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APPROXIMATION OF THE TEMPERATURE INTEGRAL IN THE EVALUATION OF THERMOANALYTICAL MEASUREMENTS

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ABSTRACT

Values of the temperature integral (i) of the Arrhenius equation have been calculated. An approximately linear relationship has been established between log i and the activation energy and between log i and the reciprocal temperature. The approximate expressions are given and the accuracy of the results obtained using these expressions is compared with the accuracies achievable using other approximations in a selected activation energy and temperature range. The applicability of various approximations is briefly discussed.

INTRODUCTION

Evaluation procedures for the determination of kinetic parameters from data obtained by thermogravimetric analysis are usually based upon an Arrhenius relationship

$$\frac{dx}{dt} = A\,e^{-E/RT}\,f(x). \tag{1}$$

In most cases thermogravimetric measurements are carried out at a constant heating rate a ($= dT/dt$). By introducing this term into eqn (1) it becomes

$$\frac{dx}{dT} = \frac{A}{a}\,e^{-E/RT}\,f(x). \tag{2}$$

When reaction rates are not directly measurable, parameters such as activation energy, pre-exponential factor and reaction order are obtained from the integrated form of eqn (2)

$$\int_0^x \frac{dx}{f(x)} = \frac{A}{a}\int_{T_0}^{T} e^{-E/RT}\,dT. \tag{3}$$

In the case of substances which are thermally stable at ambient temperature, values of the integral on the right-hand side of eqn (3) from $T = 0$°K to the usual value of T_0 (*i.e.* ambient temperature) are negligibly small compared to those between T_0

and the ordinary reaction temperatures. Therefore the boundaries in eqn (3) can be replaced by $T = 0$ and T for such substances.
The integrated form of eqn (3) can be conveniently expressed as

$$F(x) = \frac{A}{a}\, i(E, T) \tag{4}$$

The temperature integral, i, has no finite analytical form and, therefore, calculations based on eqn (4) require either numerically computed, and eventually tabulated, values of i, or the use of approximate formulae.

In this paper approximate expressions for the integral previously reported are examined, and further possibilities for approximation are discussed. The principal requirements are that the approximation should give accuracy over a wide range of values for the parameters calculated and that calculations should be easy to perform.

METHOD

The two most significant approximations are those described by Murray and White[1] and Doyle[2]. They have been employed in more recent studies[3–6], either unchanged or in modified forms. Integration of the right-hand side of eqn (3) can be simplified by replacing $-E/RT$ by a single variable. Thus if $y = -E/RT$, eqn (3) becomes

$$F(x) = \frac{AE}{aR} \int_{-\infty}^{y} \frac{e^y}{y^2}\, dy \tag{5}$$

which, after integration, can be written:

$$F(x) = \frac{AE}{aR}\, p(y). \tag{6}$$

The term $p(y)$ can be approximated in several ways. Murray and White used the asymptotic expansion:

$$p(y) = \frac{e^y}{y^2}\left(1 + \frac{2!}{y} + \frac{3!}{y^2} + \frac{4!}{y^3} + \ldots\right) \tag{7}$$

If all but the first two terms of the expansion are ignored, this becomes:

$$i \simeq \frac{RT^2}{E}\, e^{-E/RT}\left(1 - \frac{2RT}{E}\right) \tag{8}$$

Doyle calculated $\log p(y)$ values for a wide range of y values, and found that within the limits $20 < |y| < 60$ the following approximation applies:

$$\log p(y) \simeq -2.315 + 0.4567y \tag{9}$$

that is

$$\log i \simeq \log(E/R) - 2.315 - 0.4567(E/RT) \tag{9a}$$

We have calculated values of the temperature integral, i, corresponding to values of T in the range 400–900 °K, with $T_0 = 0$, and activation energies in the range 30–90 kcal/mole. Some values of log i are shown in Table 1.

TABLE 1

NEGATIVE LOGARITHMS OF THE ARRHENIUS TEMPERATURE INTEGRAL i

T (°K)	*E (kcal/mole)*						
	30	*40*	*50*	*60*	*70*	*80*	*90*
400	15.3876	20.9709	26.5282	32.0689	37.5979	43.1184	48.6323
500	11.9208	16.4101	20.8740	25.3214	29.7573	34.1847	38.6057
600	9.5820	13.3417	17.0764	20.7948	24.5019	28.2006	31.8928
700	7.8920	11.1303	14.3439	17.5415	20.7279	23.9059	27.0776
800	6.6101	9.4571	12.2797	15.0866	17.8823	20.6699	23.4511
900	5.6019	8.1443	10.6623	13.1657	15.6575	18.1413	20.6187

There is an approximately linear relationship between log i and reciprocal temperature and log i and activation energy, at constant activation energy and temperature respectively. These correlations can be expressed by the following linear equations:

$$\log i \simeq B + CE \qquad T = \text{constant} \tag{10}$$

$$\log i \simeq Z + Y(1/T) \qquad E = \text{constant} \tag{11}$$

The correlations were evaluated and the constants were determined using regression calculations. It was found that slopes and intercepts of eqns (10) and (11) varied significantly with temperature and activation energy respectively, and that the parameters B, C, Z, and Y could be expressed as follows:

$$B \simeq D + H \log(1/T) \tag{12}$$

$$C \simeq K(1/T)^L \tag{13}$$

$$Z \simeq P + Q \log E \tag{14}$$

$$Y \simeq ME^N \tag{15}$$

The constants D, H, K, L, P, Q, M, and N were calculated using further regression analysis, and eqns (10) and (11) could now be expressed in a numerical form:

$$\log i \simeq 1.955715 - 1.91591 \log\left(\frac{1000}{T}\right) - 0.225414\, E\left(\frac{1000}{T}\right)^{0.980413} \tag{16}$$

$$\log i \simeq 3.542051 - 0.915784 \log E - 0.269645\, E^{0.958229}\left(\frac{1000}{T}\right) \tag{17}$$

where E is in kcal/mole and T in °K.

CALCULATIONS AND DISCUSSION

Calculations were carried out on a computer and accuracies of both input and output data were to six decimal places. The temperature integral, i, was calculated using a Gaussian 32-point integration formula with weights and abscissae to eight decimal places.

Correlation coefficients for eqns (10) to (15) are shown in Table 2.

TABLE 2

LINEAR CORRELATION COEFFICIENTS OF EQUATIONS RELATING KINETIC PARAMETERS

Equation	*Variables*	*Correlation coefficient*
10	$\log i$, E	-0.999998 to -0.999991
12	B, $\log (1000/T)$	-0.999990
13	$\log -C$, $\log (1000/T)$	$+0.999998$
11	$\log i$, $(1000/T)$	-0.999969 to -0.999996
14	Z, $\log E$	-0.999919
15	$\log (-Y)$, $\log E$	$+0.999980$

In order to check the accuracies of eqns (16) and (17) and the approximations used by Murray and White[1] and Doyle[2], we calculated log i values corresponding to the data shown in Table 1 using these equations and approximations. The error caused by approximation, defined as follows:

$$\Delta = \frac{\log i_{\mathrm{real}} - \log i_{\mathrm{approx}}}{\log i_{\mathrm{real}}} \, 100\,(\%) \tag{18}$$

is shown in Table 3. This method of error representation has been chosen because it was found to be more characteristic of the situation than an overall error value for each method.

Of the approximation methods examined that of Murray and White[1] gave the most accurate results. There is, however, a limitation to its use, namely that the activation energy cannot be derived in an explicit single form. For this reason other workers[3,4] have preferred to utilize other relationships or to ignore the variation of the $(1-2RT/E)$ term as compared to that of the other terms of eqn (8)[5]. This latter treatment naturally decreases the accuracy of the approximation. Results obtained from eqns (16) and (17) and by Doyle's approximation[2] are of comparable accuracy. Between the specified $20<|y|<60$ limits eqn (16) is more, while eqn (17) is less, satisfactory than equation (9a). However, the error of approximation does not exceed 0.8 per cent when eqns (16) and (17) are used, and is generally considerably smaller. An advantage of eqns (16) and (17) is that they cover a wider range of E/RT values than does eqn (9a) without a significant change in accuracy. A disadvantage is that their analytical form is more complicated than that of eqn (9a) and, consequently, they are more difficult to use.

TABLES 3

PERCENTAGE ERROR VALUES USING APPROXIMATION PROCEDURES TO DETERMINE THE ARRHENIUS TEMPERATURE INTEGRAL *i*

T (°*K*)	*E* (*kcal/mole*)						
	30	*40*	*50*	*60*	*70*	*80*	*90*
	A. The method of Murray and White[1]						
400	−0.0114	−0.0047	−0.0024	−0.0015	−0.0009	−0.0006	−0.0004
500	−0.0227	−0.0094	−0.0048	−0.0027	−0.0017	−0.0011	−0.0008
600	−0.0403	−0.0165	−0.0083	−0.0048	−0.0030	−0.0020	−0.0014
700	−0.0660	−0.0267	−0.0134	−0.0077	−0.0048	−0.0032	−0.0022
800	−0.1021	−0.0408	−0.0203	−0.0116	−0.0072	−0.0048	−0.0034
900	−0.1514	−0.0596	−0.0295	−0.0167	−0.0104	−0.0069	−0.0048
	B. The method of Doyle[2]						
400	0.0234	−0.1786	−0.4995	−0.8170	−1.1046	−1.3594	−1.5841
500	−0.1147	0.0074	−0.1794	−0.4356	−0.6951	−0.9386	−1.1610
600	−0.5503	−0.0067	−0.0129	−0.1801	−0.3930	−0.6116	−0.8214
700	−1.2679	−0.1988	0.0214	−0.0311	−0.1807	−0.3627	−0.5510
800	−2.2690	−0.5575	−0.0635	0.0238	−0.0466	−0.1812	−0.3481
900	−3.5690	−1.0785	−0.2598	−0.0068	0.0172	−0.0596	−0.1816
	C. The use of equation (16)						
400	−0.1590	0.1132	0.1732	0.1604	0.1207	0.0712	0.0195
500	−0.3586	−0.0052	0.0743	0.0609	0.0130	−0.0473	−0.1107
600	−0.4785	−0.0420	0.0559	0.0457	−0.0161	−0.0878	−0.1632
700	−0.5376	−0.0172	0.0969	0.0782	0.0111	−0.0729	−0.1608
800	−0.5454	0.0584	0.1856	0.1609	0.0819	−0.0155	−0.1169
900	−0.5062	0.1793	0.3153	0.2814	0.1884	0.0761	−0.0397
	D. The use of equation (17)						
400	0.2704	−0.3248	−0.4145	−0.3310	−0.1717	0.0209	0.2270
500	0.6213	−0.0371	−0.1884	−0.1416	−0.0073	0.1671	0.3593
600	0.7789	0.0552	−0.1192	−0.0832	0.0450	0.2514	0.4046
700	0.7045	−0.0248	−0.1863	−0.1373	0.0015	0.1803	0.3761
800	0.4068	−0.2645	−0.3772	−0.2923	−0.1271	0.0716	0.2829
900	−0.1168	−0.6585	−0.6846	−0.5409	−0.3338	−0.1040	0.1310

It is not possible to express a simple preference for any one of these approximations *i.e.*, to answer the question as to which one is the most advantageous to use in a particular evaluation procedure. The choice will depend on the accuracy required, since this will decide how rigorous the mathematical treatment needs to be.

Since in most practical cases the approximate value of the activation energy can be estimated beforehand, it is possible to choose a formula which gives the most accurate values for this parameter in a given temperature range by using tables like 3B, 3C, and 3D. The approach to the evaluation could involve plotting log F(x)

against the reciprocal temperature, followed by use of an equation obtained by combining eqn (4) with either eqns (9a) or (17) to interpret the slope of the plot in terms of activation energy. Alternatively, the last two equations can be used in conjunction with a plot of log a against the reciprocal temperature, an approach based on a procedure described by Ozawa[6].

From points of identical conversion on thermogravimetric traces obtained at different heating rates, E can be calculated on the basis of eqns (9a) or (16), thus: from (9a):

$$E = \frac{\log (a_2/a_1)}{\left(\frac{0.4567}{R}\right)\left(\frac{1}{T_1} - \frac{1}{T_2}\right)} \tag{19}$$

from (16):

$$E = \frac{\log (a_2/a_1) - 1.91591 \log (T_2/T_1)}{0.225414\left[\left(\frac{1000}{T_1}\right)^{0.980413} - \left(\frac{1000}{T_2}\right)^{0.980413}\right]} \tag{20}$$

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