Journal of Thermal Analysis, Vol. 28 (1983) 147–153

ISOBARIC THERMOANALYTICAL STUDY OF THE DECOMPOSITION PROCESS OF INTERSTITIAL GRAPHITE–IRON(III) CHLORIDE COMPOUNDS

V. L. Solozhenko, I. V. Arkhangelsky, Ya. A. Kalashnikov and *N. A. Chernova*

CHEMICAL FACULTY, MOSCOW STATE UNIVERSITY, MOSCOW, U.S.S.R.

(Received March 28, 1983)

First-step and second-step interstitial graphite – $FeCl_3$ compounds were studied by isobaric thermal analysis in the temperature interval of 298 . . . 750 K and pressure interval of 10 . . . 700 Torr. ΔH^0 and ΔS^0 values were obtained for the processes

$$C_6FeCl_3 \rightarrow 0.5\, C_{12}FeCl_3 + 0.5\, FeCl_{3(s)}$$

$$C_6FeCl_3 \rightarrow 6\,C + FeCl_{3(s)} \quad \text{and} \quad C_{12}FeCl_3 \rightarrow 12\,C + FeCl_{3(s)}$$

It was demonstrated that the thermal decomposition process of the interstitial graphite compounds investigated proceeds in stages. Temperature dependence of the heat capacity of the studied compounds was determined in the temperature interval of 298 . . . 570 K.

The interstitial graphite compound (IGC) formed with $FeCl_3$ is one of the best-known graphite compounds formed with metal chlorides [1]. However, in spite of the compound having been studied intensely for the past 50 years, there still exists no clear picture of the mechanism of its thermal decomposition, and no data of its thermodynamic characteristics are at disposal.

It should be noted that the only attempt to determine certain thermodynamic values characterizing the decomposition of $FeCl_3$–IGC has been made by Kozlov and Petrov [2]. It was based on tensimetric data of the system $FeCl_3$ – natural graphite at temperatures between 400 and 1100 K. When, however, we calculated the enthalpy of sublimation of iron(III) chloride using the data listed in that work, we obtained a value of 38.1 kJ/mol, differing substantially from the value of 67.4 kJ/mol generally accepted for the temperature in question [3]. We hence believe that the values of ΔH and ΔS obtained by the cited authors for the steps of the interstitial compound cannot be satisfactorily accurate.

The objective of this work was to determine ΔH and ΔS for the decomposition processes of step I and step II $FeCl_3$–IGC by isobaric thermal analysis of these compounds in the temperature range of 298 . . . 750 K. This method has been earlier successfully applied to determine enthalpies of evaporation of various metals [4, 5] and heat of decomposition of some alkali earth carbonates and hydroxides [6].

Experimental

The studied interstitial graphite compounds containing $FeCl_3$ were prepared by introducing anhydrous iron(III) chloride from the gas phase into graphite (grade MGOSCh, grain size 50 . . . 60 μm) at 580 . . . 630 K during a period up to 4 days. The technique of synthesis and chemical analysis and the results of X-ray spectrography and Mössbauer spectroscopy of the compounds formed have been described in detail in an earlier paper [7]. For thermoanalytical studies we used step I and step II $FeCl_3$–IGC specimens with saturated layer thicknesses of 0.938 nm; compositions were $C_{5.9\pm0.1}FeCl_{3.0\pm0.1}$ and $C_{11.9\pm0.1}FeCl_{3.0\pm0.1}$, resp. Because of the hygroscopic nature of the compounds all operations were performed in dry nitrogen.

The essence of the isobaric thermoanalytical method utilized to determine thermodynamic characteristics of processes type $A_{(s)} \rightarrow B_{(s)} + C_{(g)}$, in the present case the decomposition of $FeCl_3$–IGC, consists in experimentally determining the relationship between process temperature and external pressure, and rectifying this relationship in the coordinates $\ln p$ *vs.* $1/T$. From the coefficients of the equation of linear regression

$$\ln p_{\text{external}} = a + b(1/T),$$

where $a = \Delta S/R$, $b = -\Delta H/R$, one obtains the values ΔH_T and ΔS_T at the temperature T of the experimental. The method's applicability in our case depends on the condition that the decomposition of the interstitial graphite compound proceeds in the diffusion area; the partial pressure of iron(III) chloride in the boundary layer on the surface of the graphite compound at the temperature corresponding to the maximum rate of the process (to the endothermic peak on the DTA curve) will then be equal to the external pressure in the system [8].

The apparatus used for isobaric thermal analysis is represented in Fig. 1. It consists of a quartz tubular reactor with a volume of 5 ml, a vacuum pump, a buffer balloon with a volume of 5 l to provide for constant pressure in the system during the ex-

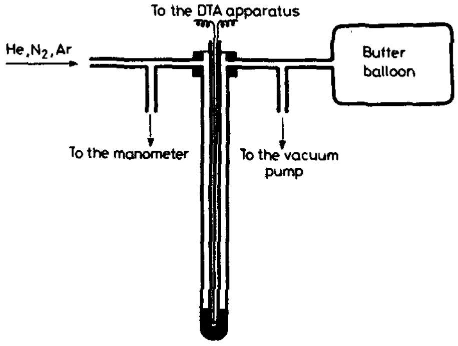

Fig. 1 Diagrammatic representation of the apparatus used for isobaric thermal analysis

periment, a mercury manometer to measure pressure with an accuracy of ±0.5 Torr, and a DTA apparatus. The latter, in turn, consists of an oven with temperature program control type PRT-1000 M, a recorder type NTP-75 and a combined chromel-alumel thermocouple. The temperatures corresponding to the endothermic peaks on the DTA curves were measured using a method described in [9], in which the melting points of high-purity (99.999%) metals, e.g. Bi, Pb, Zn are utilized as base points. The accuracy of temperature measurement was ±1 K. Sample masses were between 50 and 100 mg. The initial graphite was used as reference standard to record DTA curves. The graphite compound was decomposed in a dry inert gas (helium, nitrogen, argon, purity 99.95%). For statistical processing of the experimental results, the temperatures of the observed endothermic peaks were measured 2...5 times at each pressure.

The products formed in the decomposition were studied by X-ray diffraction and Mössbauer spectroscopy. To follow the individual stages of the decomposition process, the reaction was frozen in at certain temperatures by sharp cooling of the reactor to 298 K, and the phase composition of the products obtained in this manner was studied by the above-cited methods.

Heat capacity of the initial graphite and of step I and step II $FeCl_3$–IGC was measured by differential scanning calorimetry, using a microcalorimeter type DSM-2. The heating rate was 0.1 K/s, sample mass was 100... 150 mg, measurement was performed in nitrogen, between 298 and 570 K, with α–Al_2O_3 as reference standard.

Discussion

The DTA curves of step I and step II $FeCl_3$–IGC recorded at fixed values of external pressure are shown in Fig. 2a and 2b, resp. No change whatever in the endothermic peak temperatures was observed over the total range of pressures studied,

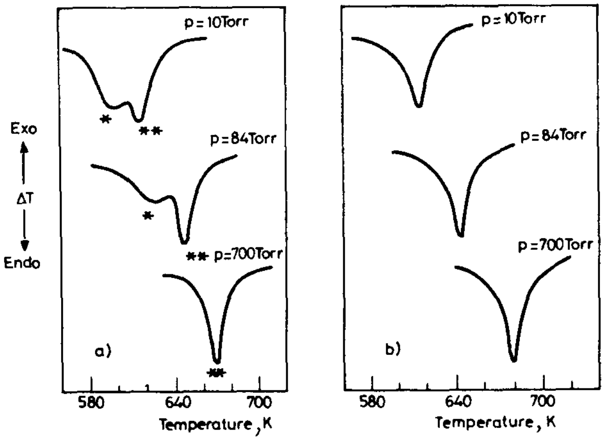

Fig. 2 DTA curves of the decomposition process of interstitial graphite compounds formed with $FeCl_3$ at various pressures. a – step I compounds, b – step II compounds

when the composition of the gas used to create the pressure (He, N_2, Ar and mixtures of these gases) was changed, nor when the compounds were diluted by some inert material. Considering the experimental conditions, namely that the decomposition was carried out in a batch reactor, the above finding confirms that the process takes place in the diffusion area and is apparently limited by intragranular diffusion.

The decomposition temperature of the studied graphite compound is defined by the vapour pressure of iron(III) chloride, this being the only gasous product of the reaction, its diffusion controlling the overall rate of reaction. The subsequent partial reaction of iron(III) chloride decomposing into iron(II) chloride and chlorine does not affect the temperature of decomposition of the interstitial compound at the pressures in question, as confirmed by the above-cited experiments performed in various gas media.

The particular feature of step I $FeCl_3$–IGC, as demonstrated by Fig. 2a, is the appearance of two endothermic peaks at low pressures. This phenomenon is obviously connected with a change in the decomposition mechanism of this compound at low external pressures. By freezing-in the equilibrium at the temperature corresponding to the inflexion point between the two endothermic peaks ($p_{ext.}$ = 10 Torr) it could be demonstrated that the first peak observed (*) corresponds to the transition of step I $FeCl_3$–IGC into step II $FeCl_3$–IGC, while the second peak (**) corresponds to the decomposition of step II $FeCl_3$–IGC into graphite. In the case of high pressures (exceeding 500 Torr) the decomposition of step I $FeCl_3$–IGC to graphite proceeds in a single stage.

The formation of step II $FeCl_3$–IGC in two-stage decomposition of the step I $FeCl_3$–IGC taking place at low pressures is also confirmed by the coincidence of the temperature of the second endothermic peak (**) on the DTA curve of the step I compound (Fig. 2a) with the temperature of the endothermic peak on the DTA curve of step II IGC (Fig. 2b) at a given pressure of the inert gas.

Utilizing the set of p, T values corresponding to the endothermic peaks on the DTA curves of decomposition of both step I and step II $FeCl_3$–IGC listed in Table 1, the relationship $\ln p = f(1/T)$ was constructed from the values for each group of endothermic peaks (Fig. 3).

Experimental data were processed on a computer type ES-1040, using the procedure described in [10]. The relationship $\ln p = f(1/T)$ was found to be linear in the decomposition of step II IGC and in the first stage of decomposition of step I IGC at low pressures (endothermic peak (*) on the DTA curve), while for the endothermic peak (**) on the DTA curve of step I, the relationship is sectionally linear, with the bend point at $T = 663 \pm 2$ K. The existence of the latter is obviously connected with the two-stage decomposition, the low-temperature branch corresponding to the transition process $IGC_{(st. II)} \rightarrow$ graphite, the high-temperature branch to the decomposition in one stage of $IGC_{(st. I)}$ into graphite.

From the coefficients of linear regression of the four straight lines describing the relationship p, T in the coordinates $\ln p$ *vs.* $(1/T)$ (cf. Fig. 3), we calculated the values ΔH_T and ΔS_T for different stages of the decomposition processes. In the calculation

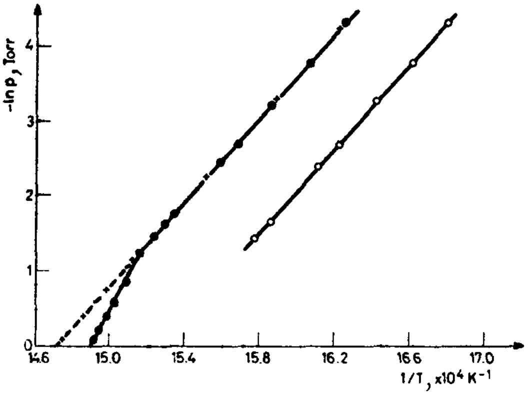

Fig. 3 Relationship ln *p* *versus* reciprocal temperature for different stages of decomposition of $FeCl_3$-IGC. ○ – endothermic peak (*) on the DTA curve of step I compound, ● – endothermic peak (**) on the DTA curve of step I compound, x – endothermic peak on the DTA curve of step II compound

Table 1 Experimental *p*, *T* data of the decomposition processes of step I and step II interstitial graphite compounds formed with $FeCl_3$

p, Torr	*T*, K		
	C_6FeCl_3		$C_{12}FeCl_2$
	endothermic peaks (*)	endothermic peaks (**)	
10	592, 593, 594, 595, 595	613, 613, 614, 614, 614	615, 616
17	600, 602	624, 625	
29	606, 607	629, 629	630, 631
50	616, 617	637, 638	
84	622	645	644, 646
142	632, 634	650, 650, 651	
148	631	651	
184	635, 636	654, 656	
242	640, 642	660, 661	661, 662
325		662, 662	
360			667, 668
411		664, 665	
519		667, 667	673, 674
610		669, 669	
700		670, 670, 671	678, 679

of the thermodynamic characteristics of both steps of the $FeCl_3$–IGC, the fact was taken into consideration that the saturated vapour of iron(III) chloride, at the temperature in question, consists to 99.97% of the dimer molecules Fe_2Cl_6 [3]. Agreement between enthalpy change in the decomposition of step I compound in the one-stage process at high pressures ($\Delta H_T = 191 \pm 33$ kJ/mol) and the overall enthalpy change in the two-stage decomposition process $IGC_{(st.I)} \rightarrow IGC_{(st.II)} \rightarrow$ graphite at low pressures ($\Delta H_T = \Delta H_T^{*} + \Delta H_T^{**} = 169 \pm 9$ kJ/mol) demonstrates the correctness of using the isobaric thermoanalytical method to determine thermodynamic characteristics in the present case.

Also, the observed agreement of the thermodynamic functions of step II IGC decomposition ($\Delta H_T = 118 \pm 6$ kJ/mol, $\Delta S_T = 174 \pm 9$ J/(mol K)) and those of the second decomposition stage of step I IGC ($\Delta H_T^{**} = 120 \pm 4$ kJ/mol, $\Delta S_T^{**} = 177 \pm 5$ J/(mol K)) conclusively evidences the correctness of the above suggested mechanism of decomposition at low pressures for step I compound.

From the experimental data obtained in the temperature interval of 298 . . . 570 K for both compounds by differential scanning calorimetry, we calculated the temperature dependence of the heat capacities. (In the temperature interval investigated, at a statistical reliability of 0.95, the error in heat capacities does not exceed 2.8%.) The results obtained were as follows (in kJ K^{-1} mol^{-1}):

$$C_{p\,(\mathrm{graphite})} = 2.0 + 0.0255\,T; \qquad C^0_{p\,298} = 9.6$$

$$C_{p\,(\mathrm{st.\,I})} = 141.7 + 0.037\,T; \qquad C^0_{p\,298} = 152.7$$

$$C_{p\,(\mathrm{st.\,II})} = 176.0 + 0.227\,T; \qquad C^0_{p\,298} = 243.6$$

Using the above values and the data from the literature on the thermodynamic properties of iron(III) chloride [3], we calculated the standard values ΔH^0 (kJ) and ΔS^0 (J/K) for the following processes:

$$C_6FeCl_3 \rightarrow 0.5\,C_{12}FeCl_{3(s)} \qquad \Delta H^0_{298} = 63 \pm 8 \qquad \Delta S^0_{298} = 83 \pm 15$$

$$C_6FeCl_3 \rightarrow 6\,C + FeCl_{3(s)} \qquad \Delta H^0_{298} = 91 \pm 13 \qquad \Delta S^0_{298} = 116 \pm 23$$

$$C_{12}FeCl_3 \rightarrow 12\,C + FeCl_{3(s)} \qquad \Delta H^0_{298} = 56 \pm 10 \qquad \Delta S^0_{298} = 64 \pm 14$$

From the above thermodynamic data we could then calculate the standard heats of formation of step I and step II $FeCl_3$–IGC. The values were – 491 ± 13 kJ/mol and – 456 ± 10 kJ/mol, resp.

The results obtained with isobaric thermal analysis hence allowed to determine some thermodynamic characteristics of the decomposition on interstitial graphite compounds formed with iron(III) chloride and demonstrated the applicability of the method for the study of similar systems.

References

1 H. Selig and L. B. Ebert, Adv. Inorg. Chem. Radiochem., 23 (1980) 281.

2 S. P. Kozlov and E. S. Petrov, Izv. Sib. otdel. AN SSSR, ser. khim. nauk, No. 7 (1978) 40.

3 I. Barin and O. Kancke, Thermochemical properties of inorganic substances, Springer, Berlin–Heidelberg–New York, Verlag Stahleisen mbH Düsseldorf, 1973.

4 J. Bohdansky and H. E. J. Schins, J. Appl. Phys., 36 (1965) 3683.

5 J. Bohdansky and H. E. J. Schins, J. Phys. Chem., 71 (1967) 213.

6 L. G. Berg, Introduction into thermography (in Russian), Nauka, Moscow, 1969.

7 V. L. Solozhenko and Ya. A. Kalashnikov, Vestn. Mosk. Univ. ser. 2, Khimiya, 22 (1981) 591.

8 D. A. Frank-Kamenitsky, Diffusion and mass transfer in chemical kinetics (in Russian), Nauka, Moscow, 1967.

9 E. M. Barrall, Thermochim. Acta, 5 (1973) 377.

10 N. A. Chernova, P. P. Melnikov, L. N. Komissarova and V. I. Spitzin, Talanta, 18 (1971) 642.

Zusammenfassung — Interstitielle Graphit-$FeCl_3$-Verbindungen wurden im Temperaturbereich von 298–750 K und im Druckbereich von 10–700 Torr mittels isobarer thermischer Analyse untersucht. Für die Reaktionen

$$C_6FeCl_3 \rightarrow 0.5\,C_{12}FeCl_3 + 0.5\,FeCl_{3(s)},$$

$$C_6FeCl_3 \rightarrow 6\,C + FeCl_{3(s)} \quad \text{und} \quad C_{12}FeCl_3 \rightarrow 12\,C + FeCl_{3(s)}$$

wurden die ΔH^0- und ΔS^0-Werte ermittelt. Die thermische Zersetzung der untersuchten interstitiellen Graphitverbindungen verläuft in mehreren Stufen. Die Temperaturanhängigkeit der Wärmekapazität der untersuchten Verbindungen wurde im Temperaturbereich von 298–570 K bestimmt.

Резюме — Проведено изобарно-термоаналитическое исследование процессов разложения ССГ с $FeCl_3$ I и II ступеней в интервале температур 298-750 K и давлений 10-700 мм рт. ст. Определены ΔH^0 (кДж) и ΔS^0 (Дж/K) следующих процессов:

$C_6FeCl_3 = 0.5\,C_{12}FeCl_3 + 0.5\,FeCl_3$ (тв.)	$\Delta H^0_{298} = 63 \pm 8$	$\Delta S^0_{298} = 83 \pm 15$
$C_6FeCl_3 = 6\,C + FeCl_3$ (тв.)	$\Delta H^0_{298} = 91 \pm 13$	$\Delta S^0_{298} = 116 \pm 23$
$C_{12}FeCl_3 = 12\,C + FeCl_3$ (тв.)	$\Delta H^0_{298} = 56 \pm 10$	$\Delta S^0_{298} = 64 \pm 14$

Показано, что процесс термического разложения слоистого соединения протекает стадийно. Определены температурные зависимости теплоемкостей исследуемых соединений в температурном интервале 298-570 K.