to 10) was studied. Multiple repeating enabled the reproducibility of the results. Despite optimization of the geometry of the condensed state, the periodical boundary conditions involving many (up to 10) molecules resulted sometimes in some anomalies due to "freezing" of molecules during the formation of the condensed state. In this case, we performed "annealing" to a high temperature when the amplitude of intra- and intermolecular motions was high. After slow cooling to 0 K followed by heating, no anomalies due to the structure of molecules or the ordered condensed substance appeared.

Figures 1—4 present for comparison the experimental and literature data for crystalline ferrocene[5] and the results obtained in this work for crystalline AF and DAF and DEF in the solid and liquid states, as well as the theoretical curves of the total energy for the substances in the condensed state and the curves of the potential energy for the substances in the gaseous state.

The curve of temperature dependence for ferrocene in the condensed state, determined by the molecular dynamics method, has a two-humped maximum of the total energy in the temperature range near 160 K (see Fig. 1, *b*). At these temperatures, the ferrocene molecules undergo intense stretching, deformation, and rotational vibrations of the ligands, resulting in a reversible change in the symmetry group of the molecule from D_{5h} to D_{5d}. Each of these motions of one Cp ring (and then of the second Cp ring to the same direction) results in a slow hindered rotation of the whole ferrocene molecule. These motions, most likely, result in the λ-transition in the temperature dependence of the heat capacity of ferrocene (see Fig. 1, *a*).[5]

Beginning from helium temperatures, ferrocene in the gaseous state exhibits a regular free rotation of Cp rings with an increasing rotation frequency and some irregular distortions of the rotation rhythm due to the combination of deformation and stretching vibrations of the Cp—M—Cp skeleton and C—H vibrations with the temperature increase (see Fig. 1, *c*). Figure 1 demonstrates the profile of changing the potential energy of gaseous ferrocene with the linear temperature increase from 0 to 300 K. The potential barrier to rotation of ligands in gaseous ferrocene can be estimated as 5—6 kJ mol^{-1}, which is close to the experimental value of 4.6 kJ mol^{-1}.[10]

The temperature dependences of the total energy of AF and DAF in the condensed state ("periodical box"*) obtained by the molecular dynamics method have no noticeable deviations from linearity (see Figs. 2, *b* and 3, *b*) in the range from 0 to 300 K. At the same time, due to intensification of stretching and deformation vibrations of the Cp—Fe and CH groups of the rings and rocking vibrations and rotations of the CO and Me groups in the acetyl substituent, the theoretical temperature dependence presented in Figs. 2, *b* and 3, *b* contains many "noises," although it is linear as a whole.

For AF in the gaseous state (see Fig. 2, *c*), an increase in the rotation frequency of the free Cp ligand is observed, and the rotation frequency of the ligand substituted by the acetyl group is much lower. These motions are most pronounced on the curve of the temperature dependence of the potential energy of AF molecules (with a linear temperature increase). Gaseous DAF in the conformation with symmetry C_i and a compensated dipole moment of organic ligands at temperatures below 300 K virtually does not exhibit a free rotation, despite many vibrational motions (see Fig. 3, *c*). Free rotation is observed in gaseous DAF only at higher temperatures (~500 K) and is characterized by variable heights of the potential barriers, which is due to the influence of vibrations.

The van der Waals volume of DEF, for which liquid is the main state (at 298 K), was determined from the density (1.184 g cm^{-3}). It is equal to 283 Å^3, *i.e.*, approximately 11.1×4.5×5.6 Å^3 (the sizes of the "box" for calculations with periodical boundary conditions). For a linear temperature increase, the temperature dependence of the total energy of DAF (determined by the molecular dynamics method) is first linear and has no anomalies, and then sharp peaks appear (see Fig. 4, *b*), which resemble in character those on the curve of the temperature dependence of DEF in the glassy, crystalline, and liquid states (see Fig. 4, *a*). Intra- and intermolecular motions of the substance are characterized by free rotation of the ethyl groups about the Cp—Et bond and inside the ethyl group and by hindered rotation of the ethylcyclopentadienyl ligands about the Cp—Fe bond, whose rotation frequency does not coincide with that of the ethyl groups. The first of them (as a lower-frequency motion) changes its direction due to the collision of two ethyl groups until the next, nonperiodical collision, because other collisions of molecules occur in the "box." The calculations by the molecular mechanics method showed that DEF has several stable states (with *trans*-, partially folded, and *cis*-positions of the ethylcyclopentadienyl rings), which is, most likely, a reason for its liquid state. The *trans*-conformer with C_i symmetry is the most stable, corresponding to the structure of gaseous DEF (an isolated molecule). The crystalline state consists, most likely, of these conformers, whereas the glassy and liquid states contain, probably, mixtures of different conformers with various stabilities. The molecular dynamics of gaseous DEF is complicated (see Fig. 4, *c*), as compared to that of ferrocene (see Fig. 1, *c*), by the nonsynchronous character of the ethyl

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* The periodical box corresponds to calculations by the molecular mechanics or molecular dynamics of a molecule or molecules in the condensed state that are present in the potential space (usually, a rectangular parallelepiped) limited with walls with periodical conditions, *i.e.*, with the operation of translation of the content of the "potential box" and energy parameters of this "cell" along three dimensions as in crystals. The "periodical box" can have large sizes and contain many molecules.

groups, which violates the regularity of the system of potential barriers to rotation.

The studies of ferrocene and some of its derivatives by the molecular dynamics method allow one to draw several conclusions on the influence of substituents in the ferrocene molecule on the basic change in both inter- and intramolecular interactions in the condensed and gaseous states. This is due to a change in the activity of different degrees of freedom in molecular and intermolecular motions when substituents are introduced into the ferrocene molecule. At the same time, the heat capacity, as a characteristic depending on the total energy of the system, reflects the main changes in molecular motions experimentally observed for the substance in both the gaseous and condensed states.

The experimental data[10] and results of numerous calculations by the molecular dynamics method[10] (including our calculation) show that for ferrocene in the gaseous state, free rotation in molecules appears beginning from helium temperatures. However, at temperatures close to 250—300 K, according to our calculations, in addition to internal rotations of the ligands and stretching vibrations of the metal—ligand and C—H bonds in ligands, deformation vibrations of the ligand—metal—ligand bonds are also activated and result in a temporal change in the linearity of these bonds. As a consequence, when the frequency of internal rotations increases (with the temperature increase), distortions of periodicity are possible, and a "jump-through" of the ligands immediately over two potential barriers is observed. The value of the latter decreases at a certain phase of deformation vibrations (the defect on the curve in Fig. 1, *c*).

As for ferrocene, free rotation of ligands beginning from helium temperatures is observed for AF in the gaseous state. It is complicated with random interactions of vibrations and rotations of the acetyl group with the free cyclopentadienyl ligand due to activation of deformation vibrations that result in the aperiodicity of rotations (see Fig. 2, *c*).

Unlike ferrocene and AF, DAF in the gaseous state at temperatures below 300 K exhibits all possible types of vibrations (see Fig. 3, *c*) and the *trans*-arrangement of the acetyl groups for which stretching and deformation vibrations and free rotation are observed is retained.

Thus, the introduction of electron-donating substituents into the ferrocene molecule results in hindrances of free rotation of the ligands, thus activating various vibrations.

Electron-donating ethyl substituents in gaseous DEF impede the free rotation of the cyclopentadienyl ligands due to the activity of the free rotation of the ethyl groups and distort its periodicity, although it is still observed (see Fig. 4, *c*), unlike 1,1-diacetylferrocene, each of whose ligands has a high dipole moment compensated in the molecule of the *trans*-conformer.

The transition of ferrocene and its derivatives to the condensed state affects noticeably the free rotation of the cyclopentadienyl ligands, which becomes hindered even in ferrocene and is manifested only at the temperature of λ-transition and higher (≥160 K) on the experimental (see Fig. 1, *a*)[5] and theoretical (see Fig. 1, *b*) curves. AF and DAF in the condensed state exhibit impeded stretching and deformation vibrations about the ligand—metal—ligand bond and all possible vibrations (including rocking) of the acetyl groups. Free rotation of the ligands or acetyl groups is absent. This affects the linear run of both the molecular dynamics curves (see Figs. 2, *b* and 3, *b*) and the experimental curve of the temperature dependence of the heat capacity (see Figs. 2, *a* and 3, *a*). Unlike ferrocene, for AF and DAF in the condensed state, the dipole-dipole interaction between molecules (AF) or their polar ligands (both compounds) contributes to the intermolecular interaction. Due to this, the mobility of the molecules in the condensed state is strongly restricted.

In DEF, which does not possess a high polarity, in the crystalline state, all vibrations that are most active in the methyl groups of ethyl substituents are hindered. When the temperature increases, rotations of ethyl groups resulting in crystal melting are activated. In the liquid state, along with these motions, hindered rotations of the ethylcyclopentadienyl ligands become active, which lead to freezing of the glassy state of DEF (with numerous conformations with different arrangements of the ethyl groups with respect to the plane of aromatic ligands in adjacent molecules) after fast cooling of the melt. This is reflected on the theoretical molecular dynamics curve (see Fig. 4, *b*) and experimental curve (see Fig. 4, *a*). Free rotation of the ligands in DEF after melting indicates predominantly van der Waals interaction between the molecules in the condensed (liquid) state distorted by intense vibrations and rotations of the ethyl groups.

The temperatures of transitions on the experimental curves of heat capacity of ferrocene (see Fig. 1, *a*) and diethylferrocene (see Fig. 4, *a*) are close to those obtained by the molecular dynamics method (see Figs. 1, *b* and 4, *b*). For the acetyl derivatives of ferrocene, the curves of the temperature dependence of the heat capacity (see Figs. 2, *a* and 3, *a*) and the molecular dynamics curves (see Figs. 2, *c* and 3, *c*) are linear.

Enthalpy of combustion and thermodynamic functions of formation

The standard enthalpies of combustion of crystalline AF and DAF and liquid DEF were determined calorimetrically at 298.15 K. The results obtained concern the following reactions:

AF: $FeC_{12}H_{12}O(cr) + 91/6\ O_2(gas) \rightarrow$

$\rightarrow 12\ CO_2(gas) + 6\ H_2O(liq) + 1/3\ Fe_3O_4(cr)$,

$$\Delta_c H^\circ{}_{298}(AF(cr)) = -6790.5 \pm 9.0\ \text{kJ mol}^{-1};$$

Table 3. Standard enthalpies ($\Delta_f H^\circ$), entropies ($\Delta_f S^\circ$), and Gibbs functions ($\Delta_f G^\circ$) of formation of ferrocene and its derivatives (T = 298.15 K)

Compound	$\Delta_f H^\circ_{298}$ /kJ mol^{-1}	$-\Delta_f S^\circ_{298}$ /J mol^{-1} K^{-1}	$\Delta_f G^\circ_{298}$ /kJ mol^{-1}
Ferrocene*(cr)	156±6	521.5±1.5	312±6
AF(cr)	−19.0±9.0	717.4±2.0	195.0±9.5
DAF(cr)	−197.5±6.5	902.5±2.0	71.5±7.0
DEF(liq)	93.5±6.0	868.9±2.0	352.5±6.5

* Ref. 5.

DAF: $FeC_{14}H_{14}O_2(cr) + 103/6\ O_2(gas) \rightarrow$
$\rightarrow 14\ CO_2(gas) + 7\ H_2O(liq) + 1/3\ Fe_3O_4(cr)$,

$\Delta_c H^\circ_{298}(DAF(cr)) = -7685.0\pm6.0$ kJ mol^{-1};

DEF: $FeC_{14}H_{18}(liq) + 19.17\ O_2(gas) \rightarrow$
$\rightarrow 14\ CO_2(gas) + 9\ H_2O(liq) + 1/3\ Fe_3O_4(cr)$,

$\Delta_c H^\circ_{298}(DEF(liq)) = -8547.6\pm5.8$ kJ mol^{-1}.

The standard enthalpies of formation at 298.15 K of crystalline AF and DAF and liquid DEF (Table 3) were calculated from the standard enthalpies of combustion of the substances and published data on the standard enthalpies of formation of gaseous CO_2 (−393.51±0.13 kJ mol^{-1}),[4] liquid water (−285.830±0.040 kJ mol^{-1}),[4] and crystalline Fe_3O_4 (−1117.1±2.1 kJ mol^{-1}).[4] For example, in the case of DEF, calculations were performed by the equation

$$\Delta_f H^\circ_{298}(DEF(liq)) = 14\Delta_f H^\circ_{298}(CO_2(gas)) + 9\Delta_f H^\circ_{298}(H_2O(liq)) + (1/3)\Delta_f H^\circ_{298}(Fe_3O_4(cr)) - \Delta_c H^\circ_{298}(DEF(liq)).$$

The standard enthalpies of formation of AF, DAF, and DEF at 298.15 K (see Table 3) were calculated from the absolute entropies of the substances under study and the same values for graphite (5.74±0.13 J mol^{-1} K^{-1}),[4] crystalline iron (27.15±0.13 J mol^{-1} K^{-1}),[4] and gaseous hydrogen (130.570±0.033 J mol^{-1} K^{-1})[4] and oxygen (205.037±0.033 J mol^{-1} K^{-1}).[4] For example, in the case of DEF, calculations were performed by the equation

$$\Delta_f S^\circ_{298}(DEF(liq)) = S^\circ_{298}(DEF(liq)) - 14S^\circ_{298}(C(gas)) - 9S^\circ_{298}(H_2(gas)) - S^\circ_{298}(Fe(cr)).$$

The Gibbs—Helmholtz equation $\Delta_f G^\circ_{298} = \Delta_f H^\circ_{298} - 298.15\Delta_f S^\circ_{298}$ was used to calculate the standard Gibbs functions of formation of crystalline AF and DAF and liquid DEF at 298.15 K (see Table 3).

Since experimental data on the temperature dependence of the vapor pressure and enthalpies of sublimation of AF and DAF are lacking, we estimated the thermodynamic functions of formation of these compounds in the gaseous phase by the quantum-chemical methods. For this purpose, we used the modified semiempirical INDO method. Ferrocene, cobaltocene, and nickelocene have almost equal melting temperatures (~446 K), isomorphous crystalline lattices, and close structures of their molecules but different ionization potentials, chemical properties, ratios of σ- and π-bonds, and populations of highest orbitals with electrons. Therefore, they were chosen as "standard" compounds for which reliable thermodynamic data are known. The enthalpies of formation of isolated $M(C_5H_5)_2$ molecules (M = Fe, Co, Ni) in the gas phase (ΔH°) were calculated taking into account the enthalpies of formation of C, H, Fe, Co, and Ni atoms in the gaseous state (715.07, 217.98, 417.00, 428.36, and 428.81 kJ mol^{-1}, respectively).[4] The quantum-mechanical parameters (σ and π) were chosen by a change in the ratio of σ—σ to π—π interactions in the metallocene molecules in such a manner that the obtained values coincided with the experimental ones. The standard enthalpies of formation of the compounds in the gas phase ($\Delta_f H^\circ$) and enthalpies of the $M—C_5H_5$ bond dissociation (Table 4) were calculated from the found ΔH° values.

Using the parameters found for ferrocene (σσ = 0.640, ππ = 0.3375), we calculated the enthalpies of formation of gaseous AF and DAF from the corresponding atoms in the gaseous state (ΔH°), enthalpies of formation of AF and DAF in the gaseous state ($\Delta_f H^\circ$), enthalpies and entropies of sublimation of crystalline AF and DAF ($\Delta_s H^\circ$, $\Delta_s S^\circ$), and enthalpies of $M—C_5H_5$ bond dissociation ($\Delta H^\circ(M—C_5H_5)$): $\Delta H^\circ = -11749$ and -13987 kJ mol^{-1}, $\Delta_f H^\circ_{298}$ = 115 and −10 kJ mol^{-1}, $\Delta_s H^\circ_{298}$ = 135 and 190 kJ mol^{-1}, $\Delta_s S^\circ_{298}$ = 450 and 640 J mol^{-1} K^{-1}, and 2 $\Delta H^\circ(M—C_5H_5)$ = 650 and 630 kJ mol^{-1} for AF and DAF, respectively.

Analysis of the absolute entropies and standard thermodynamic functions of formation of crystalline ferrocene, AF, and DAF showed that all indicated proper-

Table 4. Enthalpies of formation of metallocenes from atoms in the gas phase (ΔH°) and from simple substances ($\Delta_f H^\circ$) and mean enthalpies of $M—C_5H_5$ bond dissociation ($\Delta H(M—C_5H_5)$)

Compound	$-\Delta H^\circ$ /kJ mol^{-1}	$\Delta_f H^\circ_{298}$/kJ mol^{-1}		$\Delta H(M—C_5H_5)$/kJ mol^{-1}	
		INDO	Thermochemical data[5]	INDO	Thermochemical data[5]
$Fe(C_5H_5)_2(gas)$	9515	233	230±6	335	352±11
$Co(C_5H_5)_2(gas)$	9447	312	307±5	295	325±12
$Ni(C_5H_5)_2(gas)$	9422	338	340±5	290	300±10

Table 5. Coefficients of equations of a linear dependence of the type $X = a + bM$

Parameter X	a	b	$\pm 2\sigma$ [a]	$\Delta(X)$ [b]
$\Delta_f H^\circ_{298}$/kJ mol^{-1}	939.0	−4.20	2.0	−177±2
$\Delta_f S^\circ_{298}$/J mol^{-1} K^{-1}	321.0	−4.54	3.0	−191±5
$\Delta_f G^\circ_{298}$/kJ mol^{-1}	842.0	−2.85	3.0	−120±3
S°_{298}/J mol^{-1} K^{-1}	−24.2	1.28	3.0	54±5

[a] Double average square error of calculated values.

[b] Group increment of the acetyl group to the value of the thermodynamic parameter of ferrocene.

Table 6. Enthalpies ($\Delta_r H^\circ$/kJ mol^{-1}), entropies ($\Delta_r S^\circ$/J mol^{-1} K^{-1}), Gibbs functions ($\Delta_r G^\circ$/kJ mol^{-1}), and equilibrium constants of reactions (1)—(3) (T = 298.15 K)

Reaction	$-\Delta_r H^\circ_{298}$	$-\Delta_r S^\circ_{298}$	$-\Delta_r G^\circ_{298}$	K_{298}
(1)	23.5	60.0	5.5	9.0
(2)	27.0	49.0	12.5	$1.5 \cdot 10^2$
(3)	280.5	291.0	193.5	$8.0 \cdot 10^{33}$

ties change linearly with an increase in the molar weight (M) of the organometallic compound (Table 5).

It can be assumed that the calculated contributions $\Delta(X)$ of the acetyl group to the corresponding thermodynamic functions of ferrocene make it possible to estimate similar properties of acetyl and 1,1′-diacetyl derivatives of cyclopentadienyl compounds of other 3d metals.

Thermodynamics of synthesis

The thermodynamic functions ($\Delta_r H^\circ$, $\Delta_r S^\circ$, $\Delta_r G^\circ$, K) of the reactions of synthesis of AF and DAF by acylation of ferrocene (reaction (1)) and acetylferrocene (reaction (2)) with acetyl chloride at 298.15 K and of reaction (3) (synthesis of DEF by hydrogenation of DAF at the same temperature) are presented in Table 6.

$$\mathrm{MeCOCl} + \mathrm{Fe(C_5H_5)_2(cr)} \rightarrow \mathrm{Fe(C_5H_5)(C_5H_4COMe)(cr)} + \mathrm{HCl(gas)} \quad (1)$$

$$\mathrm{MeCOCl} + \mathrm{Fe(C_5H_5)(C_5H_4COMe)(cr)} \rightarrow \mathrm{Fe(C_5H_4COMe)_2(cr)} + \mathrm{HCl(gas)} \quad (2)$$

$$\mathrm{Fe(C_5H_4COMe)_2(cr)} + 4\ \mathrm{H_2(gas)} \rightarrow \mathrm{Fe(C_5H_4Et)_2(cr)} + 2\ \mathrm{H_2O(liq)} \quad (3)$$

Calculations were performed using the following correlations:

$$\Delta_r H^\circ_{298} = \sum_j \nu_j \Delta_f H^\circ_{298}(j) - \sum_i \nu_i \Delta_f H^\circ_{298}(i);$$

$$\Delta_r S^\circ_{298} = \sum_j \nu_j S^\circ_{298}(j) - \sum_i \nu_i S^\circ_{298}(i);$$

$$\Delta_r G^\circ_{298} = \Delta_r H^\circ_{298} - 298.15 \Delta_r S^\circ_{298};$$

$$K = \exp[-\Delta_r G^\circ/(RT)],$$

where the symbols "j" and "i" are attributed to the products and initial reagents, respectively;

$\Delta_f H^\circ_{298} = -243.93$ (MeCOCl(gas)),[11]
92.30 kJ mol^{-1} (HCl(gas))[11];

$S^\circ_{298} = 294.85$ (MeCOCl(gas)),[11]
186.70 J mol^{-1} K^{-1} (HCl(gas)).[11]

The results in Table 6 show that already at 298.15 K the yield of AF in reaction (1) is 90.0 mol.%, the yield of DAF in reaction (2) is 99.5 mol.%, and the equilibrium of reaction (3) is almost completely shifted toward formation of DEF.

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