

Note

COMPUTER-DETERMINED KINETIC PARAMETERS (E AND n) FROM DTA CURVES

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One of the authors previously reported expressions for the estimation of the kinetic parameters, activation energy (E) and reaction order (n), from TG traces assuming an n -type mechanism [1]. These expressions were subsequently transformed so that the resulting equations could be applied to DTA traces [2,3]. By means of the transformed equations (TES), DTA traces for various inorganic and polymeric materials could be analyzed quantitatively for E and n . However, prior to the estimation of E , it was initially necessary to estimate the value of n . This could be accomplished by graphical or laborious iteration procedures, which posed a serious limitation to the use of the TES—until the advent of the relatively affordable micro-processor.

In the following, a computer algorithm/program (CP) will be presented which will allow the rapid estimation of n and E from DTA (and DSC, with appropriate modifications) traces. The CP will be applied to sodium bicarbonate (SB), benzenediazonium chloride (BDC), and finally to polypropylene (PP).

THEORY

The following TES have been previously derived [2,3]

$$F(T) = (\tilde{a}_1/\tilde{a}_2)^n \left[1 - (\tilde{a}_1/AR)^{1-n} \right] / \left[1 - (\tilde{a}_2/AR)^{1-n} \right] \quad \text{for } n \neq 1 \quad (1)$$

$$E/R = \left[(1-n)T^2(DT) \right] / \left\{ (AR)(\tilde{a}/AR)^n \left[1 - (\tilde{a}/AR)^{1-n} \right] \right\} \quad \text{for } n \neq 1 \quad (2)$$

where, $F(T) = (T_1/T_2)^2 [(DT)_1/(DT)_2]$; AR = total thermogram area, i.e., $\int_{T_i}^{\infty} (DT)dT$; DT = height of the DTA curve from a baseline; T = temperature (K); and, $\tilde{a} = \int_T^{\infty} (DT)dT$. Although eqns. (1) and (2) only apply strictly when $n \neq 1$, they can generally be applied in this paper since in the CP employed, n cannot equal unity exactly.

In order to ascertain the value of n in eqn. (1), the CP employs an iteration method. Thus, if we let $LH = F(T)$ and RHS equal the right-hand-side of eqn. (1), then as n is increased from 0.10001 to 2 in increments of 0.1, the value of the deviation, i.e., absolute value of $(LH-RHS)$, will approach a minimum value as the appropriate value of n is neared. When such a value is reached, then increments of n of 0.01 are applied to the value of n immediately preceding the n -value which gave the minimum value, in order to obtain more refined n -values. This is carried out for various data pairs and an average n -value is obtained (\bar{n}). Once \bar{n} has been determined, various values of E/R can be calculated from eqn. (2). Finally, an average E -value (\bar{E}) is determined. In order to minimize the effects of experimental errors, the data were "scrambled" prior to use so that no two values of \bar{a}/AR were close to each other.

TESTING THE METHOD

In order to test the preceding equations, DTA traces were employed for an aqueous solution of BDC [4,5], SB [6], and PP [7]. The CP used is presented in the Appendix along with a typical run and corresponding results for SB. Five data sets were used for SB (cf. line 300), and are given in the following order, respectively: \bar{a}/AR , T (K), and DT ($^{\circ}C$). Since it was known from previous work that $n \neq 1$ for SB decomposition, line 120 was used to obtain n to two places (for the sake of neatness). However, in general, the first part of line 120 (preceding "PRINT N") should not be used (else, eqns. (1) and (2) may become invalid).

From the results of the run for SB, it can be seen that $\bar{n} = 0.75 \pm 0.04$ and $\bar{E} = 22.8 \text{ kcal mol}^{-1}$. Values for SB have been reported to range as follows: $n = 0.68-0.85$ and $E = 22-25 \text{ kcal mol}^{-1}$ [2,6,8,9]. In a similar manner as for SB, the following average values of n and E were obtained for BDC and PP, respectively: 1.01 ± 0.05 and $29.9 \text{ kcal mol}^{-1}$ (lit.[2-5,10], 1-1.1 and 28-30 kcal mol^{-1}); 0.86 ± 0.14 and $57.8 \text{ kcal mol}^{-1}$ (lit.[2,11,12], 0.78-1 and 55-65 kcal mol^{-1}).

APPENDIX

Computer program and run for the determination of E and n from a DTA trace for the decomposition of SB.

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5  REM ***COMPUTER-DETD. KINETIC PARAMETERS (E AND N) FROM DTA TRACES***
7  :
10 TEXT : HOME
15 :
20 DA = 5: REM NO. DATA SETS
25 :
30 FOR J = 1 TO DA: READ AA(J),T(J),DT(J): NEXT
35 :
40 DIM N(20)
45 :
50 N1 = .10001:N2 = .1:N(0) = 100:CC = 0:AR = 72: REM 'AR'= TOTAL AREA (D
    EG*DEG)
55 :
60 FOR J = 1 TO DA - 1
65 :
70 F(J) = (T(J) / T(J + 1)) ^ 2 * (DT(J) / DT(J + 1)):LH = F(J)
75 :
80 DEF FN F(N) = (AA(J) / AA(J + 1)) ^ N * (1 - (AA(J)) ^ (1 - N)) / (1 -
    (AA(J + 1)) ^ (1 - N))
85 :
90 PRINT " N"; TAB( 12)" RHS"; TAB( 17)" DEVIATN": FOR K = 1 TO 50: PRINT
    "-";: NEXT K: PRINT
95 :
100 FOR N = N1 TO 2 STEP N2
105 :
110 CC = CC + 1
115 :
120 N = INT (N * 1E2 + .5) / 1E2: PRINT N; TAB( 12); INT ( FN F(N) * 1E5 +
    .5) / 1E5; TAB( 15);
125 :
130 N(CC) = ABS (LH - FN F(N)):N(CC) = INT (N(CC) * 1E7 + .5) / 1E7: PRINT
    N(CC)
135 :
140 IF N(CC) > N(CC - 1) THEN DN(J) = N(CC - 1): GOTO 160
145 :
150 NEXT N
155 :
160 DD = DD + 1: IF DD = 2 THEN PRINT : PRINT " FOR A DEVIATN. OF "DN(J);
    " VALUE #"J;" OF N=";:NN(J) = N - N2: PRINT NN(J):DD = 0:CC = 0:N1 =
    .10001:N2 = .1: FOR K = 1 TO 50: PRINT "-";: NEXT K: PRINT : GET A*: PRINT
    : NEXT J: GOTO 190
165 :
170 CC = 0:N1 = N - 2 * N2:N2 = N2 / 10
175 :
180 GOTO 100
185 :
190 PRINT : PRINT " VALUES OF REACTION ORDER (N) AND THEIR DEVIATNS. ARE:
    ": PRINT : FOR K = 1 TO DA - 1: PRINT " N= ";NN(K);" AND DEVIATN.= "
    DN(K):SS = SS + NN(K): NEXT K

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195 :
200 AV = INT (SS / (DA - 1) * 1E2 + .5) / 1E2: PRINT : PRINT " AVG. N= ";
    AV;" AND MEAN DEVIATN.= ";;: FOR LL = 1 TO DA - 1:MD = MD + ABS (AV -
    NN(LL)): NEXT LL:MD = MD / (DA - A): PRINT MD
205 :
210 PRINT : PRINT : PRINT " VALUES OF ACTIVN. ENERGY (E) CALCD. ARE: "; PRINT
    : FOR M = 1 TO 5:E(M) = ((1 - AV) * (T(M)) ^ 2 * DT(M)) / (AR * AA(M)
    ^ (AV) * (1 - AA(M) ^ (1 - AV))):EE = EE + E(M): NEXT M:EE = EE / DA
215 :
220 FOR MM = 1 TO 5: PRINT " E= " INT (E(MM) * 2)" CAL/MOLE": NEXT MM: PRINT
    : PRINT " AVG. E= " INT (EE * 2)" CAL/MOLE"
225 :
300 DATA .8,406,.91,.40,423,1.90,.5,421,1.78,-.25,431,1.86,-.75,408,1.07: REM
    NAHCO3, 5 DATA SETS

300 DATA .8,406,.91,.40,423,1.90,.5,421,1.78,-.25,431,1.86,-.75,408,1.07: REM
    NAHCO3, 5 DATA SETS

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N	RHS	DEVIATN
.1	.34722	.0939999
.2	.36146	.0797598
.3	.37605	.0651764
.4	.39097	.0502565
.5	.40622	.0350078
.6	.42178	.0194391
.7	.43766	3.5597E-03
.8	.45384	.0126199
.6	.42178	.0194391
.61	.42336	.0178649
.62	.42494	.0162877
.63	.42652	.0147074
.64	.4281	.013124
.65	.42969	.0115376
.66	.43128	9.9481E-03
.67	.43287	8.3555E-03
.68	.43446	6.7599E-03
.69	.43606	5.1613E-03
.7	.43766	3.5597E-03
.71	.43927	1.9551E-03
.72	.44088	3.474E-04
.73	.44249	1.2632E-03

FOR A DEVIATN. OF 3.474E-04 VALUE #1 OF N=.72

N	RHS	DEVIATN
.1	1.18338	.1058007
.2	1.16733	.0897442
.3	1.15182	.074236
.4	1.13684	.0592632
.5	1.12239	.0448131
.6	1.10845	.0308728
.7	1.09501	.0174298
.8	1.08205	4.4718E-03
.9	1.06957	8.0138E-03
.7	1.09501	.0174298
.71	1.09369	.0161124
.72	1.09238	.0147998
.73	1.09107	.0134921
.74	1.08977	.0121891
.75	1.08847	.010891
.76	1.08718	9.5976E-03
.77	1.08589	8.309E-03
.78	1.08461	7.0252E-03
.79	1.08333	5.7461E-03
.8	1.08205	4.4718E-03
.81	1.08078	3.2022E-03
.82	1.07952	1.9373E-03
.83	1.07826	6.77E-04
.84	1.077	5.785E-04
.85	1.07575	1.8293E-03

FOR A DEVIATN. OF 5.785E-04 VALUE #2 OF N=.84

N	RHS	DEVIATN
.1	.69782	.2152759
.2	.72963	.1834628
.3	.76205	.151048
.4	.795	.1180944
.5	.82843	.0846694
.6	.86225	.0508447
.7	.8964	.0166956
.8	.9308	.0176995
.6	.86225	.0508447
.61	.86565	.0474431
.62	.86906	.0440384
.63	.87247	.0406305
.64	.87588	.0372197
.65	.87929	.0338059
.66	.88271	.0303892
.67	.88613	.0269698
.68	.88955	.0235477
.69	.89297	.0201229
.7	.8964	.0166956
.71	.89983	.0132658
.72	.90326	9.8337E-03
.73	.9067	6.3993E-03
.74	.91013	2.9626E-03
.75	.91357	4.762E-04
.76	.91701	3.9171E-03

FOR A DEVIATN. OF 4.762E-04 VALUE #3 OF N=.75

N	RHS	DEVIATN
.1	2.79979	.8599634
.2	2.61665	.6768172
.3	2.449	.509172
.4	2.29544	.3556161
.5	2.1547	.2148718
.6	2.02561	.0857825
.7	1.90713	.0326992
.8	1.79831	.1415219
.6	2.02561	.0857825
.61	2.0133	.0734734
.62	2.0011	.0612693
.63	1.989	.0491692
.64	1.977	.0371721
.65	1.96511	.0252772
.66	1.95331	.0134834
.67	1.94162	1.7898E-03
.68	1.93002	9.8046E-03

FOR A DEVIATN. OF 1.7898E-03 VALUE #4 OF N=.67

VALUES OF REACTION ORDER (N) AND THEIR DEVIATNS. ARE:

N= .72 AND DEVIATN.= 3.474E-04
 N= .84 AND DEVIATN.= 5.785E-04
 N= .75 AND DEVIATN.= 4.762E-04
 N= .67 AND DEVIATN.= 1.7898E-03

AVG. N= .75 AND MEAN DEVIATN.= .04

VALUES OF ACTIVN. ENERGY (E) CALCD. ARE:

E= 22695 CAL/MOLE
 E= 22926 CAL/MOLE
 E= 23158 CAL/MOLE
 E= 23170 CAL/MOLE
 E= 22116 CAL/MOLE

AVG. E= 22813 CAL/MOLE

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