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Note

COMPUTER-DETERMINED KINETIC PARAMETERS FROM TG CURVES. PART IV

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In Part III [1], kinetic parameters, i.e. activation energy, E, and reaction order, n, were satisfactorily estimated by means of an algorithm and several rational approximations (RA) for the integral of the Arrhenius function. It is the aim of this paper to utilize additional approximations for this integral and to compare them in order to determine which can be used most advantageously.

In addition to the RA previously employed [cf. eqns. (2) and (6) of ref. 1], the following expressions will be investigated [2–4]

$$T \cdot \exp(-x) \cdot \frac{(x^2 + 10x + 18)}{(x^3 + 12x^2 + 36x + 24)} \tag{1}$$

$$T \cdot \exp(-x) \cdot \frac{(x+4)}{(x^2 + 6x + 6)} \tag{2}$$

$$T \cdot \exp(-x) \cdot \frac{1}{(x+2)} \tag{3}$$

$$T \cdot x \cdot \exp(-x) \cdot \frac{1}{(x+2)(x-\mathrm{d})} \tag{4}$$

$$T \cdot \exp(-x) \cdot \frac{1}{x} \cdot \left(1 - \frac{2!}{x} + \frac{3!}{x^2} + \text{---} + \frac{(-1)^N (N+1)!}{x^N}\right) \tag{5}$$

$$T \cdot \exp(-x) \cdot \left(0.0000035 + \frac{0.99871}{x} - \frac{1.98487646}{x^2} + \frac{4.9482092}{x^3} - \frac{11.7850792}{x^4} + \ldots\right) \tag{6}$$

$$T \cdot \exp(-x) \cdot \frac{1}{(x+1)} \cdot \left(1 - \frac{1}{(x+2)} + \frac{2}{(x+2)(x+3)} - \frac{4}{(x+2)(x+3)\,(x+4)} + \frac{14}{(x+2)\ldots(x+5)} + \ldots\right) \tag{7}$$

where T = absolute temperature (K); $x = E/RT$; and $d = 16/(x^2 - 4x + 84)$. Equa-

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tions (1)–(3) represent 3rd, 2nd, and 1st degree RA, respectively [eqn. (3) is also known as the Gorbachev approximation [2,5]]. Equation (4) was presented by Zsako [6]; eqn. (5) was derived using integration by parts ($N = 2$ in Table 1); eqn. (6) was obtained by expansion in series of Bernoulli numbers [4] and this series is represented in Table 1 by terms up to and including the x^3 terms; and eqn. (7) is known as the Schlomilch expansion [4] and is represented in Table 1 by terms up to and including the third term in the expansion, i.e. $2/[(x+2)(x+3)]$.

In Table 1 are shown the values of E, n, PD [1], and relative computer time (RCT) (a high-level language was used) obtained from theoretical data [7] using eqns. (1)–(7) and the 4th degree RA previously employed [1] (however, E was now varied by ±2 kcal mole^{-1}). RCT was estimated based on an assumed value of 1 for the 4th degree RA, and applies to "unrefined" values [1] for E and n. The values of E, n, and PD in parentheses indicate "refined" values [1]. From the table, it can be seen that eqns. (3) and (4) afforded unsatisfactory refined values of E and n for theoretical data (theory, $E = 28$, $n = 0.50$). Thus, RCT is not given for these expressions. It may be further noted that the lower limits of x for eqns. (1), (2), (5), (6) and (7) are 10, 20, 16 (10 has also been reported), 2, 15, respectively [2–4].

Equations (1), (2) and (5)–(7) were employed to determine E, n and PD from sodium bicarbonate, teflon, and magnesium hydroxide data [7] employing the algorithm in Part III. Values of N from 2 to 8 in eqn. (5) were found to afford satisfactory unrefined and refined values of E and n so that only the truncated form of eqn. (5) with $N = 2$ was employed. Also, the series in eqn. (6) containing terms up to and including either the 3rd or 4th degree yielded similar results so that this series

TABLE 1

Comparisons of various expressions for the integral of the Arrhenius function

Eqn used	Data used [7]	E (kcal mole^{-1})	n	Percent deviation [1]	Relative computer time
4th deg RA	Theoretical	28	0.50	0.041	1
		(28	0.50	0.041)	
(1)	Theoretical	28	0.50	0.042	0.87
		(28	0.50	0.042)	
(2)	Theoretical	28	0.50	0.042	0.75
		(28	0.50	0.042)	
(3)	Theoretical	28	0.50	0.044	
		(27.2	0.44	0.042)	
(4)	Theoretical	28	0.50	0.043	
		(27.2	0.44	0.043)	
(5)	Theoretical	28	0.50	0.041	0.75
		(28	0.50	0.041)	
(6)	Theoretical	28	0.50	0.042	1.25
		(28	0.50	0.042)	
(7)	Theoretical	28	0.50	0.042	0.80
		(28	0.50	0.042)	

was truncated after the x^3 term. Similarly, when the Schlomilch equation, eqn. (7), contained only the 1st three terms or the 1st five terms, almost identical results for E, n, and PD were obtained so that this expansion only containing the 1st three terms was used. Almost identical unrefined and refined values of E, n and PG were obtained using eqns. (1), (2), (6), or (7) for sodium bicarbonate, teflon, and magnesium hydroxide, respectively (refined values are given in parentheses): 24, 0.80, 0.013 (24, 0.80, 0.013); 65, 0.95, 0.014 (64.6, 0.93, 0.0017); 53, 1.35, 0.016 (53.8, 1.41, 0.0011). Equation (5) gave the following corresponding values: 24, 0.80, 0.011 (24, 0.80, 0.011); 65, 0.95, 0.014 (64.6, 0.93, 0.00080); 53, 1.35, 0.016 (53.8, 1.41, 0.0016). From the preceding, except for values of PD, values of E and n obtained from eqns. (1), (2), and (5)–(7) are identical.

From Table 1, it is difficult to decide which of eqns. (1), (2) and (5)–(7) would be best to use with the previously described algorithm [1]. Three factors must be taken into account: the lower limit for x, and the values of RCT and PD. In practice, the lower limit of x is generally much greater than 15 so that, except for eqn. (2), this limit does not appear to be a deciding factor. (In regard to the preceding statement, the lower limits of x for the theoretical data and for sodium bicarbonate, teflon, and magnesium hydroxide varied from ca. 25 to 40.) Also, PD values are almost identical. Thus, RCT values appear to be deciding factors and from Table 1, the most advantageous equations to use with the previously described algorithm [1] become [omitting eqn. (2)] in order of preference: (5), (7), (1) and (6). However, when low computer times are involved, then the RCT values become less significant.

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