Iso-conversional kinetic analysis of quaternary glass re-crystallization

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Abstract

Iso-conversional kinetic analysis is popular in scientific community for analyzing solid-state reactions (e.g., glass/amorphous and amorphous/crystal phase transformations, re-crystallization etc). It is a recognized significant tool to achieve useful outcomes for the solid state reaction under consideration. Present work is devoted to explore some insights of thermally activated crystallization using various heating rates (VHR) method. We have examined the correlation between iso-conversional activation energy and iso-conversional rate of crystal growth. In fact, we have observed the compensation law and iso-kinetic relationship using two different approaches for the study of crystallization phenomenon that drives thermally in an Arrhenian manner.

Moreover, we found that the estimated intercepts and gradients (i.e., Meyer-Neldel energy and Meyer-Neldel pre-factor respectively) for both approaches also vary linearly and both sets are remarkably identical. These results approach to an inference for ensuring the equivalence of compensation law and iso-kinetic relationship and provide an understanding of various advanced materials in physical chemistry, materials sciences and solid-state physics.

Keywords: Physical chemistry, Physics methods
1. Introduction

The use of iso-conversional methods is common in the physical chemistry for the analysis of the kinetics of the thermally activated solid-state reactions. The complex physico-chemical alterations that arise during a thermally activated event are analyzed by differential scanning calorimetry (DSC) technique in terms of multi-step processes occurring concurrently at different rates. Thus, it becomes logical that the activation energies for such processes cannot be equal and therefore overall activation energy (or effective activation energy) may be dependent on the degree of conversion [1].

The analysis of crystallization kinetics of non-crystalline solids can be done using experimental data obtained from state of art DSC technique under two different conditions. In first condition, the sample is quickly heated near crystallization region and maintained at such temperature. In other words, the reaction evolution is recorded under isothermal condition [2]. The linear heating rate program is another substitute that provides the recording of the reaction growth under non-isothermal condition [3, 4]. Several procedures have been proposed for determining the activation energy and the kinetic model from data obtained under rising temperature conditions [3, 4]. More often, isothermal crystallization is a common practice due to the convenience of theoretical treatment of the obtained data, however, isothermal crystallization are usually performed in a smaller temperature window. In fact, the calorimetric studies of crystallization in non-isothermal mode are more consequential than isothermal kinetic studies since they are analogous to conventional industrial processing. Non-isothermal methods are further divided into two main categories for study of reaction kinetics: (i) iso-conversional (model-free) methods [5, 6, 7] and (ii) model-fitting methods [8]. The benefit of the iso-conversional methods over the model-fitting methods is the ability of determination of the activation energy at progressive extent of conversion (α) without assuming any reaction model. The model fitting methods involve the fitting of different reaction models to experimental data for simultaneous determination of the constant kinetic parameters [9, 10].

However, the model fitting methods consist of numerous shortcomings out of which the major trouble is the failure of these methods in estimation of the reaction model uniquely. This is the main reason of choosing the model-free methods over these methods. The determination of various kinetic parameters at different volume fractions of crystallization by using VHR method is in fashion and this approach has become popular in thermal analysis community [11, 12].

In present script, we have used VHR method as a tool to disclose some new facts of crystallization phenomenon in selenium rich multicomponent glasses. Selenium is well-known phase change material [13] and the calorimetric study of crystal growth of selenium and Se rich glasses is subject of great interest [14, 15]. Various
research groups have used iso-conversional methods in diversified scientific areas in last one decade [16, 17, 18, 19, 20, 21, 22].

Kinematical studies of the crystallization processes in chalcogen (Se, Te and S) rich materials (e.g., non-oxide glasses and amorphous semiconductors) in bulk and thin film forms [23, 24, 25, 26, 27, 28] are of particular interest because they are directly linked with such significant phenomena (like memory type of switching, reversible optical recording, etc) that are the basis of practical applications [23, 24, 25, 26, 27, 28]. In recent and old past, silver containing chalcogenide glasses were intensively studied owing to their potential applications [29, 30, 31, 32]. Hence we have opted silver containing multicomponent glasses for present study. Particularly, we prepared quaternary $\text{Se}_{78-x}\text{Te}_{20}\text{Sn}_{2}\text{Ag}_{x}$ ($x = 2, 4, 6$) glasses for this purpose. The three samples have been designated as STSA-1, STSA-2 and STSA-3 corresponding to values 2, 4 and 6 of silver composition $x$. The use of VHR method is done to establish a correlation between iso-conversional activation energy and rate constant from the data obtained by non-isothermal differential scanning calorimetry (DSC) in crystallization region.

2. Model

The kinetic model of Johnson-Mehl-Avrami (JMA) [33, 34, 35] is used as universal theory of crystallization kinetics in various materials. JMA model describes the calorimetric data of DSC in terms of volume fraction crystallized $\alpha$ in time ($t$) according to following relation:

$$\alpha = 1 - \exp\left\{-(Kt)^n\right\}$$  \hspace{1cm} (1)

The symbol $n$ in above equation is well-known Avrami index while $K$ is the rate constant that plays the role of the effectual overall reaction rate constant to describe the nucleation rate as well as the growth rate. Usually, it shows the Arrhenian temperature dependence:

$$K = K_0 \exp\left(\frac{-E}{RT}\right)$$  \hspace{1cm} (2)

In Eq. (2), the pre-factor $K_0$ associates with the probability of collisions between molecular species, $E$ is the overall crystallization activation energy involved in the crystallization process, $T$ denotes the absolute temperature and $R$ is well-known gas constant. When calorimetric measurements are done in DSC cell under non-isothermal conditions by imposing a heating rate $\beta = dT/dt$, then following linear temporal variation of temperature is observed:

$$T = T_0 + \beta t$$  \hspace{1cm} (3)

Here, $T_0$ is the on-set temperature of crystallization.
Now think about the exothermic peaks observed in crystallization regime corresponding to various heating rates and consider the common values $\alpha_i$ of ($0 \leq i \leq 1$) crystallization fraction $\alpha$ so that Eq. (1), takes the form:

$$\alpha = 1 - \exp\{-K_it_i^n\}$$  

(4)

\&

$$K_i = (K_0)_i \exp\left(-\frac{E_i}{R_T}i\right)$$

(5)

From Eqs. (4) and (5), one can easily understand that $t_i$ and $T_i$ are the time and temperature respectively analogous to the crystallization fraction $\alpha_i$ at heating rates $\beta_j$.

Rearranging Eq. (4) and taking the logarithm on both sides, we have

$$\ln(1 - \alpha_i) = -(K_it_i)^n$$

or

$$[-\ln(1 - \alpha_i)]^{1/n} = K_it_i$$

(6)

Eliminating $K_i$ from Eqs. (5) and (6), we have

$$\frac{[-\ln(1 - \alpha_i)]^{1/n}}{(K_0)_i} = t_i \exp\left(-\frac{E_i}{R_T}i\right)$$

or

$$t_i = \phi_i \exp\left(\frac{E_i}{R_T}i\right)$$

(7)

Here we have used a substitution:

$$\phi_i = \frac{[-\ln(1 - \alpha_i)]^{1/n}}{(K_0)_i}$$

(8)

Taking logarithm of Eq. (7), we have

$$\ln t_i = \ln \phi_i + \left(\frac{E_i}{R_T}i\right)$$

(9)

This equation indicates a linear relation between $\ln t_i$ and $1/T_i$ whose slope provides the value of $E_i$ and intercept is $\ln \phi_i$.

Now, let us consider two different values $\alpha_j$ and $\alpha_k$ of extent of crystallization so that we can express intercept $\ln \phi_i$ in following forms with the help of Eqs. (8) and (9):
\[ \phi_j = \ln \left\{ \frac{-\ln(1 - \alpha_j)^{1/n}}{(K_0)_j} \right\} \]  \hspace{1cm} (10)

and

\[ \phi_k = \ln \left\{ \frac{-\ln(1 - \alpha_k)^{1/n}}{(K_0)_k} \right\} \]  \hspace{1cm} (11)

From suitable mathematical rearrangements of expressions obtained after taking the exponential of Eqs. (10) and (11), we get the following expressions for pre-factor \( K_0 \):

\[ (K_0)_j = \frac{\left[ -\ln(1 - \alpha_j)^{1/n} \right]}{\exp(\ln \phi_j)} \]  \hspace{1cm} (12)

and

\[ (K_0)_k = \frac{\left[ -\ln(1 - \alpha_k)^{1/n} \right]}{\exp(\ln \phi_k)} \]  \hspace{1cm} (13)

Above analysis provide us the inclusive set of the parameters of crystallization kinetics (iso-conversional activation energy \( E \), the over-all reaction order \( n \) and iso-conversional pre-factor \( K_0 \)).

Let us presume that we have accessible values of rate constant and corresponding activation energy for some reaction measured at diverse temperatures, then these can readily be correlated by means of the Arrhenian temperature dependence:

\[ K = K_0 \exp \left( \frac{-E}{RT} \right) \]  \hspace{1cm} (14)

Now consider the existence of analogous data for a succession of strictly related reactions (symbolized by an index \( i \)). In such circumstances, we obtain a sequence of values of rate constants \( (K_i) \), pre-exponential factors \( (K_0)_i \) and activation energies \( E_i \) independently related by following equation:

\[ K_i = (K_0)_i \exp \left( \frac{-E_i}{RT} \right) \]  \hspace{1cm} (15)

The aforesaid linear connection between \( \ln K_0 \) and \( E \) can be written in the form:

\[ \ln (K_0)_i = \ln (K)_{iso} + \frac{E_i}{RT_{iso}} \]  \hspace{1cm} (16)

In light of Eqs. (15) and (16), we obtain:

\[ K_i = (K)_{iso} \exp \left[ -E_i \left( \frac{1}{RT} - \frac{1}{RT_{iso}} \right) \right] \]  \hspace{1cm} (17)
From Eq. (17), it is clear that \( \ln K_i \) versus \( 1/T \) plot provides a set of straight lines having an intersection point of ordinate \( \ln(K_{i\text{iso}}) \) and an abscissa \( 1/T_{i\text{iso}} \).

In the same manner, when one considers the following famous thermodynamic relation that is applicable for all chemical equilibrium processes:

\[
\Delta H = \Delta G + T \Delta S
\]

then the Eqs. (16) and (17) form the basis of iso-kinetic relationship (IKR) [37]. The credit to observe such type of correlation firstly goes to Constable who found a linear relationship between the logarithm of the pre-exponential factor and the activation energies of the dehydrogenation of alcohol using different copper oxide catalysts [37]. Later some other researchers observed this kind of relationship in other kinds of catalytic studies [38]. They used a special name for this relationship as “compensation effect”.

It is interesting to note that differential form can be derived for such effects, specifically the IKR and compensation effect. Leffler and Grunwald defined an operator \( \delta \) that describes the deviation of separate values within the series under consideration. Quantitatively, the compensation effect for a solitary interaction mechanism can be expressed by following relation that refers to the slope of a linear plot between \( \ln(K_{i\text{o}}) \) and \( E_i \) with a slope given by:

\[
\frac{\delta(\ln K_{i\text{o}})}{\delta E} = \frac{1}{T_{i\text{iso}}}
\]

On the equal footage, if we use a continuous parameter \( \xi \) rather than the distinct \( i \)-values then the IKR takes the following form:

\[
\left\{ \frac{\partial(\ln K)}{\partial \xi} \right\}_{1/T_{i\text{iso}}} = 0
\]

\[ \text{(20)} \]

**Fig. 1.** Diverse illustrations of the compensation effect (see upper panel) and the IKR (see lower panel) in differential form (L.H.S.) and an integral form (R.H.S.).
This equation indicates the existence of a minimum difference of \( \ln K \) values within the series at a particular temperature \( T_{iso} \).

Diversified research groups observed such correlations in a variety of research areas (e.g., Langmuir monolayer, micro-emulsion, micellization, food chemistry, solution thermodynamics etc) and they defined similar relationship according to their case studies (e.g., the compensation effect, the enthalpy-entropy relationship, the \( \theta \)-rule in heterogeneous catalysis, the Meyer-Neldel rule in conductivity of metals, the Zawadzki-Bretschnajder rule, the Smith-Topley effect etc) [39, 40]. Fig. 1 summarizes the illustrations of diversified inter-relations/formulations of the effects that were observed in past.

3. Results

Quaternary glasses alloys of STSA system were prepared by conventional melt-quench technique. The details of melt-quench technique are given in [36]. Surface morphology of quenched materials was characterized by SEM technique. SEM picture of as-prepared sample of STSA-1 is shown in Fig. 2 that clearly shows the

![Fig. 2. SEM images of as-prepared sample of STSA-1 alloy.](image1)

![Fig. 3. TEM images of as-prepared sample of STSA-2 alloy.](image2)
absence of any crystal growth. TEM pictures of these samples also reveal the same observation as it has no discernible structure but a diffuse ring was observed in its electron diffraction pattern (see an exemplary TEM picture of STSA-2 in Fig. 3 and the inset of figure). XRD technique was also used for the confirmation of glassy nature of as-prepared samples. Fig. 4 shows the XRD pattern of as-prepared sample of STSA-3. The lack of any sharp peak in XRD pattern was the direct confirmation of the over-all glassy nature of the sample. Akin XRD patterns were obtained for as-prepared samples of other two glasses.

Thermal behavior of preset multi-component glasses was investigated using differential scanning calorimeter (TA Instruments, USA; Model: Q20 MDSC). The identical mass (~5 mg) of powder of each sample was heated in DSC unit at a constant heating rate and the changes in heat flow with respect to an empty
Table 1. Values of set \((T_i, t_i)\) for present samples for \(i = 0.3\).

| Heating rate \(\beta\) (K/min) | STSA-1 \(\alpha_3 = 0.3\) | STSA-2 \(\alpha_3 = 0.3\) | STSA-3 \(\alpha_3 = 0.3\) |
|-------------------------------|-----------------------------|-----------------------------|-----------------------------|
| \(T_3\) (K) \(t_3\) (s) | \(T_3\) (K) \(t_3\) (s) | \(T_3\) (K) \(t_3\) (s) |
| 5 | 390.3 | 215.5 | 391.0 | 248.6 | 393.7 | 277.2 |
| 10 | 396.6 | 99.2 | 399.0 | 134.2 | 399.1 | 105.6 |
| 15 | 400.4 | 72.4 | 403.4 | 90.3 | 405.8 | 85.4 |
| 20 | 403.1 | 59.1 | 404.4 | 66.2 | 409.6 | 71.9 |

Fig. 6. Temperature dependence of \(\alpha_i\) for present samples.
reference pan were measured at four heating rates 5, 10, 15 and 20 K/min. The temperature precision of this equipment is ±0.1 K with an average standard error of about ±1 K in the measured values.

The distinct glass/crystal phase transition is confirmed by appearance of well-defined exothermic peaks in DSC scans. Such DSC scans obtained at different heating rates are shown in Fig. 5 for as-prepared samples. In DSC scan, the fraction “$\alpha$” (extent of conversion) crystallized at any temperature $T$ has been determined by the simple formula: $\alpha = A_T / A$. Here $A$ is the total area of exothermic peak between the temperature $T_b$ where the peak begins (i.e. starting of the crystallization) and the temperature $T_f$ where the peak is finished (i.e. ending of the crystallization). $A_T$ is the partial area of exothermic peak between the temperatures $T_b$ and $T$. The plots of Fig. 6 show the temperature dependence of $\alpha$ at

### Table 2. Values of set ($T_i$, $t_i$) for present samples for $i = 0.6$.

| Heating rate $\beta$ (K/min) | STSA-1 | | STSA-2 | | STSA-3 |
|-----------------------------|--------|---|--------|---|--------|
| $\alpha_3 = 0.6$            | $\alpha_3 = 0.6$ | $\alpha_3 = 0.6$ |
| $T_6$ (K)      | $t_6$ (s) | $T_6$ (K) | $t_6$ (s) | $T_6$ (K) | $t_6$ (s) |
| 5             | 397.4 | 301.2 | 400.8 | 366.0 | 400.5 | 358.4 |
| 10            | 404.4 | 145.6 | 409.8 | 199.4 | 405.3 | 142.6 |
| 15            | 409.2 | 107.6 | 414.4 | 134.3 | 414.2 | 119.0 |
| 20            | 411.7 | 84.9 | 415.5 | 99.5 | 417.3 | 95.1 |

![Fig. 7. Plots of ln $t_i$ versus 1000/$T_i$ for present samples.](image-url)
Table 3. Values of iso-conversional activation energy of crystallization $E_i$ obtained by VHR method, KAS and FWO methods.

| $\alpha_i$ | STSA-1 | STSA-2 | STSA-3 |
|------------|---------|---------|---------|
|            | $E_i$ (kJ/mol) | $E_i$ (kJ/mol) | $E_i$ (kJ/mol) |
| VHR | KAS | FWO | VHR | KAS | FWO | VHR | KAS | FWO |
| 0.1 | 155.5 | 148.1 | 146.9 | 110.1 | 115.7 | 116.1 | 137.6 | 122.6 | 122.8 |
| 0.2 | 150.1 | 146.5 | 145.1 | 120.4 | 121.4 | 121.6 | 109.7 | 108.5 | 109.4 |
| 0.3 | 132.8 | 134.5 | 134.2 | 121.2 | 121.8 | 122 | 105.9 | 106 | 107.1 |
| 0.4 | 132.2 | 134.2 | 133.9 | 118.5 | 117.4 | 118 | 106.5 | 106.4 | 107.5 |
| 0.5 | 124.5 | 128.4 | 128.4 | 118.9 | 119.9 | 120.3 | 99.8 | 101.9 | 103.3 |
| 0.6 | 118.2 | 122.9 | 123.2 | 114.3 | 116.1 | 116.8 | 93.8 | 97.3 | 98.95 |
| 0.7 | 116.6 | 121.4 | 121.9 | 110.9 | 113.2 | 114.1 | 86.2 | 91.46 | 93.43 |
| 0.8 | 108.6 | 114.5 | 115.4 | 100 | 104 | 105.5 | 93.4 | 97.19 | 98.93 |
| 0.9 | 105.8 | 111.6 | 112.7 | 92.7 | 100.8 | 102.5 | 95.5 | 99.18 | 100.9 |

Fig. 8. Plots of ln ($K_0$) versus $E_i$ (first approach).
four different heating rates for STSA glasses. The values of temperature $T_i$ and time $t_i$ corresponding to $\alpha_i$ ($i = 0.1, 0.2, \ldots, 0.8, 0.9$) were noted. As an example, we have shown the values of set ($T_i, t_i$) for present samples for $i = 0.3$ and 0.6 in Tables 1 and 2 respectively. Similar data was obtained for other values of $i$. The plots of $\ln t_i$ versus $1000/T_i$ for different values of $\alpha_i$ ($i = 0.1, 0.2, \ldots, 0.8, 0.9$) are shown in Fig. 7 for quaternary glass of STSA-1. Similar plots were obtained for other two samples.

4. Discussion

From the slopes of these plots we have obtained the values of iso-conversional activation energy of crystallization $E_i$. We determined the values of $E_i$ using two
standard well-known model-free methods (KAS and FWO methods) \cite{41, 42, 43, 44, 45, 46}. The values of $E_i$ obtained by VHR, KAS and FWO methods are given in Table 3 for comparison. This Table clearly shows the good agreement between the values of $E_i$; thereby proves the applicability of VHR method.

As clear from Eq.(9) that the intercepts of these plots provide the values of $\ln \phi_i$, so we can determine the pre-factor ($K_0$) of iso-conversional crystallization rate $K_i$ using either of Eqs. (12) and (13). Knowing the $K_i$ values of present samples corresponding to iso-conversional crystallization energy $E_i$ values, we have plotted the graphs of $\ln(K_0)$ against $E_i$. Such plots are shown in Fig. 8. From Fig. 8, it is obvious that each plot is a line with correlation coefficient $\sim 1$. Physically, it means that $\ln(K_0)$ increases linearly with rise in $E_i$. Thus, the iso-conversional kinetic parameters $\ln(K_0)$ and $E_i$ obeys following relationship:

$$\ln(K_0)_i = \ln(K_0) + \frac{E_i}{RT_0} \quad (21)$$

The correlation expressed in Eq. (21) is analogous to Eq. (16); thereby indicating the applicability of compensation effect for iso-conversional crystallization in present samples.

In next step, we have changed our approach to see the presence of compensation effect for a particular value of extent of crystallization $\alpha$. For this, we plotted the

**Table 4.** Values of slopes $m_1$, $m_2$ and intercepts $c_1$, $c_2$ of straight lines expressed by relations (23) and (24).

| Relation (23) | Relation (24) |
|--------------|--------------|
| $m_1$        | $m_2$        |
| $c_1$        | $c_2$        |
| 0.071        | 0.076        |
| 2.06         | 2.03         |

![Plot between slope ln $K_{00}$ and intercept $RT_0$ obtained from Relation (22)](image-url)
graphs between \( \ln K_0 \) and \( E \) using their data obtained for present samples at different values of \( \alpha \). We have used least square method for the curve fitting and we have shown the values of the square of correlation coefficient \( (R^2) \) corresponding to each \( \ln K_0 \) versus \( E \) plot in Fig. 9. It is explicable from this figure that the plots of \( \ln K_0 \) against crystallization activation energy \( E \) are the straight line of high-quality correlation coefficient; thereby indicating that \( K_0 \) varies exponentially with \( E \) according to Meyer-Neldel relation [47]:

\[
K_0 = K_{00} \exp\left( \frac{E}{RT_0} \right)
\]  

From the slopes and intercepts of the lines shown by Eqs. (21) and (22), we have collected the corresponding data of \([ (RT_0)_i, \ln (K_{00})_i ]\) and \([ RT_0, \ln K_{00} ]\) respectively. It is interesting to mention here that when we have plotted graphs for these two cases then surprisingly again we have observed the straight lines of good correlation coefficients (see Figs. 10 and 11). From these plots it is clear that both lines are almost identical. Therefore, one can express these straight lines by following expressions:

\[
\ln(K_{00})_i = m_1 \cdot (RT_0)_i + c_1
\]

\[
\ln K_{00} = m_2 \cdot RT_0 + c_2
\]

Here \( m_1, m_2 \) are the slopes of straight lines expressed by relations (23) and (24) while \( c_1, c_2 \) are their corresponding intercepts. This type of co-relation has been observed by us and other groups in the series of thermally activated phenomena [48]. Such co-relation is widely known as Further Meyer-Neldel relation (FMNR) [48]. The values of both sets [i.e., \( (m_1, c_1) \) and \( (m_2, c_2) \)] are given in Table 4. From this table, it is obvious that \( m_1 \approx m_2 \) and \( c_1 \approx c_2 \). Thus, we arrive at almost same results from the curve fitting of both \([ (RT_0)_i, \ln (K_{00})_i ]\) and \([ RT_0, \ln K_{00} ]\) data. In other words, this indicates the equivalence between iso-kinetic effect and compensation effect.

5. Conclusions

It is well-known that IKR and compensation rule are still not accepted universally owing to lack of uniform and general clarification of the phenomena under considerations. However, various case studies are being reported by the communities of biology, physical chemistry and solid state physics progressively for diverse thermally activated phenomena occurring in different types of materials. For the iso-conversional re-crystallization and crystal growth during constant heating, both IKR and compensation rule are not renowned, and therefore one purpose of present script is to demonstrate their applicability. We have successfully observed the presence of IKR and compensation effect in iso-conversional re-crystallization of three quaternary glasses of STSA system.
Further, the aforesaid studies play a significant role for calibration and verification of experimental data (Arrhenius pre-factor and the activation energy involved in the phenomenon under consideration) for their linear fitting. In past such studies have been demonstrated to be valid for over-all activation energy and pre-factor of non-isothermal crystallization by our group and other authors using model-fitting methods, but here we have first time reported the Meyer-Neldel correlation between the iso-conversional activation energy and iso-conversional pre-factor using two different approaches.

Last but not the least; we have used the experimental data of MN pre-factor and MN activation energy for the investigation of FMNR and found the applicability of FMNR successfully. We have also observed that the slopes and intercepts are almost identical which are obtained from the linear plots between MN pre-factor and MN activation energy for both cases. This indicates the equivalence of IKR and compensation rule.

**Declarations**

**Author contribution statement**

Ankita Srivastava: Analyzed and interpreted the data.

Namrata Chandel: Performed the experiments.

Neeraj Mehta: Conceived and designed the experiments; Analyzed and interpreted the data; Wrote the paper.

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**Competing interest statement**

The authors declare no conflict of interest.

**Additional information**

No additional information is available for this paper.

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