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Note

A new limited-range equation for use in non-isothermal thermogravimetric analysis

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During the last decade, several workers have made use of thermogravimetric (TG) and derivative thermogravimetric (DTG) traces for evaluating kinetic parameters[1]. The usual rate expression in this context can be put in the form,

$$d\alpha/dT = (Z/\phi)(1-\alpha)^n \exp(-E/RT) \tag{1}$$

where α = fraction decomposed at temperature T, Z = preexponential term, ϕ = heating rate (dT/dt), n = order of reaction, E = energy of activation and R = gas constant.

Rearranging and putting eqn (1) in the definite integral form gives:

$$\int_0^{\alpha} d\alpha/(1-\alpha)^n = (Z/\phi) \int_0^T \exp(-E/RT)\,dT \tag{2}$$

The main difficulty in using eqn (2) concerns the integration of the temperature-dependent integral, $\int_0^T \exp(-E/RT)\,dT$. It is a special case of the incomplete gamma function[2] and two solutions suitable for further manipulation have been given[3–5] and compared by Doyle[6]. Various approximations have also been made to integrate the aforesaid integral[1].

Van Krevelen et al.[7] have used an empirical approximation,

$$\exp(-E/RT) \approx [(T/T_s)e^{-1}]^{(E/RT_s)} \tag{3}$$

where T_s is the DTG peak temperature. However, recently, Dharwadkar and Karkhanawala[8] have criticized the undue importance attached to T_s by earlier workers in this field, on the ground that T_s, for the same system, varies with factors such as heating rate, sample size and sample mass. They point out that T_i, the temperature of the initiation of the reaction, is independent of these factors and may be taken as a constant for the same system. Such a view has also been generally accepted by most of the recent workers.

As an alternative to the Van Krevelen approximation, we wish to propose a new approximation using T_i instead of T_s.

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Let

$$\exp(-E/RT) \approx [(T/T_i)e^{-1}]^{(E/RT_i)} \tag{4}$$

An empirical constant x may be introduced in eqn (4) in order to make the LHS term as nearly equal as possible to the RHS term, so that we may write

$$\exp(-E/RT) = [(T/T_i)^x e^{-1}]^{(E/RT_i)} \tag{5}$$

where x is constant for a limited range. Of particular interest to us here would be a range where T/T_i varies from 1 to 1.25 because the greater part of the decomposition process would take place within this range. We may evaluate x as follows:

Taking logarithms, eqn (5) becomes

$$(-E/RT) = [x \ln(T/T_i) - 1](E/RT_i) \tag{6}$$

Putting $T/T_i = m$ and rearranging,

$$-1/m = [x \ln m - 1] \tag{7}$$

Even though eqn (7) is, strictly speaking, non-linear, a plot of $1/m$ versus $\ln m$ is found to be a straight line for a limited range ($1 < m < 1.25$), with the slope equal to $-x$; x is found to be 0.89 by the least squares method (correlation coefficient $= 1.00$) (cf. Fig. 1).

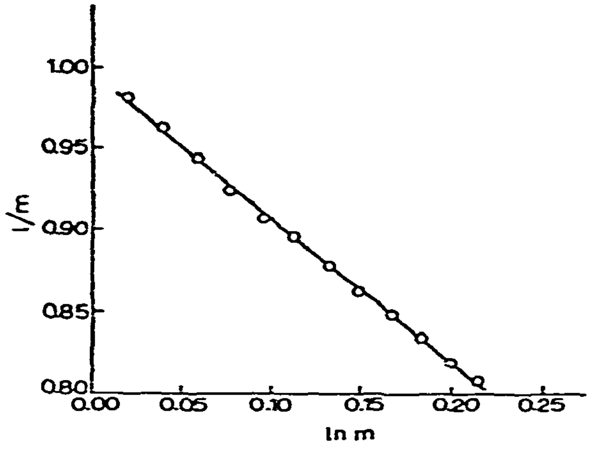

Fig. 1. Limited-range linearity between $1/m$ and $\ln m$.

On the basis of the new approximations suggested in eqn (5) we may integrate eqn (2) to get

$$\left[\frac{1-(1-\alpha)^{(1-n)}}{1-n}\right] = \left[\frac{Z\exp(-\beta/x)}{\phi T_i^{\beta}}\right]\left[\frac{T^{(\beta+1)}}{\beta+1}\right] \tag{8}$$

where $\beta = (xE/RT_i)$

TABLE 1

COMPARISON OF CALCULATED ACTIVATION ENERGY VALUES

Substance	*Decomposition stage*	*Ref. No.*[a] *for source of data*	*E (kJ mole^{-1}), calculated from the equation suggested by*						
			The present authors	*Van Krevelen*[7]	*Coats–Redfern*[3]	*Horowitz–Metzger*[9]	*Šatava*[14]	*MacCallum–Tanner*[15]	*Zsako*[12]
Cadmium thiourea reineckate	1	10	116.2	120.9	115.2	125.1	—	—	—
Cadmium thiourea reineckate	2	10	128.0	133.6	122.2	143.6	—	—	—
Copper diethyl dithiocarbamate	1	11	261.6	258.7	246.7	264.7	—	258.5	—
Nickel diethyl dithiocarbamate	1	11	265.2	275.1	261.6	282.3	—	256.4	—
Cobalt [(dimethyl glyoxime)$_2$-(*p*-ethyl aniline)$_2$] CNS	1	12	120.3	—	—	175.7[b]	—	—	120.9[b]
Cobalt [(dimethyl glyoxime)$_2$-(γ-picoline)$_2$] CNS	1	12	119.0	—	—	138.7[b]	—	—	118.4[b]
Theoretical TG trace for a substance X with *E* = 113.0 kJ mol^{-1}	1	13	117.7±0.2	—	—	—	132.4±2.5[a]	113.0±4.5[a]	—

[a] See under References. [b] Values calculated by earlier workers.

Taking logarithms and rearranging,

$$\log\left[\frac{1-(1-\alpha)^{(1-n)}}{1-n}\right] = \log\left[\frac{Z\exp(-\beta/x)}{\phi T_i^{\beta}(\beta+1)}\right] + (\beta+1)\log T \tag{9}$$

For the special case $n = 1$, the LHS of eqn (9) becomes $\log[-\ln(1-\alpha)]$. A plot of the LHS expression versus $\log T$ would be a straight line, from whose slope E can be computed; knowing E, Z can be evaluated from the intercept. Prior determination of n is necessary as is also the case with Van Krevelen's equation and with the integral methods. An approximate value of n for this purpose can be obtained by the method suggested by Horowitz and Metzger[9]. It may be noted that eqn (9) does not make use of the highly "procedural" T_s, but uses the more characteristic T_i instead.

The new equation was applied for thermal decomposition data reported in the literature and was found to give satisfactory results. Table 1 presents kinetic parameters for some complexes calculated by using the present equation as well as the equations suggested by earlier workers. It may be seen from Table 1 that the

TABLE 2

DATA SHOWING THE APPLICABILITY OF THE EQUATION[a] $1/m = A - x\ln m$
standard deviation = 0.180%.

m	*x ln m*	*A − x ln m*	*1/m*	*Deviation*	*% deviation*
1.01	0.0088	0.9867	0.9901	−0.0034	−0.343
1.02	0.0175	0.9780	0.9804	−0.0024	−0.245
1.03	0.0262	0.9693	0.9709	−0.0016	−0.165
1.04	0.0348	0.9607	0.9615	−0.0008	−0.083
1.05	0.0435	0.9520	0.9524	−0.0004	−0.042
1.06	0.0519	0.9436	0.9434	+0.0002	+0.021
1.07	0.0603	0.9352	0.9346	+0.0006	+0.064
1.08	0.0685	0.9270	0.9259	+0.0011	+0.119
1.09	0.0767	0.9188	0.9174	+0.0014	+0.153
1.10	0.0849	0.9106	0.9091	+0.0015	+0.165
1.11	0.0929	0.9026	0.9009	+0.0017	+0.189
1.12	0.1009	0.8946	0.8929	+0.0017	+0.190
1.13	0.1088	0.8867	0.8850	+0.0017	+0.192
1.14	0.1166	0.8789	0.8772	+0.0017	+0.194
1.15	0.1245	0.8710	0.8696	+0.0014	+0.161
1.16	0.1322	0.8633	0.8621	+0.0012	+0.139
1.17	0.1398	0.8557	0.8547	+0.0010	+0.117
1.18	0.1475	0.8480	0.8475	+0.0005	+0.059
1.19	0.1547	0.8408	0.8403	+0.0005	+0.060
1.20	0.1624	0.8331	0.8333	−0.0002	−0.024
1.21	0.1697	0.8258	0.8264	−0.0006	−0.073
1.22	0.1771	0.8184	0.8197	−0.0013	−0.159
1.23	0.1843	0.8112	0.8130	−0.0018	−0.221
1.24	0.1914	0.8041	0.8065	−0.0024	−0.298
1.25	0.1986	0.7969	0.8000	−0.0031	−0.388

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[a] The equation given in the text of the paper, i.e., $1/m = 1 - x\ln m$, after linearisation by the least-squares technique becomes $1/m = A - x\ln m$, where $A = 0.9955$ and $x = 0.8898$.

parameters obtained by using the present equation lie generally close to those obtained by using the earlier equations. The new equation seems to possess the accuracy associated with the integral methods as well as the computational advantage of the Van Krevelen equation; at the same time, it has the advantage of employing the more reliable T_i instead of T_s used by Van Krevelen.

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