

DERIVATION OF THE KISSINGER EQUATION FOR NON-ISOTHERMAL GLASS TRANSITION PEAKS

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A brief derivation of the Kissinger's equation for analysis of experimental data of non-isothermal glass transition peaks based on the free volume model is given. This equation was applied successfully to $\text{Cu}_{0.3}(\text{SSe}_{20})_{0.7}$ chalcogenide glass for different heating rates. For granted this model, the obtained glass transition activation energy, E_g must be constant throughout the whole glass transition temperature range. This required that T_g to be determined for three characteristic temperature points for each DSC curve.

Keywords: chalcogenide glass, DSC, phase transitions

Introduction

When a chalcogenide glass is heated at a constant heating rate in a differential scanning calorimetry (DSC) experiment, the glass undergoes structural changes and eventually crystallizes. In addition to the large exothermal crystallization peak, the DSC trace shows an endothermic peak before crystallization occurs: the glass transition peak. This calorimetric glass transition is generally considered to be due to changes in the amorphous structure, which approaches a thermodynamic equilibrium state as the temperature of the system is increased [1–7].

The objective of the present work is to derive the Kissinger equation in terms of the free volume model [8] and the importance of testing the activation energy for constancy throughout the glass transition for granted this model. This is the first attempt to check the validity of the Kissinger plot throughout the whole glass transition temperature range.

Theoretical analysis

In the free volume model, the concentration of structure defects c is related to the reduced free volume x [8] through [9]

$$c = \exp\left(-\frac{1}{x}\right) \quad (1)$$

In equilibrium, the defect concentration depends on temperature T through [6]

$$c_e = \exp\left(-\frac{B}{T-T_0}\right) \quad (2)$$

where $x_e = (T-T_0)/B$ is the equilibrium free volume; T_0 and B are constants of unit K . When the defect concentration is not in equilibrium, it will approach the equilibrium value. The rate of change of the defect concentration is in that case equal to [9]

$$\frac{dc}{dt} = -kc(c-c_e) \quad (3)$$

The rate constant k has an Arrhenian temperature dependence:

$$k = k_0 \exp\left(-\frac{E}{RT}\right) \quad (4)$$

where E is the activation energy for the migration of the structural defects in J mol^{-1} , R is the universal gas constant and k_0 is pre-exponential factor or frequency factor. From Eqs (1)–(3), it follows that the rate of change of the free volume is given by

$$\frac{dx}{dt} = -kx^2(c-c_e) \quad (5)$$

There are three different methods in treating Eq. (5) to obtain the Kissinger's equation for the glass transition peak.

First method

In this method, we expand Eq. (1) around the equilibrium free volume, x_e , gives

$$\exp\left(-\frac{1}{x}\right) = \exp\left(-\frac{1}{x_e}\right) + \frac{1}{x_e^2} \exp\left(-\frac{1}{x_e}\right)(x-x_e) + \dots \quad (6)$$

Substituting into Eq. (5) yields

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$$\frac{dx}{dt} \approx -k \frac{x^2}{x_e^2} (x-x_e) \exp\left(-\frac{1}{x_e}\right) \quad (7)$$

Recently, Ruitenberg [1] disregarded the quadratic terms in Eq. (7) by assuming $x^2/x_e^2=1$ without giving a reasonable scientific reason for that assumption.

It is convenient to assume that near the glass transition peak

$$\frac{x^2}{x_e^2} \exp\left(-\frac{1}{x_e}\right) = \text{constant} = A \quad (8)$$

and the value of x_e is almost a constant with respect to time. Hence:

$$\frac{dx}{dt} = -kA(x-x_e) \quad (9)$$

Taking the derivative of Eq. (9) with respect to time, one obtains

$$\frac{d^2x}{dt^2} = -A \left\{ k \frac{dx}{dt} + (x-x_e) \frac{dk}{dt} \right\} \quad (10)$$

From Eq. (9) into Eq. (10) and taking the derivative of Eq. (4) with respect to time. Thus Eq. (10) becomes

$$\frac{d^2x}{dt^2} = -Ak \left[-kA + \frac{\alpha E}{RT^2} \right] (x-x_e) \quad (11)$$

with $T=\alpha t$ where α is the heating rate. It is assumed that the maximum rate of change in free volume occurs at the glass transition peak at temperature T_g . Setting Eq. (11) to zero gives

$$k_g A = \frac{\alpha E_g}{RT_g^2} \quad (12)$$

or in logarithmic form

$$\ln\left(\frac{\alpha}{T_g^2}\right) = \ln\left(\frac{Ak_0 R}{E_g}\right) - \frac{E_g}{RT_g} \quad (13)$$

or

$$\ln\left(\frac{\alpha}{T_g^2}\right) = \text{constant} - \frac{E_g}{RT_g} \quad (14)$$

Equation (14) represent the Kissinger equation for the glass transition peak. If the values of α/T_g^2 can be identified in a series of endotherms taken at different heating rates, the plot of $\ln(\alpha/T_g^2)$ vs. $1/T_g$ should be a straight line with a slope $(-E_g/R)$.

Second method

By rearranging Eq. (5) and integrating, one obtains

$$\int_{x_0}^{x'} \frac{dx}{x^2(c-c_e)} = -k_0 \int_0^{t'} e^{-E_g/RT} dt \equiv G(x') \quad (15)$$

The integration is carried out from the free volume in the material prior the scan, x_0 until some fraction of the reduced free volume x' . A typical value for $x_0=0.0315$ for an annealed amorphous was taken [10].

The function $G(x') = \int_{x_0}^{x'} \frac{dx}{x^2(c-c_e)}$ is independent of the

heating rate used to obtain the reduced free volume fraction x' .

The time integral in Eq. (16) is transformed to a temperature integral, yielding

$$G(x') = -\frac{k_0}{\alpha} \int_{T_0}^{T'} e^{-E_g/RT} dT \quad (16)$$

The integral is further transformed by substituting $y=E_g/RT$

$$G(x') = -\frac{k_0 E_g}{R\alpha} \int_{y_0}^{y'} \frac{e^{-y}}{y^2} dy \quad (17)$$

This integral can be evaluated using the exponential integral function if it assumed that $T_0 \ll T'$, so that y_0 can be taken as ∞ . The exponential integral function, $E(-y)$, is represented by several approximate analytical expressions. The most convenient expression for the present problem is given by Abramovitz and Stegun [11, 12]

$$E(-y) = \frac{-e^{-y}}{y} \left(1 - \frac{1}{y} + \frac{2}{y^2} - \frac{6}{y^3} \dots + \frac{(-1)^n n!}{y^n} \right) \quad (18)$$

when $y_0 = \infty$, the integral in Eq. (17) can be expressed [12, 13] as

$$\int_{\infty}^{y'} \frac{e^{-y}}{y^2} dy = \frac{-e^{-y'}}{y'} - E_i(-y') \quad (19)$$

for $y'(=E_g/RT) \gg 1$, the integral becomes

$$\int_{\infty}^{y'} \frac{e^{-y}}{y^2} dy = \frac{-e^{-y'}}{y'} + \frac{e^{-y'}}{y'} \left[1 - \frac{1}{y'} \right] = \frac{-e^{-y'}}{y'^2} \quad (20)$$

Substituting Eq. (20) in Eq. (17), one obtains

$$G(x') = \frac{RK_0}{\alpha E_g} T^2 e^{\frac{E_g}{RT}} = \frac{RT^2 K}{\alpha E_g} \quad (21)$$

The integral over x yields

$$G(x') = \frac{1}{c_e} \ln \left(\frac{1-c_e e^{x'}}{1-c_e e^{x_0}} \right) \quad (22)$$

Finally, Eq. (17) becomes

$$\frac{1}{c_e} \ln \left(\frac{1 - c_e e^{\frac{1}{x'}}}{1 - c_e e^{\frac{1}{x_0}}} \right) = \frac{k_0 R T^2}{\alpha E_g} e^{-(E_g/RT)} \quad (23)$$

Or in logarithmic form at the glass transition peak maximum

$$\begin{aligned} \ln \left(\frac{\alpha}{T_g^2} \right) &= \ln \left(\frac{k_0 R}{E_g} \right) - \ln[G(x')] - \frac{E_g}{RT_g} \\ &= \text{constant} - \frac{E_g}{RT_g} \end{aligned} \quad (24)$$

The value of E_g is determined from a plot of $\ln(\alpha/T_g^2)$ vs. $1/T_g$ taken at different heating rates. This plot, according to Eqs (14) and (24) is a straight line, whose slope is E_g/R .

Third method

Returning to Eq. (5) with substituting $u=kx^2$, Eq. (5) yields

$$\dot{x} = -u(c - c_e) \quad (25)$$

If the rate of change in free volume is maximum at the glass transition peak, T_g , the position of the peak is given by

$$\begin{aligned} \dot{x} &= -u\dot{c} - (c - c_e)\dot{u} = 0 \\ &= -k\dot{x}[c + 2x(c + c_e)] + x^2\dot{k}(c - c_e) = 0 \end{aligned} \quad (26)$$

where $\dot{x} = dx/dt$, $\ddot{x} = d^2x/dt^2$, $\dot{c} = dc/dt = e^{-1/x}(\dot{x}/x^2)$, $\dot{u} = 2kx\dot{x} + x^2\dot{k}$ and c_e is almost a constant with respect to time.

From Eq. (4)

$$\dot{k} = \frac{\alpha E_g}{RT_g^2} k \quad (27)$$

then

$$-k_0 e^{-\frac{E_g}{RT_g}} [c + 2x(c + c_e)] = \frac{\alpha E_g}{RT_g^2} k \quad (28)$$

or in logarithmic form

$$\ln \left(\frac{\alpha}{T_g^2} \right) = \ln \left(\frac{R}{k_0 E_g} \right) + \ln[c + 2x(c + c_e)] - \frac{E_g}{RT_g} \quad (29)$$

$$\ln \left(\frac{\alpha}{T_g^2} \right) = \text{constant} - \frac{E_g}{RT_g} \quad (30)$$

Equation (30) represents the Kissinger equation like Eqs (14) and (24).

Experimental

The $\text{Cu}_{0.3}(\text{SSe}_{20})_{0.7}$ chalcogenide glass has been prepared by the quenching technique [12, 14].

Differential Scanning Calorimetry (DSC) was performed on a Shimadzu DSC-50 instrument with selected heating rates $2\text{--}30^\circ\text{C min}^{-1}$ in the range $30\text{--}600^\circ\text{C}$. The temperature precision of the equipment is $\pm 0.2^\circ\text{C}$. The samples with masses of ≈ 15 mg encapsulated in conventional platinum sample pans in an atmosphere of dry nitrogen at a flow of 30 mL min^{-1} . The instrument was calibrated prior to measurement by using high purity metal standards (In, Pb and Zn) with known latent heat. The values of the glass transition temperature (T_g), the onset temperature of crystallization (T_c), the peak temperature of crystallization (T_p) and the melting temperature (T_m) were determined by using the microprocessor of the apparatus.

Results and discussion

A typical set of DSC outputs for different heating rates ranging from 2 to $30^\circ\text{C min}^{-1}$ is shown for $\text{Cu}_{0.3}(\text{SSe}_{20})_{0.7}$ chalcogenide glass in Fig. 1. For granting the application of the Kissinger's equation to the glass transition endothermic peak, T_g was determined by using three different definitions [15, 16] as shown in Fig. 2: the extrapolated onset of the heat capacity break (designated T_{g1}), the inflection point in the rapidly rising part of the heat capacity curve (designated T_{g2}), and the heat capacity maximum (designated T_{g3}).

The values of the glass transition activation energy, E_g (kJ mol^{-1}) was obtained from the slope of $\ln(\alpha/T_g^2)$ vs. $1000/T_g$ plots given in Fig. 3, and the constant value in Eqs (14), (24) and (30) from the intercepts. Table 1 shows the values of the glass transi-

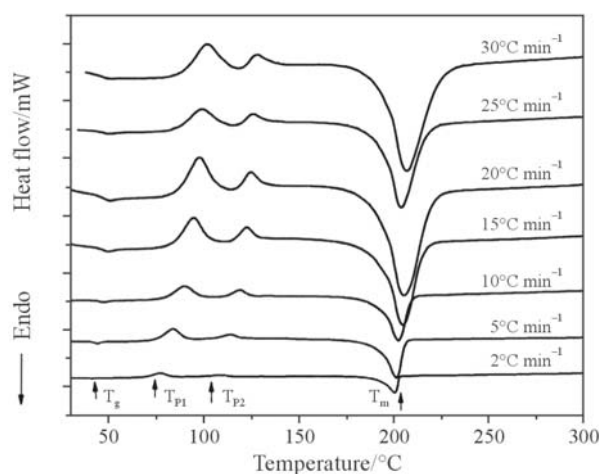


Fig. 1 DSC traces for the as-prepared $\text{Cu}_{0.3}(\text{SSe}_{20})_{0.7}$ chalcogenide glass at different heating rates

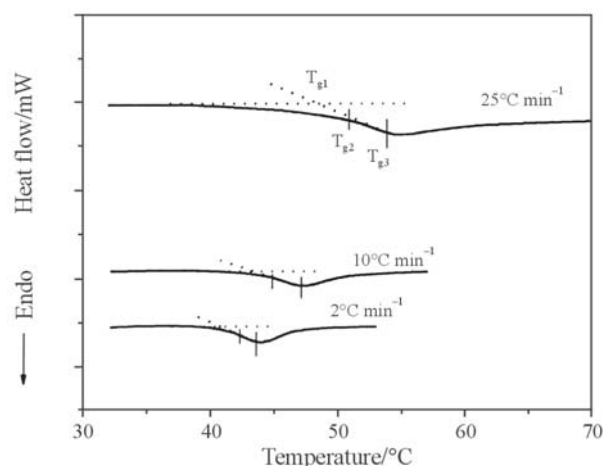


Fig. 2 DSC traces for the $\text{Cu}_{0.3}(\text{SSe}_{20})_{0.7}$ chalcogenide glass showing the T_g dependence on the heating rate

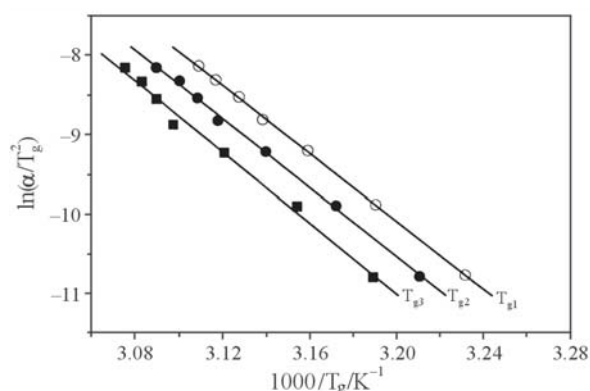


Fig. 3 Plot of $\ln(\alpha/T_g^2)$ vs. $1000/T_g$ for $\text{Cu}_{0.3}(\text{SSe}_{20})_{0.7}$ chalcogenide glass

Table 1 Activation energy and constant for all temperatures at T_g

	$E_g/\text{kJ mol}^{-1}$	Constant*
T_{g1}	178.57 ± 2.10	71.731
T_{g2}	177.73 ± 2.81	68.701
T_{g3}	177.49 ± 2.45	68.007

*Constant values in Eq. (14), (24) and (30)

tion activation energy and the constant values for all the temperatures of T_g . We notice that the values of the activation energy as they are calculated with the Kissinger method are slightly the same within the scatter of the data. Regardless of the T_g definition

(Fig. 2), the value of the glass transition activation energy E_g remained constant throughout the glass transition temperature range. The average calculated value of E_g is $177.93 \pm 1.42 \text{ kJ mol}^{-1}$. This is the first attempt to check the validity of the Kissinger plot throughout the whole glass transition temperature range.

Conclusions

The application of the Kissinger equation to the transition in $\text{Cu}_{0.3}(\text{SSe}_{20})_{0.7}$ chalcogenide glass can be used to determine and test the constancy of the glass transition activation energy, E_g throughout the glass transition temperature range. This model demonstrates that the E_g -value is constant throughout the whole glass transition temperature range and to be $177.93 \pm 1.42 \text{ kJ mol}^{-1}$.

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