

**EFFECT OF TIME ON CONCENTRATION-DEPENDENT  
INTERDIFFUSION COEFFICIENT IN Cu-Ge ALLOY SYSTEM**

**BY**

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## **ABSTRACT**

Diffusion controlled processes offer a number of advantages in a wide range of material and metallurgical processes which include phase transformations, sintering and surface treatments. Thus, the subject of diffusion has garnered considerable scholarly interest in recent times. Isothermal interdiffusion coefficients are critical parameters that significantly influence material performance evaluations and analyses used to characterize these processes. In the literature, there is the general assumption that this parameter is solely a function of temperature and concentration. However, previous studies also suggest that time has an effect resultant of the diffusion-induced stresses evident within systems.

This research work experimentally verifies the time effect on concentration-dependent interdiffusion coefficient in a copper-germanium- (Cu-Ge) binary system at different temperatures. In calculating this parameter for this system, a recently developed fully explicit numerical diffusion model-coupled with the forward simulation method is employed to avoid the inherent shortcomings of conventional models such as the Boltzmann-Matano, Sauer Freise, Wagner, and Hall methods.

The obtained results which are attributable to the concept of diffusion-induced stress show time variations in interdiffusion coefficients under isothermal conditions. These findings contradict the widely accepted notion that interdiffusion coefficients depend solely on concentration and temperature. Moreover, the commonly expected direct proportionality between diffusion kinetics and temperature as predicted by Arrhenius behavior may not hold true for all time durations.

## **DEDICATION**

This thesis is dedicated to Almighty God for all He has done

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## **LIST OF ABBREVIATIONS**

BM – Boltzmann-Matano

SF – Sauer-Freise

SEM – Scanning electron microscope

DIS – Diffusion-induced stress

FSM – Forward simulation method

HM – Hall method

EDM – Electron discharge machining

EDS – Energy dispersive x-ray spectroscopy

# CHAPTER ONE

## INTRODUCTION

### 1.1 Background Information

Atomic diffusion is a process which entails the mass transport of atoms through atomic motion. This process plays a crucial role in the investigation of phase transformations in metals and semi-conductors. The properties of engineering materials can be changed by modifying their microstructure through a material process that induces phase changes.

A number of different industries have applied the principle of solid state mass transport to influence and predict the performance of engineering materials for over 150 years including the aerospace, automobile, biomedical, and electronic (doping of semi-conductors during the fabrication of microelectronic devices) industries and energy sectors,- amongst others [1]. Industries involved in material processing frequently employ phase transformation techniques such as carburization, coating, diffusion bonding, heat treatments and sintering to improve the properties of engineering materials thereby optimizing their performance.

In recent times, diffusion is being used in a number of metallurgical processes such as carburizing, where steel alloys or iron is subjected to a high temperature carbon-rich environment to enable diffusion. This process alters the surface composition of the material, thus resulting in increased hardness and enhanced wear resistance [2]. Another process includes the manufacturing of complex circuitry on silicon chips. This is achieved by introducing dopant atoms onto silicon wafers through diffusion, which allows for the accurate control of the electrical properties thereby enabling the production of electrical components [3]. Additionally, other applications include the development of solid electrolytes which facilitate ion transport in advanced battery and fuel cell

applications, and solid state material joining processes such as diffusion bonding and brazing. Hence, a thorough understanding of solid state diffusion can advance developments in industries that rely on accurate material design and processing techniques.

The fundamental laws that govern diffusion controlled processes are called the Fick's laws of diffusion which will be elaborated in Chapter 2. The Fick's equations rely on an essential parameter known as the diffusion coefficient which plays a key role in diffusion equations as well as diffusion related analyses and predictions. This parameter characterizes how readily and quickly particles migrate through a material. Consequently, the accuracy of analyses that involve controlled processes is contingent on the reliability of the diffusion coefficient. This parameter is widely recognized to be concentration-dependent and thus termed the concentration-dependent interdiffusion coefficient  $D(c)$  or chemical diffusion coefficient [4], [5].

In the literature, it is largely assumed that  $D(c)$  is a material constant and does not vary under isothermal conditions. However, this assumption may be fundamentally flawed due to the difference in atomic sizes between the solute and solvent atoms. This leads to changes in the lattice parameter of the host material during diffusion. As the solute concentration varies across the material, these changes in the lattice parameter produce internal stresses within the crystal structure of the host [6-9]. The stress that results from diffusion induced strain is termed diffusion-induced stress (DIS). According to Jain and Van Overstraeten [8], the solute concentration gradient within a crystal lattice influences diffusion-induced strain and eventually, the diffusion coefficient. Furthermore, Larche and Cahn [7] showed that long-range elastic interactions that arise from compositional inhomogeneity contribute substantial non-local stress effects to diffusion fluxes. This behavior was interpreted as a deviation from Fick's law of solid state diffusion.

A number of investigations have theoretically and experimentally verified the existence of DIS and some studies have confirmed the influence of DIS on diffusion coefficients[6], [9-16]. The diffusion coefficient is theoretically concentration-dependent because the solute concentration influences the concentration gradient, which in turn, affects DIS which governs diffusion behavior. This concentration-dependence have been verified by a number of studies; see for example, [4] and [17].

## **1.2 Research Motivation**

Concentration-dependent interdiffusion coefficients derived from the classical Fick's second law of diffusion are assumed to remain constant under isothermal conditions without any time effect [18]. However emerging theoretical and experimental research work has presented evidence that challenge the validity of this assumption. Furthermore, the Arrhenius equation describes temperature dependent interdiffusion coefficients under non-isothermal conditions [19]. Wang et al. [4] showed that the interdiffusion coefficient in an Arrhenius equation may exhibit systematic variation with concentration as a result of the dependence of the interdiffusion coefficient on the solute concentration. Moreover, the majority of existing studies in the literature that address concentration-dependent interdiffusion coefficient typically use a fixed diffusion time across different temperature conditions with no consideration of a possible time effect.

Variations in diffusion behavior have been attributed to multiple factors that change the concentration gradient during the diffusion process. As a result, the stress and strain in the diffusion system are affected, thereby changing the diffusion coefficient. The emergence of DIS has prompted investigations of the long-standing assumption that concentration-dependent interdiffusion coefficient are not influenced by time dependent effects.

Recently, Olaye and Ojo [20] developed a fully explicit numerical diffusion model coupled with the forward simulation method (FSM) [21] to evaluate concentration-dependent interdiffusion coefficients. This method has addressed the inherent limitations in conventional models such as the Boltzmann-Matano (BM), Sauer-Freise (SF), Wagner, and Hall methods.

### **1.3 Research Objectives**

Using the recently developed approach in Olaye and Ojo [20], the main objective of this work is to investigate the effect of time on isothermal concentration-dependent interdiffusion coefficients in a copper-germanium (Cu-Ge) binary system

### **1.4 Major Work Performed and Key Findings**

A number of experiments are carried out in this study for pure Cu/Cu 3 at.% Ge for different temperatures at different diffusion times. The concentration profiles are obtained post diffusion treatment by sectioning the samples and carrying out micro-analyses specifically with the use of an energy dispersive x-ray analyzer (EDS) alongside a scanning electron microscope (SEM). At least five concentration profiles are obtained for each sample and smoothened. Afterwards, the numerical diffusion model in Olaye and Ojo [20] and FSM are employed to determine the concentration-dependent interdiffusion coefficients.

Concentration-dependent interdiffusion coefficients are plotted for various conditions with the use of standard deviation error bars, impurity diffusion coefficients and average interdiffusivity for each sample are investigated. Furthermore, the resulting interdiffusion coefficient data are used to produce Arrhenius plots.

Based on an analysis of the acquired results, this research work provides evidence that concentration-dependent interdiffusion coefficients observed under isothermal conditions vary

significantly with time. This variation shows the influence of the concentration gradients on interdiffusion coefficients. Consequently, this behavior greatly suggests the underlying effects of DIS.

## **1.5 Thesis Structure**

This thesis consists of six chapters. Chapter 1 is the introduction, which provides a general introduction of the thesis subject, research motivation, research objective along with a brief description of the major work performed, key findings and thesis structure. Chapter 2 is the literature review, which entails a review of the related existing literature including studies on solid-state diffusion, diffusion mechanisms and governing equations. The chapter also explores the conventional methods in evaluating diffusion coefficients and the concept of DIS. Chapter 3 is the methodology chapter, which extensively elaborates on the experimental work. The sample preparation of the starting materials, diffusion treatment conditions, data acquisition technique and procedures in the numerical approach are discussed. Chapter 4 provides the results and a discussion of the concentration-dependent interdiffusion and impurity diffusion coefficients. The attributes of the DIS as the underlying factor of the variations in this parameter and the significance of the time effects observed are also discussed. Chapter 5 provides a detailed summary of the major findings and the conclusion drawn from this research work. Finally, Chapter 6 is the conclusion chapter, which highlights the limitations of this work and provides future recommendations in this research area to advance the subject matter.

## CHAPTER TWO

### LITERATURE REVIEW

#### 2.1 Brief Overview of Diffusion

A number of physical material processes, such as homogenization, sintering, creep at elevated temperatures, diffusion brazing and most phase transformation processes are dependent on solid state mass transfer which is characterized by the movement of atoms within a crystal lattice. The rate of these material processes frequently used in the engineering industries are governed by the rate of diffusion [22].

##### 2.1.1 Fick's first law of diffusion

In 1855, German physicist Adolf Fick [23] pioneered the phenomenological law that governs diffusion, and proposed that in a one-dimensional-system, the flux of particles such as atoms, molecules or ions driven by concentration gradients could be mathematically described as:

$$J = -D(c) \frac{\partial c}{\partial x} \quad (2.1)$$

where  $J$  is the flux (mol /m<sup>2</sup>s),  $D$  is the diffusion coefficient (m<sup>2</sup>/s),  $c$  is the concentration of diffusing species and  $x$  is the distance in the direction of the diffusion (m).

Note that Fick's first law of diffusion is applicable only under steady-state conditions where the composition remains constant over time. Furthermore, the system is influenced solely by the concentration gradient [24].

### 2.1.2 Fick's second law of diffusion

Practical diffusion situations are usually non-steady state conditions whereby the diffusion flux and concentration gradient at a particular location within a solid change over time which result in net build up or depletion of diffusion species [25]. Under this condition, Fick's second law is mathematically described as:

$$\frac{\partial C}{\partial t} = \frac{\partial}{\partial x} \left( D(c) \frac{\partial c}{\partial x} \right) \quad (2.2)$$

If  $D$  is independent of the position, Fick's second law is expressed as:

$$\frac{\partial C}{\partial t} = D(c) \frac{\partial^2 c}{\partial x^2} \quad (2.3)$$

## 2.2 Mechanisms of diffusion

From an atomic viewpoint, the stepwise migration of atoms from one lattice site to another defines diffusion. In reality, atoms in solids are in constant motion, and change positions frequently. Two conditions must be met for atoms to migrate within a lattice site:

- i. there must be an adjacent vacant site, and
- ii. the atoms must have a certain amount of energy (vibrational in nature) to break the bonds with the neighboring atoms and cause some lattice distortion during the movement. At a certain temperature, the magnitude of the vibrational energies causes a small fraction of the total number of atoms to undergo diffusive motion, with this fraction increasing with rising temperatures [25].

Hence, these conditions are significantly dependent on temperature which points to the temperature dependence of diffusion [22].

### 2.2.1 Vacancy Diffusion

Vacancy diffusion involves the movement of atoms from its normal lattice site to a neighboring vacant lattice site. This process requires vacancies to be present and the degree to which vacancy diffusion occurs is dependent on the number of defects present. A substantial number of vacancies exist in metals at elevated temperatures. Considering that diffusing atoms and vacancies exchange positions, the movement of an atom in one direction results in a vacancy moving in the opposite direction. This mechanism facilitates both self-diffusion and interdiffusion; the former involves a host atom as the migrating atom while the latter involves an impurity atom as the migrating atom. However, in the case of interdiffusion, the impurity atoms substitute for the host atoms [25].

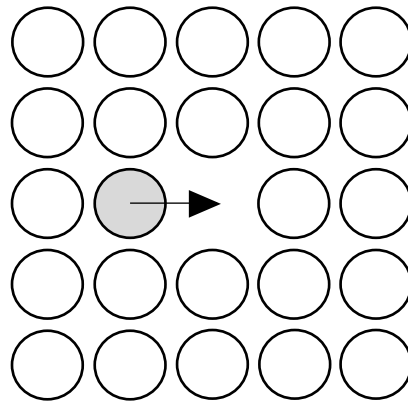


Fig. 2.1 Vacancy diffusion mechanism [26]

### 2.2.2 Interstitial Diffusion

Interstitial diffusion is defined by the migration of atoms into vacant interstitial sites. Interstitial atoms often occupy octahedral and/or tetrahedral interstitial sites in face centered cubic and body

centered cubic structures. The formation of an interstitial solid solution occurs basically by the occupancy of solute atoms which are significantly smaller than the solvent atoms in interstitial sites. Given that there is significantly low concentration of impurities in a lattice structure, atomic migrations are easily accommodated by the nearest neighboring interstitial positions. Impurities such as hydrogen, carbon, nitrogen, and oxygen often occupy these interstitial sites. Compared to vacancy diffusion, interstitial diffusion is faster because interstitial atoms are smaller and more mobile, and an empty adjacent interstitial site is more likely to be present than a vacancy. In both ferrite and austenite steels, carbon atoms occupy the interstitial sites, so carbon diffusion occurs through the successive jumps of carbon atoms from one interstitial site to another [22], [27], [28].

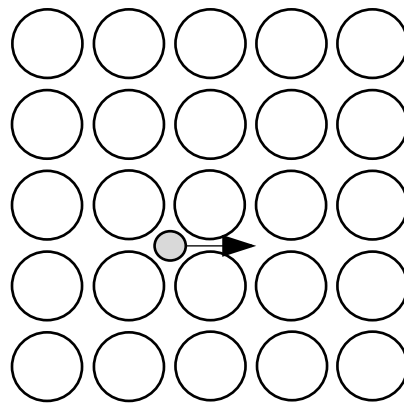


Fig. 2.2 Interstitial diffusion mechanism [25]

### 2.3 Driving forces of diffusion

Diffusion may occur with or without the presence of a driving force. In the latter, the components diffuse randomly by optimizing the systems entropy. The diffusion of small amounts of radioisotope  $A^*$  in  $A$  is one such example [29]. The potential that accounts for energy storage from the addition of a component defines the driving force. Hence, the driving force of a component constitutes all supplemental potentials including the chemical potential that arises to the total force

for that component[30]. With the presence of a driving force, the rate of diffusion is dependent upon the direction of the driving force. Typically, multiple driving forces can act simultaneously and influence the behavior of a system [31].

### 2.3.1 Chemical Potential

Thermodynamic driving forces are the result of composition differences which are inherent in the majority of material systems. Consequently, the components will diffuse along their chemical gradient potential. From a phenomenological perspective, the diffusive flux  $J_i$  of component  $i$  is directly proportional to the gradient of the chemical potential

$$J_i \propto -\frac{d\mu_i}{dx} \quad (2.4)$$

Sometimes specific components diffuse against their concentration gradient, which is known as uphill diffusion. However, it is important to note that even during this phenomenon, the components always diffuse down their chemical potential gradient [31].

### 2.3.2 Electropotential

A widely acknowledged theory suggests that an atom in its activated state impedes the flow of electrons more than an atom in a lattice site. Moving electrons responsible for electric current transfer collides with these activated atoms which results in the transfer of momentum that influences diffusive jumps in the same direction as the conduction electrons. This also restricts migrations in the opposite direction [32]. Electrotransport in metals is initiated by the electric

potential gradient on account of the cross effect between diffusing species and flux of the conducting electrons present. In integrated circuit devices, this phenomenon is crucial in narrow metal conductors that form current carrying vias (conductive pathways that connect the different layers of a circuit board) [33].

### **2.3.3 Thermopotential**

Temperature gradients triggers the decomposition of an initially homogeneous alloy and diffusion of components. In an alloy where diffusion occurs interstitially, the interstitial atoms migrate upwards or downwards the temperature gradient depending on the nature of the interstitials and host elements. When the vacancy mechanism predominates diffusion, the diffusion process is additionally modified by differences in the vacancy concentration at different temperature ranges [31].

### **2.3.4 Stress potential**

Another factor that may induce driving forces in a system is the presence of stress that is either externally applied or internal stresses initiated by dislocations or cracks under load. For example, in the deposition of thin films, interfacial stress that is generated during the process significantly impacts nucleation and diffusion processes [31].

## **2.4 Experimental methods for diffusion measurements**

In studying solid state diffusion, there are a number of experimental approaches that are used to measure diffusion, which are conventionally categorized under two overarching methods; namely, direct and indirect methods.

### **2.4.1 Direct Methods**

Direct methods are sensitive to long range diffusion and therefore regarded as macroscopic. They are established based on Fick's laws of diffusion and the phenomenological definition of diffusion coefficients. The movement of atoms against the concentration gradient is employed in determining the rate of change of the concentration gradient [31], [34]. Tracer and chemical diffusions and Rutherford back scattering are some of the direct methods used in diffusion studies on solids.

- i. Tracer diffusion: a standard radiotracer technique used to study self and solute diffusion provided that the radioactive isotope of the element is available. This allows a wide range of diffusivities to be measured given that both mechanical and sputter sectioning techniques are employed for depth profiling. Furthermore, tracer diffusion is highly sensitive due to the use of nuclear counting facilities and thus selective for specific elements.
- ii. Chemical diffusion: generally utilized for studying interdiffusion and includes the following techniques:
  - a. Secondary ion mass spectroscopy (SIMS) - utilizes sputter profiling and is applicable for short diffusion distances and low diffusivities;
  - b. Auger electron spectroscopy - identifies dissimilar elements but not isotopes of the same element. Hence, this technique is relevant for foreign atoms. Similar to SIMS,

auger electron spectroscopy also uses sputter profiling and employed for short diffusion distances and low diffusivities; and

- c. Electron probe microanalysis (EPMA) - a primary tool for the investigation of interdiffusion coefficients and is equally appropriate for analyzing large diffusivities. However, the depth resolution is restricted by the size of the specimen volume that the electron beam excites.
- iii. Rutherford back scattering (RBS): a nuclear process that involves the use of ion beams of milli-electron volts of energy for profile analyses. Since the acquirable penetration depth and energy scattering of beams in this technique are limited to small diffusivities, RBS is widely used for heavy solutes over a wide solvent window [34].

#### **2.4.2 Indirect Methods**

In solid and liquid states, indirect methods pertain to various physical phenomena influenced by the thermal migration of atoms. Typically, thermally activated atomic jumps require zero chemical potential gradients. However, it is usually appropriate to track relaxation processes that involve atomic jumps to correct deviation from equilibrium. They are not directly based on Fick's law. Variables such as relaxation time, relaxation rate or line widths are measured and the mean residence time is deduced from these measurements by using:

- i. Impedance spectroscopy (IS): used to measure the intricate conductivity of ion-conducting materials as a function of frequency, and
- ii. Nuclear magnetic relaxation (NMR): used for materials with large gyromagnetic ratios and minimal non-diffusive contributions to relaxation rates or line width. This technique can accommodate a wide range of diffusivities [31], [34].

## **2.5 Diffusion Coefficients**

Diffusion coefficients, a proportionality constant of Fick's first law of diffusion and often denoted as ( $D$ ), are an essential parameter which describes the rate at which atoms, ions or molecules spread within a medium. They characterize how the concentration of species varies over time and distance [1], [35]. The diffusing species in a system are dependent on a number of factors including the temperature, nature of the diffusing species, viscosity, etc. [36]. The four common types of diffusion coefficients are tracer (self and impurity tracer diffusion coefficients), intrinsic, interdiffusion, and average interdiffusion coefficients.

### **2.5.1 Tracer diffusion coefficients**

In the literature, diffusion studies that involve trace elements which are identified by their radioactivity or isotopic mass require only a minimal amount of the diffusing species. Despite the need for a concentration gradient of the tracer element for the diffusion process, the overall concentration of the sample remains effectively the same due to the extremely low tracer content. On an atomistic perspective, this implies the individual tracer atoms diffuse independently uninterrupted by interactions with other tracer atoms. As a result, this yields tracer diffusion coefficients that are independent of the tracer concentration [1].

Tracer diffusion experiments can produce two distinct types of diffusion coefficients depending on the chemical composition of the host material and the nature of the isotopic tracer employed. They are self-diffusion and impurity tracer diffusion coefficients. The former are defined based on the diffusion behavior of atoms that are often radioactive isotopes within a chemically identical, nonradioactive pure metal. Since both the tracer and host have the same chemical identity, this

type of diffusion reflects the intrinsic mobility of the species. The latter pertains to the diffusion of a minute quantity of a tracer element within a chemically distinct pure metal. The diffusion coefficient is determined by analyzing the spatial variation in the tracer concentration, typically inferred from the intensity of radioactive emissions after a fixed diffusion time [17] .

### **2.5.2 Intrinsic diffusion coefficients**

Intrinsic diffusion coefficients which are also referred to as component diffusion coefficients, are denoted as  $D_A$  and  $D_B$  and characterize the individual movement of species  $A$  and  $B$  within an  $AB$  alloy relative to the fixed lattice framework. These coefficients are primarily of fundamental physical interest and typically the diffusion rates of  $A$  and  $B$  differ from one another. Consequently, during an interdiffusion experiment, a net atomic flux occurs across each lattice plane. Assuming the conservation of lattice sites, this imbalance in atomic flux necessitates the movement of lattice planes relative to the sample-fixed coordinate system within the diffusion zone. This displacement is accommodated through the formation and elimination of vacancies on opposite sides of the diffusion interface. This relative movement of the lattice planes with respect to the sample reference frame is known as the Kirkendall effect [37].

### **2.5.3 Interdiffusion coefficients**

From a general standpoint, diffusion flux is directly proportional to the gradient of the chemical potential. In dilute systems or ideal solid solutions, the chemical potential shows a direct proportionality to the concentration gradient. The chemical potential gradient creates an internal driving force that governs the diffusion process. In a binary  $A - B$  alloy system, intermixing can

be described by using an interdiffusion coefficient that varies with concentration, which is denoted as  $D(c)$ . Within a binary alloy, a single interdiffusion coefficient characterizes the interdiffusion process; this process arises from the individual atomic movement of species  $A$  and  $B$  with each generally possessing distinct intrinsic diffusion coefficients [1].

#### 2.5.4 Average Interdiffusion Coefficient

The average interdiffusion coefficient,  $D_{ave}(C)$ , functions as a unique coefficient that characterizes diffusion behavior across the entire concentration range, thereby enabling systematic comparison with diffusion coefficients obtained under different conditions [38], [39]. Over a specified concentration range, the average interdiffusivity can be determined by evaluating the interdiffusion flux along the diffusion zone.

$$D_{ave} = \frac{\int_{x_L}^{x_R} J dx}{C_L - C_R} = \frac{\int_{C_L}^{C_R} D(C) dc}{C_R - C_L} \quad (2.5)$$

Equation 2.5 is the equivalent of the mean value theorem for interdiffusion coefficients against the concentration.  $x_L$  and  $x_R$  are the positions that correspond to the extreme left and right of the diffusion zone while  $C_L$  and  $C_R$  represent concentrations at the left and right ends, respectively.

#### 2.6 Conventional methods for evaluating interdiffusion coefficients

Studies on solid state diffusion in binary systems have provided a number of different approaches for evaluating interdiffusion coefficients which include the BM, SF, Wagner and Hall methods.

### 2.6.1 Boltzmann-Matano method

The BM method is used to transform Fick's second law into a non-linear ordinary differential equation, which can be used to determine concentration-dependent interdiffusion coefficients from an experimentally obtained concentration profile. Matano [40] proposed suitable boundary conditions for an interdiffusion experiment that involves a binary diffusion couple of two semi-infinite bars joined at time  $t = 0$  as follows:

$$C = C_L \text{ for } (x < 0 \text{ at } t = 0),$$

$$C = C_R \text{ for } (x > 0 \text{ at } t = 0)$$

After a diffusion annealing time of  $t$ , the concentration profile of  $C(x)$  is measured based on Figure 2.3.

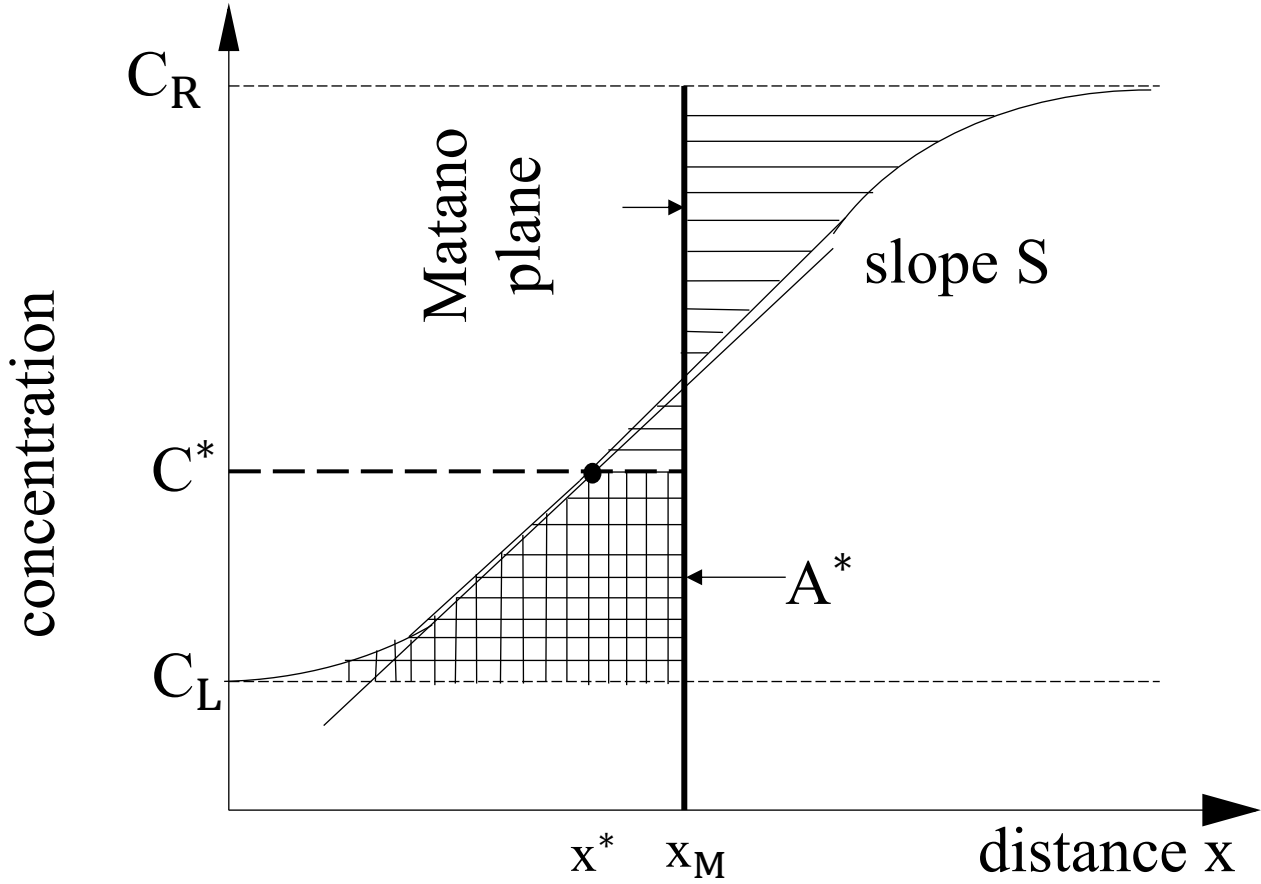


Fig. 2.3 Schematic of BM method for binary diffusion couple with starting compositions  $C_L$  and  $C_R$  [41]

Therefore, the BM equation is given as:

$$\tilde{D}(C^*) = -\frac{1}{2t} \frac{\int_{C_L}^{C^*} (x - x_m) dC}{(dC/dx)_{C^*}} \quad (2.6)$$

This relation can be used to determine the interdiffusion coefficient  $\tilde{D}$  at any concentration  $C^*$  with a known  $x_m$ .

$x_m$  is the Matano plane and can be determined by using a conservation condition expressed as:

$$\int_{-\infty}^{x_m} [C(x) - C_L] dx = \int_{x_m}^{\infty} [C_R - C(x)] dx \quad (2.7)$$

where  $C_L$  and  $C_R$  indicate the concentration at the extreme left and extreme right of the profile, respectively.

Unfortunately, the BM approach is only viable for infinite systems. Thus, the method can be applied to an experiment provided the concentration ranges are away from the end of the systems boundaries. In addition, this approach could amount to significant errors in evaluating  $D(c)$  near the end-member compositions as the area  $A^*$  and slope  $S$  in Figure 2.3 decreases substantially as they move farther away from the Matano plane [41].

### 2.6.2 Sauer-Freise method

Sauer and Freise [42] developed an approach to solve interdiffusion coefficients which eliminates the need for accurately locating the Matano plane. This method accommodates volume change as a result of interdiffusion. The interdiffusion coefficient is calculated as a function of the concentration by introducing a normalized concentration variable:

$$Y = \frac{C - C_R}{C_L - C_R} \quad (2.8)$$

where  $C_R$  and  $C_L$  are the concentrations at the left and right of the penetration profile, respectively. Furthermore, where no volume change occurs, the solution is expressed as [43]:

$$D(C) = \frac{1}{2t * \frac{dc}{dx}} \left[ (1 - Y) \int_{x^*}^{\infty} (C^* - C_R) dx + Y \int_{-\infty}^{x^*} (C_L - C^*) dx \right] \quad (2.9)$$

where  $C^*$  is the specific concentration at location  $x^*$ .

### 2.6.3 Wagner Method

The Wagner method is employed to evaluate the  $D(c)$  in systems where the assumption of an ideal molar volume does not hold [44]. Additionally, this approach eliminates the need to locate the Matano interface position. The Wagner relation is expressed as:

$$D(Y_i^*) = \frac{1}{2t} \frac{V_m^*}{\left(\frac{dY_i}{dx}\right)_{Y_i^*}} \left[ (1 - Y_i^*) \int_{x^{-\infty}}^{x^*} \frac{Y_i}{V_m} dx + Y_i^* \int_{x^*}^{x^{+\infty}} \frac{(1 - Y_i)}{V_m} dx \right] \quad (2.10)$$

Where the composition of the normalized variable with respect to component  $i$  is expressed as:

$$Y_i = \frac{N_i - N_i^-}{N_i^+ - N_i^-} \quad (2.11)$$

### 2.6.4 Hall Method

The Hall method is an analytical method to evaluate different diffusion coefficients at the extremes of a concentration profile. The key condition for the Hall method is the need for one side of the diffusion couple to have zero composition. In the following, additional transformation is applied to the dilute end of the composition profile:

$$C = \operatorname{erfc}(u) \quad (2.12)$$

$$\text{where } \operatorname{erfc}(u) \equiv 1/2 (1 + \operatorname{erf}(u)) \quad (2.13)$$

$$u = h\lambda + k \quad (2.14)$$

$$\lambda = \frac{x - x_m}{\sqrt{t}} \quad (2.15)$$

Hall [45] presumed that the dilute end of the profile exhibits distinct linear behavior and evaluated the derivative as well as the integral term in  $D(C)$  by using:

$$\frac{dC}{dx} = \frac{1}{\sqrt{t}} \frac{dC}{d\lambda} = \frac{1}{\sqrt{t}} \frac{h}{\sqrt{\pi}} \exp(-u^2) \quad (2.16)$$

$$\int_0^{C^*} (x - x_m) dC = \sqrt{t} \int_0^{C^*} \lambda dC = -\sqrt{t} \left( \frac{1}{2h\sqrt{\pi}} \exp(-u^2) + \frac{kC}{h} \right) \quad (2.17)$$

Thus, the final expression of the equation in the Hall method is derived from combining Equations 2.16, 2.17, and the BM equation (Equation 2.6) to obtain:

$$D(C) = \frac{1}{4h^2} + \frac{k\sqrt{\pi}}{2h^2} \exp(u^2) \operatorname{erfc}(u) \quad (2.18)$$

### 2.6.5 Forward Simulation Method

Although conventional methods such as the BM and SF methods are simple to use, they often result in notable uncertainties in evaluating diffusion coefficients particularly for the extremes of systems concentration profiles. However, in recent times with remarkable advancements in computational power and numerical techniques, the need to minimize errors and uncertainties is of greater importance and expected to play a vital role in future research [46].

The FSM is acknowledged as a reliable approach for determining concentration-dependent diffusion coefficients  $D(c)$  and impurity diffusion coefficients from experimental profiles. In addition, this approach is suitable for evaluating interdiffusion coefficients with weak or strong dependence on solute concentration and applicable for both finite and infinite system [27-35]. Consequently, the FSM can be applied for one-dimensional planar, two-dimensional cylindrical and three-dimensional spherical coordinate systems [54].

### 2.7 Diffusion Induced Stress

One of the pioneering studies on DIS is that of Prussin [55] who explained that dislocations are produced due to stress that arises during the diffusion process and their distribution is

influenced by solute diffusion. Subsequently, the concept of DIS has garnered considerable research focus after this pioneering study.

Due to variations in partial volume and atomic mobilities of individual components during interdiffusion, imbalance in the volume transport can arise. As a result, a stress-free deformation field may develop with contractions occurring at one side of the diffusion couple and expansion at the other side [37-42]. Available stress relaxation mechanisms such as the Kirkendall effect, creep, dislocation slips or bending within the system significantly impact these diffusion-induced stresses [6], [56], [57]. DIS tends to form inherently as a result of the mass transfer between dissimilar atoms. As such, these generated internal stresses enhance the thermodynamic potential for atomic diffusion, that is, the gradient effect, thereby altering the value of the diffusion coefficient [12].

The classical Darken analysis on interdiffusion has neglected the stress field generated by stress-free strains based on the assumption that stress relaxation occurs fully and immediately. Thus the Darken theory only accounts for convective transport effects, like the Kirkendall shift [18].

In addition, DIS relaxation does not occur at the same rate as its generation, thus indicating that the relaxation process is not fast enough to immediately counteract the buildup of DIS. Olaye [17] reported that the rate of DIS relaxation is influenced by the viscosity of the diffusion system. Therefore, factors such as the composition of the diffusion system, diffusion treatment temperature, etc. can affect the DIS by altering the viscosity of the system.

## **CHAPTER THREE**

### **METHODOLOGY**

This chapter provides the details on the materials, experimental procedures (cold rolling, sectioning and drilling, annealing, thermal diffusion coupling and electrodeposition) and numerical approaches used in this study to ensure that accurate and reliable data are obtained.

#### **3.1 Materials**

Cu-based alloy (Ge at. 3%) plates purchased from ACI Alloys Inc. (USA) and pure Cu were used for the experiments. The two materials were prepared and bonded to produce a diffusion couple, which will be discussed later in this chapter.

#### **3.2 Cold rolling**

Cold rolling is a highly effective manufacturing process in which metals are passed through rollers at an ambient temperature proven to enhance their strength, formability and dimensional precision. As the sample plates are fed into the large rollers, the compression and elongation processes permanently alter their structure. The samples used for shorter diffusion times (5, 25 and 75 hours) were rolled to a thickness of 1.5 mm for both the pure Cu and Cu alloy (Ge at. 3%). However, the pure Cu samples used for longer diffusion times (150 and 450 hours) were rolled to a thickness of 3 mm while Cu alloy (Ge at. 3%) was rolled to a thickness of 1.5 mm. A thicker pure Cu sample is necessary to accommodate solute penetration with longer diffusion times. This process also allows for the uniform distribution of the alloy elements across the entire sample area as the sample was produced by using a casting method.

### **3.3 Sectioning and drilling**

The samples were then sectioned by using an electric discharge machine (EDM) for precise material removal. The efficiency in this regard is the elimination of the mechanical force or pressure in the system which may result in micro cracks or deformation. Furthermore, the smaller samples were drilled to ensure that they were securely positioned during the subsequent electrodeposition process.

### **3.4 Annealing treatment**

As a result of the cold rolling and drilling processes, stresses and dislocations were induced in the system due to plastic deformation. Dislocations and grain boundaries are linear defects which facilitate short-circuit pathways, thereby increasing diffusivity. Olaye and Ojo [59] highlighted the pivotal role of a pre-annealing treatment to eliminate mechanical residual stresses which may have been introduced into the system and allow grain growth at a higher temperature above actual diffusion treatment temperatures. In doing so, this eliminates grain growth and the possibility that it will interfere with the actual diffusion process at lower temperatures.

The Cu alloy (Ge at. 3%) samples were annealed at 900°C for 48 hours which is a suitable temperature and time condition to initiate recrystallization. To replace deformed grain structures with new strain-free grains and relax the internal stresses, the Cu alloy and pure Cu samples were annealed at 1030°C for 2 hours in an electric furnace. The samples were encapsulated in a quartz tube backfilled with high purity argon gas.

### **3.5 Thermal diffusion coupling**

Generally, there are two approaches in the preparation of diffusion couples with a well-established contact interface: 1) pre-contracted techniques such as electroplating, and 2) pressing techniques such as hot isostatic pressing, frictional welding or by employing a special fixture [60]. The latter which is employed in this study involves force being applied to the assembly jig to promote close contact between samples. Following the process discussed in the previous section, a rigorous metallurgical sample preparation process was carried out on the intended surfaces of the pure Cu and Cu alloy (Ge at. 3%) that were to be thermally bonded. This preparation process involved grinding the samples with 240, 600 and 1200 grit silicon carbide (SiC) papers after which the samples were polished with 6 micron and 1 micron diamond suspensions on a polisher. This process ensures complete removal of possible oxide layers on the surface of the samples as well as providing smooth and uniform bonding surfaces. The outer surfaces were coated with Nicrobraz® Stop-Off, which is a solvent that provides a barrier against any diffusion that may occur between the samples and stainless steel jig in addition to preventing the samples from sticking to the jig.

The prepared samples assembled on a stainless steel jig were then inserted in a high vacuum LABVAC II brazing furnace (GCA Corporation) at 600°C for 1 hour in order for diffusion bonding to take place.

### **3.6 Electrodeposition**

Okoye et al. [61] described electrodeposition which is also known as electroplating as an electrochemical process in which solid deposits are formed on the surface of a conductive material through electrolysis. This involves coating a conductive substrate with a thin layer of the desired

material by applying an electric current which involves extracting the cations of the material from an electrolyte solution. An anode and a cathode are immersed into an electrolyte solution whereby an electrical current is applied continuously. The current drives negatively charged ions (anions) towards the anode and positively charged ions to the cathode, thus resulting in uniform metal plating on the desired part.

Electroplating is carried out on thermally bonded diffusion couples primarily to eliminate the possibility of galvanic corrosion. For galvanic corrosion to occur, metals must be electrochemically dissimilar, exposed to the same electrolyte and connected electrically; all these conditions have to be satisfied. These conditions are found for the samples in this study. The metals are electrochemically dissimilar, electrically connected through thermal bonding and exposed to the same environment. Thus this process ensures the environment perceives the sample as a single metal.

Electrodeposits are formed through the passage of an electric current in an electrochemical cell, which in this case, is a three electrode setup: the working electrode (cathode, thermally bonded Cu/CuGe sample), counter-electrode (anode) and reference electrode (saturated calomel electrode) immersed in an electrolyte solution. The working electrode is the object where deposition occurs, while the counter-electrode completes the electrical circuit. The electrolyte solution, typically an aqueous solution of metal salts, contains positive and negative ions. When an external voltage is applied, the charged species move via diffusion towards the electrodes. At the electrode surface, ionic conduction transitions to electronic conduction, thus leading to electrochemical redox reactions that drive the reduction or oxidation of the ionic species, and enhancing electrodeposition.

## **Electrodeposition procedures**

To ensure proper metal deposition on the surface of the samples, several procedures need to be carried out, including chemical cleaning and activation, electroplating assembly, and process control.

### **3.6.1 Chemical cleaning and activation**

Chemical cleaning and activation involves cleaning the surface of the working electrode of grease, oil or other impurities. The samples were inserted into a hot sodium hydroxide (NaOH) solution for twenty minutes after which, they were immersed in distilled water. Furthermore, the samples were immersed in dilute hydrochloric acid (HCL) and dilute sulfuric acid (H<sub>2</sub>SO<sub>4</sub>) for a minute and thirty seconds, respectively, to activate the surface, thereby ensuring a strong bond between the diffusion couple and protective coating.

### **3.6.2 Electroplating assembly**

After chemical cleaning and activation, the electrolytic cell was assembled. The cleaned samples were inserted into a glass vessel that contained a Cu (II) sulfate plating solution (CuSO<sub>4</sub>), which is the source of the Cu ions (Cu<sup>2+</sup>) for deposition.

In Figure 3.1, a counter electrode (CE) which is the pure Cu plate where oxidation occurs, Cu atoms are dissolved into Cu<sup>2+</sup> ions thus replenishing the electrolyte solution with metal ions.



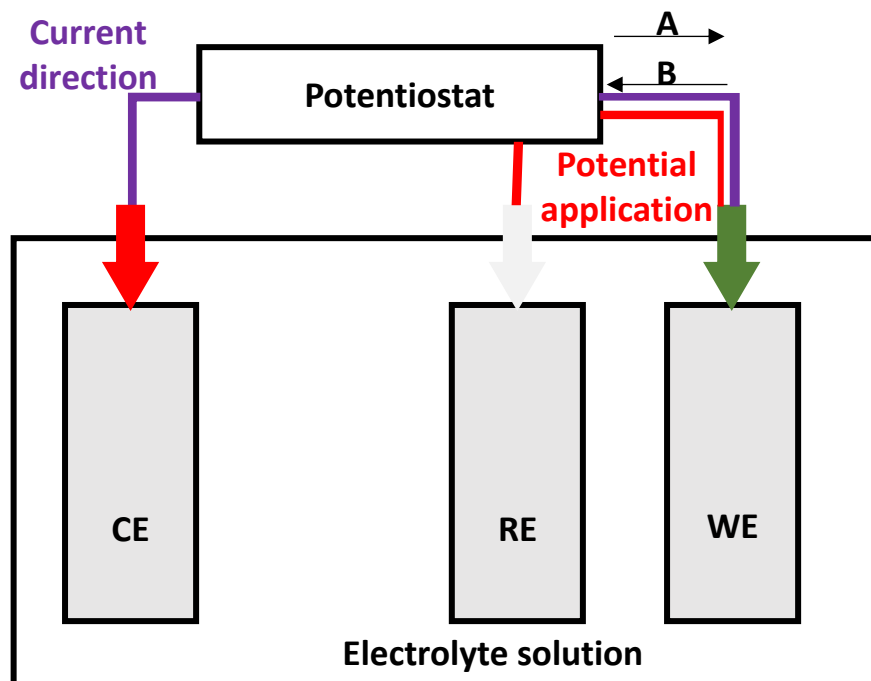


Fig. 3.1 Schematic of electroplating assembly [62]

Also in the figure, the reference electrode (RE) is a saturated potassium chloride (KCL) solution that acts as a reference to the potential applied at the working electrode (WE). The WE is the thermally bonded CuGe/Cu diffusion couple. This is where pure Cu is deposited from the reduction of the  $\text{Cu}^{2+}$  ions within the electrolyte.



Finally, the A and B arrows depict the current and electron flows, respectively during oxidation

### **3.6.3 Process Control**

A VersaSTAT\_3 potentiostat was employed to control the electrodeposition process with a current density of  $10 \text{ mA/cm}^2$  that determines the rate of deposition of Cu onto the samples. During this process, the current density and electrodeposition timing were carefully monitored to ensure uniform plating.

After the electrodeposition process, the samples were rinsed thoroughly in distilled water and left to air dry.

### **3.7 Isothermal diffusion treatments**

Subsequent to the electrodeposition, the samples were encapsulated in quartz tubes backfilled with high purity argon gas. This provides an inert atmosphere to eliminate the possibility of any further reactions. Table 3.1 provides the information on diffusion treatment conditions.

Table 3.1 Diffusion treatment conditions

| <i>Temp/ Time</i> | <i>1hr</i> | <i>5 hrs</i> | <i>25 hrs</i> | <i>75 hrs</i> | <i>150 hrs</i> | <i>450 hrs</i> |
|-------------------|------------|--------------|---------------|---------------|----------------|----------------|
| <i>550°C</i>      |            | ✓            | ✓             | ✓             | ✓              | ✓              |
| <i>600°C</i>      |            | ✓            | ✓             | ✓             | ✓              | ✓              |
| <i>650°C</i>      |            | ✓            | ✓             | ✓             | ✓              | ✓              |
| <i>700°C</i>      | ✓          | ✓            | ✓             | ✓             | ✓              | ✓              |
| <i>750°C</i>      | ✓          | ✓            | ✓             | ✓             | ✓              | ✓              |
| <i>800°C</i>      | ✓          | ✓            | ✓             | ✓             | ✓              | ✓              |

### 3.8 Standard metallographic preparation of samples

The standard metallographic preparation of the metal or alloy samples involves a variety of operation steps for further metallographic examination which would allow for the assessment of the material structure and composition by using a light microscope or SEM. The steps include sectioning, mounting, grinding, polishing and optical microscopy:

- i. Sectioning: The heat treated diffusion couples were sectioned perpendicular to the joined plane thereby exposing the cross-sectional view of the joint. This was carried out by using an EDM for accuracy, and water served as the coolant to minimize overheating and changing of the microstructure of the material and analysis itself.

- ii. Mounting: involves embedding the cut sample in phenolic resin (bakelite) to provide support and enhance workability. Mounting was carried out on a mounting press that provides heat of up to 180°C and pressure of about 27-30 MPa followed by cooling under pressure [63].
- iii. Grinding: carried out to reduce the extent of surface irregularities and deformations from the sectioning process. Grinding was achieved by using SiC abrasive papers with grit sizes of P200, P600 and P1200. An efficient grinding process requires a careful smoothening of the sample surface progressively with the use of coarse-to-fine abrasive papers in order to minimize excessive material loss and promote a uniform surface finishing. Then, the samples were rinsed thoroughly with water.
- iv. Polishing: a crucial step in sample preparation as scratches from the grinding need to be completely eliminated. Rough polishing was first carried out by using a 6 micron polishing abrasive cloth with diamond suspension as the lubricant after which the samples were immersed in an ethanol solution for ultrasonic cleaning to prevent contamination caused by the coarse abrasive. The samples were finally polished with a finer 1 micron abrasive with polishing time and force kept to a minimum to eliminate any further surface irregularities.
- v. Optical Microscopy: the samples were viewed under an optical microscope for visual inspection. This microscope utilizes visible light and a range of lenses to generate magnified images of the sample. This is done to examine the surface quality of the sample, thus ensuring that it is void of artifacts.

### **3.9 Sample Measurement and Analysis**

The data were obtained and analyzed through scanning electron microscopy. The SEM is a highly versatile tool used for examining the microstructure morphology and analyzing chemical compositions [64]. Energy dispersive X-ray spectroscopy is an analytical technique used in combination with scanning electron microscopy to determine the elemental composition or composition gradient of a sample. This is done when the electron beam of the SEM interacts with the sample. This excites the atoms thereby causing them to exhibit characteristic X-rays. The EDS captures these X-rays and determines the elements present by analyzing their unique energy levels. The measured resolutions with the EDS are approximately one micron which is influenced by the inherent characteristics of the electron-matter interaction volume [65]. This limitation thus indicates that for a reliable result, the concentration profile must have at least 1 at.% per 1 micron minimum. Hence, the least measurable diffusion penetration depth in this work of CuGe (3 at.% Ge) is 3 microns for reliable data.

#### **Sample Measurement**

The samples were each carefully positioned on the SEM. At least five concentration profiles were taken per sample to minimize errors, improve accuracy and allow for reproducibility. These line scans were acquired perpendicular to the joint interface of the diffusion couple; that is, Cu/CuGe (3 at. % Ge) using EDS on a Phillip XL 30 ESEM. To eliminate data randomness and discrete data noise, the five concentration profiles were smoothened and averaged into a single profile by using the simple moving average technique in [66]. It should be noted that smoothening was carried out with care to avoid over-fitting to smoothness and experimental data loss.

### 3.10 Governing equations of numerical model

The novel numerical model developed in Olaye and Ojo [19], [67-68] for evaluating interdiffusion coefficients from experimental data employs a hybrid approach that involves a fully explicit finite difference analysis with the Leapfrog/Dufort-Frankel scheme. This approach adequately eliminates the need for non-trivial simplifications that have the tendency to reduce the accuracy of fully implicit solutions. Thus, this model ensures numerical stability and minimizes the influence of simplified assumptions.

The governing equations used for this model are:

$$r^{\lambda-1} \frac{\partial c(r, t)}{\partial t} = \frac{\partial}{\partial r} \left( r^{\lambda-1} D_A[c(r, t)] \frac{\partial c(r, t)}{\partial r} \right) \quad 0 \leq r \leq s(t) \quad (3.3)$$

$$r^{\lambda-1} \frac{\partial c(r, t)}{\partial t} = \frac{\partial}{\partial r} \left( r^{\lambda-1} D_B[c(r, t)] \frac{\partial c(r, t)}{\partial r} \right) \quad s(t) \leq r \leq R \quad (3.4)$$

$$D_A[c(r, t)] \frac{\partial c(r, t)}{\partial t} \Big|_{r=s(t)^-} - D_B[c(r, t)] \frac{\partial c(r, t)}{\partial t} \Big|_{r=s(t)^+} = [C_B - C_A] \frac{ds}{dt} \quad r = s(t) \quad (3.5)$$

### 3.11 Forward Simulation Method

To calculate interdiffusion coefficients from the acquired experimental data, the model in [20] was coupled with the FSM. This involves an iterative process whereby  $D(c)$  was evaluated through an inverse relationship between the concentration gradient and diffusion coefficient. A numerical

method that can solve Fick's second law in single or multi-phase systems is necessary to execute the FSM. The numerical method employed to solve Fick's second law for simulation in this work has been discussed comprehensively in [19-20], [67-71]. The procedure is as follows:

- i. Estimation of initial function: An initial approximation of  $D(c)$  is made by using a conventional method such as the BM method with the following function:

$$D = \exp(F(c)) \quad (3.6)$$

where  $F(c)$  is a polynomial function;

- ii. Profile simulation: Using the numerical model capable of solving Fick's second law, a numerical experimental profile is simulated with the use of experimental time, initial condition and estimated  $D(c)$ ;
- iii. Comparison between experimental and simulated profiles: made between the numerically obtained concentration profile and experimentally obtained profile. The least square method is often employed to measure the discrepancies between the experimental and simulated profiles;
- iv. Evaluating errors: A preset tolerance error value of less than or equal to 0.001 is considered acceptable. The simulation is terminated if the obtained error value is satisfied;
- v. Adjusting  $D(c)$  function: If the resultant error is larger than the preset tolerance value, the interdiffusion coefficient function is adjusted by using Equation 3.7. Steps i. to iii. are repeated until the experimental and simulated concentration profiles converge with a permissible error value. Equation 3.7 is used to adjust the interdiffusion coefficients.

$$D(c)_{new} = D(c)_{old} * \frac{\frac{dx}{dc}_{Experiment}}{\frac{dx}{dc}_{Simulated}} \quad (3.7)$$

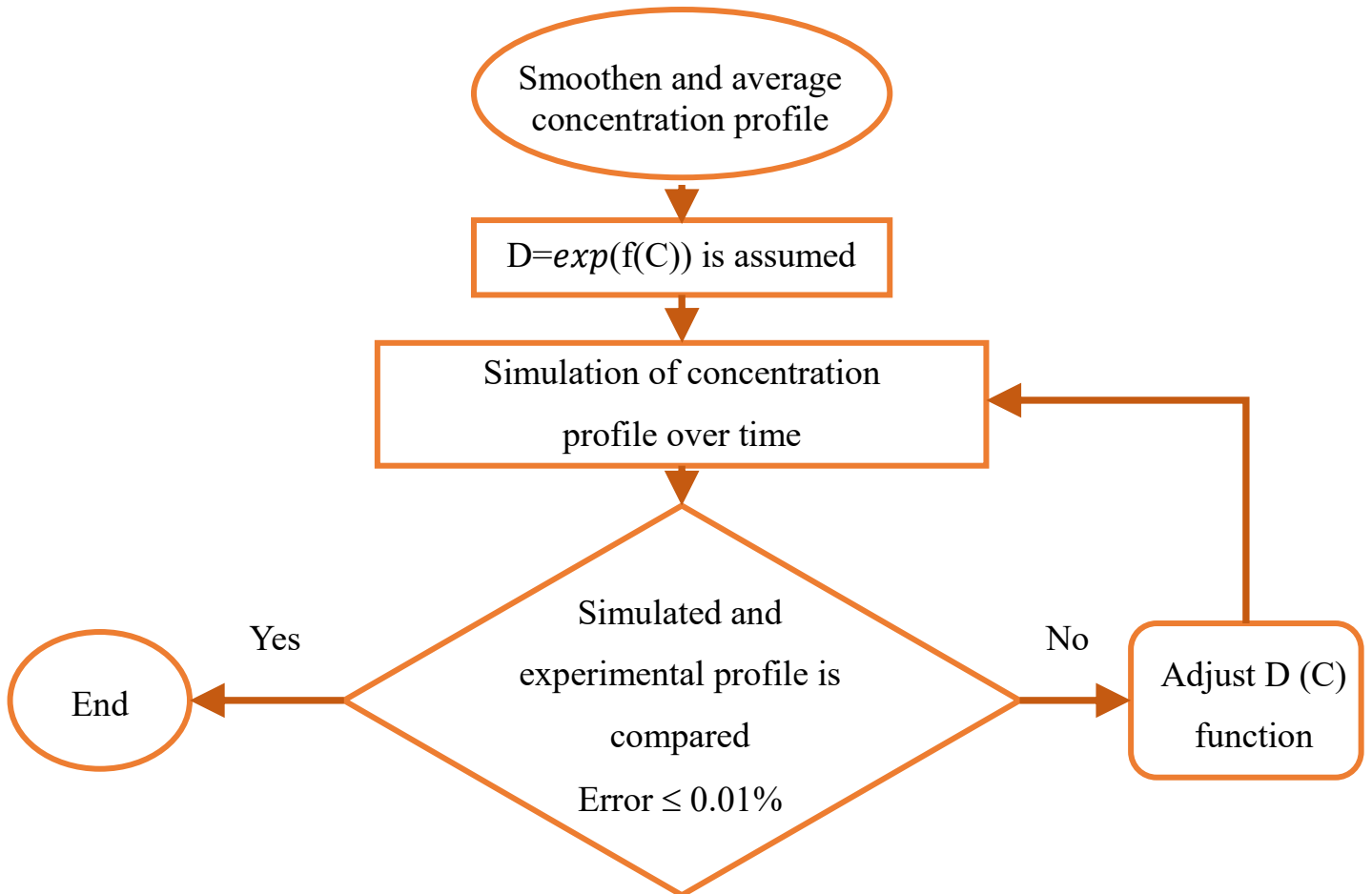


Fig. 3.2 Schematic diagram of FSM

## CHAPTER FOUR

### RESULTS AND DISCUSSION

In this chapter, the results and discussion of the time effect on concentration-dependent interdiffusion coefficients in the Cu/CuGe alloy system are presented, which are attributable to the DIS within the system.

#### 4.1 Validation of Numerical Model

The numerical model in this study analyzes a system by utilizing two experimentally obtained concentration profiles to extract the interdiffusion coefficient. This is a numerical inverse method capable of capturing concentration-dependent interdiffusion coefficients in scenarios that involve non-uniform solute distribution. Traditional approaches for determining interdiffusion coefficients are limited by the assumption of an idealized initial condition: solute concentration distribution as a step-function of space prior to diffusion [72-74] . However, real diffusion applications often involve multiple diffusion treatments at various temperatures, therefore this approach is a more applicable methodology.

Hence, this numerical approach enables accurate estimation of the interdiffusion coefficient when a non-uniform solute distribution is present before the actual diffusion treatment. This is achieved by solving Fick's second law of diffusion to simulate the concentration profile from an estimated interdiffusion coefficient. The numerical model coupled with FSM is used to calculate the interdiffusion coefficient based on a non-uniform initial solute distribution which then produces the interdiffusion coefficient needed to obtain the final concentration profile by using the initial concentration profile as the initial condition [75]. In this study, the initial condition is the concentration profile obtained after the diffusion bonding process where a pre-diffusion has

occurred. This is termed as the “0 hr” condition which serves as the initial condition in the numerical model, thereby accounting for the pre-existing non-uniform solute distribution.

The results from the numerical model were validated by using FSM to adjust the interdiffusion coefficient function until the accepted tolerance value was reached (see Figure 3.2). Figures 4.1 and 4.2 plot the actual and simulated profiles for 1 hour and 450 hours at 800°C, respectively. A notable agreement is observed between the two profiles which confirms the reliability of the numerical model.

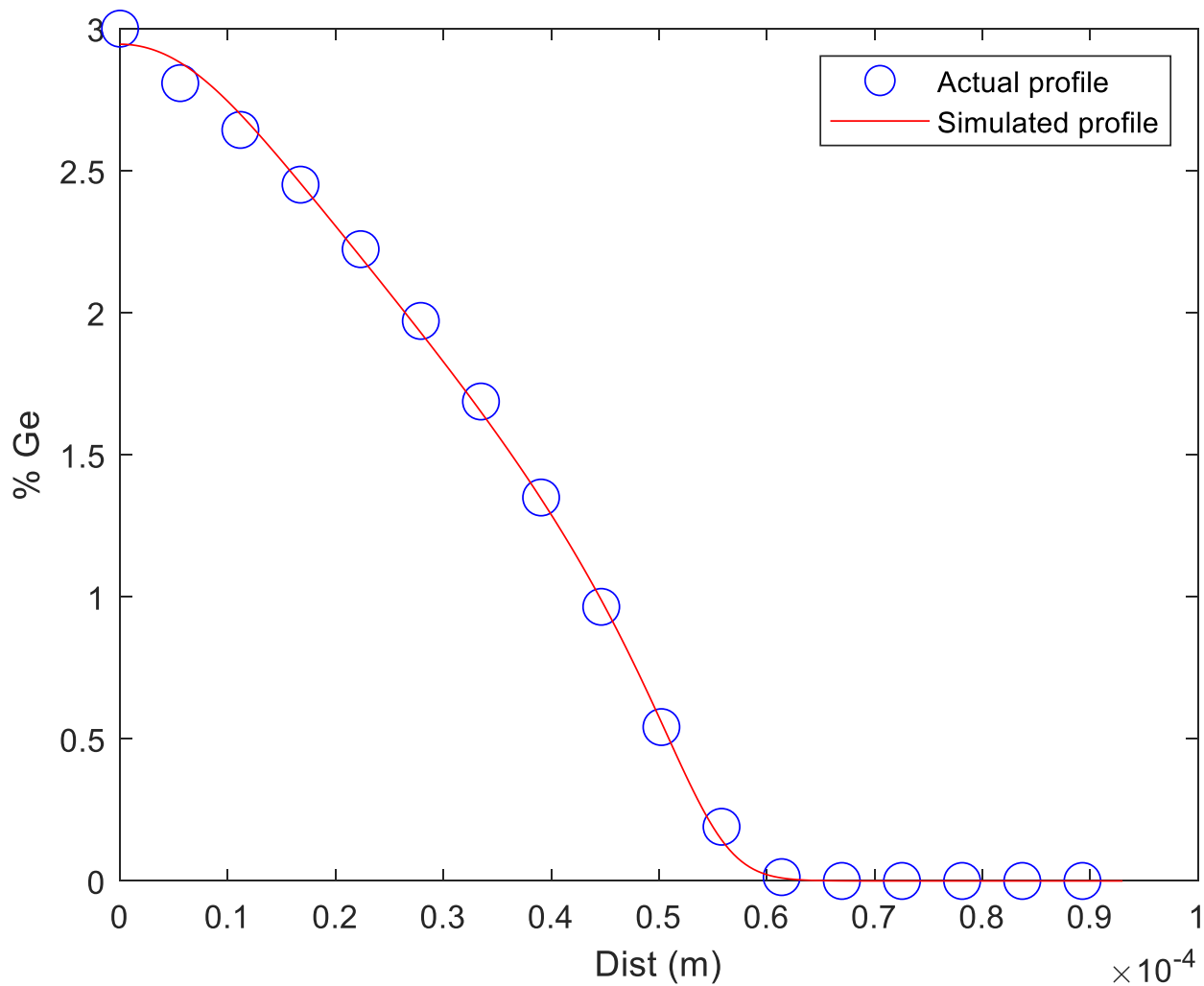


Fig. 4.1 Actual vs simulated profile for 1hr at 800°C

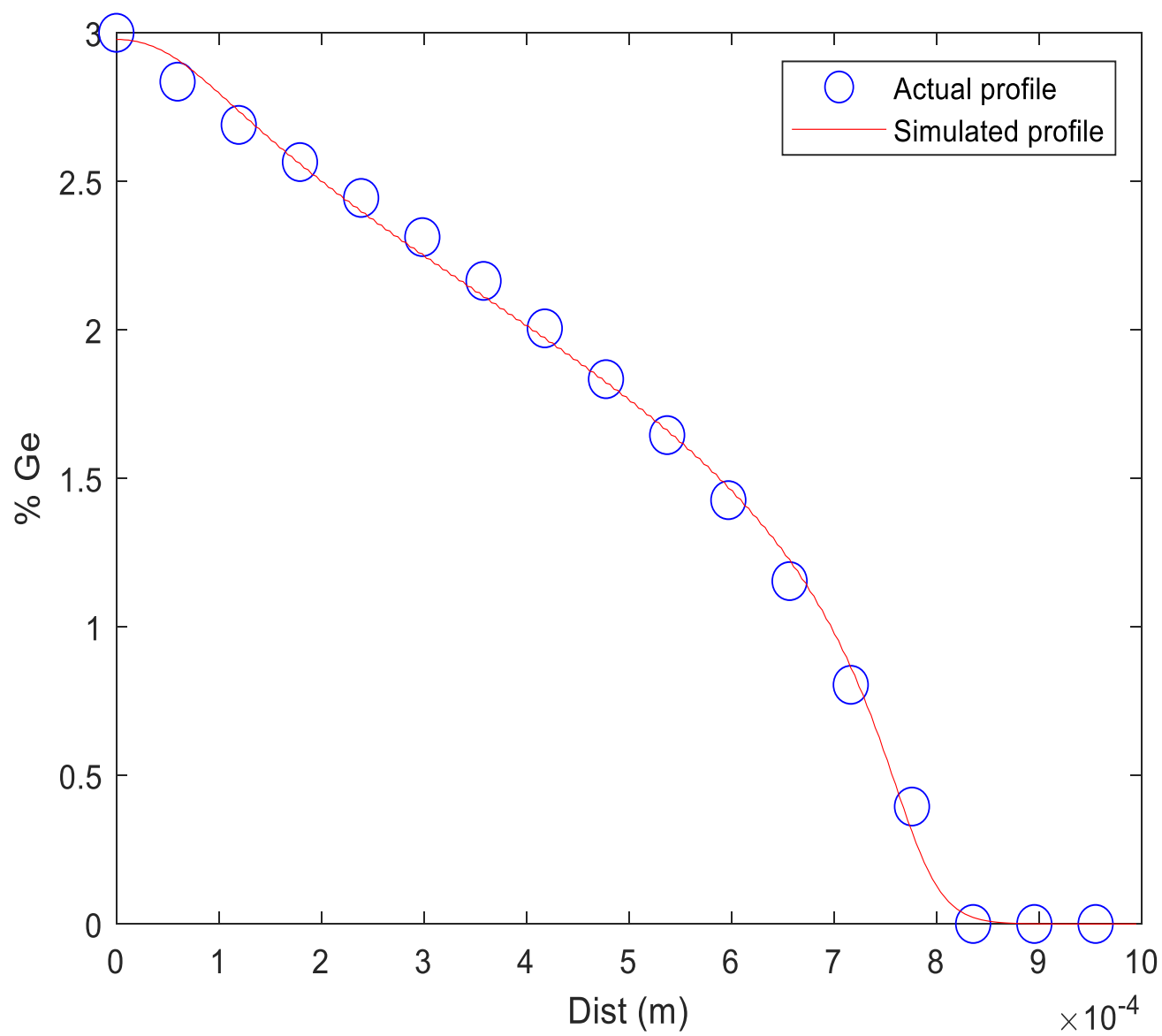


Fig. 4.2 Actual vs simulated profile for 450 hrs at 800°C

## **4.2 Effect of Time on Interdiffusion Coefficient $D(c)$**

Time is a significant variable that alters concentration gradients at specific concentrations thereby resulting in DIS changes. These changes further influence the diffusion coefficients in a system [17]. As a result, the occurrence of the time effect on the interdiffusion coefficients is verified under isothermal conditions of 550°C, 600°C, 650°C, 700°C, 750°C and 800°C for durations of 5, 25, 75, 150 and 450 hours. To maintain conciseness, typical datasets are presented. Furthermore, comparisons are made between various times for evaluation purposes and to quantify the significance of any time variations observed.

### **4.2.1 Effect of Time on Concentration-dependent Interdiffusion Coefficient $D(c)$ in CuGe alloy/ pure Cu at 600°C**

The CuGe alloy/ pure Cu diffusion couple underwent annealing at a constant temperature of 600°C for different diffusion times of 5, 25, 75, 150 and 450 hours. The numerical model in Olaye and Ojo [20] was coupled with the forward simulation model to evaluate the interdiffusion coefficients against solute concentration at the five different diffusion holding times. A comparison is made between the short diffusion time of 5 hours and long diffusion times of 25, 75, 150 and 450 hours.

The result in Figure 4.3 is a plot of the interdiffusion coefficients against the concentration points with error bars from 0-3 at. % Ge. The figure shows an apparent variation of the interdiffusion coefficients between 5 and 25 hours. This is particularly evident between 0 at. % Ge and approximately 0.7 at. % Ge, and even more evident towards the Ge abundant region of 1.6 at % Ge to the maximum solute concentration. A comparable pattern is observed in Figure 4.4 where a significant variation is towards the Ge rich region for 0-5 hours vs 0-75 hours. For the maximum diffusion treatment duration of 450 hours, this trend is not particularly observed. Instead, the

significant variation in  $D(c)$  can be observed from 0.3 at. % Ge to 1.7 at. % and is reduced as the solute concentration increases. Also, a slight error bar overlap is evident in Figure 4.5 for 0-5 hours vs 0-150 hours which shows a less apparent difference between the two conditions. However, the percentage increase between their average interdiffusivity values is even higher than the empirically derived benchmark of experimental uncertainty. The average interdiffusivity for all concentration ranges were evaluated which ranged between  $6.02 \times 10^{-16} \text{ m}^2/\text{s}$  at 0-5 hours and  $3.73 \times 10^{-16} \text{ m}^2/\text{s}$  at 0-25 hours as presented in Table 4.1. Furthermore, the substantial increase in average interdiffusivity values across the considered time intervals in Table 4.2 undoubtedly indicates the time effect of  $D(c)$  under isothermal conditions of 600°C in the Cu-Ge system.

Thus, the change in  $D(c)$  with time observed in the present work is attributable to the occurrence of DIS as previously analyzed and suggested in the literature [17].

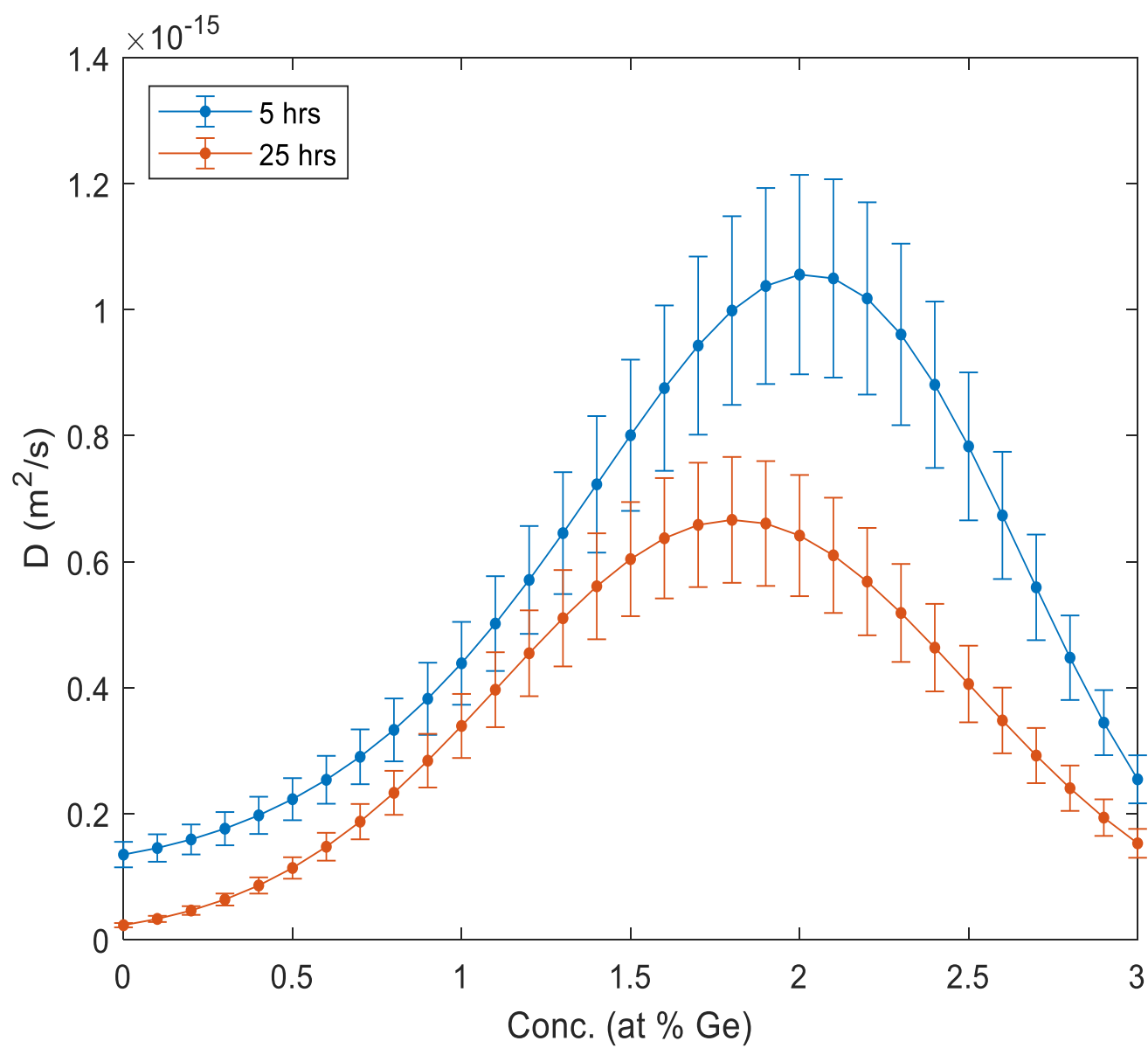


Fig. 4.3 Concentration-dependent interdiffusion coefficient operative between 0-5 hrs vs 0-25 hrs at 600°C

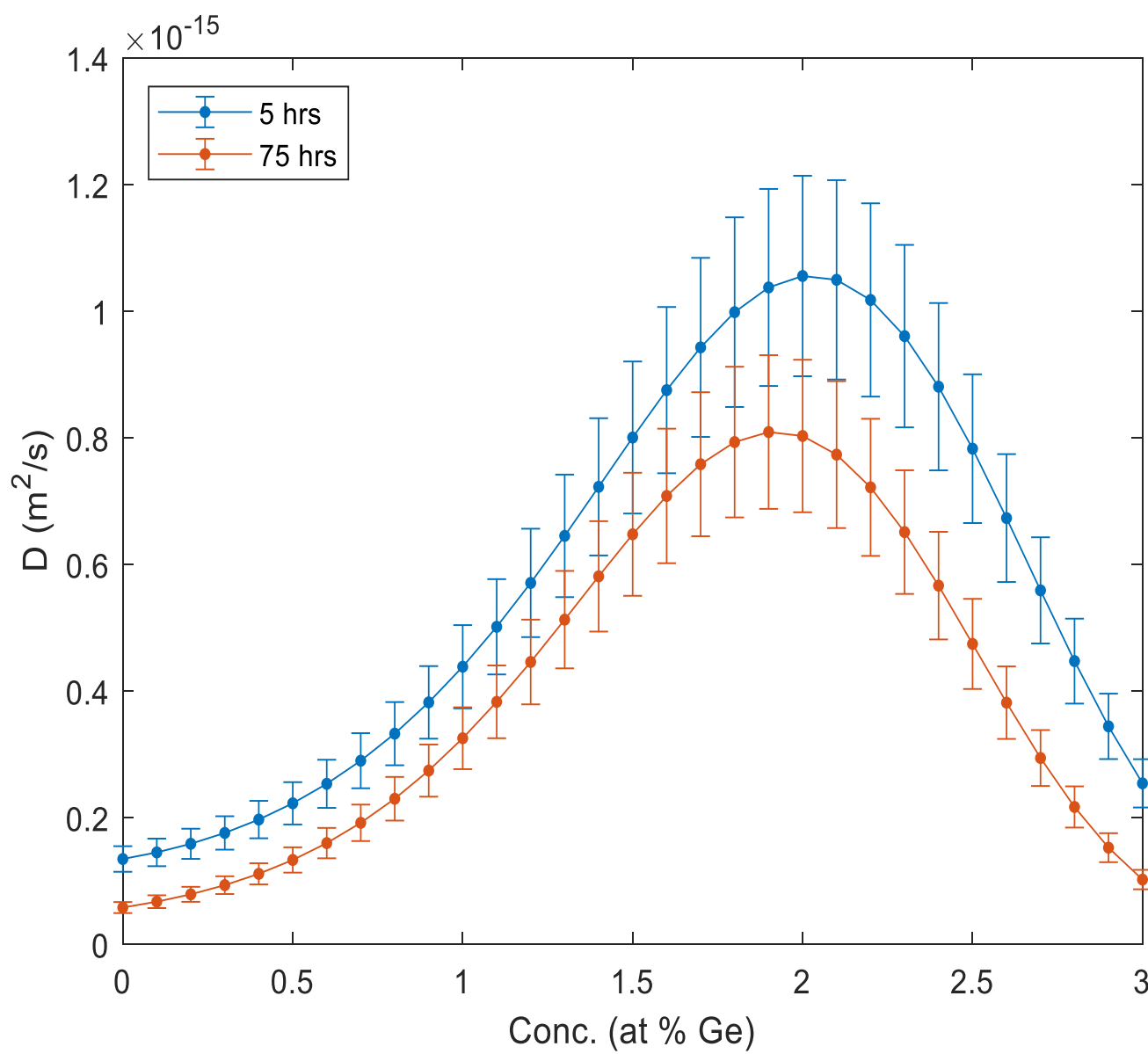


Fig. 4.4 Concentration-dependent interdiffusion coefficient operative between 0-5 hrs vs 0-75 hrs at  $600^\circ\text{C}$

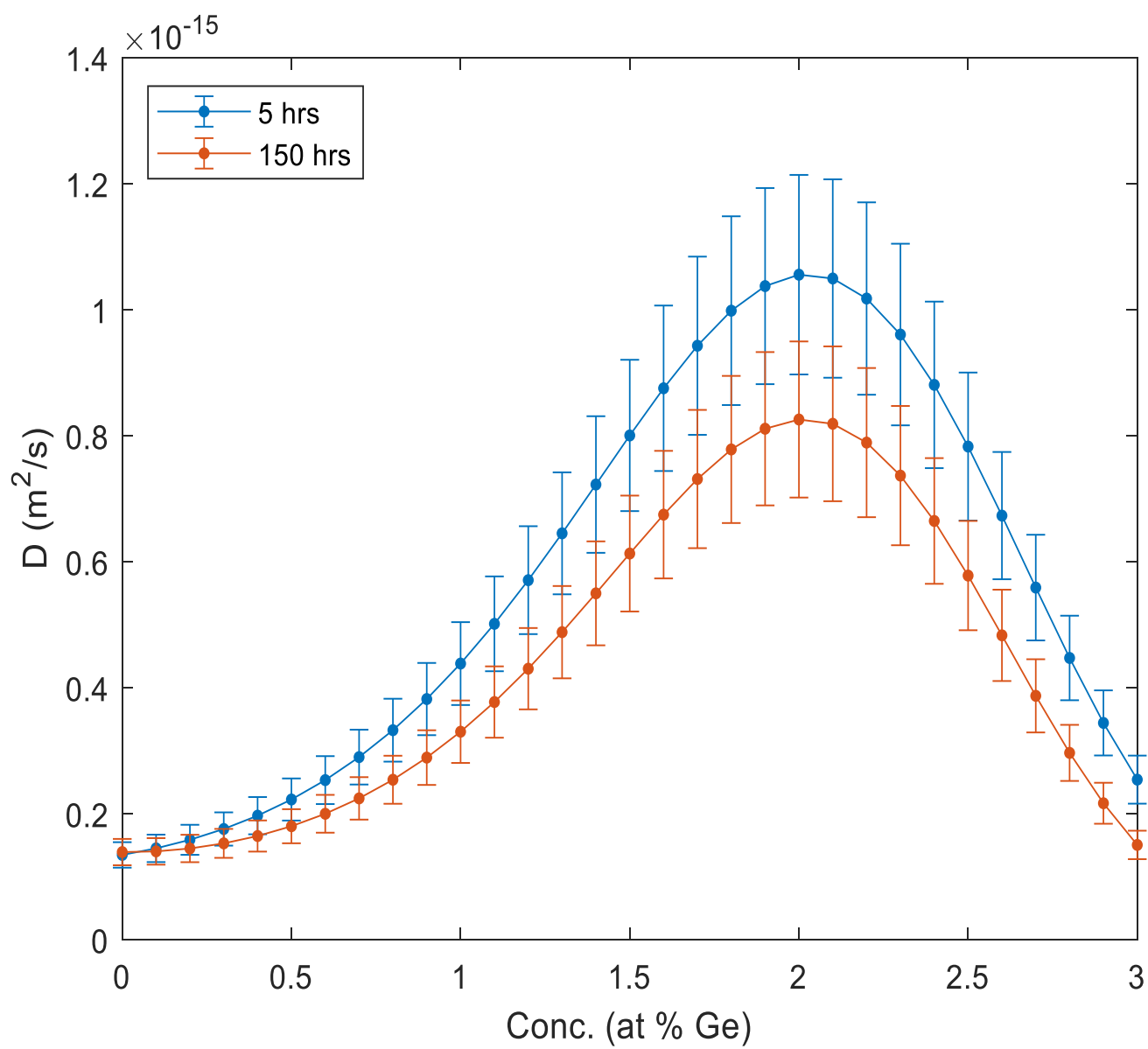


Fig. 4.5 Concentration-dependent interdiffusion coefficient operative between 0-5 hrs vs 0-150 hrs at 600°C

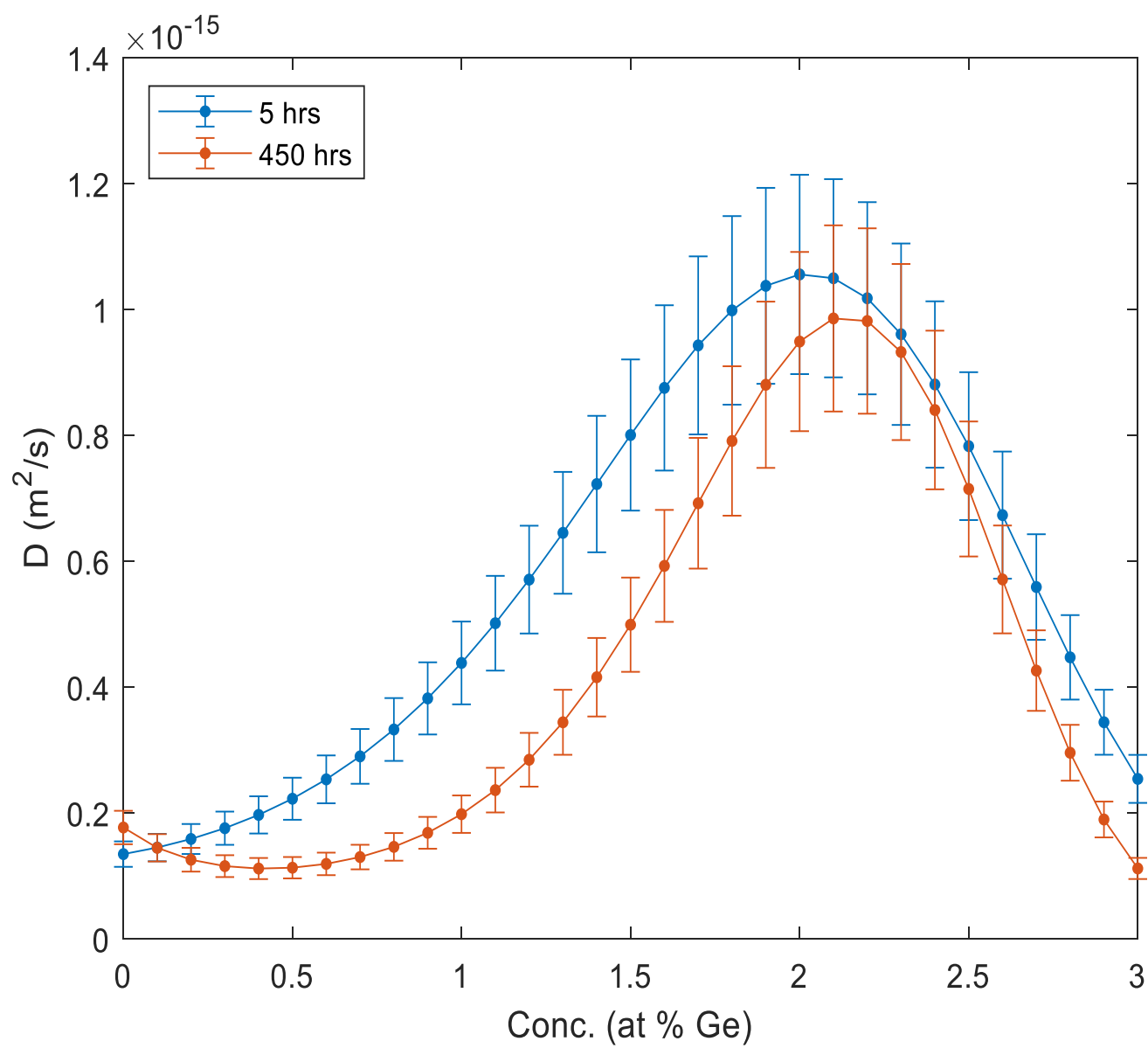


Fig. 4.6 Concentration-dependent interdiffusion coefficient operative between 0-5 hrs vs 0-450 hrs at  $600^\circ\text{C}$

Table 4.1 Average interdiffusion coefficients for different time intervals

| <b>Time Interval</b> | <b>D<sub>average</sub> (m<sup>2</sup>/s)</b> |
|----------------------|----------------------------------------------|
| 0-5 hrs              | 6.02E-16                                     |
| 0-25 hrs             | 3.73E-16                                     |
| 0-75 hrs             | 4.21E-16                                     |
| 0-150 hrs            | 4.61E-16                                     |
| 0-450 hrs            | 4.60E-16                                     |

Table 4.2 Percentage increase in D<sub>average</sub> between time intervals

| <b>Time Interval</b>  | <b>D<sub>average</sub> Percentage Increase</b> |
|-----------------------|------------------------------------------------|
| 0-5 hrs and 0-25 hrs  | 61.3%                                          |
| 0-5 hrs and 0-75 hrs  | 43.1%                                          |
| 0-5 hrs and 0-150 hrs | 30.6%                                          |
| 0-5 hrs and 0-450 hrs | 31%                                            |

#### 4.2.2 Effect of Time on Concentration-dependent Interdiffusion Coefficient $D(c)$ in CuGe alloy/ pure Cu at 700°C

In addition to annealing at a constant temperature of 600°C, annealing at a constant temperature of 700°C was systematically evaluated to verify the time effect on  $D(c)$  for 5, 25, 75, 150 and 450 hours. The plotted  $D(c)$  curves with error bars compare short and longer diffusion times at 700°C; see Figures 4.7 - 4.10. The  $D_{\text{average}}$  values and their corresponding percentage increase are shown in Tables 4.3 and 4.4, respectively. The deviation in the  $D(c)$  profiles is apparent towards the Ge rich region. That is, from 1.4 at. % to 3 at. % solute concentration, the 5 hours vs 25 hours condition is similar to those at 600°C. A comparison of 5 hours vs 75 hours show enhanced variability across the entire concentration range with 5 hours having higher  $D(c)$  values. The plots of 5 hours vs 150 hours and 5 hours vs 450 hours in Figures 4.9 and 4.10 respectively exhibit similar patterns and variations evident throughout the concentration points.

Moreover, the calculated average interdiffusion coefficient values in Table 4.3 show a consistent and progressive decline across all of the diffusion times, which indicates a time-dependent reduction in interdiffusivity from the shortest to the longest diffusion annealing times. Furthermore, the highest percentage increase in average interdiffusivity is between 5 and 450 hours thus resulting in a 149.2% increase. Notably, all  $D_{\text{average}}$  percentage increases compared through all durations markedly surpass the benchmark of experimental uncertainty.

Consequently, beyond the observations made at 600°C, it is further confirmed that  $D(c)$  exhibits a strong dependence on time and as suggested in [17], the observed changes of  $D(c)$  with time is due to the occurrence of DIS.

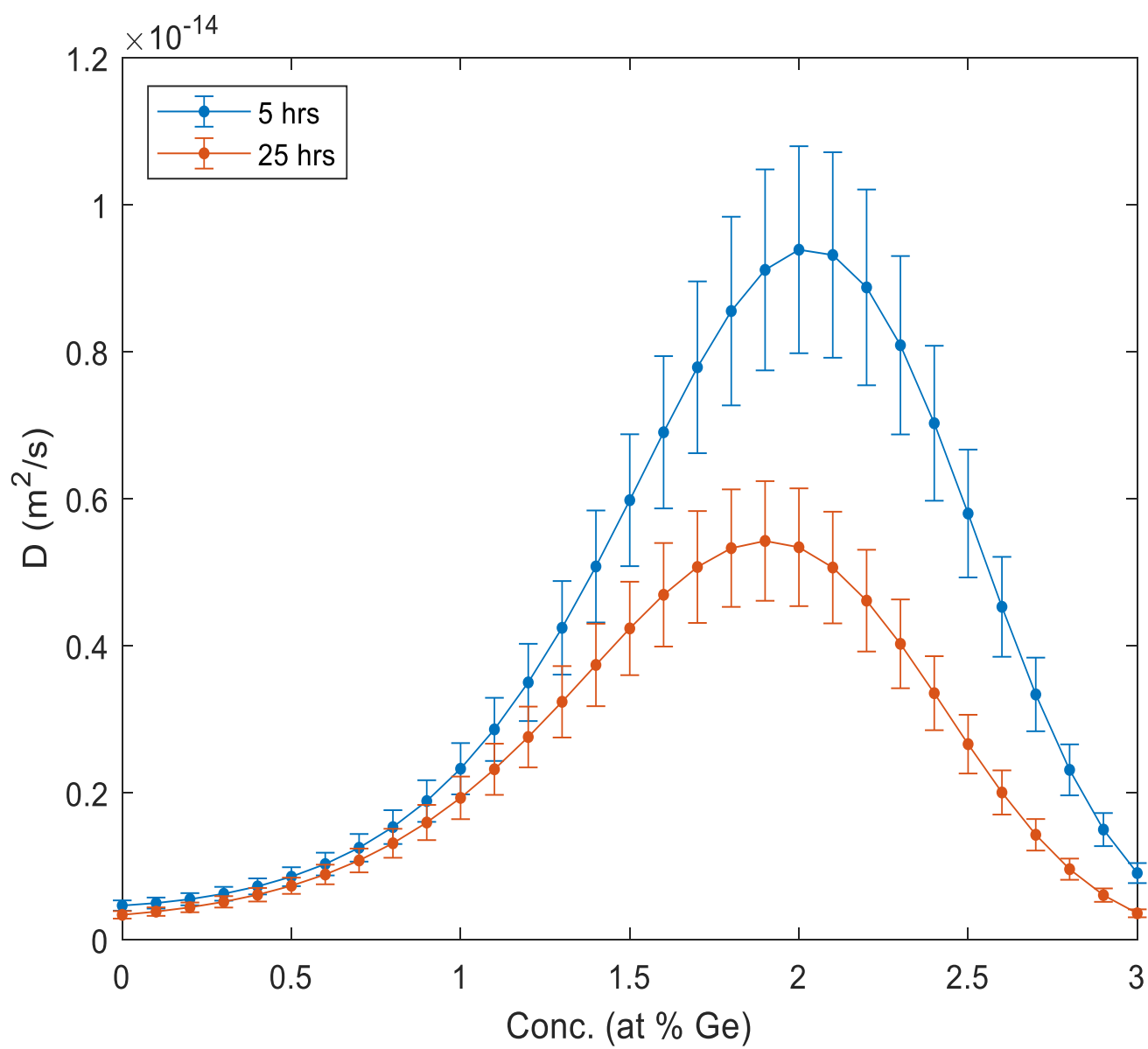


Fig. 4.7 Concentration-dependent interdiffusion coefficient operative between 0-5 hrs vs 0-25 hrs at  $700^\circ\text{C}$

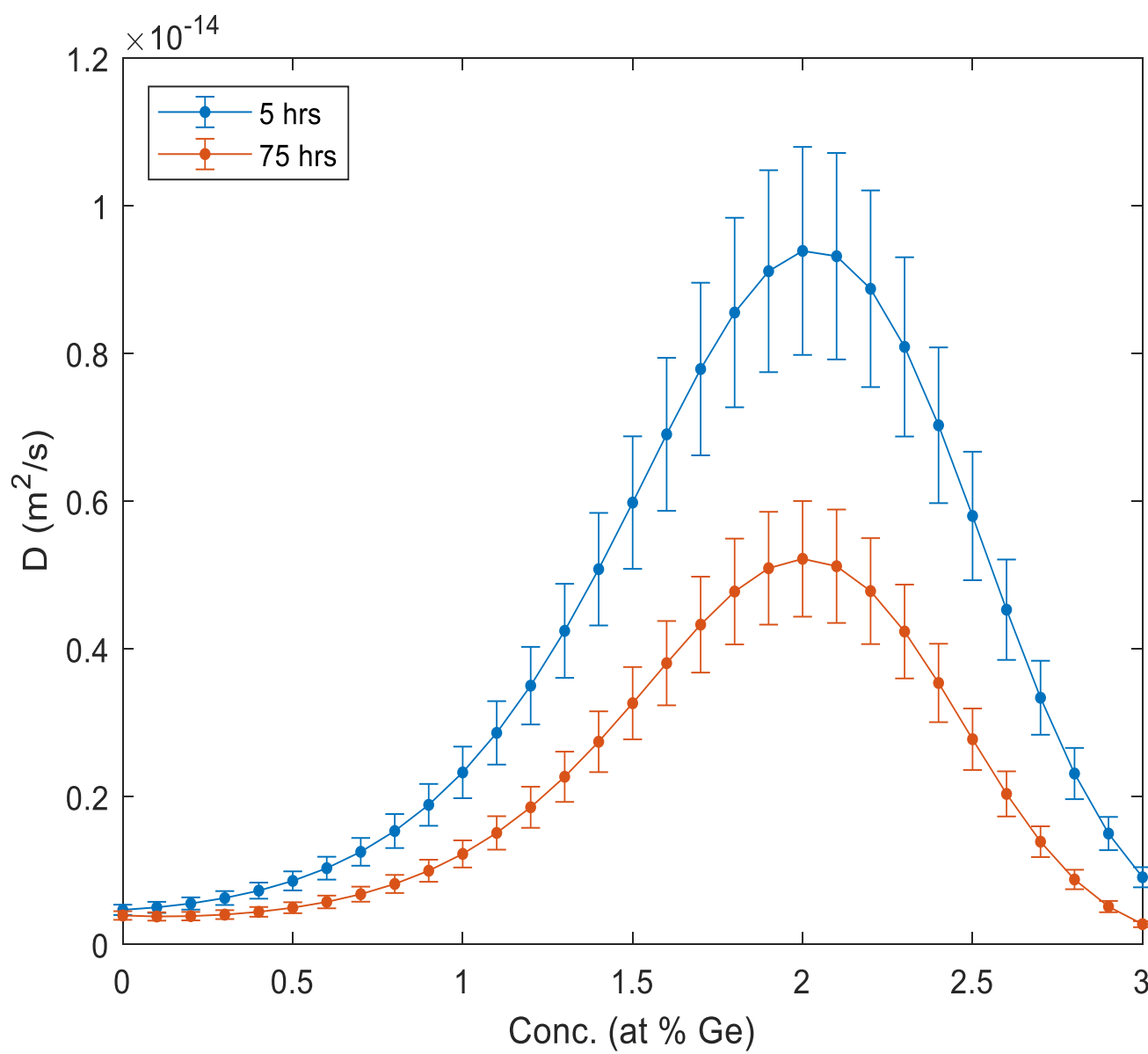


Fig. 4.8 Concentration-dependent interdiffusion coefficient operative between 0-5 hrs vs 0-75 hrs at 700°C

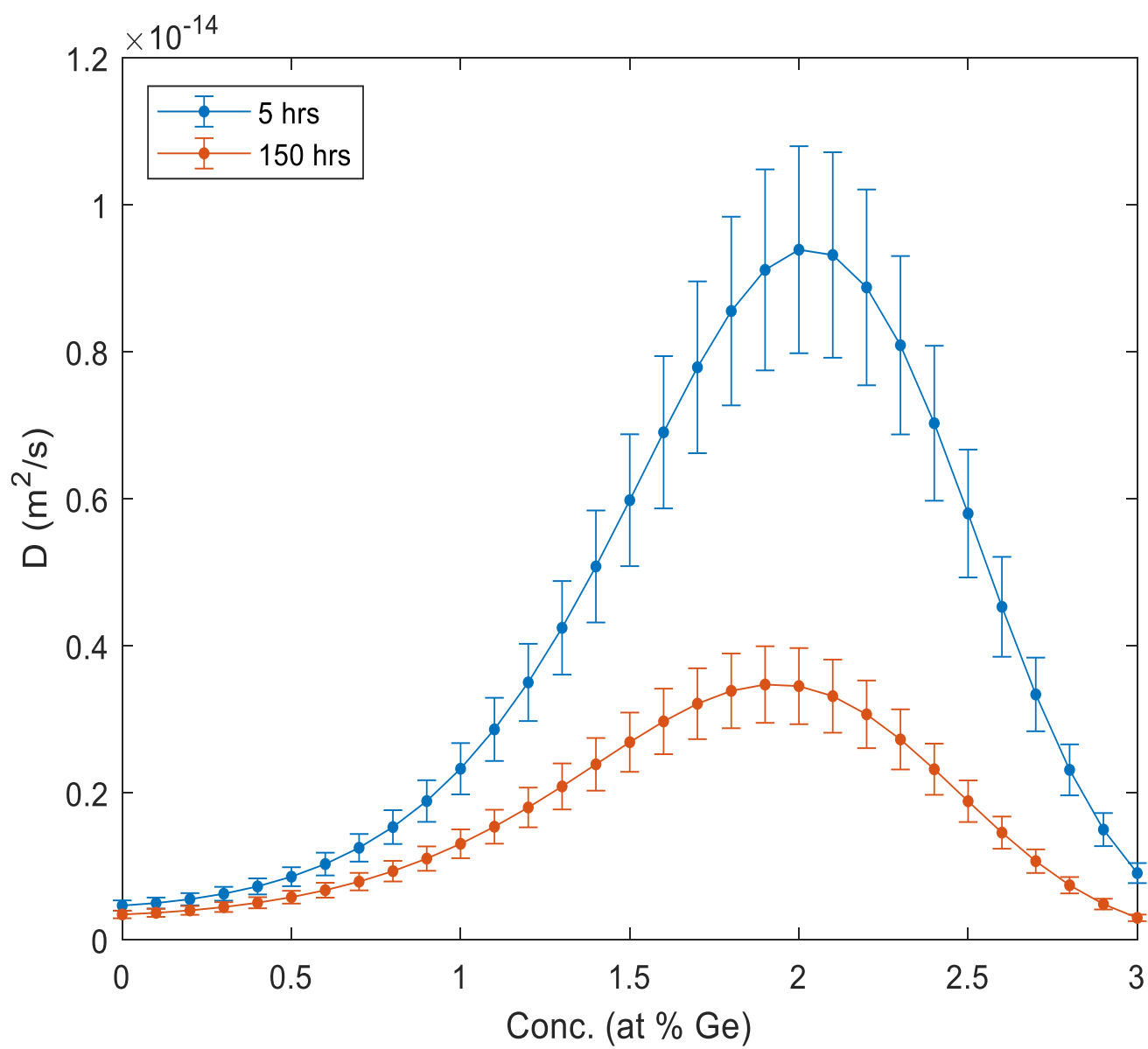


Fig. 4.9 Concentration-dependent interdiffusion coefficient operative between 0-5 hrs vs 0-150 hrs at  $700^\circ\text{C}$

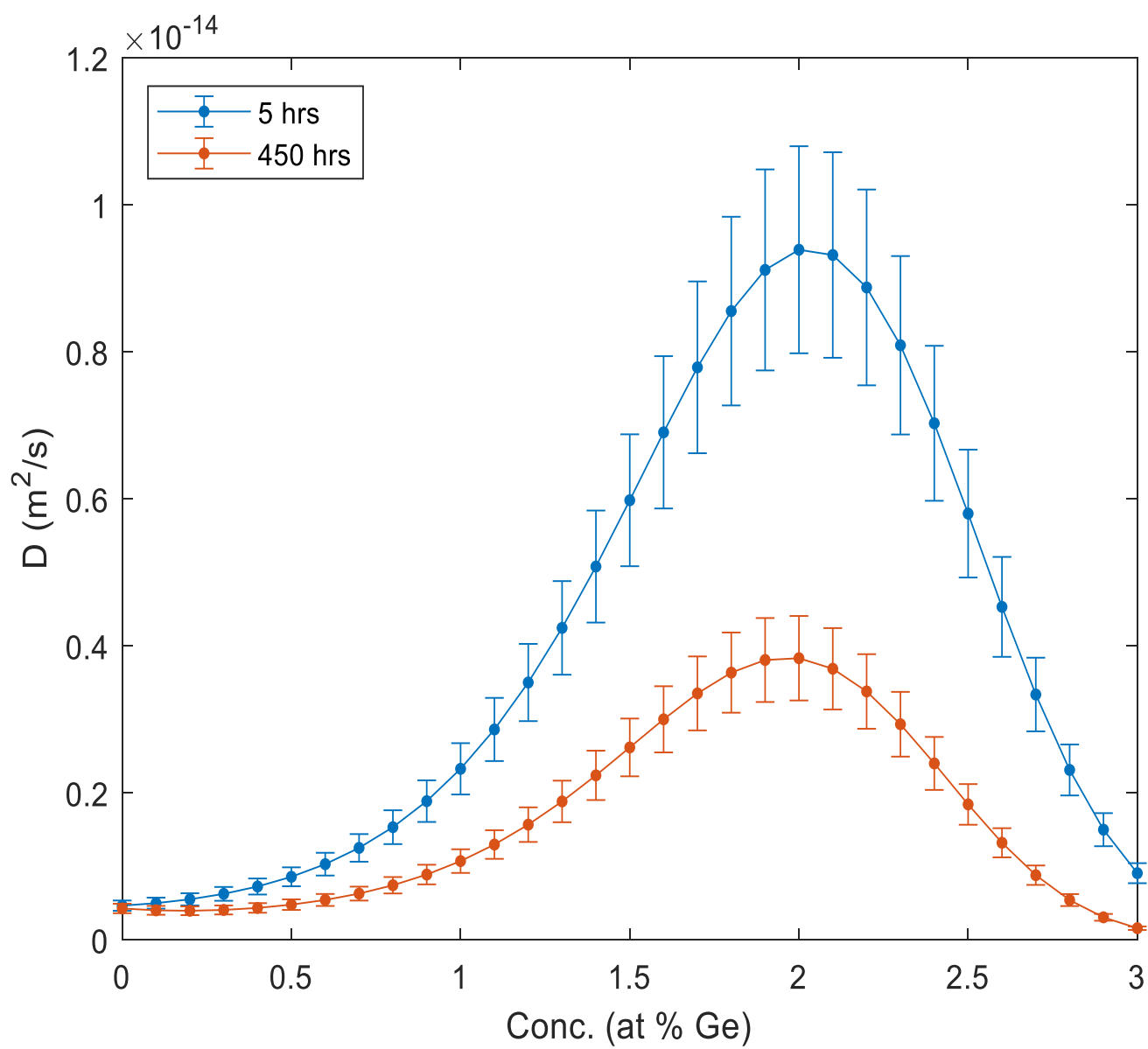


Fig. 4.10 Concentration-dependent interdiffusion coefficient operative between 0-5 hrs vs 0-450 hrs at 700°C

Table 4.3 Average interdiffusion coefficients for different time intervals

| <b>Time Interval</b> | <b>D<sub>average</sub> (m<sup>2</sup>/s)</b> |
|----------------------|----------------------------------------------|
| 0-5 hrs              | 4.35E-15                                     |
| 0-25 hrs             | 2.65E-15                                     |
| 0-75 hrs             | 2.31E-15                                     |
| 0-150 hrs            | 1.77E-15                                     |
| 0-450 hrs            | 1.74E-15                                     |

Table 4.4 Percentage increase in D<sub>average</sub> between time intervals

| <b>Time Interval</b>  | <b>Percentage Increase</b> |
|-----------------------|----------------------------|
| 0-5 hrs and 0-25 hrs  | 64.0%                      |
| 0-5 hrs and 0-75 hrs  | 88.4%                      |
| 0-5 hrs and 0-150 hrs | 145.5%                     |
| 0-5 hrs and 0-450 hrs | 149.2%                     |

#### **4.2.3 Effect of Time on Concentration-dependent Interdiffusion Coefficient $D(c)$ in CuGe alloy/ pure Cu at 800°C**

At a higher temperature of 800°C, the influence of time on the interdiffusion coefficient was examined by using the same time intervals as those used in the previously discussed isothermal conditions. Across all the  $D(c)$  profiles compared, there is a general absence of significant overlap indicated by the standard deviation error bars, except for a limited concentration range of 0 at. % - 1.4 at. % as shown in Figure 4.14. This observation clearly deviates from the anticipated behavior of  $D(c)$  as reported in the existing literature [18].

Notably, an unconventional trend is observed at this temperature: longer diffusion times such, as 25, 75, 150 and 450 hours exhibit higher interdiffusion coefficients than that of 5 hours. This finding is supported both graphically in the plots and  $D_{\text{average}}$  values provided in Table 4.5. This behavior appears to be exclusive to this condition compared to the other temperatures studied; moreover, it challenges the traditional understanding derived from the interdiffusion framework of Darken which assumes DIS is relieved immediately during diffusion [18]. Also, this behavior indicates the influence of an additional driving force within the system during longer diffusion periods. Specifically, the emergence of a stress gradient appears to act alongside the concentration gradient thereby contributing to the overall interdiffusion process. This strongly suggests the presence of DIS as previously analyzed and suggested in the literature [17]. The average interdiffusion coefficient for the considered time intervals and percentage increase are presented in Tables 4.5 and 4.6, respectively.

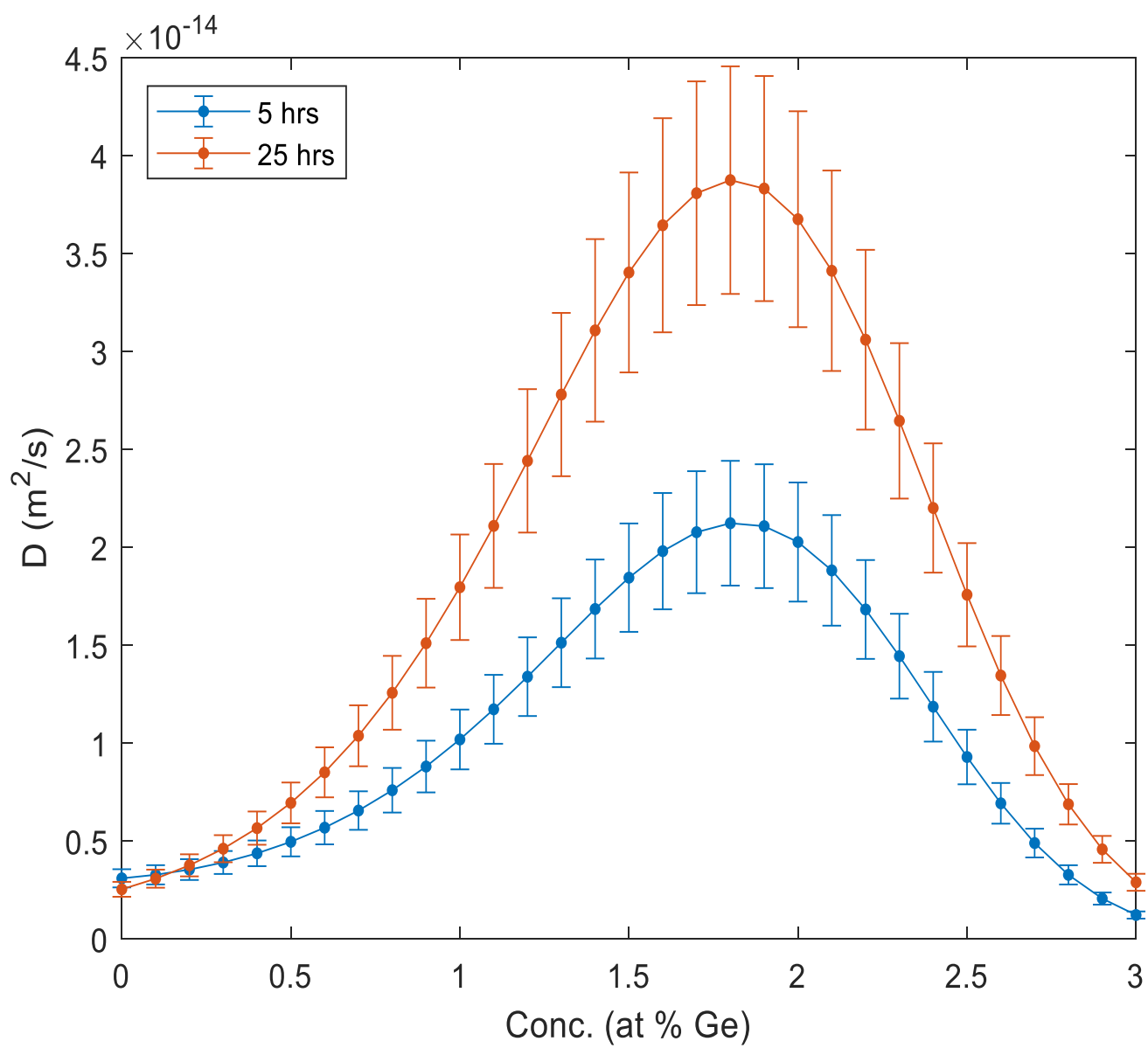


Fig. 4.11 Concentration-dependent interdiffusion coefficient operative between 0-5 hrs vs 0-25 hrs at  $800^\circ\text{C}$

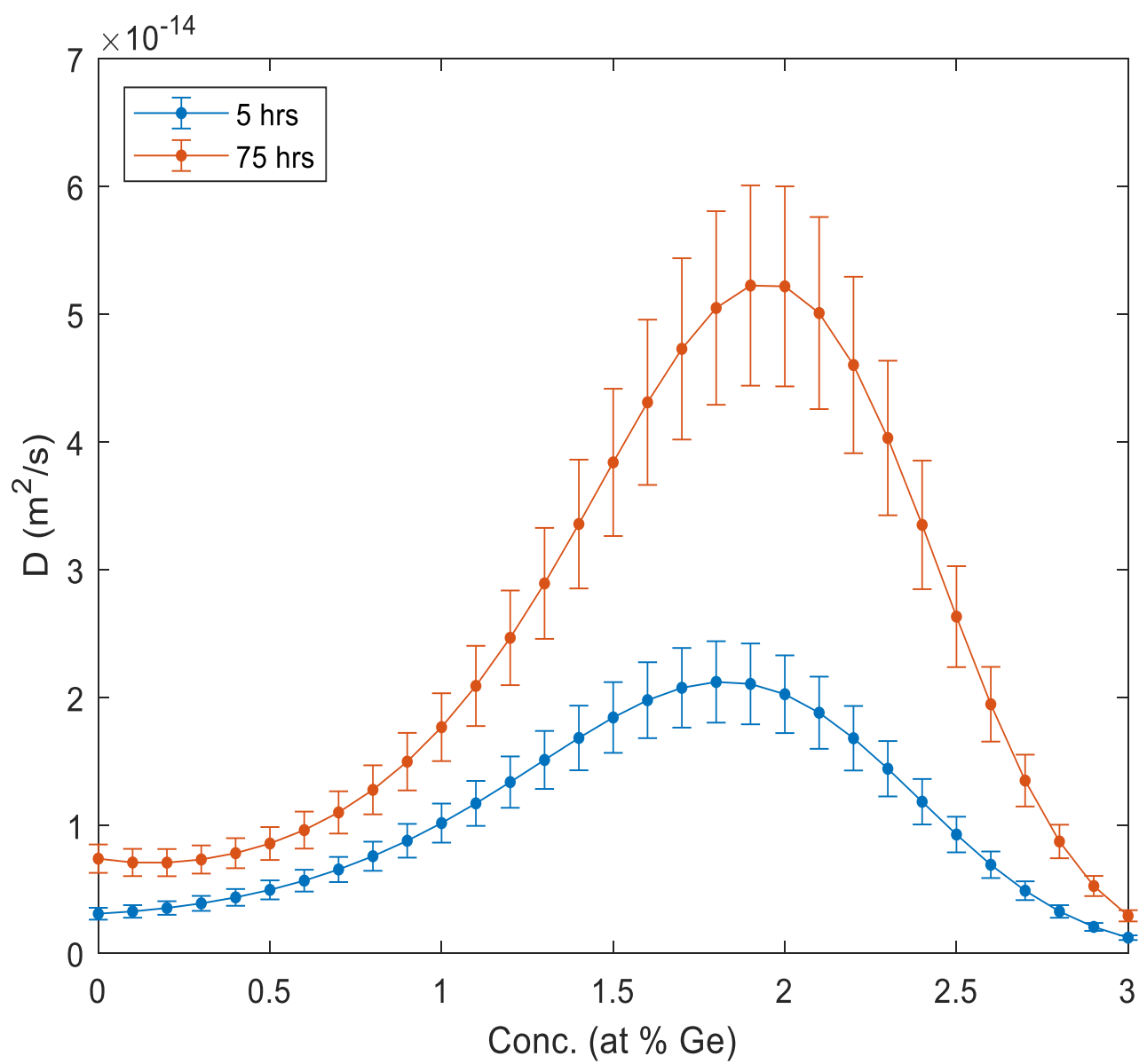


Fig. 4.12 Concentration-dependent interdiffusion coefficient operative between 0-5 hrs vs 0-75 hrs at  $800^\circ\text{C}$

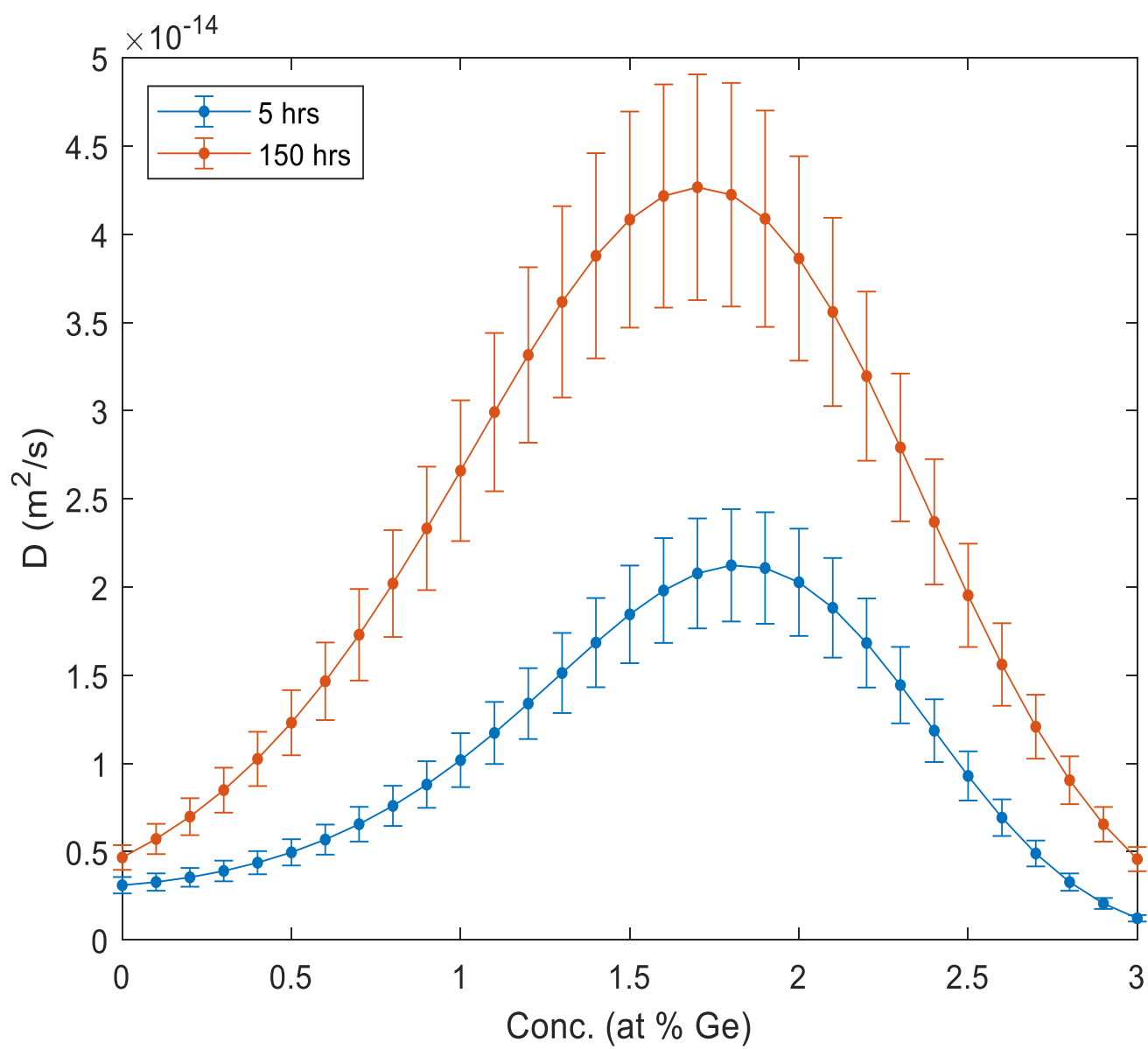


Fig. 4.13 Concentration-dependent interdiffusion coefficient operative between 0-5 hrs vs 0-150 hrs at  $800^\circ\text{C}$

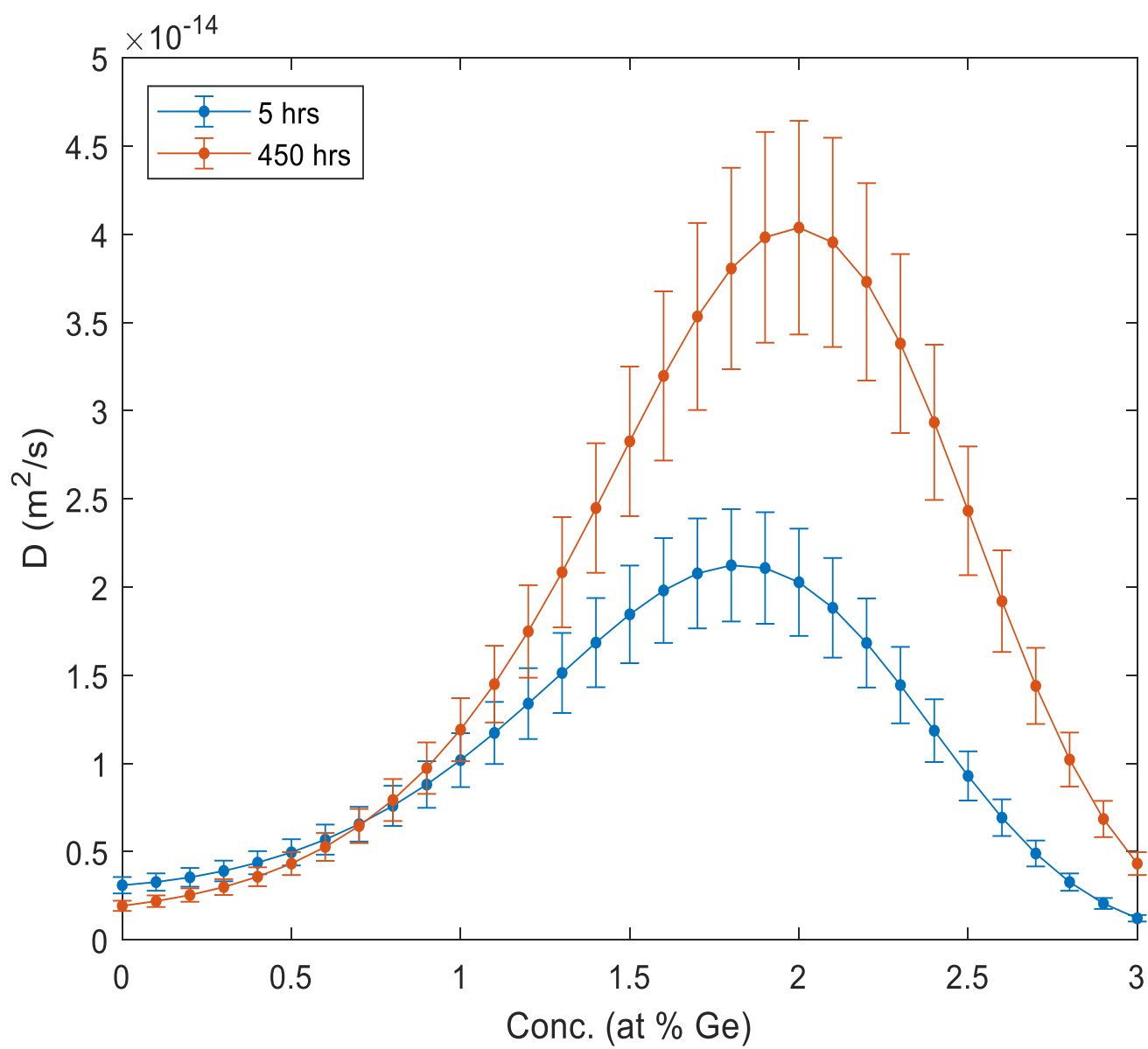


Fig. 4.14 Concentration-dependent interdiffusion coefficient operative between 0-5 hrs vs 0-450 hrs at  $800^\circ\text{C}$

Table 4.5 Average interdiffusion coefficients for different time intervals

| Time Interval | $D_{\text{average}}$ (m <sup>2</sup> /s) |
|---------------|------------------------------------------|
| 0-5 hrs       | 1.15E-14                                 |
| 0-25 hrs      | 2.01E-14                                 |
| 0-75 hrs      | 2.57E-14                                 |
| 0-150 hrs     | 2.48E-14                                 |
| 0-450 hrs     | 1.97E-14                                 |

Table 4.6 Percentage increase in  $D_{\text{average}}$  between time intervals

| Time Interval         | Percentage Increase |
|-----------------------|---------------------|
| 0-5 hrs and 0-25 hrs  | 75.6%               |
| 0-5 hrs and 0-75 hrs  | 123.8%              |
| 0-5 hrs and 0-150 hrs | 116.6%              |
| 0-5 hrs and 0-450 hrs | 72.1%               |

### 4.3 Effect of Time on Impurity Diffusion Coefficients

The radioactive tracer method is a well-established technique for evaluating impurity diffusion coefficients. However, its major limitations include the lack of availability of suitable radioactive isotopes and the process itself requires significant resources [1]. These drawbacks have been mitigated by applying a numerical model [17] which is shown to be reliable in calculating impurity diffusion coefficients. This method is coupled with the FSM to determine the impurity diffusion coefficients in this research work. To facilitate the investigation of the time effect on impurity diffusion coefficients, this method is applied to specifically analyze Ge diffusion as a solute in a Cu solvent at various temperatures and different holding times, including their corresponding percentage increase in the various conditions presented in Tables 4.7, 4.8 and 4.9.

The significant percentage increase observed while comparing the different diffusion times show the effect of time on the impurity diffusion coefficients at a constant temperature of 600°C. A similar pattern of the impurity diffusion coefficients that vary with time is also observed under the different isothermal conditions studied. While the variations observed at 700°C are comparatively minor, the percentage increase for 0-5 vs 0-25 hours and 0-150 vs 0-450 hours exceeds the 15% threshold for experimental uncertainty.

Overall, the widely acknowledged assumption that  $D(c)$  remains constant under isothermal conditions is not substantiated by the analysis in this study. This deviation from the results in the literature introduces potential inaccuracies which may have negative consequences in real life applications. Furthermore, it has been shown in this investigation that impurity diffusion coefficients evolve as a function of time due to the influence of DIS within the system. This necessitates a reconsideration of steady-state diffusion models in such binary alloy systems.

Table 4.7 Impurity diffusion coefficient of Ge solute in Cu solvent with respective percentage increases at 600°C

| Time      | D (m <sup>2</sup> /s) | Time Interval           | Percentage Increase |
|-----------|-----------------------|-------------------------|---------------------|
| 0-5 hrs   | 1.3E-16               | –                       | –                   |
| 0-25 hrs  | 2.3E-17               | 0-5 hrs and 0-25 hrs    | 493.8%              |
| 0-75 hrs  | 5.8E-17               | 0-25 hrs and 0-75 hrs   | 155.9%              |
| 0-150 hrs | 1.4E-16               | 0-75 hrs and 0-150 hrs  | 139.8%              |
| 0-450 hrs | 1.8E-16               | 0-150 hrs and 0-450 hrs | 27.1%               |

Table 4.8 Impurity diffusion coefficient of Ge solute in Cu solvent with respective percentage increases at 700°C

| Time Interval | D (m <sup>2</sup> /s) | Time Interval           | Percentage Increase |
|---------------|-----------------------|-------------------------|---------------------|
| 0-5 hrs       | 4.7E-16               | –                       | –                   |
| 0-25 hrs      | 3.4E-16               | 0-5 hrs and 0-25 hrs    | 37.1%               |
| 0-75 hrs      | 3.9E-16               | 0-25 hrs and 0-75 hrs   | 14.7%               |
| 0-150 hrs     | 3.5E-16               | 0-75 hrs and 0-150 hrs  | 13.0%               |
| 0-450 hrs     | 4.3E-16               | 0-150 hrs and 0-450 hrs | 24.0%               |

Table 4.9 Impurity diffusion coefficient of Ge solute in Cu solvent with respective percentage increases at 800°C

| Time Interval | D (m <sup>2</sup> /s) | Time Interval           | Percentage Increase |
|---------------|-----------------------|-------------------------|---------------------|
| 0-1 hr        | 9.0E-15               | —                       | —                   |
| 0-5 hrs       | 3.1E-15               | 0-1 hr and 0-5 hrs      | 192.2%              |
| 0-25 hrs      | 2.5E-15               | 0-5 hrs and 0-25 hrs    | 22.2%               |
| 0-75 hrs      | 7.4E-15               | 0-25 hrs and 0-75 hrs   | 192.0%              |
| 0-150 hrs     | 4.7E-15               | 0-75 hrs and 0-150 hrs  | 58.6%               |
| 0-450 hrs     | 1.9E-15               | 0-150 hrs and 0-450 hrs | 142.1%              |

#### 4.4 Effect of Temperature on Concentration-dependent Interdiffusion Coefficient $D(c)$

The Arrhenius relationship describes the variation of the interdiffusion coefficient  $D(c)$  with temperature under non-isothermal conditions. Wang et al. [4] stated that activation energy and frequency factors in an Arrhenius relationship can vary systematically with concentration as interdiffusion coefficients differ with concentration. The relationship between interdiffusion coefficients and temperature is given by the classical Arrhenius law:

$$D(C) = D_o(C) \exp\left(\frac{-Q_d(C)}{RT}\right)$$

where  $D_o(c)$  denotes the frequency factor which is the frequency of collisions between diffusing particles and  $Q_d(c)$  denotes the activation energy for diffusion which is the minimum energy required for one mole of atom to make a diffusive motion [76].  $R$  and  $T$  represent the gas constant and absolute temperature (Kelvin), respectively.

To validate the Arrhenius equation, Figures 4.15 - 4.19 plot the natural logarithm against the inverse of temperature in Kelvin at a magnitude of  $10^4$  where the temperature dependence of the interdiffusion coefficient follows the Arrhenius law.

In general, a straight line negative slope is commonly observed in Figures 4.15 - 4.19 for all concentrations and time, thus indicating the temperature dependence of the interdiffusion coefficients, that is; as  $1/T$  decreases, the rate constant  $\ln D$  increases. However, in some specific cases such as at a Ge concentration of 3 at. % for 5 hours of diffusion, the highest  $\ln D$  value is observed at a lower temperature which deviates from the Arrhenius relationship. Furthermore, this deviation is also observed at 3 at. % Ge for 450 hours in Figure 4.19 and 2 at. % Ge for 25 and 75 hours in Figures 4.16 and 4.17, respectively. The Arrhenius plots for the impurity diffusion

coefficients that correspond to all durations of diffusion under investigation in this study are presented in Figures 4.20 and 4.21. The temperature dependence of the impurity diffusion coefficients exhibit a trend similar to that observed for  $D(c)$  at higher concentrations. Although this is observed only for 5 and 25 hours, the impurity diffusion coefficients are comparatively higher at lower temperatures relative to higher temperatures.

Generally, this inverse temperature dependence deviates from the classical Arrhenius relationship where diffusivity typically increases with temperature and is indicative of underlying stress-related effects such as DIS.

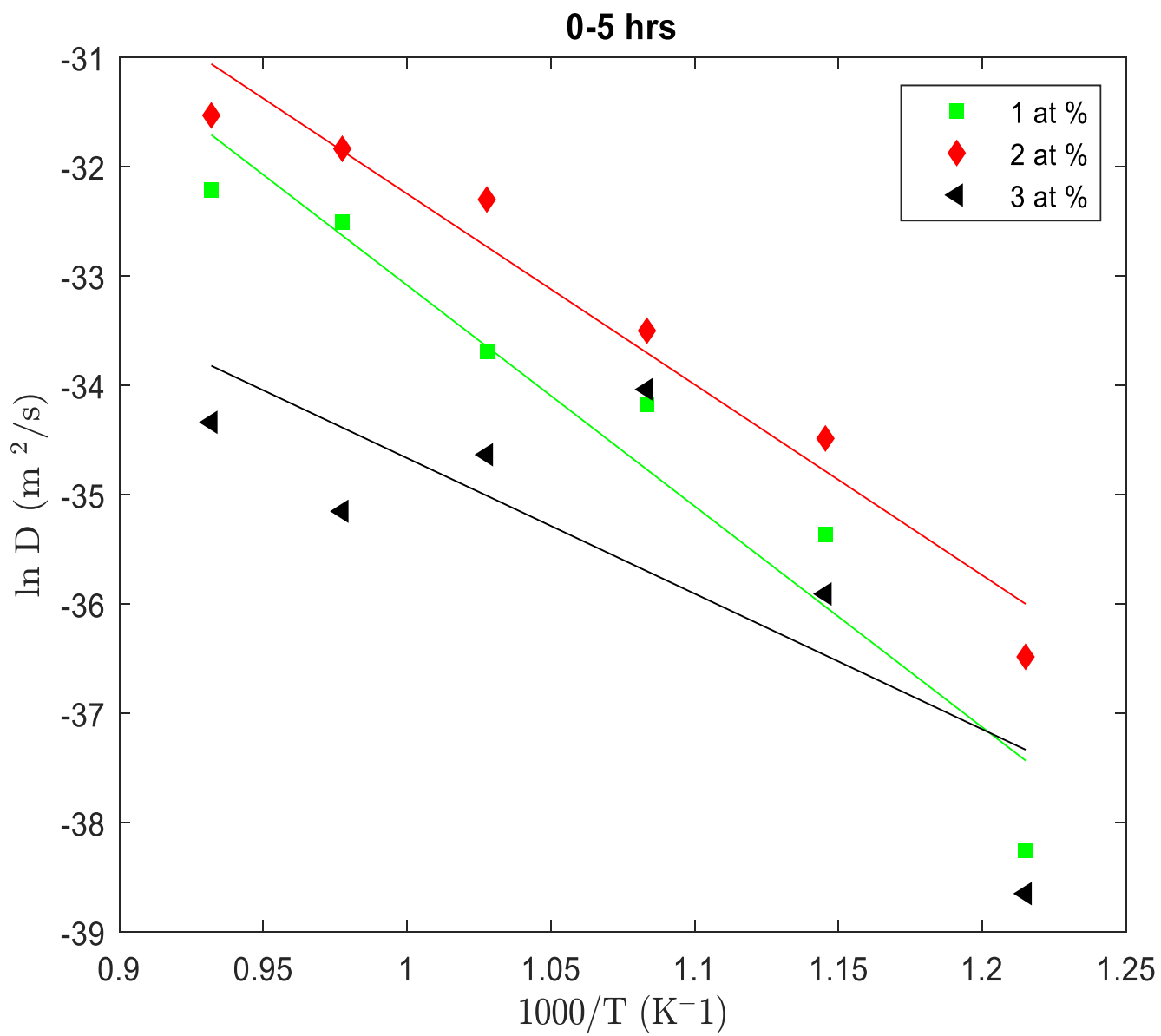


Fig. 4.15 Temperature dependence of interdiffusion coefficient after 5 hours

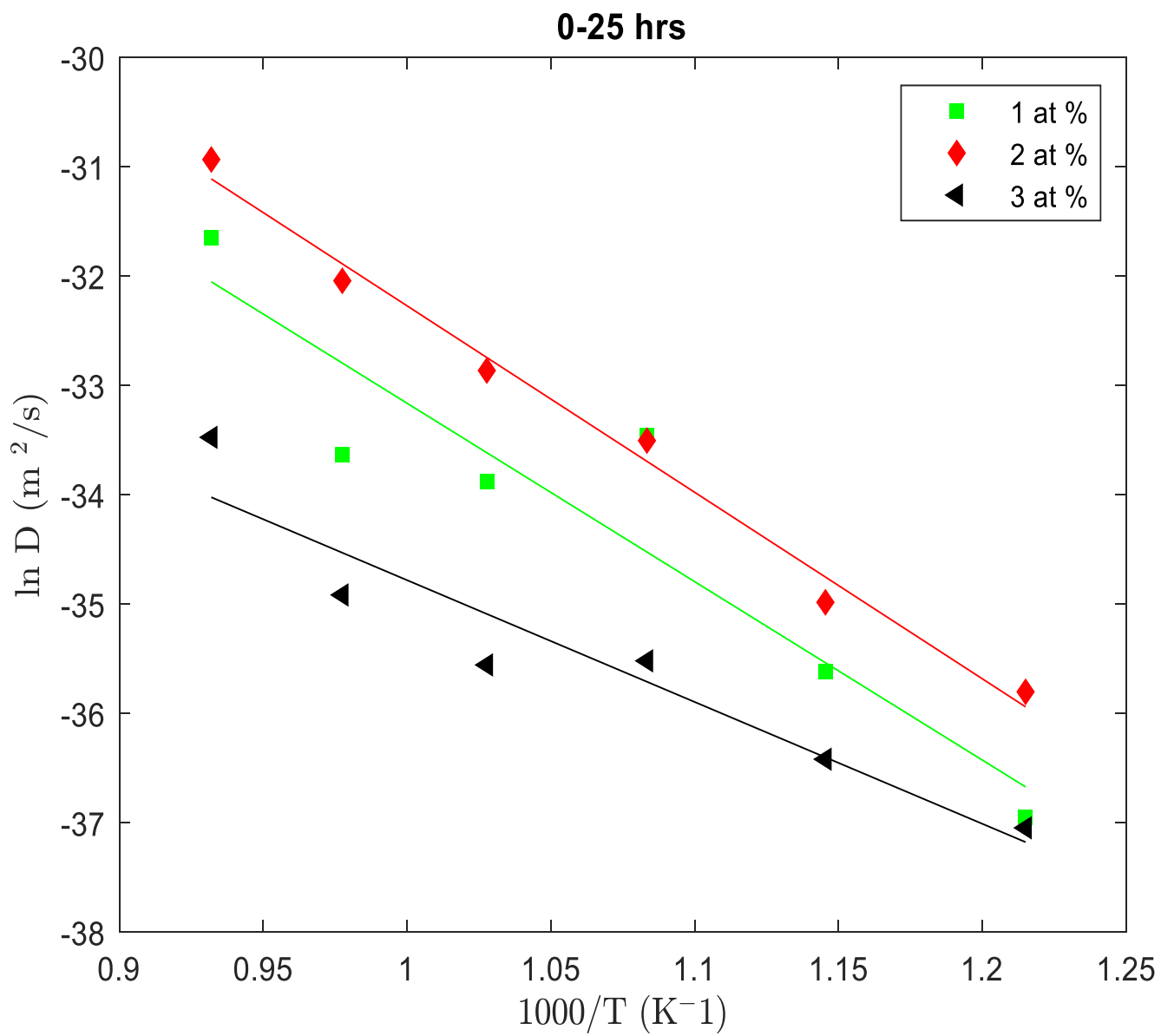


Fig. 4.16 Temperature dependence of interdiffusion coefficient after 25 hours

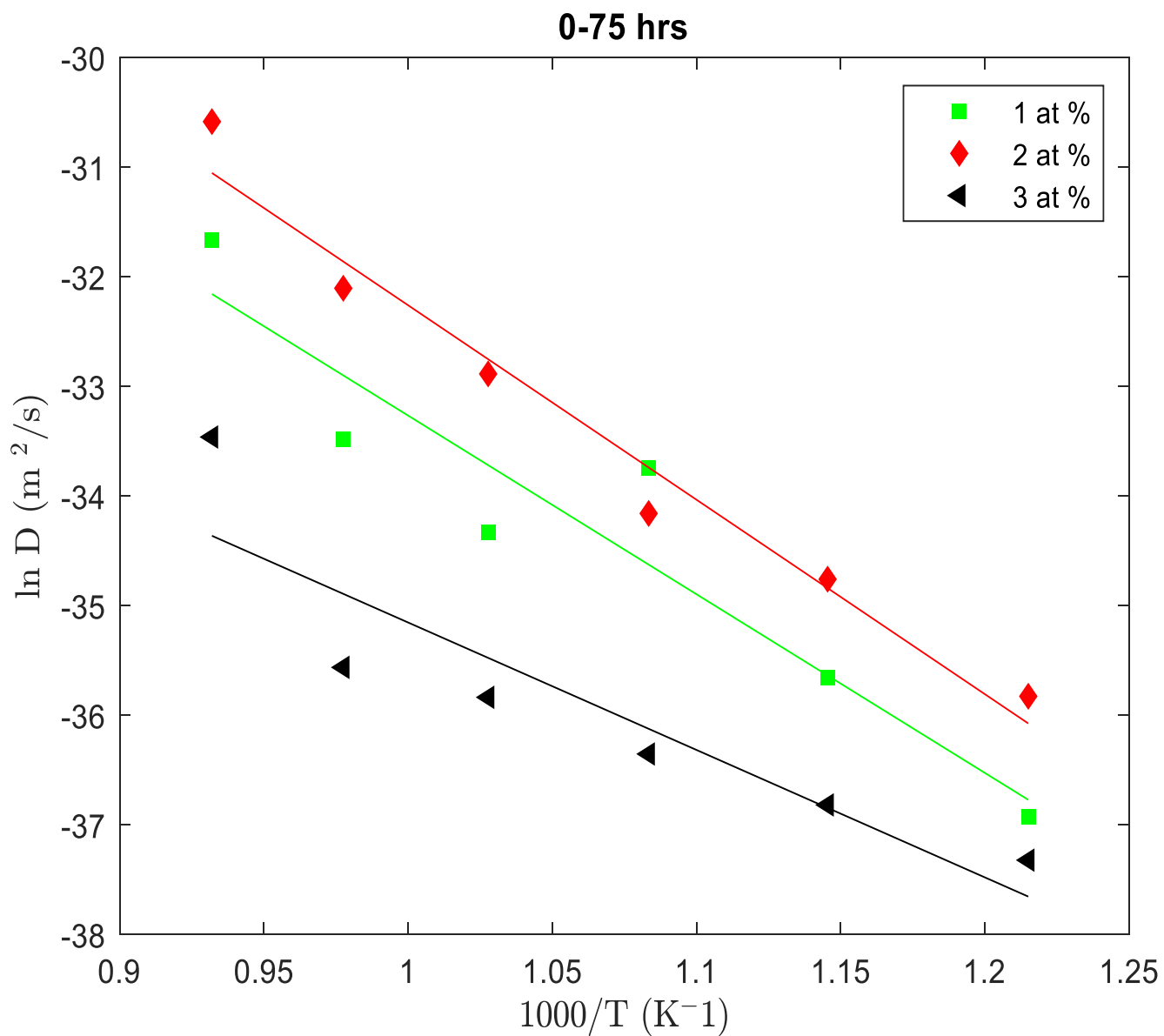


Fig. 4.17 Temperature dependence of interdiffusion coefficient after 75 hours

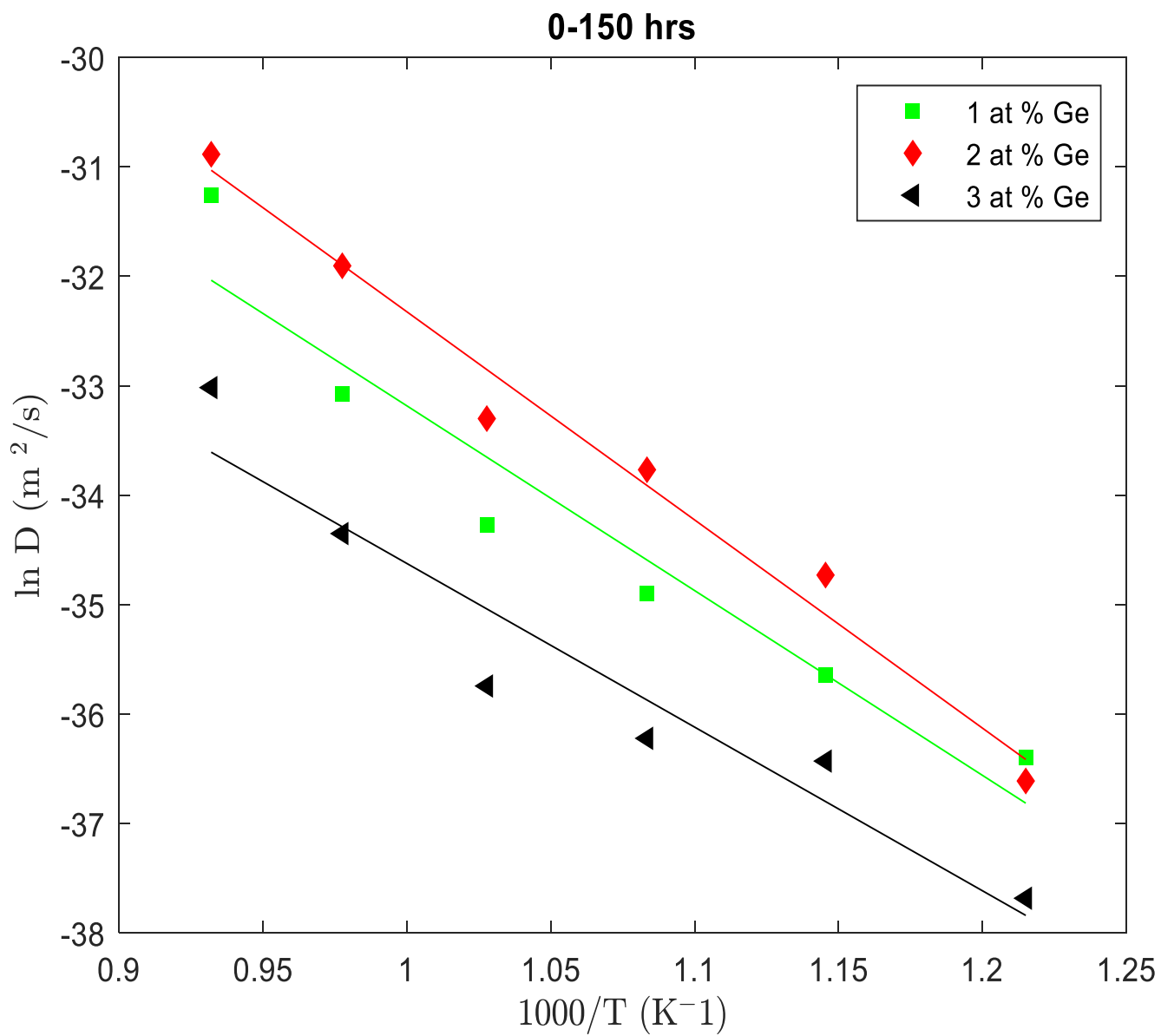


Fig. 4.18 Temperature dependence of interdiffusion coefficient after 150 hours

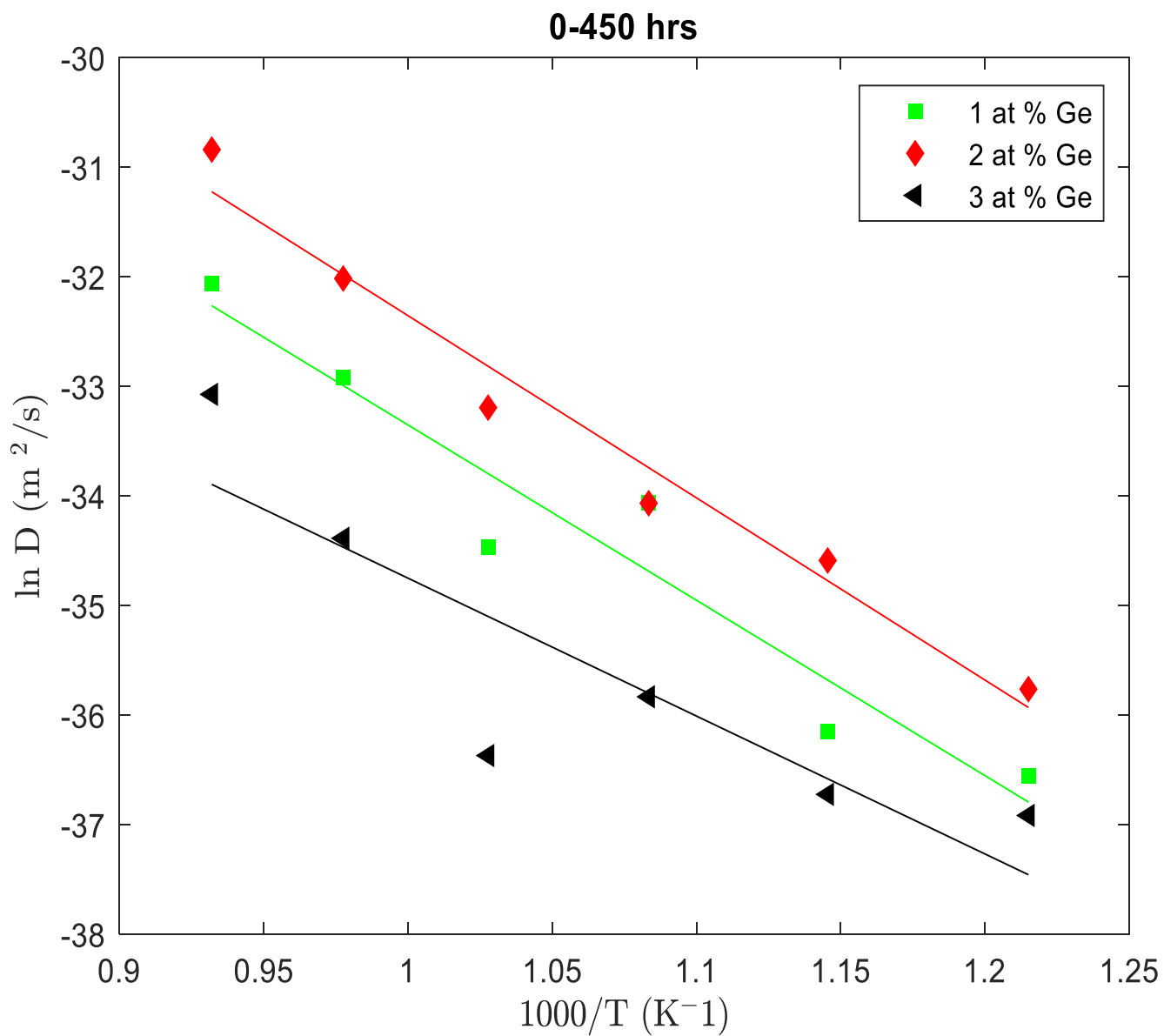


Fig. 4.19 Temperature dependence of interdiffusion coefficient after 450 hours

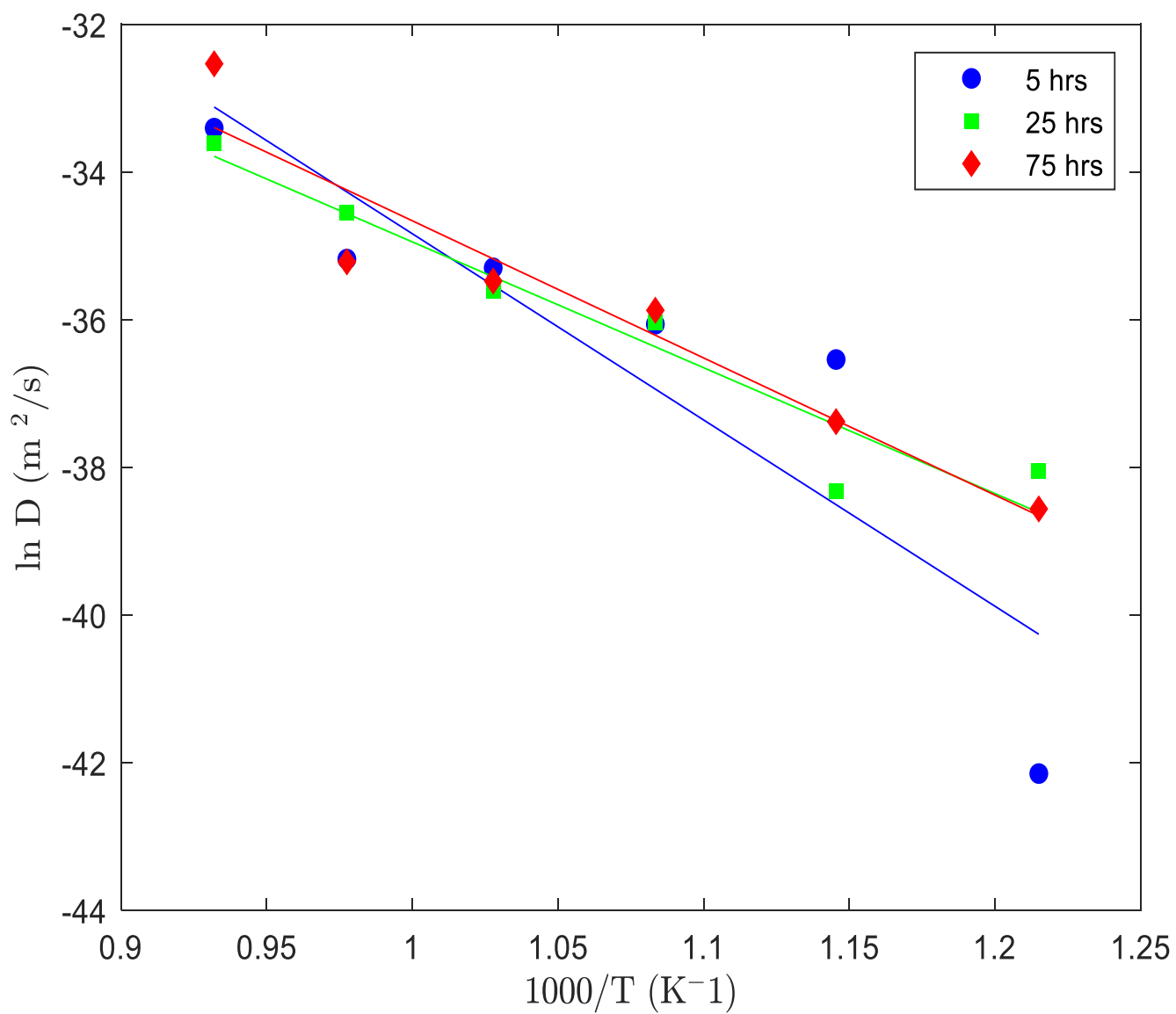


Fig. 4.20 Temperature dependence of impurity diffusion coefficient after 5, 25 and 75 hours

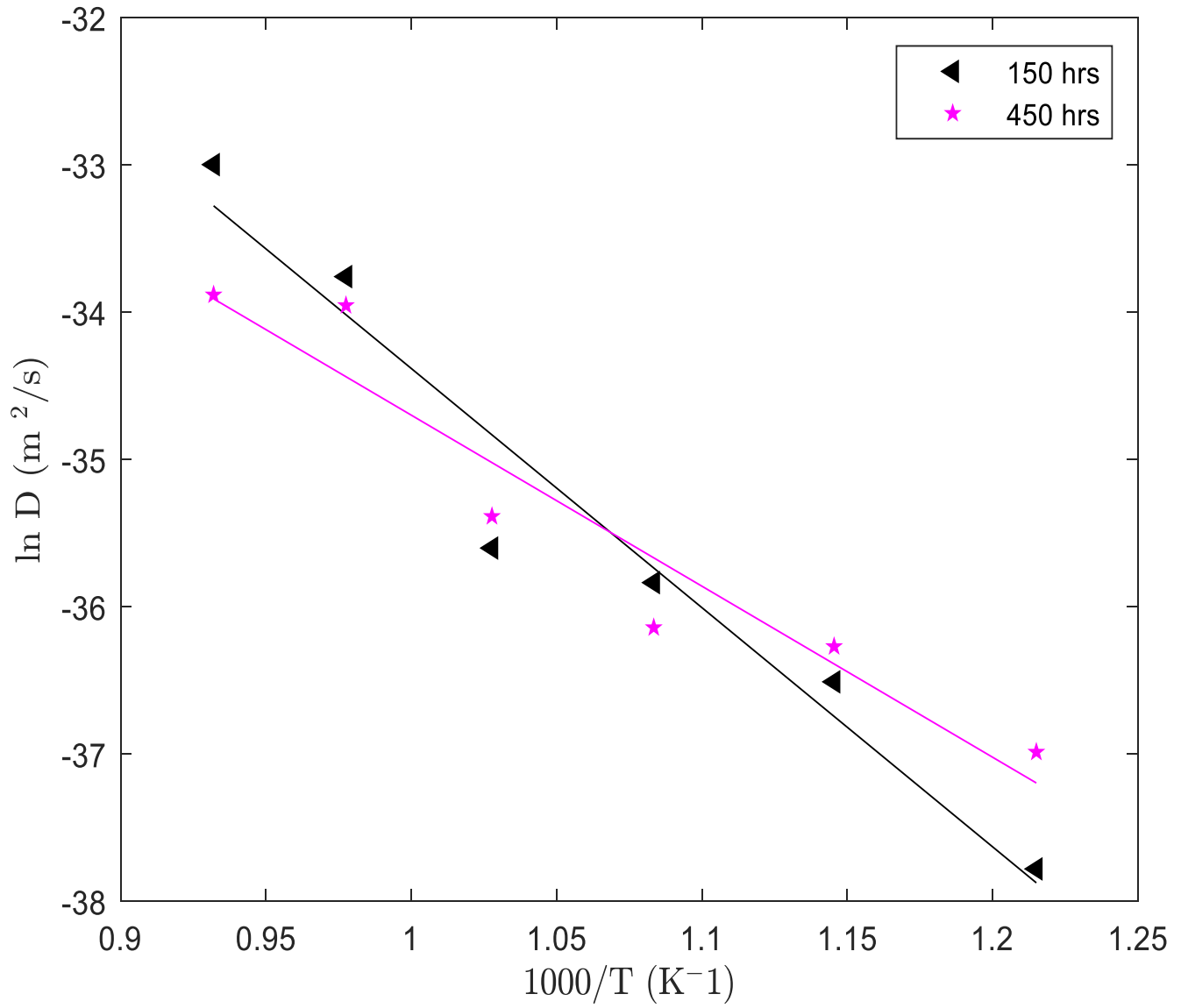


Fig. 4.21 Temperature dependence of impurity diffusion coefficient after 150 and 450 hours

#### 4.4.1 Concentration-dependent Diffusion Frequency Factor $D_o$ and Activation Energy $Q_d$

The concentration-dependent diffusion frequency factor and activation energy are derived directly from the Arrhenius plots where the data points were fitted with straight lines by using linear regression; the intercept and slope are then used to calculate frequency factor, and activation energy, respectively. In general, the reliability of the evaluated concentration-dependent frequency factor and activation energy can be substantially improved when diffusion couples are systematically investigated at various temperatures [77]. Thus, a large number of diffusion heat treatments at different temperatures are carried out to enhance the validity in this analysis.

The interdiffusion coefficients obtained at 0-5 , 0-25, 0-75, 0-150 and 0-450 hours at 550°C, 600°C, 650°C, 700°C, 750°C and 800°C were used to evaluate the concentration-dependent frequency factor  $D_o(c)$  and activation energy  $Q_d(c)$ .

Table 4.10 show that the values of  $D_o(c)$  range from  $5.4 \times 10^{-11}$  to  $6.7 \times 10^{-5} \text{ m}^2/\text{s}$  while the values of  $Q_d(c)$  range from 92.6 to 209.7 kJ/mol-K.

The obtained results from this Cu-Ge binary system distinctly show that both  $D_o(c)$  and  $Q_d(c)$  vary over time contrary to the notable patterns reported in the literature. Provided that these parameters exhibit ideal time-independent behaviors, it would be expected that the frequency factor  $D_o(c)$  and activation energy  $Q_d(c)$  values across all of the diffusion times would equate. On the contrary, the observed differences suggest systematical variations.

Laik et al. [77] described a notable behavior in the form of a decrease in both  $D_o(c)$  and  $Q_d(c)$  with increasing aluminum solute concentration in a pure Zr/ Zr 2.8 at. % Al alloy system. This pattern indicated the linear variation of  $D_o(c)$  and  $Q_d(c)$  with solute concentration. In this study, a comparable decrease in  $D_o(c)$  and  $Q_d(c)$  with increasing Ge solute concentration is observed

only at a specific diffusion time of 5 hours. After 5 hours, no consistent or discernible pattern can be observed across the other diffusion times. In certain cases,  $D_o(c)$  and  $Q_d(c)$  increase at lower Ge concentrations followed by a decline at higher concentrations and in other cases, the reverse behavior was observed.

Overall, these variations of  $D_o(c)$  and  $Q_d(c)$  with time are due to the effects of time on the interdiffusion coefficients attributable to diffusion induced stresses/strains within the system.

Table 4.10 Concentration-dependent frequency factor and activation energy values in Cu/Cu 3 at.

% Ge system

| Ge at.<br>% | 0-5 hours                                 |                       |                    | 0-25 hours                                |                       |                    | 0-75 hours                                |                       |                    |
|-------------|-------------------------------------------|-----------------------|--------------------|-------------------------------------------|-----------------------|--------------------|-------------------------------------------|-----------------------|--------------------|
|             | D <sub>0</sub> (c)<br>(m <sup>2</sup> /s) | ln D <sub>0</sub> (c) | Q <sub>d</sub> (c) | D <sub>0</sub> (c)<br>(m <sup>2</sup> /s) | ln D <sub>0</sub> (c) | Q <sub>d</sub> (c) | D <sub>0</sub> (c)<br>(m <sup>2</sup> /s) | ln D <sub>0</sub> (c) | Q <sub>d</sub> (c) |
| 0           | 6.69E-05                                  | -9.6                  | 209.7              | 1.67E-08                                  | -17.9                 | 141.7              | 1.03E-07                                  | -16.1                 | 154.4              |
| 1           | 2.57E-06                                  | -12.9                 | 168.1              | 4.83E-08                                  | -16.8                 | 135.7              | 4.27E-08                                  | -17.0                 | 135.5              |
| 2           | 3.72E-07                                  | -14.8                 | 145.0              | 2.46E-07                                  | -15.2                 | 141.2              | 4.94E-07                                  | -14.5                 | 147.5              |
| 3           | 2.15E-10                                  | -22.3                 | 103.1              | 5.41E-11                                  | -23.6                 | 92.6               | 6.05E-11                                  | -23.5                 | 96.7               |
| Ge at.<br>% | 0-150 hours                               |                       |                    | 0-450 hours                               |                       |                    |                                           |                       |                    |
|             | D <sub>0</sub> (c) (m <sup>2</sup> /s)    | ln D <sub>0</sub> (c) | Q <sub>d</sub> (c) | D <sub>0</sub> (c) (m <sup>2</sup> /s)    | ln D <sub>0</sub> (c) | Q <sub>d</sub> (c) |                                           |                       |                    |
| 0           | 1.32E-08                                  | -18.1                 | 135.0              | 9.41E-11                                  | -23.1                 | 96.5               |                                           |                       |                    |
| 1           | 8.30E-08                                  | -16.3                 | 140.4              | 2.92E-08                                  | -17.3                 | 133.1              |                                           |                       |                    |
| 2           | 1.67E-06                                  | -13.3                 | 158.1              | 1.48E-07                                  | -15.7                 | 138.3              |                                           |                       |                    |
| 3           | 2.86E-09                                  | -19.7                 | 124.3              | 2.36E-10                                  | -22.2                 | 104.6              |                                           |                       |                    |

#### 4.5 Anomalous behavior of $D(c)$ with temperature

Under typical diffusion conditions, it is expected that diffusivity increases with increases in temperature for **ALL** concentrations. However, for specific ranges of concentration and diffusion times, an anomalous trend is observed where the diffusivity decreases as temperature increases. This is observed for 0.5 at. % Ge. –  $\approx$  1.5 at. % Ge in Figures 4.22, 4.23 and 4.25. The  $D(c)$  at a lower temperature of 650°C within this range is larger than those at a higher temperature of 700°C and 750°C in some cases. A theoretical analysis has showed that this abnormal behavior is due to the occurrence of DIS [17]. It is important to note however, that this anomalous behavior is not consistent across all diffusion times as shown in Figure 4.24 with a diffusion time of 150 hours.

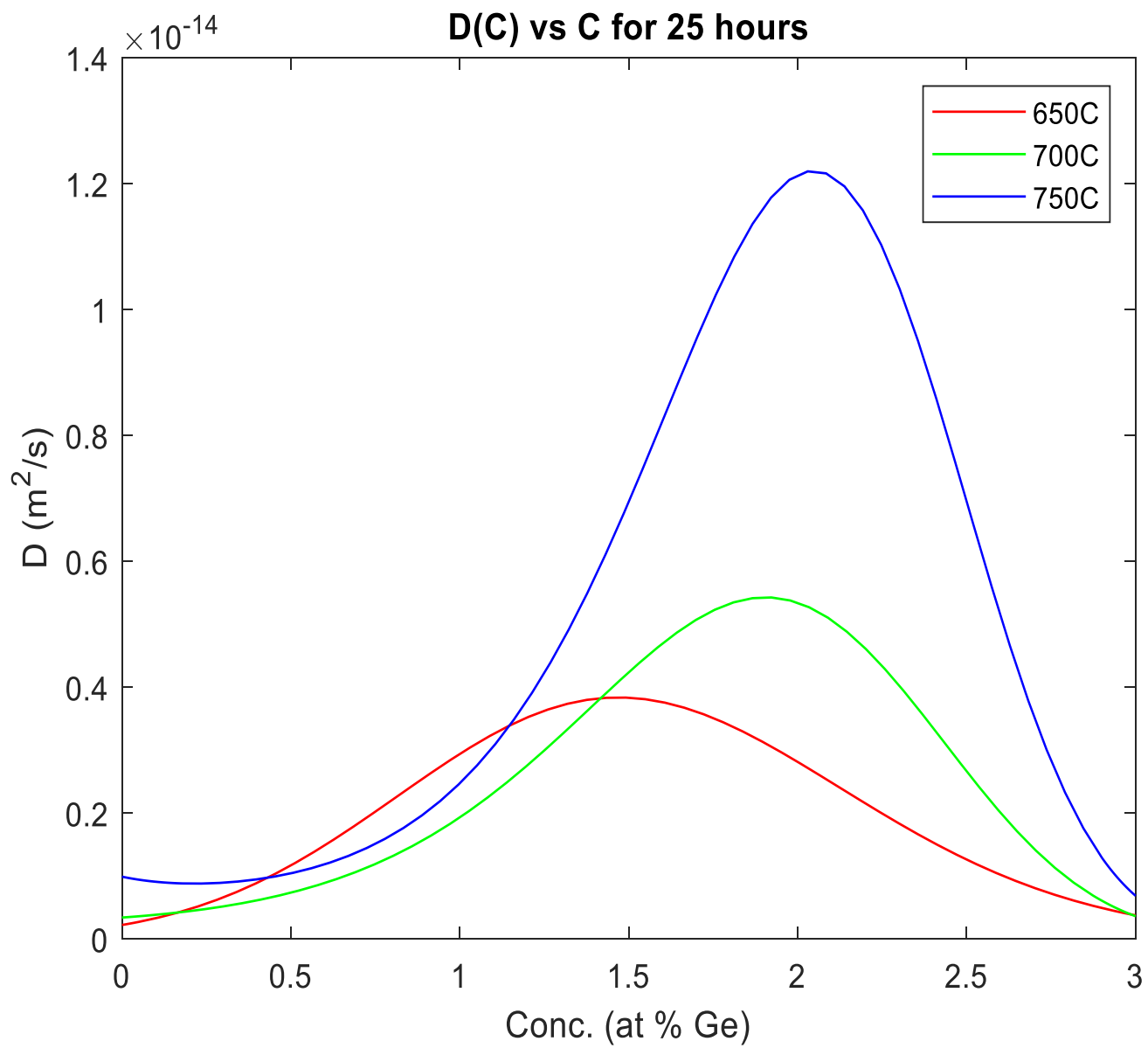


Fig. 4.22 Interdiffusion coefficient against concentration plot after 25 hours at 650°C, 700°C and 750°C

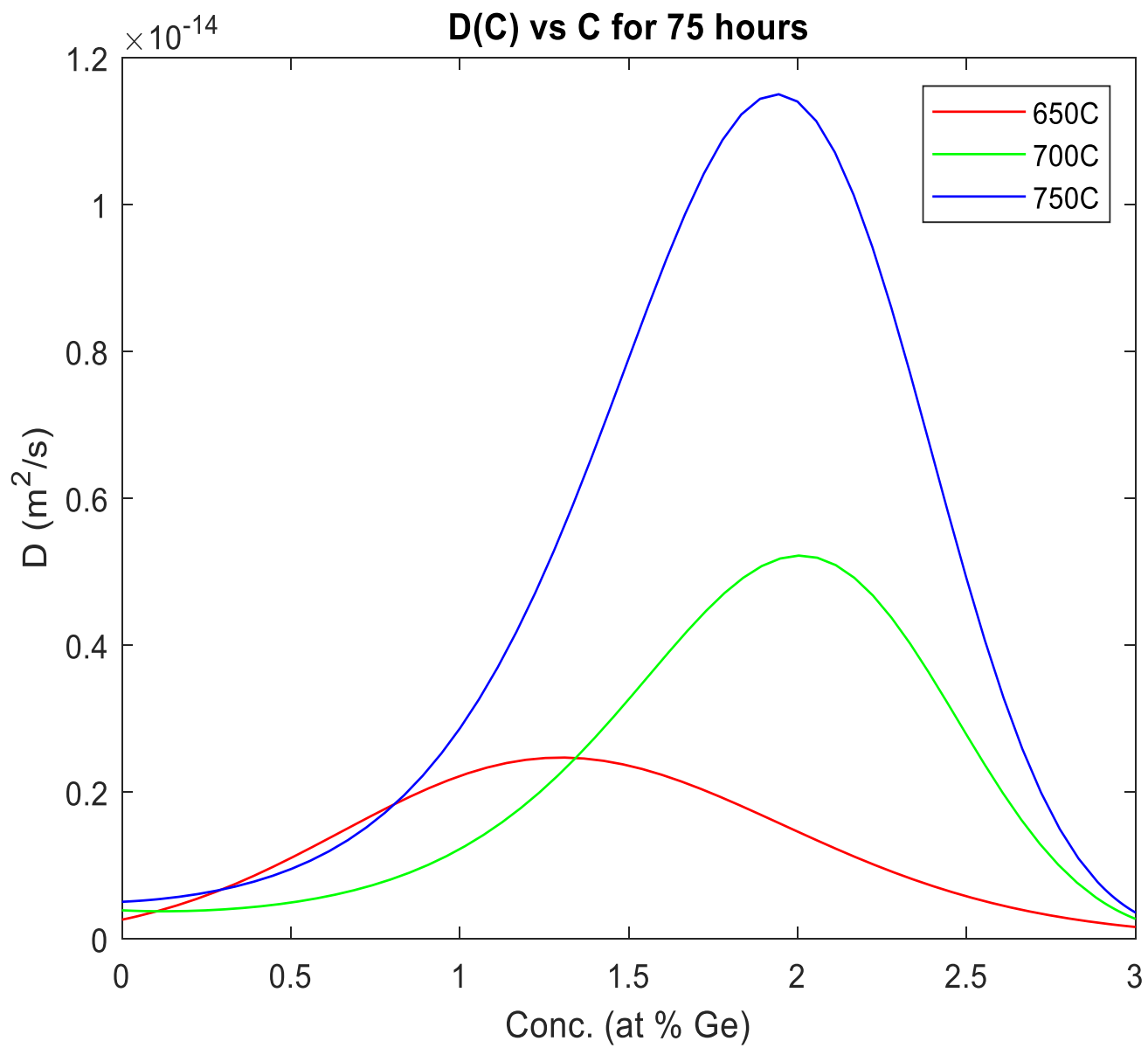


Fig. 4.23 Interdiffusion coefficient against concentration plot after 75 hours at 650°C, 700°C and 750°C

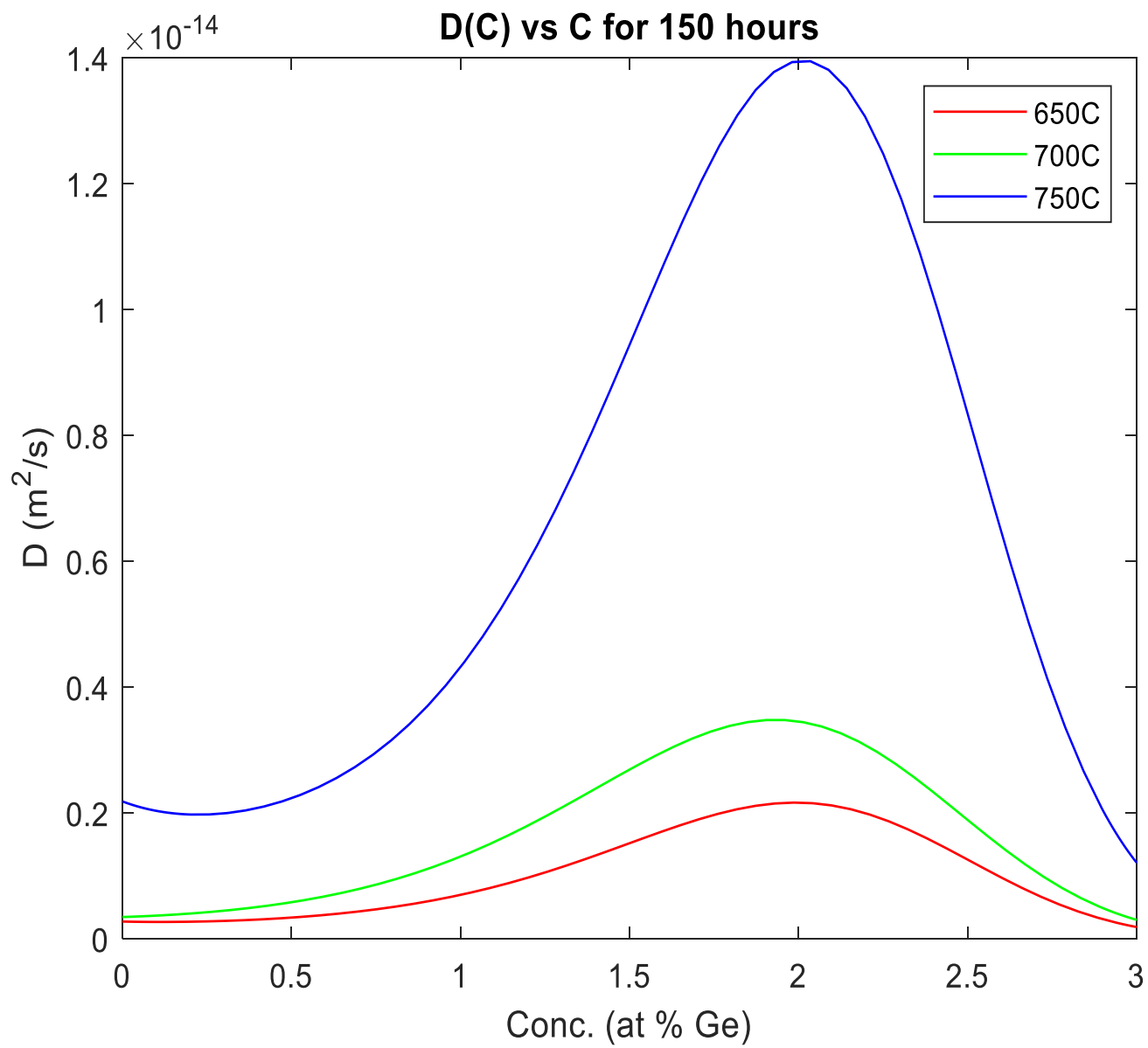


Fig. 4.24 Interdiffusion coefficient against concentration plot after 150 hours at 650°C, 700°C and 750°C

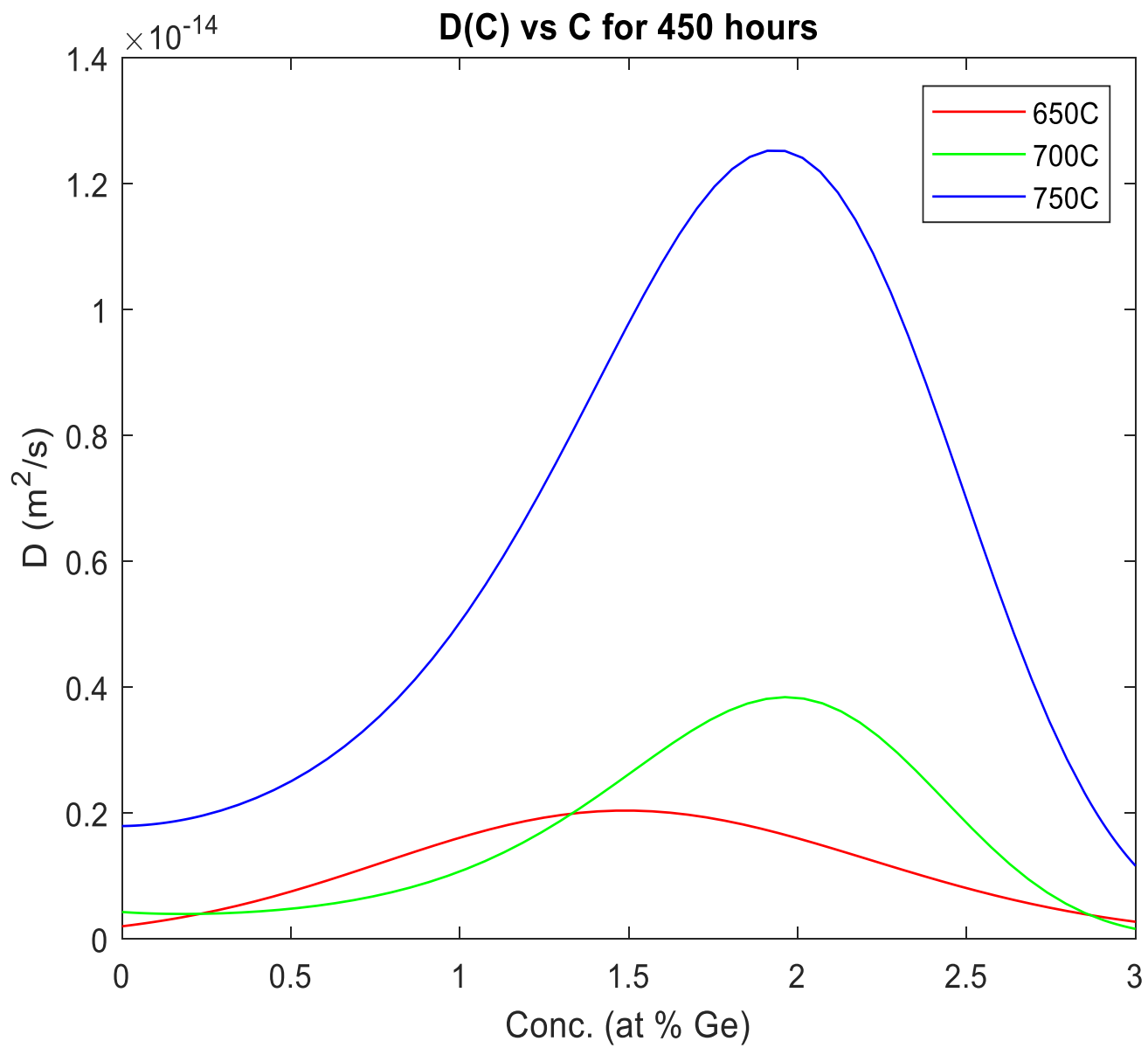


Fig. 4.25 Interdiffusion coefficient against concentration plot after 450 hours at 650°C, 700°C and 750°C

#### 4.6 Significance of the effect of time on $D(c)$

A widely accepted approach by researchers for determining  $D(c)$  involves the use of a single diffusion time. In doing this, it is generally assumed in the literature that  $D(c)$  obtained at longer diffusion times under isothermal conditions can be used to model diffusion at any time and a given temperature. To verify this prevailing assumption, the calculated  $D(c)$  for a long diffusion time of 450 hours is used to simulate the concentration profile after 5 hours at 700°C and 800°C. Following this, a comparison is made between the simulated concentration profile at 5 hours and the actual experimental profile obtained after 5 hours, and the results are presented in Figures 4.26 and 4.27.

The simulated concentration profile at 5 hours derived using  $D(c)$  obtained from 450 hours display variations indicative with error bars from the experimental concentration profiles at 5 hours. This discrepancy indicates the time dependence of  $D(c)$  attributable to the occurrence of DIS. Consequently, the assumption that  $D(c)$  values obtained at longer diffusion times at a given temperature can be used to model any diffusion duration may result in considerable inaccuracies.

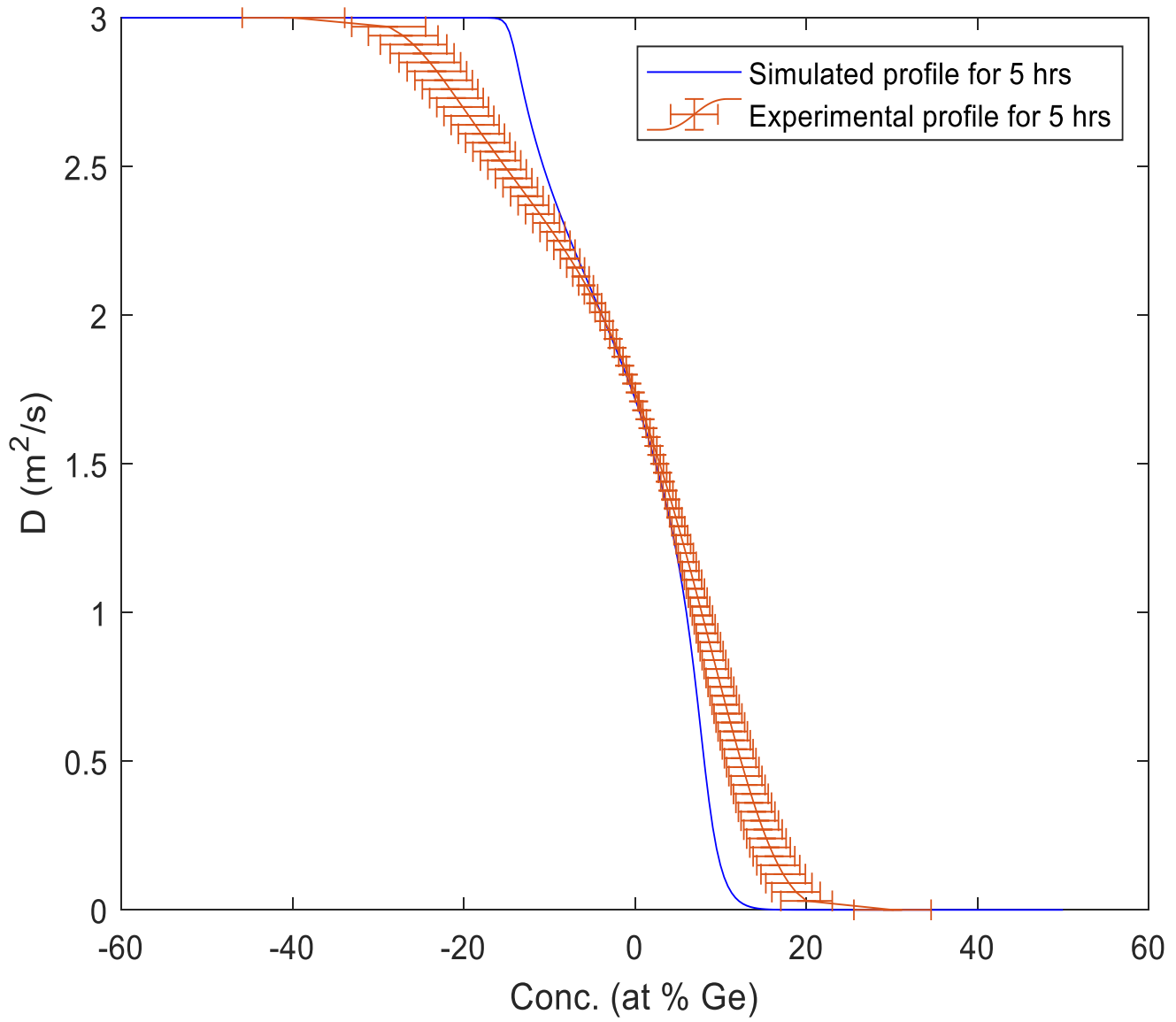


Fig. 4.16 Comparison of simulated 5 hrs profile obtained with  $D(c)$  of 450 hrs and actual experimental 5hrs concentration profile at 700 °C

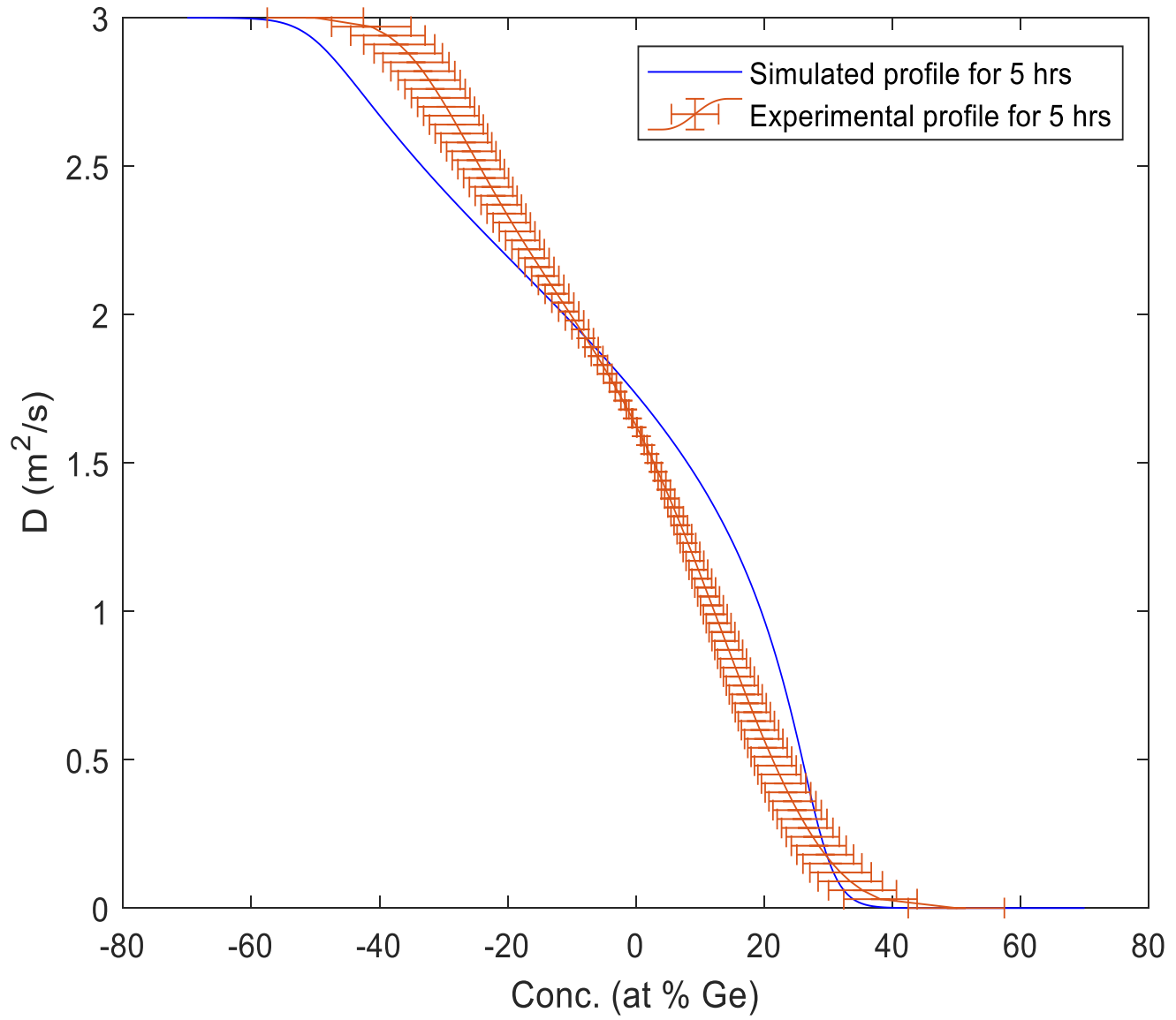


Fig. 4.27 Comparison of simulated 5 hrs profile obtained with  $D(c)$  of 450 hrs and actual experimental 5hrs concentration profile at 800°C

Finally, to validate the importance of using appropriate  $D(c)$  for diffusion analysis, the  $D(c)$  obtained after a specific diffusion time is used to simulate the concentration profile at that time. A comparison is made in Figures 4.28 and 4.29 between the simulated concentration profile at 5 hours and experimental concentration profile obtained after 5 hours. Evidently, the simulated profile falls within the region of the experimental profile indicated using error bars as shown in Figures 4.28 and 4.29. Therefore, the scenarios demonstrated in this section, that is; employing  $D(c)$  obtained after a long diffusion time to predict concentration profiles at shorter durations, and using  $D(c)$  after a specific time to reproduce the concentration profiles at that same time further substantiates that  $D(c)$  evolves over time at constant temperatures.

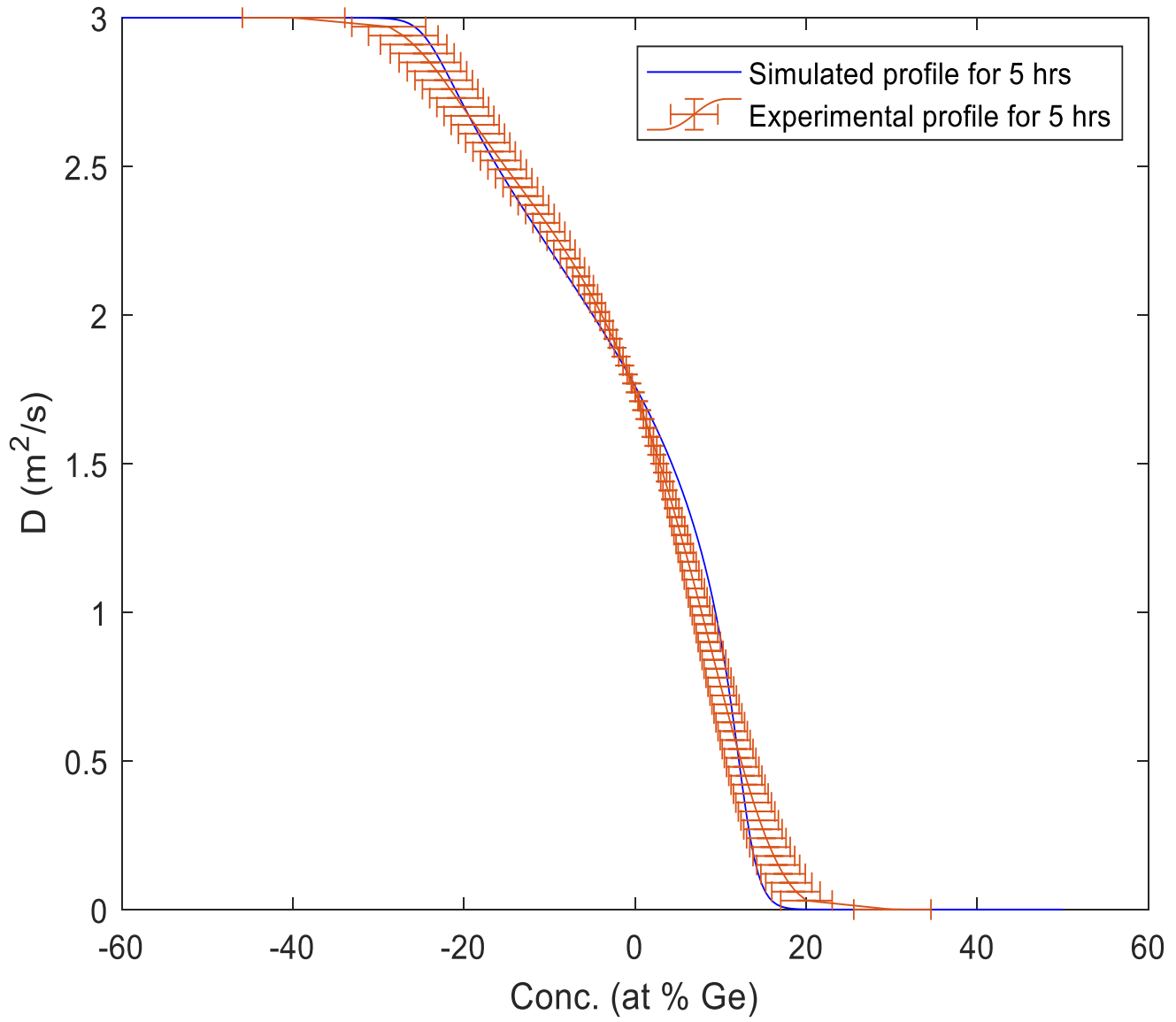


Figure 4.38 Comparison of simulated 5 hrs profile obtained with  $D(c)$  of 5 hrs and actual experimental 5hrs concentration profile at 700 °C

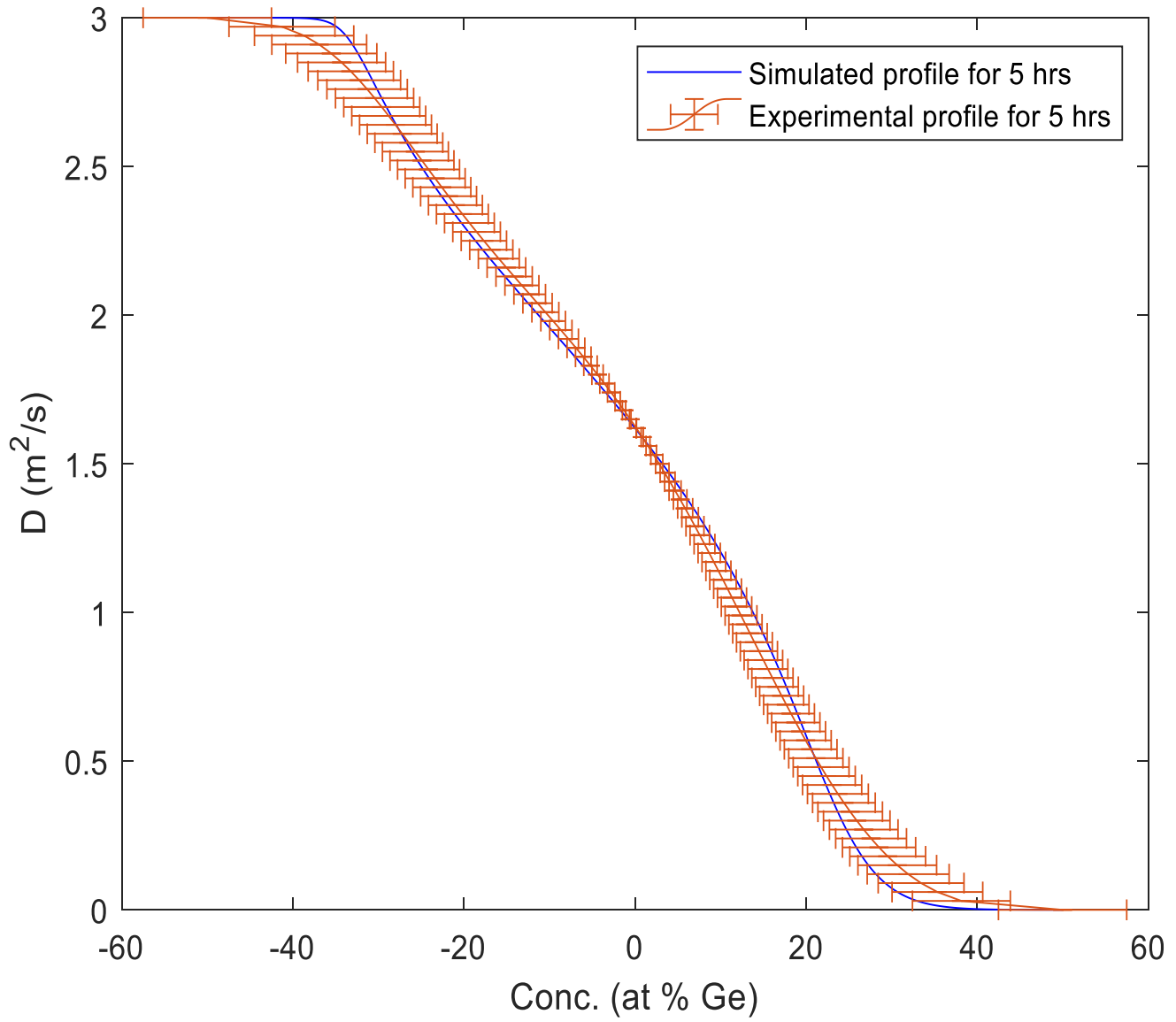


Figure 4.49 Comparison of simulated 5 hrs profile obtained with  $D(c)$  of 5 hrs and actual experimental 5hrs concentration profile at 800°C

## CHAPTER FIVE

### SUMMARY AND CONCLUSIONS

The effect of time on concentration-dependent interdiffusion coefficient has been investigated for diffusion times of 5, 25, 75, 150 and 450 hours at temperatures that range from 550°C to 800°C with 50°C intervals of increase. These results are calculated by using a newly developed robust numerical diffusion model in [20] that does not have the shortcomings of traditional models, including the BM, SF, Hall, and Wagner methods.

The main findings of this research work are summarized as follows:

- i. Concentration-dependent interdiffusion coefficient is observed to vary with time across the temperature range studied.
- ii. Likewise, the impurity diffusion coefficient of Ge in Cu is found to isothermally vary with time at all the temperatures used in this study.
- iii. Isothermal variations in both the concentration-dependent interdiffusion coefficient and impurity diffusion coefficient are attributable to the concept of diffusion-induced stress.
- iv. It is observed that, at certain concentrations and diffusion times, the diffusion coefficient anomalously decreases with increasing temperature. This behavior is a distinctive feature of diffusion-induced stress and thus serves as a clear indication of its occurrence in the present work.

## **CHAPTER SIX**

### **FUTURE WORK AND RECOMMENDATIONS**

The following items are recommended for future work related to this study:

- i. The effect of time on concentration-dependent interdiffusion coefficients should be explored when the diffusion interface in the Cu-Ge alloy system migrates in 2D and 3D.
- ii. The newly developed numerical model in [20] employed in this research work only applies to binary systems. Therefore, future studies need to investigate concentration-dependent interdiffusion coefficients in ternary and multicomponent systems. The latter, such as advanced high strength steel alloys or high entropy alloys, are recommended, as recently, there is high demand for multicomponent systems in nuclear and automotive applications.

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