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ENTHALPY RELAXATION IN GLASSES
Regression analysis of integral DSC data

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Abstract

A new method of calculation of parameters of enthalpy relaxation models is proposed. Regression analysis treatment compares the experimental and calculated values of relaxation enthalpy. The experimental values of relaxation enthalpy are obtained by numerical integration of the difference between the two DSC curves. Contrary to the overall shape of the DSC curve the integral values are not affected by particular heat flow conditions during the DSC experiment. The Narayanaswamy's numerical model based on the Kohlrausch–William–Watts relaxation function was used to calculate the theoretical values of relaxation enthalpy. The application of the proposed method on the DSC experimental data of enthalpy relaxation of As_2Se_3 is shown.

Keywords: DSC, glass, regression analysis, relaxation

Introduction

Two types of methods of DSC enthalpy relaxation data analysis are usually used [1]. The methods of the first type are based on the investigation of the dependence of significant points of the DSC curve (maxima or inflex points, for example) on the experimental conditions (heating/cooling rate, thermal history of the sample). In this case the information contained in a large number of DSC experimental data points is lost [1]. On the contrary, the methods of the second group are based on the curve fitting of the whole DSC curve (e.g. our previous work [3]). In this case, all experimental DSC points are used in the regression analysis. However, the experimental data are partially influenced by the inner thermal heat exchange conditions in the DSC experimental arrangement. The enthalpy relaxation models do not explicitly handle these effects and, consequently, the obtained estimates of the parameters of particular relaxation model may be biased.

The method proposed in the present work tends to overcome both disadvantages mentioned above.

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Theory

According to the Tool’s concept of fictive temperature [4, 5], the specific enthalpy of a glassy sample can be expressed as a function of the enthalpy fictive temperature $T_{\mathrm{f,H}}$, and the thermodynamic temperature T:

$$H(T,T_{\mathrm{f,H}})=H(T_{\mathrm{r}},T_{\mathrm{r}})+\int_{\mathrm{T_f}}^{\mathrm{T_{f,H}}}C_{\mathrm{pm}}(T')\mathrm{d}T'+\int_{\mathrm{T_{f,}H}}^{\mathrm{T}}C_{\mathrm{pg}}(T')\mathrm{d}T' \tag{1}$$

where C_{pm}, C_{pg} are specific isobaric heat capacities of metastable melt and glass, respectively, and T_{r} is an arbitrary sufficiently high reference temperature at which the sample is in a metastable thermodynamic equilibrium. According to Scherer and Narayanaswamy [4, 6], the fictive temperature can be calculated for an arbitrary temperature–time schedule $T(t)$:

$$T_{\mathrm{f,H}}(t)=T(t)-\int_0^{\mathrm{t}}\mathrm{d}t'\left(\frac{\mathrm{d}T}{\mathrm{d}t}\right)_{\mathrm{t'}}M_{\mathrm{H}}[\xi(t)-\xi(t')] \tag{2}$$

where M_{H} is a Kohlrausch–William–Watts (KWW) relaxation function [4, 7]:

$$M_{\mathrm{H}}(\xi)=\exp(-\xi^{\mathrm{b}}) \tag{3}$$

where b is the non-exponentiality parameters ($0<b\leq 1$) and ξ is the dimensionless relaxation time:

$$\xi(t)=\int_0^{\mathrm{t}}\frac{\mathrm{d}t'}{\tau_{\mathrm{H}}(t')} \tag{4}$$

According to Scherer and Moynihan [4, 8], the enthalpy relaxation time is expressed as a function of thermodynamic and fictive temperature:

$$\tau_{\mathrm{H}}=\tau_0\exp\left[\frac{x\Delta h^*}{RT}+\frac{(1-x)\Delta h^*}{RT_{\mathrm{f,H}}}\right] \tag{5}$$

where x is the non-linearity parameter ($0\leq x\leq 1$), Δh^* is the apparent activation energy, τ_0 is the relaxation time at infinite temperature, and R is the universal gas constant. In the case of metastable equilibrium $T=T_{\mathrm{f,H}}$ holds. The apparent activation enthalpy, Δh^*, equals to the activation enthalpy of metastable equilibrium viscous flow, when the same temperature exponential course of flow and enthalpy relaxation time is assumed.

The term relaxation enthalpy is used for the enthalpy change during an isothermal temperature regime [2, 9, 10]. When the isotherm at temperature T_{iso} starts at time t_1, then for any time $t_2\geq t_1$ the relaxation time is defined as $t_{\mathrm{rel}}=t_2-t_1$. Supposing the linear temperature dependence of specific isobaric heat capacities in the form:

$$C_{\mathrm{pm}}(T)=C_{\mathrm{pm,0}}+C_{\mathrm{pm,1}}T \quad \text{and} \quad C_{\mathrm{pg}}(T)=C_{\mathrm{pg,0}}+C_{\mathrm{pg,1}}T \tag{6}$$

the relaxation enthalpy can be expressed as follows:

$$H_{\mathrm{rel}}(T_{\mathrm{iso}},t_{\mathrm{rel}})=H(T_{\mathrm{iso}},T_{\mathrm{f,H}}(t_2))-H(T_{\mathrm{iso}},T_{\mathrm{f,H}}(t_1))= \\ =[T_{\mathrm{f,H}}(t_2)-T_{\mathrm{f,H}}(t_1)]\left\{\Delta C_{\mathrm{p0}}+\frac{1}{2}\Delta C_{\mathrm{p1}}[T_{\mathrm{f,H}}(t_2)+T_{\mathrm{f,H}}(t_1)]\right\} \tag{7}$$

where

$$\Delta C_{\mathrm{pk}}=C_{\mathrm{pm,k}}-C_{\mathrm{pg,k}} \quad k=1,2 \tag{8}$$

Simplified schemes of glass formation and enthalpy relaxation are presented in Figs 1 and 2.

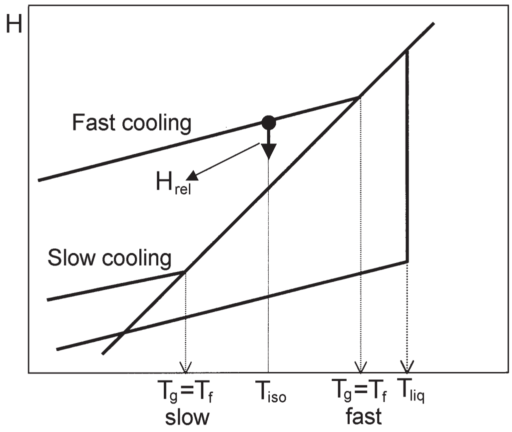

Fig. 1 An outline of glass formation for slow and fast cooling of a glass-forming melt: H_{rel} – relaxation enthalpy, T_g – glass transition temperature, T_f – Tool's fictive temperature, T_{iso} – temperature of relaxation isotherm

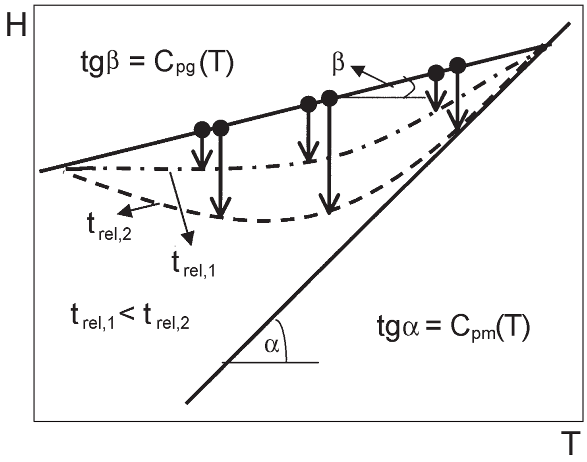

Fig. 2 An outline of the enthalpy relaxation

In the infinite relaxation time limit, the relaxation enthalpy approaches the value

$$\begin{aligned} &H_{\mathrm{rel}}(T_{\mathrm{iso}},\infty)=H(T_{\mathrm{iso}},T_{\mathrm{f,H}}(\infty))=T_{\mathrm{iso}}-H(T_{\mathrm{iso}},T_{\mathrm{f,H}}(t_1))= \\ &=[T_{\mathrm{iso}}-T_{\mathrm{f,H}}(t_1)]\left\{\Delta C_{\mathrm{p0}}+\frac{1}{2}\Delta C_{\mathrm{p1}}[T_{\mathrm{iso}}+T_{\mathrm{f,H}}(t_1)]\right\}\end{aligned} \tag{9}$$

and the stage of relaxation process can be quantified with a relative relaxation value:

$$P_{\mathrm{rel}}=100\frac{H_{\mathrm{rel}}(T_{\mathrm{iso}},t_{\mathrm{rel}})}{H_{\mathrm{rel}}(T,\infty)}\% \tag{10}$$

Only in the case of temperature independent isobaric heat capacities, i.e. only when $\Delta C_{\mathrm{p1}}=0$, the relative enthalpy relaxation value may be expressed by the enthalpy fictive temperature:

$$\frac{P_{\mathrm{rel}}}{\%}=100\frac{T_{\mathrm{f,H}}(t_2)-T_{\mathrm{f,H}}(t_1)}{T_{\mathrm{iso}}-T_{\mathrm{f,H}}(t_2)} \tag{11}$$

Method

Using the common non-linear least squares method, the sum of squares between experimental and calculated values of relaxation enthalpies is minimized:

$$F(b,A,B,q,\Delta C_{\mathrm{p0}},\Delta C_{\mathrm{p1}})=\sum_{i=1}^{\mathrm{M_{iso}}}\sum_{k=1}^{\mathrm{N_i}}[H_{\mathrm{rel}}^{\mathrm{calc}}(T_{\mathrm{iso,i}},t_{\mathrm{rel,i,k}})-H_{\mathrm{rel}}^{\mathrm{exp}}(T_{\mathrm{iso,i}},t_{\mathrm{rel,i,k}})]^2 \tag{12}$$

where M_{iso} is the number of relaxation isotherms and N_{i} is the number of relaxation times at the *i*-th relaxation temperature. Parameters *A*, *B*, and *q* defined by the relationships:

$$A\log\tau_0 B=0.43429\frac{\Delta h^*}{R} q=100\log\frac{x}{1-x} \tag{13}$$

are used in numerical minimization for convenience. Using *A* and *q* instead of τ_0 and *x* avoids the need of constraint minimization.

As a result, the best estimates of unknown parameters ΔC_{p0}, ΔC_{p1}, *x*, Δh^* and τ_0 of relaxation model are obtained:

$$F(b^*,A^*,B^*,q^*,\Delta C_{\mathrm{p0}}^*,\Delta C_{\mathrm{p1}}^*)=F(\boldsymbol{X}^*)=\min \tag{14}$$

The corresponding standard deviations $s(X_{\mathrm{i}})$, co-variances $\mathrm{cov}(X_{\mathrm{i}},X_{\mathrm{j}})$, and intercorrelation coefficients $\mathrm{r}(X_{\mathrm{i}},X_{\mathrm{j}})$ are obtained by quadratic approximation of the sum of squares hyper-surface around the minimum value F_{min}:

$$F(b,A,B,q,\Delta C_{\mathrm{p0}},\Delta C_{\mathrm{p1}})-F(b^*,A^*,B^*,q^*,\Delta C^*_{\mathrm{p0}},\Delta C^*_{\mathrm{p1}})=\Delta\boldsymbol{X}^{\mathrm{T}}\boldsymbol{A}\Delta\boldsymbol{X} \tag{15}$$

$$s(X_i)=\left[\frac{(A^{-1})_{ii}F_{\min}}{N_{\exp}-6}\right]^{1/2} \tag{16}$$

$$\mathrm{cov}(X_i,X_j)=\left[\frac{(A^{-1})_{ij}F_{\min}}{N_{\exp}-6}\right]^{1/2} \tag{17}$$

$$r(X_i,X_j)=\frac{\mathrm{cov}(X_i,X_j)}{s(X_i)s(X_j)} \tag{18}$$

where

$$\Delta \boldsymbol{X}^{\mathrm{T}}\equiv\{b-b^*,A-A^*,B-B^*,q-q^*,\Delta C_{\mathrm{p0}}-\Delta C^*_{\mathrm{p0}},\Delta C_{\mathrm{p1}}-\Delta C^*_{\mathrm{p1}}\} \tag{19}$$

and the total number of experimental points $N_{\exp}$ is given by the sum

$$N_{\exp}=\sum_{i=1}^{M_{\mathrm{iso}}}N_i \tag{20}$$

Results and discussion

The method was applied to the enthalpy relaxation data (Fig. 3) obtained by Černošková *et al.* [9] for As_2Se_3 glass. The glass samples were prepared by spontaneous cooing of glass melt in ambient atmosphere. The value of 450±2 K was reported for the glass transition temperature of the glass [9]. The cooling rate of 5 K min^{-1} was used in our calculations. Other details of experimental procedure are given in reference [9]. A non-linear regression analysis based on simplex minimization method was performed on a PC using an in-house created Fortran code. Basic statistical characteristics of obtained fit are summarized in Table 1. Calculated and experimentally

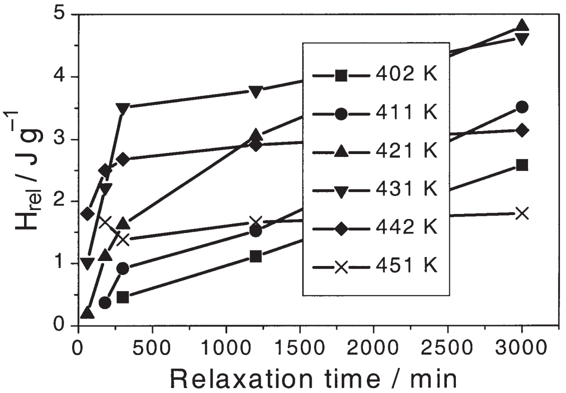

Fig. 3 Experimental enthalpy relaxation data of As_2Se_3, reference [9]. The lines connecting individual relaxation isotherms are plotted for eye guidance only

acquired values of relaxation enthalpies are compared graphically in Fig. 4. As an example, the situation is shown in detail for two arbitrarily chosen relaxation isotherms, i.e. for T_{iso}= 430.9 K in Fig. 5 and for T_{iso}= 441.8 K in Fig. 6.

Table 1 Basic statistical characteristics of obtained fit

Characteristic	Numerical value
Number of experimental points	29
Number of degrees of freedom	23
Standard deviation of approximation	0.33 J g^{-1}
Variance of experimental values	6.38 J^2 g^{-2}
Variance of residuals	0.33 J^2 g^{-2}
Fisher's *F*-statistics	57

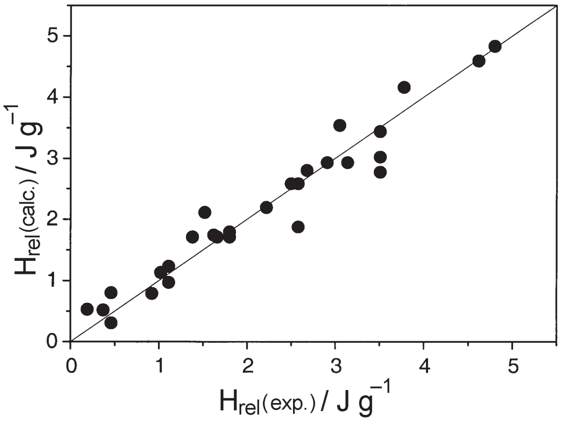

Fig. 4 The comparison of experimental (exp.) and calculated (calc.) relaxation enthalpies

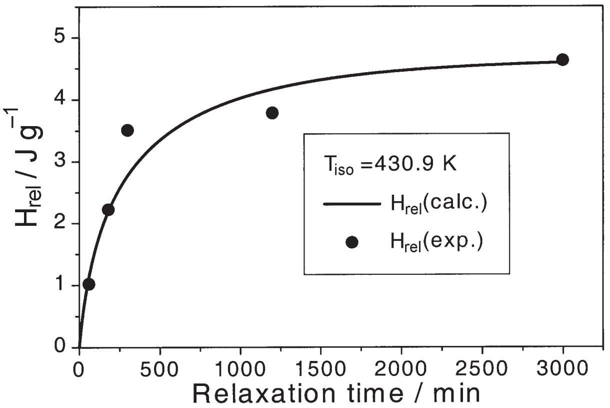

Fig. 5 Relaxation at 430.9 K. Full line – calculated values, circles – experimental values

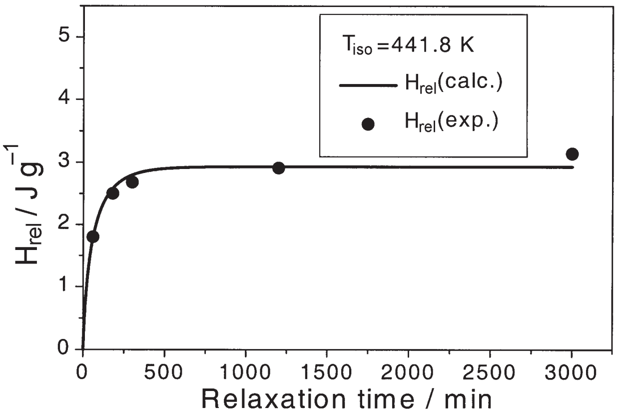

Fig. 6 Relaxation at 441.8 K. Full line – calculated values, circles – experimental values

The differences between the calculated and experimental values of the relaxation enthalpy are randomly distributed (Fig. 4), and the value of standard deviation of approximation of 0.33 J g^{-1} K^{-1} (Table 1) corresponds to the experimental error [9]. The significance of the overall fit is confirmed by the relatively high value (F=57) of the Fisher's F-statistics (Table 2), defined as the ratio of the variance of the experimental relaxation enthalpy data to the variance of regression residuals.

Table 2 Results of regression analysis – best estimates X_i^* standard deviations s(X_i^*), correlation coefficient i(X_i^*,X_j^*), covariance cov(X_i^*,X_j^*), and heat capacity differences calculated at various temperature close to the T_g value

Parameter	X_i^*	s(X_i^*)	$t(X_i^*)$
b	0.898	0.18	5.0
A=log(τ_0/min)	–30.19	0.27	112
B	15013	118	127
q	36.44	11.1	3.3
ΔC_{p0} /J g^{-1} K^{-1}	0.84016	0.5270	1.6
ΔC_{p1} /J g^{-1} K^{-1}	–0.0015384	0.00117	1.3
$r(\Delta C_{p0}, \Delta C_{p1})$	0.9998	–	–
cov($\Delta C_{p0}, \Delta C_{p1}$)	–0.0006144	–	–
ΔC_p(400 K)/J g^{-1} K^{-1}	0.225	0.072	3.1
ΔC_p(425 K)/J g^{-1} K^{-1}	0.186	0.052	3.6
ΔC_p(450 K)/J g^{-1} K^{-1}	0.148	0.044	3.4
Δh^*/kJ mol^{-1}	287.4	2.3	127
x	0.70	0.05	14

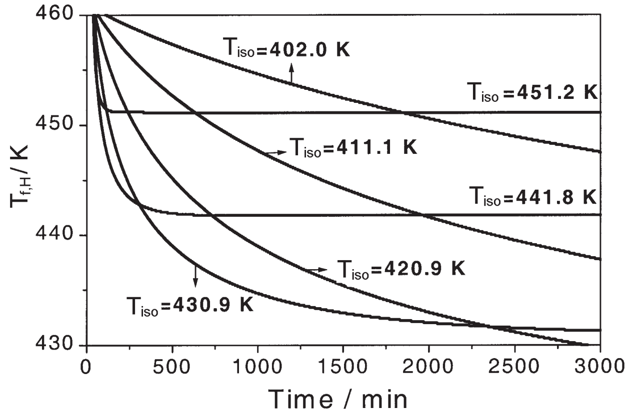

Fig. 7 Time dependence of the structural temperature in the course of an isothermal relaxation

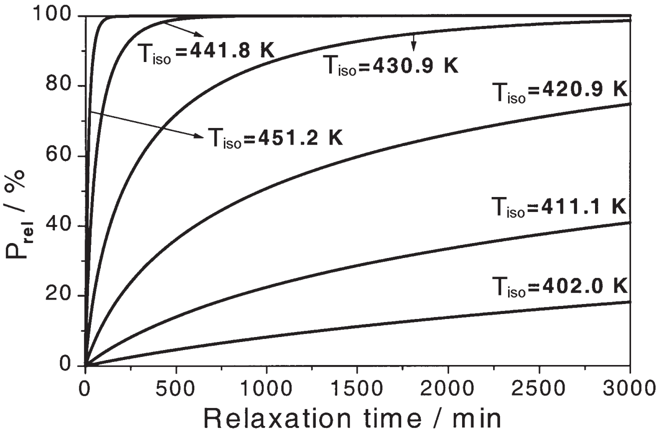

Fig. 8 Time dependence of relative enthalpy relaxation in the course of an isothermal relaxation

Time dependences of structural temperature, $T_{\mathrm{f,H}}$, in the course of isothermal relaxation are for various isotherms compared in Fig. 7. It is worth noting, that the structure moves towards its equilibrium position practically instantly when the isothermal temperature reaches the value close to the reported [9] range of glass transition temperature (T_g= 448–452 K). The same can be seen in Fig. 8, where the time dependences of relative enthalpy relaxation, P_{rel}, are compared for different isothermal temperatures.

More detailed statistical analysis of results obtained is given in Table 2. Comparing the values of t-statistics with the 99% significance critical value $t_{\mathrm{crit}}(0.01)=2.5$, one can see (Table 2), that the regression analysis does not give significant individual estimates of ΔC_{p0} and ΔC_{p1}. This fact can be attributed to the strong linear correlation between estimates of these parameters as it is indicated by the high value of corresponding correlation coefficient of 0.9998 (Table 2). On the other hand, if the $\Delta C_p(T)$ value is evaluated for temperature T near T_g

$$\Delta C_p(T)=\Delta C_{p0}+\Delta C_{p1}T \tag{21}$$

and the corresponding standard deviation, $s[\Delta C_p(T)]$, is obtained using

$$s^2[\Delta C_p(T)]=s^2(\Delta C_{p0})+T^2s^2(\Delta C_{p1})+2T\,\mathrm{cov}(\Delta C_{p0},\,\Delta C_{p1}) \tag{22}$$

then the t-statistics indicates the statistical significance of $\Delta C_p(T)$ (Table 2). The obtained confidence intervals of $\Delta C_p(T)$ are in a good agreement with the temperature independent value of 0.21 J g^{-1} K^{-1} reported by Málek [10].

The estimate of Δh^* value, 287.4±2.3 kJ mol^{-1}, corresponds with the value of activation energy of the equilibrium viscous flow E_η=292±5 kJ mol^{-1} reported by Málek [10], thus confirming the equivalence between the kinetics of enthalpy relaxation and structural relaxation.

The estimated values of non-linearity parameter, x=0.70±0.05, and non-exponentiality parameter, b=0.90±0.18, can be compared with the values x=0.51±0.02 and b=0.76±0.06 found by Málek [10] for volume relaxation of As_2Se_3 glass. It seems that while the non-exponentiality parameters are almost the same, the non-linearity parameters significantly differ. The same value of non-exponentiality parameters can be rationalized when we realize, that the non-exponentiality parameter defines the width of the relaxation time distribution function [11], and supposing that the distribution of relaxation times is closely related to the glass structure.

On the other hand, it must be stated here, that all presented parameter estimates are – to a various extent – dependent on the supposed cooling rate, which was only approximately estimated in the present work. Therefore, the experimental enthalpy relaxation values are needed for glasses prepared by controlled cooling.

Conclusions

The proposed method is suitable for regression analysis of DSC enthalpy relaxation data. The statistical analysis confirmed the plausibility of the used mathematical model. The statistical significance of parameters' estimates was enhanced due to the fact, that all points of the DSC curve were included in the integral experimental data. The samples with controlled thermal history are to be used for the more precise estimation of parameters of enthalpy relaxation model.

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