

# Crystallization in glass-forming aqueous solutions during warming: numerical construction of non-isothermal DSC thermocurves during warming from isothermal data. Application to 42.5% w/w 1,2-propanediol/water

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## Abstract

The Johnson–Avrami–Mehl model for isothermal crystallization in glasses has been applied for non-isothermal conditions. The general equation for the crystallization is deduced from this model and applied to the glass-forming 42.5% w/w 1,2-propanediol/water solution. The general equation is a generalized integral equation which underlines the difficulties associated with information deduced directly from non-isothermal experiments. The presented constructions of the thermocurves show good agreement with the experimental results for the devitrification temperatures and for the amount of crystallization versus the warming rate.

## INTRODUCTION

The determination of the amount of crystallization for glass-forming aqueous solutions is of importance for cryobiological purposes [1] and also for more general purposes concerning non-crystalline materials [2–7]. Different approaches for the determination of kinetics parameters from non-isothermal experiments have already been discussed in numerous papers [2–7]. However, the problem associated with applying the Johnson–Avrami–Mehl isothermal model to non-isothermal conditions has never been clearly addressed. In the present paper, the general equations for the crystallization during warming in glasses above the glass transition are deduced for the Johnson–Mehl–Avrami (JMA) model and are tested in a particular solution to confirm the suitability of the JMA model for kinetics purposes.

## MATERIALS

The experiments were made on a Perkin-Elmer DSC-4, with samples of 1,2-propanediol (99+ % from Aldrich) diluted in de-ionized water to a final

concentration of 42.5% w/w. The sample was filtered through a 0.22  $\mu\text{m}$  filter prior to the experiments.

Isothermal experiments and the determination of the kinetics parameters have been previously reported [8]. The non-isothermal experiments were carried out by cooling the samples at 40°C min<sup>-1</sup> to -140°C, which is below the glass transition, and warmed back beyond the melting temperature at 2, 5, 10, 20, 40 and 80°C min<sup>-1</sup>. The calibration of the DSC-4 is done using different melting temperatures of pure compounds during warming versus temperature and versus warming rate [9].

## THEORY

The main logical assumption for the elaboration of the general equation is to assume that the JMA model can be applied at different temperatures above the glass transition  $T_g$  until the end of melting temperature  $T_m$ . In a general term, the JMA model gives a general relationship between the crystallization fraction  $X$  with the time of exposure  $t$  at the considered temperature  $T$  with [10]

$$X = 1 - \exp[-(Kt)^n] \quad (1)$$

$$K = K_0 \exp[-E_K/R\Theta] \quad (2)$$

with  $\Theta = T$  for Arrhenius behavior or  $\Theta = T - T_0$  for a Vogel–Fulcher–Tamman behavior, depending on the fragility of the glassy state [11], and  $n$  being the Avrami exponent which depends on the crystal geometry and the crystallization process involved [10].

The more problematic aspect is to pass from isothermal to non-isothermal conditions. Equation (1) gives a monotonic mapping from the time compact set,  $t \in [0, \infty]$ , to be the compact set,  $X \in [0, 1]$ . The inverse function can therefore be used for the determination of an equivalent unique time  $t^*$  corresponding to the crystallization fraction seen by the sample at the considered temperature  $T$ . If the sample is taken at a temperature  $T \in [T_g, T_m]$  as the sample is warmed at a warming rate  $V$ , during the increase of temperature  $dT$ , corresponding to a very small time  $dt$ , the crystallization fraction will increase by

$$dX(t^*) = nK^n t^{*(n-1)} [1 - X(t^*)] dt \quad (3)$$

which is the standard differential presentation of the JAM kinetics model. Note that the times  $t^*$  and  $t$  are different because they are defined by different mechanisms:  $t^*$  is defined as a fictive time seen by the sample as the sample sees the fraction crystallized  $X(t^*)$  at the temperature  $T$  with  $X(t^*)$ , and  $t$  is the time of the scanning thermocurve. Another equation is

needed to complete eqn. (3)

$$X(t^*) = \left[ Q_i + \int_{T_g}^T dQ \right] / Q_{\max}^*(T) \quad (4)$$

where  $Q_i$  is the amount of crystallization heat during the initial cooling, the integral represents the amount of crystallization heat during warming up to the temperature  $T$ , and  $Q_{\max}^*(T)$  is the maximum amount of crystallization heat at the corresponding temperature  $T$  for the solution having a solute concentration corresponding to a melting temperature  $T_m$ . Assuming that the JMA model is still applicable to the scaled time  $t^*$ , this can be replaced in eqn. (3) by substituting  $(Kt^*)^{(n-1)}$  from eqn. (1)

$$dX(t^*) = nK \exp[(1 - 1/n) \ln\{-\ln[1 - X(t^*)]\}] [1 - X(t^*)] dt \quad (5)$$

Multiplying each side by  $Q_{\max}^*(T)$  makes the left side  $dQ(T)$ , i.e. the heat produced during the time  $dt$  at the temperature  $T$

$$dQ(T) = nK \exp[(1 - 1/n) \ln\{-\ln[1 - X(t^*)]\}] [1 - X(t^*)] Q_{\max}^*(T) dt \quad (6)$$

with eqn. (4) as a complementary equation. By taking the differential equation of eqn. (4)

$$dX = (dQ(T))/Q_{\max}^*(T) - X(dQ_{\max}^*(T))/Q_{\max}^*(T) \quad (7)$$

Extracting  $dQ(T)$  leads to the general differential equation

$$dXQ_{\max}^* + X dQ_{\max}^* = nK \exp[(1 - 1/n) \ln\{-\ln[1 - X]\}] (1 - X) Q_{\max}^* dt \quad (8)$$

The system of eqns. (8) and (4) gives the general integral equation system of the crystallization during non-isothermal conditions. For a constant heating rate,  $dt$  is substituted by  $dT/V$  in eqn. (8) or eqn. (6). A more general non-isothermal equation can be applied by substituting  $dt$  by a more general relation between  $dt$  and  $dT$ . This equation can be difficult to resolve as different factors can be dependent on different physical factors, such as the Avrami exponent  $n$  which can depend on the solute concentration and on the temperature domain, as noticed for ice formation in some aqueous solutions [12]. Another unknown problem is to be able to access the function  $Q_{\max}^*(T)$  in a functional form.

## APPLICATION AND RESULTS

The chosen solution was a solution of 42.5% w/w 1,2-propanediol in water because of its conveniently repeatable behavior, and as a complement to previous work on the determination of JMA kinetics parameters in isothermal conditions [8]. To resolve the general system of eqns. (4) and

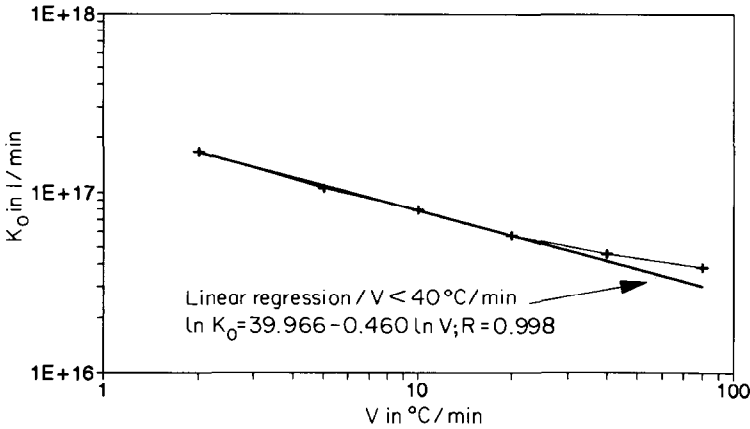


Fig. 1. Variation in the pre-exponential factor  $K_0$  of the Avrami constant  $K(T)$  with the warming rate  $V$  for isothermal crystallization in the glass-forming aqueous solution of 42.5% w/w 1,2-propanediol in water. Both  $K_0$  and  $V$  are reported in logarithmic scale. the warming rate  $V$  is the rate at which the sample is warmed to the isothermal temperature. The linear regression from the four lower warming rates is also reported.

(6), further assumptions have been made. As for the isothermal study, the variation of  $K(T)$  is assumed to follow an Arrhenius model [8], and it is assumed that the Avrami exponent  $n$  is not temperature dependent. Therefore, the JMA kinetics parameters are taken directly from a previous study [8]. In this work, it was also shown that the value  $K_0$  for  $K(T)$  is dependent on the nucleus density and therefore depends on the warming rate  $V$ , as reported in Fig. 1 where the slope is the inverse of the Avrami

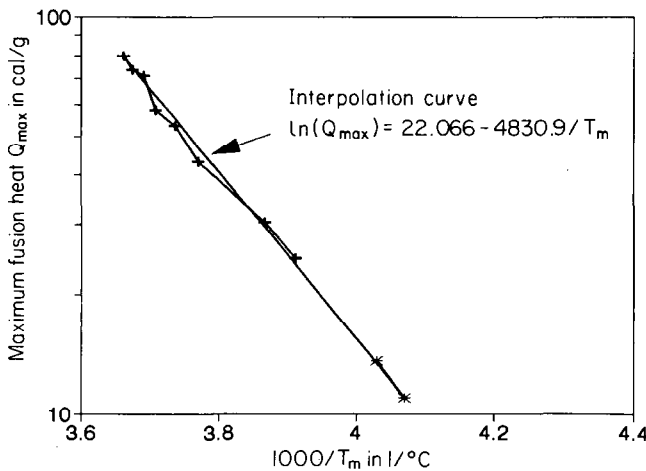


Fig. 2. Maximum heat of fusion  $Q_{max}$  plotted in a logarithmic scale as a function of  $1000/T_m$  for the binary system water-1,2-propanediol.  $T_m$  is the end of melting temperature in the phase diagram of this binary system: +, values taken from refs. 13 and 14; \*, this work.

exponent  $n = 2.17$  previously determined experimentally [8]. As suggested in ref. 8, the values for  $V > 40^\circ\text{C min}^{-1}$  are higher due to the nuclei formed and stabilized during the initial cooling which can no longer be neglected. Above this warming rate,  $K_0$  will vary less, becoming constant at high warming rates. The variations of  $K_0$  can be reported in eqn. (6) for  $K(T)$ .

A more difficult step is to define the function  $Q_{\max}(T_m)$  as the maximum amount of crystallization heat for the solute concentration corresponding to a melting temperature  $T_m$ . An experimental variation of the maximum heat of crystallization versus  $1000/T_m$  is reported in Fig. 2, with an approximated interpolation curve being

$$Q_{\max}(T_m) = Q_0 \exp[-A/T_m] \quad (9)$$

with experimental values taken from refs. 13 and 14, and completed by values from the present work for higher solute concentrations.

The step to access the maximum crystallization  $Q_{\max}^*(T)$  at a temperature

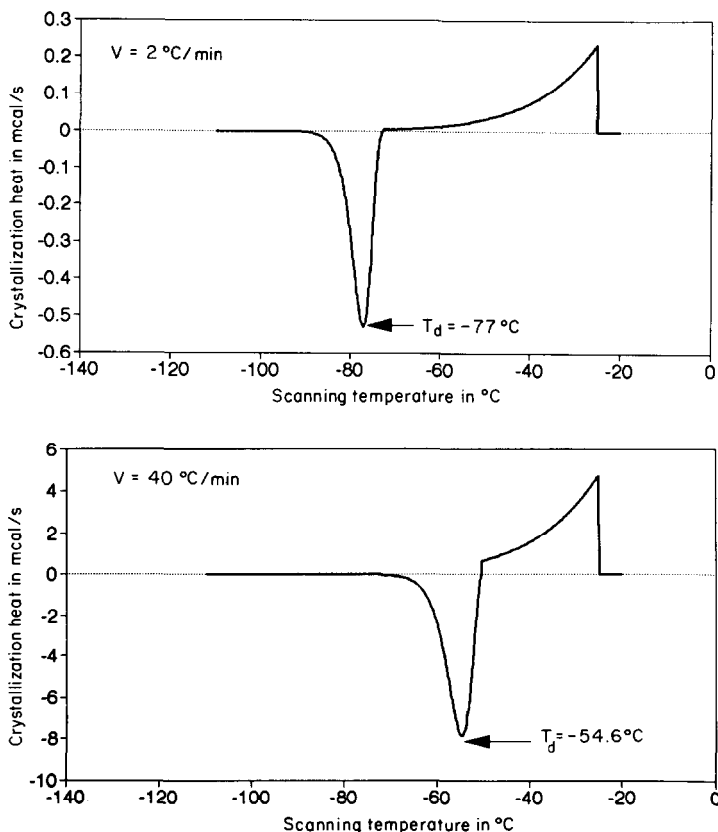


Fig. 3. Calculated thermocurves during warming for the glass-forming aqueous solution of 42.5% w/w 1,2-propanediol in water. The upper curve corresponds to a warming rate of  $2^\circ\text{C min}^{-1}$  and the lower curve to a warming rate of  $40^\circ\text{C min}^{-1}$ .  $T_d$  is the devitrification temperature.

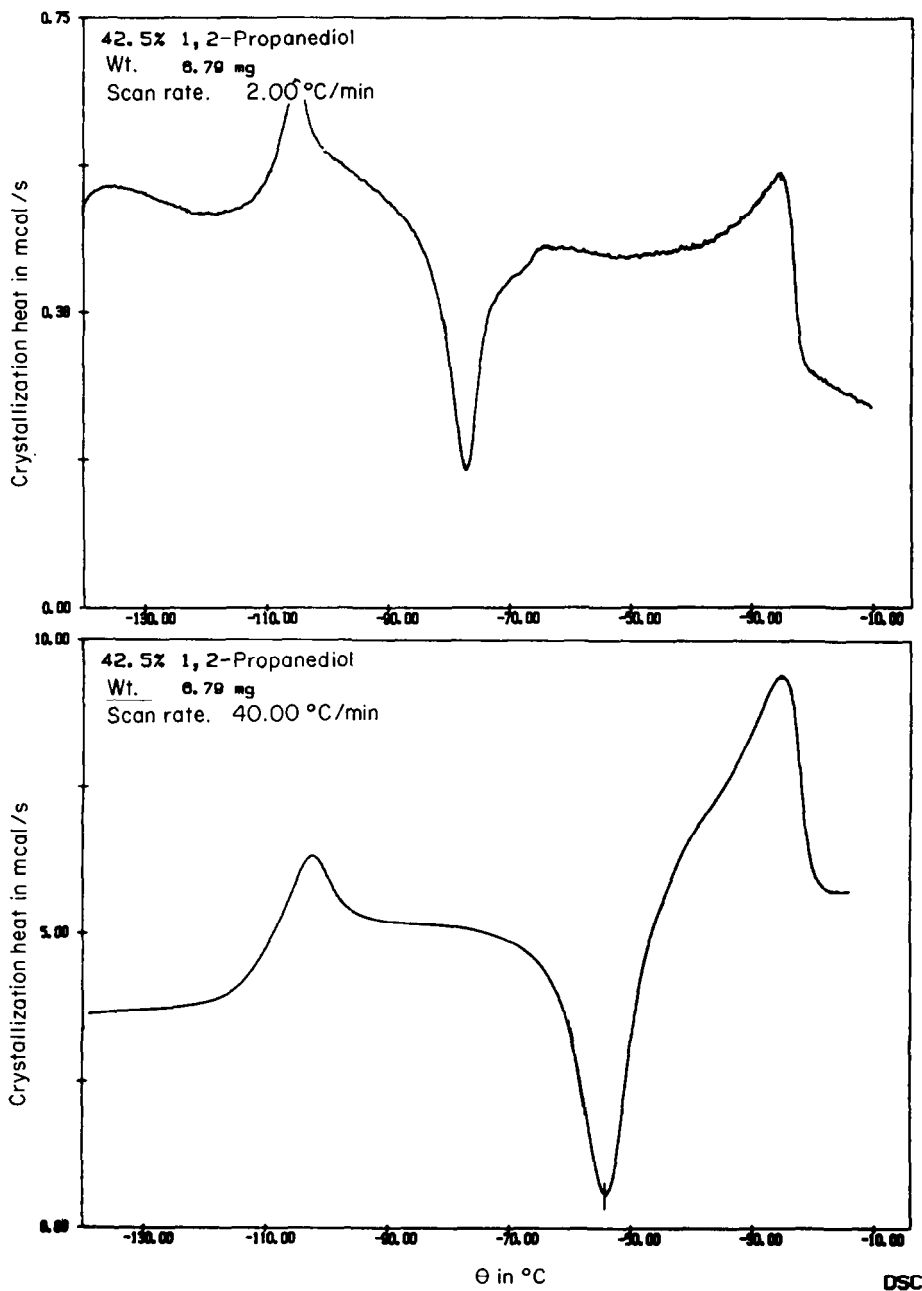


Fig. 4. Experimental thermocurves during warming recorded on the DSC-4 for a sample of 42.5% w/w 1,2-propanediol in water. The same weight is used for the determination of the thermocurves in Fig. 3. The upper thermocurve corresponds to a warming rate of  $2^{\circ}\text{C min}^{-1}$  and the lower to a warming rate of  $40^{\circ}\text{C min}^{-1}$ . The temperature scale was corrected prior to drawing. The errors on the experimental temperatures are  $\pm 0.2^{\circ}\text{C}$ , and on the experimental energies, less than 2% from the DSC-4 calibration.

$T$  of a solution having a melting temperature  $T_m$ , is then simple: it is the difference between the amount of corresponding to the initial solute concentration (or  $T_m$ ) and the amount corresponding to a solute concentration having a melting temperature  $T$ . Therefore

$$Q_{\max}^*(T) = Q_{\max}(T_m) - Q_{\max}(T) \quad (10)$$

$$Q_{\max}^*(T) = Q_0[\exp(-A/T_m) - \exp(-A/T)] \quad (11)$$

Equation (9) can then be reported in eqn. (6). To recover the units of the thermocurves, the quantity measured in the DSC-4 is the energy delivered to the sample to warm it per second; therefore it is  $[dQ/dT]MV/60$ , with  $M$  being the mass of the sample,  $V$  the warming rate in  $^{\circ}\text{C min}^{-1}$  converted to  $^{\circ}\text{C s}^{-1}$  by the factor 60, and  $dQ$  the energy calculated numerically step by step with a  $dT$  given to determine  $dQ/dT$ . The choice of  $Q_i$  has been taken as a rough approximation of the amount of crystallization due to the presence of stable nuclei in the glass after the initial cooling, as previously observed [8] with a value of  $10^{-6} \text{ cal g}^{-1}$ . The other parameters are taken from Figs. 1 and 2.

Figure 3 shows two examples of the thermocurves for warming rates of 2 and  $40^{\circ}\text{C min}^{-1}$ , with the devitrification temperatures  $T_d$  reported on the side of the crystallization peaks. For comparison, the corresponding experimental thermocurves recorded in the DSC-4 are shown in Fig. 4. There is good accord between the calculated and experimental thermocurves. For a better comparison, the devitrification temperatures and the maximum crystallization heats are reported in Fig. 5 for the calculated and

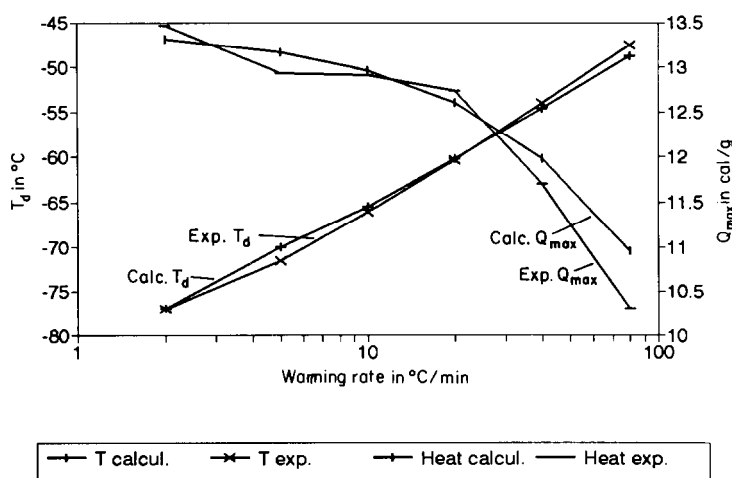


Fig. 5. Comparison of the experimental and calculated results for 42.5% w/w 1,2-propanediol in water for the devitrification temperature  $T_d$  corresponding to the maximum crystallization rate, and for the maximum crystallization heat-max achieved during warming, both plotted as functions of the warming rates. The errors of measurement are similar to those in Fig. 4.

experimental thermograms. These close results began to diverge for warming rates above  $40^{\circ}\text{C min}^{-1}$ , especially for the maximum crystallization heat.

## DISCUSSION

The present general integral equation for crystallization in glasses during warming can be applied with the same parameters determined with the JMA kinetics model for isothermal conditions. The present application of this equation to 42.5% w/w 1,2-propanediol in water, glassified during a cooling of  $40^{\circ}\text{C min}^{-1}$ , supports the use of the generalized equation for glass-forming aqueous solutions. It can also be used for other glass-forming systems.

For the present application, the experimental and calculated results are very close, as seen in Fig. 5. The sensitivity of the crystallization to the density of stable nuclei in the solution underlines the effect of the thermal history of the samples for the determination of the JMA model parameters. The approximation of  $Q_{\max}(T_m)$  by the experimental data is needed, but a variation in the parameters has little effect on the calculated results of  $T_d$ . Only a small variation in the maximum amount of crystallization heat versus warming rate can be observed. However, the values of  $n$ ,  $K$  and  $E_K$  are more critical and result in a translation of the whole set of devitrification temperatures  $T_d$  versus the warming rates for independent variations of the parameters. However, in a similar set of experiments, these three parameters are linked to an internal compensation of each other, being non-independent parameters. Therefore adjustments from previous data to improve the fit of the data have not been attempted. Continuous variations of the three parameters as a matrix can lead to a better fit for the present experimental thermocurves.

## CONCLUSION

It has been possible to deduce a general integral equation from the isothermal Johnson–Avrami–Mehl model for crystallization in glasses during warming. This equation has been applied to a glass-forming aqueous solution of 42.5% w/w 1,2-propanediol in water, with good agreement between the experimental observations and calculated results. These observations support the fact that the JMA model still applied to non-isothermal conditions through the generalized integral equation eqn. (6) with eqn. (4). As noticed in eqn. (8), the effect of the function  $Q_{\max}^*$  is important as the driven force for the crystallization. Most of the non-isothermal theories for crystallization neglect this, remaining more mathematically oriented. The only theory that so far considers this driven



force is that presented by Boutron, who introduced a term  $T_m - T$  in his differential equation [15]. This theory also gives good results but remains strongly experimental.

The generalized equation presented can also be used for generalized non-isothermal conditions represented by the function  $T = f(t)$ , where  $f$  is a general function which also reflects on the fact that the function  $K_0$  is also dependent on the time  $t$  to which it is related through the warming rate  $V$  in the present experiments.

The most important conclusion of this work is to confirm the possibility of applying the generalized system of eqns. (6) and (4), with the JMA parameters being obtained from only one experiment. Then, knowing these different parameters, calculations can be effectuated for the determination of the thermal behavior of the glass during warming, for example the minimum warming rate needed to limit the crystallization to a known fraction, as for TTT-curve determinations.

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