On the activation energy of the glass transition process

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Annotation. Calculation of the temperature dependence of the activation energy of the glass transition process $U(T)$ of amorphous organic polymers and inorganic glasses with the use of the Williams-Landel-Ferry equation for the relaxation time (viscosity) is proposed. The estimates made are in satisfactory agreement with experiment. The nature of the $U(T)$ dependence is discussed.

Key words: glass transition, viscosity, relaxation time, activation energy.

Introduction

The nature of the transition of an amorphous substance from a liquid to a glassy state remains one of the unsolved problems. The glass transition of a liquid is closely related to an increase in viscosity upon cooling the melt. In this case, the activation energy of the glass transition process, as a rule, coincides with the activation energy of a viscous flow (relaxation time) in the region of the liquid-glass transition.

The temperature dependence of the viscosity of simple low-viscosity liquids such as acetone is successfully described by the equation of Ya.I. Frenkel [1]

$$\eta = \eta_0 \exp \left( \frac{U}{RT} \right)$$  \hspace{1cm} (1)

with constant activation energy $U = \text{const.}$ Here $\eta_0$ is the preexponential factor, $R$ – is the gas constant.

However, for glass-forming melts in formula (1), the activation energy in the glass transition region rather strongly depends on temperature: $U = U(T)$. In this regard, empirical viscosity equations are proposed, which implicitly take into account this dependence $U(T)$. Among them, the WLF (Williams-Landel-Ferry) ratio is widespread [2, 3]

$$\ln a_1 = -C_1 \frac{T - T_g}{T - T_g + C_2}, \quad a_1 = \frac{\tau(T)}{\tau(T_g)} \equiv \frac{\eta(T)}{\eta(T_g)},$$  \hspace{1cm} (2)

where $C_1$ and $C_2$ are empirical constants, $T_g$ is the glass transition temperature, $\tau$ is the relaxation time.

The validity of this equation has been shown in many works for various vitrifying systems [2-4].

Earlier, a conclusion and justification of this expression was proposed without specifying the functions $\tau(T)$ and $\eta(T)$ [5].

The present work is devoted to the assessment of the temperature dependence of the activation energy of the glass transition process $U(T)$ using data on the parameters of the WLF equation $C_1$ and $C_2$.

Calculation of the temperature dependence of the activation energy of glass transition using the Williams-Landel-Ferry equation

It is easy to verify that the WLF equation (2) is algebraically derived from the well-known Vogel – Fulcher – Tamman relation [4].
\[ \eta = \eta_0 \exp \left( \frac{B_0}{T - T_g} \right), \] (3)

where the empirical constant \( B_0 \) has the dimension of temperature and is measured in kelvin. Moreover, their parameters turn out to be related by the equalities

\[ B_0 = C_1 C_2, \] (4)

\[ T_p = T_g - C_2. \] (5)

From a comparison of formulas for viscosity (1) and (3), assuming the preexponential factors in them to be equal, we obtain the following dependence of the activation energy of viscous flow on temperature

\[ U = \frac{B_0 RT}{T - T_p}. \] (6)

Since for many amorphous polymers and inorganic glasses the values of the parameters of the WLF equation \( C_1 \) and \( C_2 \) are known [2 - 4], using expressions (4) and (5), it is expedient to pass from dependence (6) to the value \( U(T) \) as a function of these parameters

\[ U = \frac{C_1 C_2 RT}{T - T_p + C_2}. \] (7)

This equality implies a simple relation for calculating the activation energy of the glass transition process \( U_g = U(T_g) \) at the glass transition temperature \( T = T_g \)

\[ U_g = C_1 R T_g. \] (8)

For sheet silicate glass, for example, \( C_1 \) and \( T_g \) are equal, respectively [6]: \( C_1 = 36 \) and \( T_g = 807 \) K, whence we have (\( R = 8.3 \) J/(mol·K)): \( U_g = 241 \) kJ/mol. The methods of relaxation spectrometry [4, 6] for this glass lead to practically the same value \( U_g = 242 \) kJ/mol.

It is known that many vitrifying systems pass from a liquid to a solid glassy state at practically the same viscosity \( \eta_g \approx \eta_g(T \to \infty) \) is also in the first approximation constant \( \eta_g \approx \text{const} \approx 10^{-3.5} \) Pa·s. Therefore, the activation energy at the glass transition temperature \( U_g = U(T_g) \) can be estimated by formula (1) at \( T = T_g \), \( \eta_g \approx \eta_g(T_g) \approx 1012 \) Pa·s and \( \eta_0 \approx 10^{-3.5} \) Pa·s [4]

\[ U_g = \left( \frac{\eta_g}{\eta_0} \right) R T_g \approx 36 R T_g, \] (9)

which practically coincides with relation (8).

Consequently, the weak dependence of the parameter of the WLF equation \( C_1 \) on the nature of the glasses: \( C_1 \approx \text{const} \approx 35 - 40 \) (Table) [2, 4] is explained by the approximate constancy of the viscosities \( \eta_g \) and \( \eta_0 \):

\[ C_1 = \ln \left( \frac{\eta_g}{\eta_0} \right). \]

### Table

Parameters of the WLF equation (2) and the activation energy of the glass transition process at \( T = T_g \) for amorphous organic polymers and inorganic glasses (data from [2, 4] were used)

| N | Amorphous substances | \( T_g \), K | \( C_1 \), K | \( C_2 \), K | \( U_g \), kJ/mol |
|---|---------------------|-------------|-------------|-------------|----------------|
| 1. | PbO – SiO₂           | 711         | 36          | 250         | 212           |
| 2. | Na₂O – B₂O₃         | 544         | 39          | 130         | 131           |
| 3. | Sheet glass          | 807         | 36          | 305         | 241           |
| 4. | Polyisobutylene      | 202         | 38          | 104         | 64            |
| 5. | Polyvinyl acetate    | 305         | 38          | 104         | 96            |
| 6. | Polyurethane         | 238         | 36          | 33          | 71            |
| 7. | Natural rubber       | 300         | 38          | 54          | 95            |

**Note:** \( U_g \) - calculation by formula (8).
Thus, to calculate $U(T)$ in the glass transition region using formula (7), it is necessary to know the values of three quantities: $C_1$, $C_2$, and $T_g$. Data on the parameters of the WLF equation $C_1$ and $C_2$, as well as on the glass transition temperature $T_g$, for many amorphous organic polymers are available in the book by Ferry [2], and for inorganic glasses - in the monograph by Sanditov and Bartenev [4]. One of the ways to define $C_1$ and $C_2$ is described in this book [4, p. 86].

In fig. 1 shows the temperature dependence of the activation energy of the glass transition process for sheet silicate glass. Curve - calculation by formula (7), and points - experimental data. The experimental points were obtained from the data on the viscosity $\log(\eta(T))$ using Eq. (1), from which the dependence $U(T)$

$$U = 2.3RT[\log(\eta(T)) - \log(\eta_g)]$$

As you can see, the points fall on the calculated curve, which confirms the applicability of the WLF formula. Similar $U - T$ plots were constructed by us for a number of organic amorphous polymers (see, for example, for polyvinyl acetate, Fig. 2).

![Figure 1](image1.png)

**Figure 1.** Temperature dependence of the activation energy of glass transition $U(T)$ for sheet silicate glass. Points - experimental data, curve - calculation by formula (7).

![Figure 2](image2.png)

**Figure 2.** Temperature dependence of the activation energy of glass transition $U(T)$ for polyvinyl acetate. Points - experimental data, curve - calculation according to equation (7).

**On the nature of the $U(T)$ dependence**

The main regularities of the glass transition process are qualitatively the same for the vast majority of amorphous substances, regardless of their nature: for inorganic glasses, amorphous organic polymers, metal amorphous alloys, aqueous solutions, chalcogenides, which is confirmed by the presence of universal equations and rules in the glass transition region [4-7].

We proceed from the idea that the physical reason for the sharp increase in the activation energy of the glass transition process with decreasing temperature is the configurational change in the structure of the glass-forming melt.
Within the framework of the model of delocalized atoms [8, 9] for glass-forming liquids, the activation energy of the glass transition (viscous flow) in Eq. (1) is the sum of two terms

\[ U = U_\infty + U_s(T), \]

where \( U_\infty \) is the potential for the transition of a kinetic unit (atom, molecule) to a new local position, \( U_s(T) \) is the potential for a configurational structural change, which is a function of temperature,

\[ U_s(T) = RT \left[ \exp\left( \frac{\Delta \varepsilon_e}{RT} \right) - 1 \right]. \]

Here, \( \Delta \varepsilon_e \) is the delocalization energy of the atom (its limiting displacement from the local equilibrium position). The delocalization of an atom is caused by the rearrangement of neighboring particles (fluctuation of short-range order) and reflects a local configurational change in the structure.

At elevated temperatures \( RT >> \Delta \varepsilon_e \), the potential of the configurational structural change is equal to zero \( U_s(T) = 0 \), and the viscosity equation (1), taking into account (11) and (12), transforms into the usual Arrhenius (Frenkel) dependence with a constant activation energy \( U = U_\infty \).

\[ \eta = \eta_0 \exp\left( \frac{U_\infty}{RT} \right). \]

From this point of view, the value of \( U_\infty \) turns out to be the high-temperature limit of the activation energy for viscous flow.

At low temperatures, in the glass transition region, the energy of atomic delocalization \( \Delta \varepsilon_e \) becomes comparable to the energy of thermal vibrations of the lattice (~ 3RT) and the relative number of delocalized atoms \( (N_d/N) \) responsible for fluidity above \( T_g \) significantly decreases according to the law [9]. The structure of the melt becomes denser, and for the activation jump of the atom to a new position, a preliminary local configurational change (“loosening”) of the structure near \( T_g \) is required: the potential for configurational structural change \( U_s(T) \) sharply increases. This explains the almost exponential growth of the activation energy of fluidity in the glass transition region.

Thus, the configurational change in the structure, which is described within the framework of the model of delocalized atoms, turns out to be responsible for the temperature dependence of the activation energy of the glass transition process (viscous flow) in the region of the transition from the liquid state to the glassy state.

**Conclusion**

For amorphous organic polymers and inorganic glasses, methods of calculating the temperature dependence of the activation energy of the glass transition process \( U(T) \) are considered. This dependence \( U(T) \) is satisfactorily described near \( T_g \) using the well-known Williams-Landel-Ferry equation for viscosity (relaxation time). Within the framework of the model of delocalized atoms, a sharp increase in the activation energy in the glass transition region is explained by an increase in the potential for a configurational change in the structure upon cooling the glass-forming melt.

**Acknowledgment**

This work was supported by the Ministry of Science and Higher Education of the Russian Federation (Grant No. 3.5406.2017 / 8.9).

**References**

1. Frenkel’ Ya I, *Kinetic Theory of Liquids*, Akad. Nauk SSSR, Moscow, 1945.
2. Ferry J D, *Viscoelastic Properties of Polymers*, John Wiley & Sons, Inc., New York, 1980.
3. Williams M L, Landel R F and Ferry J D, 1955 *J. Amer. Chem. Soc.* 77, 3701.
4. Sanditov D S and Bartenov G M, *Physical Properties of Disordered Structures*, Nauka, Novosibirsk, 1982.
5. Sanditov D S and Razumovskaya I V, 2018 *Polym. Sci., Ser. A* 60, 156.
6. Bartenev G M and Sanditov D S, *Relaxation Processes in Glassy Systems*, Nauka, Novosibirsk, 1986.
7. Rostiashvili V G, Irzhak V I and Rozenberg B A, *Glass Transitions in Polymers*, Khimiya, Leningrad 1987.
8. Sanditov D S, 2012 *J. Exp. Theor. Phys.* 115, 112
9. Sanditov D S and Ojovan M I, 2019 *Phys.-Usp.* 62, 111