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A MODIFICATION TO THE FREEMAN AND CARROLL METHOD FOR THE ANALYSIS OF THE KINETICS OF NON-ISOTHERMAL PROCESSES

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An analysis of the mathematical treatment employed in the Freeman and Carroll method has showed the existence of large errors in the determination of the order of the kinetic equation. A modification is proposed which allows that this error to be reduced.

The Freeman and Carroll method [1] for the kinetic analysis of non-isothermal decomposition processes is still frequently used despite of the great number of other methods proposed. Some workers [2,3] conclude that this method gives the most satisfactory results, while others [4] arrive at the opposite conclusion. In general, as the Freeman and Carroll method postulates a kinetic equation of the type

$$-\frac{dx}{dt} = Kx^n \tag{1}$$

good agreement should be expected for those processes whose kinetics can be expressed by equation (1), where x represents the amount of the substance still to decompose at time t.

However, this method has a disadvantage that results directly from the mathematical treatment of the data and is independent of the validity of the kinetic equation proposed. From equation (1), if a linear dependence of temperature with time is assumed, a linear equation

$$Y = \frac{-E}{R} X + n \tag{2}$$

can be derived, where

$$Y = \frac{\Delta \ln (d\alpha/dt)}{\Delta \ln (1-\alpha)} \quad \text{and} \quad X = \frac{\Delta (1/T)}{\ln (1-\alpha)}$$

and E, R, T, n and α have their usual meaning.

A straight line is fitted to the X_i, Y_i pairs obtained from the data measured in the thermal curve, normally by the least squares method. The gradient of the line gives the parameter E, while the ordinate at the origin gives n. However, the validity of the values obtained in this way needs to be examined by analysing the statistical treatment used.

Firstly, (and this comment is valid for any regression analysis on a group of X_i, Y_i pairs) the problem is to select which is the straight line which best fits the cluster of points obtained experimentally. Although the regression of Y on X is normally determined, it is obvious that the regression of X on Y could equally be used. In addition, the line which passes through the greatest number of points could also be chosen. It is evident that the problem as posed above does not have an answer as the best line depends on the optimization criterion selected, which in these cases under discussion will be arbitrary. Thus a factor of uncertainty is introduced which in some cases can be irrelevant but here is of the utmost importance. The calculation of the X_i, Y_i pairs also leads to values of X_i which are very close to each other, which makes the angular coefficient of the regression line of Y on X

$$\beta_{YX} = \frac{r\,\sigma_Y}{\sigma_X}$$

very large.

In addition, even if the cluster of points fits the line very well, the gradient of this line, $-E/R$, has a very large absolute value (of the order of 20.000 for a typical value of E =170 kJ.mole^{-1}) while means that a small error in this value, as a result of the scatter of the points obtained, gives rise to a considerable error in the ordinate at the origin of the line (2). This indicates that the values of n obtained by this method have, in general, a dubious significance as the following example will show:

For a regression line

$$Y - \bar{Y} = r\,\frac{\sigma_Y}{\sigma_X}\,(X - \bar{X})$$

the standard deviation of the ordinate is given by

$$Y = \sigma_Y\,(1 - r^2)^{\frac{1}{2}}$$

where r is the coefficient of correlation.

For a typical group of values of the ordinate Y between -20 and 1:

$$Y = -20, -10, -6, -2, 0, 1$$

σ_Y is found to be 7.22 and, on assuming a good correlation r = 0.99, the probable error in n is given by

$$n = 7.22 \cdot (1 - 0.99^2)^{\frac{1}{2}} \cong \pm 1$$

Thus the value of n obtained is associated with a large error which can be of the order of 100% or more if, as is frequent, the dispersion of the cluster of points is larger that in the example taken.

The method proposed here permits this uncertainty in the value of n to be eliminated by a modification to the Freeman and Carroll treatment.

Assuming that the temperature varies linearly with time and that x is also linearly related to the fraction reacted gives:

$$\begin{aligned} x &= p\ (1 - \alpha) \\ T &= b + at \end{aligned} \qquad (3)$$

and so equation [1] becomes

$$\alpha' = \frac{d\alpha}{dT} = q \cdot k \cdot\ (1 - \alpha)^n$$

On introducing the value of k given by the Arrhenius equation

$$\alpha' = c \cdot e^{-E/RT}\ (1 - \alpha)^n$$

And differentiating with respect to T gives

$$\alpha'' = \frac{E}{RT^2}\ \alpha' - n\frac{(\alpha')^2}{(1-\alpha)}$$

Therefore, at the point where the decomposition rate is maximum, α' = max., $\alpha'' = 0$, and

$$\frac{E}{nR} = \left[\frac{\alpha' T^2}{(1-\alpha)}\right]_{\alpha'=\max.} = Q \qquad (4)$$

As the Freeman and Carroll line (2) will pass through the centre of gravity of the cluster of the points $(\bar{Y}, \bar{X})$:

$$\bar{Y} = -\frac{E}{R}\bar{X} + n \qquad (5)$$

Combining equations [4] and [5] gives

$$n = \frac{\bar{Y}}{1 - Q\bar{X}} \tag{6}$$

$$E = \frac{RQ\bar{Y}}{1 - Q\bar{X}} \tag{7}$$

with an error in n considerably smaller than that which results from the direct applicaton of the Freeman and Carroll method, as the treatment presented here allows the unanswerable question of which is the best fit straight line to be avoided.

Equations (6) and (7) have been applied to various cases [5,6], and the results obtained compared with those obtained from other isothermal and non isothermal methods. The agreement obtained for the values of n has been considerably better than when the order of the reaction is taken to be equal to the ordinate at the origin of the Freeman and Carroll line.

Note: It is important to realize that the value of α' which appears in equation (4) is $d\alpha/dT$. As by normal experimentation $d\alpha/dt$ is determinated, to calculate the coefficient Q it should be remembered that from equation (3)

$$\alpha' = \frac{d\alpha}{d\bar{T}} = \frac{1}{a}\,\frac{d\alpha}{dt}$$

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