

DETERMINATION OF REACTION KINETIC PARAMETERS FROM VARIABLE TEMPERATURE DSC OR DTA

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An equation is derived for evaluating the kinetic parameters of a transformation from variable temperature DSC or DTA, taking account of the variation in the reaction rate constant with time and temperature. Kinetic parameters for the crystallization of a ZrF_4 – BaF_2 – LaF_3 glass are calculated using this equation.

Differential scanning calorimetry (DSC) and differential thermal analysis (DTA) are versatile thermoanalytical techniques for studying the kinetics of phase transformations and other processes. DTA is a dynamic technique in which time and temperature variables are intermixed; it cannot be used for isothermal experiments. DSC can be employed for both isothermal and non-isothermal studies.

Various mathematical analyses of non-isothermal solid state transformations from DSC and DTA measurements have been reported (see ref. [1] for a review). Most of these analyses used the Johnson–Mehl–Avrami (JMA) transformation equation [2, 3] and were derived under severely limiting and often incorrect assumptions, without taking proper account of the change in reaction rate constant with time and temperature.

Yinnon and Uhlmann [1] critically assessed these analyses and showed that most of them were based on incorrect equations, except for the approach of Augis and Bennet [4]. Even the procedure of Augis and Bennet is questionable, because they did not take proper account of the temperature dependence of the reaction rate constant.

In this paper an equation for evaluating the kinetic parameters of a transformation from non-isothermal DSC or DTA is derived with special attention to appropriate assumptions and conditions. This equation is used to calculate the kinetic parameters for the crystallization of a ZrF_4 – BaF_2 – LaF_3 glass and compared with the values of the parameters obtained from other analyses.

Mathematical treatment

Isothermal kinetics of phase transformations often fit the Johnson–Mehl–Avrami (JMA) equation [2, 3]:

$$-\ln(1-x) = (kt)^n \quad (1)$$

where x is the volume-fraction transformed after time t , n the dimensionless Avrami exponent, and k the reaction rate constant, whose temperature dependence can be expressed by the Arrhenius equation:

$$k = \nu \exp \left[-\frac{E}{RT} \right] \quad (2)$$

where ν is the frequency factor, E the activation energy of the overall process, R the gas constant, and T the isothermal temperature in degrees kelvin. In isothermal transformations ν and E are usually not functions of time or degree of transformation. Over narrow ranges of temperature ν and E can be constant, but over wider ranges of temperature transformations can depend on nucleation and growth rates that have complicated temperature dependencies. For example, both nucleation and growth rates often have maxima as a function of temperature, so they do not fit eq. (2) with constant ν and E . In this work ν and E are assumed to be independent of temperature, which should be valid for transformations with a constant number of nuclei and a growth rate with ν and E constant, or for narrow ranges of temperature.

In DSC or DTA experiments, the temperature is changed at a constant rate α ($= dT/dt$), so that

$$T = T_i + \alpha t \quad (3)$$

where T_i is the initial temperature and T is the temperature after a time t . The reaction factor k is no longer a constant but changes with time:

$$k(t) = \nu \exp \left[-\frac{E}{R(T_i + \alpha t)} \right] \quad (4)$$

The volume of particles is given by $\int_0^t k(t) dt$, so the JMA relation becomes:

$$-\ln(1-x) = \left[\int_0^t k(t) dt \right]^n \quad (5)$$

or

$$x = 1 - \exp[-u^n] \quad (6)$$

where

$$u = \int_0^t k(t) dt \quad (7)$$

when the temperature is constant, eq. (5) reduces to equation (1).

At each temperature T in a DSC experiment, the deflection from the baseline is assumed to be proportional to the instantaneous reaction rate. This assumption requires that the sample temperature is uniform, so that the interface temperature is negligibly affected by the liberation of the latent heat of transformation at the growth interface. The studies of Uhlmann et al. [6, 7] on the glass forming systems $\text{Na}_2\text{O} \cdot 2\text{SiO}_2$ [6] and GeO_2 [7], of Briggs and Carruthers [8] on CaO-MgO-SiO_2

glasses, and of Chen [9] on metallic glasses support this assumption. However, if the rate of crystal growth is high the temperature may not be uniform, as shown by Laird and Bergeron [10] for the $\text{PbO} \cdot 2 \text{B}_2\text{O}_3$ glass and by Morley [11] for $\text{Li}_2\text{O}-\text{SiO}_2$ glasses.

If the rate of transformation is a maximum at the DSC or DTA peak, the position of the peak is given by:

$$\ddot{x} = [\dot{u}u - \dot{u}^2(nu^n - n + 1)]nu^{(n-2)}(1-x) = 0 \quad (8)$$

where $\dot{x} = dx/dt$, $\dot{u} = du/dt$, and $\ddot{u} = d^2u/dt^2$.

From eq. (7)

$$\dot{u} = k(t) \quad (9)$$

and

$$\ddot{u} = qk \quad (10)$$

where

$$q = \frac{E\alpha}{RT^2} \quad (11)$$

Equation (7) can be evaluated by introducing a new variable:

$$y = \frac{E}{R(T_i + \alpha t)} \quad (12)$$

so that

$$dy = -q dt \quad (13)$$

Substituting eqs (4), (12) and (13) into eq. (7), one gets

$$u = \int_{y_{t=0}}^{y_{t=t}} \nu \exp(-y) \left(-\frac{1}{q}\right) dy = \frac{\nu}{q} \{ \exp(-y)_{t=t} - \exp(-y)_{t=0} \}$$

when $T_i \ll T$, $\exp(-y)_{t=0} \ll \exp(-y)_{t=t}$, then

$$u \approx \frac{\nu}{q} \exp(-y)_{t=t}$$

or

$$u \approx \frac{k}{q} \quad (14)$$

Then from eqs (10) and (14)

$$\ddot{u} = q^2 u \quad (15)$$

The preceding relations can be used to calculate T_p , the temperature at the maximum of the DSC or DTA peak.

From eq. (8)

$$\frac{\ddot{u}}{\dot{u}^2} = nu^n - n + 1 \quad (16)$$

and from eqs (9), (10) and (14):

$$\frac{\ddot{u}}{\dot{u}^2} = \frac{(qk) \left(\frac{k}{q}\right)}{k^2} = 1 \quad (17)$$

Hence from eqs (16), (17) and (14), the condition for the peak maximum becomes

$$k = q \quad (18)$$

Substituting values of k and q from eqs (4) and (11), one gets

$$\nu \exp\left(-\frac{E}{RT_p}\right) = \frac{E\alpha}{RT_p^2} \quad (19)$$

or in logarithmic form:

$$\ln\left(\frac{T_p^2}{\alpha}\right) = \ln\left(\frac{E}{R}\right) - \ln \nu + \frac{E}{RT_p} \quad (20)$$

which is the equation showing the change in T_p with α . A plot of $\ln [T_p^2/\alpha]$ vs. $1/T_p$ obtained at various heating rates should be linear with slope E/R and intercept $[\ln(E/R) - \ln \nu]$. If E/R is calculated from the slope, the frequency factor ν can be calculated from the intercept.

Table 1 Comparison of kinetic parameters for crystallization of ZrF_4 - BaF_2 - LaF_3 glass calculated from DSC studies using different mathematical analyses

Method	Reaction parameters		Reference
	ν, s^{-1}	$E, kJ mol^{-1}$	
Isothermal DSC:			
$\ln k$ vs. $1/T$ plot	7×10^{21}	302	Bansal et al. [13]
Non-isothermal DSC:			
$\ln \alpha$ vs. $1/T_p$ plot [15]	—	325	[13]
$\ln [\alpha/(T_p - T_i)]$ vs. $1/T_p$ plot [16]	2×10^{21}	315	[13]
$\ln [T_p^2/\alpha]$ vs. $1/T_p$ plot	6×10^{22}	314	Present work

Equation (20) is the same as those derived by Kissinger [12] and Chen [9], using entirely different approaches. Equation (20) is being used to evaluate the kinetic parameters for the crystallization of various heavy metal fluoride glasses [13, 14]. Values of the reaction parameters for the crystallization of a ZrF_4 - BaF_2 - LaF_3 (62-33-5 mol%) glass calculated by least-squares fitting of the non-isothermal DSC

experimental data to eq. (20) are presented in Table 1 and compared with those obtained from other methods. The agreement between the present method and the isothermal DSC is quite good.

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References

- 1 H. Yinnon and D. R. Uhlmann, *J. Non-Cryst. Solids*, 54 (1983) 253.
- 2 W. A. Johnson and R. F. Mehl, *Trans. Am. Inst. Min. Metall. Engrs.*, 135 (1939) 416.
- 3 M. Avrami, *J. Chem. Phys.*, 7 (1939) 1103; 8 (1940) 212; 9 (1941) 177.
- 4 J. A. Augis and J. D. Bennett, *J. Thermal Anal.*, 13 (1978) 283.
- 5 H. J. Borchartd and F. Daniels, *J. Am. Chem. Soc.*, 79 (1957) 41.
- 6 G. S. Meiling and D. R. Uhlmann, *Phys. Chem. Glasses*, 8 (1967) 62.
- 7 P. J. Vergano and D. R. Uhlmann, *Phys. Chem. Glasses*, 11 (1970) 30.
- 8 J. Briggs and T. G. Carruthers, *Phys. Chem. Glasses*, 17 (1976) 30.
- 9 H. S. Chen, *J. Non-Cryst. Solids*, 27 (1978) 257.
- 10 J. A. Laird and C. G. Bergeron, *J. Am. Ceram. Soc.*, 51 (1968) 60.
- 11 J. G. Morley, *Glass Technol.*, 6 (1965) 77.
- 12 H. E. Kissinger, *J. Res. Nat. Bur. Stds.*, 57 (1956) 217; *Anal. Chem.* 29 (1957) 1702.
- 13 N. P. Bansal, A. J. Bruce, R. H. Doremus and C. T. Moynihan, Paper presented at the Second International Symposium on Halide Glasses, August 2–5, 1983, Troy, New York, USA.
- 14 N. P. Bansal, A. J. Bruce, R. H. Doremus and C. T. Moynihan, unpublished work.
- 15 T. Ozawa, *J. Thermal Anal.*, 2 (1970) 301.
- 16 J. A. Augis and J. D. Bennett, *J. Thermal Anal.*, 13 (1978) 283.

Zusammenfassung — Es wird eine Gleichung zur Bestimmung der kinetischen Parameter einer Umwandlung aus DSC- und DTA-Messungen bei variabler Temperatur abgeleitet, die den Veränderungen der Reaktionsgeschwindigkeit mit der Zeit und der Temperatur Rechnung trägt. Kinetische Parameter der Kristallisation von ZrF_4 - BaF_2 - LaF_3 -Glas werden unter Benutzung dieser Gleichung berechnet.

Резюме — Исходя из переменной температуры ДСК или ДТА, выведено уравнение для оценочных кинетических параметров преобразования, учитывая изменение константы скорости реакции с температурой и временем. Используя это уравнение, были вычислены кинетические параметры кристаллизации стекол состава ZrF_4 - BaF_2 - LaF_3 .