REPLY TO COMMENTS ON "DETERMINATION OF REACTION KINETIC PARAMETERS FROM VARIABLE TEMPERATURE DSC OR DTA"

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We do not agree with Dey and Chakrabarty that Eq. (20) in our paper [1] is invalid. A recent paper by Bansal et al. [2] deals with the point raised by them.

The original Johnson–Mehl–Avrami (JMA) equation was derived for an isothermal transformation. For the non-isothermal case, the JMA equation can be written as:

$$-\ln (1-x) = [\int_0^t k(t)\, dt]^n \tag{1}$$

where x is the volume fraction transformed after time t, n is the Avrami exponent which is related to the morphology of crystal growth, and $k(t)$ is the reaction rate constant whose temperature dependence, at least within a narrow temperature range, can be expressed by the Arrhenius equation:

$$k = v \exp (-E/RT) \tag{2}$$

where v is the attempt frequency, E the effective overall activation energy, R the gas constant and T the temperature in Kelvin.

To solve equation (1), one has to evaluate [1, 2] the integral:

$$- \int_{E/RT_i}^{y_t} e^{-y}(RT^2/E\alpha)\, dy \tag{3}$$

where $y = E/RT$. When the activation energy is high the T^2 term contributes a negligible change, compared to the exponential term, to the function under the integral sign [2]. For example, in our studies [1–4] on the crystallization kinetics of the infrared-transmitting fluoride glasses, a temperature change from 620 K to 670 K changes T^2 by 17% and e^{-y} by a factor of 100. Thus it is reasonable to take the T^2 term outside the integral sign, and also the term from the lower limit is negligible. The result is the equation:

$$\ln (T_p^{2/\alpha}) = \ln (E/R) - \ln v + (E/RT_p) \tag{4}$$

Over a limited temperature interval, Eq. (4) applies, as shown in our studies [1–4] on the crystallization of the fluorozirconate glasses. The values of the kinetic parameters evaluated from Eq. (4) using non-isothermal differential scanning calorimetry (DSC) for various ZrF_4 glasses were in good agreement with the values obtained from independent isothermal DSC studies.

Neither Equation (4) nor Eq. (2), which gives the temperature dependence of the crystallization rate parameter k, are valid over large temperature intervals. The glass crystallization rate becomes a maximum at a certain temperature, because of the opposing effects of viscosity and the thermodynamic driving force (undercooling) for crystallization; at higher temperatures close to the melting point of the crystals, the undercooling and hence the rate of crystallization become small.

Since Eq. (2) does not give the temperature dependence of k under these conditions, the treatment of Dey and Chakraborty is not valid at these temperatures. Their integrals may allow one to!extend slightly the temperature range of data that can be examined, but they did not explore this possibility.

We emphasize that our treatment and Eq. (2) are valid over particular temperature ranges of experimental data; if Eq. (2) is not applicable, a more general integration of Eq. (1), not given by Dey and Chakraborty, is required.

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References

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