
PHASE
TRANSITIONS

Glass-Transition Temperature and Cooling Rate of Glass-Forming Melts

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Abstract—A new derivation of the Bartenev equation has been proposed for the glass-transition temperature as a function of the cooling rate with allowance for the dependence on the activation energy for the liquid–glass transition.

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1. INTRODUCTION

Unlike phase transition temperatures, the glass-formation temperature of a liquid, T_g , depends only weakly on the cooling rate $q = dT/dt$ of the glass-forming liquid. Establishing the interrelation between these quantities is an important part of the theory of the glass state. It is also important for practical applications, e.g., for development of annealing regimes for glass.

In 1951, Bartenev [1] proposed one of the optimal explicit dependences of the glass-formation temperature on the cooling rate of melt:

$$\frac{1}{T_g} = a_1 - a_2 \log q, \quad (1)$$

where a_1 and a_2 are empiric constants. The Bartenev equation (1) was obtained on the basis of his glass-formation criterion

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

and the known formula for the relaxation time:

$$\tau = \tau_0 \exp\left(\frac{U}{kT}\right), \quad (3)$$

written for the glass-formation temperature ($T = T_g$, $\tau = \tau_g$). Here, C is an empiric parameter, τ_g is the relaxation time τ at T_g , U is the activation energy for the glass-formation process, which, when deriving Eq. (1), was supposed to be constant (independent of temperature),

$$U = \text{const}, \quad (4)$$

and τ_0 is the period of vibration of a molecule in the equilibrium position.

In 1954, from other assumptions (independent of Bartenev's work [1]), the same expression was obtained by Ritland¹ [2]. Therefore, (1) sometimes is referred to as the Bartenev–Ritland equation [3–5].

Numerous experiments show [1–10] that relationship (1) satisfactorily describes the dependence $T_g = T_g(q)$ in a fairly wide range of cooling rates (Fig. 1). However, in Luk'yanov's experiment [6, 7], for a number of glasses, a deviation from the Bartenev equation at relatively high cooling rates was observed (Fig. 2). In our opinion, the most probable reason for this deviation is the assumption that the activation energy for the glass-formation process (4) is constant. It has been known for a long time that, in the region of the liquid–glass transition, the activation energy sharply increases [3]. In recent years, attempts have been undertaken to improve the Bartenev equation by using a more appropriate temperature dependence $\tau(T)$ of the structural relaxation than the simple exponential (3) with $U = \text{const}$ [3–5].

The present work is devoted to deriving a formula for the dependence of the glass-formation temperature on the cooling rate by using one of the most widely accepted temperature dependence of the activation energy for glass formation [11–16], which obtains a definite interpretation in the framework of the activation theory and the model of delocalized atoms [17, 18].

¹There are no reference to Bartenev's paper [1] in Ritland's work [2].

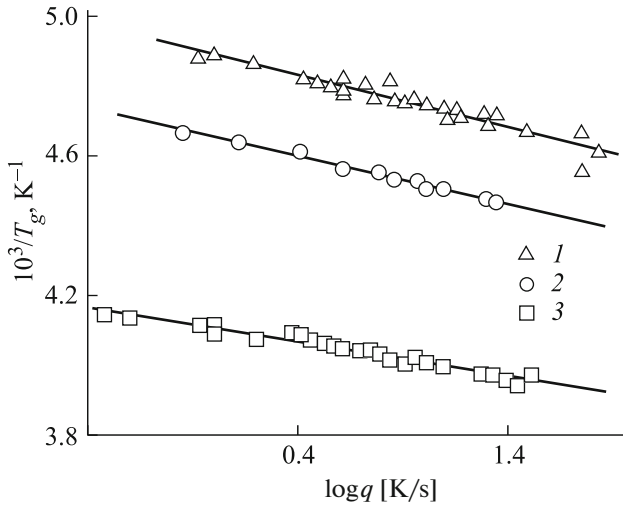


Fig. 1. Reciprocal glass-formation temperature $1/T_g$ vs. the logarithm of the melt cooling rate, $\log q$, [8] for caoutchoucs (1) SKS-30, (2) SKN-18 (2), and (3) SKN-40.

2. THEORY

The activation energy for the transition of a molecule (kinetic unit) of glass-forming liquid from one equilibrium position to another in a wide temperature interval can be represented by the following relationship [19–21]:

$$U = U_\infty + bkT \left[\exp\left(\frac{\Delta\epsilon_e}{kT}\right) - 1 \right], \quad (5)$$

where U_∞ is the high-temperature limit of the activation energy, $\Delta\epsilon_e$ is the energy for delocalization of an atom (its displacement from the equilibrium), and b is a coefficient on the order of unity (below we set $b \cong 1$ [19]).

At low temperatures in the glass-formation region, in this expression, the unity in brackets and the first term U_∞ may be neglected as compared to the exponential dependence of the second term, which significantly simplifies dependence (5):

$$U \cong kT \exp\left(\frac{\Delta\epsilon_e}{kT}\right). \quad (6)$$

Taking into account this equality, equation (3) for the relaxation time at the glass-formation temperature $T = T_g$ can be rewritten in the “double-exponential” form:

$$\tau_g = \tau_0 \exp\left[\exp\left(\frac{\Delta\epsilon_e}{kT_g}\right)\right]. \quad (7)$$

The kind of dependence (double exponential) for molecular kinetic processes in glass-forming liquids in the glass-formation region were proposed by Shishkin [14], Bredbury [13], and other authors [11, 12, 15, 16] in the form of empirical and semiempirical relationships.

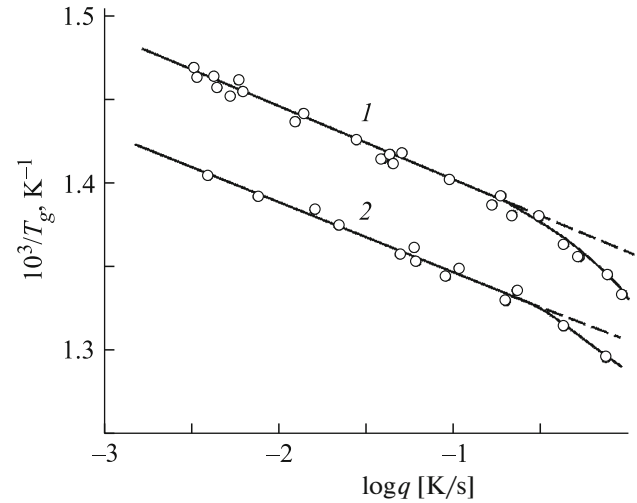


Fig. 2. Glass-formation temperature vs. melt cooling rate for lead-silicate glasses in the $1/T_g - \log q$ coordinates with the content PbO, mol %: (1) 30 and (2) 52, according to data [6, 7].

Substituting into equality (2) the relaxation time τ_g from formula (7), after some transformations, we obtain the following equation:

$$\frac{1}{T_g} = a_1 + b_1 \ln\left(1 - \frac{\ln q}{b_2}\right), \quad (8)$$

where $b_1 = k/\Delta\epsilon_e$, $b_2 = \ln(C/\tau_0)$, and $a_1 = b_1 \ln b_2$.

Thus, in the framework of this approach, the dependence of the glass-formation temperature on the cooling rate, $T_g(q)$, is weak, because q enters into expression (8) under the double logarithm.

3. DISCUSSION OF RESULTS

Setting $\tau_0 \approx 10^{-12}$ s and $C \approx 10$ K for the standard cooling rate ($q = 0.05$ K/s) [6–8], we have the estimate $b_2 = \ln(C/\tau_0) \approx 30$. At comparatively low cooling rates $\ln q \ll b_2$, we expand the logarithm on the right-hand side of (8) in a series and retain only its first term

$$\ln\left(1 - \frac{\ln q}{b_2}\right) \approx -\frac{\ln q}{b_2} - \dots$$

Then, equality (8) passes into Bartenev equation (1),

$$\frac{1}{T_g} = a_1 - \left(\frac{b_1}{b_2}\right) \ln q \quad (9)$$

if $a_2 = b_1/b_2$. Hence, the Bartenev equation is valid for not very high cooling rates: $\ln q \ll 30$. Indeed, as was noted above, with an increase in the cooling rate, for a number of glasses, a deviation from dependence (1) is observed (Fig. 2). Note that the parameter C in glass-formation equation (2) depends only weakly on the cooling rate q via $T_g(q)$ [22]. However, T_g depends on q logarithmically and, in addition, C enters into rela-

tionship (8) under the sign of logarithm. Therefore, the parameter C may be considered practically constant, which is confirmed by the validity of the Bartenev equation at moderate cooling rates.

4. CONCLUSIONS

Thus, the derivation of Bartenev equation (1) with allowance for the temperature dependence of the activation energy for the glass-formation process (6) shows that this equation is valid at not very high cooling rates of glass-forming liquids: $\ln q \ll 30$. In future studies, it is of interest to apply formula (8), obtained above, in a wide range of cooling and heating rates.

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