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THERMAL STUDY OF FAST REACTIONS BY MEANS OF APPARATUS CONNECTED DIRECTLY TO A COMPUTER

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An automated system of thermal analysis is described for the study of fast exothermic reactions (intensive burning, self-inflammation, transition from the non-equilibrium state to the equilibrium state, etc.). The system includes a complex of technical means for connecting the measuring instrument with the computer (hardware), and a special mathematical supply (software).

The use of this system provides data required for thermal and chemical calculations in the high-temperature range.

Two examples of DTA data-processing are presented.

Thermal analysis methods are often ineffective in studies of fast transformations such as intense burning, inflammation, flashing, crystallization of glasses, isomerization, etc., owing to the discrepancy between the dynamical properties of the applied apparatus and the character of the signal to be recorded.

Thus, the usually-applied oscillographic methods of recording thermal curves [1] only cover the initial (low-temperature) range of chemical transformations. That part of the thermal curve which corresponds to maximum rates of reaction is usually discontinuous, and hence the study of high-temperature decomposition becomes impossible. The often-applied extrapolation to high temperatures of physical-chemical parameters obtained under slow decomposition conditions is by no means always justified [2, 3].

The resolution and accuracy of thermal analysis methods can be substantially increased by the numerical transformation of the measurement signals, and their direct input into a computer for recording and processing. In addition to increased versatility and accuracy, it thereby becomes possible to obtain basically new data on the character of high-temperature decompositions.

The automated system of thermal analysis dealt with in this paper includes a complex of thechnical means and a special mathematical supply.

The system is presented diagramatically in Fig. 1. The signals of the temperature transmitters are introduced into the transformer unit where commutation, amplification and analogue-digital transformation proceed. The signals, now in the digital form, are forwarded along the connecting channel and are fed in the course of the experiment into the operative memory of the computer. The control signals elaborated by the electronic block are taken up in the processing unit that sets the required operating conditions of the computer.

Measured information is introduced according to a special program stored in the operative memory of the computer. The maximum input speed is 1000 ten-digit numbers per second. Experimental data introduced into the memory of the computer are written on magnetic tape after the experiment is finished, or, if required, are immediately processed by means of a set of special mathematical programs.

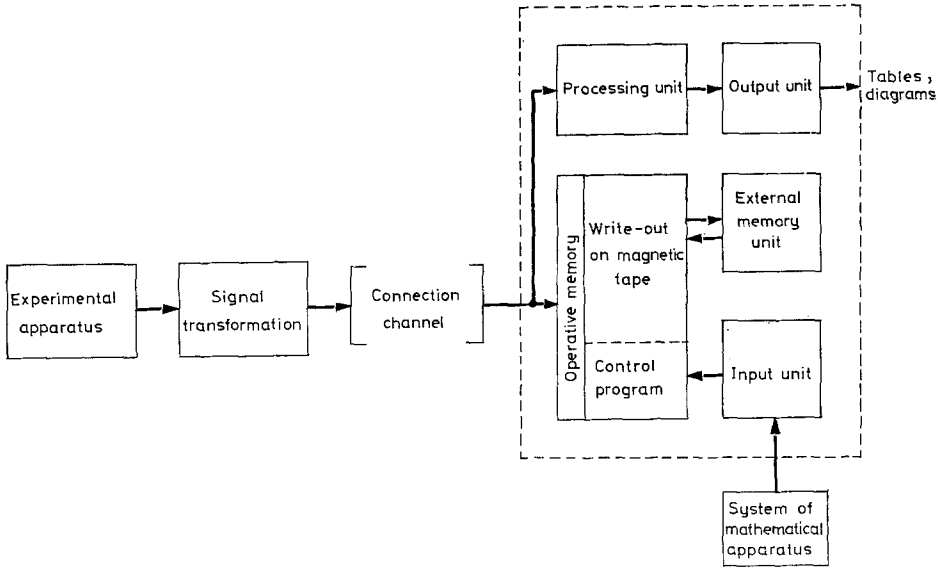

Fig. 1. Block scheme of the apparatus

The data-processing algorithms ensure print-out of the results, viz. the thermal curve, in tabular and diagramatic form, and the values of the calculated characteristics of the thermal effect.

These algorithms include:

calibration of the transmitters by polynomials ensuring optimum approach;
scaling of the measurement signals;
smoothing-out of experimental data;
separation and formation of peaks;
discrete integration;
dynamical correction of temperature transmitters;
algorithms of presentation of data.

Processing of the data of one experiment on the Minks-22 computer requires 5–7 minutes of computer time.

In Figs 2 and 3 result of two DTA experiments are presented in the form obtained directly from the computer. First, experimental conditions are printed.

* ИСХОДНЫЕ ДАННЫЕ

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KOMP=25 NAV=15.

ХАРАКТЕРИСТИКИ ЭФФЕКТА

НАЧАЛЬНАЯ ТЕМПЕРАТУРА,ГРАД МАКСИМАЛЬНАЯ ТЕМПЕРАТУРА,ГРАД

298,4 1621,3

ДЛИТЕЛЬНОСТЬ,ИСЕК ПЛОЩАДЬ,ГРАД.СЕК

180 131,64

ДИФФЕРЕНЦИРОВАННАЯ ТЕРМОГРАММА (ТЕМПЕРАТУРА,ГРАД-ВРЕМЯ,ИСЕК)

0,00	-40	868,91	460	410,15	960
0,00	-30	840,62	470	404,83	970
0,00	-20	812,35	480	404,22	980
0,00	-10	808,06	490	395,16	990
0,00	0	808,29	500	374,97	1000
53,67	10	999,88	510	355,70	1010
26,82	20	782,35	520	362,97	1020
96,78	30	770,43	530	372,68	1030
273,40	40	752,29	540	372,31	1040
458,06	50	697,91	550	362,64	1050
651,10	60	649,50	560	359,23	1060
682,42	70	671,77	570	354,06	1070
565,23	80	702,09	580	351,49	1080
519,45	90	705,65	590	343,87	1090
797,69	100	681,57	600	331,61	1100
1242,59	110	668,87	610	328,63	1110
1359,16	120	656,97	620	325,28	1120
1121,37	130	651,72	630	329,43	1130
1276,42	140	637,17	640	328,88	1140
1272,03	150	613,28	650	324,49	1150
1381,61	160	591,48	660	316,92	1160
1326,97	170	593,33	670	313,30	1170
1330,24	180	598,92	680	310,91	1180
1327,84	190	594,15	690	305,16	1190
1316,58	200	581,59	700	300,72	1200
1310,10	210	573,03	710	297,91	1210
1306,50	220	564,59	720	295,20	1220
1292,57	230	554,92	730	292,69	1230
1269,78	240	546,14	740	289,29	1240
1246,18	250	538,43	750	283,13	1250
1240,40	260	536,76	760	292,84	1260
1233,71	270	519,43	770	272,35	1270
1225,66	280	538,82	780	218,92	1280
1192,30	290	498,10	790	182,04	1290
1131,51	300	386,91	800	190,47	1300
1078,32	310	296,19	810	229,52	1310
1085,38	320	381,21	820	257,73	1320
1167,42	330	476,16	830	257,84	1330
1095,94	340	507,90	840	241,05	1340
1053,04	350	476,87	850	242,14	1350
1021,59	360	473,19	860	354,24	1360
1013,85	370	466,93	870	506,68	1370
1005,83	380	459,23	880	521,09	1380
1017,83	390	452,77	890	301,62	1390
961,75	400	443,41	900	149,89	1400
842,84	410	439,89	910	0,00	1410
746,85	420	433,32	920	0,00	1420
689,11	430	426,61	930	0,00	1430
803,59	440	419,93	940	0,00	1440
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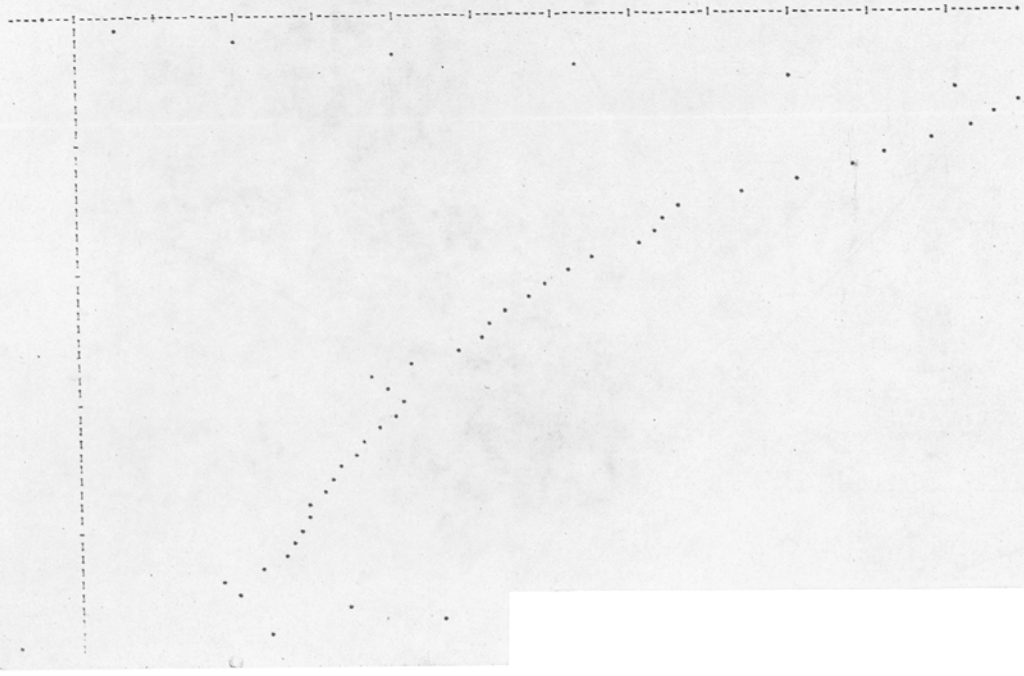

Fig. 2. DTA data and curve of polyethylene

ИСХОДНЫЕ ДАННЫЕ

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KCORR=10 NAV=80

N=0

ХАРАКТЕРИСТИКИ ЭФФЕКТА

НАЧАЛЬНАЯ ТЕМПЕРАТУРА,ГРАД МАКСИМАЛЬНАЯ ТЕМПЕРАТУРА,ГРАД

294,9 1436,1

ДЛИТЕЛЬНОСТЬ,НСЕК ПЛОЩАДЬ,ГРАД.СЕК

800 368,75

ДИФФЕРЕНЦИАЛЬНАЯ ТЕРМОГРАММА (ТЕМПЕРАТУРА,ГРАД-ВРЕМЯ,НСЕК)

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0,00	-200	165,53	4800
0,00	-100	160,16	4900
0,00	0	151,95	5000
10,60	100	153,73	5100
103,71	200	151,97	5200
221,85	300	138,31	5300
340,53	400	139,85	5400
551,34	500	146,56	5500
839,26	600	140,00	5600
1054,77	700	132,04	5700
1141,23	800	130,37	5800
1134,88	900	145,53	5900
1104,33	1000	142,58	6000
1057,16	1100	136,03	6100
999,50	1200	133,92	6200
944,22	1300	130,66	6300
884,31	1400	123,59	6400
811,08	1500	113,84	6500
734,66	1600	108,72	6600
683,74	1700	108,34	6700
648,07	1800	109,36	6800
612,83	1900	109,23	6900
574,77	2000	109,24	7000
531,54	2100	109,14	7100
489,75	2200	109,10	7200
461,00	2300	109,63	7300
437,55	2400	111,17	7400
403,18	2500	113,81	7500
377,41	2600	115,43	7600
362,70	2700	109,52	7700
340,55	2800	98,44	7800
317,27	2900	0,00	7900
304,83	3000	0,00	8000
289,59	3100	0,00	8100
271,77	3200	0,00	8200
260,18	3300	0,00	8300
246,86	3400		
227,21	3500		
225,54	3600		
229,71	3700		
215,02	3800		
179,73	3900		
147,57	4000		
133,15	4100		
132,75	4200		
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148,77	4400		
162,52	4500		

N1=1 M=1

МАСШТАБ 1:9,027394

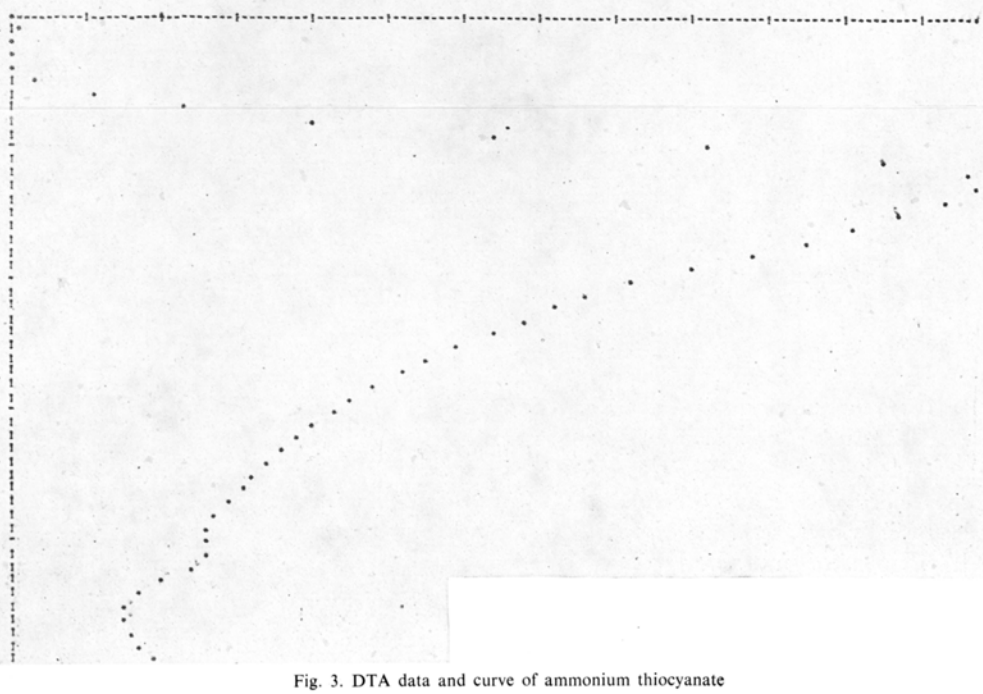

Fig. 3. DTA data and curve of ammonium thiocyanate

Then follow the calculated characteristics of the thermal effect (period of time and area are calculated up to the maximum of the peak). Finally, the differential thermal curve is printed in both tabular and diagramatic form. The table includes all temperature values measured at the corresponding moments of time.

The number of points of the exothermic peak printed in the table depends on the duration of the thermal effect and on the chosen discretization frequency of the signal. The diagram is constructed by means of points, whose number is preset by the experimenter. These points are uniformly selected by the computer from the data in the table. In the presented examples, the diagrams are constructed from 50 points.

Fig. 2 gives DTA results for the burning of polyethylene in the presence of an oxidizing agent (sample weight 15 mg, rate of heating 20 °C/min, discretization time 10 msec).

Fig. 3 shows the oxidation of ammonium thiocyanate (sample weight 80 mg, rate of heating 20 °C/min, discretization time 100 msec).

As demonstrated by these examples, the use of computers in the course of thermal analysis leads to new data on fast reactions in the high-temperature range. These data may serve as the basis for corresponding thermal and kinetic calculations.

References

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RÉSUMÉ — On décrit un système automatique d'analyse thermique pour l'étude de réactions exothermiques rapides (combustion intense, autoinflammation, transition de l'état de non-équilibre à celui d'équilibre, etc. . . .). Le système comprend un ensemble de moyens techniques pour coupler l'instrument de mesure à l'ordinateur et à l'appareillage mathématique spécial.

L'utilisation de ce système permet d'obtenir les données nécessaires aux calculs des effets thermiques et chimiques dans le domaine des températures élevées.

On présente deux exemples du traitement des données de l'ATD.

ZUSAMMENFASSUNG — Ein automatisches Thermoanalyse-System zum Studium schneller exothermer Reaktionen (intensives Brennen, Selbstzündung, Übergang vom Nicht-Gleichgewichtszustand in den Gleichgewichtszustand usw.) wird beschrieben. Das System enthält eine Reihe technischer Vorrichtungen zur Verbindung des Meßgerätes mit dem Komputer und dem speziellen mathematischen Apparat.

Die Anwendung dieses Systems ermöglicht die Ermittelung von Daten, welche zu thermischen und chemischen Berechnungen im Hochtemperatur-Bereich nötig sind.

Zwei Beispiele der DTA-Datenverarbeitung werden gegeben.

Резюме — Описывается автоматизированная система термического анализа для исследований быстрых экзотермических реакций (интенсивное горение, самовоспламенение, переход из неравновесного состояния в равновесное и др.). Система включает в себя комплекс технических средств связи экспериментальной установки с ЭВМ и специальное математическое обеспечение.

Отмечается, что использование системы позволяет получать данные, необходимые для проведения тепловых и химических расчетов в высокотемпературной области.

Приводятся результаты, полученные с помощью системы при обработке данных ДТА конкретных веществ.