

# MODELING OF THE REVERSIBLE PART OF STEPSCAN DSC MEASUREMENT OF THE GLASS TRANSITION

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*The reversible part of StepScan DSC record of a glass in the region of the glass transition was interpreted as a measure of the conversion degree  $\alpha$  of the  $A \leftrightarrow B$  type equilibrium reaction identified with a reversible part of glass  $\leftrightarrow$  undercooled melt transition. The temperature course of the conversion degree,  $\alpha(T)$ , was expressed in terms of the temperature dependence of the equilibrium constant alternatively with the temperature dependent and temperature independent reaction enthalpy. Experimental data of eight various inorganic and organic glasses were fitted by the proposed model. The formalism of temperature independent formal reaction enthalpy was sufficient to reach an acceptable quality of the fit, i.e. the fit accuracy level of an average experimental error. The model of temperature dependent formal reaction enthalpy was found inappropriate due to strong inter-correlations between the regression parameters. In contrary to the previously reported model the proposed model yields the maximum conversion rate at the conversion degree lower than 0.5.*

## INTRODUCTION

The new experimental techniques, a dynamic differential scanning calorimetry (DDSC) and StepScan DSC, brings a new insight into study of the glass transition. Both methods enable to split the glass transition into two types of processes - the fast one (denoted as in-phase, thermodynamic or storage process) and the slow one (out-of-phase, kinetic or loss process). It was found that so-called thermodynamic process of the glass transition is completely independent on the thermal history of glass, and on the direction and rate of temperature change, and thus this process depends only on the sample chemical composition [1,2]. Beside it the thermal history of a glass including also the exothermic change during the melt-glass transition and the endothermic change in the opposite direction is thus reflected exclusively in the so-called kinetic part of glass transition [1-4].

It is worth mentioning, that this experimental finding is, strictly speaking, in contradiction with the commonly accepted theory of the glass transition phenomenon, which is contemporary explained on purely kinetic basis [5, 6], and not as a consequence of the second

order phase transition. It has to be stated here, that solving of this problem is beyond the scope of the present paper.

The thermodynamic part of glass transition has been the subject of recent study [7, 8]. It was found that this part could be regarded as glass  $\leftrightarrow$  undercooled melt transition with a conversion degree  $\alpha$  dependent (at isobaric conditions) on thermodynamic temperature only. This equilibrium can be described well by the empirical equation [7, 8]

$$\alpha(T) = 1 - \exp[-(T/T_g')^n] \quad (1)$$

where  $T$  is thermodynamic temperature,  $T_g'$  is the glass transition temperature, which is unambiguously determined from the position of point of inflexion on the reversible part of StepScan DSC record. Thus, in the frame of StepScan DSC method, the  $T_g'$  value is considered as the experimental value of the glass transition temperature. In contrary to the common phenomenological treatment, this value is independent of experimental conditions, i.e. of the heating rate, and of the thermal history of the measured sample. The parameter  $n$ , representing the slope of the glass transition curve  $C_p$  vs.  $T$ , varies in a wide range of values depending on the che-

mical composition of the non-crystalline material. The conversion degree  $\alpha$  is calculated from the temperature dependence of reversible heat capacity  $C_p(\text{rev}, T)$  obtained from the DDSC experiment:

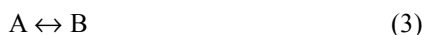
$$\alpha(T) = \frac{C_p(\text{rev}, T) - C_p(\text{rev}, \text{glass})}{C_p(\text{rev}, \text{melt}) - C_p(\text{rev}, \text{glass})} = \frac{C_p(\text{rev}, T) - C_p(\text{rev}, \text{glass})}{\Delta C_p} \quad (2)$$

where  $C_p(\text{rev}, \text{melt})/C_p(\text{rev}, \text{glass})$  is identified with the maximum/minimum value of the measured sigmoid  $C_p(\text{rev}, T)$  curve.

The present paper aims to propose a model of the conversion degree temperature dependence based on the theory of chemical equilibrium reactions, i.e. on the temperature dependence of equilibrium constant given by the equation of van't Hoff's reaction isobar [9].

## THEORETICAL

We assume instantaneous formation of equilibrium between two structural arrangements denoted for simplicity as A (the low temperature form, i.e. the glass) and B (the high temperature form, i.e. meta-stable or under-cooled melt):



In the case of the standard state of pure substance at the pressure and temperature of the system, the ratio of equilibrium mole fractions of A and B can be expressed by the corresponding equilibrium constant  $K$ :

$$K(T) = \frac{x(B)}{x(A)} = \frac{x(B)}{1 - x(B)} = \frac{\alpha}{1 - \alpha} \quad (4)$$

or

$$\alpha = \frac{K(T)}{1 + K(T)} \quad (5)$$

where  $\alpha$  is the conversion degree (transformation ratio).

Further we assume that the composition independent partial molar enthalpies of A and B are equal to corresponding molar quantities  $H_A$  and  $H_B$ . Introducing the temperature independent isobaric molar heat capacities  $C_{p,A}$  and  $C_{p,B}$  of pure substances A and B the temperature dependence of  $H_A$  and  $H_B$  can be expressed in a simple linear form:

$$H_X(T) = H_X(T_r) + C_{p,X}(T - T_r), \quad X = A, B \quad (6)$$

where  $T_r$  is an arbitrary reference temperature ( $T_r = 298$  K in our case).

The temperature dependence of equilibrium constant  $K$  is given by the van't Hoff's equation:

$$\left( \frac{\partial \ln K}{\partial T} \right) = \frac{\Delta H(T)}{RT^2} = \frac{H_B(T) - H_A(T)}{RT^2} \quad (7)$$

where  $R$  is the universal molar gas constant (8.314 J/molK),

$T$  - thermodynamic temperature, and the reaction enthalpy  $\Delta H$  at temperature  $T$  is expressed by the molar enthalpies of hypothetical pure substances A and B:

$$\begin{aligned} \Delta H(T) &= H_B(T) - H_A(T) = \Delta H(T_r) + \Delta C_p(T - T_r) = \\ &= \Delta H_r + \Delta C_p(T - T_r) \end{aligned} \quad (8)$$

where the temperature independent reaction heat capacity is given by:

$$\Delta C_p = C_{p,B} - C_{p,A} \quad (9)$$

The integration of equation (7) gives an analytic expression for the  $K(T)$  dependence in the form:

$$K(T) = K_0 \exp\left(\frac{T_r \Delta C_p - \Delta H_r}{RT}\right) \exp\left(\frac{\Delta C_p}{R} \ln T\right) \quad (10)$$

where

$$K_0 = K_r \exp\left(\frac{\Delta H_r}{RT_r}\right) \exp\left(-\frac{\Delta C_p}{R}\right) \exp\left(-\frac{\Delta C_p}{R} \ln T_r\right) \quad (11)$$

where  $K_r = K(T_r)$ .

Inserting the equation (10) into the equation (5) results in an analytic expression for  $\alpha(T)$  dependence with three unknown parameters  $K_r$ ,  $\Delta H_r$ , and  $\Delta C_p$ . These can be obtained by standard non-linear regression treatment by minimization of the sum of squares of deviations between the experimental (i.e. obtained from the equation (2)) and calculated  $\alpha$  values.

## EXPERIMENTAL

A new stepwise DSC technique, the StepScan method (Perkin-Elmer) [10], was used. This method facilitates determination of accurate specific heat capacity data and allows separation of  $C_p$  (reversible or thermodynamic part) from slow irreversible kinetic events, i.e. from relaxation processes. It is a stepwise technique, based on repeated measurement of the heat flow,  $dQ/dt$ , of a known amount of sample at a constant heating or cooling rate,  $q^\pm$ , which is compared with the heat flow in adjacent isotherm. The scanning steps are selected to be in regular intervals (1°C was used in this case), and heating and cooling rates in the scanning steps  $\pm 1^\circ\text{C}/\text{min}$  and/or  $\pm 100^\circ\text{C}/\text{min}$  were selected. The isothermal dwell is software controlled, and depends on the response of the sample. The maximal allowed heat flow difference during isotherm was  $\Delta(dQ/dt) = \pm 0.0001$  mW per approximately 10 s before the next step commenced. This way, enthalpy changes of slow processes accompanying the glass transition can be separated from the isobaric heat capacity temperature dependence. Both the glass transition temperature and the change of isobaric heat capacity,  $\Delta C_p$ , were found independent on experimental conditions (especially on heating or cooling rate) and thermal history of glass [1].

As<sub>2</sub>Se<sub>3</sub>, As<sub>2</sub>S<sub>3</sub> and Se bulk glasses were prepared by conventional method of direct synthesis from high-purity elements (5N) in evacuated silica ampoules in a rocking furnace and quenched in air. The oxide glass LiPbPBO (40Li<sub>2</sub>O:10PbO:10B<sub>2</sub>O<sub>3</sub>:40P<sub>2</sub>O<sub>5</sub>) was prepared by melting of oxides and melt was consequently cooled on a cold copper plate. The lead-silica glass NBS 711 is a commercial product [11]. The barium crystal glass RONA was taken from the industrial production of the glasswork RONA, j.s.c. Lednické Rovne. The poly(styrene-co-acrylonitrile), 75/25, PSA, from BASF, and a commercial product based on poly(ethylen terephthalate), PET, were used as polymer samples. Samples (of approximately 10 mg weight) were placed into sealed aluminium pans and measured using Pyris 1 DSC (Perkin-Elmer).

## RESULTS AND DISCUSSION

The results or regression analysis treatment are summarized in table 1 and in figures 1, 2. In the first step, all three regression parameters ( $K_r$ ,  $\Delta H_r$ , and  $\Delta C_p$ ) were estimated for each sample. As can be seen from table 1 (rows where  $N_{\text{par}} = 3$ ), the obtained values of standard deviation of approximation,  $s_{\text{appr}}$ , as well as the high values of Fisher's  $F$ -statistics (defined as the ratio between the variance of experimental points and the variance of residuals) confirm the high quality of obtained fit. From graphic outputs in figures 1,2 is obvious, that lower quality of the fit, i.e. higher values of  $s_{\text{appr}}$  and, simultaneously, lower value of  $F$ , were observed only for the experimental data of evidently poorer qua-

lity, e.g. in cases (c) and (d) in figure 1 and case (d) in figure 2. In case (c) of figure 2, the value of  $C_p(\text{rev, glass})$  was probably chosen too low. However, analyzing the standard deviations of obtained parameters' estimates (table 1) one can observe that the standard deviations of regression estimates of  $\Delta C_p$  are extremely high. This is the consequence of a strong linear bound between the  $\Delta H_r$  and  $\Delta C_p$  parameters, i.e. their individual values cannot be found by regression treatment. From physical point of view this situation resulted from small changes of  $\Delta H(T)$  value in relatively narrow temperature range in which the transition takes place. Therefore the regression treatment was repeated with the fixed value of  $\Delta C_p = 0$ , i.e. supposing the temperature independent  $\Delta H$  value given by  $\Delta H_r$ . As can be seen from the statistical characteristics reported in tab. 1, the obtained two-parametric regression is almost of the same quality as the previous three-parametric one. The best indication resides in overlapping of full and dashed curves representing the calculated values of the three- and two-parametric fits in figures 1, 2. Obviously, due to  $\Delta C_p = 0$  assumption, the  $\Delta H_r$  estimates are higher for the two-parametric regression. Thus the reversible part of the StepScan DSC glass transition curve can be described with sufficient accuracy by the constant reaction enthalpy model based on the standard thermodynamic relationship for temperature dependence of the reaction equilibrium constant.

Another question arises in connection with more subtle characteristics of the proposed model. Namely the position of the inflexion point on the  $\alpha(T)$  has to be discussed, as the previous model [7, 8] fixed this point strongly to the value of  $\alpha = (1 - 1/e) = 0.632$ .

Table 1. Results of non-linear regression analysis:  $N_{\text{par}}$  - number of parameters, parameters' estimates  $\pm$  theirs standard deviations,  $s_{\text{appr}}$  - standard deviation of approximation,  $F$  - Fischer's  $F$ -statistics.

System	$N_{\text{par}}$	$-\log K_r$	$\Delta H_r$ (kJ/mol)	$\Delta C_p$ (J/mol/K)	$s_{\text{appr}}$	$F$
As <sub>2</sub> S <sub>3</sub>	2	21.84±0.03	328.3±0.4	0	0.014	568
	3	21.33±0.02	315.2±0.5	73±4	0.014	578
As <sub>2</sub> Se <sub>3</sub>	2	22.94±0.11	371.0±1.8	0	0.020	307
	3	22.49±0.11	358.5±2.0	77±27	0.020	301
LiPbPBO Glass	2	37.95±0.12	421.9±1.3	0	0.033	90
	3	36.94±0.12	403.3±1.4	61±11	0.033	89
NBS711 Glass	2	41.98±0.12	402.0±1.1	0	0.028	137
	3	41.43±0.13	393.5±1.2	20±8	0.029	134
RONA Glass	2	80.02±0.10	711.6±0.9	0	0.025	151
	3	78.75±0.11	694.5±1.0	32±5	0.025	148
Se	2	4.94±0.07	578.9±8.1	0	0.019	345
	3	4.94±0.07	578.3±18.1	41±1559	0.019	339
PET	2	10.94±0.14	465.9±5.9	0	0.037	70
	3	10.92±0.15	464.0±6.7	62±281	0.038	68
PSACN25	2	10.59±0.16	285.1±4.2	0	0.039	83
	3	10.51±0.16	280.9±5.0	50±124	0.039	81

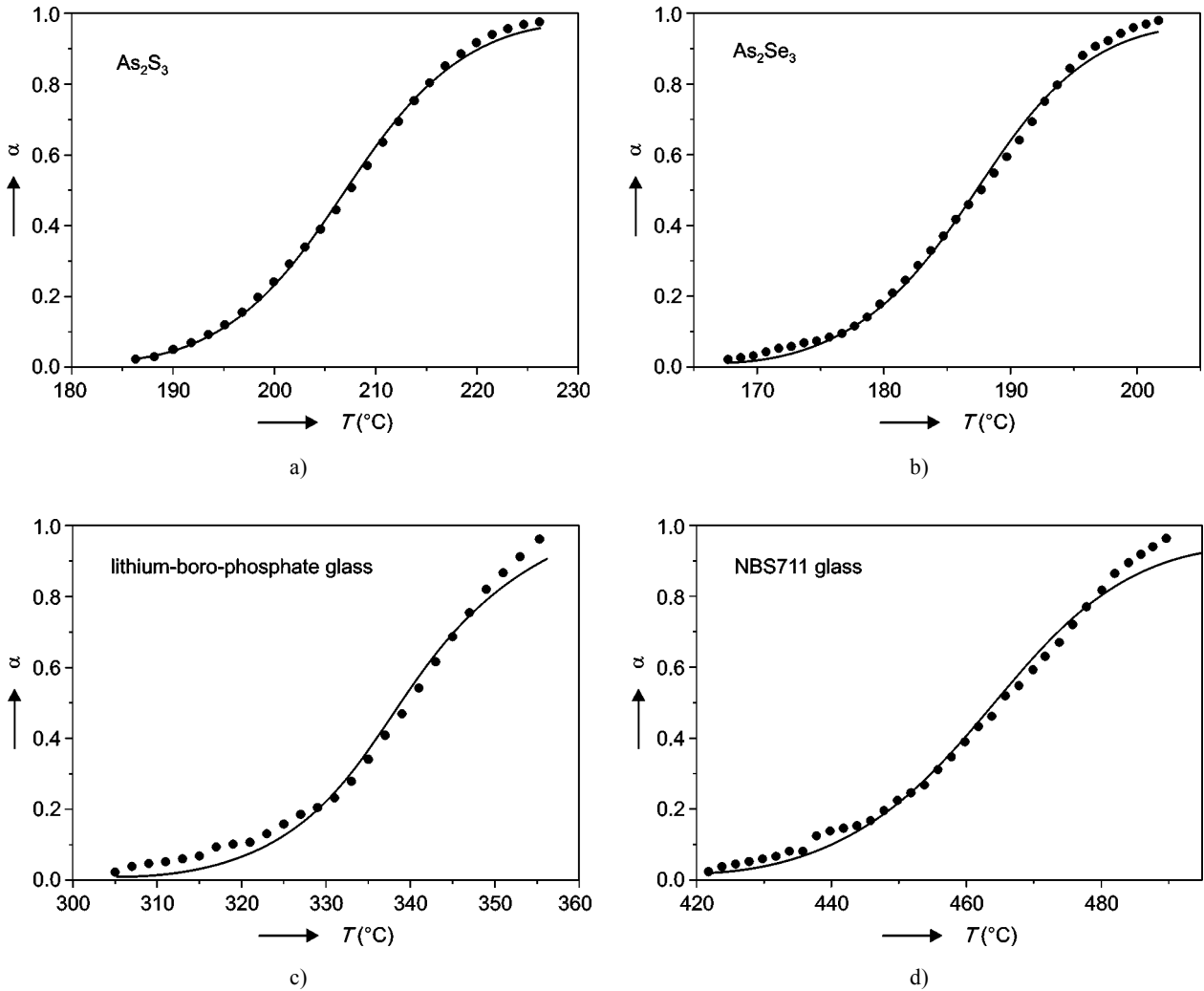


Figure 1. The comparison of experimental data (solid points) and calculated values of the two-parametric model (full line). The results of the three-parametric model (invisible dashed line) are indistinguishable from the two-parametric model in the used scale of  $\alpha$  axes; a)  $As_2S_3$ , b)  $As_2Se_3$ , c) LiPbPBO glass, d) NBS711 glass.

The slope of the temperature dependence of the conversion,  $\alpha$ , can be obtained by the derivative of the definition equation (5), i.e.

$$\left(\frac{\partial \alpha}{\partial T}\right)_P = \frac{1}{(K+1)^2} \left(\frac{\partial K}{\partial T}\right)_P \quad (12)$$

Proceeding to the second derivative we obtain

$$\left(\frac{\partial^2 \alpha}{\partial T^2}\right)_P = \frac{1}{(K+1)^2} \left[ \frac{-2}{K+1} \left(\frac{\partial K}{\partial T}\right)_P^2 + \left(\frac{\partial^2 K}{\partial T^2}\right)_P \right] \quad (13)$$

We assume that in a limited temperature range the reaction enthalpy  $\Delta H$ , can be considered as temperature independent, i.e.

$$\left(\frac{\partial \Delta H}{\partial T}\right)_P = 0 \quad (14)$$

Then the equation of reaction isobar can be rewritten in the form

$$\left(\frac{\partial K}{\partial T}\right)_P = K \frac{\Delta H}{RT^2} \quad (15)$$

Proceeding to the second derivative we obtain after some rearrangement

$$\left(\frac{\partial^2 K}{\partial T^2}\right)_P = K \frac{\Delta H}{RT^3} \left(\frac{\Delta H}{RT} - 2\right) \quad (16)$$

The temperature of maximum temperature conversion change,  $T_i$ , and, simultaneously, of the inflexion point of the  $\alpha(T)$  dependence can be determined by solving the equation

$$\left(\frac{\partial^2 \alpha}{\partial T^2}\right)_P = 0 \quad (17)$$

Substituting the equation (15) and equation (16) into the equation (13) we obtain

$$\left(\frac{\partial^2 \alpha}{\partial T^2}\right)_p = \frac{K}{(K+1)^2} \frac{\Delta_r H}{RT^3} \left(\frac{1-K}{1+K} \frac{\Delta_r H}{RT} - 2\right) \quad (18)$$

From equation (17) then for the determination of the inflexion point temperature follows the implicit equation

$$\frac{1 - K(T_i)}{1 + K(T_i)} \frac{\Delta H}{RT_i} - 2 = 0 \quad (19)$$

Substituting the equation (5) into the equation (19) allows us to calculate the conversion degree in the inflexion point, i.e.

$$(1 - 2\alpha_i) \frac{\Delta H}{RT_i} - 2 = 0 \quad (20)$$

or

$$\alpha_i = \frac{1}{2} - \frac{RT_i}{\Delta H} \quad (21)$$

thus the maximum slope of the temperature dependence of  $\alpha$  is reached before a half-conversion point.

We can therefore conclude that the proposed model, in principle, differs from the previous model [7, 8] with respect to the position of maximum conversion rate temperature. More detailed analysis will be needed to solve the question about the principal reason of such strict location of this point. In the case of the previous model these feature resulted from its formal similarity with exponential relaxation model, or with the Avrami equation [12] describing the crystallization kinetics.

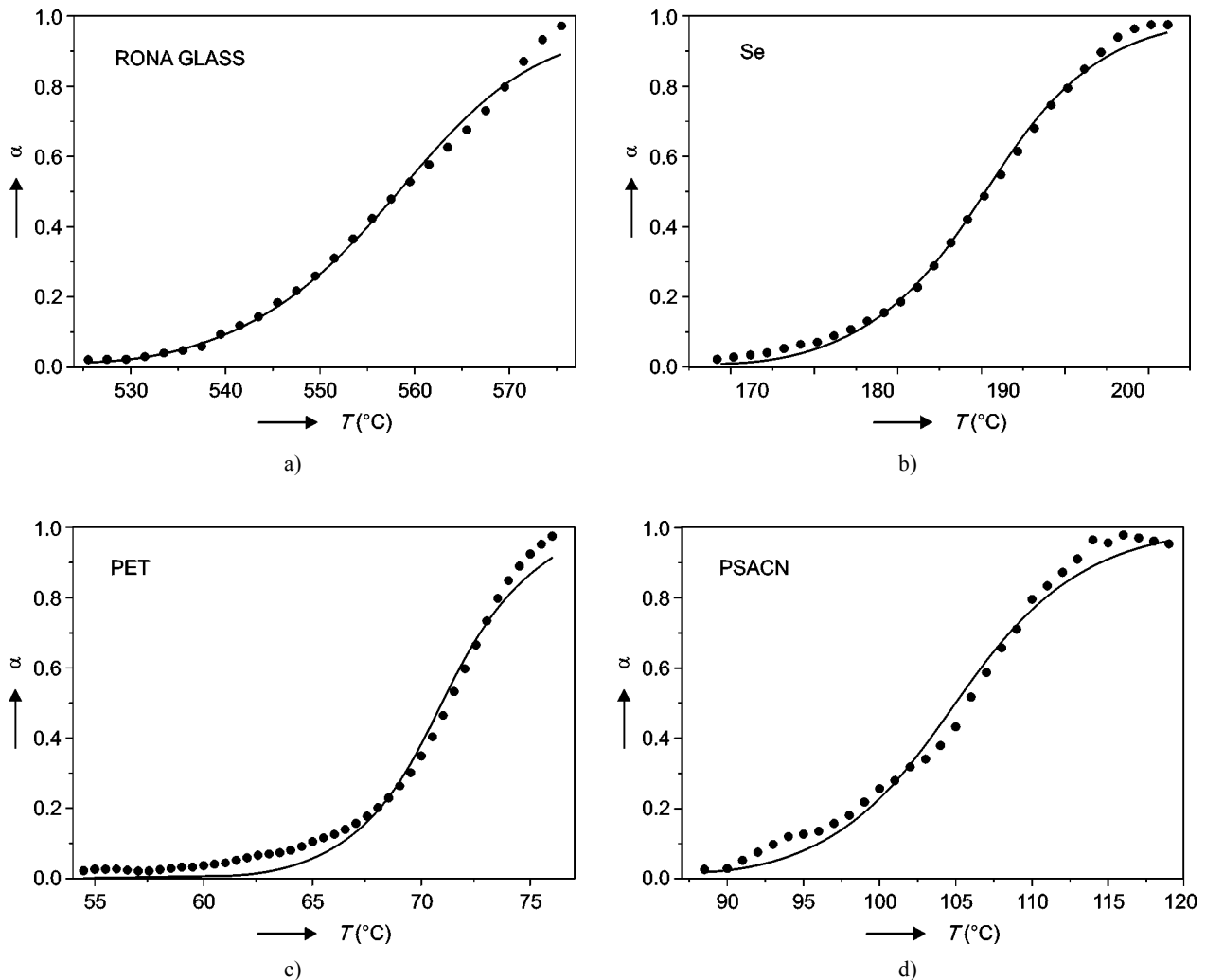


Figure 2. The comparison of experimental data (solid points) and calculated values of the two-parametric model (full line). The results of the three-parametric model (invisible dashed line) are indistinguishable from the two-parametric model in the used scale of  $\alpha$  axes; a) RONA glass, b) Selenium, c) Polyethylene, d) Polystyrene-ACN co-polymer.

## CONCLUSIONS

The proposed thermodynamic model is inherently consistent with the character of the reversible part of StepScan DSC measurement, where a thermodynamic equilibrium between the over-cooled liquid and glass is observed. On the other hand, this new feature of the glass transition needs a further and more detailed investigation.

The model describes the experimental data with sufficient accuracy reaching the level of experimental errors.

The temperature independent value of reaction enthalpy is sufficient for achievement of acceptable quality of the fit.

The proposed model, in principle, differs from the previous model [7, 8] with respect to the position of maximum conversion rate temperature. A more detailed experimental and theoretical analysis is probably needed to address this discrepancy.

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## References

1. Černošek Z., Holubová J., Černošková E., Liška M.: *J. Optoelectron. Adv. Mat.* 4, 489 (2002).
2. Boolchand P., Georgiev D. G., Goodman B.: *J. Optoelectron. Adv. Mat.* 3, 703 (2001).
3. Boolchand P., Georgiev D. G., Micoulaut M.: *J. Optoelectron. Adv. Mat.* 4, 823 (2002).
4. Cai L., Boolchand P.: *Phil. Mag.* B82, 1649 (2002).
5. Sipp A., Richet P.: *J. Non-Cryst. Solids* 298, 202 (2002).
6. Rao K. J.: *Structural Chemistry of Glasses*, Elsevier, Amsterdam 2002.
7. Holubová J., Černošek Z., Černošková E.: *Conf. on Non-Crystalline Inorganic Materials 2003*, April 8-12, 2003, Bonn, Germany, Book of Abstracts, p. 99.

8. Holubová J.: Thesis, University Pardubice, Pardubice 2004.
9. Atkins P.W.: *Physical Chemistry*, 3<sup>rd</sup> ed., p. 221-224, W. H. Freeman Comp., New York 1986.
10. Merzlyakov M., Schick C.: *Thermochim. Acta* 380, 5 (2001).
11. Certificate of Viscosity Values, Standard Sample No. 711 Lead-Silica Glass, U.S. Department of Commerce, National Bureau of Standards, Washington, D.C. 20235.
12. Avrami M.: *J. Chem. Phys.* 7, 1103 (1939).

## MODEL REVERZIBILNEJ ČASTI DSC ZÁZNAMU SKLENÉHO PRECHODU MERANEJ METÓDOU STEPSCAN

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Reverzibilná časť StepScan DSC záznamu skleného prechodu bola formálne termodynamicky opísaná pomocou stupňa konverzie  $\alpha$  rovnovážnej reakcie typu  $A \leftrightarrow B$ , stotožnenej s reverzibilnou časťou prechodu sklo  $\leftrightarrow$  metastabilná podchladená tavenina. Teplotná závislosť stupňa konverzie  $\alpha(T)$  sa vyjadřila pomocou teplotnej závislosti rovnovážnej konštanty uvedenej reakcie opísanej rovnicou reakčnej izobary s teplotne závislou alebo s teplotne nezávislou hodnotou štandardnej reakčnej entalpie. Uvedeným modelom sa metódou nelineárnej regresnej analýzy opísali experimentálne dáta získané StepScan DSC meraniami skleného prechodu ôsmich rôznych organických i anorganických skiel. Formalizmus teplotne nezávislej hodnoty štandardnej reakčnej entalpie postačoval na získanie dostatočne presného preloženia experimentálnych dát. Model vychádzajúci z teplotne závislej hodnoty štandardnej reakčnej entalpie sa ukázal ako v regresnej analýze nepoužiteľný z dôvodu silnej korelácie medzi regresnými parametrami. V rozpore s modelom navrhnutým v predchádzajúcich prácach, vyvinutý model poskytuje maximálnu smernicu teplotnej závislosti stupňa konverzie pri hodnote stupňa konverzie menšej ako 0,5.