

PHASE TRANSITIONS

Cooling Rate of Melts and Glass Transition Temperature

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Received May 13, 2016

Abstract—The recently obtained equation for the dependence of the glass transition temperature on the cooling rate of a melt has been considered and compared with the experimental data. The kinetic criterion of glass transition has been discussed.

DOI: 10.1134/S106378341702024X

1. INTRODUCTION

The establishment of the nature of glass transition of a liquid is one of the important unsolved problems in the physics of the glassy state [1]. In contrast to conventional phase transitions, the process of transition from a liquid to a glass is characterized by the dependence of the glass transition temperature T_g on the cooling rate of the melt $q = dT/dt$. For this dependence, the following new equation has recently been proposed in [2]:

$$\frac{1}{T_g} = a_1 + b_1 \ln \left(1 - \frac{\ln q}{b_2} \right), \quad (1)$$

where $b_1 = k/\Delta\epsilon_e$, $b_2 = \ln(C/\tau_0)$, and $a_1 = b_1 \ln b_2$. Here, k is the Boltzmann constant; $\Delta\epsilon_e$ is the delocalization energy of an atom, i.e., the energy of displacement of an atom from the equilibrium position [3]; τ_0 is the vibration period of an atom in the equilibrium position; C is the empirical parameter in the glass transition criterion proposed by Bartenev [4, 5],

$$q\tau_g = C, \quad (2)$$

τ_g is the structural relaxation time τ at the glass transition temperature.

It was shown that, under the condition

$$\ln q \ll b_2, \quad (3)$$

and for $a_2 = b_1/b_2$, relationship (1) is transformed into the well-known Bartenev empirical equation [4, 5]

$$\frac{1}{T_g} = a_1 - a_2 \ln q. \quad (4)$$

However, the correspondence of relationship (1) to the experimental data was not verified [2].

This study is devoted to the comparison of relationship (1) with the available experimental data.

2. CALCULATION AND DISCUSSION OF THE RESULTS

Let us estimate the order of magnitude of the parameter b_2 . For vitreous systems of the same class, the parameter C in equality (2) can be taken as a constant $C \approx \text{const}$ [4, 5] or as the coefficient of proportionality between the cooling rate q and the inverse structural relaxation time $1/\tau_g$: the higher is the cooling rate q , the shorter is the structural relaxation time τ_g . By assuming that $\tau_0 \approx 10^{-12}$ s and $C \approx 10$ K [6, 7], we obtain the approximate estimate of the parameter b_2 :

$$b_2 = \ln(C/\tau_0) \approx 30. \quad (5)$$

Here, the expression under the logarithm sign (C/τ_0) has the dimension of degrees Kelvin per second (K/s). The cooling rate under the logarithm sign has the same dimension: $\ln q$ [K/s]. The ratio $\ln q/b_2$ in equality (1) is a dimensionless quantity.

In order to verify relationship (1), we can now construct the corresponding plots in the coordinates

$$\frac{1}{T_g} - \ln \left(1 - \frac{\ln q}{30} \right).$$

As can be seen from Figs. 1 and 2, the experimental data [8, 9] plotted in these coordinates lie on straight lines, which confirms the validity of relationship (1).

From condition (3) and estimate (5), it follows that the Bartenev equation (4) is valid at not very high cooling rates of glass-forming melts: $\ln q \ll 30$. In actual fact, at relatively high values of cooling rates q for a number of glasses, for example, for vitreous boric

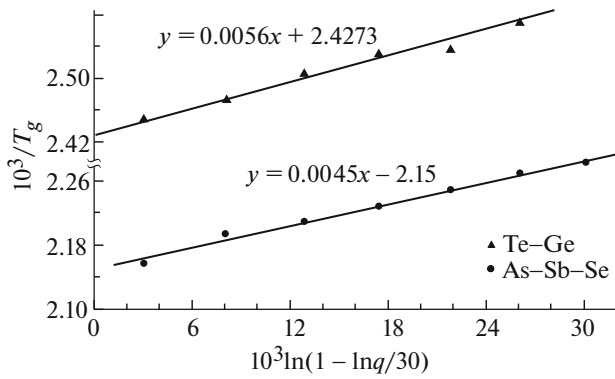


Fig. 1. Dependences of the glass transition temperature on the cooling rate for the As–Sb–Se and Te–Ge glasses in the coordinates of equation (1): $1/T_g - \ln[1 - (\ln q/30)]$. The concentrations of As/Sb/Se and Te/Ge (in mol %) in the glasses are 32.91/7.64/59.45 and 90.87/9.13, respectively. The parameters of equality (1) are as follows: $a_1 = 2.1 \times 10^{-3} \text{ K}^{-1}$ and $b_1 = 4.5 \times 10^{-3} \text{ K}^{-1}$ for the As–Sb–Se glass and $a_1 = 2.4 \times 10^{-3} \text{ K}^{-1}$ and $b_1 = 5.6 \times 10^{-3} \text{ K}^{-1}$ for the Te–Ge glass. The data taken from [8] are used.

anhydride B_2O_3 and lead silicate glasses, there is a deviation from the straight line in the $1/T_g - \log q$ coordinates (Fig. 3) [2]. It is important to note that, for the aforementioned glasses, there are no deviations from straight lines in the coordinates corresponding to the new equation (1) (Fig. 2).

Thus, this relationship (1) is in satisfactory agreement with the experimental data over a wider range of cooling rates as compared to the Bartenev equation (4).

Let us now briefly discuss the criterion of glass transition (2).

In the series of papers [1, 10], Schmelzer and his colleagues formulated a slightly different approach to the kinetic criterion of glass transition

$$\left(\frac{1}{T} \left| \frac{dT}{dt} \right| \tau \right) \Big|_{T=T_g} = C_0, \quad C_0 \approx 1. \quad (6)$$

In the consideration of this relationship, Nemilov [11] drew his attention to the fact that, for oxide (for example, silicate) glasses, according to equality (6), the product $q\tau_g$ at the temperature $T = T_g$ should correspond to the value of $q\tau_g \approx T_g \approx 700\text{--}800 \text{ K}$. However, this is in contradiction with the classical relaxation theories of glass transition [12, 13], as well as with typical values of the product $q\tau_g \approx (5\text{--}20)$ [5, 7, 9, 11].

If we now divide both sides of the Bartenev equality (2) by the glass transition temperature T_g , then, in accordance with the previously obtained result [6], we arrive at the relationship, which can be considered as the generalized Bartenev criterion of glass transition

$$\frac{q}{T_g} \tau_g = C^*. \quad (7)$$

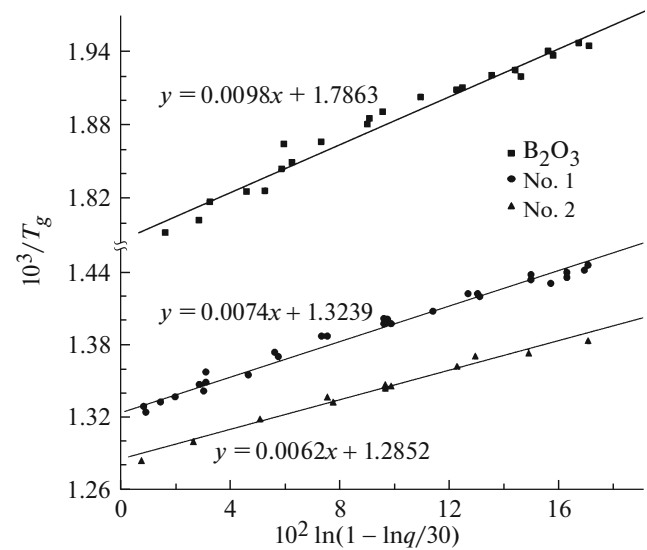


Fig. 2. Dependences $T_g = T_g(q)$ for lead silicate glasses nos. 1 and 2 and for boric anhydride B_2O_3 in the $1/T_g - \ln[1 - (\ln q/30)]$ coordinates. The data taken from [5, 9] are used. The concentrations of PbO in glasses nos. 1 and 2 are 30 and 52 mol %, respectively. The parameters of equation (1) are as follows: $a_1 = 1.3 \times 10^{-3} \text{ K}^{-1}$ and $b_1 = 7.4 \times 10^{-3} \text{ K}^{-1}$ for glass no. 1, $a_1 = 1.2 \times 10^{-3} \text{ K}^{-1}$ and $b_1 = 6.2 \times 10^{-3} \text{ K}^{-1}$ for glass no. 2, and $a_1 = 1.7 \times 10^{-3} \text{ K}^{-1}$ and $b_1 = 9.8 \times 10^{-3} \text{ K}^{-1}$ for boric anhydride B_2O_3 .

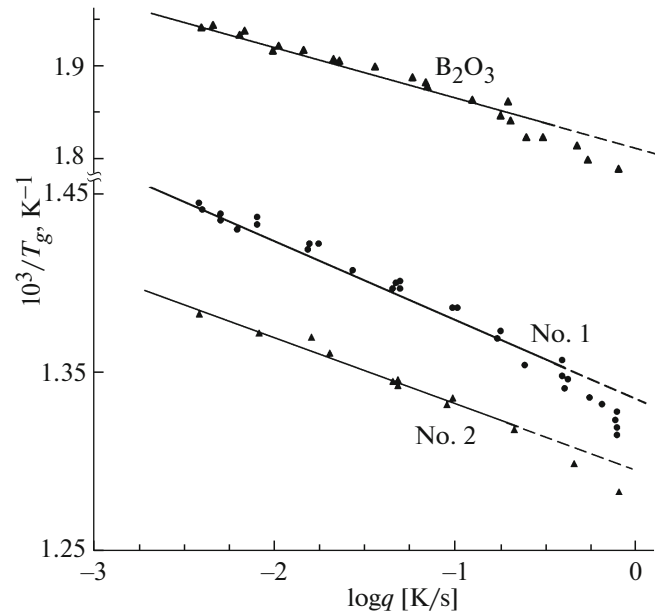


Fig. 3. Dependences of $1/T_g$ on $\log q$ for vitreous boric anhydride B_2O_3 and lead silicate glasses nos. 1 and 2 [5, 9].

Here, C^* is, in fact, a universal constant [6]:

$$C^* = \frac{C}{T_g} = \frac{f_g}{\ln(1/f_g)} \approx \text{const} \approx 0.007, \quad (8)$$

$f_g = (\Delta V_e/V)_{T=T_g}$ is the fraction of the fluctuation volume frozen at the glass transition temperature. The fluctuation volume of an amorphous material ΔV_e is caused by thermal displacements of atoms from their equilibrium positions:

$$\Delta V_e = N_e \Delta v_e,$$

where N_e is the number of delocalized atoms and Δv_e is the elementary fluctuation volume required for the delocalization of an atom, i.e., for its displacement from the equilibrium position. The fluctuation volume fraction f_g depends weakly on the nature of glasses. For the vast majority of vitreous systems, the fluctuation volume fraction is a universal quantity: $f_g \approx \text{const} \approx 0.025$ [3, 6]. At the glass transition temperature, the process of delocalization of an atom is frozen.

By analogy with expression (6), the glass transition criterion (7) can be written in the generalized form

$$\left(\frac{1}{T} \left| \frac{dT}{dt} \right| \tau \right) \Big|_{T=T_g} = C^*, \quad C^* \approx 7 \times 10^{-3}. \quad (9)$$

The proposed condition for the liquid-to-glass transition (9), in contrast to condition (6), does not contradict the classical relaxation theories [12, 13]. For the product $q\tau_g$, as applied to oxide glasses ($T_g \approx 700\text{--}800$ K), this condition gives the following order of magnitude:

$$q\tau_g = C^* T_g \approx (5\text{--}6) \text{ K},$$

which is in agreement with typical “standard” data for the product $q\tau_g$ [7].

3. CONCLUSIONS

Thus, the well-known Bartenev empirical equation (4) is valid at not very high cooling rates of glass-forming melts: $\ln q \ll 30$. The generalized equation (1) describes the dependence $T_g = T_g(q)$ over a fairly wide range of cooling rates. The proposed condition for the liquid-to-glass transition (relationship (7)) can be

considered as a modification of the kinetic glass-transition criterion (6) formulated by Schmelzer and his colleagues, and also as an extension of the condition for the transition from a liquid to a glass according to Bartenev (relationship (2)).

ACKNOWLEDGMENTS

This study was supported by the Ministry of Education and Science of the Russian Federation (project no. 1932).

REFERENCES

1. T. V. Tropin, J. W. Schmelzer, and V. L. Aksenov, *Phys.—Usp.* **59** (1), 42 (2016).
2. D. S. Sanditov, S. Sh. Sangadiev, and M. V. Darmaev, *Phys. Solid State* **58** (10), 2078 (2016).
3. D. S. Sanditov, *J. Exp. Theor. Phys.* **115** (1), 112 (2012).
4. G. M. Bartenev, *Dokl. Akad. Nauk SSSR* **76** (2), 227 (1951).
5. G. M. Bartenev, *The Structure and Mechanical Properties of Inorganic Glasses* (Stroiizdat, Moscow, 1966; Wolters-Noordhoff, Rijn, The Netherlands, 1970).
6. D. S. Sanditov, M. V. Darmaev, and B. D. Sanditov, *Phys. Solid State* **57** (8), 1666 (2015).
7. D. S. Sanditov, M. V. Darmaev, and B. D. Sanditov, *Phys. Solid State* **58** (2), 382 (2016).
8. *MDL @ SciGlass—7.8* (Institute of Theoretical Chemistry, Shrewsbury, 2012). www.sciglass.info.
9. G. M. Bartenev and I. A. Luk'yanov, *Zh. Fiz. Khim.* **29**, 1486 (1955).
10. T. V. Tropin, J. W. P. Schmelzer, I. Gutzov, and C. J. Schick, *Chem. Phys.* **136**, 124502 (2012).
11. S. V. Nemilov, *Glass Phys. Chem.* **39** (6), 609 (2013).
12. M. V. Vol'kenshtein and O. B. Ptitsyn, *Zh. Tekh. Fiz.* **26**, 2204 (1956).
13. F. Simon, *Z. Anorg. Allg. Chem.* **203**, 219 (1931).

Translated by O. Borovik-Romanova