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Note

COMPUTER-DETERMINED KINETIC PARAMETERS FROM TG CURVES. PART XIX

LEO REICH, PAUL ALLEN, JR. * and S.S. STIVALA

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

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In a recent publication [1], the authors derived an expression applicable to non-isothermal TG (NITG) curves (DSC curves can also be used) which related conversion (α), temperature [T (K)], reaction order (n) and slope (RT). From such an expression it was possible to obtain an empirical cubic equation which afforded satisfactory values of n for the cases tested. In the present paper, a similar derivation will be employed to obtain an expression which can be used to estimate both n and activation energy (E) concurrently from similar experimental curves. The preceding expression will then be tested for two theoretical cases and for benzenediazonium chloride (BDC). Then a similar procedure will be applied to theoretical isothermal TG (ITG) data in order to yield values of n and rate constant (k) concurrently.

THEORY

It can be readily shown (cf. ref. 1) that for NITG curves

$$F\left[(1-\alpha)^{n}-(1-\alpha)\right]/\left[(RT)T^{2}\right]=FR(1-n)/E \quad (1)$$

where F is an arbitrary scaling factor, R is the gas constant and $RT = \mathrm{d}\alpha/\mathrm{d}T$. From eqn. (1) it can readily be perceived that the right-hand side (RH) can be set equal to a constant (K) and that once K (average) has been determined, E can then be calculated. Values of the left-hand side (LH) of eqn. (1) were calculated for various particular n values and for the various data sets which consisted of values of α, T and RT. Then average K values and their standard deviations (SD) were estimated from the LH values for the various particular n values used. Initially, n values were incremented in 0.100001 steps (ST) (so that n could not equal unity exactly). However, after

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* Professor Emeritus (deceased).

attaining a minimum SD value, the corresponding n value was decreased by ST and n values were now incremented in steps of ST/10 until a minimum SD value was again obtained. The proper value of n (and hence of E) was considered to be that value which afforded the minimum SD value. Also, since RH values in eqn. (1) were expected to be very small, a scaling factor of 10000 was introduced so that resulting values could be more easily handled.

It can also be shown that for ITG curves [2]

$$\left[1-(1-\alpha)^{(1-n)}\right]/t=k(1-n) \qquad (2)$$

where k is the rate constant and t is the reaction time. By employing a procedure similar to the preceding used for NITG, values of k and n could

TABLE 1

Results from the computer analysis of eqn. (1) for standard deviation, reaction order and average K, using theoretical NITG data [3]

Data: 05741, 708, 0.001679, 0.10012, 726, 0.0027201, 0.19673, 750, 0.0047245, 0.26693, 762, 0.0059205, 0.40193, 780, 0.0076313, 0.50868, 792, 0.0084064, 0.62223, 804, 0.0085916, 0.73334, 816, 0.0079942, 0.83129, 828, 0.0066134, 0.90715, 840, 0.0047235: REM BOHME THEOR DATA/10 SETS → $n=1.00/E=30.2$

Std. dev.	n	Avg. K
0.473518	0.10	0.983529
0.336644	0.20	0.814684
0.232789	0.30	0.667158
0.155044	0.40	0.537376
0.097963	0.50	0.422418
0.057247	0.60	0.319901
0.029505	0.70	0.227869
0.012055	0.80	0.144719
0.002779	0.90	0.069125
0.000000	1.00	−0.000006
0.002388	1.10	−0.063582
0.002779	0.90	0.069125
0.002233	0.91	0.061937
0.001751	0.92	0.054813
0.001330	0.93	0.047752
0.000969	0.94	0.040752
0.000668	0.95	0.033812
0.000424	0.96	0.026933
0.000237	0.97	0.020112
0.000104	0.98	0.013349
0.000026	0.99	0.006643
0.000000	1.00	−0.000006
0.000026	1.01	−0.006600

Final values: $n=1.00$, $E=30.20$ kcal mol^{-1}, std. dev. = 0.00000 be determined simultaneously. The ITG data now consisted of pairs of α–t values and no scaling factor was employed.

TESTING THE METHOD

The preceding method for NITG data was tested using theoretical TG data and data for BDC. In Tables 1–3, the data used (given in the order: α, T and RT) are depicted in line numbers 1000, 1200 and 1400. From Table 1, the theoretical data used [3] afforded final values of $n = 1.00$ and $E = 30.2$ kcal mol^{-1} (lit. [3], 1 and 30). Theoretical TG data ($n = 1/2$, $E = 28$ kcal mol^{-1}) were also tested in Table 2. From this table, it can be seen that final values were $n = 0.50$ and $E = 28.0$, in excellent agreement with the theoretical values. Data from the DTA decomposition of BDC in aqueous solution are given in Table 3 [4]. From this table, final values were $n = 1.00$ and $E = 29.7$ kcal mol^{-1}, in good agreement with anticipated results (lit. [4–7], 1–1.1 and 28–30).

TABLE 2

Results from the computer analysis of eqn. (1) for standard deviation, reaction order and average K, using theoretical NITG data

Data: 084601, 400, 0.007239, 0.131895, 405, 0.01086, 0.201953, 410, 0.015872, 0.302608, 415, 0.022388, 0.441051, 420, 0.029949, 0.618692, 425, 0.036614, 0.818781, 430, 0.037022, 0.978827, 435, 0.018398:REM THEOR DATA/8 SETS → $n = 0.50/E = 28$

Std. dev.	n	Avg. K
0.420794	0.10	0.883284
0.233548	0.20	0.712187
0.114571	0.30	0.572876
0.041713	0.40	0.456567
0.000005	0.50	0.357140
0.020670	0.60	0.270308
0.041713	0.40	0.456567
0.036339	0.41	0.445947
0.031261	0.42	0.435490
0.026467	0.43	0.425191
0.021946	0.44	0.415044
0.017688	0.45	0.405046
0.013683	0.46	0.395192
0.009921	0.47	0.385479
0.006393	0.48	0.375901
0.003089	0.49	0.366456
0.000005	0.50	0.357140
0.002878	0.51	0.347948

Final values: $n = 0.50$, $E = 28.00$ kcal mol^{-1}, std. dev. = 0.00000

TABLE 3

Results from the computer analysis of eqn. (1) for standard deviation, reaction order and average K, using DTA data from the decomposition of BDC [4]

Data: 0.54, 308.2, 0.00851094, 0.1171, 313.2, 0.0165843, 0.2369, 318.2, 0.0297812, 0.4386, 323.2, 0.0457304, 0.6202, 327.2, 0.051235, 0.7684, 330.2, 0.0468596, 0.9317, 334.4, 0.0238532: REM BORCHARDT THESIS/7 SETS/ON2CL/$RH=1$/TBL VII/P.90 → $n=1.00$, $E=29.7$

Std. dev.	n	Avg. K
0.710269	0.10	1.078814
0.493758	0.20	0.879136
0.334474	0.30	0.710037
0.218726	0.40	0.565322
0.136096	0.50	0.440154
0.078663	0.60	0.330749
0.040407	0.70	0.234136
0.016753	0.80	0.147976
0.004218	0.90	0.070418
0.000000	1.00	−0.000006
0.002722	1.10	−0.064468
0.004218	0.90	0.070418
0.003467	0.91	0.063076
0.002798	0.92	0.055804
0.002207	0.93	0.048600
0.001693	0.94	0.041464
0.001252	0.95	0.034394
0.000881	0.96	0.027388
0.000577	0.97	0.020447
0.000335	0.98	0.013568
0.000146	0.99	0.006751
0.000000	1.00	−0.000006
0.000122	1.01	−0.006703

Final values: $n=1.00$, $E=29.73$ kcal mol^{-1}, std. dev. = 0.00000

The effect of significant figures (SF) on the results obtained in Tables 1–3 were next examined. When the data in these tables (α and RT) were reduced to 2 SF, the following results were obtained for n and E (kcal mol^{-1}), respectively: Table 1, 1.00 and 30.2; Table 2, 0.50 and 28.1; Table 3, 1.00 and 29.7. From the preceding, it can be seen that there were no significant changes in the values of n and E when the SF were reduced to 2.

When the preceding procedure for NITG data was applied to theoretical ITG data [8] using eqn. (2), the following values of n and k were obtained, respectively, using 3 SF: 0.67 and 0.02193 (lit. [8], 2/3 and 0.0219). When only 2 SF were employed, n and k values were, respectively, 0.66 and 0.02169.

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