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Step-wise kinetics of natural physical ageing in arsenic selenide glasses

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Abstract

The long-term kinetics of physical ageing at ambient temperature is studied in Se-rich As–Se glasses using the conventional differential scanning calorimetry technique. It is analysed through the changes in the structural relaxation parameters occurring during the glass-to-supercooled liquid transition in the heating mode. Along with the time dependences of the glass transition temperature (T_g) and partial area (A) under the endothermic relaxation peak, the enthalpy losses (ΔH) and calculated fictive temperature (T_F) are analysed as key parameters, characterizing the kinetics of physical ageing. The latter is shown to have step-wise character, revealing some kinds of subsequent plateaus and steep regions. A phenomenological description of physical ageing in the investigated glasses is proposed on the basis of an alignment–shrinkage mechanism and first-order kinetic equations.

(Some figures may appear in colour only in the online journal)

1. Introduction

Physical ageing is known to be an important concern for amorphous polymers, pharmaceuticals, gels and glasses, because it results in a time drift of such important bulk properties as density, modulus, brittleness, permeability, impact strength, fracture energy, deformation, etc [1–4]. The effect of physical ageing in silicate glasses at ambient temperature was first documented by Joule as early as 1884 [5]. To date, the kinetics of changes in the physical–chemical properties of many silicate glasses at room temperature has been studied on timescales from several hours to decades [6, 7]. On the basis of these data, the two-stage microstructural model of physical ageing was proposed [8]. During the first stage, it is assumed that loosely packed local regions of ~ 0.5 – 1 nm dimensions spontaneously collapse at a rate related to the Johari–Goldstein (JG) β -relaxation, approaching their equilibrium size at a particular ageing temperature [8]. In the

second stage, the elastic energy appearing in the immediate surroundings of these collapsed regions biases the potential energy minimum in a two-site model for oxygen atom displacement and dissipates into the surrounding network via an α -relaxation-controlled mechanism [8]. Consequently, the volume of the glass decreases homogeneously following exponential law kinetics [6–8]. However, silicate glasses, as a rule, are characterized by over-constrained networks and, consequently, very slow kinetics of physical ageing at room temperature, which is far below their glass transition temperature (T_g) [9]. Therefore, the natural physical ageing in these materials (at present, the maximum documented kinetics is for the Joule thermometer, for an ageing duration of about ~ 40 years) [5] is far from complete, which can be estimated by the fictive temperature of the aged glasses [9–13]. As a result, the exponential law, which is assumed for physical ageing kinetics in silicate glasses [6–8], can be only a partial case describing the initial part of the below- T_g relaxation kinetics. On the other hand, the full physical ageing

kinetics in oxide glasses can be studied at elevated (near- T_g) temperatures, but its mechanism can be significantly different, owing to a number of reasons like the temperature dependence of the network constraints, etc [14].

In order to develop a realistic picture and understand the fundamental nature of physical ageing below T_g , its complete kinetics should be analysed at various temperatures different from T_g . To date, most of the full kinetics are obtained at temperatures not exceeding ~ 15 – 20 K below T_g , while comprehensive investigations for greater departures from T_g are scarce. In our view, the most suitable objects for kinetic studies of physical ageing could be the chalcogenide glasses (ChGs)—melt-quenched glassy alloys of chalcogen atoms (S, Se, Te, but not O) with some elements from the IV to V groups [15–17]. These materials have lower T_g in comparison to silicate glasses and, as a consequence, they possess faster kinetics of physical ageing at ambient conditions (the relaxation constant τ depends directly on the ageing temperature) [12, 13]. This allows study of an almost complete picture of physical ageing (not an initial part of the ageing kinetics as in the case of silicate glasses) within acceptable experimental timescales (\sim tens of years) [9, 11]. Additionally, the wide glass-forming regions of typical chalcogenide systems permit bulk glasses of the same chemical origin with different fragilities and connectivities that are nearly impossible to realize in silicate glasses [15, 16]. Therefore, it is possible to investigate the influence of these parameters on the physical ageing effects. As model objects, ChGs have several advantages over polymers too. The main one is the possibility, in principle, to obtain high purity and homogeneous materials, which are nearly impossible to achieve in polymers because of the specificity of their fabrication procedure [1, 3]. Then, a typical ChG network is built mostly of covalent chemical bonds and their structural parameters have been evaluated for many years, even if some important discussions remain on their actuality [15–17].

Notwithstanding, a little is known about the kinetics and microstructural mechanisms of physical ageing in ChGs, which became a subject of deep studies only after the discovery of their semiconducting properties in the middle of the 1950s [18]. There are still contradictory data on both the overall possibility of ChG ageing, and the timescale of this process [9, 11, 19, 20]. Simultaneously, a number of peculiarities different from silicate glasses should be noted when studying the physical ageing in ChGs. The much lower dissociation energies of chalcogenide bonds (within the ~ 1.5 – 2.8 eV range) in comparison to that of the Si–O bond (~ 4.6 eV) [15, 17, 21], together with homoatomic chalcogen–chalcogen bond formation (in the case of silicate glasses O–O bonds do not exist) [20], introduce an additional possibility for covalent bond redistribution accompanying the many-body relaxation processes of physical ageing in ChG [22]. Thus, in the case of short chalcogen chains it was established that long-term physical ageing in under-constrained vitreous matrices is accompanied by re-conformation of some Se–Se shared $\text{AsSe}_{3/2}$ pyramids (As–Se–Se–As structural fragments) into directly corner-shared (via As–Se–As bridges) pyramids and Se–Se–Se chain-like fragments [22].

Aligning–shrinkage processes of Se chains followed by general shrinkage of the under-constrained glass network are assumed as the main microstructural mechanisms of physical ageing in Se-rich ChGs [23]. However, the long-time kinetics of physical ageing at ambient conditions has not been studied for any known ChG. Only episodic studies have been performed for some Se-containing compositions (including pure Se) [24], but on timescales of no more than a few months [19, 20]. As we will show in this paper, the timescale is very important owing to the step-wise character of enthalpy relaxation, which can lead to misleading conclusions on the saturation of physical ageing after short periods of isothermal storage [19, 20, 24].

In this paper we analyse the long-term (over 25 years) kinetics of natural (ambient conditions, dark storage) physical ageing in an under-constrained Se-based ChG of the binary As–Se system, studied with the differential scanning calorimetry (DSC) technique. A unified phenomenological description of physical ageing in covalent glasses is being developed on the basis of these results.

2. Experimental details

Samples of binary $\text{As}_x\text{Se}_{100-x}$ glasses ($x = 0, 10, 20, 30$ and 40) were prepared in 1985 by the conventional melt-quenching route in evacuated quartz ampoules from a mixture of high purity (99.999%) As and Se constituents. The furnace was rocked to obtain the most homogeneous melt. All ingots were quenched by switching off the furnace. Then, all samples were sealed in hermetic plastic bags and stored in the dark under average room conditions ($T_a \approx 300$ K) for nearly two decades before our calorimetric experiments. The amorphous state of the as-prepared and aged ChGs was controlled visually by a characteristic conch-like fracture and x-ray diffraction patterns typical for glassy substances. The purity and composition of the samples were confirmed by x-ray photoelectron survey and As/Se 3d core level spectra recorded using a high-resolution Scienta ESCA-300 spectrometer with a monochromatic Al $K\alpha$ source (1486.6 eV) [25].

DSC measurements were performed on a NETZSCH 404/3/F microcalorimeter pre-calibrated with a set of standard elements, the DSC curves being recorded in the ambient atmosphere with a $q = 5$ K min^{-1} heating rate. The same calibration procedure was repeated each time during the routine kinetics measurements. Three independent DSC measurements were performed in each case to confirm the reproducibility of the results. Then, the raw DSC data were processed using the NETZSCH PC software package.

A typical rejuvenation procedure was applied to the 25-year aged samples in order to achieve a state close to the initial as-prepared one [1, 9–11, 26]. It comprised heating of the aged samples above their glass transition temperature (T_g), waiting for equilibrium at $T_g + 30$ K and subsequent cooling in a chosen regime at the same rate ($q = 5$ K min^{-1}). This rejuvenation procedure was performed directly in the NETZSCH 404/3/F microcalorimeter. Then, identical batches of rejuvenated samples were additionally

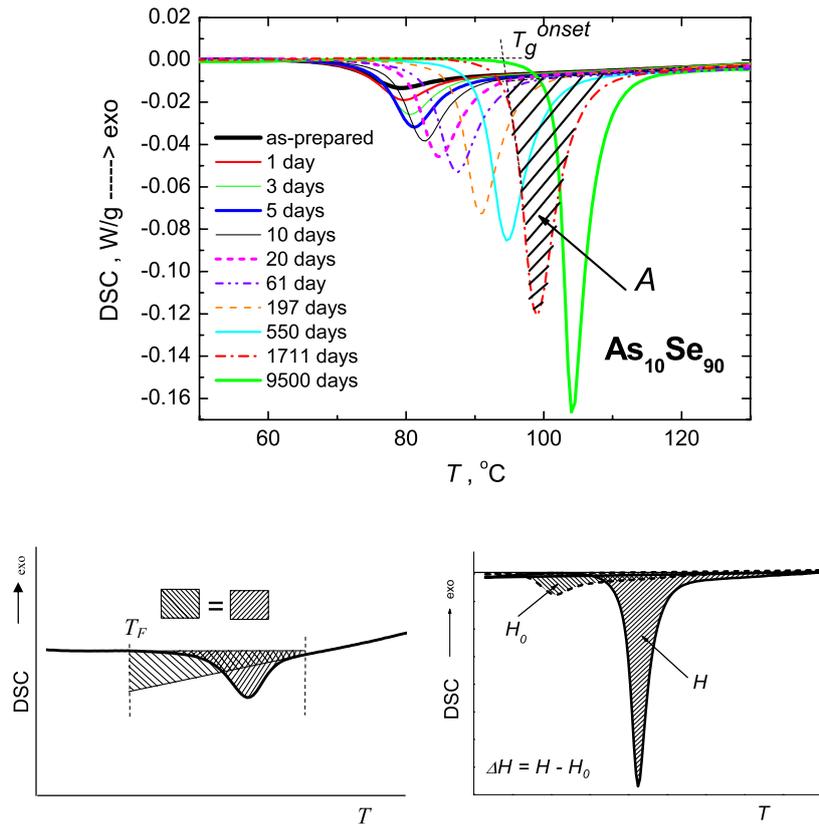


Figure 1. Typical DSC curves recorded after certain periods of storage in the dark at room conditions of $As_{10}Se_{90}$ glass and the method for A and T_g^{onset} determination (upper panel); methods to determine the fictive temperature T_F from the DSC curves and enthalpy changes ΔH (bottom panel).

stored at the same ambient conditions and measured routinely after certain periods (up to 6 years). Thus, the kinetic curves were obtained in a *real-time* and *backward-rejuvenation chronology*, assuming that the rejuvenated samples were quite close to the as-prepared ones.

3. Results

It was shown previously that physical ageing in As_xSe_{100-x} ChGs, associated with slow structural relaxation towards thermodynamic equilibrium of supercooled liquid, was a property of all Se-rich compositions ($x < 40$) [9, 27]. The physical ageing in ChGs with $x > 40$ (as determined from DSC measurements) was not so significant even after prolonged storage at ambient conditions [9, 27]. The effect in the stoichiometric $As_{40}Se_{60}$ composition, which possesses an optimally constrained glass backbone in terms of the Phillips–Thorpe rigidity theory [28], was not observed at all. Thus far, it was concluded that Se-rich ChGs kept at ambient conditions far below the glass transition temperature T_g or subjected to different external influences lose their excess of configurational entropy, enthalpy or free volume (gained at the stage of synthesis) to reach a more favourable thermodynamic state.

This ageing behaviour is well revealed by the DSC technique through distinguishable changes in the glass transition region [9, 11, 27]. A strong endothermic peak

superimposed on the endothermic step of the glass transition signal and its displacement towards higher temperatures, appearing as a result of prolonged storage/annealing [9, 11, 27], photoexposure [29, 30] or maintenance in stationary high-energy radiation fields [31, 32], was attributed to the enthalpy relaxation caused by these factors. The difference in the area under the DSC signal of aged and rejuvenated ChGs, calculated as shown in figure 1 (bottom panel), is directly proportional to the enthalpy losses ΔH . Along with the ΔH value, the changes in the glass transition temperature (estimated as the onset T_g^{onset} , midpoint T_g^{mid} , inflection T_g^{infl} or endset T_g^{end} value) and partial area A under the endothermic peak (figure 1, upper panel), as well as the fictive temperature T_F (calculated according to Moynihan’s area method [10], figure 1) could be analysed as main parameters for characterization of the kinetics of physical ageing in the investigated As_xSe_{100-x} glasses.

Typical DSC curves recorded after some specific periods of natural storage are shown in figure 1 (upper panel) for the example of $As_{10}Se_{90}$ glass. Two obvious processes could be identified in the kinetic behaviour of these curves: the changes in the area A under the endothermic peak (or ΔA provided the area of the rejuvenated sample A_0 is subtracted) and T_g values. The kinetic curves for the T_g^{onset} , T_g^{mid} , T_g^{infl} and T_g^{end} values as determined from DSC scans had essentially the same behaviour. Therefore, in our further consideration

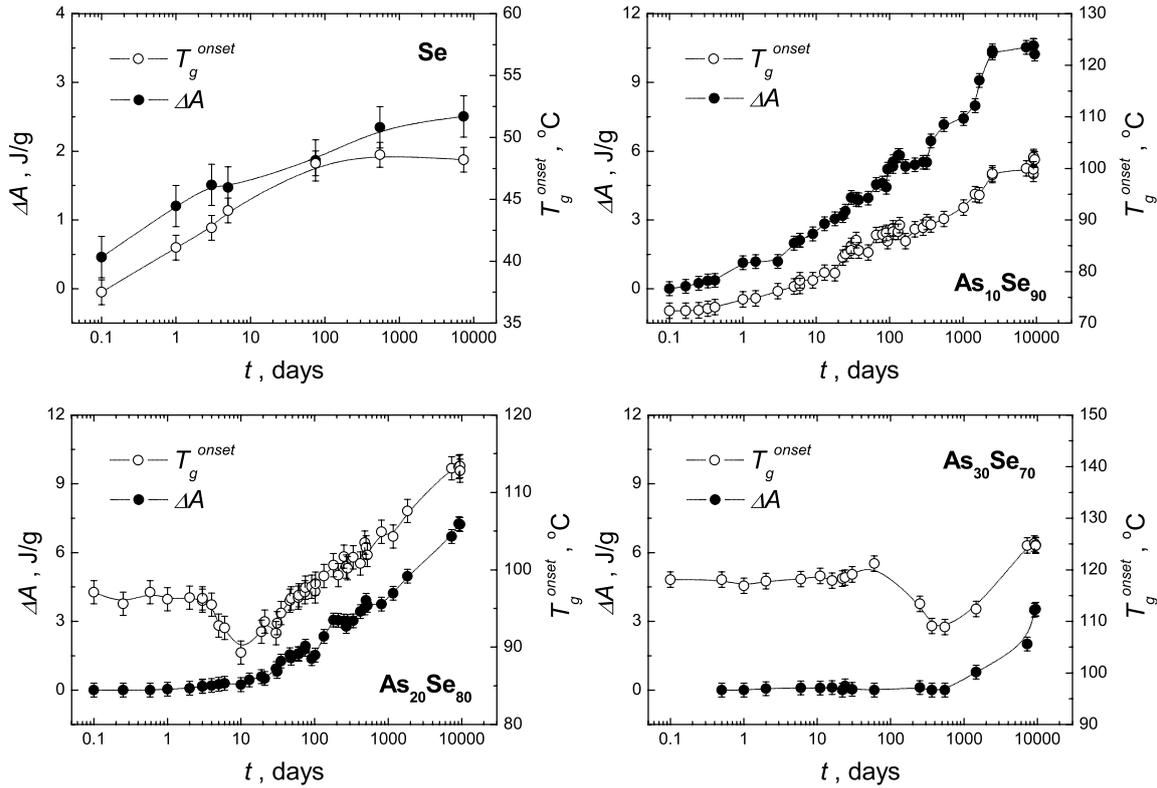


Figure 2. The kinetics of changes in the partial area under the endothermic peak ΔA and the onset value of the glass transition T_g^{onset} caused by long-term dark storage of Se-rich As–Se glasses. The lines are drawn as guides for the eyes.

we shall focus only on the $T_g^{\text{onset}}(t)$ dependence as a typical representative. The kinetic curves for ΔA and T_g^{onset} in $\text{As}_x\text{Se}_{100-x}$ glasses with $x < 40$ are shown in figure 2.

Different regions can be distinguished in the ageing kinetics expressed through T_g^{onset} values. At the beginning stage of physical ageing, a decrease in T_g^{onset} can be noticed (see the curves for $\text{As}_{20}\text{Se}_{80}$ and $\text{As}_{30}\text{Se}_{70}$ glasses in figure 2). It is followed by a region of significant increase in T_g^{onset} during longer periods of natural storage in the dark. The time limits for these regions depend essentially on the fragility (composition) of the investigated ChG. It is clearly seen that the duration of the first region is largest for $\text{As}_{30}\text{Se}_{70}$ glass, which possesses the lowest fragility index among the studied $\text{As}_x\text{Se}_{100-x}$ glasses with $x < 40$. At the same time, in pure glassy Se (as well as in $\text{As}_{10}\text{Se}_{90}$ glass) the first region in the T_g^{onset} kinetics is not observed, most probably because it is too short in comparison with the experimental timescale (determined by the time needed for unambiguous measurement of the DSC curve at a given rate q).

The peculiarities in the ΔA kinetic behaviour can be emphasized too (figure 2). Plateaus in the time dependences, where ΔA does not change essentially, can be noticed for the investigated samples, but the protocol used for the present kinetic studies does not allow unambiguous identification of their characteristics (number, duration, position, etc). More careful *in situ* investigations are needed to fully characterize this effect.

The time dependences of the enthalpy losses ΔH and fictive temperature T_F values, determined according to

Moynihans’ graphic method [10], are shown in figure 3. In general, the fictive temperature T_F is known to approach the ageing temperature (T_a) over time ($T_a \approx 300$ K, in the case of natural physical ageing under consideration) [9, 11]. Therefore, it can serve as a good indicator of the completeness of physical ageing. According to the present data, the physical ageing is fully completed for vitreous Se ($T_F \approx 300$ K) and almost completed for the $\text{As}_{10}\text{Se}_{90}$ sample ($T_F \approx 305$ K) after nearly two decades of ambient storage in the dark. In contrast to these samples, the physical ageing for $\text{As}_{20}\text{Se}_{80}$ and, more markedly, for $\text{As}_{30}\text{Se}_{70}$ ChG is far from complete, since the corresponding T_F values are far from the ageing (room) temperature. Therefore, we have captured different stages of physical ageing in the $\text{As}_x\text{Se}_{100-x}$ glasses: the beginning stage exemplified by vitreous $\text{As}_{30}\text{Se}_{70}$, the intermediate fragment of physical ageing kinetics in $\text{As}_{20}\text{Se}_{80}$ glass, the almost full picture of physical ageing in vitreous $\text{As}_{10}\text{Se}_{90}$ and the saturation stage for the example of vitreous Se. The case of $\text{As}_{10}\text{Se}_{90}$ ChG is the most intriguing one, since it gives the possibility to analyse the overall kinetics at one time.

As is evident from figure 3, the ΔH and T_F kinetic curves exhibit clear plateaus and steep regions testifying to the non-elementary mechanism of physical ageing in the studied $\text{As}_x\text{Se}_{100-x}$ ChGs. Similar peculiarities in ΔH were also observed previously for some other glasses [20, 33, 34] and polymers [35–37], but were usually ignored during interpretation of the results and kinetics analysis. We believe that this circumstance may be a reason for the discrepancy between the timescales of the physical ageing effect in

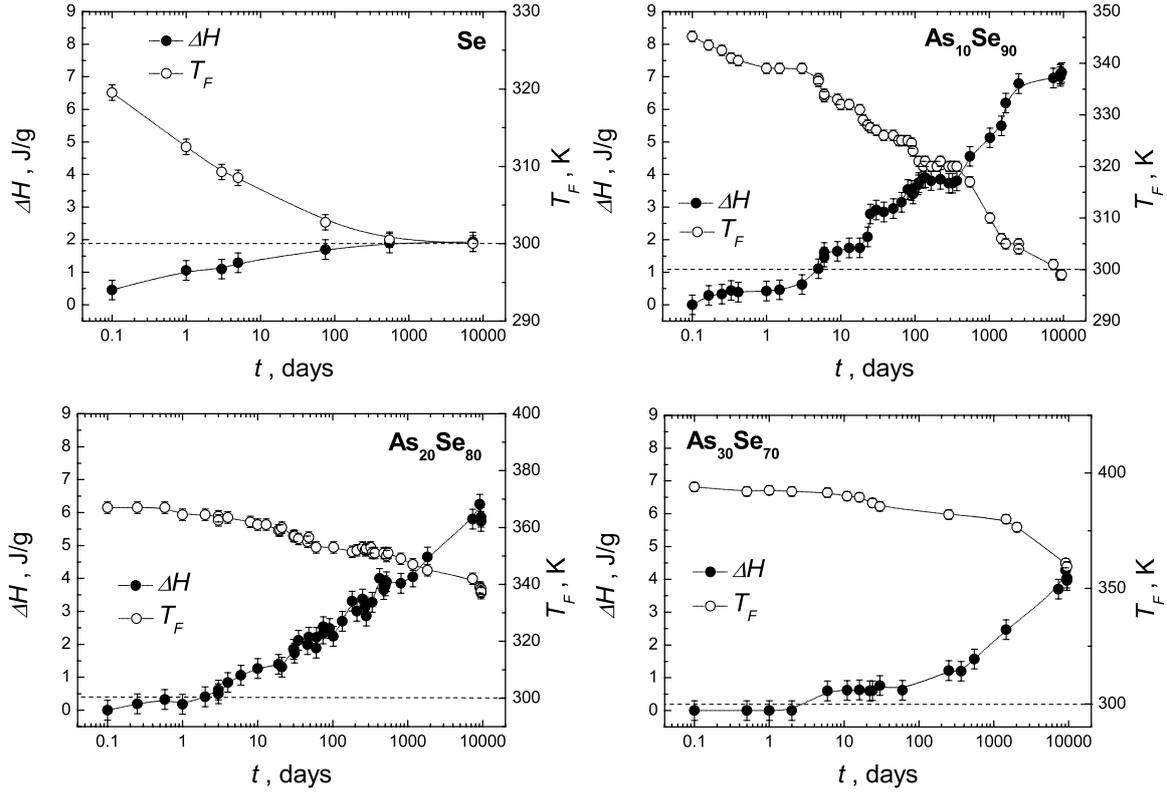


Figure 3. The kinetics of enthalpy losses ΔH and fictive temperature T_F caused by long-term dark storage of Se-rich As–Se glasses. The lines are drawn as guides for the eyes.

ChGs reported by different authors. Dramatic deviations from the extrapolated liquid-like behaviour (when the glass system reaches a limiting T_F different from T_a), observed in some glassy polymers [38, 39], can also be well explained by the existence of plateaus in the $\Delta H(t)$ dependences. In these cases the experiments could be terminated just at the time when the kinetics reached a first noticeable plateau (intermediate stage), while a longer timescale was needed to capture the full behaviour.

Now let us consider the possible mechanisms of the observed physical ageing phenomenon and its appropriate phenomenological description.

4. Discussion

4.1. General assumptions

In general, the time evolution of the departure from equilibrium of any physical quantity, $\delta(t)$, during isothermal ageing can be represented by Kohlrausch's stretched exponential function [12, 13]

$$\delta(t) = \delta_0 \exp \left\{ - \left(\int_0^t \frac{dt}{\tau} \right)^\beta \right\}, \quad (1)$$

where δ_0 is the initial departure of the physical quantity from equilibrium, τ is the effective time constant and the fractional exponent β is a so-called stretching parameter (also known as the non-exponentiality or dispersivity index), ranging between

0 (highly-dispersive process) and 1 (single-exponential relaxation).

Then, the nonlinearity of the structural recovery can be accounted for by an appropriate model for τ determination, like the Tool–Narayananaswamy–Moynihan (TNM) [40] and Kovacs–Aklonis–Hutchinson–Ramos (KAHR) models [41] or the Hodge–Scherer expression [42], which can be considered as equivalent. None of these models address the microscopic nature of structural relaxation, describing only the time behaviour of macroscopic physical quantities. The most frequently used one is the TNM model [40, 43], giving an effective time constant τ with respect to the apparent activation energy E_a as

$$\tau = \tau_0 \exp \left\{ y \frac{E_a}{RT} + \frac{(1-y)E_a}{RT_F} \right\}, \quad (2)$$

where y is the structural factor ($0 \leq y \leq 1$) and R is the ideal gas constant.

This model, however, cannot take account of the temperature or the structural dependence of β , if any [12, 13]. Thus, for structural glasses it is generally assumed that β is ageing time independent as per fitting by the TNM model.

At the same time it is also shown that various relaxing properties including the enthalpy, volume, stress, strain and refractive index behave differently in the glass transition region even for the same sample and have different model parameters [1, 12, 44–48]. The β and τ values can depend also on the waiting time t below the glass transition temperature. In particular, a large increase in τ accompanied by a decrease

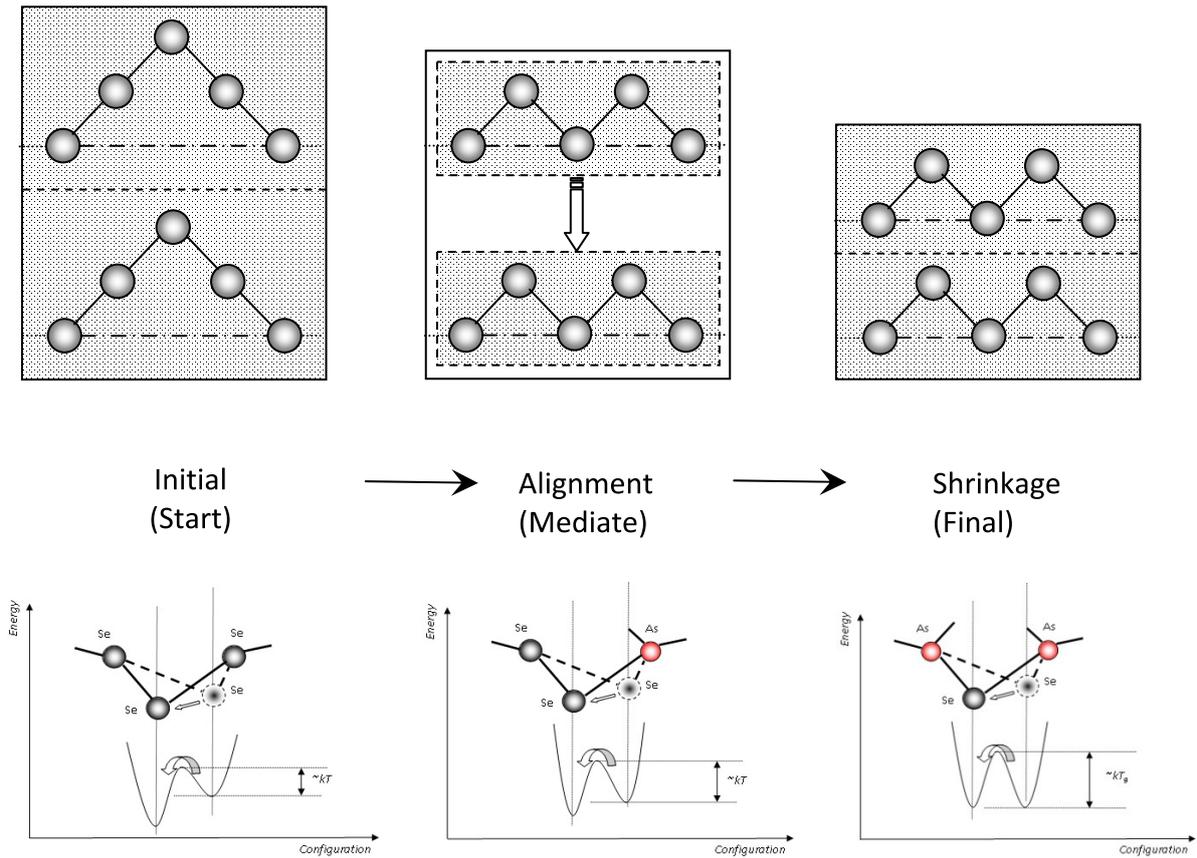


Figure 4. Schematic illustration of the physical ageing mechanism in Se-rich ChGs according to the double-well potential concept.

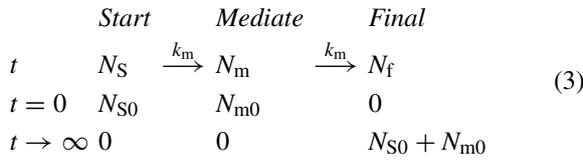
in β upon ageing is testified to by studying colloidal suspensions [12, 46, 48]. On the other hand, increase in β is expected with increase of the nonlinearity γ of the system [42] and temperature (in the case of thermorheologically complex systems) [12, 13, 48, 49]. Again, the lower the $(T_F - T_a)$ value, the faster the glassy system approaches equilibrium because of the $\tau(T)$ dependence [12, 13, 48]. All these correlations cause a lot of complications in developing a master empirical equation capable of describing the physical ageing kinetics in complex systems like ChGs.

In contrast to numerous approaches to explaining equation (1) [12, 13, 47, 48], we start from a pure atomistic understanding of physical ageing in ChGs rather than theoretical modelling. We try to approach the problem of a phenomenological description of physical ageing from its microstructural origin and correlate it with real structural perturbations occurring in a glass network in the deep supercooled regime far below T_g .

Recent experimental investigations and theoretical achievements suggest that physical ageing well below T_g occurs through the Johari–Goldstein (JG) β -relaxation mechanism [12, 50], which can be considered as the initiating process (precedent) for α -relaxation events [12]. Structural data obtained for a number of Se-rich As–Se glasses suggest that the mechanism of physical ageing in ChGs is based on the elementary relaxation acts (twisting) of inner Se atoms within double-well potentials (DWPs) associated with

the high flexibility of chalcogen bonds [22, 23, 50]. In the first approximation, these twisted Se atoms (associated with *cis-trans* reconfigurations of the Se atoms in the chain) [23] can be accepted as elementary JG β -relaxation precursors [50]. They should result in the appearance of collapsed (aligned) Se-based regions in a glass network and, consequently, a local free volume released by twisted atoms (figure 4). Like in the case of oxide glasses [8], we can assume that the appearance (agglomeration) of local free volumes around the collapsed Se-based regions is accompanied by the appearance of elastic strains in their immediate surroundings. We believe that this initial stage of physical ageing is responsible for the lowering of T_g^{onset} during the first period of natural storage [50], as is obvious from figure 2 for $\text{As}_{20}\text{Se}_{80}$ and $\text{As}_{30}\text{Se}_{70}$ glasses. When the accumulated elastic energy is high enough, cooperative rearrangements can occur, eliminating the redundant free volume from the considered local region, which leads to lowering of the internal energy of the system at this particular local scale. When they occur on a larger scale these processes should lead to a general shrinkage of the glass network. Therefore, in the second stage of physical ageing in ChGs, a general shrinkage of the glass network takes place, which can be assigned to a JG β -relaxation-facilitated α -relaxation event (figure 4). We believe that this is a reason for the increase in T_g^{onset} and enthalpy losses ΔH observed with the DSC technique for longer periods of natural storage (figures 2 and 3).

Let us consider the process of twisting of Se atoms within the DWP in more detail. Three possible DWPs can be assumed for Se atoms owing to their immediate surrounding $-\text{Se}-\text{Se}-\text{Se}-$, $=\text{As}-\text{Se}-\text{Se}-$ and $=\text{As}-\text{Se}-\text{As}=\text{}$ (figure 4). Obviously, they differ by energetic parameters, which are determined by the type of surrounding atoms (As or Se). Owing to the magnitude of the physical ageing effect in the investigated $\text{As}_x\text{Se}_{100-x}$ ChGs [9, 27], the lowest barrier for Se twisting is expected for the $\text{Se}-\text{Se}-\text{Se}$ DWP, while the highest one is expected for the $\text{As}-\text{Se}-\text{As}$ surrounding. Let us denote the average relative probability of a Se atom twisting within the above DWPs (or alignment rate) as k_m and the probability of further atomic shrinkage (the shrinkage rate) as k_f . Then, the overall process of physical ageing can be schematically presented by the following diagram:



where N_S denotes the concentration of atomic sites described by the DWP as precursors for Se twisting (N_{S0} is their initial concentration), N_m is the concentration of precursors for shrinkage, which originate from the preliminary stage of DWP twisting (N_{m0} is the initial concentration of twisted Se atoms), N_f is the concentration of atomic sites, affected by general shrinkage of the network.

It is obvious that at each time the overall amount of inter-balanced sites is held,

$$N_S + N_m + N_f = N_{S0} + N_{m0}. \quad (4)$$

Then, if k_m and k_f are independent of time, the classic first-order differential rate equations, which govern the changes in the concentration of twisted (the mediate alignment stage) and densified (the final shrinkage stage) atomic sites, for the considered network can be composed as follows:

$$\frac{dN_m}{dt} = k_m N_S - k_f N_m, \quad \frac{dN_f}{dt} = k_f N_m. \quad (5)$$

Solutions of the rate equations (5) can be considered in terms of the microstructural mechanism for physical ageing illustrated in figure 4.

In the case where the measured property (e.g. T_g , ΔA , ΔH , T_F , etc) is sensitive to both stages of physical ageing in figure 4 (the mediate and final), the following *master equation* should be used to describe the physical ageing kinetics:

$$F(t) = N_m(t) + N_f(t) = N_{m0} + N_{S0}(1 - e^{-k_m t}). \quad (6)$$

We believe that this is the case for the ΔH or T_F kinetics obtained from the DSC data, which are supposed to reflect the overall mechanism of physical ageing.

If the measured physical quantity is sensitive to one of the stages in figure 4 (like volumetric measurements or T_g^{onset} , for example), then each component of the master equation (6)

should be considered separately as follows:

$$N_m(t) = \frac{N_{S0}k_m}{k_f - k_m} e^{-k_m t} - \left(\frac{N_{S0}k_m}{k_f - k_m} - N_{m0} \right) e^{-k_f t}, \quad (7)$$

$$\begin{aligned}
 N_f(t) &= (N_{S0} + N_{m0}) - \frac{N_{S0}k_f}{k_f - k_m} N_{S0} e^{-k_m t} \\
 &+ \left(\frac{N_{S0}k_m}{k_f - k_m} - N_{m0} \right) e^{-k_f t}.
 \end{aligned} \quad (8)$$

Two other possibilities are to be analysed in view of the above solutions.

- (1) The mechanism in figure 4 occurs once during the overall physical ageing with the k_m and k_f rates dependent on the time (reflecting the statistical distribution of the atomic sites involved in the alignment–shrinkage process).
- (2) The process in figure 4 is routinely repeated in such a way that the final stage in figure 4 becomes the initial stage for the subsequent alignment–shrinkage process of the newly formed network (*serial* processes), or, alternatively, the independent relaxation processes in figure 4 with different k_m and k_f rates occur simultaneously (*parallel* processes).

4.2. Time-dependent relaxation rates

In the first case, it is necessary to consider the dependence of the rates k_m and k_f on the time t .

Let us assume the existence of a single fractional exponent β to describe the statistical distributions of atomic sites involved in the alignment–shrinkage processes of physical ageing. Then, in accordance with the general principle of relaxation [51, 52], the Kohlrausch relaxation function (1) can be derived from simple exponential kinetics (6)–(8) by introducing the change of dimensionless variable $kt \rightarrow (kt)^\beta = \xi$, where $0 \leq \beta \leq 1$, $k = k_m + k_f$. In this case we start with a new set of rate equations with respect to ξ

$$k \frac{dN_m}{d\xi} = k_m N_S - k_f N_m, \quad k \frac{dN_f}{d\xi} = k_f N_m. \quad (9)$$

By solving equations (9) in the same manner as (5), we obtain a new *dispersivity-related master equation* instead of the previous (6)

$$F(t) = N_m(t) + N_f(t) = N_{m0} + N_{S0} \left(1 - e^{-\left(\frac{t}{\tau_m}\right)^\beta} \right) \quad (10)$$

with individual components defined as

$$\begin{aligned}
 N_f(t) &= (N_{S0} + N_{m0}) - \frac{N_{S0}k_f}{k_f - k_m} e^{-\left(\frac{t}{\tau_m}\right)^\beta} \\
 &+ \left(\frac{N_{S0}k_m}{k_f - k_m} - N_{m0} \right) e^{-\left(\frac{t}{\tau_f}\right)^\beta},
 \end{aligned} \quad (11)$$

$$N_m(t) = \frac{N_{S0}k_m}{k_f - k_m} e^{-\left(\frac{t}{\tau_m}\right)^\beta} - \left(\frac{N_{S0}k_m}{k_f - k_m} - N_{m0} \right) e^{-\left(\frac{t}{\tau_f}\right)^\beta}, \quad (12)$$

where $\tau_f = \frac{1}{k_f^\beta}$, $\tau_m = \frac{1}{k_m^\beta}$ and $k_f \neq k_m$.

Table 1. Fitting parameters describing the relaxation kinetics of physical ageing in glassy As–Se with respect to equation (10).

Glass composition	Effective time constant, τ_m (days)	Non-exponentiality index, β
Se	$\sim 2 \times 10^{-1}$	0.16
As ₁₀ Se ₉₀	$\sim 7 \times 10^2$	0.25
As ₂₀ Se ₈₀	$\sim 10^3$	0.28
As ₃₀ Se ₇₀	$\sim 10^5$	0.35

A straightforward fitting of the experimentally measured $\Delta H(t)$ curves with equation (10) gives τ_m and β values as summarized in table 1. It can be seen that the further we are from completeness of physical ageing, the higher β is. These changes, however, are not very drastic, varying around the 0.30 ± 0.05 value for glasses with As content (table 1). This value is typical for polymer materials, having β in the range of 0.2–0.3 [1, 48]. According to the obtained data, a slight decrease in the β parameter is expected during physical ageing, in good agreement with studies in colloidal suspensions [12, 46]. On the other hand, the effective time constant τ_m increases by over ~ 6 orders of magnitude with increasing As content from 0 to 30 at.% in the samples (table 1) or, equivalently, with increasing connectivity of their glass backbone, which determines T_g . Such a drastic dependence is characteristic for the time constant of α -relaxation with changing T_a/T_g (in our case $T_a \approx 300$ K, while T_g changes with composition) [13].

A few partial cases of spontaneous structural relaxation need to be discussed in addition to the above general solutions (10)–(12). The first one is due to the case when the as-prepared glass started to age with zero population of atomic sites in the mediate state of diagram (3). This hypothetical condition can be simply derived from the above equations (10)–(12) by putting $N_{m0} = 0$,

$$F(t) = N_m(t) + N_f(t) = N_{S0} \left(1 - e^{-\left(\frac{t}{\tau_m}\right)^\beta} \right), \quad (13)$$

$$N_f(t) = N_{S0} \left(1 - \frac{k_f}{k_f - k_m} e^{-\left(\frac{t}{\tau_m}\right)^\beta} + \frac{k_m}{k_f - k_m} e^{-\left(\frac{t}{\tau_f}\right)^\beta} \right), \quad (14)$$

$$N_m(t) = N_{S0} \frac{k_m}{k_f - k_m} \left(e^{-\left(\frac{t}{\tau_m}\right)^\beta} - e^{-\left(\frac{t}{\tau_f}\right)^\beta} \right). \quad (15)$$

The second situation can occur if the physical ageing is far from completeness or, alternatively, if only the initial stage of physical ageing is captured. Then $N_f \ll N_{S0} + N_{m0}$, so $N_S \approx N_{S0} + N_{m0} - N_m$ and $N_f(t)$ attains a mixed stretched-power-exponential form

$$N_f(t) = \frac{k_f(k_f N_{m0} - k_m N_{S0})}{k} + \frac{k_f k_m}{k} (N_{S0} + N_{m0}) \times (kt)^\beta - \frac{k_f(k_f N_{m0} - k_m N_{S0})}{k} e^{-(kt)^\beta}. \quad (16)$$

At the same time, the $N_m(t)$ remains its stretched exponential behaviour

$$N_m(t) = \frac{k_m}{k} (N_{S0} + N_{m0}) + \frac{k_f N_{m0} - k_m N_{S0}}{k} e^{-(kt)^\beta}. \quad (17)$$

In this case, the general form of the master equation determined as a sum of equations (16) and (17) includes an additional power-law functional component, which indeed was experimentally observed in the relaxation kinetics of many glass formers and is also known as a ‘glass’ relaxation function [53]. Additionally, if no atomic sites are in the initial moment in the mediate state ($N_{m0} = 0$), equations (16) and (17) can be further simplified as follows:

$$N_f(t) = \frac{k_f k_m N_{S0}}{k} (e^{-(kt)^\beta} + (kt)^\beta - 1), \quad (18)$$

$$N_m(t) = \frac{k_m N_{S0}}{k} (1 - e^{-(kt)^\beta}). \quad (19)$$

Several important conclusions can be drawn from the above considerations. First of all, if the measured physical quantity reflects both processes (the mediate and final stages), stretched exponential relaxation is expected for physical ageing. Otherwise, if the measured physical quantity depends more on the changes occurring during the first or second stage of ageing, the corresponding kinetic curves will be more complicated, involving superposition of different functions.

4.3. Complex scenario of relaxation

Another way to obtain the Kohlrausch relaxation function (1) is to assume the mathematical approximation of the physical ageing by a weighted superposition of separate contributions from single-exponential Debye relaxation processes [54, 55],

$$F(t) = \int_0^\infty g(\tau) e^{-\frac{t}{\tau}} d\tau. \quad (20)$$

Such an assumption was frequently used in the past to interpret the dispersion of structural α -relaxation as a superposition of exponential relaxation processes with different relaxation times τ_i weighted by g_i [12, 54, 55]. Macroscopic mechanical and dielectric measurements never supported or refuted this interpretation. Whether the stretched exponential behaviour of the relaxation originates from exponentially relaxing heterogeneous domains or intrinsic non-exponentially relaxing ones is still a subject of rigorous debate within the scientific community.

As follows from figure 5, the overall relaxation function describing the ΔH kinetics in As₁₀Se₉₀ glass (with almost complete physical ageing) behaves in a manner like a *sequence (series)* of continuously growing inputs, each of them being represented by a single-exponential function with individual τ_i . Altogether, they can be well enveloped by a generalized stretched exponential function with $\beta = 0.25$ and $\tau \cong 7 \times 10^2$ days (figure 5). Arbitrarily, the same result can be obtained by assuming a superposition of *parallel* processes, which involve independent single-exponential relaxators of growing time constants (from days to years, see figure 5) and magnitudes. A similar picture was developed on the basis of hierarchically constrained dynamics by Palmer *et al* [55], showing that a series interpretation is more plausible.

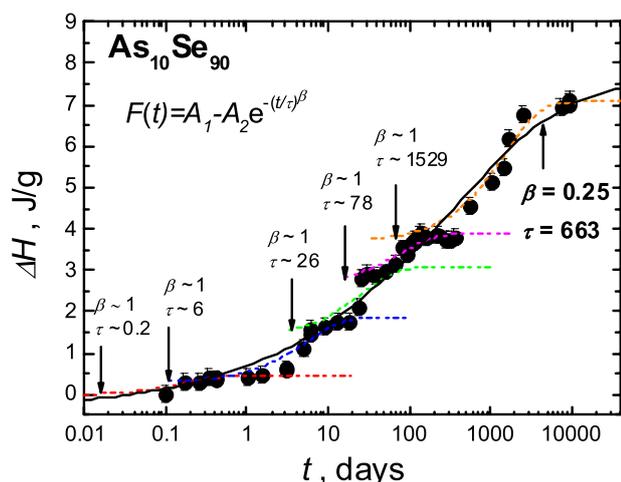


Figure 5. A fit (solid curve) of the experimental $\Delta H(t)$ data of $\text{As}_{10}\text{Se}_{90}$ glass with a stretched exponential relaxation function of the type of equation (10) (τ is given in days, A_1 and A_2 are constants). Fitting curves (dashed) and corresponding fit parameters (τ and β) are also shown for each observed steep region. The parameter β approaches unity for individual region fits, but retains an ~ 0.25 value for the overall kinetics.

Therefore, from the present findings, it can be speculated that the stretched exponential α -relaxation in ChGs originates from series JG β -relaxation processes, each of them being described by a simple single-exponential function. Within this assumption, the α -relaxation-controlled event can be considered as a termination process for JG β -relaxation, which triggers the system into the ‘initial’ state in figure 4. Then, all of the processes start as before, but with growing energetic barriers and time constants involved.

This picture is supported by recent investigations of the atomic dynamics at the nanoscale in network glasses [56]. The proposed phenomenological model can also explain the exponential behaviour of natural physical ageing in silicate glasses [6–8]. In the latter case, the beginning stage of the physical ageing is captured and, therefore, it should be well fitted by a simple exponent rather than a stretched exponential function. This conclusion is well confirmed by the present studies, where the fractional parameter β , used to describe the overall $\Delta H(t)$ kinetics, increases with departure from completeness of physical ageing, the tendency corresponding to transition from $\text{As}_{10}\text{Se}_{90}$ towards $\text{As}_{30}\text{Se}_{70}$ glass (table 1).

5. Conclusions

Despite the extensive experimental and theoretical work on the problem of physical ageing in network glasses, our understanding of this phenomenon is still at the stage of infancy. Thus, contrary to expectations, the kinetics of changes in the onset value of the glass transition temperature (T_g), the partial area (A) under the endothermic peak, the enthalpy losses (ΔH) and the fictive temperature (T_F) caused by storage of Se-rich As–Se glasses in the dark at room temperature for ~ 25 years exhibit a well-expressed step-wise character, showing some kinds of plateaus and

steep regions. A phenomenological description can be derived sufficiently from the alignment–shrinkage microstructural mechanism of physical ageing. In particular, exponential, stretched exponential and power-law relaxation functions can be obtained directly within the developed approach by choosing appropriate controlled parameters and starting conditions, postulating time dependence/independence of the relaxation rates or assuming superposition of parallel/sequent alignment–shrinkage processes with different relaxation times. According to the experimentally obtained enthalpy relaxation kinetic curves, the latter possibility is more plausible. To fully confirm the proposed phenomenological model one needs to measure the full kinetics of physical ageing at various temperatures in detail, using glasses of different fragilities and network dimensionalities (connectivities). The obtained conclusions can be generalized towards a wider class of materials, including oxide glasses and glassy polymers.

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