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KINETIC ANALYSIS OF THERMOGRAVIMETRIC DATA. XII.

A NOMOGRAM METHOD OF DERIVING KINETIC PARAMETERS

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Shape and position parameters ∇, Δ and τ are proposed for the characterization of TG curves and are defined by Eqs (6), (7) and (8), respectively. These parameters being reduced to the standard "conditions" $n = 0$ and $q = 1/6$ K sec^{-1}, the nomogram given in Fig. 1 can be constructed by means fo Eqs (9), (11) and (12). An iteration method is proposed, allowing derivation of the kinetic parameters n, E and Z of simple thermal decomposition reactions, from the parameters n, E and Z, by using the empirica formulae (9), (10), (11) and (12) and the nomogram. Table 3 contains data necessary to construct this nomogram.

Kinetic analysis of thermogravimetric data is frequently made on the basis of the following hypotheses [1]:

1. The reaction rate can be expressed as

$$\frac{d\alpha}{dt} = k(1 - \alpha)^n \tag{1}$$

where α is the conversion, i.e. the fraction of the initial compound reacted, t is time, k the apparent rate constant, and n the apparent reaction order.

2. The apparent rate constant obeys the following Arrhenius law:

$$k = Z \exp(-E/RT) \tag{2}$$

where R is the gas constant, E the apparent activation energy, T the absolute temperature, and Z will be referred to as the pre-exponential factor.

If TG data are obtained under dynamic temperature conditions, by the use of a linear temperature program with a constant heating rate $dT/dt = q$, the equation of the TG curve, derived by Doyle [2] from Eqs (1) and (2), can be written as

$$g(\alpha) = \frac{ZE}{Rq} p(x) \tag{3}$$

where $g(\alpha)$ is the conversion integral

$$g(\alpha) = \int_0^{\alpha'} \frac{d\alpha}{(1 - \alpha)^n} \tag{4}$$

and $p(x)$ the exponential integral

$$p(x) = -\int_0^x \frac{e^{-u}}{u^2}\,du \tag{5}$$

with $u = E/RT$.

Equation (3) allows the derivation of the kinetic parameters n, E and Z from experimental TG curves.

In our previous paper [3] theoretical TG curves were constructed by using Eq. (3), and the influence of the heating rate and of the kinetic parameters n, E and Z upon the shape and position of the TG curves was studied. The main conclusions were as follows:

1. Increasing q shifts the TG curves towards higher temperatures and slightly reduces their slope.
2. Increasing n does not affect the first portion of the TG curve, but it reduces the slope of the curve, especially at higher α values.
3. Increasing E shifts the TG curves towards higher temperatures and slightly reduces their slope.
4. Increasing Z shifts the TG curves towards lower temperatures and increases their slope.

As shown by Ozawa [4], by performing a graphical plot of $(1 - \alpha)$ *vs.* $\vartheta = 1/T$, the shifts of theoretical TG curves due to the modification of q become perfectly parallel. Further, the analysis of theoretical TG curves, constructed as functions of ϑ, has shown the possibility of deriving the apparent reaction order directly from the shape of the TG curve. For this purpose the following parameter was defined [5]:

$$\nabla = \frac{\vartheta_{0.5} - \vartheta_{0.9}}{\vartheta_{0.1} - \vartheta_{0.9}} \tag{6}$$

where ϑ_α is the reciprocal temperature at which the conversion reaches the value α. By variation of E from 10 to 60 kcal/mole and of Z from 10^2 to 10^{33} sec^{-1}, the parameter ∇ has been shown to depend to a first approximation only upon the apparent reaction order, *viz.* to be almost a linear function of n.

Shape and position of TG curves

The shape of a TG curve can be well characterized by means of the parameter ∇ defined above, together with the width of the temperature interval in which the thermal decomposition occurs. We propose to characterize this width by means of the following parameter:

$$\Delta = 10^6(\vartheta_{0.1} - \vartheta_{0.5}) \tag{7}$$

which is not much affected by the apparent reaction order value.

As far as the position of the TG curves is concerned, this could be characterized, for example, by means of the reciprocal temperature of 10% conversion. Thus, we propose to take for this purpose the following parameter:

$$\tau = 10^3 \vartheta_{0.1}. \tag{8}$$

In order to clarify the influence of the heating rate and of the kinetic parameters upon the shape and position of TG curves, the parameters ∇, Δ and τ have been calculated for a great number of theoretical TG curves. The region investigated can be given by the lower and upper limits of the parameters systematically varied during these calculations. These limits are the following:

$1/96\ \mathrm{K\ sec^{-1}} \leq q \leq 8/3\ \mathrm{K\ sec^{-1}} \qquad 0 \leq n \leq 2$

$7\ \mathrm{kcal/mole} \leq E \leq 400\ \mathrm{kcal/mole} \qquad 10^{-3}\ \mathrm{sec^{-1}} \leq Z \leq 10^{300}\ \mathrm{sec^{-1}}$.

Even in this region the restriction $0.5 \leq \tau \leq 5$ has been used, i.e. we considered only reactions reaching the 10% conversion in the temperature interval from 200 K to 2000 K.

Calculations have been made by means of Eq. (3). Since $x \geq 1.75$ in all cases considered in our calculations, the exponential integral values have been calculated by means of an empirical formula proposed in our previous paper [6], this approximation ensuring sufficient accuracy in the entire region investigated [7].

Results of these calculations are illustrated by Tables 1 and 2, containing a few examples. Table 1 shows the influence of E and Z values upon the shape param-

Table 1

Influence of E and Z upon the parameters ∇, Δ and τ. ($n = 1$, $q = 8/3\ \mathrm{K\ sec^{-1}}$)

	E, kcal/mole \ log Z	10	20 s	40	80	160
∇	0	0.3753	0.3771	0.3786	0.3799	0.3810
	4	0.3859	0.3862	0.3864	0.3866	0.3868
	8	0.3879	0.3879	0.3880	0.3881	0.3881
	16	0.3888	0.3888	0.3888	0.3888	0.3888
Δ	0	279.5	142.7	72.7	37.0	18.8
	4	326.2	164.0	82.4	41.4	20.8
	8	342.9	171.9	86.1	43.2	21.6
	16	356.0	178.1	89.1	44.6	22.3
τ	0	1.1841	0.6454	0.3499	0.1887	0.1013
	4	2.7101	1.4157	0.7383	0.3844	0.1999
	8	4.3595	2.2431	1.1533	0.5926	0.3042
	16	7.7942	3.9627	2.0142	1.0235	0.5200

Table 2

Influence of n and q upon the parameters Δ, ∇ and τ

	n / q, K/sec	E = 10 kcal/mole, log Z = 0			E = 160 kcal/mole, log Z = 16		
		0	1	2	0	1	2
∇	8/3	0.2601	0.3753	0.4758	0.2673	0.3888	0.4994
	1/6	0.2630	0.3810	0.4861	0.2673	0.3889	0.4995
	1/96	0.2646	0.3839	0.4912	0.2673	0.3889	0.4995
Δ	8/3	240.3	279.5	323.6	19.1	22.3	26.0
	1/6	257.4	300.1	348.5	19.1	22.4	26.1
	1/96	268.9	313.9	365.1	19.2	22.4	26.2
τ	8/3	1.1920	1.1841	1.1760	0.5206	0.5200	0.5193
	1/6	1.6299	1.6215	1.6128	0.5535	0.5529	0.5523
	1/96	2.0894	2.0806	2.0716	0.5865	0.5859	0.5853

eters ∇ and Δ and upon the position parameter τ in the case of first-order reactions, at a heating rate of $q = 8/3$ K sec^{-1}. It is apparent that ∇ is practically not influenced by either E or Z. In contrast, Δ is mainly determined by the E value and is relatively little influenced by Z. The position parameter τ varies in parallel with Δ, but in this case the influence of Z is also very important.

In Table 2 the influence of the apparent reaction order and of the heating rate is presented in the case of two $E-Z$ pairs, representing the extremities of the region covered by Table 1. In both cases, the shape parameters ∇ and Δ are affected to the same extent by the variation of n, but the variation of the heating rate has a quite different influence upon the same ∇ and Δ parameters in the two cases considered above. If E and Z are large, the heating rate has practically no effect, but if E and Z are small, the effect of the heating rate cannot be neglected, especially in the case of Δ. As far as the position parameter τ is concerned, it is practically not influenced by n, especially if E and Z are large, but it depends on the heating rate to an important extent, especially if E and Z have small values.

Reduced characteristics of TG curves

Since, in the case of large E and Z values, the shape parameters are practically not influenced by the heating rate, and the position parameter has practically the same value, irrespective of the reaction order n, an attempt has been made to obtain some reduced characteristics of TG curves, by eliminating the influence of the heating rate and of certain kinetic parameters.

Taking into account the almost constant value of ∇ for a given reaction order, our first aim was to obtain a reduced parameter ∇^*, depending exclusively on n and

E, $\frac{\text{kcal}}{\text{mole}}$		log Z −3	−2	−1	0	1	2	3	4	5	6	7	8	9
7	τ^*	0.7996	1.2407	1.7277	2.2460	2.7865	3.3434	3.9128	4.4920	5.0790	–	–	–	–
	Δ^*	267.7	314.4	344.4	365.0	379.8	390.8	399.1	405.8	411.0	–	–	–	–
8	τ^*	0.7206	1.1093	1.5374	1.9922	2.4661	2.9541	3.4529	3.9601	4.4741	4.9936	–	–	–
	Δ^*	237.2	276.9	302.6	320.3	333.0	342.4	349.6	355.3	359.9	363.7	–	–	–
9	τ^*	0.6571	1.0048	1.3868	1.7920	2.2140	2.6484	3.0921	3.5433	4.0005	4.4625	4.9285	–	–
	Δ^*	213.1	247.5	270.0	285.3	296.5	304.8	311.0	316.0	320.1	323.4	326.1	–	–
10	τ^*	0.6049	0.9195	1.2644	1.6299	2.0103	2.4016	2.8015	3.2077	3.6192	4.0353	4.4547	4.8776	–
	Δ^*	193.6	223.9	243.7	257.3	267.2	274.5	280.1	284.6	288.2	291.1	293.6	295.7	–
11	τ^*	0.5640	0.8486	1.1625	1.4958	1.8437	2.2002	2.5640	2.9331	3.3070	3.6847	4.0668	4.4526	4.8378
	Δ^*	177.6	204.5	222.1	234.4	243.3	249.8	254.8	258.9	262.1	264.8	267.0	268.8	270.6
12	τ^*	0.5236	0.7882	1.0772	1.3830	1.7008	2.0275	2.3613	2.7001	3.0444	3.3904	3.7405	4.0926	4.4472
	Δ^*	163.7	188.1	204.1	215.2	223.3	229.2	233.8	237.5	240.5	242.9	244.9	246.5	248.1
13	τ^*	0.4836	0.7366	1.0047	1.2870	1.5808	1.8825	2.1900	2.5026	2.8197	3.1404	3.4639	3.7903	4.1175
	Δ^*	151.0	174.3	188.8	198.9	206.2	211.6	215.8	219.2	221.9	224.1	226.0	227.5	228.9
14	τ^*	–	0.6916	0.9405	1.2033	1.4763	1.7568	2.0433	2.3340	2.6286	2.9260	3.2262	3.5283	3.8322
	Δ^*	–	162.3	175.7	185.0	191.7	196.7	200.7	203.8	206.2	208.2	210.0	211.5	212.7
15	τ^*	–	0.6521	0.8849	1.1306	1.3863	1.6487	1.9163	2.1875	2.4619	2.7392	3.0187	3.3006	3.5839
	Δ^*	–	152.0	164.3	172.9	179.1	183.7	187.3	190.2	192.6	194.4	196.0	197.3	198.4
16	τ^*	–	0.6174	0.8360	1.0666	1.3059	1.5516	1.8019	2.0571	2.3152	2.5755	2.8384	3.1026	3.3686
	Δ^*	–	142.9	154.4	162.3	168.1	172.4	175.7	178.4	180.6	182.4	183.8	185.0	186.1
17	τ^*	–	0.5862	0.7926	1.0091	1.2358	1.4668	1.7026	1.9426	2.1853	2.4310	2.6788	2.9283	3.1787
	Δ^*	–	134.9	145.6	153.0	158.4	162.4	165.5	168.0	170.0	171.7	173.0	174.2	175.2
18	τ^*	–	0.5584	0.7533	0.9588	1.1718	1.3905	1.6135	1.8402	2.0694	2.3012	2.5348	2.7699	3.0068
	Δ^*	–	127.6	137.6	144.6	149.6	153.4	156.4	158.7	160.6	162.1	163.4	164.5	165.5
19	τ^*	–	0.5334	0.7181	0.9130	1.1153	1.3222	1.5334	1.7478	1.9648	2.1850	2.4071	2.6309	2.8550
	Δ^*	–	121.2	130.5	137.1	141.8	145.4	148.2	150.3	152.0	153.5	154.7	155.7	156.6
20	τ^*	–	0.5103	0.6863	0.8715	1.0635	1.2606	1.4614	1.6655	1.8723	2.0807	2.2907	2.5026	2.7155
	Δ^*	–	115.3	124.2	130.3	134.8	138.3	140.9	142.9	144.6	146.0	147.1	148.1	149.0
22	τ^*	–	–	0.6319	0.7996	0.9741	1.1536	1.3366	1.5220	1.7099	1.8992	2.0903	2.2826	2.4758
	Δ^*	–	–	113.2	118.5	122.5	125.6	127.9	129.8	131.3	132.6	133.6	134.5	135.3
24	τ^*	–	–	0.5839	0.7388	0.8991	1.0636	1.2311	1.4015	1.5738	1.7477	1.9227	2.0996	2.2767
	Δ^*	–	–	104.0	109.0	112.6	115.3	117.4	119.2	120.6	121.7	122.7	123.5	124.2
26	τ^*	–	–	0.5439	0.6868	0.8350	0.9871	1.1416	1.2986	1.4572	1.6177	1.7799	1.9438	2.1079
	Δ^*	–	–	96.2	100.8	104.1	106.6	108.5	110.1	111.4	112.4	113.3	114.0	114.7
28	τ^*	–	–	0.5092	0.6423	0.7800	0.9212	1.0653	1.2111	1.3589	1.5081	1.6582	1.8098	1.9619
	Δ^*	–	–	89.5	93.6	96.7	99.0	100.8	102.2	103.4	104.4	105.2	105.9	106.5
30	τ^*	–	–	–	0.6034	0.7319	0.8638	0.9982	1.1352	1.2725	1.4112	1.5512	1.6928	1.8350
	Δ^*	–	–	–	87.5	90.3	92.4	94.1	95.4	96.5	97.4	98.2	98.8	99.4
32	τ^*	–	–	–	0.5689	0.6896	0.8133	0.9395	1.0672	1.1962	1.3272	1.4586	1.5913	1.7245
	Δ^*	–	–	–	82.1	84.7	86.7	88.3	89.5	90.5	91.4	92.1	92.7	93.3
36	τ^*	–	–	–	0.5111	0.6186	0.7286	0.8407	0.9545	1.0695	1.1857	1.3029	1.4205	1.5389
	Δ^*	–	–	–	73.1	75.5	77.1	78.5	79.7	80.6	81.3	81.9	82.4	82.9
40	τ^*	–	–	–	–	0.5612	0.6604	0.7614	0.8637	0.9673	1.0719	1.1769	1.2833	1.3896
	Δ^*	–	–	–	–	68.0	69.6	70.8	71.7	72.5	73.2	73.8	74.2	74.7
45	τ^*	–	–	–	–	0.5015	0.5901	0.6800	0.7712	0.8634	0.9568	1.0507	1.1452	1.2401
	Δ^*	–	–	–	–	60.1	62.0	63.0	63.7	64.4	65.0	65.5	65.9	66.3
60	τ^*	–	–	–	–	–	0.5361	0.6168	0.6990	0.7820	0.8657	0.9500	1.0349	1.1202
	Δ^*	–	–	–	–	–	55.8	56.8	57.5	58.1	58.6	59.1	59.4	59.7
55	τ^*	–	–	–	–	–	–	0.5644	0.6389	0.7136	0.7889	0.8651	0.9419	1.0194
	Δ^*	–	–	–	–	–	–	51.7	52.3	52.9	53.3	53.7	54.0	54.3
60	τ^*	–	–	–	–	–	–	0.5199	0.5879	1.6569	0.7269	0.7971	0.8680	0.9392
	Δ^*	–	–	–	–	–	–	47.3	47.9	48.4	48.8	49.2	49.5	49.8
70	τ^*	–	–	–	–	–	–	–	0.5053	0.5654	0.6257	0.6867	0.7480	0.8092
	Δ^*	–	–	–	–	–	–	–	40.8	41.3	41.8	42.1	42.4	42.7
80	τ^*	–	–	–	–	–	–	–	–	0.4998	0.5518	0.6045	0.6577	0.7111
	Δ^*	–	–	–	–	–	–	–	–	36.2	36.7	37.0	37.2	37.4
90	τ^*	–	–	–	–	–	–	–	–	–	–	0.5415	0.5873	0.6336
	Δ^*	–	–	–	–	–	–	–	–	–	–	32.8	33.0	33.2
100	τ^*	–	–	–	–	–	–	–	–	–	–	–	0.5303	0.5729
	Δ^*	–	–	–	–	–	–	–	–	–	–	–	29.8	30.0
120	τ^*	–	–	–	–	–	–	–	–	–	–	–	–	–
	Δ^*	–	–	–	–	–	–	–	–	–	–	–	–	–
150	τ^*	–	–	–	–	–	–	–	–	–	–	–	–	–
	Δ^*	–	–	–	–	–	–	–	–	–	–	–	–	–
200	τ^*	–	–	–	–	–	–	–	–	–	–	–	–	–
	Δ^*	–	–	–	–	–	–	–	–	–	–	–	–	–
300	τ^*	–	–	–	–	–	–	–	–	–	–	–	–	–
	Δ^*	–	–	–	–	–	–	–	–	–	–	–	–	–
400	τ^*	–	–	–	–	–	–	–	–	–	–	–	–	–
	Δ^*	–	–	–	–	–	–	–	–	–	–	–	–	–

Table 3

Reduced parameters τ^* and Δ^* as function of kinetic parameters E and Z

10	11	12	13	14	16	18	20	22	24	28	32	36	40	45	50	60	70	80	100	150	200	300
—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
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—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
4.8036	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
249.3	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
4.4462	4.7744	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
230.0	231.1	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
4.1378	4.4446	4.7529	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
213.7	214.6	215.5	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
3.8696	4.1565	4.4447	4.7327	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
199.4	200.3	201.1	201.9	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
3.6361	3.9046	4.1745	4.4453	4.7166	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
187.0	187.9	188.6	189.3	189.8	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
3.4299	3.6819	3.9350	4.1888	4.4428	4.9614	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
176.1	176.9	177.5	178.2	178.7	179.7	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
3.2443	3.4834	3.7229	3.9637	4.2049	4.6895	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
166.3	167.0	167.6	168.3	168.8	169.7	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
3.0793	3.3053	3.5330	3.7604	3.9893	4.4480	4.9068	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
157.4	158.1	158.6	159.2	159.7	160.5	161.2	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
2.9297	3.1447	3.3605	3.5767	3.7943	4.2305	4.6675	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
149.7	150.4	150.9	151.5	151.9	152.6	153.3	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
2.6697	2.8657	3.0628	3.2603	3.4579	3.8547	4.2517	4.6488	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
135.9	136.5	137.0	137.5	137.9	138.6	139.4	139.7	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
2.4556	2.6347	2.8147	2.9949	3.1763	3.5399	3.9046	4.2716	4.6398	→	—	—	—	—	—	—	—	—	—	—	—	—	—
124.8	125.4	125.8	126.3	126.6	127.3	127.9	128.3	128.7	—	—	—	—	—	—	—	—	—	—	—	—	—	—
2.2726	2.4379	2.6042	2.7706	2.9378	3.2738	3.6124	3.9520	4.2952	4.6436	—	—	—	—	—	—	—	—	—	—	—	—	—
115.2	115.7	116.1	116.6	116.9	117.5	118.1	118.5	118.8	119.0	—	—	—	—	—	—	—	—	—	—	—	—	—
2.1150	2.2683	2.4229	2.5775	2.7330	3.0446	3.3568	3.6719	3.9869	4.3030	4.9371	—	—	—	—	—	—	—	—	—	—	—	—
107.0	107.4	107.8	108.2	108.6	109.1	109.6	110.0	110.3	110.5	111.1	—	—	—	—	—	—	—	—	—	—	—	—
1.9778	2.1212	2.2654	2.4101	2.5552	2.8460	3.1381	3.4304	3.7240	4.0184	3.6096	—	—	—	—	—	—	—	—	—	—	—	—
99.8	100.2	100.6	100.9	101.2	101.7	102.2	102.5	102.8	103.0	103.5	—	—	—	—	—	—	—	—	—	—	—	—
1.8585	1.9929	2.1279	2.2631	2.3992	2.6720	2.9460	3.2209	3.4969	3.7732	4.3280	4.8848	—	—	—	—	—	—	—	—	—	—	—
93.7	94.1	94.4	94.7	95.0	95.5	95.9	96.2	96.5	96.7	97.1	97.4	—	—	—	—	—	—	—	—	—	—	—
1.6581	1.7773	1.8976	2.0179	2.1388	2.3813	2.6251	2.8693	3.1141	3.3602	3.8534	4.3484	4.8447	—	—	—	—	—	—	—	—	—	—
83.3	83.6	83.9	84.3	84.4	84.9	85.3	85.6	85.8	85.9	86.3	86.6	86.8	—	—	—	—	—	—	—	—	—	—
1.4972	1.6044	1.7128	1.8209	1.9299	2.1482	2.3674	2.5874	2.8080	3.0293	3.4732	3.9187	4.3654	4.8131	—	—	—	—	—	—	—	—	—
75.0	75.3	75.5	75.8	76.0	76.4	76.7	77.0	77.2	77.4	77.7	78.0	78.2	78.3	—	—	—	—	—	—	—	—	—
1.3352	1.4308	1.5268	1.6229	1.7192	1.9128	2.1070	2.3016	2.4977	2.6948	3.0924	3.4928	3.8848	4.2901	4.7973	—	—	—	—	—	—	—	—
66.6	66.9	67.1	67.3	67.5	67.9	68.2	68.4	68.6	68.8	69.0	69.2	69.4	69.6	69.7	—	—	—	—	—	—	—	—
1.2061	1.2923	1.3787	1.4654	1.5524	1.7270	1.9024	2.0784	2.2549	2.4320	2.7872	3.1436	3.5010	3.8591	4.3080	4.7572	—	—	—	—	—	—	—
60.0	60.3	60.5	60.7	60.9	61.1	61.3	61.5	61.7	61.9	62.2	62.4	62.6	62.6	62.7	62.8	—	—	—	—	—	—	—
1.1975	1.1757	1.2543	1.3331	1.4121	1.5709	1.7304	1.8909	2.0516	2.2124	2.5354	2.8594	3.1840	3.5092	3.9182	4.3277	—	—	—	—	—	—	—
54.5	54.8	55.0	55.2	55.4	55.6	55.8	56.0	56.2	56.4	56.6	56.7	56.9	57.0	57.1	57.2	—	—	—	—	—	—	—
1.0107	1.0826	1.1546	1.2267	1.2994	1.4450	1.5911	1.7378	1.8848	2.0325	2.3285	2.6255	2.9234	3.2219	3.5959	3.9703	4.7211	—	—	—	—	—	—
50.0	50.2	50.4	50.6	50.7	51.0	51.2	51.3	51.5	51.6	51.8	51.9	52.1	52.2	52.3	52.4	52.6	—	—	—	—	—	—
0.8717	0.9337	0.9958	1.0580	1.1203	1.2449	1.3701	1.4953	1.6206	1.7459	1.9979	2.2500	2.5025	2.7554	3.0744	3.3936	4.0319	4.6718	—	—	—	—	—
42.9	43.0	43.1	43.3	43.5	43.7	43.8	43.9	44.0	44.1	44.3	44.5	44.6	44.7	44.8	44.9	45.0	45.1	—	—	—	—	—
0.7648	0.8187	0.8727	0.9269	0.9814	1.0906	1.1999	1.3103	1.4208	1.5313	1.7533	1.9761	2.1995	2.4234	2.7040	2.9848	3.5479	4.1124	4.6775	—	—	—	—
37.6	37.7	37.8	38.0	38.1	38.3	38.4	38.5	38.6	38.7	38.8	39.0	39.1	39.2	39.3	39.3	39.4	39.5	39.6	—	—	—	—
0.6811	0.7285	0.7767	0.8249	0.8733	0.9705	1.0676	1.1653	1.2628	1.3613	1.5581	1.7557	1.9541	2.1533	2.4029	2.6537	3.1551	3.6588	4.1635	—	—	—	—
33.4	33.5	33.6	33.7	33.8	34.0	34.1	34.2	34.2	34.3	34.5	34.7	34.7	34.8	34.8	34.9	35.0	35.1	35.1	—	—	—	—
0.6160	0.6591	0.7024	0.7458	0.7893	0.8767	0.9643	1.0525	1.1407	1.2293	1.4070	1.5852	1.7639	1.9431	2.1673	2.3922	2.8427	3.2929	3.7463	4.6524	—	—	—
30.1	30.2	30.3	30.4	30.4	30.6	30.7	30.8	30.8	30.9	31.1	31.2	31.3	31.4	31.5	31.5	31.6	31.6	31.6	31.7	—	—	—
0.5198	0.5553	0.5911	0.6271	0.6633	0.7362	0.8093	0.8827	0.9567	1.0309	1.1801	1.3299	1.4800	1.6301	1.8176	2.0056	2.3814	2.7566	3.1334	3.8894	—	—	—
25.1	25.2	25.3	25.4	25.4	25.6	25.7	25.7	25.8	25.8	25.9	26.0	26.0	26.1	26.2	26.3	26.3	26.4	26.4	26.4	—	—	—
—	—	—	0.5023	0.5313	0.5896	0.6481	0.7068	0.7657	0.8248	0.9432	1.0621	1.1812	1.3006	1.4503	1.6001	1.9004	2.2015	2.5029	3.1069	4.6207	—	—
—	—	—	20.3	20.3	20.4	20.5	20.5	20.6	20.7	20.7	20.8	20.8	20.9	20.9	21.0	21.0	21.0	21.1	21.1	21.1	—	—
—	—	—	—	—	—	—	0.5329	0.5770	0.6213	0.7102	0.7993	0.8887	0.9783	1.0905	1.2029	1.4281	1.6589	1.8800	2.3330	3.4684	4.6060	—
—	—	—	—	—	—	—	15.4	15.4	15.4	15.6	15.6	15.6	15.7	15.7	15.8	15.8	15.8	15.8	15.8	15.9	15.9	—
—	—	—	—	—	—	—	—	—	—	—	0.5355	0.5951	0.6548	0.7293	0.8045	0.9547	1.1052	1.2560	1.5580	2.3149	3.0733	4.5923
—	—	—	—	—	—	—	—	—	—	—	10.4	10.4	10.4	10.4	10.4	10.5	10.5	10.6	10.6	10.6	10.6	10.6
—	—	—	—	—	—	—	—	—	—	—	—	—	—	0.5484	0.6048	0.7175	0.8304	0.9434	1.1699	1.7376	2.3064	3.4457
—	—	—	—	—	—	—	—	—	—	—	—	—	—	7.8	7.8	7.9	7.9	7.9	7.9	7.9	7.9	8.0

independent of q, E and Z. The systematic study of the influence of q, E and Z upon the numerical value of ∇ allowed us to obtain an empirical formula reducing ∇ to a value depending exclusively on n, corresponding to the ∇ value for very large E and Z parameters. The formula obtained can be written as follows:

$$\nabla^* = \nabla + 1.42\frac{a}{b}10^{-2} \tag{9}$$

where

$$a = (1 + 0.6n + 0.25n^2)\left(2 - \frac{1}{3}\log q\right)$$

$$b = [2.3 - \log q + 0.15(\log q)^2]\left(\log E - 2 - \frac{1}{3}\log q\right)$$
$$[1 + 0.5\log Z + 7(\log Z)^2 10^{-2}].$$

This reduced, or corrected shape parameter depends only on n and enables us to obtain the apparent reaction order from this parameter, according to the following empirical formula:

$$n = \frac{1.272 - \sqrt{1.618 - 2.2(\nabla^* - 0.2675)}}{0.11}. \tag{10}$$

Further, an attempt has been made to obtain reduced Δ^* and τ^* values which would be independent of n and q. For this purpose the heating rate $q = 1/6$ K sec^{-1} (10 K min^{-1}) and the reaction order $n = 0$ were chosen as standard "conditions" and empirical formulae able to reduce all Δ and τ values to these standard conditions were sought.

Analysis of the calculated Δ values led us to the following expression:

$$\Delta^* = \frac{\Delta + c}{1 + 0.16n + 0.011n^2 - d} \tag{11}$$

with

$$c = \frac{[7.1 - 5(\log E - 6)][2.443 + 3.473\log q + 0.428(\log q)^2]\,10^4}{E[4 + 1.5\log Z + 0.16(\log Z)^2]}$$

$$d = \frac{12n(n + 3)[1.353 + 0.535\log q + 0.103(\log q)^2]10^{-3}}{(4 + 3\log Z)(\log E - 1)}.$$

In a similar way, from theoretical τ values the following empirical formula has been derived:

$$\tau^* = \tau + \frac{(4 + \log Z)e - f}{(4 + \log Z)E} \tag{12}$$

with

$$e = 101n + 4550(\log q + 0.778)$$
$$f = 16.6(\log q + 4.39)n + 300(\log q + 0.778)(\log q + 11.75).$$

Both Δ^* and τ^* depend on E and Z, and an infinite number of $\Delta^* - \tau^*$ pairs belong to a constant E or Z value. Thus, a nomogram can be obtained, by giving in $\Delta^* - \tau^*$ co-ordinates a curve family corresponding to different E values, and another curve family corresponding to different Z values. The data presented in Table 3 enable us to construct this nomogram for the whole region investigated in this paper. Several curves of this nomogram are given in Fig. 1.

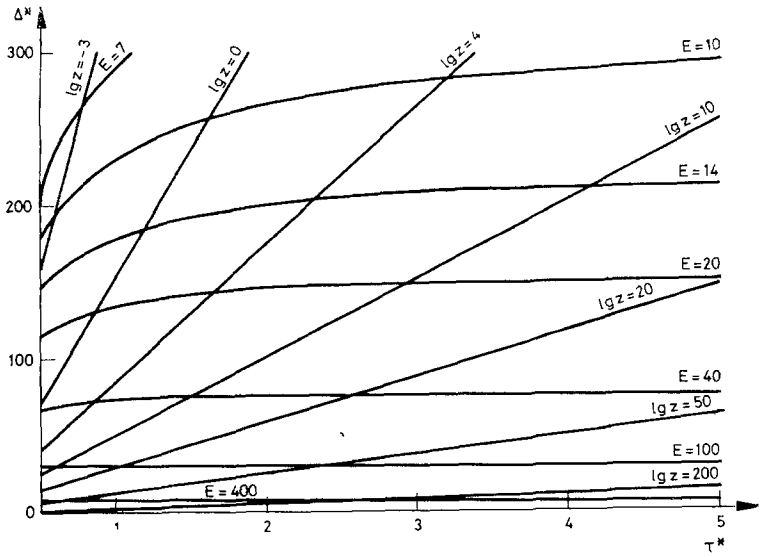

Fig. 1. Nomogram, representing E and log Z as a function of the reduced parameters τ^* and Δ^*. (E values are given in kcal/mole^{-1}, Z values in sec^{-1})

The nomogram method

The nomogram given in Fig. 1 enables us to propose an iteration procedure of deriving kinetic parameters from the shape and position parameters of the TG curve. On the basis of the TG curve, one can determine the $\vartheta_{0.1}$, $\vartheta_{0.5}$ and $\vartheta_{0.9}$ values for a given thermal decomposition step, i.e. for a portion of the TG curve situated between two successive weight loss stops. Via these three reciprocal temperature values, parameters ∇, Δ and τ can be calculated according to Eqs (6), (7) and (8).

In the first iteration cycle the apparent reaction order n_1 is calculated by means of Eq. (10), by using the experimentally obtained ∇ value instead of the reduced parameter ∇^*. The reduced shape parameter Δ_1^* is calculated by means of Eq. (11), by using the n_1 value obtained above, and by taking $c = d = 0$. As far as the position parameter is concerned, we take $\tau_1^* = \tau$. By using these Δ_1^* and τ_1^* values, by means of the nomogram given in Fig. 1, or constructed with more details on the basis of the data given in Table 3, we obtain the first approximation of the kinetic parameters, *viz.* E_1 and log Z_1.

In a higher, e.g. the i-th iteration cycle, ∇_i^* is calculated by means of Eq. (9). The constants a and b are calculated by using the heating rate q and the n_{i-1}, E_{i-1}, $\log Z_{i-1}$ values obtained in the $(i-1)$-th iteration cycle. This ∇_i^* value is used for the calculation of n_i, by means of Eq. (10). Δ_i^* and τ_i^* are calculated by means of Eqs (11) and (12), by using the q, n_i, E_{i-1} and $\log Z_{i-1}$ values for the calculation of the constants c, d, e and f.

This iteration procedure is continued until the system of reduced parameters becomes self-consistent, i.e. until the k-th approximation of the reduced parameters (and of the kinetic parameters) is equal to the $(k-1)$-th approximation.

Verification on theoretical TG curves

The procedure given above is rapidly convergent and the second or third iteration cycle already gives a self-consistent system of ∇^*, Δ^*, τ^*, n, E and Z values.

As an example, theoretical curves corresponding to $n = 1$, $E = 20$ kcal/mole, $Z = 10^4\ \mathrm{sec}^{-1}$ and to different heating rates have been chosen. Their shape and position parameters, together with the reduced parameters and kinetic parameters obtained in the first three iteration cycles, are presented in Table 4. It is obvious

Table 4

Shape and position parameters x_0, reduced parameters x_i^* and kinetic parameters y_i obtained in the i-th iteration cycle. ($n = 1$, $E = 20$ kcal/mole, $Z = 10^4\ \mathrm{sec}^{-1}$, heating rate q K sec^{-1})

x	q	x_0	x_1^*	x_2^*	x_3^*	y	y_1	y_2	y_3
	8/3	0.3862	0.3862	0.3902	0.3891		0.97	1.01	1.00
∇	1/6	0.3870	0.3870	0.3888	0.3000	n	0.98	1.00	1.00
	8/3	0.3875	0.3875	0.3884	0.3887		0.98	0.99	1.0
	8/3	164.03	140.63	142.41	142.41		20.0	20.0	20.0
Δ	1/6	167.09	143.11	142.89	142.89	E	20.0	20.0	20.0
	1/96	169.46	145.05	143.72	143.38		20.0	19.9	19.9
	8/3	1.4157	1.4157	1.6619	1.6668		2.8	4.0	4.0
τ	1/6	1.6609	1.6609	1.6656	1.6656	$\log Z$	4.0	4.0	4.0
	1/96	1.9098	1.9098	1.6595	1.6610		5.2	3.9	4.0

that in the case of the standard heating rate $q = 1/6$ K sec^{-1}, even the first iteration cycle practically gives the true values of the kinetic parameters. If q is not the standard one, the first iteration cycle gives wrong Z values, but in the second or third cycle errors are already eliminated.

Verification on experimental TG curves

The TG curve of $Ca(COO)_2 \cdot H_2O$ has been recorded by means of a MOM derivatograph; sample weight 750 mg; $q = 10$ K min^{-1}. Decomposition stages I, II and III have been submitted to kinetic analysis by means of the nomogram method proposed in the present paper. The results given in Table 5 are compared to the kinetic parameters derived from the same curve by means of the Coats–Redfern method [8], presented in the last column of the Table (y_{CR}). The log Z values in this column have been obtained by means of the following relation [9]:

$$\log Z = \log g(\alpha) - \log p(x) + \log Rq - \log E \qquad (13)$$

derived from Eq. (3).

As seen from Table 5, the kinetic parameters derived by means of the nomogram and of the Coats–Readfern method are sufficiently close to each other in the

Table 5

Shape and position parameters x_0, reduced parameters x_i^* and kinetic parameters y_i corresponding to the i-th iteration cycle, derived from the experimental TG curve of $Ca(COO)_2 \cdot H_2O$ · $q = 1/6$ K sec^{-1}

Reaction		x_0	x_1^*	x_2^*	y	y_1	y_2	y_{CR}
I	∇	0.3555	0.3555	0.3573	n	0.71	0.73	0.67
	Δ	232.7	207.9	207.5	E	13.7	13.7	13.3
	τ	2.279	2.279	2.284	log Z	3.6	3.6	3.5
II	∇	0.5722	0.5722	0.5723	n	2.71	2.71	1.00
	Δ	33.8	22.3	22.3	E	140	140	263.1 51.0
	τ	1.396	1.396	1.398	log Z	40	40	78.0 13.0
III	∇	0.3293	0.3293	0.3301	n	0.50	0.50	0.50
	Δ	72.7	67.1	67.2	E	43.3	43.3	42.6
	τ	0.9555	0.9555	0.9556	log Z	5.6	5.6	5.5

case of reactions I and III, which are simple endothermic decomposition reactions. In contrast, reaction II is an exothermic reaction and even the shapes of the DTA and DTG curves show it not to be a simple process. The Coats–Redfern plot gives two intersecting straight lines for $n = 1$, corresponding to two kinetic stages with different E and Z values, given in Table 5. In this case ∇ is quite large and generally a value of $\nabla > 0.4$ might indicate the complex character of the process, i.e. the impossibility of characterizing the decomposition stage by means of a single $E - Z$ pair. Thus, if $\nabla > 0.4$ is found, the simple or complex character of the process is to be tested, e.g. by performing a Coats–Redfern linearization, corresponding to the n value given by Eq. (10).

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RÉSUMÉ — Pour caractériser les courbes TG, on propose les paramètres de forme et de position ∇, Δ et τ définis par les équations (6), (7) et (8). En réduisant ces paramètres aux "conditions" standards $n = 0$ et $q = 1/6$ K sec^{-1}, à l'aide des équations (9), (11) et (12), le nomogramme donné dans la figure 1 peut être construit. On propose une méthode d'itération pour déduire les paramètres cinétiques n, E et Z à partir des paramètres ∇, Δ et τ dans le cas des réactions simples de décomposition thermique, en utilisant les formules empiriques (9), (10), (11) et (12) ainsi que le nomogramme. Le tableau 3 contient les données nécessaires pour construire ce nomogramme.

ZUSAMMENFASSUNG — Die Gestalts- und Positionsparameter ∇, Δ und τ werden zur Charakterisierung von TG-Kurven vorgeschlagen, bzw. durch die Gleichungen (6), (7) und (8) definiert. Durch Reduktion dieser Parameter auf die "Standardbedingungen" $n = 0$ und $q = 1/6$ K sec^{-1} mit Hilfe der Gleichungen (9), (11) und (12) kann das Nomogramm in Abb. 1 konstruiert werden. Eine Iterationsmethode wird vorgeschlagen, welche die Ableitung der kinetischen Parameter, n, E und Z einfacher thermischer Zersetzungsreaktionen aus den Parametern ∇, Δ and τ unter Anwendung der empirischen Formeln (9), (10), (11) und (12) sowie des Nomogramms ermöglicht. Tabelle 3 enthält die zur Konstruktion des Nomogramms nötigen Angaben.

Резюме — Предложены параметри формы и положения ∇, Δ и τ для характеристики кривых ТГ и определяемых, соответственно, уравнениями (6), (7) и (8). Эти параметры приведены к нормальным «условиям» $n = 0$ и $q = 1/6$ К сек$^{-1}$ и номограмма, приведенная на рис. 1, может быть построена посредством уравнений (9), (11) и (12). Предложен итерационный метод, позволяющий вывести кинетические параметры n, E и Z простых реакций термического разложения, исходя из ∇, Δ и τ параметров и используя эмпирические формулы (9), (10), (11) и (12) и номограмму. Таблица 3 содержит данные, необходимые для построения этой номограммы.