Thermochimica Acta, 106 (1986) 379–387
Elsevier Science Publishers B.V., Amsterdam – Printed in The Netherlands

Note

COMPUTER-DETERMINED KINETIC PARAMETERS FROM TG CURVES. PART XVII

LEO REICH, L.Z. POLLARA * and S.S. STIVALA

Department of Chemistry and Chemical Engineering, Stevens Institute of Technology, Hoboken, NJ 07030 (U.S.A.)

(Received 14 March 1986)

In a previous paper [1], a computer method was presented for the analysis of non-isothermal TG (NITG) data for mechanism and activation energy. In the present communication, the preceding method was modified considerably and then applied to "n-type" decompositions to determine activation energy (E) and reaction order (n) simultaneously. This modified procedure was implemented by means of a computer-generated spreadsheet and was applied to theoretical data, benzenediazonium chloride (BDC), teflon (TF), magnesium hydroxide (MH) and calcium oxalate monohydrate (COX).

THEORY

For an "n-type" unimolecular (or pseudo-unimolecular) decomposition carried out by means of NITG, it can be readily shown [2] that (assuming $1 \gg 2RT/E$)

$$\ln\left\{\left[1-(1-\alpha)^{(1-n)}\right]/T^2(1-n)\right\} = -E/RT + K \tag{1}$$

where α = degree of conversion, $K = ln(AR/\beta E)$ and should be constant at any particular value of n and of heating rate (β), and A = pre-exponential factor. (Although eqn. (1) does not hold for $n = 1$, this need not concern us since values of n can be used which are very close to unity.) If we let the left-hand side of eqn. (1) be denoted by Y, we may write

$$Y + (\mathrm{SL}/T) = K \tag{2}$$

where, $\mathrm{SL} = E/R$.

* Polymer Processing Institute.

0040-6031/86/$03.50

RESULTS AND DISCUSSION

The computer procedure employed can be described as follows. Various values of n were assumed to be valid (initially 0.1 increments were used). Then using α–T (K) pairs of NITG data, eqn. (1), and a least-squares treatment, a value of SL could be determined for any particular value of n. The resulting value of SL was next used with the various data pairs to estimate K-values from eqn. (2) and the standard deviation (SD) of these K-values was determined. This process was repeated for various n-values until a minimun SD-value [SD(min)] was obtained. The entire process was repeated again using n-values (in 0.01 increments) which were close to that value of n which afforded SD(min). Final values of n and SL ($= E/R$) were taken as those at the resulting SD (min). The preceding iteration procedure was implemented by means of a computer-generated spreadsheet called MSPLAN. This particular spreadsheet (Radio Shack) is a subset of the full-fledged Microsoft MULTIPLAN spreadsheet and was found to be satisfactory for the E and n determinations carried out in this work. Although this spreadsheet analysis is relatively slow compared with a similar analysis via computer programming, it has certain advantages, such as providing neat formats of data and results, and possessing automatic functions for summations (SUM) and SD calculations (STDEV). Worksheet data and results are presented in the various tables that follow. (In order to save space, only portions of some worksheets are presented.)

Tables 1A, 1B and 1C depict worksheet analyses for SL and n using theoretical data ($n = 1/2$ and $E = 28$ kcal mol^{-1}) [3]. When three or more significant figures (SF) were used for conversion, the SD (min) value obtained at $n = 0.50$ (SL = 14000) was much smaller than corresponding values of SD obtained at $n = 0.49$ and 0.51. However, when only two SF were used for conversion values, the SD-values at $n = 0.49$ and 0.51 were much closer to that at $n = 0.50$ (Table 1C). Thus, it is highly recommended, based on these results, that when the described method is used three or more SF be used for conversion data (and that SD-values be much less then 0.05). Theoretical data values ($n = 1$ and $E = 30$ kcal mol^{-1}) [4] are again employed in Table 2. From this table, it can be readily observed that SD(min) occurs when $n = 1$ and SL = 15100.

Data [5] and worksheet results are presented in Table 3 for the decomposition of BDC in aqueous solution. From these results, it can be observed that SD(min) occurs when $n = 1.03$ and SL = 14656 (from refs. 5–8, $n =$ 1–1.1 and $E = 28$–38 kcal mol^{-1}). Data [9] and worksheet results for the decomposition of MH are presented in Table 4. From this table, values of n and SL at SD(min) are, respectively, 1.64 and 28805 (from refs. 3, 9–12, $n = 1.3$–1.8 and $E = 53$–57 kcal mol^{-1}). Table 5 depicts data [13] and results for the decomposition of COX. From this table, it can be seen that $n = 0.92$ and SL = 9745 (from refs. 6, 13–14, $n = 0.74$–1 and $E = 18$–22

TABLE 1A

Worksheet analysis of theoretical data with more than three SF for n and SL values

Conversion, C	T (K)	X = $-1/T$	YN = $[1-(1-C)^{(1-n)}]/(1-n)$	YD = $T \times T$	Y = ln(YN/YD)	XX = X×X	XY = X×Y	Y + (E/RT) = INT
0.1319	405	−0.00246914	0.136753384	164025	−13.9973502	6.09663E-06	0.034561359	20.84244822
0.20197	410	−0.00243902	0.213822495	168100	−13.5749234	5.94884E-06	0.033109569	20.83999946
0.30263	415	−0.00240964	0.330982224	172225	−13.1622476	5.80636E-06	0.031716259	20.83803758
0.44108	420	−0.00238095	0.507585949	176400	−12.7585986	5.66893E-06	0.030377616	20.83692128
0.61872	425	−0.00235294	0.77187078	180625	−12.3631165	5.53633E-06	0.029089686	20.83716205
0.73858	428	−0.00233645	0.989171928	183184	−12.1291335	5.45899E-06	0.028339097	20.83843277
0.81881	430	−0.00232558	1.165712657	184900	−11.9742378	5.40833E-06	0.027847065	20.83999097
0.92696	433	−0.00230947	1.490042102	187489	−11.7426711	5.33365E-06	0.027119333	20.84420737
		#DIV/0!	0	0	#DIV/0!	#DIV/0!	#DIV/0!	#DIV/0!
		#DIV/0!	0	0	#DIV/0!	#DIV/0!	#DIV/0!	#DIV/0!
		#DIV/0!	0	0	#DIV/0!	#DIV/0!	#DIV/0!	#DIV/0!
Summations:		−0.01902319			−101.702279	4.52581E-05	0.242159983	0.002578906
n	0.3	0.4	0.5	0.6	0.48	0.49	0.51	0.52
SL = slope	12951	13464	14000	14560	13891	13945	14505	14110
SD	0.0235	0.0123	0.000016471	0.0134	0.00255	0.00129	0.00128	0.00258

TABLE 1B

Worksheet analysis of theoretical data with three SF for n and SL values

Conversion, C	0.132	0.202	0.303	0.441	0.619	0.819	0.927	
T (K)	405	410	415	420	425	430	433	
n	0.3	0.4	0.5	0.6	0.48	0.49	0.51	0.52
SL = slope	12924	13448	13997	14572	13885	13941	14053	14110
SD	0.025	0.01306	0.000478	0.01413	0.002778	0.001476	0.001402	0.002736

TABLE 1C

Worksheet analysis of theoretical data with 2-SF for n and SL values

Conversion, C	0.13	0.2	0.3	0.44	0.62	0.82	0.93	
T (K)	405	410	415	420	425	430	433	
n	0.3	0.4	0.5	0.6	0.48	0.49	0.51	0.52
SL = slope	13055	13584	14139	14720	14026	14082	14196	14253
SD	0.0253	0.01319	0.001639	0.01479	0.003022	0.002	0.00228	0.00342

TABLE 2

Worksheet analysis of theoretical data for n and SL values

Conversion, C	T (K)	$X = -1/T$	$YN = [1-(1-C)^{(1-n)}]/(1-n)$	$YD = T \times T$	$Y = \ln(YN/YD)$	$XX = X \times X$	$XY = X \times Y$	$Y + (E/RT) = INT$	
0.020877	678	−0.00147493	0.021102458	459684	−16.8966603	2.17541E-06	0.024921328	5.441633501	
0.05741	708	−0.00141243	0.059158844	501264	−15.9524174	1.99496E-06	0.022531663	5.439338588	
0.10012	726	−0.00137741	0.105605226	527076	−15.4231475	1.89726E-06	0.021244005	5.438234396	
0.19673	750	−0.00133333	0.219544976	562500	−14.7563446	1.77778E-06	0.019675126	5.437473051	
0.30805	768	−0.00130208	0.369600934	589824	−14.2829109	1.69542E-06	0.01859754	5.43761415	
0.45399	786	−0.00127226	0.608794483	617796	−13.8301881	1.61866E-06	0.017595659	5.438721832	
0.56512	798	−0.00125313	0.839657445	636804	−13.5389785	1.57034E-06	0.016966138	5.440173438	
0.67875	810	−0.00123457	1.148528225	656100	−13.2555872	1.52416E-06	0.016364922	5.44239211	
0.7846	822	−0.00121655	1.559071807	675684	−12.9793901	1.47998E-06	0.015790012	5.445625944	
0.87237	834	−0.00119904	2.101586635	695556	−12.7097742	1.4377E-06	0.015239537	5.450133735	
0.95713	852	−0.00117371	3.250897845	725904	−12.3162418	1.37759E-06	0.014455683	5.460006078	
Summations:		−0.01066015			−117.936234	1.4254E-05	0.157896382	0.001822322	
n	0.3	0.4	0.5	0.6	0.7	0.8	0.9	0.99999	1.1
SL = slope	13675	13868	14065	14266	14470	14677	14888	15102	15320
SD	0.0576	0.0501	0.0423	0.0343	0.0261	0.0176	0.00894	1.68608E-05	0.00919
n	0.98	0.99	1.01	1.02	–				
SL = slope	15059	15080	15124	15145	15145.36322				
SD	0.0018	0.000901	0.000912	0.00182	0.001822322				

TABLE 3

Worksheet analysis of data for the decomposition of BDC for n and SL values

Conversion, C	T (K)	$X = -1/T$	$YN = [1-(1-C)]^{(1-n)}]/(1-n)$	$YD = T \times T$	$Y = \ln(YN/YD)$	$XX = X \times X$	$XY = X \times Y$	$Y + (E/RT) = INT$
0.054	308.2	−0.00324465	0.055574389	94987.24	−14.3515307	1.05277E-05	0.046565641	33.35141909
0.1171	313.2	−0.00319285	0.124854072	98094.24	−13.5742936	1.01943E-05	0.043340656	33.36711483
0.2369	318.2	−0.00314268	0.271833437	101251.24	−12.827926	9.87642E-06	0.040314035	33.37587385
0.4386	323.2	−0.00309406	0.58403923	104458.24	−12.0943298	9.5732E-06	0.037420575	33.39468357
0.6202	327.2	−0.00305623	0.987099559	107059.84	−11.5941276	9.34057E-06	0.035434375	33.33878535
0.7684	330.2	−0.00302847	1.506382849	109032.04	−11.1896858	9.17162E-06	0.033887601	33.33499357
0.9317	334.4	−0.00299043	2.833202578	111823.36	−10.583268	8.94268E-06	0.031648529	33.38218983
		#DIV/0!	0	0	#DIV/0!	#DIV/0!	#DIV/0!	#DIV/0!
		#DIV/0!	0	0	#DIV/0!	#DIV/0!	#DIV/0!	#DIV/0!
		#DIV/0!	0	0	#DIV/0!	#DIV/0!	#DIV/0!	#DIV/0!
		#DIV/0!	0	0	#DIV/0!	#DIV/0!	#DIV/0!	#DIV/0!
Summations:		−0.02174936			−86.2151614	6.76265E-05	0.268611412	0.022572983
n	0.4	0.5	0.6	0.7	0.8	0.9	0.99999	1.1
SL = slope	12094	12456	12834	13229	13642	14071	14518	14983
SD	0.116	0.102	0.0866	0.0702	0.0531	0.03604	0.02351	0.02752
n	0.98	0.99	1.01	1.02	1.03	1.04	–	–
SL = slope	14427	14473	14564	14610	14656	14702	14702.04911	14702.04911
SD	0.02513	0.02424	0.02296	0.02261	0.02248	0.02257	0.022572983	0.022572983

TABLE 4

Worksheet analysis of data for the decomposition of MH for n and SL values

Conversion, C	0.1777	0.262	0.3485	0.4715	0.59	0.6538	7107	0.7563
T (K)	645	652	657	664	670	674	677	680
n	1.1	1.2	1.3	1.4	1.5	1.6	1.7	1.8
SL = slope	24269	25067	25884	26720	27576	28450	29344	30256
SD	0.0317	0.0274	0.0231	0.019	0.0155	0.0134	0.0136	0.0162
n	1.58	1.59	1.61	1.62	1.63	1.64	1.65	1.66
SL = slope	28274	28362	28539	28627	28716	28805	28895	28984
SD	0.01365	0.01351	0.01329	0.01321	0.01316	0.01314	0.013144	0.013174

TABLE 5

Worksheet analysis of data for the decomposition of COX for n and SL values

Conversion, C	0.075	0.205	0.305	0.442	0.607	0.773	
T (K)	443.2	463.2	473.2	483.2	493.2	503.2	
N	0.5	0.6	0.7	0.8	0.9	0.99999	1.1
SL = slope	8786	9005	9230	9461	9697	9939	10187
SD	0.0426	0.0343	0.0261	0.0185	0.01385	0.01586	0.02344
n	0.91	0.92	0.93	0.94	–	–	–
SL = slope	9721	9745	9769	9794	9793.543562	9793.543562	9793.543562
SD	0.01371	0.01364	0.01366	0.01375	0.013748501	0.013748501	0.013748501

TABLE 6A

Worksheet analysis of seven pairs of data for the decomposition of TF for n and SL values

Conversion, C	0.016	0.087	0.216	0.333	0.489	0.663	0.826	
T (K)	773.2	803.2	823.2	833.2	843.2	853.2	863.2	
n	0.5	0.6	0.7	0.8	0.9	0.99999	1.1	–
SL = slope	30322	30823	31337	31864	32406	32961	33529	33073.31067
SD	0.0795	0.0661	0.0524	0.0389	0.02716	0.02169	0.02795	0.02200676
n	0.98	0.99	1.01	1.02	–	–	–	–
SL = slope	32849	32905	33017	33073	33073.31067	33073.31067	33073.31067	33073.31067
SD	0.02191	0.02173	0.02178	0.022	0.02200676	0.02200676	0.02200676	0.02200676

TABLE 6B

Worksheet analysis of nine pairs of data for the decomposition of TG for n and SL values

Conversion, C	0.016	0.087	0.138	0.216	0.333	0.489	0.663	0.826 0.967
T (K)	773.2	803.2	813.2	823.2	833.2	843.2	853.2	863.2 873.2
n	0.5	0.6	0.7	0.8	0.9	0.99999	–	–
SL = slope	29523	30273	31064	31896	32769	33684	32239.81049	32239.81049
SD	0.941	0.0723	0.0508	0.0354	0.0406	0.0646	0.034411182	0.034411182
n	0.81	0.82	0.83	0.84	–	–	–	–
SL = slope	31981	32067	32153	32240	32239.81049	32239.81049	32239.81049	32239.81049
SD	0.0348	0.0344	0.0343	0.0344	0.034411182	0.034411182	0.034411182	0.034411182

kcal mol^{-1}). Finally, data [15] and results for TF are shown in Tables 6A and 6B. From these tables, there appears to be some inconsistency in the data. Thus, Tables 6A and 6B afford the following results for n and SL, respectively: 0.99 and 32905; 0.83 and 32153 (from refs. 3, 15, $n = 1$ and $E = 66–68$ kcal mol^{-1}).

From the preceding, the procedure presented for the estimation of n and E and its implementation by means of worksheet analysis affords values of n and E/R from the various $\alpha - T$ (K) data pairs tested, in satisfactory agreement with corresponding theoretical and reported values.

REFERENCES

1 L. Reich and S.S. Stivala, Thermochim. Acta, 73 (1984) 165.
2 L. Reich, L.Z. Pollara and S.S. Stivala, Thermochim. Acta, 90 (1985) 189.
3 L. Reich and S.S. Stivala, Thermochim. Acta, 24 (1978) 9.
4 K. Bohme, S. Boy, K. Heide and W. Holand, Thermochim. Acta, 23 (1978) 17.
5 H.J. Borchardt, Ph.D. Dissertation, University of Wisconsin, 1956.
6 L. Reich, J. Appl. Polym. Sci., 10 (1966) 465.
7 L. Reich and S.S. Stivala, Thermochim. Acta, 66 (1983) 383.
8 L. Reich and S.S. Stivala, Thermochim. Acta, 84 (1985) 385.
9 P.H. Fong and D.T.Y. Chen, Thermochim. Acta, 18 (1977) 273.
10 L. Reich and S.S. Stivala, Thermochim. Acta, 36 (1980) 103.
11 L. Reich and S.S. Stivala, Thermochim. Acta, 87 (1985) 347.
12 L. Reich and S.S. Stivala, Thermochim. Acta, 98 (1986) 359.
13 L. Reich and S.S. Stivala, Thermochim. Acta, 25 (1978) 367.
14 V. Marcu and E. Segal, Thermochim. Acta, 20 (1977) 211.
15 C.D. Doyle, J. Appl. Polym. Sci., 5 (1961) 285.