Journal of Optoelectronics and Advanced Materials, Vol. 4, No. 3, September 2002, p. 489 - 503

# ENTHALPIC RELAXATION AND THE GLASS TRANSITION

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Enthalpic relaxation was investigated on the $As_2Se_3$ bulk glass with perfectly defined thermal history by differential scanning calorimetry (DSC). The relaxation enthalpy change, $\Delta H$, the parameters of the Tool-Narayanaswamy-Moynihan (TNM) relaxation model and the parameter of non-exponentiality, $\beta$, were evaluated. It was found that $\beta$ is both temperature and time dependent. The value of enthalpy change necessary to reach a metastable equilibrium is less than that assumed on the base of a linear extrapolation of H(T) of a supercooled liquid. The glass transition was studied by a new stepwise DSC technique on the bulk $As_2Se_3$ and $As_2S_3$ glasses. The glass transition was found to be a superposition of two parts: a reversible or thermodynamic component, reflecting temperature changes of vibrational amplitudes, and an irreversible or kinetic process, so-called enthalpy relaxation. The value of the glass transition temperature, $T_g$, determined from the thermodynamic part of the glass transition was found to be independent on both the heating/cooling rate and the thermal history of glass. The $T_g$ depends only on the chemical composition of the glass and thus it could be regarded as a material constant. Therefore the heating/cooling rate dependence of $T_g$, known from DSC or DTA measurements, is caused by a kinetic process with relaxation time dependent on structure and temperature.

(Received June 20, 2002; accepted July 22, 2002)

*Keywords*: Enthalpic relaxation, Non-exponentiality, Glass transition, StepScan

## 1. Introduction

Detailed study of non-crystalline solids has been important for more than half a century. Glassy materials have still larger and larger utilization in technical practice lately. It is in connection with an effort to get under control preparation of glasses with well-defined properties and their long lifetime. For this reason broad attention has been paid to processes, which are taking place in glass after its preparation. Study of reorganization of glass structure is very important not only from point of view of basic research but for technology in material engineering as well.

The glassy state is generally the non-equilibrium one and is characterized by an excess of thermodynamic properties (e.g. enthalpy, entropy, volume). The as-quenched and thus non-equilibrium glass seeks to attain a lower energy metastable equilibrium especially if this one is held at temperature not too far below the glass transition temperature. This time dependent variation in physical properties following glass formation is called structural or enthalpic relaxation if the change of enthalpy is the studied thermodynamic property [1]. While the glass transition has been described as "fast" process associated primarily with the vibrational degrees of freedom, the subsequent slow structural relaxation is connected with a change in the frozen liquid structure [2]. So the relaxation kinetics of glasses is determined not only by the thermodynamic temperature T but also by the instantaneous structure of the glass, which is characterized by fictive temperature $T_f$, firstly introduced by Tool [3]. The fictive temperature is defined as the temperature at which the observed value of an intensive property would be the equilibrium one. During relaxation $T_f$ approaches relaxation temperature $T_r$. In the metastable equilibrium $T_f = T_r$ and the departure from equilibrium is measured by $|T_f - T|$. The initial non-equilibrium state of glass is not unique but depends on the conditions of glass formation and the relaxation process is strongly influenced by the complete thermal history of glass.

Besides the great interest of structural relaxation the considerable attention has paid to the glass transition. Historically, the glass transition has been observed in undercooled liquids and, therefore, is regarded as a characteristic property of liquids. Later experiments, however, showed that this phenomenon is quite common in non-crystalline materials prepared by various methods other than traditional liquid cooling, see [4] and references cited in.

The glass transition temperature is ”defined” by various inconsistent manners, for example:

i) The glass transition temperature denotes a temperature for which relaxation times in the supercooled liquid become longer than typical observation times. The ratio between these two times, the Deborah number, is approximately unity for $T=T_g$. (Prophetess Deborah declared that what appeared to mortals to be stationary are not necessarily so to an eternal deity.)

ii) The glass transition temperature is the one at which the viscosity of the supercooled liquid reaches a value $10^{13}$ Poise. It is important to note that the viscosity is continuous through $T_g$, exhibiting none of the discontinuities observed in heat capacity [5] and thus this definition has no physical meaning.

iii) The glass transition temperature is the one at which configurational entropy vanishes during melt cooling.

Notwithstanding these ”definitions” the glass transition is characterized by a gradual break in slope of extensive thermodynamic variables (enthalpy, entropy and volume). The region over which the changes of slope occur is termed glass transition region. This region is usually characterized by midpoint temperature called glass transition temperature, $T_g$. Continuous change of extensive thermodynamic variables through the glass transition implies that there must be a discontinuity in derivative variables at $T_g$, such as a heat capacity or a coefficient of thermal expansion. Such differences are used to distinguish two classes of glass forming liquids - strong and fragile liquid [6]. For review on supercooled liquids and the glass transition refer to [7] and references cited in.

It is well-known that $T_g$ is not regarded as a material constant because when measured for instance by DSC it depends on many parameters as for instance heating rate, $q^+$, [8-10], the cooling rate, $q^-$, [10,11] and the physical aging [9,12,13]. If the $T_g$ is determined by heating the temperature obtained often differs from the one from cooling measurement. These values of $T_g$ may vary in the range of 10 to 20 % depending on difference of cooling rates and heating rates.

The nature of the glass transition is very complex and poorly understood so far. It is clear that regarding long structural relaxation time relatively to laboratory time scale during measurement the material is out of thermodynamic equilibrium. Elimination of this influence of scanning rate on determining of $T_g$ was the main aim of some models. An expression relating dependence of $T_g$ on the cooling rate was derived by Kovacs [14]. More often a linear dependence of $T_g$ on $\ln(q^+)$ proposed by Lasocka [15] has been used. Extrapolation of the experimental results to $q^\pm = 0$ K/min in order to obtain the "correct" glass transition temperature has been suggested [16]. It must be noted that logarithmic dependence lacks of physical meaning when $q^\pm$ is less then 1 K/min or limited to infinity and thus logarithmic model only hardly can be correct.

The main aim of this work is the study of enthalpic relaxation on bulk glassy material with perfectly known thermal history using below-mentioned theoretical background. The greatest attention will be paid to the study of both time and temperature dependence of relaxation parameters of the Tool-Narayanaswamy-Moynihan (TNM) model.

Furthermore the attention was paid to obtain more information on the glass transition by comparing the results obtained by conventional DSC with the ones acquired from stepwise DSC technique in the state near thermal equilibrium. We intend to find dependence of $T_g$ on $q^+$ and $q^-$ without restriction, in contrast to Lasocka's equation [15]. We also try decide whether it is possible to extrapolate the conventional DSC glass transition temperatures obtained at various heating and cooling rates to some rate (probably zero or infinity) to estimate "correct" $T_g$.

The $As_2Se_3$ was used for relaxation experiments. Both $As_2Se_3$ and $As_2S_3$ bulk glasses were used as model ones for glass transition study. These glasses can be easily prepared as homogeneous even by very slow cooling of melts without crystallization. They were, also measured using very low cooling rates. This is a very rare case and one can hardly find better inorganic model glasses with stoichiometric composition. Indispensable is also the fact that these glasses are widely used for basic research as well as for utilization in technical practice [17]. The obtained results concerning $T_g$ were proved, also, on non-chalcogenide glass: lead-silicate glass NBS 711 [18].

## 2. Experimental

### 2.1 Model of enthalpic relaxation

Enthalpic relaxation (physical aging, structural relaxation) of glassy materials has been studied by a number of techniques, but in particular the differential scanning calorimetry (DSC) has been used extensively to measure the kinetics of enthalpic relaxation of glasses.

According to the Tool's concept of fictive temperature, the specific enthalpy of a glassy sample can be expressed as a function of fictive temperature $T_f$ and thermodynamic temperature T:

$$H(T,T_f) = H(T_0,T_0) + \int_{T_r}^{T_f} C_{pm}(T')dT' + \int_{T_f}^{T} C_{pg}(T')dT' \,, \tag{1}$$

where $C_{pm}$, $C_{pg}$ are specific isobaric heat capacities of metastable melt and glass, respectively, and $T_0$ is an arbitrary sufficiently high reference temperature at which the sample is in a metastable thermodynamic equilibrium. Narayanaswamy generalized Tool's model [19] by allowing for distribution of relaxation time and obtained the following expression for the fictive temperature that can be calculated for any thermal history:

$$T_f(t) = T(t) - \int_0^t dt' \left(\frac{dT}{dt}\right)_{t'} M_H[\xi(t) - \xi(t')] \,. \tag{2}$$

$M_H$ is a Kohlrausch-William-Watts (KWW) relaxation function:

$$M_H(\xi) = \exp\left(-\xi^{\beta}\right), \tag{3}$$

$\beta$ is the non-exponentiality parameter ($0 < \beta \le 1$), which is inversely proportional to the width of a distribution of relaxation times of independent relaxation processes. $\xi$ is the dimensionless reduced relaxation time:

$$\xi(t) = \int_0^t \frac{dt'}{\tau(t')} \,. \tag{4}$$

The contribution to the relaxation time $\tau(T,T_f)$, simply $\tau$, from both the temperature and fictive temperature is controlled by a non-linearity parameter x ($0 \le x \le 1$) according to the Tool-Narayanaswamy-Moynihan (TNM) equation [11]:

$$\tau = \tau_0 \exp\left[\frac{x\Delta h^*}{RT} + \frac{(1-x)\Delta h^*}{RT_f}\right], \tag{5}$$

where $\tau_0$ is a constant, $\Delta h^*$ is an apparent activation energy, R is the universal gas constant.

The time course of the normalized molar heat capacity $C_{p,eff}(t)$, e.g. the DSC measurement output, may be obtained from the definition:

$$C_{p,eff}(t) = C_{pg}[T(t)] + \left\{C_{pm}[T_f(t)] - C_{pg}[T_f(t)]\right\}\frac{dT_f}{dT} \,, \tag{6}$$

On the assumption of the temperature independence of $C_{pm}$ and a linear temperature dependence of $C_{pg}$

$$C_{pg}(t) = C_{pg,0} + C_{pg,1}T \tag{7}$$

and using Eqs.(1)-(6) $C_{p,eff}(t)$ may be calculated for an arbitrary time-temperature schedule. The unknown parameters of the proposed model may be estimated by using the standard non-linear least-squares model, i.e. minimizing the target function F:

$$F(C_{pg,0}, C_{pg,1}, C_{pm}, \tau_0, x, \Delta h^*, \beta) = \int_0^{t_{max}} \left[C_{p,eff}^{calc}(t) - C_{p,eff}^{exp}(t)\right]^2 dt\,, \qquad (8)$$

where $t_{max}$ is the time of completion of the DSC experiment.

### 2.2. Samples preparation

Bulk glasses of $As_2Se_3$ and $As_2S_3$ compositions were prepared by direct synthesis from high-purity elements (5N) in evacuated silica ampoules in a rocking furnace (800 °C, 24 h). After synthesis and homogenization the ampoules containing the melt were quenched in air. The lead-silica glass NBS 711 was a commercial product [18].

### 2.3. Enthalpic relaxation

Perkin-Elmer Pyris 1 DSC calorimeter was used for enthalpic relaxation measurements. All experiments were carried out without removing the sample from the instrument. To ensure good thermal contact of glass and aluminium pan and to minimize the thermal gradient inside sample thin disks (thickness less than 1 mm) of glassy sample for relaxation study were prepared directly in calorimeter. Encapsulated powder of bulk glass (approx. 10 mg) was melted and equilibrated at 420 °C ($T_m(As_2Se_3)$ = 375 °C) and subsequently cooled to 50 °C with rate $q^-$ = -100 °C/min. Glass prepared by such way was immediately heated by heating rate $q^+$ = +100 °C onto relaxation temperature $T_r$. After isothermal relaxation the sample was cooled down to the temperature 50 °C by cooling rate q = -100 °C/min. After this the DSC curve was recorded up to 420 °C by heating rate $q^+$ = +20 °C/min. This scan was used for computer simulation. A baseline was obtained by repeating this procedure but storing at the ageing temperature for zero time.

Glasses were isothermally relaxed at temperatures 145, 150, 155, 160, 165 and 170 °C with duration between 15 minutes and 35 hours. All in-instrument steps were computer controlled using Pyris 1 software.

### 2.4. The glass transition

Conventional DSC measurements were carried out using of DSC 7 calorimeter and new stepwise technique was carried on the Pyris 1 DSC (both Perkin-Elmer) with special software. Powdered glassy samples (weigh around 4 mg for conventional DSC and 10 mg for StepScan measurements, see below) were encapsulated into sealed aluminium pans. Glassy samples used in the glass transition study were prepared directly in calorimeter, see Sec. 2.3.

Conventional DSC scans were done using heating and cooling rates $q^{\pm}$ = (1 – 20) °C /min.

New stepwise measurement between states close to thermal equilibrium of glass performed by the StepScan™ method [20] (Perkin Elmer) was used. This method facilitates the taking of accurate specific heat capacity data and allows separating $C_p$ (reversible or thermodynamic component) from slow irreversible kinetic events. The scanning steps are selected to be at regular intervals. In our measurement the heating or cooling rate in the scanning steps was selected from the range ±(2 to 20) °C /min. The isotherm duration is software controlled and depends on the response of the sample. The maximal allowed heat flow difference during isotherm was $\Delta Q = \pm 0.0005$ mW per approximately 10 s. Enthalpy changes of slow actions that accompanies glass transition can be separated from the isobaric heat capacity temperature dependence in this manner. Both glass transition temperature and $\Delta C_p$ independent on experimental conditions (especially on heating or cooling rate) and thermal history of glass were obtained.

Glass transition temperature, $T_g$, and $\Delta C_p$ measured by StepScan are labeled by superscript "eq" in the following text, i.e., $T_g^{eq}$, $\Delta C_p^{eq}$.

## 3. Results

### 3.1. Enthalpic relaxation

Generally the relaxation enthalpy ΔH corresponds to area of so called overshoot on the DSC heating scan. The values of ΔH were obtained as a difference between overshoot areas of relaxed glass scan and non-relaxed glass one used as a baseline. The relaxation enthalpy ΔH increases with increasing time (or duration) of relaxation, $t_r$, at every relaxation temperature, $T_r$, used for isothermal aging. Relaxation enthalpy, ΔH, reaches its limit value, $\Delta H_{eq}(T_f = T_r)$ after the sufficiently long time, $t_r$, at each isothermal relaxation. This means that glass achieves a metastable equilibrium at given temperature. The dependence of obtained values of $\Delta H_{eq}$ on relaxation temperature is shown in Fig. 1. When relaxation temperature decreases the value of $\Delta H_{eq}$ increases, but not linearly. At relaxation temperatures sufficiently below $T_g$ ($T_r$ ~ ($T_g$ - 30 °C) in our study) the enthalpy change from non-relaxed glass to metastable equilibrium achieves its final value $\Delta H_{eq}^{max}$. This value does not change with further decreasing of $T_r$, see Fig. 1. For $As_2Se_3$ glass the maximal enthalpic change is $\Delta H_{eq}^{max}(As_2Se_3)$ ~ 6.4 kJ/mol.

Obtained final DSC curves were normalised such that the isobaric specific heat, $C_p$, passes from zero to unity as the sample goes from glassy state to the equilibrium liquid like state on heating. When above mentioned model of enthalpic relaxation was used and all normalised DSC scans were computer simulated with using thermal history beginning in glass formation, the complete set of parameters of TNM model were obtained for each of relaxation. This set contains the parameter of non-exponentiality, β, non-linearity, x, fictive temperature, $T_f$, and apparent activation energy, $\Delta h^*$.

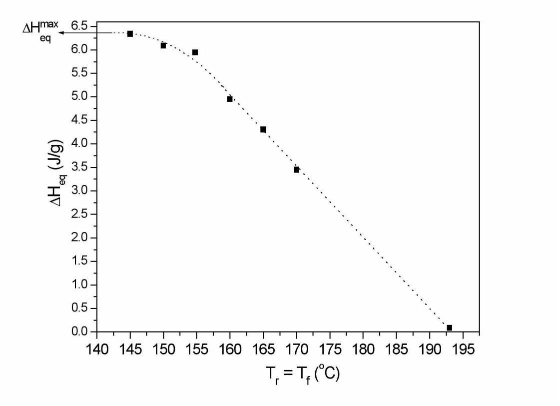

Fig 1. The dependence of pseudo-equilibrium value $\Delta H_{eq}$ on relaxation temperature $T_r$. The curve is only a guideline for eyes.

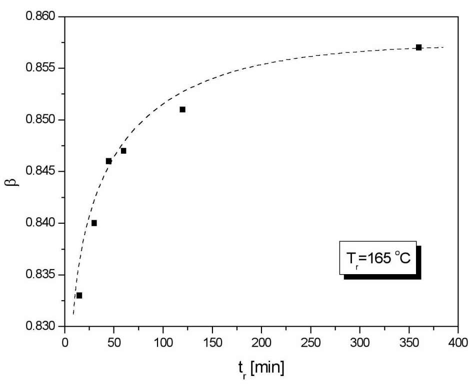

Fig. 2. The time dependence of non-exponentiality parameter β at relaxation temperature 165 °C. The curve is only a guideline for eyes.

The main attention has been paid to the study of behaviour of non-exponentiality parameter β. This parameter was found not to be constant in both the time scale of isothermal relaxation and the temperature scale of the set of $T_r$. Non-exponentiality parameter increases with increasing time of relaxation at every relaxation temperature used. The time dependence of β at relaxation temperature 165 °C is shown in the Fig. 2. As one can see at Fig. 2, after sufficiently long duration of relaxation (when $T_f = T_r$) the parameter β achieves its final value $\beta_{eq}(T_r)$ corresponding to the metastable equilibrium structure of glass at $T_r$.

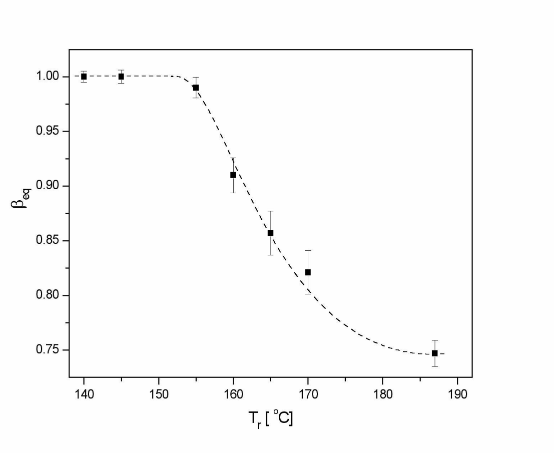

Fig. 3 The dependence of parameter $\beta_{eq}$ ($T_f = T_r$) on the relaxation temperature $T_r$. The curve is only a guideline for eyes.

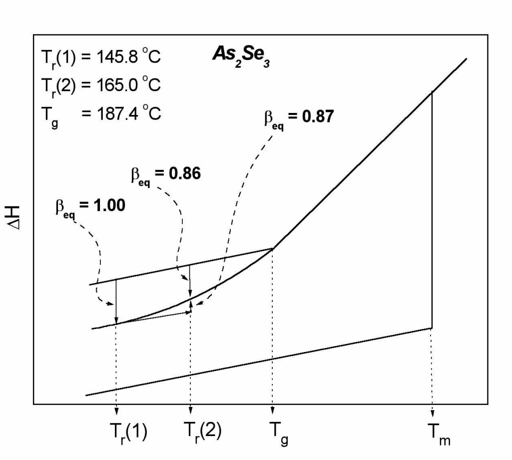

Fig. 4 Qualitative concept of enthalpic relaxation. The values of parameter $\beta_{eq}$ (for $T_f = T_r$) were obtained experimentally.

Value of β increases when the $T_r$ decreases, see Fig. 3. Based on these results we can conclude that the non-exponentiality parameter is both time and temperature dependent, $\beta = f(t_r, T_r)$.

We found that for given relaxation temperature the value of $\beta_{eq}(T_r)$ is independent on the way in which the glass reached its metastable equilibrium at given temperature, Fig. 4. The as-quenched glass was subsequently completely relaxed at $T_f = T_r$ = 165 °C and the value of $\beta_{eq}$ = 0.86. Another sample of glass was completely relaxed at $T_f = T_r$ = 145 °C ($\beta_{eq}$ = 1.00) and after temperature jump it was completely relaxed again at $T_r$ = 165 °C. The $\beta_{eq}$ was then found 0.87, within error the same as it was found in previous experiment. It is necessary to emphasize that the first relaxation at 165 °C is the exothermic process and the second one is the endothermic process, see Fig. 4.

In the case when the change of the relaxation enthalpy reaches its maximal value, $\Delta H_{eq}^{max}$ (as it was mentioned above) the value of $\beta_{eq}$ reached its maximal value $\beta_{eq}^{max} = 1$, see Fig. 5.

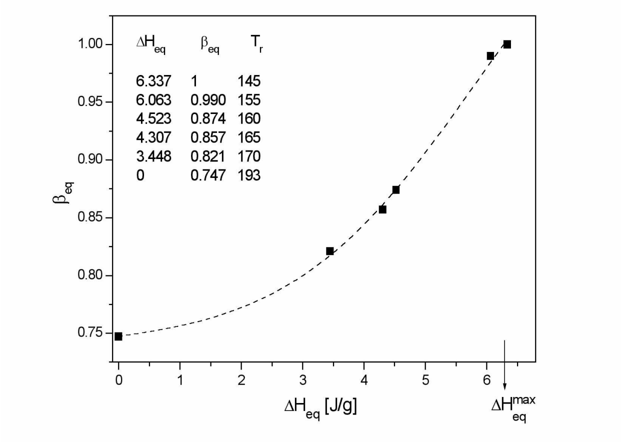

Fig. 5. The dependence of the parameter $\beta_{eq}$ on the enthalpy change $\Delta H_{eq}$ between non-relaxed state of as-quenched glass and metastable equilibrium at the same temperature, see inset.

Non-linearity parameter, x, increases as $T_f$ is getting near $T_r$ during isothermal relaxation. This parameter was found in range 0.60 - 0.75 and these values reflect relatively small influence of structure to relaxation time. During annealing this influence still decreases.

The apparent activation energy is nearly constant and independent on both temperature and time of relaxation, $\Delta h^*(As_2Se_3)$ = 263 ± 15 kJ/mol.

### 3.2. The glass transition

Typical StepScan DSC traces of $As_2S_3$ melt cooling through the glass transition region and trace of $As_2S_3$ glass heating are shown in Fig. 6. The reversible (thermodynamic) component, $C_p$, and enthalpic change corresponding to irreversible (kinetic) one are separated.

Results of DSC measurement of glassy $As_2Se_3$ by StepScan are collected in Tab. 1. Reversible (thermodynamic) parts are shown in Figs. 7 (including NBS 711 glass) and 8. When glass is formed the exothermic peak is clearly seen in Fig. 6, as well as both exothermic undershoot and endothermic overshoot when glass is heated and undergoes glass transformation. The temperature of overshoot maximum is always lower than the thermodynamic $T_g^{eq}$, $T_p < T_g^{eq}$, Tab. 1 and Fig. 6, contrary to the conventional DSC where $T_p > T_g$ every time. Remind that $T_g^{eq}$ and $T_g$ were determined as the temperature of $\Delta C_p^{eq}$ (StepScan) and/or heat flow difference, $\Delta Q$, (conventional DSC) midpoint between glass and undercooled liquid.

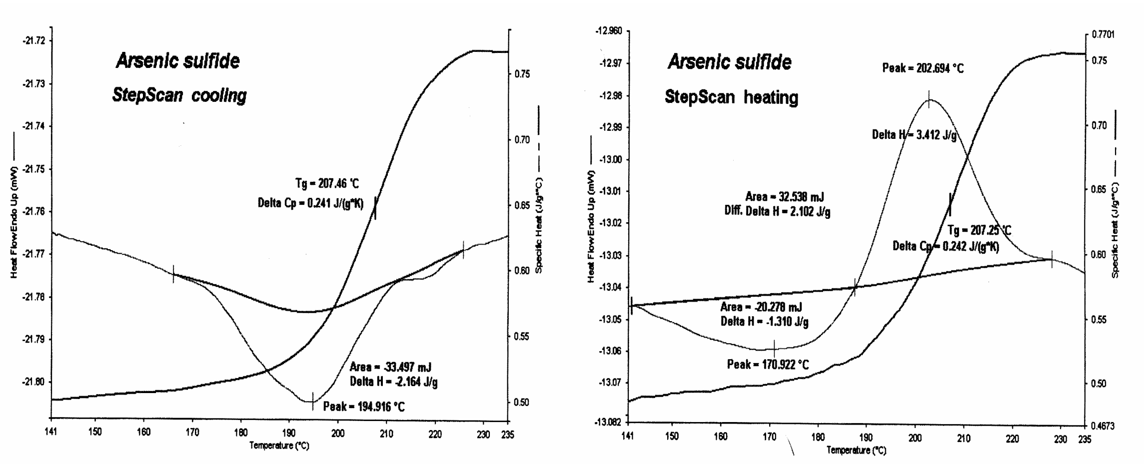

Fig. 6 Typical results of DSC StepScan method. On the irreversible part of cooling scan is seen exothermic peak ($\Delta H$ = -2.16 J/g). On heating scan both exothermic undershoot ($\Delta H$ = -1.31 J/g) and endothermic overshoot ($\Delta H$ = +3.14 J/g) are seen and their difference is within experimental error equal to enthalpic change in course of glass formation. Reversible parts ($C_p$ vs. T) are identical for cooling and heating.

When the undercooled liquid was cooled to obtain glass the exothermic change in the glass transition region was observed on irreversible component, Fig. 6. Its enthalpy is independent on cooling rate within experimental error, contrary to enthalpy of irreversible changes obtained during heating, confront results each other in Tab. 1. Temperatures of maxima or minima of enthalpic peaks depend on heating or cooling rate as well as on thermal history of glass, Table 1.

Important result shown in Fig. 7 clearly demonstrates that the $C_p$ measurement close to isothermal equilibrium when irreversible component is separated removes completely both well-known hysteresis of thermal capacity and shape difference during heating and cooling. Temperature dependence of $C_p$ obtained by this way is independent on both heating/cooling rate and thermal history. Similar result was found also for organic polymer [21].

Table 1. Experimental results obtained by StepScan. Values of $T_g^{eq}$ and $\Delta C_p^{eq}$ were obtained from reversible part, temperature of kinetic peak, $T_p$, and enthalpy of kinetic process, $\Delta H_p$, from irreversible part of the StepScan measurement.

| | | **$As_2Se_3$**<br>$T_g^{eq}$ = 187.47 ± 0.41 °C<br>$\Delta C_p^{eq}$ = 0.187 ± 0.001 J/(g·°C) | | **$As_2S_3$**<br>$T_g^{eq}$ = 207.50 ± 0.22 °C<br>$\Delta C_p^{eq}$ = 0.240 ± 0.011 J/(g·°C) | |
|---|---|---|---|---|---|
| **Thermal history** | **q [°C/min]** | **$T_p$ [°C]** | **$\Delta H_p$ [J/g]** | **$T_p$ [°C]** | **$\Delta H_p$ [J/g]** |
| As-quenched | +2 | 182.09 | +2.98 | 202.28 | +2.59 |
| Relaxed[1, 2] | +2 | 183.39 | +5.12 | 196.47 | +7.85 |
| As-quenched | +5 | 182.96 | +2.67 | | |
| Relaxed[3] | +5 | 185.87 | +9.04 | | |
| As-quenched | +20 | 183.40 | +2.80 | 203.06 | +4.67 |
| Glass formation | -2 | 173.67 | -2.79 | 195.56 | -3.25 |
| Glass formation | -10 | 182.86 | -2.73 | | |
| Glass formation | -20 | 183.64 | -2.78 | 199.06 | -3.32 |

[1] $As_2Se_3$ glass relaxed 2 hrs. at 160 °C

[2] $As_2S_3$ glass relaxed 2 hrs. at 170 °C

[3] $As_2Se_3$ glass relaxed 166 hrs. at 145 °C, fully relaxed glass ($T_f$ = 145 °C)

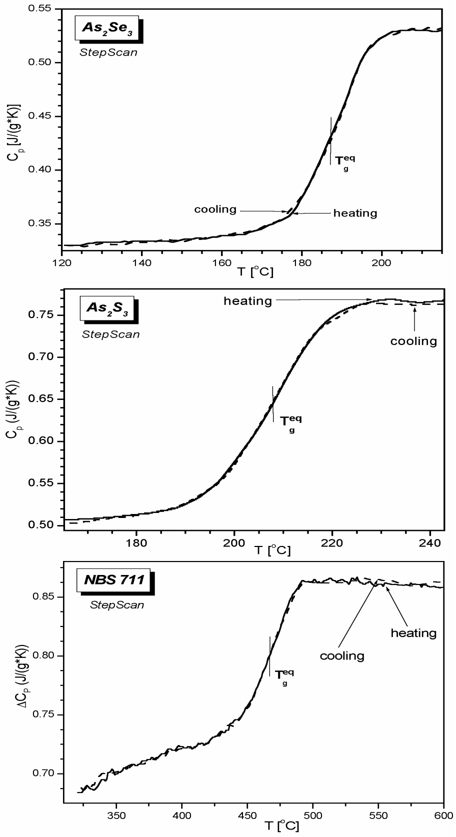

Fig. 7. Reversible (thermodynamic) part of the glass transition. StepScan method, Pyris 1 DSC.

It is well known that conventional DSC traces gained during cooling and heating differ significantly in the shape and thus also in the value of the specific heat capacity change, $\Delta C_p$, e.g. [22-26]. This is also well known that the value of glass transition temperature, $T_g$, is dependent on heating and cooling rate, $q^+$ and $q^-$, and with increasing rates, $q^\pm$, the glass transition temperature increases, see e.g. [15,23].

Results of our conventional DSC experiments carried out at different heating or cooling rates are in Figs. 8A, B. Part A show the dependence of $T_g$ on the heating rate. It is pointed out, that dependence of $T_g$ on heating rate, Fig. 8A doesn't need to be logarithmic contrary to Lasocka's proposal [15]. The application of two-phase exponential association equation (also known as pseudo-first order association kinetics eq.), Fig. 8A, allows us to extrapolate the $T_g$ values from zero heating rate even to the infinity. The values of $T_g$ obtained in this manner are more realistic compared to application of logarithmic dependence. Glass transition temperatures obtained by StepScan, $T_g^{eq}$, are represented by shaded stripe with width of 2*(std. deviation) of $T_g^{eq}$, Fig. 8A. Very surprising is dependence of $\Delta C_p$ on heating and cooling rates obtained by conventional DSC, Fig. 8B, which wasn't published and systematically studied yet. It shows namely that $\Delta C_p$ determined either from heating or cooling scans going to be significantly different when rates $q^\pm$ decrease. On the other hand the values of $\Delta C_p^{eq}$ are practically constant (Fig. 8B, half-filled circles and Tab. 1). In other words the application of the new method of measurement eliminates the influence of thermal history of glass and also influences of heating or cooling rate on the glass transition temperature, $T_g^{eq}$, and on the $\Delta C_p^{eq}$. It can be easily shown that the sum of thermodynamic and kinetic components is equivalent to the conventional DSC scan at the same heating rate.

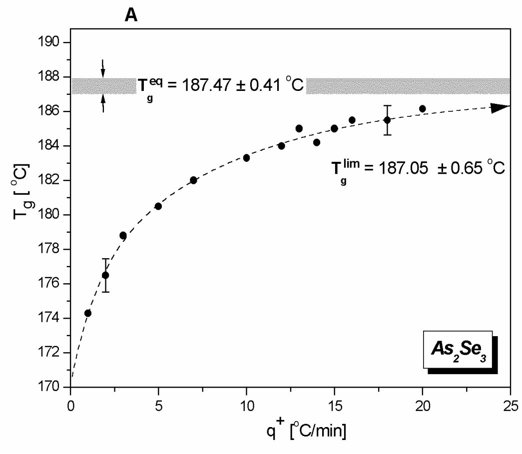

Fig. 8A. Heating rate dependence of the glass transition temperature, $T_g$, obtained by conventional DSC (full circles). The $T_g^{eq}$, obtained by StepScan, is represented by shaded stripe of width 2*(std. deviation) of $T_g^{eq}$.

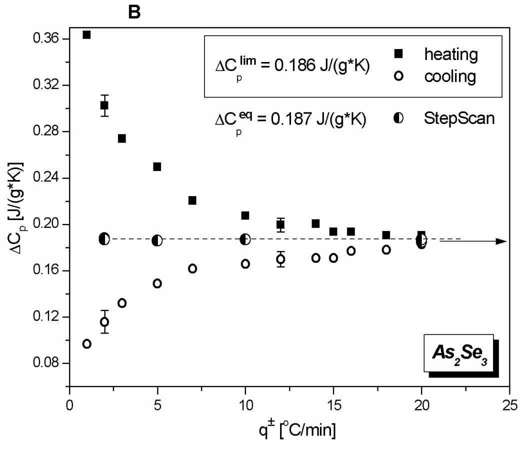

Fig. 8B. The heating/cooling rate dependence of both $\Delta C_p$ (conventional DSC) and $\Delta C_p^{eq}$ (StepScan). The radius of half-filled circles is equal to 2*(std. deviation) of $\Delta C_p^{eq}$.

## 4. Discussion

### 4.1. Enthalpic relaxation

We have found that glass reached the metastable equilibrium at each of relaxation temperature we used. Corresponding limiting value of the enthalpy change, $\Delta H_{eq}(T_r)$, are indispensable lower than the expected values from linear extrapolation of melt equilibrium enthalpy, see Fig. 9. This figure is based on our experimental results. At certain temperature, $T_o$, sufficiently below the glass transition temperature, the enthalpy loss achieves its maximal value $\Delta H_{eq}^{max}$. This one is invariant at temperatures lower than $T_o$ for relaxed glass. For $As_2Se_3$ glass it was found $T_o \sim 155$ °C and $\Delta H_{eq}^{max} \sim 6.4$ kJ/mol. The changes of H(T) of fully relaxed glass at temperature lower than $T_o$ bear on the changes of vibrational enthalpy. These changes are the same as for crystal of the same chemical composition because of known fact that heat capacities for both the crystalline and glassy states of most of materials are essentially the same [5,27,28], except at ultra-low temperatures [27], and arise from vibrational contributions. As one can see in the Fig. 5 the curve of metastable equilibrium has the same slope as that one of non-relaxed glass. It corresponds with our results hereafter in this paper that the specific heat is insensitive on the thermal history of a glass. All these facts confirm our assumption that metastable equilibrium is not identical with equilibrium linearly extrapolated of the equilibrium enthalpy above $T_g$, see Fig. 5. This conclusion agrees with some works, published lately [28-30], that linear extrapolation of equilibrium enthalpy of the liquid state above $T_g$ to this one below $T_g$ is unrealistic.

The obtained dependence of non-exponentiality parameter $\beta = f(t_r, T_r)$ need to be interpreted in two steps. Firstly we focus our attention on $\beta = f(t_r)$, thus on results obtained from isothermal relaxation ($T_r$ = const.).

The relaxation function, which is frequently simplified by KWW stretched exponential Eq. (3), may be expressed by a sum of exponential terms of N individual simultaneous relaxation processes [31]:

$$M_H = \sum_{i=1}^{N} w_i \exp\left[-\frac{t}{\tau_{0i}}\right] \approx \exp\left[-\left(\frac{t'}{\tau_0}\right)^{\beta}\right], \qquad (9)$$

where $w_i$ are weighting factors, $\tau_{0i}$ are independent relaxation times and t is duration of isothermal relaxation. In the right part of Eq. (9) the KWW parameter $\tau_0$ means relaxation time of all relaxation processes at actual time t' and $\beta$ reflects the variation of weighting factors $w_i$ (the distribution of relaxation times) in this time. From the theories describing structural relaxation it follows that the non-exponentiality parameter is inversely proportional to the distribution of structural relaxation times. $\beta = 1$ corresponds to a single relaxation time and as $\beta$ decreases the distribution broadens. We believe it is a justifiable assumption that in the course of relaxation to the metastable equilibrium, $T_f \rightarrow T_r$, the number of independent relaxation processes decreases in consequence of decreasing disorder. Therefore the experimentally found growth of parameter $\beta$ during the isothermal relaxation, Fig. 2, may be interpreted as a consequence of restriction of relaxation times distribution when structure becomes relaxed.

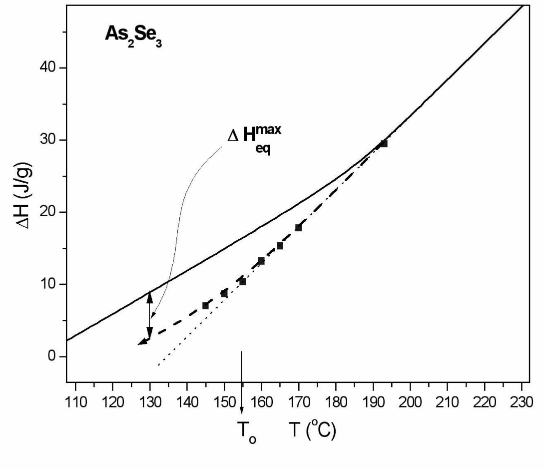

Fig. 9. Real enthalpic temperature dependence observed on glass during isothermal relaxation at annealing temperatures below glass transition. Full lines are calculated from $C_p$ measurement during glass formation and points ($\Delta H_{eq}$) reflect the results of isothermal relaxation. Compare with Fig. 1.

Dependence of non-exponentiality parameter on relaxation temperature, $\beta = f(T_r)$, is interesting especially in case of its limit value $\beta_{eq}$, thus for $T_f = T_r$, Fig. 3. These values, inversely proportional to the distribution of relaxation times of glass in the metastable equilibrium, have shown namely that with decreasing temperature the metastable equilibrium structure approaches the state with only one relaxation time ($\beta_{eq}^{max} = 1$ at the temperature $T_r \leq T_o$). This structure is characterized also by a final relaxation enthalpy, $\Delta H_{eq}^{max}$, Fig. 5, as it was mentioned above. In contrast to our results some researchers found, especially on organic polymers, that β decreases when temperature decreases [32,33]. According to our opinion these results are only hardly compatible with the idea of structural relaxation. The metastable equilibrium structure becomes denser when temperature goes down and the number of independent relaxation processes goes down, as well. Consequently distribution of relaxation times becomes narrower and thus β rises up.

We have also found out that $\beta_{eq}$ does not depend on fact whether metastable equilibrium was reached by exothermic or by endothermic relaxation, Fig. 4. Therefore non-exponentiality parameter of metastable equilibrium is path independent.

We can conclude that it would be better to express the parameter β dependent on the structure of glass than on the time of relaxation $t_r$. While the time increases constantly from the beginning of process irrespective of relaxation extent, the change of the structure of glass is finite. The change of the structure is described by the change of fictive temperature, $T_f$. Then we may summarize that β depends on thermodynamic temperature and simultaneously on fictive temperature, $\beta(T_r, T_f)$.

According to our results there is directly proposed conception that in the glass transition region the glass may be viewed as an equilibrium mixture - supercooled liquid ↔ glass. Starting from the upper temperature end of a glass transition region when temperature decreases this equilibrium moves towards the glass and at the temperature $T_o$ the supercooled liquid completely disappears and vice versa. Temperature dependence of isobaric specific heat in the glass transition interval also supports this concept. In the case of studied glass this change of the total quantity of $\Delta C_p$ is also finished practically at the temperature $T_o$. The fact that the overwhelming majority of studies of the relaxation have been done in the glass transition region, e.g. [34], probably due to strongly increasing time-consumption at lower temperatures is worthy of remark.

### 4.2. The glass transition

Conventional DSC measurements of the glass transition temperature showed that the glass transition temperature $T_g$ approaches StepScan $T_g^{eq}$ in the case of sufficiently high heating rates, Fig. 8A. It is clear that the explanation of known heating/cooling rate dependence of the glass transition temperature should be searched in relaxation times of processes in the glass transition region. The temperature dependence of reversible (thermodynamic) $C_p$, essentially the change of vibrational amplitudes, is rapid enough in comparison with experimental time of DSC technique and thus this reversible part cannot be influenced by the rate of temperature changes. To elucidate the experimental results it is necessary to focus attention on irreversible (kinetic) component, because of strong temperature and structure dependent relaxation time $\tau(T,T_f)$, simply τ. One can expect that this fact should influence considerably the shape of the non-isothermal DSC scans.

The kinetics of isothermal structural relaxation, $T = T_r = \text{const.}$, can be expressed:

$$\frac{dT_f}{dt} \approx \frac{|T_f - T|}{\tau(T, T_f)}. \tag{10}$$

For non-isothermal relaxation kinetics this equation can be rewritten in the form:

$$\frac{dT_f}{dT} \approx \frac{1}{q}\frac{|T_f - T|}{\tau(T, T_f)}, \tag{11}$$

where q is the heating rate, $q = \frac{dT}{dt}$.

For the forthcoming discussion on influence of non-isothermal structural relaxation on the shape of conventional DSC curve, and thus on the $T_g$ and $\Delta C_p$ values, refer to Fig. 10.

We shall discuss heating scan at first. Provided that $(T_f > T)_{T<Tg}$, then the glass relaxes exothermally toward the equilibrium structure at T. It manifests itself as so-called undershoot on the non-isothermal

DSC scan, see Fig. 6. On the other hand when $(T_f < T)_{T<Tg}$ the relaxation is endothermic and its typical overshoot is found at the temperature above conventional DSC glass transition temperature. In the limit case of $(T_f = T)_{T<Tg}$ the glass is in metastable equilibrium. It is important to point out here that this is the case only when $T_f$ crosses line $T = T_f$. At this moment exothermic relaxation changes to endothermic one, Fig. 10. Because the relaxation time, $\tau$, increases exponentially with decreasing temperature so at glass formation structural relaxation time is much longer than experimental time, $\tau >> t$, for the temperatures not much lower than $T_g$ ($T \sim T_g - 10$ °C). As a matter of fact the fictive temperature of non-relaxed glasses is practically always substantially higher than thermodynamic temperature ($T_f >> T$). It results in well-known fact that during glass heating the exothermic relaxation (undershoot) can be observed in many cases. Its magnitude depends on the difference between the rate of glass formation (the rate of cooling) and the rate of following heating. In case of a low heating rates the equilibrium structure can be reached, $(T_f = T)_{T<Tg}$, and crossed. In such case further increasing of temperature leads to departure from equilibrium and subsequent endothermic process proceeds toward a new equilibrium. Thus an overshoot begins to appear at DSC scan. Very slow heating of quickly cooled glass, represented by curve 2 in Fig. 7, leads to deep undershoot and very small overshoot when conventional DSC is used. Resulting shape of DSC scan is known as so-called pre-peak, or sub-$T_g$ peak. Origin of this is unclear up to now, see e.g. [35,36]. When non-relaxed or only slightly relaxed glass is heated with sufficiently high rate the exothermic undershoot decreases and at the same the endothermic overshoot shifts up to higher temperature because the equality $(T_f = T)_{T<Tg}$ is reached at higher temperature, see Fig. 10.

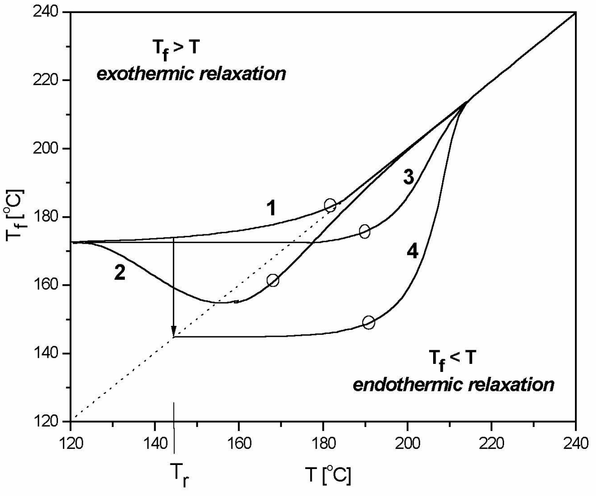

Fig. 10. A schematic drawing of relation between fictive (structural) temperature, $T_f$, and thermodynamic temperature, T. Circles indicate the points corresponding to conventional DSC glass transition temperatures. Curves: 1 – cooling, 2 – slowly heated non-relaxed glass, 3 – quickly heated non-relaxed glass, 4 – quickly heated glass fully relaxed at $T_r$. See text for details.

Relaxation kinetics influences not only determination of the glass transition temperature but it also crucially affects the value of isobaric specific heat capacity change, $\Delta C_p$, in course of glass transition. The dependence of the specific heat capacity change on heating/cooling rate is shown on Fig. 8B. When the rate, $q^{\pm}$, rises up the change of specific heat limits to constant equal to StepScan $\Delta C_p^{eq}$, Fig. 8B, in the same manner as a glass transition temperature does, Fig. 8A. The explanation is simple: when a glass is heated the relaxation proceeds and because the quicker heating the lower extent of relaxation and therefore shallower undershoot tends to produce a lower value of $\Delta C_p$, closer to the correct value of heat capacity difference. In the case of sufficiently high heating rate the glass almost don't relax exothermally at the temperature decreases below $T_g$ and thus $\Delta C_p \sim \Delta C_p^{eq}$.

With regard to conventional DSC cooling scan the explanation is not very clear. During cooling of the melt the exothermic process (relaxation) takes place in and below the glass transition region, Fig. 6. Now it should be pointed out that the conventional DSC doesn't measure directly the specific heat but only the heat flow and the later is higher in the glass than in the melt. Therefore when melt is cooled and glass is formed the heat flow of exothermal changes is subtracted from the growth of heat flow during glass transition, Fig. 11. It leads, consequently to erroneous lower values of both $T_g$ and $\Delta C_p$ obtained from conventional DSC cooling scan, as it is demonstrated on Fig. 11. At increasing cooling rates the extent of relaxation decreases and $\Delta C_p$ tends to $\Delta C_p^{eq}$, Fig. 8B.

The opposite sign of heat flow of the glass transition and of the exothermic structural relaxation during cooling and, on the other hand, the same sign of changes of both heat flow components, when the heated glass undergos the glass transformation, causes the completely different shape of conventional DSC traces. These differences led to erroneous conclusion that when the melt is cooled through the glass transition region there is not exothermal counterpart to endothermic overshoot.

From the aforesaid it is obvious that the value of glass transition temperature obtained by conventional DSC is strongly affected by the facts that i) relaxation kinetic affects significantly shape of DSC scan, and that ii) glass transition temperature is actually determined on an ascending part of irreversible endothermic overshoot added on the reversible $C_p(T)$ dependence.

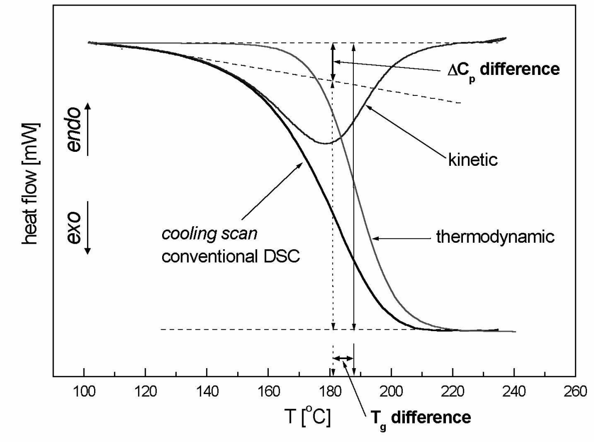

Fig. 11. The influence of exothermic process on the shape of conventional DSC cooling scans in course of glass transformation. Errors of determination of both $T_g$ and $\Delta C_p$ are indicated.

The heating rate dependence of the overshoot peak shift is widely used for the determination ofthe apparent activation energy of relaxation, e.g. [37]. Heating rate dependence of the glass transition temperature has been used to find the activation energy of either the glass transition [37-39] or the activation energy of relaxation [40]. From our results it is evident that both relaxation peak and $T_g$ shift bear on relaxation and thus it doesn't surprise that the obtained activation energies of relaxation and of glass transition are very close to each other. Their difference is caused only by the fact that in the first case the peak shift and in the second one the shift of the ascending part of endothermic overshoot is used, but always it is only more less good estimation of activation energy of relaxation.

It's clear that with use of conventional DSC it is possible only to approach more or less correctly the values of $T_g^{eq}$ and $\Delta C_p^{eq}$ (characteristic values of reversible changes). However, for the full thermo-analytical characterization of glass it is necessary to characterize not only reversible (thermodynamic or vibrational) component but also the irreversible (kinetic or structural) one.

## 5. Conclusions

The isothermal relaxation was studied on glasses with perfectly defined thermal history. It was found that enthalpies of metastable equilibria at temperatures below glass transition region are higher than the ones obtained at the same temperatures by linear extrapolation of H(T) of a supercooled liquid, Fig. 9. In view of this result the extrapolation should not be used generally for definition of metastable equilibrium of glass.

It was found that parameter $\beta$ increases with increasing duration of isothermal relaxation, it means that $\beta$ is structurally dependent, $\beta(T_f)$. The metastable equilibrium is also characterized by equilibrium non-linearity parameter, $\beta_{eq}(T_r)$, and its value does not depend on the way by which the equilibrium is reached. Contrary to previously published results $\beta_{eq}(T_r)$ increases with decreasing supercooling. Thus we can summarized that the non-exponentiality parameter depends on both temperature and structure, $\beta(T_r,T_f)$, as well as the relaxation time does.

At lower relaxation temperatures ($T_r < T_o$) the completely relaxed glass may be characterized by the maximal value of parameter of non-exponentiality ($\beta_{eq} = 1$) and also by the maximal relaxation enthalpy change $\Delta H_{eq}^{max}$ which does not change furthermore. This allows us to conclude that at low relaxation temperatures the glass reaches the state with the lowest energy and with further decreasing of relaxation temperature the glass does not relax yet.

It was found that the glass transition is in fact a superposition of thermodynamic process (the changes of vibrational amplitudes) and kinetic one (also called structural relaxation). The glass transition temperature and shape of the temperature dependence of the isobaric specific heat are invariant on both heating/cooling rate and a thermal history of glass, too. Beside constant $T_g$, the exothermic change in course of glass transition was found. The well-known heating/cooling rate dependencies of a glass transition temperature, as well as curve shape and position and enthalpy of undershoot and overshoot, when conventional DSC is used, bear only on kinetic processes. From aforesaid it follows that conventional DSC studies of glass transition kinetics are the same, in principle, as the studies of enthalpic relaxation. Since the glass transition temperature depends only on chemical composition of glass, see also [41], but not on its thermal history, it can be regarded as a material constant. Unambiguous way of determination of the glass transition temperature independent on a rate, $q^{\pm}$, is crucial for obtaining comparable values of various frequently used glass characterizing parameters, e.g. Hruby's criterion [42] or fragility [43].

It is plausible that when appropriate model of structural relaxation would be used the computer processing of the conventional DSC data could be separated onto reversible part (temperature dependent isobaric heat capacity) and irreversible (kinetic) part. The set of parameters completely characterizing the actual state of glass, i. e., $T_g$, $C_{p,g}$, $\Delta C_p$, $T_f$, x, $\beta$, $\Delta h^*$ and $\Delta H$ could be obtained by this way.

## Acknowledgements

This work was supported by The Ministry of Education of Czech Republic under the projects MSM LN00A028 and 253100001 and by The Slovak Grant Agency for Science under grant No. VEGA 1/7008/20.

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