

This is a repository copy of *The activation energy temperature dependence for viscous flow of chalcogenides*.

White Rose Research Online URL for this paper: <u>https://eprints.whiterose.ac.uk/213343/</u>

Version: Published Version

Article:

Mashanov, A.A., Ojovan, M.I. orcid.org/0000-0001-8928-4879, Darmaev, M.V. orcid.org/0000-0001-5270-5860 et al. (1 more author) (2024) The activation energy temperature dependence for viscous flow of chalcogenides. Applied Sciences, 14 (10). 4319. ISSN 2076-3417

https://doi.org/10.3390/app14104319

Reuse

This article is distributed under the terms of the Creative Commons Attribution (CC BY) licence. This licence allows you to distribute, remix, tweak, and build upon the work, even commercially, as long as you credit the authors for the original work. More information and the full terms of the licence here: https://creativecommons.org/licenses/

Takedown

If you consider content in White Rose Research Online to be in breach of UK law, please notify us by emailing eprints@whiterose.ac.uk including the URL of the record and the reason for the withdrawal request.



eprints@whiterose.ac.uk https://eprints.whiterose.ac.uk/





Article The Activation Energy Temperature Dependence for Viscous Flow of Chalcogenides

Alexey A. Mashanov¹, Michael I. Ojovan^{2,3,*}, Migmar V. Darmaev^{1,4}, and Irina V. Razumovskaya⁵

- ¹ Department of General and Theoretical Physics, Banzarov Buryat State University, Ulan-Ude 670000, Russia; mashanov@bsu.ru (A.A.M.); darmaev@bsu.ru (M.V.D.)
- ² Department of Materials Science and Engineering, The University of Sheffield, Sheffield S1 3JD, UK
- ³ Department of Radiochemistry, Lomonosov Moscow State University, Moscow 119991, Russia
- ⁴ Institute of Physical Materials Science, Siberian Branch of the Russian Academy of Sciences, Ulan-Ude 670047, Russia
- ⁵ Department of Theoretical Physics, Moscow State Pedagogical University, Moscow 119435, Russia; e-irinarasum9@mail.ru
- * Correspondence: m.ojovan@sheffield.ac.uk; Tel.: +44-788-389-1379

Abstract: For some chalcogenide glasses, the temperature dependence of the activation energy E(T) of viscous flow in the glass transition region was calculated using the Williams–Landel–Ferry (WLF) equation. A method for determining the activation energy of viscous flow as a function of temperature is proposed using the Taylor expansion of the function E(T) using the example of chalcogenide glasses As-Se, Ge-Se, Sb-Ge-Se, P-Se, and AsSe-TISe. The calculation results showed that the temperature dependence of the activation energy for the Ge-Se, As-Se, P-Se, and AsSe systems is satisfactorily described by a polynomial of the second degree, and for Sb-Ge-Se glass by a polynomial of the third degree. The purpose of this work is to compare the values of the coefficients obtained from the Taylor series expansion of E(T) with the characteristics of the E(T) versus $(T - T_g)$ curves obtained directly from the experimental temperature dependence of viscosity. The nature of the dependence E(T) is briefly discussed.

Keywords: glass transition; viscosity; activation energy; WLF equation; chalcogenide glasses

1. Introduction

Viscosity arises because of a transfer of momentum between material layers moving at different velocities and quantifies the resistance of the material to flow with the Frenkel equation commonly used for the temperature dependence of viscosity [1–5]:

$$\eta = \eta_0 \exp\left(\frac{E}{RT}\right),\tag{1}$$

where η_0 is the pre-exponential coefficient, *E* is the activation energy of viscous flow, *T* is the temperature, and *R* is the universal gas constant. For glass-forming melts, the activation energy of viscosity is a well-defined constant only asymptotically at high temperatures at which the viscosities are low, i.e., $log(\eta/Poise) < 3$ and $E = E_L = 80-300$ kJ/mol [2], whereas the pre-exponential coefficient η_0 was shown to be the high-temperature viscosity limit within logarithmic approximation [4]. In the glass transition range of temperatures $T \sim T_g$, where T_g is the glass transition temperature, the activation energy of the viscous flow of glass-forming melts has a strong temperature dependence E = E(T) increasing on the decrease in temperature from its lowest value E_L in the melts ($T >> T_g$) to its highest value in the glassy state ($T < T_g$) $E_H = 400-800$ kJ/mol [2]. Following [3–6], we observe that the viscous flow in glass-forming melts exhibits three temperature ranges, as illustrated by Figure 1.



Citation: Mashanov, A.A.; Ojovan, M.I.; Darmaev, M.V.; Razumovskaya, I.V. The Activation Energy Temperature Dependence for Viscous Flow of Chalcogenides. *Appl. Sci.* 2024, 14, 4319. https://doi.org/ 10.3390/app14104319

Academic Editors: Alejandro Rodríguez Pascual and Luigi Biolzi

Received: 20 March 2024 Revised: 3 May 2024 Accepted: 16 May 2024 Published: 20 May 2024



Copyright: © 2024 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/).



Figure 1. The viscosity regimes of chalcogenide glasses and melts [6].

Namely, the temperature regimes of viscosity are as follows:

- 1. Low temperatures $T < T_g$: isostructural Arrhenius-type law viscosity of the glass ($E = E_H$);
- 2. Intermediate temperatures $T_g < T < T_A$: non-Arrhenius-type law formally expressed with an exponent *E* with variable activation energy of viscosity E = E(T);
- 3. High temperatures $T > T_A$: Arrhenius-type law viscosity ($E = E_L$).

The crossover temperature T_A is assumed to be close to the liquidus temperature T_{liq} , at which the material is completely melted [5]. It was recently shown [7] that regardless of the type of glass-forming liquid, the crossover temperature is given by the universal Equation (2):

$$T_A = kT_m,\tag{2}$$

where T_m is the melting temperature and $k = 1.1 \pm 0.15$ (see for details Figure 3b of reference [7]). In addition, the T_A of certain glass families, such as float and nuclear waste glasses, can be defined using a fixed viscosity value which is independent of composition [8]. Figure 1 also provides the universal viscosity equation [3], which is valid at all temperatures although it requires at least four parameters to be fitted to experimental data–the so-called Douglas–Doremus–Ojovan (DDO) double-exponential model (see Chapter 8 of Ref. [8]).

This work is devoted to estimating the temperature dependence of the activation energy of viscous flow for several chalcogenide compositions within the temperature range (2): $T_g < T < T_A$. Chalcogenide vitreous materials are used in the development of nonvolatile memory techniques both for selectors and storing data in memory cells. Various compositions are used in infrared and fiber optics, sensors and devices utilizing the properties of these glasses. Research of such materials has great prospects in electronics and optics. We have selected chalcogenide glasses as the main objects of the study because for these materials there are experimental data on viscosity available in a wide temperature range. For them, the expansion of the activation energy function E(T) into a Taylor series is acceptable. The method proposed can be expanded to include other glass-forming compositions.

2. Modeling the Viscosity

Many useful models of the viscosity of amorphous materials have been proposed for the temperature range (2) (see the overviews [1–5]), among which we can note the two most developed and frequently used models, namely the Vogel–Fulcher–Tammann (VFT) equation [9–11], and the Williams–Landel–Ferry (WLF) equation [12,13]:

$$\eta = \eta_0 \exp\left(\frac{B_0}{T - T_0}\right),\tag{3}$$

$$\log a_T = -C_1 \frac{T - T_r}{T - T_r + C_2},$$
(4)

where η_0 and B_0 are temperature-independent constants and material-dependent parameters, a_T is the relative viscosity $a_T = \eta(T)/\eta(T_g)$, C_1 and C_2 are empirical temperatureindependent constants, T_r is the reference temperature typically taken as the glass transition temperature $T_r = T_g$. The validity of these equations has been demonstrated in many works for various glass-forming systems, e.g., see Refs. [1-5,14-20]. We note that the activation energy of viscous flow starts to decrease exactly at temperatures exceeding T_g , see e.g., Figure 1 of Ref. [5] and Figures 1, 2, and 4 of Ref. [19]. The WLF equation is known to correctly describe the molecular kinetic processes in the glass transition region and provide fairly exact temperature dependence of relaxation time $\tau(T)$ and the viscosity $\eta(T)$ within the glass transition range of temperatures for amorphous materials of various natures such as polymers, organic, and inorganic glasses, and metallic amorphous alloys [14–20]. It is known that the WLF equation can be derived in [16] without specifying the functional dependence $\eta(T)$ based on the series expansion of function $ln(\eta(T))$ near the T_g with respect to the small dimensionless parameter $\lambda = (T - T_g)/T_g \ll 1$. This led to following Equation (5) in terms of natural logarithms (ln) rather than decimal (log) logarithms while assuming $T_r = T_g$:

$$\ln a_T = -\left(\frac{A^2}{B}\right) \frac{T - T_g}{T - T_g + \left(\frac{A}{B}T_g\right)}, \text{ where } A = -\frac{\partial \ln \eta}{\partial \left(T/T_g\right)} \bigg|_{T = T_g}, B = \frac{1}{2} \frac{\partial^2 \ln \eta}{\partial \left(T/T_g\right)^2} \bigg|_{T = T_g}$$
(5)

From here, the WLF equation constants C_1 and C_2 acquire a physical meaning, expressed through the derivative parameters A and B:

$$C_1 = \frac{A^2}{B}, \text{ and } C_2 = \frac{A}{B}T_g, \tag{6}$$

Additionally, we observe that the VFT and WLF equations are equivalent if we suppose that:

Either
$$B_0 = C_1 C_2 ln 10$$
 in (4) or $B_0 = C_1 C_2$ in (5), and $T_0 = T_g - C_2$ (7)

Equating Formulas (1) and (3) and taking into account that $\eta_0 = const$, we obtain the following expression for determining the activation energy of viscous flow on temperature:

$$E(T) = \frac{B_0 RT}{T - T_0} \tag{8}$$

Accounting for (7) we can rewrite it using (5) as:

$$E(T) = \frac{C_1 C_2 R T}{T - T_g + C_2}$$
(9)

We conclude from (9) that in order to calculate the variable activation energy of viscous flow within the temperature range (2) it is necessary to know the values of three parameters: C_1 , C_2 , and T_g . From Equation (9) it follows the following expression for determining the activation energy at the liquid-glass transition $E_g = E(T_g)$:

$$E_g = C_1 R T_g. \tag{10}$$

The validity and usefulness of Equations (9) and (10) were checked for several chalcogenide materials, as described below.

The resulting Equations (9) and (10) can be effectively used to predict E_g . The calculation results show a good agreement with data obtained using relaxation spectrometry methods. For example, it was found that the activation energy at the glass transition temperature of silicate glass is 241 kJ/mol according to Formula (10), and $E_g = 242$ kJ/mol according to relaxation spectroscopy data [21].

3. Materials and Methods

We have analyzed the activation energies of the viscous flow within the temperature range (2) for the following three families of glasses: As-Se, Sb-Ge-Se, and Ge-Se. Figures 2–4 show the temperature dependence of the activation energy E(T). Theoretical dependences were calculated using Equation (9), whereas the points in the plots represent experimental data taken from [20–25].



Figure 2. Temperature dependence of the activation energy of viscous flow E(T) of As-Se molten glass. The content of As is 3 mol.%, Se—97 mol.%. Points and experimental data from [20], curve calculation using Formula (9), $T_g = 316$ K.



Figure 3. Temperature dependence of the activation energy of viscous flow E(T) for Sb-Ge-Se molten glass. Sb content—20 mol.%, Ge—10 mol.%, Se—70 mol.%. Points and experimental data from [24], curve calculation using Formula (9), $T_g = 424$ K.

The dots in these figures indicate the values obtained from the logarithms of viscosity $log(\eta(T))$ according to reference [19] and using the equation:

$$E(T) = ln10 \times RT[log(\eta(T)) - log(\eta_0)].$$

$$(11)$$

Figures 2–4 reveal that the experimental points practically coincide with those calculated, which is confirmed by the low values of the Pearson chi-square divergence criterion. This confirms the good applicability of the WLF equation. Table 1 presents data for two empirical coefficients of the WLF equation and the glass transition temperature for the analyzed compositions, as well as the activation energy of the liquid-glass transition at T_g , calculated using Formula (10). The viscosity of the chalcogenide systems under consideration at various temperatures was measured by the penetration method with error on a logarithmic scale ± 0.05 [20–25].



Figure 4. Temperature dependence of the activation energy of viscous flow E(T) for Ge-Se molten glass. Ge content—92 mol.%, Se—8 mol.%. Points and experimental data from [22], curve calculation using Formula (9), $T_g = 352$ K.

Table 1. Parameters of WLF Equation (4) and activation energy of the glass transition process at $T = T_g$ (data from Refs. [20–25] were used).

N₂		Composition, mo	ти	0	0 K	E 11/	
	As		Se	-1_{g} , K	\mathcal{C}_1	С ₂ , К	$E_{g_{f}}$ KJ/mol
1.	3		97	316	11.5	39.0	30.1
2.	5		95	320	12.3	45.9	32.8
3.	10		90	331	15.4	87.1	42.6
4.	25		75	364	17.5	152.3	53.0
5.	50		50	440	15.1	130.5	55.2
	Ge		Se				
1.	8		92	352	14.1	82.9	41.2
2.	10		90	356	23.0	237.3	68.2
3.	15		85	396	18.3	209.6	60.2
4.	17		83	411	17.5	224.0	60.0
5.	20		80	430	20.6	327.7	73.7
	Sb	Ge	Se				
1.	5	10	85	370	20.5	206.4	63.2
2.	10	10	80	391	15.3	122.3	49.8
3.	5	15	80	408	14.2	140.9	48.3
4.	15	10	75	403	14.7	130.3	49.3
5.	10	15	75	422	21.1	233.5	74.0
6.	20	10	70	424	12.3	87.6	43.5
7.	15	15	70	445	13.6	118.0	50.3
8.	10	20	70	480	10.6	85.4	42.6
9.	20	15	65	489	10.8	66.1	43.9

4. Theoretical

Let us expand the temperature-dependent activation energy of viscous flow E(T) near the T_g into a Taylor series in terms of a small temperature increment with a small parameter available in the system $\lambda = (T - T_g)/T_g \ll 1$, limiting the expansion to the first three terms of the series [24]:

$$E = E_g - D_1 (T - T_g) + D_2 (T - T_g)^2 \text{ where } D_1 = -\left(\frac{\partial E}{\partial T}\right)_{T_g}, D_2 = \frac{1}{2} \left(\frac{\partial^2 E}{\partial T^2}\right)_{T_g}.$$
 (12)

The small parameter in expansion (12) is the dimensionless quantity λ , but T_g to the first and second powers is hidden in the coefficients D_1 and D_2 . From Equation (1), it follows that:

$$-\frac{\partial \ln \eta}{\partial (T/T_g)} = -\frac{T_g}{R} \left[\frac{1}{T} \left(\frac{\partial E}{\partial T} \right) - \frac{E}{T^2} \right]$$
(13)

According to Equation (5), for parameter *A*, we obtain the relation:

$$A = -\frac{\partial ln \eta}{\partial (T/T_g)} \bigg|_{T=T_g} = -\frac{1}{R} \left[\left(\frac{\partial E}{\partial T} \right)_{T_g} - \frac{E_g}{T_g} \right] = \frac{D_1}{R} + \frac{E_g}{RT_g},$$
(14)

where we accounted for the definition of D_1 from (12). The parameter A is given in Equations (5) and (6) by:

$$A = \frac{C_1}{C_2} T_g \tag{15}$$

Equations (14) and (15) in turn give the following equality:

$$D_1 = \frac{C_1 R T_g}{C_2} - \frac{E_g}{T_g},$$
 (16)

which considering $E_g = C_1 R T_g$ transforms into the following equation:

$$D_1 = C_1 R \left(\frac{T_g}{C_2} - 1 \right) \tag{17}$$

We find the formula for coefficient D_2 from the calculations as follows:

$$\frac{1}{2}\frac{\partial^2 ln \eta}{\partial (T/T_g)^2} = \frac{T_g^2}{2}\frac{\partial}{\partial T}\left(\frac{\partial ln \eta}{\partial T}\right) = \frac{T_g^2}{2R}\frac{\partial}{\partial T}\left[\frac{1}{T}\frac{\partial E}{\partial T} - \frac{E}{T^2}\right] = \frac{T_g^2}{2R}\left\{\frac{1}{T}\left(\frac{\partial^2 E}{\partial T^2}\right) - \frac{1}{T^2}\left(\frac{\partial E}{\partial T}\right) - \frac{1}{T^2}\left(\frac{\partial E}{\partial T}\right) + \frac{2E}{T^3}\right\}$$
(18)

The coefficient *B* is given accordingly by:

$$B = \frac{1}{2} \frac{\partial^2 ln \eta}{\partial (T/T_g)^2} \bigg|_{T=T_g} = \frac{T_g}{R} \bigg\{ D_2 + \frac{D_1}{T_g} + \frac{E_g}{T_g^2} \bigg\}$$
(19)

Further, in this relation for D_1 , we consider expression (16), resulting in:

$$B = \frac{T_g}{R} \left\{ D_2 + \frac{1}{T_g} \left(\frac{C_1}{C_2} R T_g - \frac{E_g}{T_g} \right) + \frac{E_g}{T_g^2} \right\} = \frac{T_g}{R} \left\{ D_2 + \frac{C_1 R}{C_2} \right\}$$
(20)

From (6) and (15), we have equality $B = C_1(T_g/C_2)^2$, which, on substitution into (20), finally gives D_2 :

$$D_2 = \frac{C_1}{C_2} R\left(\frac{T_g}{C_2} - 1\right) \tag{21}$$

If we go a slightly different route and use a joint transformation of expressions (12) and (1) with the concomitant finding of differentials A and B, then we can obtain equivalent data. Thus, the activation energy of viscous flow is represented in the form of a Taylor series in the temperature range (2) in the form:

$$E = E_g \left[1 - \left(\frac{1}{C_2} - \frac{1}{T_g} \right) (T - T_g) + \frac{1}{C_2} \left(\frac{1}{C_2} - \frac{1}{T_g} \right) (T - T_g)^2 \right] = E_g \left\{ 1 - \left(\frac{1}{C_2} - \frac{1}{T_g} \right) (T - T_g) \left(1 - \frac{1}{C_2} \right) (T - T_g) \right\}$$
(22)

The following assumption holds: in a given series, it is possible to limit ourselves to only the linear term if it is much larger than the next one. This is possible if the following condition is met:

(

$$T - T_g) << C_2 \tag{23}$$

Thus, based on three known quantities (C_1 , C_2 , and T_g), and using Equations (12), (18), and (22), it is possible to calculate the dependence of the activation energy of viscous flow on the temperature in the temperature range (2). Table 2 contains the coefficients D_1 and D_2 for the chalcogenide glasses analyzed, which are compared with the characteristics of the activation energy E(T) versus $(T - T_g)$ plots obtained directly from the experimentally known temperature dependence of viscosity [20–25].

Table 2. Parameters of Equations (17) and (21). Data for viscosities used are from Refs. [20-25].

	Composition mal 9/		Calculated Using (17) and (21)		Polynomial of 2nd Degree			Polynomial of 3rd Degree			
N⁰	Compo	osition,	, MOI. %	<i>D</i> ₁	<i>D</i> ₂	D_1	D ₂	R ²	D_1	D ₂	R ²
	Sb	Ge	Se								
1.	5	10	85	0.135	0.0007	0.446	0.0013	0.995	0.261	0.0030	0.998
2.	10	10	80	0.280	0.0023	0.372	0.0050	0.998	0.293	0.0019	0.995
3.	5	15	80	0.225	0.0016	0.361	0.0010	0.998	0.316	0.0052	0.995
4.	15	10	75	0.256	0.0020	0.554	0.0022	0.995	0.399	0.0012	0.999
5.	10	15	75	0.141	0.0006	0.310	0.0018	0.998	0.213	0.0024	0.999
6.	20	10	70	0.394	0.0045	0.529	0.0021	0.998	0.524	0.0003	0.999
7.	15	15	70	0.313	0.0027	0.447	0.0013	0.995	0.324	0.0017	0.999
8.	10	20	70	0.409	0.0048	0.326	0.0070	0.998	0.291	0.0001	0.993
9.	20	15	65	0.575	0.0087	0.482	0.0014	0.991	0.358	0.0031	0.997
Ge Se											
1.	8		92	0.380	0.0046	0.514	0.0001	0.988	0.779	0.0063	0.998
2.	10		90	0.496	0.0004	0.547	0.0015	0.998	0.651	0.0029	0.999
3.	15		85	0.135	0.0006	0.342	0.0006	0.998	0.398	0.0012	0.999
4.	17		83	0.122	0.0005	0.308	0.0005	0.998	0.385	0.0012	0.998
5.	20		80	0.153	0.0002	0.272	0.0003	0.998	0.250	0.002	0.998
	As		Se								
1.	3		97	0.677	0.0173	0.682	0.0028	0.980	1.027	0.0107	0.993
2.	5		95	0.611	0.0133	0.756	0.0033	0.987	1.074	0.0108	0.997
3.	10		90	0.360	0.0041	0.773	0.0031	0.988	1.076	0.0092	0.996
4.	25		75	0.203	0.0013	0.488	0.0009	0.997	0.403	0.0003	0.998
5.	50		50	0.298	0.0023	0.486	0.0011	0.987	0.742	0.0047	0.998
	Р		Se								
1.	10		90	0.180	0.0004	0.272	0.0003	0.998	0.289	0.0030	0.998
2.	20		80	0.124	0.0002	0.524	0.0008	0.998	0.459	0.0007	0.998
3.	28.57		71.43	0.100	0.0004	0.236	0.0002	0.999	0.215	0.0018	0.999
4.	40		60	0.064	0.0001	0.019	0.0003	0.998	0.096	0.0001	0.999
	AsSe		TlSe								
1.	66.6		33.4	0.441	0.0053	0.440	0.0017	0.999	0.457	0.0057	0.999
AsSe											
1.	100		0.131	0.0005	0.151	0.0005	0.999	0.146	0.0030	0.989	

Note. The dimensions of coefficients are as follows: $[D_1] = [kJ/mol \cdot K]; [D_2] = [kJ/mol \cdot K^2].$

The parameters of the function E(T) versus $(T - T_g)$ expressed as a polynomial of the second degree were calculated using the Microsoft Excel spreadsheet software, with results shown in Figures 5–7, where the dots indicate the dependence of the activation energy on the temperature difference, obtained according to Formula (1) using experimental data from [20–25].



Figure 5. Results of processing the temperature dependence of the activation energy of viscous flow for As-Se molten glass. The content of As is 3 mol.%, Se—97 mol.%. Points and experimental data taken from [20], curve polynomials.



Figure 6. Results of processing the temperature dependence of the activation energy of viscous flow for Ge-Se molten glass. The content of Ge is 8 mol.%, Se—92 mol.%. Points and experimental data from [22], curve polynomials.

In a sufficiently large temperature range, however, the contribution of the third-degree term in the Taylor series may increase, which affects the estimate of the effective value of D_2 . In this regard, in the calculations of the required energy, a polynomial was used to the appropriate extent. Nevertheless, taking into account the application of this assumption, the data obtained turned out to conform well with the experiment.

Thus, we conclude that the temperature dependence of the activation energy in a wide temperature range for chalcogenide glasses Ge-Se, As-Se, P-Se, As-Se-Tl-Se, and As-Se

is satisfactorily described by a second-degree polynomial, and for Sb-Ge-Se glass by a third-degree polynomial dependence.



Figure 7. Results of processing the temperature dependence of the activation energy of viscous flow for Sb-Ge-Se molten glass. The content of Sb is 20 mol.%, Ge—10 mol.%, Se—70 mol.%. Points and experimental data from [24], curve polynomials.

5. Discussion

As research shows, many substances with disordered structures and initially different natures, such as different classes of glasses, polymers, metal alloys, etc., have similar mechanisms of transitioning from a liquid to a glassy state. This fact is also justified by the discovery in the region of the liquid-glass transition of general rules suitable for different classes of substances [1–4,14–19,26–29]. A significant increase in the activation energy of viscous flow with decreasing temperature is a consequence of a change in the configuration of the structure of the melt, which passes into the glassy state [3,30,31].

It is known [3] that the activation energy of a viscous flow consists of a pair of components due to the processes of breaking bonds (formation of defects according to Mott [32]) and due to the movement of broken bonds, called configurons [33]. This division of the above energy into a pair of components was first proposed by Ya. I. Frenkel [1]. It was then further developed in the works of Duglas [34], Angell and Rao [28], Filipovich [30], Nemilov [31], Doremus [35], and later by the Sheffield School of Glass [36], also known as the DDO model [8]. In a more rigorous approach, E(T) should be understood as the free energy of activation, as is customary in the classical works of Eyring [37].

The developed model of delocalized atoms [37-40] assumes that for melts transforming into a glassy state, the activation energy E(T) in Equation (1) is also decomposed into two components:

$$E(T) = E_{\infty} + E_s(T) \tag{24}$$

where E_{∞} is the potential for the transition of a structural kinetic unit (atom, molecule) to a new local position, and $E_S(T)$ is the potential for a configurational change of structure, which is a function of temperature [28,38,39]:

$$E_s(T) = RT \left[exp\left(\frac{\Delta \varepsilon_e}{RT}\right) - 1 \right]$$
(25)

Here $\Delta \varepsilon_e$ is the delocalization energy of the atom, characterizing the critical deviation of the kinetic unit from the point with the minimum energy. Such a deviation of a kinetic unit is possible with a spatial change in its immediate environment. This process can be considered as a transformation of the structural configuration at the local level. The energy of change

in the structure configuration $E_S(T)$ tends to zero in on the case of increasing temperature when $RT \gg \Delta \varepsilon_e$. Then, expression (1), taking into account Equations (24) and (25), takes the form of the Arrhenius equation with one potential E_{∞} .

$$\eta = \eta_0 \exp\left(\frac{E_{\infty}}{RT}\right) \tag{26}$$

Thus, the component $E\infty$ can have the value of the activation energy of the viscous flow at a temperature tending to infinity; in this case $E_{\infty} = E_H$.

When the temperature decreases to values around T_g , the energy begins to decrease exponentially $exp(-\Delta \varepsilon_e/kT)$ [27,38]. As a result of such a sharp decrease, $\Delta \varepsilon_e$ becomes comparable to the energy of thermal vibrations of the lattice (~3 *RT*) and the relative number of delocalized atoms (N_e/N). As a result of a sharp decrease in the delocalization energy, the structure of the glassy substance (melt) begins to compact, and rearrangement of the kinetic unit will require a local change in the configuration in its vicinity, which leads to a sharp increase in the potential for changing the configuration of the structure $E_S(T)$. In this way, we can explain the exponential increase in the activation energy of the melt in the glass transition region. The model noted in the work explains how a change in the relative position of the kinetic units of the structure affects the dynamics of the activation energy values when the temperature changes in the range close to T_g .

6. Conclusions

The article describes the possibilities of determining the activation energy E(T) at various temperatures for the chalcogenide glasses under study. To analyze the dependence of E(T) at temperatures close to the glass transition temperature, the WLF equation can be used as a first approximation with sufficient reliability. A method is shown for expanding the above dependence into a Taylor series in the range near T_g . The calculation results showed that the temperature dependence of the activation energy for the Ge-Se, As-Se, P-Se, AsSe-TISe, and AsSe systems is satisfactorily described by a polynomial of the second degree, and for Sb-Ge-Se glass by a polynomial of the third degree. For Sb-Ge-Se systems, the values of coefficients D_1 and D_2 at corresponding temperatures are in the range from 0.135 to 0.575 kJ/mol·K and from 0.0007 to 0.0087 kJ/mol·K², respectively. For other studied compositions, the values of D_1 and D_2 are approximately in the same ranges. Using the model described in this article, it is shown that the exponential increase in activation energy at T_g follows from an increase in the potential for restructuring the structure during the transition from the liquid to the glassy state.

Author Contributions: Conceptualization, A.A.M. and I.V.R.; methodology, A.A.M. and M.V.D.; validation, A.A.M., M.I.O., M.V.D. and I.V.R.; formal analysis, A.A.M., M.I.O., M.V.D. and I.V.R.; resources, A.A.M.; data curation, A.A.M., M.I.O., M.V.D. and I.V.R.; writing—original draft preparation, M.V.D.; writing—review and editing, A.A.M., M.I.O., M.V.D. and I.V.R.; funding acquisition, A.A.M. and M.V.D. All authors have read and agreed to the published version of the manuscript.

Funding: This research was funded with the support of the Banzarov Buryat State University Federal State Budgetary Educational Institution of Higher Education, grant No. 24-03-01.

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: The original contributions presented in the study are included in the article, further inquiries can be directed to the corresponding author.

Conflicts of Interest: The authors declare no conflicts of interest.

References

- 1. Frenkel, J. Kinetic Theory of Liquids; Oxford University Press: Oxford, UK, 1946.
- 2. Volf, M.B. *Mathematical Approach to Glass;* Elsevier: Amsterdam, The Netherlands, 1988.
- 3. Zaccone, A. Viscosity of Supercooled Liquids. In *Theory of Disordered Solids*; Lecture Notes in Physics; Springer: Cham, Switzerland, 2023; Volume 1015. [CrossRef]
- 4. Zheng, Q.; Mauro, J.C. Viscosity of glass-forming systems. J. Am. Ceram. Soc. 2016, 100, 6–25. [CrossRef]
- 5. Deubener, J. Viscosity of glass-forming melts. In *Encyclopedia of Glass Science, Technology, History, and Culture;* Wiley: New York, NY, USA, 2021; Chapter 4.1; pp. 431–451.
- 6. Ojovan, M.I.; Louzguine-Luzgin, D.V. On Crossover Temperatures of Viscous Flow Related to Structural Rearrangements in Liquids. *Materials* **2024**, *17*, 1261. [CrossRef] [PubMed]
- 7. Galimzyanov, B.; Doronina, M.; Mokshin, A. Arrhenius Crossover Temperature of Glass-Forming Liquids Predicted by an Artificial Neural Network. *Materials* **2023**, *16*, 1127. [CrossRef] [PubMed]
- Hrma, P.; Ferkl, P.; Kruger, A.A. Arrhenian to non-Arrhenian crossover in glass melt viscosity. J. Non-Cryst. Solids 2023, 619, 122556. [CrossRef]
- 9. Vogel, D.H. Das Temperaturabhaengigkeitsgesetz der Viskositaet von Fluessigkeiten. Phys. Zeit. 1921, 22, 645–646.
- 10. Fulcher, G. Analysis of Recent Measurements of the Viscosity of Glasses. J. Am. Ceram. Soc. 1925, 8, 339–355. [CrossRef]
- 11. Tammann, G.; Hesse, W. Die Abhängigkeit der Viscosität von der Temperatur bie unterkühlten Flüssigkeiten. *Z. Anorg. Allg. Chem.* **1926**, *156*, 245–257. [CrossRef]
- 12. Williams, M.L.; Landel, R.F.; Ferry, J.D. The Temperature Dependence of Relaxation Mechanisms in Amorphous Polymers and Other Glass-forming Liquids. *J. Am. Chem. Soc.* **1955**, 77, 3701–3707. [CrossRef]
- 13. Ferry, J.D. Viscoelastic Properties of Polymers; Wiley: New York, NY, USA, 1970.
- 14. Sanditov, D.S.; Bartenev, G.M. Physical Properties of Disordered Structures, Nauka: Novosibirsk, Russia, 1982.
- 15. Xu, W.-S.; Douglas, J.F.; Sun, Z.-Y. Polymer Glass Formation: Role of Activation Free Energy, Configurational Entropy, and Collective Motion. *Macromolecules* **2021**, *54*, 3001–3303. [CrossRef]
- 16. Razumovskaya, I.V.; Bartenev, G.M. Glassy state. In *Proceedings of the All-Union Conference on Glassy State, Leningrad, USSR,* 1971; Nauka: Leningrad, Russia, 1971; p. 34.
- 17. Sanditov, D.S.; Razumovskaya, I.V. New Approach to Justification of the Williams–Landel–Ferry Equation. *Polym. Sci. Ser. A* **2018**, *60*, 156–161. [CrossRef]
- 18. Sanditov, D.S.; Darmaev, M.V.; Sanditov, B.D. Application of the model of delocalized atoms to metallic glasses. *Tech. Phys.* 2017, 62, 53–57. [CrossRef]
- 19. Richet, P.; Conradt, R.; Takada, A.; Dyon, J. (Eds.) *Encyclopedia of Glass Science, Technology, History, and Culture*; Wiley: Hoboken, NJ, USA, 2021; 1568p.
- 20. Nemilov, S.V.; Petrovskii, G.T. A Study of the Viscosity of Glasses in the As-Se System. Zh. Prikl. Khim. 1963, 36, 977-981.
- 21. Sanditov, D.S.; Mashanov, A.A.; Razumovskaya, I.V. On the temperature dependence of the glass transition activation energy. *Polym. Sci. Ser. A* 2020, *62*, 588–596. [CrossRef]
- 22. Nemilov, S.V. Viscosity and Structure of Glasses in the Selenium–Germanium System. Zh. Prikl. Khim. 1964, 37, 1020–1024.
- 23. Orlova, G.M.; Kolomeitseva, S.E.; Timonov, A.S.; Kuznetsova, O.A. Viscosity and thermal expansion of glasses of the P–Se–Te system. *Fizika i Khimiya Stekla* 1979, *5*, 546–549.
- 24. Korepanova, N.A.; Chalabyan, G.A.; Orlova, G.M. Viscosity and elasticity of glass Sb-Ge-Se systems. *Zh. Prikl. Khim.* **1976**, *49*, 1173–1174.
- 25. Orlova, G.M.; Udalov, S.S.; Manakhova, E.N. Elastic and thermal properties of glasses of the AsSe–TlSe, As2Se3–Tl2Se systems. *Fizika i Khimiya Stekla* **1985**, *11*, 215–218.
- 26. Bartenev, G.M.; Sanditov, D.S. Relaxation Processes in Glassy Systems; Novosibirsk: Nauka, Russia, 1986; 238p.
- 27. Rostiashvili, V.G.; Irzhak, V.I.; Rosenberg, B.A. *Glass Transition of Polymers. L.: Chemistry*; 1987; 192p. Available online: https://www.studmed.ru/rostiashvili-vg-irzhak-vi-rozenberg-ba-steklovanie-polimerov_dec103142dd.html (accessed on 25 October 2023).
- 28. Angell, C.A.; Rao, K.J. Configurational excitations in condensed, and the "bond lattice" model for the liquid-glass transition. *J. Chem. Phys.* **1972**, *57*, 470–481. [CrossRef]
- 29. Darmaev, M.V.; Ojovan, M.I.; Mashanov, A.A.; Chimytov, T.A. The Temperature Interval of the Liquid–Glass Transition of Amorphous Polymers and Low Molecular Weight Amorphous Substances. *Appl. Sci.* 2023, *13*, 2742. [CrossRef]
- 30. Filipovich, V.N. Vacancy-diffusion theory of viscosity of SiO₂ and GeO₂ glasses with low R₂O content. *Phys. Chem. Glass* **1975**, 1, 426–431.
- 31. Nemilov, S.V. The nature of viscous flow of glasses with a frozen structure and some consequences of the valence-configuration theory of fluidity. *Phys. Chem. Glass* **1978**, *4*, 662–674.
- 32. Mott, N.F. The viscosity of silicon dioxide. Philos. Mag. 1987, B56, 257-262. [CrossRef]
- 33. Ojovan, M.I.; Louzguine-Luzgin, D.V. On Structural Rearrangements during the Vitrification of Molten Copper. *Materials* **2022**, 15, 1313. [CrossRef] [PubMed]
- 34. Douglas, R.W. The flow of glass. J. Soc. Glass Technol. 1949, 33, 138-162.
- 35. Doremus, R.H. Viscosity of silica. J. Appl. Phys. 2002, 92, 7619–7629. [CrossRef]

- 36. Ojovan, M.I.; Travis, K.P.; Hand, R.J. Thermodynamic parameters of bonds in glassy materials from viscosity-temperature relationships. *J. Phys. Condens. Matter* 2007, *19*, 415107. [CrossRef]
- 37. Glasstone, S.; Laidler, K.J.; Eyring, H. *The Theory of Rate Processes: The Kinetics of Chemical Reactions, Viscosity, Diffusion and Electrochemical Phenomena*; McGraw-Hill Book Company, Incorporated: Tokyo, Japan, 1941; 611p.
- 38. Sanditov, D.S. Model of delocalized atoms in the physics of the vitreous state. J. Exp. Theor. Phys. 2012, 115, 112–124. [CrossRef]
- 39. Sanditov, D.S.; Ojovan, M.I. Relaxation aspects of the liquid—Glass transition. *Phys. Uspekhi* 2019, 62, 111–130. [CrossRef]
- 40. Sanditov, D.S.; Ojovan, M.I.; Darmaev, M.V. Glass transition criterion and plastic deformation of glass. *Phys. B* 2020, *582*, 411914. [CrossRef]

Disclaimer/Publisher's Note: The statements, opinions and data contained in all publications are solely those of the individual author(s) and contributor(s) and not of MDPI and/or the editor(s). MDPI and/or the editor(s) disclaim responsibility for any injury to people or property resulting from any ideas, methods, instructions or products referred to in the content.