Information From Differential Scanning Calorimetry

The goal is to find two parameters, which, when plotted one against the other, will result in a straight line. From the slope of such a line, some important parameters of the process could be calculated (for instance the overall effective activation energy E or the order of reaction n).

The fraction crystallized **a** in terms of nucleation rate J and crystal growth rate G is:

$$a = 1 - exp\left[-g\int_0^t J_o\left(\int_{t'}^t Gd\boldsymbol{t}\right)^m dt'\right] \tag{1}$$

For interface-controlled growth or diffusion controlled growth with G independent of time, $m=1,2$ *and 3* depending on the dimension of growth. For diffusion controlled growth where $G\sim t^{-1/2}$ $m=1/2, 1, 3/2. +1$

For anisotropic growth $\prod_i \int G_i d\boldsymbol{t}_i$

For constant J, G
$$a = 1 - exp\left(-gJ_o G^m t^n\right), \quad n=m+1$$

$$a = 1 - exp\left[-Kt^n\right] \tag{2}$$

$$K = K_o\, exp\left(-\frac{E}{RT}\right)$$

In general neither the activation energy E_N nor the activation energy for linear crystallization E_G are constant. As the process takes place in a narrow temperature region they are taken as effective values in this region.

$$E = E_n + mE_G$$

Interpretations of results:
$$T = T_o + qt$$

Ozawa method *to determine n*

$$a = 1 - \exp\left[-K\left(\frac{T - T_o}{q}\right)^n\right] \qquad (3)$$

Taking twice the logarithm
$$\left.\frac{d[\ln(-\ln(1-a))]}{d\ln q}\right|_T = -n \qquad \text{Here } a \text{ is obtained at the same}$$
temperature from a number of crystallization experiments taken at different heating rates.

All other methods involve as a first step differentiation of eq.(2) with respect to time

Piloyan-Borchardt

$$\boxed{\dot{a} = (1-a)nKt^m\left(1 + \frac{\dot{K}}{K}\right)} \qquad (4)$$

$$\dot{K} = \frac{dK}{dT}\frac{dT}{dt} = q\frac{d}{dT}\left[K_o\, exp\left(-\frac{E}{RT}\right)\right] = \frac{qEK_o}{RT^2}exp\left(-\frac{E}{RT}\right) \qquad (5)$$

$$\boxed{\dot{a} = (1-a)nKt^m(1+bt) \qquad ; \qquad b = \frac{qE}{RT^2}} \qquad (***)$$

If $T_o << T$ *than at* $\gg E/RT$

assumption !!?? *E/RT << 1 !!??*

$$\dot{a} \approx (1-a)nKt^m$$

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Dependence of $\dot{X}$ on $\boldsymbol{a}$ and t

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assumption: It is possible to define

$$\dot{\boldsymbol{a}} = k(x)h(T)$$

The time can be expressed in terms of $\boldsymbol{a}$ as:

$$t = \left[\frac{-ln(1-\boldsymbol{a})}{K}\right]^{1/n} \quad ; \quad t = \frac{T - T_o}{q}$$

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Coats-Redfern-Sestak method determines activation energy

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Assumes that $k(\boldsymbol{a})=(1-\boldsymbol{a})^n$

from $\dot{\boldsymbol{a}} = k(\boldsymbol{a})K_o e^{-\frac{E}{RT}}$

by rearranging the above expression and integrating

$$\int_0^{X'} \frac{d\boldsymbol{a}}{k(\boldsymbol{a})} = K_o \int_0^{t'} e^{-\frac{E}{RT}} dt \equiv U(\boldsymbol{a'}) \quad \text{The function } U(\boldsymbol{a'}) \text{ is independent on the heating}$$

rate used to obtain the crystallized fraction $\boldsymbol{a'}$

The time integral is transformed to temperature integral

$$U(\boldsymbol{a'}) = \frac{K_o}{q} \int_{T_o}^{T''} e^{-\frac{E}{RT}} dT = \frac{K_o E}{Rq} \int_{y_o}^{y''} \frac{e^{-y}}{y^2} dy \quad ; \quad y = \frac{E}{RT} \tag{*}$$

If we start at $T_o << T'$ (below T_g so that no crystallization takes place in this region we may assume $T_o \circledR 0$, i.e. $y_o = ¥$

Exponent integral function

$$\int \frac{e^{-y}}{y^2} dy = -\frac{e^{-y}}{y} + Ei(y)$$

$$E_i(y) = \frac{e^{-y}}{y}\left(1 - \frac{1!}{y} + \frac{2!}{y^2} ... + \frac{(-1)^n n!}{y^n}\right)$$

$$Ei(y) = -\boldsymbol{g} - ln\, y + \left(\frac{y}{1.1!} - \frac{y^2}{2.2!} + \frac{y^3}{3.3!} - ...\right) \quad , \gamma = 0.5772$$

for $y' >> 1$ the integral (*) becomes

$$\int_{\infty}^{y'} \frac{e^{-y}}{y^2}\, dy \approx -\frac{e^{-y'^2}}{y'^2}$$

If $\quad k(a) \approx (1-a)[-ln(1-a)]^{\frac{n-1}{n}}$

then $\quad U(a') = [-ln(1-a')]^{1/n} = \dfrac{K_o RT'^2}{Eq} e^{-\frac{E}{RT'}}$

Essential is that for a given a', $\ U(a')=const$

$$\frac{K_o RT'^2}{Eq} e^{-\frac{E}{RT}} = const$$

$$ln\frac{T'^2}{q} - \frac{E}{RT'} = Const \quad \textbf{This is known as Ozawa-Chen method}$$

Ozawa used a simpler approximation and find coordinates
ln q against 1/T'.

If a fixed *a'* is determined in a series of exotherms at different heating rates, the plot of *ln T'²/q vs 1/T'* should be a straight line with a slope *E/R*.

Derivation of Coats-Sestac-Redfern for E/RT >> 1

From Eq.(***) , since *qt/T~1*

$$\overset{\bullet}{a} = (1-a)nKt^m \frac{qE}{RT^2}$$

$$\int_0^{X'} \frac{da}{(1-a)ln(1-a)} = ln[-ln(1-a)] = \frac{E}{R}\int_0^{T'} \frac{dT}{T^2} = -\frac{E}{RT'}$$

Bennet has shown that at temperature of the peak T_p the degree of transformation $a_p \gg 0.63$ *DOES NOT DEPEND ON HEATING RATE OR THE ORDER OF THE REACTION*

$$a(t) = 1 - exp\left\{ -c_g \int\limits_0^t J(t') \left[\int\limits_0^{t-t'} G(t'')dt'' \right]^d dt' \right\}$$

This is the evolution of the crystallized fraction of the volume. It is controlled by two basic parameters – the crystallite nucleation and growth rates *J and G*

Growth	Shape	c_g
1D	Needle	$2A_o$
2D	Disk	πH_o
2D	Square prism	$4H_o$
3D	Sphere	$4\pi/3$
3D	cube	8

A_o – constant cross section area of needle; H_o constant thickness of the prism

H. Yinnon, D. Uhlmann, J. Non Cryst Sol. 54 (1983) 253