DIFFUSION OF GERMANIUM AND SILVER IN SILICA GLASS

by

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A thesis submitted for the Degree of Doctor of Philosophy in the Australian National University.

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April 1974.
"DJER BASUKI MAWA BEJA"

("AS YE SOW SO SHALL YE REAP")

old Indonesian proverb.

The work contained in this thesis is my own except where another source is acknowledged.

M.S.A. SASTROAMIDJOJO.
I wish to express my gratitude to Dr. A.J. Mortlock for his advice and supervision during the course of this investigation and Dr. R.P. Agarwala for his kind and persistent interest during critical stages of my work. Thanks are also extended to Mr. D.M. Price for informative guidance in practical procedures, Mr. L. Batt and Mr. J. Robinson, for valuable technical assistance and Mr. K. Smith for assistance with photography.

General assistance was offered by many individuals at the Australian National University. In this respect I would especially thank Dr. M.I. Whitecross and Mrs. A. Petterson of the Department of Botany, School of General Studies for their assistance with electron microscopy, Mr. J.H. Pennington of the Department of Geology, School of General Studies for his help with x-ray diffraction analysis and Dr. D.C. Doetschman of the Research School of Chemistry for criticism and helpful suggestions.

Scanning electron microscopy analysis was done in the laboratory of Dr. Barry Filshie, Division of Entomology, C.S.I.R.O., Canberra, with the assistance of Mr. Colin Beaton and my debt to both is hereby gratefully acknowledged. The assistance of Dr. J.N. Boland of the T.E.M. facilities R.S.E.S, Australian National University, is also hereby gratefully acknowledged.

I am indebted to my fellow research students for friendly co-operation and discussion in particular Mr. M. Marshall, Mr. H.R. Foster, Mr. T. Solaga and Mr. S. Takabayasi. Spiritual support of ancestors, parents, my wife, Pustika and my children, Sena Gumira and Adjiputranto was of vital importance as was the interest and cheerful encouragement of Pietermella van de Donk, Nicolina Maria Kootkar and, last but not least, Inez Jean Selina Lenora Harding.
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ABSTRACT

In the past a substantial amount of work has been carried out on tracer diffusion in metals and several different mechanisms have been proposed to explain the mode of diffusion in a crystalline lattice. However, relatively little work exists on the diffusion in supercooled liquids like glass (Homosil) used in the present studies. These studies were carried out with the purpose of elucidating the different mechanisms operating in this type of structure. It was found that the diffusion of germanium and silver in glass (Homosil) exhibited three definite regions (I, II and III) in the concentration vs. penetration distance profiles. These have been interpreted as being due to

(I) contamination by radioactive grinding and polishing debris

(II) diffusion through "holes" or "cavities" in the glass network; diffusion mechanisms are similar to interstitial, vacancy and exchange mechanisms in crystalline solids

(III) diffusion along "channels" or paths of enhanced diffusivity in the network.

Plots of log D vs $\frac{1}{T}$ showed two straight-line regions separated by a transformation region in the vicinity of 570°C. The change in slope (activation energy) in going from the low temperature region to the high temperature region has been tentatively explained on the basis of the effects of charge and size of the diffusing ion in a network which changes with temperature.
The least-squares Arrhenius parameters for region II of the concentration vs. penetration distance profiles were as follows:

for germanium:
\[
D = 8.2 \times 10^{-10} \exp \left[ -\frac{(0.70 \pm 0.06) \text{eV}}{kT} \right] \text{cm}^2/\text{sec} \text{ between 570°C and 956°C}
\]
\[
D = 1.1 \times 10^{-12} \exp \left[ -\frac{(0.21 \pm 0.03) \text{eV}}{kT} \right] \text{cm}^2/\text{sec} \text{ between 413°C and 570°C}
\]

for silver:
\[
D = 6.9 \times 10^{-2} \exp \left[ -\frac{(1.51 \pm 0.02) \text{eV}}{kT} \right] \text{cm}^2/\text{sec} \text{ between 570°C and 948°C}
\]
\[
D = 1.0 \times 10^{-5} \exp \left[ -\frac{(0.48 \pm 0.02) \text{eV}}{kT} \right] \text{cm}^2/\text{sec} \text{ between 441°C and 570°C}.
\]

A decreasing diffusivity with increasing temperature has been observed in region III. It is believed that this is an anomaly not seen in specimens which had been pre-annealed for a long time at high temperature. The enhanced diffusivity in this region is believed to take place along "channels", paths of high diffusivity, akin to "dislocation pipe-diffusion" in regular crystals.

Diffusion of a mixture of $^{68}\text{Ge}$ and $^{71}\text{Ge}$ also of a mixture of $^{105}\text{Ag}$ and $^{110}\text{Ag}$ was carried out to investigate correlation effects.

With the data from the isotope effect experiments, the correlation factor could be computed.

Depending on whether a "one-atom" jump or a "two-atom" jump was considered, the quantity $f\Delta K$ was computed to be as follows:

<table>
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<th>$f\Delta K$</th>
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<td>$n = 1$</td>
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<tr>
<td>Ag</td>
<td>0.6 ± 0.2</td>
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<tr>
<td>Ge</td>
<td>0.7 ± 0.3</td>
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in which \( n \) gives the number of atoms involved in the diffusion jump.

On the basis of considerations pertaining to the charge and size of the diffusing ion in a changing network configuration and taking into account the values of \( f \), it was believed to be likely that germanium diffused by an interstitialcy mechanism in region II. In the case of silver diffusion, the diffusion mechanisms possible in region II are: vacancy, interstitialcy and exchange mechanism.

X-ray diffraction analyses of powdered specimens have been made to determine if devitrification had taken place in the course of the diffusion anneal. No devitrification could be detected.

Electron micrographs by ordinary and scanning electronmicroscopy have been obtained to find evidence for regions of higher diffusivity. Differences in surface granulation have been observed for specimens annealed at different temperatures. The functional relationship between annealing time, temperature and granular size, however, has not been established.

Qualitatively the electron micrographs do not exclude the existence of regions of weaker bonding and by implication paths of enhanced diffusivity. This possibility has been invoked to support the explanations given for the anomalous diffusion behaviour in region III.
SUMMARY OF CHAPTER I

The general theory of diffusion is given as a basis for plotting experimental data. Fick's first and second equations are given. The absolute rate reaction theory and the "dynamical method" developed by Rice are briefly touched upon.

A number of diffusion mechanisms for diffusion in regular crystal lattices (i.e. structures with long range order) are listed. Vacancy, interstitial, interstitialcy and dislocation diffusion mechanisms are singled out for illustration, and a redefinition of vacancy, interstitial and interstitialcy mechanisms as applicable to ionic diffusion in glass is given along lines suggested by Haven and Stevels.

The general nature of glass is discussed with special emphasis on structure and thermal history. It is pointed out that, broadly speaking, two major schools of thought exist concerning the structure of glass, (1) the extended random network theory, and (2) the "crystallite" hypothesis.

Several models are discussed of which, for the purpose of this thesis, the extended random network and its modification by Tilton (the "vitron" model) are the most important.

Special care is taken in selecting "two-dimensional" and "three-dimensional" representations of a glass network, since in an explanation of diffusion processes diffusion pathways are often hard to visualize, especially in a three-dimensional random network like glass.
CHAPTER I

INTRODUCTION

I.1 Preliminaries

In the solid state physical and chemical properties depend on the forces by which the geometrical units in the crystal lattice are bound together and on the arrangement of the arrays of atoms, clusters of molecules and of single atoms or molecules.

The forces between atoms and atomic scale defects in these materials could easily be studied by determining the rates of diffusion of atoms. The study of the rate of diffusion helps in elucidating the various reactions taking part in phase transformations, solubility, creep, grain growth and recrystallization.

Earlier studies of transport phenomena were devoted mainly to the study of diffusion in metals although later on with the advancement of different techniques and the availability of pure tracers, it has been extended to the study of diffusion in ceramics and glasses.

The present study concerns itself with the diffusion in glass because this material does not exhibit long range periodicity of atomic structure and is also distinguished from the other solids by the lack of crystallinity.

The study of impurity transport in glass should throw light on the mode of diffusion in super-cooled non-crystalline structures and will help to elucidate different processes involved in diffusion compared to those in metals.

For such a study proper understanding of diffusion equations and the basis of diffusion is important.
I.2 Theory of Diffusion

The driving force for diffusion can be said to be the difference in chemical potential between different parts of the system [1].

The rate of diffusion depends not only on the magnitude of the driving force but also on the kind of matrix. In most solids the rate of diffusion at room temperature is much less than the rates found for gases and liquids. To obtain measurable diffusion it is therefore necessary to let diffusion in solid take place at high temperatures. In this way not only will the diffusing particles have more molecular motion at higher temperatures, but also the lattice of the solid would have expanded thus making the migration of the diffusing particles easier.

Mathematically the diffusion process may be represented in relation to the chemical potential gradient by

\[ I = -L \frac{\partial \mu}{\partial x} \]  \hspace{1cm} (1)

where 
- \( I \) = current of diffusing particles per unit area of section;
- \( \mu \) = the chemical potential of the diffusing matter;
- \( L \) = a proportionality constant.

Equation (1) holds for diffusion in one direction when only one species is diffusing. To generalize equation (1), one must replace it by a sum of similar terms over all diffusing species and over \( x, y, z \).

Heat conduction in solids is considered a process very similar to that of diffusion. This was recognized in 1855 by Fick who expressed the rate of transfer of diffusing materials in isotropic substances as

\[ J = -D \frac{\partial C}{\partial x} \]  \hspace{1cm} (2)

where 
- \( J \) = amount of material diffusing per unit area of section per unit time;
D = the diffusion coefficient;
C = concentration of the diffusing species;
x = the space co-ordinate normal to the section.

It should be remembered that the two basic assumptions involved are

(1) proportionality of the particle flux to the gradient of particle concentration

(2) conservation of the number of particles per unit volume [3].

Consider a cylindrical volume between two planes perpendicular to the axis of symmetry and of unit cross-section [3]. Let these planes be p and \( p^1 \) at \( x \) and \( x + dx \) respectively, \( J(x) \) be the flux traversing \( p \) at \( x \) and \( J(x + dx) \) be the flux of particles traversing \( p^1 \) at \( x + dx \) and the flux be directed from left to right. In a unit time the amount of material accumulating in the cylindrical volume will be the difference of the flux entering through \( p \) at \( x \) and leaving through \( p^1 \) at \( x + dx \), or

\[
[J(x) - J(x + dx)] \, dt \tag{3}
\]

which in the limit becomes

\[
- \frac{3J}{3x} \, dx \, dt . \tag{4}
\]

The amount given by equation (4) can be considered as the variation of the number of atoms in volume \( dx \) or \( dCdx \) in which \( dC \) gives the variation in concentration. It follows that

\[
\frac{\partial C}{\partial t} = - \frac{3J}{3x} \tag{5}
\]

This equation is called the conservation equation. Combining equations (2) and (5) one can write
\[
\frac{\partial C}{\partial t} = \frac{\partial}{\partial x} \left( D \frac{\partial C}{\partial x} \right)
\]

or

\[
\frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial x^2}
\]  \hspace{1cm} (6)

when \(D\) is independent of \(x\).

Equation (6) expresses the behaviour in a region in which \(\frac{\partial C}{\partial x}\) varies with time [3] and is called Fick's second Law whereas equation (2) is known as Fick's first Law.

The importance of equation (6) lies in the fact that the solution of this equation, e.g., the function \(C(x, t)\) depends on the initial and final boundary conditions imposed by the experiment.

In practice, one sets up the experiment in such a fashion that a simple solution of equation (6) is applicable. This will be the case if one works in a so-called infinite medium, where the solute concentration is significant only in a layer much thinner in the \(x\)-direction, the direction of diffusion, than the thickness of the matrix as a whole; for example, a thin layer of radioactive material to be diffused "sandwiched" between two thick pieces of material.

The similarity of equation (1) and (2) is evident and they can be related by

\[
D = kT G^* \quad \text{where} \quad L = kT G^* \quad .
\]  \hspace{1cm} (7)

\(k\) = Boltzmann's constant;

\(T\) = absolute temperature;

\(G^*\) = the mobility.

Equation (7) was first derived by Nernst in 1888.

For ionic mobilities in solutions one can obtain the same information from conductivity data as can be obtained from diffusion experiments.

Consider the diffusion in the \(x\) direction from a plane source.
The diffusing material is at the surface of the diffusion medium in a thin layer so that for \( x > 0 \), \( C \to 0 \) as \( t \to 0 \) and for \( x = 0 \), \( C \to \infty \) as \( t \to 0 \). For a thickness of deposit small compared to \( \sqrt{D t} \), the solution is a simple Gaussian and one can write

\[
C = \frac{M}{\sqrt{\pi Dt}} \exp \left( -\frac{x^2}{4Dt} \right)
\]

(8)

where \( M \) = amount of deposit on the surface. \( \int_0^\infty C \, dx = M \) for all \( t > 0 \) [107].

For the same initial conditions but for \( C(0) = C_s \), a constant, for \( t > 0 \) the diffusion is represented by

\[
C = C_s \text{erfc} \left( \frac{x}{2\sqrt{Dt}} \right)
\]

(9)

The temperature dependence of the diffusion coefficient can usually be expressed thus:

\[
D = D_0 \exp \left( -\frac{Q}{RT} \right)
\]

(10)

where

- \( R \) = the gas constant;
- \( T \) = the absolute temperature.

This equation was first proposed by Arrhenius for the rate constant in chemical reactions. \( D_0 \) is called the "frequency factor" and \( Q \) is called the "activation energy".

The motion of the diffusing particle can be considered as a random walk and a theory of diffusion in crystalline phases has been developed which assumes the diffusing particle to move by a series of jumps from one site to the other. The frequency of such jumps is dependent on the ability of the diffusing particle to pass the free energy barrier.

The diffusion coefficient for such diffusion can be represented
by

\[ D = \gamma \nu^* \lambda^2 \exp (- \Delta G/RT) \]
\[ = \gamma \nu^* \exp (\Delta S/R) \exp (- \Delta H/RT) \]  

(11)

where \( \gamma \) = numerical constant depending on geometry and mechanism of diffusion;
\( \nu^* \) = vibration frequency of diffusing atom;
\( \Delta G \) = Gibbs free energy of activation per mole;
\( \Delta S \) = entropy of activation per mole;
\( \Delta H \) = enthalpy of activation per mole;
\( \lambda \) = jump distance of diffusing particle.

Another model for the diffusion through solids is based upon the actual atomic displacement of the diffusing atom and the displacements of its neighbours.

The amplitude of the thermal vibration of the atom in the direction of diffusion has to be sufficiently large in order to carry the atom from one stable configuration to another. Another requirement is that atoms that obstruct the jump of the diffusing atom must move a sufficient distance from each other so as to allow the diffusing particle to pass between them.

Rice [4] considered the case of harmonically bound atoms. For diffusion the required amplitude of vibrational motion of the diffusing atom has to be of the order of half the distance between two lattice sites. The direction of the vibration is in the direction of diffusion.

It was further assumed that the diffusing atom achieved the amplitude of vibration needed much less frequently than the barrier atoms achieve their smaller amplitudes of vibration. Pair correlation functions between the diffusing atom and the nearest neighbour atoms have also to be considered.

For an idealized harmonic crystal the values of \( D_0 \) and \( Q \) in equation (10) become
\[ D_0 = \alpha^2 \bar{v} \exp \left[ \left( \Delta S_f + \Sigma \frac{\Delta S}{k} \right) \right] \]  
(12)

and

\[ Q = \Delta H_t + E_0 + \Sigma E_1 + \Delta H \]  
(13)

where

- \( \alpha \) = lattice parameter;
- \( \bar{v} \) = weighted frequency factor;
- \( \Delta S_f \) = entropy of vacancy formation;
- \( \Delta S \) = changes in entropy;
- \( \Delta H_t \) = enthalpy of vacancy formation;
- \( \Delta H \) = changes in enthalpy;
- \( E_0 \) = the energy required for the diffusing atom to attain the critical amplitude of motion for the jump;
- \( E_1 \) = the energy for the barrier atom to have appropriate vibrational amplitude for the jump to take place.

The method just developed could be called the dynamical method while the one leading up to equation (11), based on absolute reaction rate theory could be called the equilibrium method.

Both methods give results which are not incompatible with equation (10). However, the exact determination of \( D_0 \) and \( Q \) of equation (10) is extremely difficult so that there is not enough evidence to prefer one theory over the other.

This shows how difficult it is to understand diffusion mechanisms in a medium which has a periodic lattice and even more so in glass which is generally referred to as having no lattice periodicity.

Most of the diffusion research has been done on metallic systems, metallic oxides and alkali halide crystal systems resulting in some insight as to how diffusion in crystalline materials take place. When one tries to understand the diffusion mechanism in glass the question arises to what
extent the picture of diffusion in crystalline materials can be applied to super-cooled liquids.

I.3 Diffusion Mechanisms

I.3.1 General Discussion

In crystalline solids diffusion mechanisms can be described in simple terms [2]. The ordered crystal lattice restricts the possible atom motions and allows a simple description of each specific atom displacement.

In a gas the diffusing atom moves through a cloud of randomly moving atoms. In both liquids and amorphous solids the atoms in the matrix are neither really arranged randomly nor have a definite periodicity.

In crystalline solids diffusion takes place through a regular array of lattice sites which are energetically favoured positions for atoms.

The basic assumption is that each diffusing atom makes a series of jumps between the various equilibrium lattice sites. The jumps are in more or less random directions and allow the atoms to migrate through the crystal.

Possible diffusion mechanisms include [2]:

(1) Exchange mechanism.
(2) Ring mechanism.
(3) Interstitial mechanism.
(4) Indirect interstitial mechanism (also called interstitialcy mechanism).
(5) Crowdion mechanism.
(6) Vacancy mechanism.
(7) Divacancy mechanism.
(8) Relaxion mechanism.
(9) Dislocation diffusion mechanism.
(10) Grain boundary diffusion mechanism.
(11) Surface diffusion mechanism.

Only the following mechanisms will be discussed:

(1) Vacancy mechanism.
(2) Interstitial mechanism.
(3) Dislocation diffusion mechanism.
(4) Grain boundary surface mechanism.
(5) Surface diffusion mechanism.

I.3.2 Vacancy Mechanism

Fig. 1 shows a regular array of atoms with one empty lattice site. The elementary atom jump in the vacancy mechanism consists of an atom jumping into a neighbouring empty site or vacancy. The position vacated by the jumping atom in its turn is then vacant, so that in effect vacancy and atom have merely exchanged positions. Each atom moves through the crystal by making a series of exchanges with the various vacancies.

I.3.3 Interstitial Mechanism

If the diffusing atom is small enough to fit into the spaces between the regular lattice sites in the matrix, it will often diffuse mainly by the interstitial mechanism, because the energy barriers tend to be smaller than for the other mechanisms in such cases. In this mechanism atoms move from one interstitial site to another and do not disturb the atoms in the regular lattice.

I.3.4 Interstitialcy (Indirect Interstitial) Mechanism

The interstitial atom is nearly equal in size to the lattice
atoms or to the lattice atoms on a given sub-lattice. In this case diffusion is most likely to occur by indirect interstitial mechanism. The interstitial atom does not move directly to another interstitial site. Instead, it moves into a normal lattice site and the atom which is originally at the lattice site is pushed into a neighbouring interstitial site as illustrated in Fig. 2.

I.3.5 Dislocation diffusion mechanisms

The theory of dislocations has been adequately developed by a number of workers and a general survey of the theory of crystal dislocations has been given by Cottrell [5] and Friedel [6].

I.3.5.1 Dislocation, grain boundary and surface diffusion mechanisms

Boundary and surface diffusion mechanisms are important in regions where the regular lattice structure breaks down. They involve line or surface discontinuities in the crystals.

It is clear that diffusion should occur more easily in the open regions of the crystal at dislocations, grain boundaries and surfaces. The detailed atomic paths in each case will depend on the particular atom configurations at each line or surface defect. Thus these mechanisms do not lend themselves to detailed kinetic analysis. Since the number of dislocations, grain boundaries and surfaces is more or less independent of temperature, diffusion by these mechanisms might have a smaller temperature dependence than by mechanisms involving point defects e.g., vacancies and interstitials. Where the concentration of point defects increases with temperature, line and surface mechanisms are relatively important at low temperatures but usually are not so important at high temperatures when compared to volume diffusion mechanisms.
FIG. 1. VACANCY MECHANISM

FIG. 2. INTERSTITIALCY (INDIRECT INTERSTITIAL) MECHANISM
Haven and Stevels (1957) [7] give a somewhat different model for the different mechanisms of diffusion in glass. In analogy with ionic transport in crystals [2] the places between the silicon-oxygen network, available for network-modifying ions [3], are divided into sites and interstitial sites. Both are places of relative potential minima, but the minima of the sites are distinctly lower than those of the interstitial sites, by say a few tenths of an electron volt (see Fig. 2a).

The number of sites depends on the composition of the glass. If a few sites are left unoccupied, they will be called vacancies analogous to the situation in the crystalline state.

In anticipation of what we will say about the diffusion of silver in vitreous silica we give here the diffusion mechanisms according to Haven and Stevels' model for the diffusion of sodium in glass [7] (see Fig. 2a).

1. "Free" transport mechanism

If the number of potential Na sites i.e. the number of places between the SiO₂-network tetrahedra available for Na-ions, is much greater than the number of Na⁺-ions, the latter can jump from one site to another without being much hindered by each other.

2. Vacancy mechanism

If the number of vacant sites (vacancies) is very low, a Na⁺-ion can only jump from one site to another if it is near a vacancy.

3. Interstitial mechanism

The Na⁺-ion travels by jumping from intersite to intersite. Mechanism (A) (short trajectory). The ion travels via a few intersites to a vacant site.
FIG. 2a. SCHEMATIC REPRESENTATION OF VARIOUS TRANSPORT MECHANISMS (POTENTIAL WELLS AND BARRIERS) ACCORDING TO HAVEN AND STEVELS [7]. ARROW INDICATES THE JUMP OF THE Na⁺ ION.

\( \odot = \text{sodium ion} \)
Mechanism (B) (long trajectory). The ion travels a very long distance before it finds a vacant site.

(4) **Interstitialcy mechanism**

An ion at intersite A can jump to a neighbouring site B, if at the same time the ion at B jumps to another intersite C. In this mechanism the ions are alternately at a site and an intersite.

### I.4 The Nature of Glass

#### I.4.1 General introduction

The lack of understanding of the structure of glass is a major obstacle in the study of diffusion in glass. It is therefore proper for the purpose of the present work to have a general picture of the nature of glass and in particular of silica glass, the material under study. Silica glasses are produced from quartz crystal powder by flame fusion (Verneuil process) [8]. Since there is no crucible material in contact with the glass there is an absence of metallic impurities.

However, the atmosphere of the hydro-oxygen flame produces an OH-content of 150-400 ppm.

Different types of silica glasses exhibit different physical properties (e.g. different absorption spectra, permeability, behaviour on irradiation) and therefore have differences in their network structure.

#### I.4.2 Thermodynamic considerations

Silica has the ability to form a super-cooled liquid by cooling down from temperatures above the melting point of the high temperature modification of cristobalite and to freeze into a solid glass. If one considers the typical behaviour of a common silicate glass as a function of temperature, it is evident that when glass forming substances cool
down the melt will undergo a modification of the structure and solidifies
to glass because of a discontinuity in thermodynamical properties such as
the enthalpy (H), the free energy (E), and the entropy (S).

Consider Fig. 3 in which;

- $T_m$ = melting or liquidus temperature
- $T_g$ = glass transition temperature
- $T_{gl.s}$ = transition temperature for slow cooling glass
- $T_{gl.f}$ = transition temperature for fast cooling glass.

Fast cooling will result in a more random structure, whereas slow
cooling will result in a glass which has a more crystal-like structure.

The structure of glass is therefore very much dependent on its
thermal history.

**I.4.3 Structure of glass**

As known from X-ray [9, 10] and neutron diffraction studies of silica
glass [11], the structural unit consists, like that of most crystalline
modifications of silica, of four oxygen atoms placed at the corners of a
tetrahedron with a silicon atom at the centre with interatomic distances as
follows: $Si - O (1.5 \text{ Å}), O - O (2.6 \text{ Å})$; the distance between Si atoms in
adjacent tetrahedrons is $3.03 \text{ Å}$ [4], see Fig. 3a, b, c, d(1), d(2), e, f(1), f(2) and Fig. 17.

While these bond distances are quite well accepted by different
workers there is still no agreement on the arrangement of the tetrahedrons
forming the composite structure. The concepts of geometrical structure of
oxide glasses are closely related. Geometrical concepts do not give an
answer to the question why a substance is able to go into the vitreous state.
FIG. 3. VOLUME VS TEMPERATURE PLOT OF GLASS FORMATION FROM THE STABLE MELT
FIG. 3a. SILICATE UNIT CONSISTING OF ONE SILICON ATOM SURROUNDED BY FOUR OXYGEN ATOMS [14]

FIG. 3b. CHAIN OF SILICATE GROUPS [14]
FIG. 3d(1) CRISTOBALITE, A HIGH TEMPERATURE FORM OF QUARTZ [14]

FIG. 3d(2) GLASS STRUCTURE. RESEMBLES DISTORTED CRISTOBALITE STRUCTURE [14]
FIG. 3c. SILICATE SHEET FORMED BY LINKED CHAINS. EACH SILICON ATOM IS IN THE CENTRE OF A TETRAHEDRON FORMED BY FOUR OXYGEN ATOMS. NOTE HEXAGONAL PATTERN OF "HOLES" IN THE SHEET [20].
**Fig. 3f(1)** TWO DIMENSIONAL REPRESENTATION OF THE DIFFERENCE BETWEEN A CRYSTAL (1) AND (2) A GLASS [21, 106].

**Fig. 3f(2)** CROSS SECTION THROUGH THE STRUCTURE OF QUARTZ GLASS ACCORDING TO OBERLIES AND DIETZEL [67].

- **●** = SILICON
- **○** = OXYGEN
Relevant data were interpreted using a more or less polymeric overall network. The undercooled melt of such polymeric substances has a high viscosity in the neighbourhood of the glass transition range and therefore nucleation and crystallization rates are very low. This means that the glass forming process is a kinetic problem and therefore depends in principle only on the rate of quenching [8]. But this is not a true interpretation since it shifts the problem from one property to another. The field strength concept is concerned with the binding forces between cations and anions. The screening theory [12] and the theory using the concept of co-ordination [13] consider the relations in and between the polyhedra. Factors like polarization, co-ordination number and, in the case of multi-component glasses, the ratio of network forming to network modifying cations [8] have to be considered.

Tilton (1957) [15] proposed a model of glass based on discrete building blocks, which he called "vitrons". As such the glass is supposed to have a semi-ordered crystalline structure.

To date no satisfactorily consistent model has emerged; broadly speaking, opinion has been divided, focussing on
(a) the extended random network concept with short range order and
(b) the crystallite hypothesis, which holds that glasses are aggregates of extremely small crystals, called crystallites.

Porai-Koshits and Eustropyev (1972) [16] stated in a seminar on the "modern state of the crystallite hypothesis of glass structure":

"The main point of the hypothesis though not always realized by the investigators, was the idea about the inhomogeneity of glass in a broad sense - geometrical, chemical and structural. At present the overwhelming majority of investigators doubt neither the existence of chemical inhomogeneity in many glasses nor the probability of formation of structural units corresponding in composition to some or other chemical compounds" and

also:
"Other methods of studying the structure of substances (electron microscopy, x-ray structural analysis et al.) despite their extensive development in recent years, do not permit, for some reason or other, to reveal the regions of increased ordering in glass. Therefore, like the infrared spectroscopic method, they cannot be used for obtaining quantitative characteristics of these regions."

In a relatively recent international conference [16] on the physics of non-crystalline solids (Sheffield University, September 1970) [17] papers presented on the topic of structure discuss mathematical models and go deeper into existing models of glass structure but nothing emerged decisively for or against the crystallite hypothesis except, maybe, an article by Seward and Uhlman [18] who conducted transmission electron-microscopy of thin sections of vitreous silica and generally discounted the presence of sub-microscopic structure in the bulk of the glass.

For the purpose of the discussions in this thesis an extended random network as proposed by Warren and his school [9, 10, 11] has been adopted.

In the section on volume diffusion a modified version of the extended network model as proposed by Vukcevich [21], has been used. For the interpretation of x-ray diffractograms the "vitron" model of Tilton [15] has been found useful.

Diffusion similar to "dislocation-pipe-diffusion" in crystals has been discussed using a variation of the extended network model as modified by Revesz (1970) [19], who assumed the presence of "channels" in the structure.

The use of different models is a practical necessity simply because of the unsettled nature of the problem of the actual microscopic structure of glass; no model which explains all the characteristic properties of vitreous silica has been constructed. One has to use different models for different sets of properties. In particular, the Vukcevich model, the Tilton "vitron" model and the Revesz "channel"
model are mutually compatible and none of them contradict the extended random network proposed by Warren [9, 10, 11].
SUMMARY OF CHAPTER II.

The purity of the glass used is indicated by the amount of metal impurities present. Factory specifications listed only four metal impurities. Fe, Cu, B and Al, all in the ppm range.

Sample preparation is described with special attention to clouding by the diffusing agent and devitrification by the heating regimen.

A diagram of the counting arrangement is given and the precautions taken to ensure that the data are not affected by systematic errors of the counting equipment or counting procedure.

X-ray and electron microscopy routines both for "ordinary" and "scanning" electron microscopy are briefly described.
CHAPTER II

EXPERIMENTAL PROCEDURES

II.1 Materials Used and Sample Preparations

The SiC glass used was designed for optical use in U.V. spectroscopy and manufactured by the Heraeus Quarzschmelze GMBH, Hanau, Germany and is known under the trade name Homosil.

Homosil has a specific gravity of 2.205 g/cm³. The impurities present in Homosil are as given below:

<table>
<thead>
<tr>
<th>ppm.</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe</td>
<td>&lt; 1</td>
</tr>
<tr>
<td>Cu</td>
<td>&lt; 1</td>
</tr>
<tr>
<td>B</td>
<td>&lt; 0.1</td>
</tr>
<tr>
<td>Al</td>
<td>&lt; 2</td>
</tr>
</tbody>
</table>

The water content amounts to 1200 ppm as reported in [11]. For the purpose of the diffusion of germanium and silver in the glass under investigation (Homosil) the glass was used in the "as received" condition. No preliminary heat treatment was given prior to deposition of the radioactive tracer. The glass specimens were 1 x 1 x 0.8 cm. A sandwich of two such specimens was heated for an appropriate time.

After the diffusion anneal the specimens were cleaned and bottom and sides were removed to a depth of about 3√Dt, (taking the largest D measured in any part of the specimen) to get rid of surface diffusion.

Serial sectioning techniques were then employed. Penetration was computed from the difference in weight of the specimen before and after each removal. Knowing the specific weight and assuming constant area the penetration can be readily computed.
II.2 X-ray Diffraction of Glass Specimens

To check on devitrification, X-ray diffractograms of the glass blocks were made after sectioning or grinding sequences had been finished. Diffractograms so obtained were compared with one taken from a glass specimen which had not undergone heat treatment (Fig. 4c, No.10).

The powdered specimens were mixed with pure silicon to provide a reference point.

Diffractograms obtained were those of specimens annealed at about 900°C, 800°C, 700°C, 600°C, 500°C and 400°C. Also, diffractograms were obtained from cristobalite to show the difference between the x-ray patterns obtained of crystalline and amorphous SiO₂.

The glass was reduced to a fine powder of approximately 350 to 400 mesh by grinding first in a small porcelain mortar and finally an agate mortar.

Smear mounts were made by transferring a small amount of the finely ground glass specimen from the agate mortar onto a standard 1 11/16" x 1" microscope slide adding a drop or two of acetone and smearing the mixture uniformly over the surface of the slide. No binding agent was used.

It has been shown [22] that no "contamination" of diffraction patterns was caused by the use of a glass slide.

Diffraction spectra for each glass specimen were obtained on a standard Siemens diffraction unit (m. 386- x -AB) with counter goniometer, pulse height analyzer (P.H.A.) and strip chart recorder.

Diffractometer parameters for optimum resolution and for scanning time of glass diffraction maxima are given as follows:

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Radiation</td>
<td>Cu Kα</td>
</tr>
<tr>
<td>Beam voltage</td>
<td>40 kV</td>
</tr>
<tr>
<td>Beam current</td>
<td>28 mA</td>
</tr>
<tr>
<td>Detector</td>
<td>scintillation counter</td>
</tr>
</tbody>
</table>
Detector voltage 1000 V
Scan Rate 1°/min.
Time constant 0.4
Divergence slit 1/2°
Attenuation 2x

X-ray diffraction patterns are given in Fig. 4 (c, d, e)

From the X-ray diffractograms conclusions can be drawn about devitrification and possibly about change of network configuration. A separate discussion will be given in Chapter IV.

II.3 Diffusion Coefficient Measurements

The residual activity of the surface after each layer was ground away was measured with a scintillation counter.

$^{71}$Ge was acquired as a GeO$_2$ powder from the Amersham Radiochemical Centre.

GeO$_2$ deposited on the glass surface and heated in the annealing furnace combined with the water present in the air and caused chemical reactions to take place in the glass specimen resulting in clouding, see Fig. 4a.

When the heating took place in vacuum or in an argon atmosphere, no such clouding was observed. In the actual experiment a drop of ammonium hydroxide on the tracer deposit gives rise to the following reaction. Germanium dioxide is known to form complex polymeric germanic acids with H$_2$O. On addition of an alkaline solution such as ammonium hydroxide, depolymerization generally occurs, producing a soluble Ge-species [23]. A deposit so treated does not cause clouding of the specimen.

$^{71}$Ge emits X-rays with an energy of 0.0092 MeV and has no radioactive daughter products. Its half-life is 11 days. Counting was done with a beryllium coated N.681 EKCO thallium
FIG. 4b. COUNTING ARRANGEMENT

1. Counting crystal
2. Lead castle
3. Glass specimen
4. Tray-holder
5. Perspex tray
6. Specimen holder

Note: The position of the specimen was marked on the specimen holder. The specimen holder fitted snugly into a hollow in the perspex tray, (see also Figs. 52, 53 and 54. Appendix IV).
FIG. 4c. (1) AND (2) X-RAY DIFFRACTOGRAMS OF SiO₂ SPECIMENS ANNEALED AT 400°C AND 511°C RESPECTIVELY. (10) X-RAY DIFFRACTOGRAM OF SiO₂ SPECIMEN PRIOR TO ANNEALING.
FIG. 4d. (3, 4, 5 and 6) X-RAY DIFFRACTOGRAMS OF SiO\textsubscript{2} SPECIMENS ANNEALED AT 598°C, 622°C, 722°C AND 800°C.
FIG. 4e. X-RAY DIFFRACTOGRAM OF $\text{SiO}_2$ SPECIMEN ANNEALED AT 924°C (7) OF A MICROSCOPE GLASS SLIDE (8) AND OF CRYSTALLINE CRISTOBALITE (9).
activated sodium iodide crystal of 0.225" thickness and 1.625" diameter. Because of the beryllium window only X-rays are absorbed and counted. A "thin" crystal was used because of the low energy of the emitted radiation. Counting apparatus consisted of a R.I.D.L. single channel analyzer where counting time could be preset.

Electronic drift was periodically checked with a plot of energy vs. threshold for a fixed voltage (1000 V) and window (0.2 mV) using $^{241}$Americium (half-life: 458 years) as a standard. The maximum of $^{71}$Ge (0.0092 MeV) and two maxima of $^{241}$Americium, the 0.033 MeV peak and the 0.060 MeV peak were found to be on a straight line and this has remained so during the whole duration of the experiments (Fig. 5c). The room in which the counting was done was air conditioned, so that temperature fluctuations in the ambient near the electronic equipment were minimized.

A lead castle was used for the specimen to reduce background and a fixed geometry was preserved at all times (see Fig. 4b)

Serial removal of layers was done by grinding on microscope slides with diamond paste. The size of the grains in the diamond paste used varied from nine microns to a quarter micron. Final polish was always done with a quarter micron paste, the finest paste available. After the removal of a layer the microscope slide used as a grinding base was discarded to prevent subsequent contamination of the residual block.

The glass specimen was ultrasonically cleaned using freon as solvent of the oily base of the diamond paste and finally the specimen was weighed with a Mettler analytical balance, accurate to five decimal places.

The above techniques were also used in the diffusion of $^{68}$Ge, $^{110m}$Ag and $^{105}$Ag. $^{68}$Ge has a half-life of 280 days and a shortlived daughter product, $^{68}$Ga (68 min). $^{68}$Ge emits only X-rays with an energy
of 0.0092 MeV (Fig. 5c). $^{110m}$Ag and $^{105}$Ag were purchased from the Amersham Radiochemical Centre and from the New England Nuclear Co. respectively.

$^{105}$Ag has a half-life of 40 days and is a $\gamma$-ray emitter.

For the diffusion of $^{105}$Ag in Homosil the 0.310 MeV peak was used. $^{110m}$Ag has a half-life of 250 days and also emits $\gamma$-rays. For the diffusion of $^{110m}$Ag the 0.656 MeV peak was used. The silver isotopes were counted using a NaI thallium activated sodium iodide crystal 2.280" thick and 2.09" in diameter coated with aluminum.

The temperature was monitored using Pt/(Pt + 10% Rh) thermocouples and continuously recorded on a Leeds and Northrup recorder.

All diffusion annealings were done in cylindrical wire wound furnaces thermostatically controlled within one Celsius degree.

The specimens were put in the furnace in fused silica tubes. For every diffusing species a different tube was used to prevent contamination. Diffusing times ranged from several hours, in the case of silver diffusion, to several months in the case of germanium diffusion.

II.4 The Isotope Effect for Germanium Diffusion in Glass

The method used in the present experiment was that of codeposition of $^{68}$Ge and $^{71}$Ge. The mixture was allowed to diffuse with subsequent serial sectioning and analysis of each section for tracer content [24].

To minimize losses during processing the following grinding technique was evolved. Circular microscopic cover glasses were araldite bonded into corrugated planchets of 1" diameter. (Figs. 55, 56. Appendix IV.)

Before bonding the planchet was slightly punched out to enlarge the volume. Grinding was done in the planchet, with the cover glass as a grinding base (Fig. 5a). After grinding, the glass specimen was carefully washed and ultrasonically cleaned. The washings so collected were decanted in the planchet followed by evaporation under an infrared lamp.
It was felt that in this way losses were minimized. The method of separation was that of half-life separation which in the present case involved two sets of counting data to be gathered separated by six months. The data for both germanium and silver isotope effect experiments were taken at two distances from the surface of the counting crystal, to make sure that the counting rate ratio observed in the isotope effect experiment was not a function of count rate.

The horizontal geometry of the planchets was preserved at all times.

Since the distance moved vertically was only 0.5 cm, air absorption could be disregarded in the case of the 0.0092 MeV X-ray radiation used in the germanium isotope effect experiment, and even more so for the 0.656 MeV γ-radiation in the silver isotope effect experiment.

No change in ratio was observed as a result of vertical displacement of the sample. So that it is clear that isotope effect did not depend on the count rate.

The usual method of checking this consists of counting successive dilutions of the same isotope mixture and in finding out if the apparent ratio of the isotopes does not change with dilution. Our method has the advantage that the samples themselves were used and no dilutions of isotope mixtures were needed as in the usual null-line experiment, and therefore no possible new errors could be introduced because of inaccuracies in preparation of dilutions [25]. Preparing radioactive dilutions can be very awkward, especially if working with small quantities.
FIG. 5. ENERGY SPECTRA OF $^{110\text{m}}\text{Ag}$ AND $^{105}\text{Ag}$ [25].
FIG. 5a. MODIFIED PLANCHET FOR GRINDING AND COUNTING PURPOSES, SEE ALSO FIGS. 55 and 56. APPENDIX IV.
FIG. 5b. COUNT RATE VS PULSE HEIGHT (VOLTS) OF $\text{Ge}^{71}$ ($0.0092$ MeV).
CALIBRATION OF SCINTILLATION COUNTER

FIG. 5c. ENERGY VS PULSE HEIGHT DIAGRAM OF 71 Ge, AND 241 Am.
II.5 The isotope effect for Silver in Glass

In the co-diffusion of $^{105}_{\text{Ag}}$ and $^{110m}_{\text{Ag}}$ the half-lives are too long to allow for a half-life separation. However, their spectra (Fig. 5), show that a separation by energy is feasible if one uses pure $^{105}_{\text{Ag}}$ and $^{110m}_{\text{Ag}}$ standards. $^{105}_{\text{Ag}}$ and $^{110m}_{\text{Ag}}$ are both gamma emitters [25]. Counter drift was checked periodically and showed that the pulse height setting for the peak did not have to be altered at any time.

The samples were counted in random order as a further precaution against drift.

For the energies involved an EKCO N609 thallium activated sodium iodide crystal was used with a thickness of 2.280" and 2.09" diameter. The crystal was aluminium coated.

II.6 Electron Microscopy of an Annealed Specimen

An annealed specimen was given a polish with quarter micron diamond paste for four minutes. It was then given a very light etch with 40% HF acid for thirty seconds. A replica was made of the surface and platinum shadowed. The electron microscope used was a J.E.M. 6.

The photographs so obtained give an idea of the condition of the surface after the sectioning sequence has been concluded.

II.7 Scanning Electron Microscopy of Specimen Surfaces

To find out what the surface of the glass looked like without having undergone polishing or etching, scanning electron microscope pictures were made of surfaces on fractured glass specimens.
In the scanning electron microscope the source is imaged onto the sample by a magnetic lens (see Fig. 6); the small spot of electrons thus formed is deflected by scanning coils to illuminate the sample point by point at sequential times; e.g. $T_1$, $T_2$, $T_3$ in Fig. 6. Secondary electrons generated where the primary beam strikes the sample are drawn to a detector and produce an electrical signal.

This signal modulates the intensity of an electron beam inside a television tube scanned in step with the spot.

The scanning electron microscope is able to provide images of three dimensional objects because in its normal mode of operation it records not the electrons passing through the specimen but the secondary electrons that are released from the sample by the electron beam impinging on it. The sample can therefore be of any size and thickness that will fit in the evacuated sample chamber [26].

Since the specimens themselves are used and not carbon replicas, the objection that some surface structures might be caused by the carbon substrate is not valid in scanning electron micrographs.

Another advantage is that scanning electron micrographs lend themselves particularly well to stereoscopic viewing. On the other hand resolution is not as good as in the ordinary non-scanning electron microscope.

Scanning electron microscopy has therefore always to be done in conjunction with ordinary electron microscopy.

Sample preparation was simple, and consisted only in sputtering a 200 Å thick layer of gold onto the crushed specimen.

Similar features to those on polished and etched glass surfaces were observed.

Fig. 43 shows the fractured surface of vitreous silica used in the present investigation and the discussion of the features seen will be given in the discussion of the "near surface effect" in Chapter IV.
FIG. 6. SCHEMATIC REPRESENTATION OF SCANNING ELECTRON MICROSCOPE ACCORDING TO EVERHART[26].
SUMMARY OF CHAPTER III.

The main content of this chapter is the presentation of the data incorporated in graphs, an analytical discussion for computational purposes and an error discussion.

The graphs show the regions and concentration vs. penetration profiles.

Short theoretical discussions are given for the isotope effect experiment for the purpose of indicating how the data can be treated computationally.

Special attention has been given to the description of the electron micrographs, since subsequent arguments based on the present electron microscopy experiment are qualitative and not quantitative.
CHAPTER III

RESULTS

III.1 The Diffusion of Silver and Germanium in Glass

III.1.1 Graphs of experimental data

Activity vs. penetration plots are given in Figs. 7, 10, 12, 14, 17 and the corresponding $2\text{erfc}^{-1}$ vs. penetration plots in Figs. 9, 11, 13, 16 and 18 respectively. Figs. 8 and 15 are activity vs. penetration plots indicating $C_s$ and $A(o)$ (see III.12) and correspond to Fig. 7 and 14 respectively. Tables I and II give the computed D-values and Figs. 19, 20, 21 and 22 show the Arrhenius plots in region II and region III.

In Figs. 7, 8, 10, 12, 14, 15 and 17 $A(x)$ denotes the residual activity obtained as follows:

$$A(x) = \frac{\text{sample} - \text{background}}{\text{standard} - \text{background}}$$

the sample count rate being taken after thickness $x$ has been removed.

III.1.2 Analytical considerations

For concentration independent diffusion Fick's second states that

$$\frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial x^2}$$

(14)

For a thin layer deposited at the plane $x = 0$ of a medium infinite in the $x$-direction, the boundary conditions are [1]:

$$C \to 0 \text{ at } t \to 0 \text{ for } |x| > 0$$

$$C \to \infty \text{ as } t \to 0 \text{ for } x = 0$$

$$\int_{-\infty}^{\infty} C(x) \, dx = M.$$

The solution of equation (14) is then

$$C = \frac{M}{2\sqrt{\pi}Dt} \exp \frac{-x^2}{4Dt}$$

(15)

where $M$ = amount of impurity initially deposited at the plane $x = 0$.

If the pre-exponential term can be assumed constant for a given annealing time a plot of $\ln C$ vs. $x^2$ will yield a straight line slope $-\frac{1}{4Dt}$.

The right hand side of Equation (15) is symmetrical with respect to $x = 0$ and for $t = 0$ is vanishing everywhere except for $x = 0$, where it becomes infinite.
For a small solubility or if the deposited layer is thick, the above boundary conditions change to

\[ C = C_s \text{ at } x = x_s \text{ for all } t \]
\[ C = 0 \text{ at } t = 0 \text{ for } x > x_s \]

and the solution of equation (14) becomes

\[ C = C_s \text{ erfc} \left(\frac{x - x_s}{2\sqrt{D}t}\right) \quad (16) \]

where \( C_s \) = solubility limit of the chemical phase
\( x_s \) = thickness of the zone of surface phases where the solute concentration is greater than \( C_s \).

This solution can be referred to as the "error function solution" and assumes \( x_s \) to be independent of time. \( x_s \) can generally be neglected.

For a study of impurity diffusion in glass, sectioning techniques can be applied using radioactive tracers.

Since the sections taken off are often very thin it is very difficult to get a concentration vs penetration distance profile because of the difficulty in collecting the material and often because the activity of the tracer is very small so that the count rate is inadequate to produce reliable data. This consideration does not apply to the isotope effect experiments which were done at a high temperature and where also, thicker sections could be taken. Boundary conditions are less critical for an analysis in which the activity remaining in the specimen is measured; also compared to serial sectioning, the problem of contamination in the residual activity method is no worse.

If in the serial sectioning method the first section is not parallel to the original interface and if subsequent sections are parallel to the first section, there will be a systematic error in the slope of the curve used to find \( D \), right through the profile [131]. With the residual activity method the error in the slope of the curve used to find \( D \) is only significant near the first section. The following calculations illustrate this for a situation in which the first section, a thickness of \( 0.2\sqrt{D}t \), was removed from half the specimen cross section and nothing from the rest of the block. Subsequent sections are supposed to to be parallel to the first (see Appendix IV for the calculations involved).
It is often better therefore to measure the activity remaining in the specimen. The profile from these measurements is an integrated profile and for the activity remaining can be written [27]

\[ A(x') = \int_{x'}^{\infty} C(x) \, dx \]  

At \( x' = 0 \) one gets

\[ A(0) = \int_{0}^{\infty} C(x) \, dx \]  

The "fractional activity remaining" \( F(x) \) is given by

\[ F(x') = A(x') / A(0) = \frac{\int_{x'}^{\infty} C(x) \, dx}{\int_{0}^{\infty} C(x) \, dx}. \] (19)

It can be shown that for a high solubility tracer [27]

\[ F(x) = \text{erfc} \left( \frac{x}{2\sqrt{Dt}} \right), \quad \text{where} \quad u = \frac{x}{2\sqrt{Dt}}. \] (20)

For a very small solubility an "error-function solution" to the diffusion is applicable.

Substituting equation (16) into equation (19) one obtains

\[ F(x') = A(x') / A(0) = \frac{\int_{x'}^{\infty} \frac{C_s}{s} \text{erfc} \left[ \frac{x}{2\sqrt{Dt}} \right] \, dx}{\int_{0}^{\infty} \frac{C_s}{s} \text{erfc} \left[ \frac{x}{2\sqrt{Dt}} \right] \, dx}. \] (21)
Standard integral table one gets

\[ F(x') = 1.772 \int_u^\infty \text{erfc} \, (u) \, du \] (22)

using the notation \( \text{ierfc} \, (a) = \int_a^\infty \text{erfc} \, y \, dy \) one can write

\[ F(x) = 1.772 \, \text{ierfc}(u) \] (23)

III.1.3 Application of the analysis to the experiments

Use of an \( \text{ierfc}^{-1} \) type of solution was thought to be appropriate because of the presence of an undissolved layer in the diffusion of both germanium and silver in glass. The same analysis therefore has been used in the diffusion of germanium and that of silver.

For several measurements of \( F(x) \) a graph of \( (2 \, \text{ierfc})^{-1} \left( \frac{F(x)}{.886} \right) \) vs penetration results in a straight line of which the slope is \( \frac{1}{2\sqrt{Dt}} \). From this \( D \) can be calculated with the help of curves like the one shown in Fig. 23, a theoretical plot of \( (2 \, \text{ierfc})^{-1}(u) \). [107]

In both the analyses the absorption of the radiations has been assumed negligible (see appendix I).

An integrated diffusion profile is given in Figs. 7, 8, 10 and 12 for the diffusion of \(^{71}\text{Ge}\) in Homosil and in Figs. 14, 15 and 17 for the diffusion of \(^{110m}\text{Ag}\).

Graphical analysis of the diffusion of Ge and Ag in Homosil is given in Figs. 9, 11, 13, 16 and 18 using the \( 2 \, \text{ierfc}^{-1} \) vs penetration plot to find

\[ D = \frac{1}{4t} \left[ \frac{x}{(2 \, \text{ierfc})^{-1} \left( \frac{F(x)}{.886} \right)} \right] \] (24)
III.2 The Isotope Effect

III.2.1 Theory of the mass effect on diffusion

Diffusion rates are determined in part by mass and there are measurable differences in the diffusion coefficient of two isotopes diffusing in a common matrix when they have different mass [28]. These measurable differences are called "isotope effects". A quite general dependence with which we can define a mass-effect as the ratio of the D's for two isotopes of the same species having masses $m_\alpha$ and $m_\beta$ is

$$\frac{D_\alpha}{D_\beta} = \left[ \frac{M_\beta}{M_\alpha} \right]^{\frac{1}{2}} \left[ \frac{M_\alpha + M_2}{M_\beta + M_2} \right]^{\frac{1}{2}}$$

(25)

where $M_2$ is the molecular mass of the matrix species. Equation (25) has been derived for the diffusion in a gas.

For the diffusion of two isotopes in a solid one obtains [24]

$$\left[ \frac{D_\alpha}{D_\beta} \right]^{-1} = f \left[ \frac{W_\alpha}{W_\beta} \right] - 1$$

(26)

where $f = \text{correlation factor}$;

$W = \text{jump frequency in impurity diffusion}$.

The correlation factor $f$, will be discussed in section IV.2.2. It suffices here to note that for the experimental measurement of $f$, the equation used is [73]:

$$\left[ \frac{D_\alpha}{D_\beta} - 1 \right] = f\Delta k \left[ \frac{M_\beta}{M_\alpha} \right]^{\frac{1}{2}}$$

(27)

where $\Delta k$ is the fraction of the transitional kinetic energy which is possessed by the solute atom at the saddle point.
III.2.2 Experimental measurement of the isotope effect in the co-diffusion of $^{68}\text{Ge}$ and $^{71}\text{Ge}$ in glass

If after diffusion, the sample is serially sectioned and the activities of the two isotopes are determined, at each section one obtains, if (15) applies:

$$C_\alpha = \frac{\text{const}}{\sqrt{D_\alpha t}} \exp \left[-\frac{x^2}{4D_\alpha t}\right]$$

$$C_\beta = \frac{\text{const}}{\sqrt{D_\beta t}} \exp \left[-\frac{x^2}{4D_\beta t}\right]$$

For the discrimination of the two tracers present to be possible their half-lives or the types of energies of the radiation they emit must be sufficiently different.

$^{71}\text{Ge}$ has a half-life of 11 days and $^{68}\text{Ge}$ has a half-life of 280 days so that the half-life difference will distinguish one from the other. The isotope ratio was calculated from two counts taken six months apart (see also appendix IV).

From equation (28) it is easily found, since the times $t$ of annealing are identical, that

$$\ln \left[ \frac{C_\alpha}{C_\beta} \right] = 1 - \left[ \frac{D_\alpha}{D_\beta} \right] \ln C_\alpha + \text{const}$$

(29)

Thus a plot of $\ln \left[ \frac{C_\alpha}{C_\beta} \right]$ vs $\ln C_\alpha$

gives a line of slope $\left[ \frac{D_\alpha}{D_\beta} \right] - 1$.

If (16), instead of (15) applies, (29) will still be approximately correct at large $x$ (Appendix III). (27) then gives $fAk$. Fig. 24 shows a plot of
\[
\frac{\ln C_{68_{\text{Ge}}}}{\ln C_{71_{\text{Ge}}}} \text{ vs } \ln C_{68_{\text{Ge}}}
\]

which gives a slope of -0.0129 by a least squares method of computation.

III.2.3 The experimental measurement of the isotope effect in the co-diffusion of $^{105}\text{Ag}$ and $^{110}\text{mAg}$ in glass

The separation of isotopes in the case of the co-deposition of $^{105}\text{Ag}$ and $^{110}\text{mAg}$ on the basis of half-life is impractical since $^{105}\text{Ag}$ has a 40.9 days half-life and $^{110}\text{mAg}$ has a 253 days half-life.

However, as their spectra show, a separation by energy is more feasible. See Fig. 5 (Chapter II).

In the present experiment the discriminator of the counter was set at two lower levels as shown in Fig. 5.

Let

\[
A = \frac{\text{counts/min in channel 2}}{\text{counts/min in channel 1}} \text{ for pure } ^{110}\text{mAg} \quad (30)
\]

and

\[
B = \frac{\text{counts/min in channel 2}}{\text{counts/min in channel 1}} \text{ for pure } ^{105}\text{Ag} \quad (31)
\]

all counts being corrected for background.

For a sample containing $X$ counts/min of $^{110}\text{mAg}$ and $Y$ counts/min of $^{105}\text{Ag}$ in channel 1 one gets

\[
X + Y = \text{Counts per min in channel 1} \quad (32)
\]

and

\[
AX + BY = \text{Counts per min in channel 2}. \quad (33)
\]

The counts in each channel are the total count above the lower level. Thus knowing $A$ and $B$ from measurements on pure $^{110}\text{mAg}$ and $^{105}\text{Ag}$ the quantity $\frac{X}{Y}$ can be determined. This quantity is proportional to
the isotopic ration and with a proper procedure of collecting and counting the sections, the constant of proportionality will be the same for all the sections. A decay correction is made to adjust all ratios to the same time.

To make sure that the isotope effect observed was not due to a systematic error in the counting set up, the sections were counted in random order.

The number of counts taken in the present experiment was of the order of $10^5$ in both channels.

Following the same reasoning as that given previously in the evaluation of the experimental results of the germanium isotope experiment the results of the silver isotope experiments are plotted as

$$\frac{\ln C_{105^{\text{Ag}}}}{\ln C_{110^{\text{mAg}}}}$$

vs $\ln C_{105^{\text{Ag}}}$ (Fig. 25) and the slope determined by the least squares method, is -0.0128.

Only sections for large $x$ were used to determine the isotope effect. The basic reason for this is that at large penetrations the shapes of the Gaussian and error function profiles are very similar. A more elaborate justification is given in Appendix III (see also Mortlock 1969 [29]).

A comparison between diffusion coefficients obtained by sectioning techniques (from the isotope effect data) and diffusion coefficients obtained by residual activity was not made since in principle residual activity and sectioning techniques are very similar; in effect they practically use the same set of data. It is not as if sectioning and autoradiography techniques had been used.
III.3 Electron Microscopy of Specimen Surfaces (see Figs. 26, 27, 28, 29, 30, 31 and 32).

Description of Surface Features of Residual Blocks

Fig. 26 Electron-micrograph of glass specimen annealed at 400°C and cooled down to room temperature. The most conspicuous feature of the surface is its corrugated appearance due to what could best be described as "staircases" or "slabs" sticking out of the matrix. This micrograph was taken at a 5000X magnification.

Fig. 32 Gives a more detailed picture of the typical "staircase" in Fig. 26. Magnification was 10,000X.

Fig. 27 Electron-micrograph of glass specimen annealed at 600°C and cooled down to room temperature. The most characteristic feature here is the triangular sub-structure very clearly visible in the right-hand corner. The "ruggedness" of the whole surface is markedly less than that at 400°C.

Fig. 28 Electron-micrograph of glass specimen annealed at 900°C and cooled down to room temperature. The surface is very smooth compared to the surfaces of the specimens annealed at 400°C and 600°C. One can definitely say that for higher temperatures, cracks or interfacial boundaries (see Fig. 28) tend to disappear leaving a more and more smooth surface.

Figs. 29, 30 and 31 are electron-micrographs of the same specimen shown in Figs. 26, 27 and 28. Magnification is 30,000X and shows a "granulation" which becomes smoother at higher temperatures. One can see a finer grain structure and a gradual disappearance of surface features.
III.4 Error considerations*

III.4.1 Experimental uncertainty

The two main sources of uncertainty are:

(i) uncertainty in annealing temperature;

(ii) uncertainty in the diffusion coefficient resulting from the limited number of counts taken.

(i) Uncertainty in annealing temperature arise from the uncertainty in the calibration of the thermocouple (less than ± 3°C), from the variation in furnace temperature readings (less than ± 2°C) and from the uncertainty of the temperature gradients in the furnace (less than 1°C). (See also Appendix IV.)

The extreme error limits are therefore ± 6°C.

The error in the diffusion coefficient associated with this temperature error is ± 7% for Ge in the high temperature region and ± 7% in the low temperature region. The corresponding values for Ag are ± 15% for the high temperature region and ± 7% for the low temperature region.

(ii) For germanium diffusion the uncertainties in the measured diffusion coefficients are:

± 10% - 50% in region II

and

± 10% - 40% in region III.

For silver diffusion

± 20% - 50% in region II

and

± 10% - 30% in region III.

The error limits were calculated from the upper and lower

* See also Appendix IV for detailed discussion.
bounds of the slopes of lines which would pass through all the error limits of the experimental points in the $2\text{ierfc}^{-1}$ vs $x$ plots.

### III.4.2 The uncertainties in the isotope effect experiment

The uncertainty calculated from the standard errors of the least squares fit of $\log e \frac{C_\alpha}{C_\beta}$ vs $\log e C_\alpha$ was, for germanium ± 30% and for silver ± 30%. 

<table>
<thead>
<tr>
<th>Temp</th>
<th>D$_{68\text{Ge}}$(cm$^2$/sec)</th>
<th>D$_{71\text{Ge}}$(cm$^2$/sec)</th>
</tr>
</thead>
<tbody>
<tr>
<td>956°C</td>
<td>$3.68 \times 10^{-13}$</td>
<td>$3.68 \times 10^{-13}$</td>
</tr>
<tr>
<td>900°C</td>
<td>$1.46 \times 10^{-13}$</td>
<td>$2.04 \times 10^{-13}$</td>
</tr>
<tr>
<td>825°C</td>
<td>$2.85 \times 10^{-13}$</td>
<td>$5.85 \times 10^{-14}$</td>
</tr>
<tr>
<td>800°C</td>
<td>$5.04 \times 10^{-14}$</td>
<td>$8.08 \times 10^{-14}$</td>
</tr>
<tr>
<td>711°C</td>
<td>$3.10 \times 10^{-14}$</td>
<td>$5.57 \times 10^{-14}$</td>
</tr>
<tr>
<td>708°C</td>
<td>$5.04 \times 10^{-14}$</td>
<td>$4.25 \times 10^{-14}$</td>
</tr>
<tr>
<td>642°C</td>
<td>$8.70 \times 10^{-14}$</td>
<td>$6.85 \times 10^{-14}$</td>
</tr>
<tr>
<td>619°C</td>
<td>$9.84 \times 10^{-14}$</td>
<td>$8.75 \times 10^{-14}$</td>
</tr>
<tr>
<td>545°C</td>
<td>$2.35 \times 10^{-13}$</td>
<td>$1.01 \times 10^{-12}$</td>
</tr>
<tr>
<td>511°C</td>
<td>$3.10 \times 10^{-14}$</td>
<td>$1.46 \times 10^{-13}$</td>
</tr>
<tr>
<td>419°C</td>
<td>$5.11 \times 10^{-14}$</td>
<td>$2.04 \times 10^{-13}$</td>
</tr>
<tr>
<td>413°C</td>
<td>$3.27 \times 10^{-14}$</td>
<td>$7.22 \times 10^{-14}$</td>
</tr>
</tbody>
</table>

**TABLE I**

**DIFFUSION OF GERMANIUM IN GLASS IN THE TEMPERATURE RANGE 956°C - 413°C**
<table>
<thead>
<tr>
<th>Temp</th>
<th>Region II</th>
<th>Region III</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$D_{110mAg}$</td>
<td>$D_{105Ag}$</td>
</tr>
<tr>
<td>948°C</td>
<td>$7.30 \times 10^{-6}$</td>
<td>$5.90 \times 10^{-6}$</td>
</tr>
<tr>
<td>912°C</td>
<td>$5.32 \times 10^{-6}$</td>
<td>$7.98 \times 10^{-6}$</td>
</tr>
<tr>
<td>755°C</td>
<td>$5.31 \times 10^{-7}$</td>
<td>$4.54 \times 10^{-5}$</td>
</tr>
<tr>
<td>722°C</td>
<td>$2.86 \times 10^{-7}$</td>
<td>$7.37 \times 10^{-5}$</td>
</tr>
<tr>
<td>622°C</td>
<td>$2.15 \times 10^{-8}$</td>
<td>$4.19 \times 10^{-4}$</td>
</tr>
<tr>
<td>598°C</td>
<td>$3.47 \times 10^{-8}$</td>
<td>$5.10 \times 10^{-4}$</td>
</tr>
<tr>
<td>511°C</td>
<td>$8.70 \times 10^{-9}$</td>
<td>$1.53 \times 10^{-3}$</td>
</tr>
<tr>
<td>482°C</td>
<td>$6.45 \times 10^{-9}$</td>
<td>$1.81 \times 10^{-3}$</td>
</tr>
<tr>
<td>441°C</td>
<td>$4.34 \times 10^{-9}$</td>
<td>$2.80 \times 10^{-3}$</td>
</tr>
<tr>
<td>441°C</td>
<td>$4.40 \times 10^{-9}$</td>
<td>$2.86 \times 10^{-3}$</td>
</tr>
</tbody>
</table>

**TABLE II**

DIFFUSION OF SILVER IN GLASS IN THE TEMPERATURE RANGE 948°C - 441°C
FIG. 7. INTEGRATED DIFFUSION PROFILE FOR THE DIFFUSION OF $^{71}$Ge IN GLASS (HOMOSIL) AT 900°C.
FIG. 8. INTEGRATED DIFFUSION PROFILE FOR $^{71}$Ge IN HOMOSIL AT 900°C (NOT DIFFERENT FROM FIG. 7) INDICATING $C_s$ AND $A(0)$. 

REGION I

REGION II

REGION III

PENETRATION ($\mu$m)

$A(x)$ (arbitrary units)

$A(0)$

$C_s$
\[ 2 \text{IERFC}^{-1} \times 10^{-2} \]

**FIG. 9.** 2ierfc\(^{-1}\) VS \(X\) PROFILE FOR THE DIFFUSION OF \(^{71}\text{Ge}\) IN HOMOSIL AT 900\(^{\circ}\)C CORRESPONDING TO FIG. 8.
FIG. 10. INTEGRATED DIFFUSION PROFILE FOR $^{71}\text{Ge}$ IN HOMOSIL AT 711°C.
FIG. 11. $2\text{ierfc}^{-1} \times 10^{-3}$ VS PENETRATION (micron) for the diffusion of $^{71}\text{Ge}$ in HOMOSIL at 711°C corresponding to integrated diffusion profile in Fig. 10.
FIG. 12. INTEGRATED DIFFUSION PROFILE FOR THE DIFFUSION OF $^{71}$Ge IN GLASS (HOMOSIL) AT 413°C.
FIG. 13. $2\text{ierfc}^{-1}$ VS $X$ PROFILE FOR THE DIFFUSION OF $^{71}\text{Ge}$ IN HOMOSIL AT 413°C CORRESPONDING TO DIFFUSION PROFILE IN FIG. 12.
FIG. 14. INTEGRATED DIFFUSION PROFILE OF 110°, Ag DIFFUSION IN GLASS (HOMOSIL) AT 948°C.
FIG. 15. INTEGRATED DIFFUSION PROFILE FOR $^{110m}_{\text{Ag}}$ IN HOMOSIL AT 948°C (NOT DIFFERENT FROM FIG. 14) INDICATING $C_s$ AND $A(0)$. 
FIG. 16. $\text{2ierfc}^{-1}$ VS. $x$ PROFILE FOR THE DIFFUSION OF Ag IN HOMOSIL AT 948°C CORRESPONDING TO INTEGRATED DIFFUSION PROFILE IN FIG. 14.
FIG. 17. INTEGRATED DIFFUSION PROFILE FOR THE DIFFUSION OF $^{110m}_{\text{Ag}}$ IN GLASS (HOMOSIL) AT 441°C.
FIG. 18. $2\text{erfc}^{-1}$ VS X PROFILE FOR THE DIFFUSION OF Ag IN HOMOSIL AT 441°C CORRESPONDING TO INTEGRATED DIFFUSION PROFILE IN FIG. 17.
FIG. 19. LOG D VS $\frac{1}{T}$ PLOT OF Ge-DIFFUSION IN GLASS (HOMOSIL) FOR REGION II.
FIG. 20. LOG D VS $\frac{1}{T}$ PLOT OF Ge-DIFFUSION IN GLASS (HOMOSIL) FOR REGION III.
FIG. 21. LOG D VS $\frac{1}{T}$ PLOT OF Ag-DIFFUSION IN GLASS (HOMOSIL)
FIG. 22. LOG D VS $\frac{1}{T}$ PLOT OF Ag-DIFFUSION IN GLASS (HOMOSIL) IN REGION III.
FIG. 23. THEORETICAL PLOT OF $2\text{erfc}^{-1}(u)$ VS $u$. 
FIG. 24. PLOT OF $\ln \frac{C_{68}}{C_{71}}$ vs $\ln C_{68}$ AND ZERO ISOTOPE EFFECT LINE WITH DATA FITTED BY LEAST-SQUARES LINES. THE ISOTOPES USED WERE Ge$_{71}$ AND Ge$_{68}$.  

**ISOTOPE EFFECT LINE**
SLOPE = -0.0129

**ZERO ISOTOPE EFFECT LINE**
SLOPE = -0.0007
FIG. 25. PLOT OF $\ln \frac{c_{105}}{c_{110m}}$ vs $\ln c_{105}$ AND ZERO ISOTOPE EFFECT LINE WITH DATA FITTED BY LEAST-SQUARES LINES. THE ISOTOPES USED WERE Ag$_{105}$ AND Ag$_{110m}$. 
FIG. 26. ELECTRON MICROGRAPH OF GLASS SURFACE AFTER ANNEALING AT 400°C AND COOLING DOWN TO ROOM TEMPERATURE

MAGN. 5000X
FIG. 27. ELECTRON-MICROGRAPH OF GLASS SURFACE AFTER ANNEALING AT 600°C AND COOLING DOWN TO ROOM TEMPERATURE.

MAGN. 5000X
FIG. 28. ELECTRON-MICROGRAPH OF GLASS SURFACE AFTER ANNEALING AT 900°C AND COOLING DOWN TO ROOM TEMPERATURE

MAGN. 5000X
FIG. 29. ELECTRON-MICROGRAPH PICTURE OF GLASS SURFACE AFTER 400°C ANNEALING AND COOLING DOWN TO ROOM TEMPERATURE. Magn. 30,000X.
FIG. 30. ELECTRON-MICROGRAPH OF GLASS SURFACE AFTER 600°C ANNEALING AND COOLING DOWN TO ROOM TEMPERATURE. Magn. 30,000X.
FIG. 31. ELECTRON-MICROGRAPH PICTURE OF GLASS SURFACE AFTER 900°C ANNEALING AND COOLING DOWN TO ROOM TEMPERATURE. Magn. 30,000X.
FIG. 32. ELECTRON-MICROGRAPH PICTURE OF GLASS SURFACE AFTER 400°C ANNEALING AND COOLING DOWN TO ROOM TEMPERATURE. Magn. 10.000X.
SUMMARY OF CHAPTER IV.

(I) Diffusion behaviour and Q variation

Discussion of the diffusion of silver and germanium is done on the following lines:

(a) each diffusing species has its diffusion behaviour compared below and above the transition region. For example, the diffusion of Ge in the low temperature region is compared with its diffusion behaviour in the high temperature region.

(b) the two diffusing species (Ge and Ag) are compared to each other, both below and above the transition region.

In both procedures (a and b) comparisons are made with:

(1) other diffusing species in the same kind of glass as used in the present investigation (e.g. sodium diffusing in vitreous silica);

(2) other diffusing species in glasses of different composition (e.g. sodium diffusing in sodium silicate glass).

Throughout, the main consideration is the effect of charge and size of a diffusing species in a matrix which has not only a random order but has also a structure dependent on its thermal history.

(II) The isotope experiment

The isotope experiment is discussed with the aid of a perfect crystal lattice. It is realized that this is an idealization justifiable only to approximate jump distances, number of nearest neighbours etc. and to visualize diffusion paths. The computed correlation factor is discussed with its bearing on the diffusion mechanisms likely to be operating.

(III) The "near-surface" region

Anomalous behaviour in the "near-surface" region is discussed and a surface contamination is thought to be the most likely explanation.
(IV) **Diffusion in region III**

Diffusion of silver and germanium in the third region, which showed an increase of diffusivity with a decrease in temperature is tentatively explained on the basis of "channel" diffusion akin to "dislocation-pipe-diffusion" in crystalline solids. It is surmised that the number or extent of the "channels" becomes progressively less with higher temperature.

(V) **Electron microscopy and X-ray analysis**

Results of electron microscopy and X-ray analysis are searched for clues regarding change of structure with change in temperature. While not contradicting the present reasoning, the results are not overly convincing.
CHAPTER IV.

DISCUSSION

IV.1  The Diffusion of Germanium and Silver in Region II.

IV.1.1  Our observations on the change in $Q$ at 570°C

Plots of $\log D$ vs $\frac{1}{T}$ are given in Fig. 19 and Fig. 21. Tables I and II list the diffusion coefficients at the different temperatures for the diffusion of germanium and silver respectively.

Neither the $\log D$ vs. $1/T$ plot of germanium (Fig. 19) nor that of silver (Fig. 21) can be fitted by a single straight line. To obtain in either case a fit within experimental error, one must fit the points in the high temperature region (614°C - 956°C for Ge, 598°C - 948°C for Ag) by one line, the points for lower temperatures by another line.

The change from the low temperature to the high temperature line occurs in what we call the transition region, which is near 570°C.

To understand the behaviour of the diffusing atoms in the high and low temperature region and in the transition region it may be worthwhile to remember that the structure of glass is very much dependent on its thermal history and it might well be that the change or variation in the rate of diffusion in the different temperature regions and in the transition regions can be correlated with the change of glass structure as a result of thermal treatment during diffusion (see also Frischat (1970) [31]).

IV.1.2  Frischat's observations on the change in $Q$ at 570°C

Before proceeding with the discussion of a model of the glass structure which can be used to account for the diffusion behaviour
observed, we will first discuss the work of Frischat [30, 32], who used almost the same kind of vitreous silica as used in the present investigation.

Frischat used $^{22}\text{Na}$ in tracer diffusion in the temperature range from 170° to 1000°C. The glass used was a commercial SiO$_2$ glass from the Heraeus-Schott factory, Hanau, Germany, with the trade name Infrasil which differs from the glass under investigation (Homosil) obtained from the same source, only in homogeneity.

A break in the Arrhenius plot was reported at about 570°C. The change in activation energy at about 570°C has been well established for sodium diffusion in several other SiO$_2$ glasses of almost the same composition (glasses under the trade names Infrasil, Homosil, Herasil and Ultrasil, all from the same source) and is independent of the H$_2$O content, of melt-residues and of the thermal history of manufacture [30, 32, 33, 53].

The transition from one region to the other was considered to be due to a phase transformation. Frischat points out that at about 570°C in quartz an α-β transition takes place.

However the trend of increase and decrease of the activation energy in Frischat's work on the diffusion of sodium in SiO$_2$ glass [32] and of the increase and decrease of the activation energy in the present investigation is dissimilar.

In Frischat's sodium diffusion the activation energy above the transition region was lower than the activation energy below the transition region. The opposite is the case in germanium and silver diffusion (see Table III).

The question arises whether the dissimilarity in trend of the variation of Q for sodium diffusion on the one hand and germanium and silver on the other was due to the different glasses used. From Frischat's
<table>
<thead>
<tr>
<th>Diffusing species</th>
<th>Matrix</th>
<th>Charge</th>
<th>Ionic Radius</th>
<th>$Q$ above transition region (eV)</th>
<th>$Q$ below transition region (eV)</th>
<th>$D_0$ cm$^2$/sec above transition region</th>
<th>$D_0$ cm$^2$/sec below transition region</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ge</td>
<td>Homosil</td>
<td>++++</td>
<td>0.53 Å</td>
<td>0.70</td>
<td>0.21</td>
<td>8.2. $10^{-10}$</td>
<td>1.1 $10^{-12}$</td>
<td>Present thesis</td>
</tr>
<tr>
<td>Ag</td>
<td>Homosil</td>
<td>+</td>
<td>1.26 Å</td>
<td>1.51</td>
<td>0.48</td>
<td>6.8. $10^{-2}$</td>
<td>1.0 $10^{-5}$</td>
<td>Present thesis</td>
</tr>
<tr>
<td>Na</td>
<td>Infrasil</td>
<td>+</td>
<td>0.94 Å</td>
<td>0.91</td>
<td>1.12</td>
<td>3.44 $10^{-2}$</td>
<td>0.398</td>
<td>[32]</td>
</tr>
<tr>
<td>Na</td>
<td>Quartz</td>
<td>+</td>
<td>0.94 Å</td>
<td>0.50</td>
<td>0.87</td>
<td>7.09. $10^{-3}$</td>
<td>0.68</td>
<td>[38]</td>
</tr>
</tbody>
</table>

**TABLE III**

Diffusion of Ge and Ag in Homosil and of Na in Infrasil and Quartz.
work on sodium diffusion in Infrasil, Herasil, Homosil and Ultrasil, which all show the same trend of variation of Q with temperature, we conclude that the dissimilarity of Q variation of sodium diffusion in Infrasil in Frischat's case and the silver diffusion in Homosil in the present thesis cannot be ascribed to the difference between Infrasil and Homosil [34].

IV.1.3 Changes of other glass properties at 570°C and explanations of the changes

The change in activation energy in going through the transition point at 573°C is explained by Frischat on the basis of structural changes taking place in the glass during heating. Frischat's assumption of a sharp transition at 573°C is not required by his explanation and is an unlikely one. In quartz the transition does not take place at exactly 573°C [45] and in cristobalite the displacive transformation is gradual and extends over a 40°C range [46]. Frischat's Arrhenius plot for sodium diffusion in SiO$_2$ glass does not suggest a sharp change in activation energy [30, 31]; in glass, with its random structure, a sharp change is not expected anyway. It is more accurate to speak of a transition region.

In glass, with its random structure, a sharp change is not to be expected anyway, and it is therefore more accurate to speak of a transition region.

Experiments in vitreous silica supporting Frischat's explanation are observation of anomalies in dielectric relaxation (Owen and Douglas [35]) micro hardness measurements by Westbrook [36], and measurements of properties of tridymite, cristobalite and quartz glass when subjected to acoustical vibrations (Deeg, [37]).

Experiments questioning Frischat's supposition of structural ("phase") changes were those of Oberlies [7], who studied glass structure with the electron microscope.
In more detail the experiments for and against Frischat's contention are as follows:

1. Anomalies in dielectric relaxation in SiO$_2$ glass at about 570°C were reported by Owen and Douglas [35] and this was mentioned by Frischat [30, 32] in support of the existence of a structural transformation.

2. Micro hardness of natural and synthetic glasses was tested by Westbrook [36] and sharp changes at 570°C were observed in hardness vs temperature plots for both natural and synthetic glass, thus supporting the idea of a phase change taking place in glass at about 570°C. Frischat quotes Westbrook's experiments, presumably to imply that structural changes required by a high-low inversion in the crystal (quartz for example) might have their close analogues in glass and hence are reflected in the diffusion-temperature behaviour as they are in the hardness-temperature behaviour in Westbrook's experiments.

It is therefore likely, according to Frischat that the changes are true structural changes which he attributes to quartz-like, pre-crystalline elements, present in the glass.

3. Mechanical properties of tridymite, cristobalite and quartz glasses, showed maxima of damping and bending vibrations at 570°C (Deeg, [37]).

4. Oberlies [100], using the electron microscope, studied the surfaces of the (fractured) specimens used by Deeg [37] and suggested that the transition at 570°C as reported by Deeg was not due to phase transformation but caused by melt-residues (quartz-like inclusions) going into new formations as seen from the varying degrees of devitrification (Oberlies, [77]).
Frischat [32] argued, however, that the transition effect could not be explained entirely by melting residues because then no change in activation energy should occur. In Frischat's experiment the difference in activation energy for the regions below and above the transition temperature is 0.20 eV. The difference of the D-values corresponds to a factor of 1.4 [32], and he concluded that the transformations represent true changes in the glass structure.

Sodium diffusion in natural quartz crystals have been measured both parallel and perpendicular to the c-axis and exhibited a transition at 573°C (Frischat, 1970) [38].

The change in the crystal structure from a lower to a higher symmetry resulted in a decrease of activation energy for diffusion from 0.88 eV to 0.50 eV [38]. Comparing the results of the sodium diffusion experiments in quartz and glass, the similar behaviour with a transition region for both glass and quartz around 570°C make it not unreasonable to assume that, in the words of Westbrook [36]:

"the glass has carried over some sort of memory or structural vestige, reminiscent of the original crystal structure".

In the present investigation the diffusion of germanium and silver in glass exhibits a decrease in activation energy going from a higher to a lower temperature region. As far as having two straight-line regions and a transition region at about 570°C is concerned, the present work resembles Frischat's.

IV.1.4 The Vukcevich model of the vitreous silica network

From the examples above it is seen that a rather abrupt change in the properties of silica glass, which occurs at about 570°C, is not confined to our results but is quite general and so any explanation should be based on the general properties of silica glass. An
explanation of diffusion behaviour based on changes in the structure of silica glass with temperature may be given in terms of a new model of silica glass proposed by Vukcevich (1971, [39]). We will first discuss his model with his justification for introducing it and then apply it to our results.

Vukcevich adopts a silicon-oxygen tetrahedron as the common structural unit in both crystalline and vitreous silicates [40]. In pure silica phases each tetrahedron is linked to four neighbouring tetrahedra by oxygen atoms which are called bridging oxygen atoms. Shape and size of tetrahedra appear not to be sensitive to the structure of a solid nor to the method of preparation.

In tetrahedrally co-ordinated silica, crystals and in glass, whether well annealed, quenched, densified or neutron irradiated [41] [11], the average (SiO) distance is always 1.61 ± 0.01 Å.

The structure of vitreous silica therefore differs from its many crystalline forms only in the way the tetrahedra are randomly oriented. This means that instead of being characterized by one Si-O-Si angle (see Fig. 32a) (defined as the oxygen-angle) silica glass is characterized by a broad distribution of Si-O-Si angles.

As an introduction to his proposed new model Vukcevich [39] reviews theoretical and experimental aspects of the anomalous behaviour of vitreous silica as reported by the different workers in the field. The term anomalous here refers to comparison with the behaviour in crystalline silica.

Cases considered are the following:

1. the increase of compressibility of silica glass with increasing pressure;

2. the increase of Young's modulus and of the shear modulus, with temperature;
FIG. 32a. CHANGE IN NETWORK CONFIGURATION WITH CHANGE IN Si-O-Si ANGLE. [39]
(3) the negative thermal expansion of vitreous silica between the absolute zero and room temperature;
(4) the large acoustic loss observed at low temperatures;
(5) the large dielectric loss;
(6) the excess specific heat and negative thermal expansion at low temperatures of vitreous silica.

Vukcevich [39] after examination of the explanations put forward for the anomalous cases listed above observed that the two elements common to all explanations were:

(1) bending of oxygen angles is not only possible but is responsible for anomalous behaviour, for example in the case of acoustic loss, compressibility and thermal properties
(2) at least locally, metastable structures can occur in vitreous silica. These will differ from the stable structure in oxygen-angle, length of Si-O bond [42] or in the configuration of the subgroups present.

Vukcevich [39] continues by drawing attention to the following:

Quartz, cristobalite and tridymite undergo a displacive $\alpha \rightarrow \beta$ transformation during heating or cooling. In all three cases the low temperature phase ($\alpha$) has a higher density than the high temperature phase ($\beta$).

Vukcevich suggests, on the basis of experimental data that the density change could be due mainly to the change in the oxygen angle during the displacive transformation and that this type of transformation cannot be explained in terms of central ionic forces commonly used to interpret physical and chemical properties of ceramic materials [43]. According to the central interatomic force model (see
Fig. 33), the cohesive energy of a crystal depends only on the distance between the atoms or molecules and has a single minimum at the equilibrium separation; \( r_0 \) in Fig. 33.

The cohesive energy of quartz, for example, can in the first approximation be regarded as a function of Si-O bond length \( (r_0) \) and Si-O-Si angle \( \phi \), with two related minima. The \( r_0 \) and \( \phi \)-values for one minimum are those of the \( \alpha \)-phase and so will be denoted by \( (r_{0\alpha}, \phi_{\alpha}) \). The \( r_0 \) and \( \phi \) values for the other minimum are those of the \( \beta \)-phase, denoted by \( (r_{0\beta}, \phi_{\beta}) \) (Fig. 34).

At low temperatures the \( (r_{0\alpha}, \phi_{\alpha}) \) minimum gives a lower cohesive energy and so we have here the corresponding equilibrium phase \( \alpha \). At high temperatures the \( (r_{0\beta}, \phi_{\beta}) \) minimum gives the lower potential energy, which corresponds to the \( \beta \)-equilibrium phase. The cohesive energy curves of tridymite and cristobalite will be different but are assumed, by Vukcevich, to have two minima also. This kind of model is distinct from central force models in which to a first approximation the cohesive energy will depend only on \( r_0 \); in that case we have only one relative minimum (Fig. 33).

From X-ray data of most silica modifications \([39,41,44]\) it is seen that the silicon-oxygen distance does not change significantly during a \( \alpha \rightarrow \beta \) transformation.

Furthermore, in the vitreous state it seems that the size of the \( \text{SiO}_4 \) tetrahedra is relatively insensitive to temperature. Similarly the densification of vitreous silica does not change the size or shape of the \( \text{SiO}_4 \) tetrahedra \([41]\). We have therefore in Fig. 34, \( r_{0\alpha} = r_{0\beta} \) and the main reason for volume changes in various silica modifications presumably will be the change in the oxygen angle \( \phi \) (Fig. 35).

The free energy function should be of the same form as the potential energy, except that the entropy term will modify the relative positions of the two minima (Fig. 36) \([39]\).
FIG. 33. CENTRAL FORCE POTENTIAL (h) AS A FUNCTION OF THE INTERATOMIC DISTANCE (r); $r_o = \text{EQUILIBRIUM INTERATOMIC DISTANCE [39].}$

FIG. 34. ISO-POTENTIAL LINES IN BOND ANGLE ($\phi$) VS INTERATOMIC DISTANCE (r) PLOT. TWO MINIMA SHOWN AT $\phi_o^\alpha, r_o^\alpha$ AND AT $\phi_o^\beta, r_o^\beta$; $r = \text{Si-O DISTANCE}; r_o^\alpha = \text{EQUILIBRIUM DISTANCE FOR } \alpha\text{-CONFIGURATION}; r_o^\beta = \text{EQUILIBRIUM DISTANCE FOR } \beta\text{-CONFIGURATION [39].}$
FIG. 35. SIMPLIFIED POTENTIAL (h) DIAGRAM DERIVED FROM FIG. 34 APPLICABLE WHEN $r_\alpha^0 = r_\beta^0$. $\phi_\alpha^0$ and $\phi_\beta^0$ are Si-O-Si EQUILIBRIUM BOND ANGLES [39].

FIG. 36. RELATIVE POSITIONS OF MINIMA IN FREE ENERGY (f) VS BOND ANGLE (\(\phi\)) PLOTS. $T_{\alpha\beta}$ = TRANSITION TEMPERATURE BETWEEN THE TWO "PHASES" [39].
IV.5 Application of the Vukcevich model to experimental results in vitreous silica

If the Vukcevich model is to be accepted, then the predictions must agree with experiment. One striking prediction which would not be predicted by other types of models, is that the $\alpha$-$\beta$ transformation is of the second order i.e. the $\alpha \neq \beta$ transformation is not sharp at one well defined temperature but gradual. Upon heating the $\alpha$-phase some of the SiO$_4$ tetrahedra will acquire enough thermal energy to "jump" over the barrier separating $\alpha$ and $\beta$-states before the main transformation takes place. This is in agreement with the current interpretation of the $\alpha$-$\beta$ transition in quartz [45].

Also the transformation in cristobalite is known to be gradual and extended over a region of about 40°C [46]. Our faith in the model is hereby justified.

In terms of the proposed angular potential the vitreous state of silica can be interpreted as an essentially random network of SiO$_4$ tetrahedra in which the oxygen angles have a definite preference for the two characteristic values $\phi^o_{\alpha}$ and $\phi^o_{\beta}$. At any given temperature and pressure a certain fraction of oxygen angles will have values scattered around the $\alpha$-minimum with a corresponding fraction scattered around the $\beta$-minimum. If the values of the two characteristic oxygen angles are within 5° to 10° of each other, the distribution of oxygen angles will have a broad peak of the type actually observed (Fig. 36a [101]).

We shall now apply the Vukcevich model to glass in order to see how the structure changes with temperature.

All three forms of crystalline silica, quartz, tridymite and cristobalite exist in the $\alpha$-phase at low temperatures and predominantly in the $\beta$-phase at high temperatures, for example at 570°C. The $\alpha$-phase has a smaller Si-O-Si angle and is of higher density.
FIG. 36a. DISTRIBUTION OF OXYGEN ANGLES ($\phi$) IN VITREOUS SILICA AT ROOM TEMPERATURE [101].
FIG. 37. MODEL OF BASIC (IDEALIZED) NETWORK STRUCTURE WITH HEXAGONAL "DOORWAYS"

= SILICON

= OXYGEN
Vitreous silica, it should be kept in mind, has a distinct structure, differing from those three crystalline forms.

Grunin, Ioffe and Zonn (1972, [47]) found the average Si-O-Si angle of vitreous silica at low temperature to be 146.8° which resembles the Si-O-Si angles of the other silica polymorphs (quartz, tridymite and cristobalite) in the β-configuration.

Thus at low temperature most of the tetrahedra in glass are frozen into the β-states. At higher temperatures the thermal energy of the atoms increases, so that the energy barrier between α and β states is more easily crossed; thus we would expect the proportion of α-states to increase with temperature until at high temperatures where there is free crossing of the energy barrier half of the glass tetrahedra will be in α-states and half in β-states.

Glass goes from a lower concentration of α-states to a higher concentration of α-states as the temperature increases. Thus, in a manner of speaking, we can say that glass goes through a transformation from the β to the α configuration as the temperature increases.

IV.1.6 Explanations of the change in Q in the transition region for silver and germanium diffusion

Since repeatedly the trend of the increase or decrease of the activation energy in two different temperature regions has been discussed it will be useful to review the influence of heating upon the glass network.

According to Vukcevich [39] heating increases the concentration of α-states, and since the volume in the α-configuration is smaller than that in the β-configuration, the final result will be a "squeezing" of the glass structure at higher temperatures.

The "squeezing" of the network on heating the glass would be
expected to cause changes in the activation energy of diffusion. Changes in the repulsive ("size") forces and Coulomb interactions caused by the reduction in interatomic distances would probably cause the activation energy to increase. For ions at network sites, (Si, Ge) the "squeezing" will decrease the amount of π-bonding and so will lead to a decrease of the bond strength with the neighbouring oxygens (Revesz, 1971 [48]), and thus would lead to a decrease in activation energy.

The observed increase in \( Q \) through the transition region indicates that for both silver and germanium it is the increase in interactions produced by the "squeezing" which is more important.

IV.1.7. Discussion of the "doorway" model

If a model is constructed with the Si-O-Si angle equal to 138° in the high temperature region we arrive at an orifice with a radius of 1.15 Å. In Fig. 39 the ionic radii of germanium (\( r = 0.53 \) Å) and silver (\( r = 1.26 \) Å) are compared to the orifice radius.

The radii of "doorways", as the orifices are often called, can also be calculated directly from the activation energies of diffusing atoms; such radii are more realistic since an ideal geometrical model is not exact.

Assuming that the diffusion activation energy equals the strain-energy to distort the network sufficiently for a diffusing atom to pass from one equilibrium site to an adjacent one, we can compute the "doorway" radius from the equation derived by Frenkel [49] and modified by Anderson and Stuart [50] in which

\[
Q = 4\pi G r_D (r - r_D)
\]

where
- \( Q \) = activation energy
- \( G \) = modulus of elasticity
- \( r_D \) = "doorway" radius
- \( r \) = radius of diffusing ion.
Values between 0.93 Å and 1.03 Å (Frenkel [49]) and 0.78 Å and 0.86 Å (Anderson and Stuart [50]) have been computed using Q values of He, N₂, and H₂.

It would thus be expected, since the "doorway" even at higher temperatures is much larger than the Ge⁴⁺ radius, that Ge⁴⁺ diffusion will not be affected by "squeezing", that is, the activation energy will not change through the transition region. The experimental results contradict this; how can this be reconciled with the "doorway" model?

A "doorway" can not only be reduced radially, it can also be squeezed by different kinds of "puckering" or other distortions [51].

Accordingly there may be a whole spectrum of "doorway" sizes, and it is possible that Ge and Ag will use different sub-groups of "doorways". For the germanium ion diffusing in vitreous silica we get for the high temperature region with Q = 0.70 eV and the modulus of elasticity G = 8.0 \times 10⁵ kp/cm² [52] a "doorway" radius of 0.49 Å. For Ag the "doorway" computed in the same way is 1.24 Å.

This suggests that the "doorways" for Ge are smaller than those for Ag so that changes in "doorway size" resulting from changes in glass structure will be just as important for Ge as for Ag.

Experimental justification for the size of the "doorway" could be found by conducting X-ray diffraction experiments on glass specimens during heat treatment identical to that used during the diffusion experiment.

IV.1.8. The change in Q in the transition region for the monovalent ions

Comparing the ratios of the activation energies below and above the transition region for sodium and potassium diffusion in the experiments by Frischat [32] and Flinn [53] we observe that in the diffusion
of sodium and potassium the activation energies change by about 20% for Na, 5% for K and the activation energy of sodium and potassium diffusion, increases in going from a high to a low temperature region [32].

However the activation energy of Ag-diffusion decreases in going from a high to a low temperature region. The difference in behaviour between K and Ag is hard to explain, as their valence is the same, their ionic radii are almost the same (since Ag has an ionic radius of 1.26 Å and K has an ionic radius of 1.35 Å) and they probably diffuse by similar mechanisms (see Section IV.1.13).

One might try and attribute the difference in behaviour to differences in the properties of the glasses used. As mentioned before, Homosil and Infrasil are very different in for example, homogeneity [54]. The glass used by Flinn, GE-204, is similar to Infrasil (Shelby, [55]).

In the light of Frischat's experiments on sodium diffusion in both Homosil and Infrasil which gave identical results it is not very likely that differences in glass properties could explain the effect (see also [34]).

The difference could be connected in some way with the relative polarizability of the ions. For Na, there is a decrease in Q as the temperature rises and for K little change, whereas for Ag there is an increase.

This order of increase of Q is also the order of increasing polarizability (0.22 Å³, 0.97 Å³, 2.4 Å³ for Na, K and Ag respectively; (Tessman, Kahn and Shockley [56]) and there may be some correlation.
IV.1.9 Discussion of the difference in magnitude between the diffusion coefficients of germanium and silver diffusion

If one looks at other available data for diffusion in vitreous silica [57, 58, 32] it seems one can discern two classes of diffusants:

(1) those with diffusion coefficients of the order of $10^{-2} - 10^{-8}$ cm$^2$/sec at about 1000°C. This class includes He, Ne, Na, Ag, Ca, K and Li;

(2) those with diffusion coefficients of the order of $10^{-12}$ cm$^2$/sec at about 1000°C. This class includes Al, Ge and O.

There seems to be a definite gap between these two classes.

The difference between Ag and Ge diffusion coefficients, at any rate, is not likely to be due to an increase in the activation energy since germanium in fact has a lower activation energy compared to silver.

Thus the difference must be due to the pre-exponential factor.

The pre-exponential factors of germanium and silver diffusion show a difference of several orders of magnitude. This is too great to be accounted for by differences in $\gamma$ or $\lambda^2$.

The question arises if the difference in size of the diffusing particle can produce a big enough difference in magnitude of the entropy, $\Delta S$, or $v^*$, the vibration frequency of the particle; the mechanism remaining constant.

This is obviously impossible for $v^*$, the vibration frequency. In the case of $\Delta S$ we should expect a marked change going through the transition region, because of the contraction of the network above the transition region; this however is not observed.

Furthermore the diffusion coefficient of lithium only differs from that of silver by about a factor of 6 (Stern, 1970 [59]) at 570°C. Lithium is only slightly larger than germanium.

It is thus hard to see how this comparatively small difference
in $D$ could be explained if the difference between the $\text{Ag}$ and $\text{Ge}$ diffusion was due only to size differences.

Thus the difference between $D_0(\text{Ag})$ and $D_0(\text{Ge})$ must be due to some factor other than size.

Bruckner [33] reviews the diffusion coefficients of cations with valencies higher than one. At $1000^\circ\text{C}$ the ratio of the different diffusion coefficients for vitreous silica is

$$D_{\text{Na}} : D_{\text{Ca}} : D_{\text{Al}} : D_0 = 1 : (2.5 \times 10^{-3}) : (1.3 \times 10^{-8}) : (1.1 \times 10^{-9})$$

indicating the effect of bond strength of these ions on the diffusion coefficient.

From these ratios it could be inferred that a higher valency correlates with a higher bond strength. This would mean that if, for example, the diffusion mechanism was an exchange mechanism, the impurities ($\text{Na}^+$, $\text{Ca}^{2+}$, $\text{Al}^{3+}$, $\text{H}^+$) in the network present are harder to dislodge, the higher the valency. This results in a lower diffusivity.

The strength of $\text{Ag}-\text{O}$ and $\text{Ge}-\text{O}$ bonds would therefore differ widely. If both $\text{Ag}$ and $\text{Ge}$ were situated at the same type of site one would expect the activation energy for $\text{Ge}$ diffusion to be higher than that for $\text{Ag}$ diffusion. This is not observed.

It is therefore very likely that the diffusing germanium and silver ions are occupying different sites.

It should be noted here, that if in other systems (like metals) large differences in $D$ are observed, it is found that these can be traced to differences in the sites occupied by the diffusing particles, e.g. diffusion of silver and gold in lead [105].
IV.1.10 The effect of thermal history of the network on diffusion

The effect of thermal history of the network and its relation to diffusion has been well illustrated in the diffusion of helium and neon through vitreous silica. It was found that whilst:

"the diffusion of helium through vitreous silica was apparently free from serious effects due to differences in thermal history of the glass, there is a definite effect on the diffusion of neon" (Srivastava, 1970, [51]), presumably because it has a rather larger atomic size than helium (see also Fig. 38). The observed differences in activation energy for neon diffusion are consistent with small variations in the size of the central orifice of a silicon-oxygen ring brought about by bond angle variation or by different amounts of "pucker" in the rings (see Fig. 38 and 39). It is usual to consider the activated jump process as the forcing of the diffusing atom from an interstice or "cavity" through a ring of silicon and oxygen into the next interstice.

It is to be expected that all gases with an atomic or molecular size greater than that of neon (r = 1.2 Å) will also show this thermal history effect [51].

It might be remarked that Srivastava in his discussion of the effect of thermal history on the diffusion of helium and neon through vitreous silica pointed out the fact that not only the activation energy but also the pre-exponential factor was clearly affected; a separation of the factors contributing to the changes in the pre-exponential factor, however, has been unsuccessful [51]. (See also Frischat's discussion of the effect of thermal history on sodium diffusion in vitreous silica [31].)
FIG. 38. PLANAR REPRESENTATION OF A PENTAGONAL RING WITH AN Si-O-Si BOND ANGLE OF 150° (1): ORIFICE RADIUS = 0.94 Å. (2): SIZE OF NEON ATOM IS (1.2 Å RADIUS) SHOWN FOR COMPARISON [51]; (3): OXYGEN; (4): SILICON.
FIG. 39. PLANAR REPRESENTATION OF HEXAGONAL RING WITH A Si-O-Si BOND ANGLE OF 138°.
ORIFICE RADIUS (2) = 1.15 Å
SIZE OF Ge RADIUS (1) = 0.53 Å
SIZE OF Ag RADIUS (3) = 1.26 Å
(4) = OXYGEN; (5) = SILICON.
IV.1.11 Diffusion of germanium in vitreous silica in region II

Germanium resembles silicon in size and charge. It is therefore not surprising that it has been found that in SiO$_2$-GeO$_2$ glasses the Ge-ions are all located on network sites, in fact, as far as can be determined (Borrelli, 1969 [60]), can be located on silicon sites.

From a table of ionic crystal radii we find that Si$^{4+}$ has a radius of 0.42 Å, Ge$^{4+}$ a radius of 0.53 Å, Al$^{3+}$ a radius of 0.51 Å and Fe$^{3+}$ a radius of 0.64 Å.

Both Al$^{3+}$ and Fe$^{3+}$ are found to be located mainly on network sites and this further supports the assumption that germanium can replace silicon in the network [32,43].

Silver will exchange with sodium or any of the other alkali metals present in silicon and so probably occurs on the same sites. Sodium and the other alkali metals are situated in the interstices of the SiO$_2$ network (Doremus, 1968 [61]). These site assignments are in harmony with our earlier deduction that Ag and Ge are at different sites.

In germanium diffusion, three points are of special interest:

1. the diffusion mechanism seems not to involve the breaking of bonds. This is indicated by the small activation energy.

2. a simple interstitial mechanism has to be excluded, because of the values found for $f$, the correlation factor (see Section IV.2.5).

3. diffusion of Al$^{3+}$ in glass [32,43] seems to support our proposed diffusion mechanism.

The diffusion mechanism here put forward tentatively, is as follows:

We assume that a small portion of the germanium ions is located in between the network. The rate determining step in the diffusion process which is reflected in the activation energy would be the exchange of a non-network germanium ion and a silicon or germanium
ion at a network site.

During the diffusion annealing it is assumed that the chains of tetrahedra are not frozen in position. It is conceivable that a tetrahedron moves or rotates in such a fashion that the oxygen ions in the tetrahedron under consideration end up in such a position that in the new configuration they are effectively bonded to both the silicon network ion and the germanium non-network ion. This would happen at the saddle point and the motion of the oxygen ions may proceed in such a way that the non-network germanium ion becomes the centre of the tetrahedron and the original network silicon ion becomes a non-network ion. This silicon ion may migrate a few steps as a non-network ion before exchanging again with a network ion.

This sort of mechanism would be well suited to diffusion in glasses since the possibility of considerable local distortion of the general configuration of tetrahedral chains is not excluded.

Only two ions actually change their position so that $f\Delta K = 0.8 \pm 0.2$ as computed for a two-atom jump (see appendix II for the relevant computation).

Since $\Delta K$ would be expected not to be very large, this means that $f$ must be close to 1 and therefore the diffusion jumps should not be very strongly correlated.

In conclusion it can be said that it is likely that germanium diffusion in silica glass proceeds by a kind of interstitialcy mechanism.

IV.1.12 The diffusion of silver in vitreous silica in region II

Silver is very different in size compared to the silicon ion and there is also a big difference in charge. This makes it plausible to suggest that the silver ions in the silica network do not substitute for the silicon ions but are found in between silicon sites.
Further evidence for silver being on network modifying sites is the ease with which silver and sodium ions can be exchanged (Stern 1968 [62]). It is known from other sources [14,39] that sodium occurs at network modifying sites in silica and silicate glasses.

The reason why tracer diffusion rates in silica fall into two categories is now obvious. The fast diffusing substances such as sodium, silver, potassium, helium and neon are those occupying non-network sites while the slow diffusing substances are those occupying network sites.

IV.1.13 Comparison of monovalent ion diffusion in vitreous silica with that in alkali silicates

We should now compare diffusion rates of monovalent ions in silicate glasses with those in vitreous silica.

We begin by considering the effect of alkali content on diffusion rates.

In pure vitreous silica each oxygen is bonded to two Si$^{4+}$ ions. When network-modifying ions are introduced into the glass, a corresponding number of oxygen ions bonded to only one Si$^{4+}$ ion is introduced. (These are called non-bridging oxygens whereas the oxygens bonded to two Si$^{4+}$ ions are called bridging oxygens.) Simultaneously, the specific volume changes, so that the volume per gm.mole oxygen increases as the alkali content increases (Stevels [64]).

The increase in alkali content will increase the atomic density causing a fall in D and a rise in Q. The corresponding increase in volume per gm.mole oxygen increases the average alkali-(or in our case silver) - oxygen distance, weakening the corresponding bonds; this will tend to cause a fall in Q and a rise in D.

Thus there are two counterbalancing effects and there are no theoretical grounds for deciding which is more important.
It is found experimentally that the diffusion coefficient of sodium or silver in vitreous silica is lower than in sodium silicate glass at a comparable temperature and that the activation energy is a little higher (Frischat, 1968 [32]). This suggests that the effect of the decrease in Na-O bond strength is more important than the blocking of paths by sodium ions.

Le Clerc [65] compared the diffusion of silver in sodium and potassium silicate glasses to that of Li, Na and K in the same glasses [see Table IV]. While table IV shows that there is a rough correlation between diffusion rate and ionic size, it is clear that the relation is not a simple one. Probably polarizability and bond strength are also important.

<table>
<thead>
<tr>
<th></th>
<th>Radius Å</th>
<th>D (cm²/sec)</th>
<th>Relative mobility* in SiO₂ glass (Ag = 1) at 570°C [66]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li⁺</td>
<td>0.60</td>
<td>4. x 10⁻⁷</td>
<td>6</td>
</tr>
<tr>
<td>Na⁺</td>
<td>0.95</td>
<td>1.1. x 10⁻¹⁰</td>
<td>4.8</td>
</tr>
<tr>
<td>Ag⁺</td>
<td>1.25</td>
<td>2.5. x 10⁻¹⁰</td>
<td>1</td>
</tr>
<tr>
<td>K⁺</td>
<td>1.33</td>
<td>3.0. x 10⁻¹²</td>
<td>0.06</td>
</tr>
</tbody>
</table>

* Given for the sake of completeness only; not further discussed.

IV.1.14 Mechanism of monovalent ion diffusion in vitreous silica and silicates

The similar behaviour of sodium and silver diffusion in vitreous silica and in sodium silicate glass further supports our earlier assumption that silver occupies non-network sites in vitreous silica (see also figs. 40, 41).
FIG. 40. GLASS MODIFYING ATOMS IN A RANDOM THREE DIMENSIONAL NETWORK. THE SODIUM ATOMS HAVE REDUCED THE AMOUNT OF CROSS-LINKING. THUS SOME OXYGEN ATOMS ARE NOW STRONGLY BONDED TO ONLY SINGLE ATOMS [14].
FIG. 41. STRUCTURE OF SODA-SILICA GLASS IN TWO DIMENSIONS. IN A TWO-DIMENSIONAL VIEW, THE SILICONS APPEAR TO BE BONDED TO THREE RATHER THAN TO FOUR OXYGEN ATOMS. IN FACT, EACH SILICON ATOM IS TETRAHEDRALLY BOUND TO FOUR OXYGEN ATOMS. EACH SILICON ATOM IS TETRAHEDRALLY BOUND TO FOUR OXYGEN ATOMS, BUT THE FOURTH IS DIRECTLY ABOVE OR BELOW THE SILICON ATOM AND THEREFORE NOT SHOWN IN THE PLANE OF THE PAPER [63].
In discussing the diffusion of network-modifying ions (including silver) it is customary to use the terms vacancy and interstitial site in a sense which is not the usual one.

In analogy to what is customary in the field of ionic transport in crystals [7] the places between the silicon-oxygen network available for network modifying ions can be divided into sites and interstitial sites. (see also Fig. 2a). Both are places of potential minima but the minima of the sites are distinctly lower than that of an interstitial site [7].

It is understood that the majority of the network modifying ions are distributed over the sites and only a few over the interstitial sites.

Some authors [64] assume that there are many more sites than cations. These sites are all roughly equivalent in energy level; each cation can therefore jump in several possible directions without being blocked by another cation, and the experimental activation energy represents simply the migration barrier.

Another possibility mentioned by Isard [68] is to assume that before migration can occur vacancies and/or interstitials must be created first, and that the experimental activation energy consists mainly of an energy of defect formation, i.e. an energy of dissociation of a cation from a normal site.

It has been suggested on the basis of correlation factor measurements that if the diffusion process involves jumps to vacant sites the accessible sites must be in linear chains with a certain proportion of side connections [68].

In a random network such as occurs in vitreous silica with its abundance of available sites this assumption would be more plausible if it can be proven that the tetrahedral chains are lying in a preferred orientation and that diffusion proceeds mainly along that direction.
Evidence from X-ray diffraction studies [41] suggests that alkali ions are paired in the glass structure, rather than uniformly dispersed.

It is accordingly likely that sodium diffuses by a two-ion mechanism, and if as suggested above, silver diffuses by a similar mechanism to sodium, then silver likewise diffuses by a two-ion mechanism.

Some have favoured an exchange mechanism for Na diffusion because thus electrical neutrality is automatically satisfied [33].

Frischat [32] suggested that the diffusing sodium ion interchanged with a sodium ion initially present in the glass network as an impurity.

A silver ion in silver diffusion could likewise be thought of as interchanging with a network modifying ion in vitreous silica. Interchange of silver and network modifying ions might not involve the breaking of strong bonds such as would occur if silver had to inter-change with a network ion such as silicon.

One concludes that at this stage of the discussion, vacancy, interstitial, interstitialcy and exchange mechanisms are possible mechanisms for the diffusion of Ag in vitreous SiO₂.

IV.1.15 Is silver diffusion in silica self diffusion?

Before leaving the discussion on silver diffusion the question might be asked: Is silver diffusion in vitreous silica self diffusion or impurity diffusion?

All authors agree that Na-diffusion in a Na₂O-SiO₂ glass is self diffusion. This is reasonable because the Na is migrating between sites occupied only by Na ions. The network-modifying sites are only occupied by Na ions, if any.
As the proportion of Na is decreased it seems reasonable that the diffusion remains self diffusion and the ordinary self-diffusion correlation factors continue to be applicable; Na is still migrating between sites occupied only by Na ions. Even in the case of tracer Na migrating in pure SiO$_2$ glass this would still be true.

Ag, like Na, occupies network-modifying sites. In Homosil glass there is a negligible proportion ($\sim$ 1 ppm) of such sites occupied so that in the diffusion zone Ag will be the main occupier of network-modifying sites of all types. Thus Ag diffusion seems to be actually self diffusion and so one should be justified in using self diffusion correlation factors.

IV.2 The Isotope Effect

IV.2.1 General theory

As indicated in III.2.1 the isotope effect was measured in order to obtain values of $f$, the correlation factor, which we shall now define and discuss theoretically.

The purpose of obtaining $f$, the correlation factor, is to get added information about the mechanism of diffusion or about the jump frequencies of the diffusing ions.

Bardeen and Herring (1952 [58]) pointed out the fact that atoms and ions do not always make random jumps. For example, in a vacancy mechanism, just after a jump has taken place, the site left by the ion has a greater probability of being unoccupied than the other neighbouring sites so that an ion has a greater probability of jumping back to the site that it has just occupied than of jumping in other directions.

Only after the probability distribution of vacancies around the particular ion has decayed to a random distribution will there be a
random jump probability for this ion.

The non-randomness of diffusion may be taken into account by introducing the correlation factor $f$ into some of the formulae involving $D$.

We shall first derive appropriate expressions for the case of random diffusion and then show how correlation modifies these.

Consider single particles $A$, each with a single charge $e$, which can jump in a crystal over a distance $\lambda$ and with probability of $P$ sec$^{-1}$ in each of $z$ directions.

Each particle makes $zP$ jumps per second; $z$ is so oriented that the three co-ordinate axes are equivalent with respect to isotropic diffusion.

If the directions of the jumps are distributed at random we can write

$$D_A = z^2 P \lambda^2.$$  \hspace{1cm} (34)

Another expression for ionic diffusivity, called the Nernst-Einstein relation, is

$$D_{\text{conduction}} = \frac{\sigma_A kT}{N e^2}. \hspace{1cm} (34a)$$

The ionic conductivity $\sigma_A$ is given by combining equation (34) and equation (34a).

$$\sigma_A = zP Ne^2 \frac{\lambda^2}{6kT}.$$  \hspace{1cm} (35)

where $N = \text{number of particles (of type A) per cm}^3$

$\lambda = \text{jump distance}$

$e = \text{electronic charge}$

$k = \text{Boltzmann constant}$

$T = \text{absolute temperature}.$
If there is a non-random distribution of the direction of successive jumps of a particle, equation (34) becomes \( D_A = f \cdot \frac{Z}{6} \nu \lambda^2 \), where \( f \) is the correlation factor, and gives a measure of the randomness of the diffusion (Barr and Le Claire [24]).

The equation for the conductivity, \( \sigma_A = zv \nu e^2 \frac{\lambda^2}{6kT} \), does not have to be modified by the correlation factor since an increased jump probability of a certain ion in one direction is counterbalanced by a decreased jump probability of another ion in the opposite direction.

If diffusion be non-random or if several particles are involved in the jump then the Nernst-Einstein relation no longer applies and one can write

\[
\frac{D_A}{\sigma} = f_{\sigma} \frac{kT}{Ne^2} \tag{36}
\]

\( f_{\sigma} = f \) when diffusion and conductivity involve charged particles moving by a vacancy mechanism, but in general they are different (Adda and Philibert [69]).

The relation between \( f \) and \( f_{\sigma} \) is given by

\[
f_{\sigma} = 2f \left( \frac{r_T}{r_0} \right)^2 \tag{37}
\]

where

\( r_T = \) correlated jump distance

\( r_0 = \) uncorrelated jump distance.

The magnitude of the correlation factor depends on the mechanism of transport and on the ionic arrangement.

Since glass does not have long range order in the structure, the above reasoning for the derivation of a correlation factor does not unqualifiedly apply to an amorphous material like glass.

Strictly speaking it would only apply to those regions where there is still some crystal like behaviour. Correlation factors calculated from isotope experimental data in glass are of uncertain validity.
The choice of diffusion mechanisms therefore should never be made, in the case of diffusion in glass, on the basis of the correlation factor alone.

IV.2.2 Calculation of correlation factors

It is with these reservations in mind that the discussion of the isotope effect is continued.

Compaan and Haven [70] have shown the correlation factor for vacancy self diffusion in crystals to be of the order of

\[ f = 1 - \frac{2}{z^*} \]  

(38)

where \( z^* \) is the number of nearest neighbours in the sublattice in which the ion moves. For example, in a two-dimensional honeycomb lattice \( z^* = 6 \) and \( f \) is therefore 0.67; in a three-dimensional, diamond lattice \( z^* = 4 \) and \( f = 0.5 \).

The exact determination of \( z^* \) in glass is difficult. As an approximation a two-dimensional model has been set up for the glass used in the present experiments (Homosil) Fig. 42.

The structure of the quartz glass in the present experiment has been investigated by Oberlies and Dietzel [103]. They found that the glass consists of a network of tetrahedral \( \text{SiO}_4 \) groups. Every Si atom is surrounded by four oxygen atoms. A network of tetrahedra arises, in which each oxygen atom belongs to two tetrahedra.

Oberlies and Dietzel assumed several models and calculated on the basis of their experimental data the most probable structure. It was found that their calculations agreed with experimental data of Warren [104] if one used hexagonal rings. Such a configuration occurs exclusively in cristobalite.

In the present case our model consists of adjacent hexagonal
structures conforming to the models set up by Oberlies, Dietzel and Warren [11, 104] (see Fig. 42).

In Fig. 42 the silicon network sites which are available for an ion jumping from C, for example, number 3, i.e. E, F and G, since these are unobstructed by oxygens. The total number of nearest neighbours (in the three hexagons) in which a diffusing particle can jump from C is therefore 9.

In the silicon sub-lattice of the glass used in the present investigation \(z^* = 9\) and \(f\) therefore is equal to 0.77 for diffusion by the vacancy mechanisms. For the interstitial and exchange mechanisms of diffusion, we deal with random processes so that for any diffusing tracer, \(f\) equals 1.

For the interstitialcy mechanism this correlation factor for self diffusion can be approximated by

\[
f = \left(1 - \frac{1}{z^*}\right)
\]  

(39)

This holds for co-linear jumps only [24,71]; \(z^*\) is the number of neighbouring interstitial sites to which an ion, located on a lattice site, can jump (see Table V).

In the case of an indirect interstitial mechanism of diffusion, lattice atoms can move to any one of three interstitial sites, A, B and D. in Fig. 42. Therefore \(z^* = 3\) and this value of \(z^*\) in equation (39) gives \(f = 0.67\). As remarked before, it is realized that the correlation factor has been derived with the aid of a model in which the atoms are arrayed in a perfect crystal lattice. This is, for glass, a highly idealized approximation, of which the general validity still has to be proved.

We do not know how the non-network ions (e.g. Ag ions) are distributed in almost pure silica and so the number of nearest neighbours cannot be predicted. For a simple interstitial or exchange mechanism
FIG. 42. TWO DIMENSIONAL LATTICE.

\[ \text{\( O = \text{OXYGEN} \)} \]

\[ \text{\( \Theta = \text{SILICON} \)} \]
If there is an excess of vacant sites (in the Haven and Stevel sense [68], as illustrated in Fig. 2a) \( f = 1 \) also. For other types of vacancy or interstitialcy mechanisms, \( f \) will depend on the number of nearest neighbours and the various possibilities are listed in Table V.

**TABLE V**

Correlation factor, \( f \), for self-diffusion relevant to different mechanisms of diffusion in vitreous silica

<table>
<thead>
<tr>
<th>ONE-BODY mechanism</th>
<th>number of possible jump directions</th>
<th>correlation factor ( f )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Interstitial</td>
<td></td>
<td>1</td>
</tr>
<tr>
<td>Vacancy</td>
<td>2</td>
<td>0</td>
</tr>
<tr>
<td>Vacancy</td>
<td>3</td>
<td>( \frac{1}{3} )</td>
</tr>
<tr>
<td>Vacancy</td>
<td>4</td>
<td>( \frac{1}{2} )</td>
</tr>
<tr>
<td>Vacancy</td>
<td>9</td>
<td>0.77</td>
</tr>
</tbody>
</table>

(as for silicon)

<table>
<thead>
<tr>
<th>TWO-BODY mechanism</th>
<th>number of possible jump directions</th>
<th>correlation factor ( f )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Interstitialcy</td>
<td>2; from lattice site</td>
<td>( \frac{1}{2} )</td>
</tr>
<tr>
<td>Interstitialcy</td>
<td>3; from lattice site</td>
<td>( \frac{1}{3} )</td>
</tr>
<tr>
<td>Exchange</td>
<td></td>
<td>1</td>
</tr>
</tbody>
</table>
In the derivation of the correlation factor (Haven and Verkerk, 1965 [72]; Barr and Le Claire [24]) discussion was based on self diffusion. It was shown that the correlation factor was a geometrical constant determined by lattice geometry and by the type of mechanism by which atomic jumps take place. Implicitly, the assumption was made that individual atoms were identifiable and that it was the diffusion of the selected atoms that was being studied.

IV.2.3 Use of the isotope effect to measure the correlation factor

Experimentally this is made possible by the use of isotope tracers. It is the diffusion of these tracers which is measured.

At present there are two methods by which correlation factors can be measured.

The first is the "mass effect" or "isotope effect" method where one compares the diffusion coefficients of two isotopes.

The "f" measured by the isotope effect method has been compared with the "f" derived from the geometrical model (cf Fig. 31).

Barr and Le Claire [24] derived the following relation:

$$f \left[1 - \frac{W_\alpha}{W_\beta}\right] = \left[1 - \frac{D_\alpha}{D_\beta}\right]. \quad (40)$$

where

- $f$ = correlation factor
- $W_\alpha$ = the jump rate of the first diffusing species (here designated by $\alpha$)
- $W_\beta$ = the jump rate of the second diffusing species (here designated by $\beta$)
- $D_\alpha$ and $D_\beta$ = diffusion coefficients for $\alpha$ and $\beta$ respectively.
This equation (40) assumes a particular form for \( f \) which does not apply for example to indirect interstitialcy diffusion [73]. However in cases studied up to now, the error is not very great [78]. Consider the ratio \( \frac{W_\alpha}{W_\beta} \), where \( W = v^* \exp \left( - \frac{\Delta F}{RT} \right) \) and \( \Delta F = \) free energy barrier for the jump. \( \Delta F \) is independent of isotope mass while \( v^* \), the vibration frequency of the diffusing atom, varies approximately inversely with the square root of the isotope mass. Then if only one atom changes its site during a migration step one can write [28]:

\[
\Delta K = \text{fraction of the kinetic energy associated with the motion of the diffusing atom leading to change in the saddle-point configuration [110]. } 0 < \Delta K < 1.
\]

If the migration step involves the simultaneous motion of \( n \) atoms, equation (41) can be written more generally [24]

\[
f(\Delta K) \left( 1 - \left( \frac{M_\beta}{M_\alpha} \right)^{1/2} \right)^{n-1}D_\alpha = \left( \frac{D_\alpha}{D_\beta} \right)^{n-1}D_\beta
\]

where \( M \) is the average mass of the matrix-atoms.

If the isotope effect for self diffusion is measured (41) or (41a), can be used to help decide what the diffusion mechanism is. The left hand side of (41) or (41a) must be less than

\[
f \left( 1 - \left( \frac{M_\beta}{M_\alpha} \right)^{1/2} \right) \quad \text{or} \quad f \left( 1 - \left( \frac{(n-1)M+M_\beta}{(n-1)M+M_\alpha} \right)^{1/2} \right)
\]

respectively, so that for each mechanism there is a maximum which cannot be exceeded.

Comparisons with the experimentally measured right hand side value of equation (41) or (41a) then enables one to eliminate mechanisms whose \( f \)-values are too small to be compatible with the left hand side.

If for a given mechanism \( \Delta K \) is known, either from theoretical work or found empirically, one can further reduce the number of possible mechanism
For correlated mechanisms (vacancy, interstitialcy) $f$ for impurity diffusion can be any value from near zero to unity. In general, one cannot determine which of these correlated mechanisms applies. One can, however, still give a lower limit to the $f$-value.

**IV.2.4 Use of conductivity experiments to obtain $f$**

If one compares the measured diffusion coefficient with the contribution to the ionic conductivity from the diffusing species, $f_\sigma$ can be determined from (36) [72]. The correlation factor so obtained is, in general, not equal to the Bardeen-Herring correlation factor.

**IV.2.5 The isotope effect for germanium diffusion**

It was found that for Ge, $\left| 1 - \frac{D_\alpha}{D_\beta} \right| = 0.015 \pm 0.007$ and for $\frac{M_\beta}{M_\alpha}^{1/2}$ we get $1.022$ ($\alpha = ^{68}\text{Ge}$ and $\beta = ^{71}\text{Ge}$). Substituting these data into (41) and (41a) the experimental values of $f\Delta K$ for Ge are $0.7 \pm 0.3$ if one atom moves during the diffusion jump as is the case in the vacancy and interstitial mechanisms and $1.0 \pm 0.5$ if two atoms move during the diffusion jump as in the exchange and interstitialcy mechanism.

The correlation factor $f$ for various mechanisms has been computed by various authors (Compaan and Herring, 1956 [74], Friauf [75], Barr and Munday [76]).

If one considers the permissible values of $f$, one-body diffusing with $f < 0.4$ and two-body mechanisms with $f < 0.5$ are excluded.

For an interstitial mechanism of diffusion $f = 1$ and in known cases of interstitial diffusion $\Delta K$ is also close to 1 (Le Claire [28]) except for the diffusion of hydrogen where quantum effects are important. See also Appendix II. Therefore a simple interstitial mechanism is unlikely, but is not excluded by the error bounds for $f\Delta K$. 
IV.2.6. The isotope effect for Ag diffusion

For Ag, \( \left[ 1 - \frac{D_{\alpha}}{D_{\beta}} \right] = 0.015 \pm 0.003 \) and \( \frac{M_{\beta}}{M_{\alpha}}^{1/2} = 1.024 \).

In the case of Ag diffusion, \( f \Delta K = 0.6 \pm 0.2 \) for a one-atom mechanism and \( 0.8 \pm 0.2 \) for a two-atom mechanism using (41) and (41a). (See Appendix II.)

Within the limits of error the correlation factor as calculated from isotope experiments in silver diffusion does not exclude vacancy, interstitialcy or exchange mechanism. It is not necessarily true that the mechanism is the same for both silver and germanium.

Which mechanism is chosen ultimately as the most likely should be decided upon after considering all the evidence; it should not be based on the outcome of the isotope experiment alone.

Finally it can be assumed that in view of the chemical similarity of silicon and germanium it can be expected that both of them diffuse by the same mechanism; our results therefore imply that silicon probably does not diffuse by an interstitial mechanism either.

In deciding on a diffusion mechanism a look at the values of the correlation factor \( f \) should be worthwhile.

The essential feature concerning the calculation of the correlation coefficient is that in the diffusion two ions jump together.

For Ag diffusion the experimental data of the isotope experiment give \( f \Delta K = 0.6 \pm 0.2 \) for a one-atom mechanism and \( f \Delta K = 0.8 \pm 0.2 \) for a two-atom mechanism (see Appendix II for the relevant calculation).

However, if only the magnitude of the correlation factor is taken into consideration, within the limits of error, vacancy, interstitialcy or exchange mechanism is in the present case still permissible.

IV.2.7. Conductivity experiments and the correlation factor \( f \) for sodium diffusion in vitreous silicates

In sodium silicate glasses the conductivity is often due predominantly to the sodium ion diffusion, so that in such cases the second
method of obtaining correlation factors (which depends on equation (36) can be used.

It is possible that silver diffusion proceeds by a similar mechanism to sodium diffusion so that the following observations are relevant.

The value of \( f_Q \) (eqn. 36) is 0.2-0.5 \([72, 79, 86]\). This is low, suggesting that the number, \( z \), of possible jump directions from a given position is small. For simple vacancy processes the approximate value of \( f = 1 - \frac{2}{z} \) gives \( f = 0, \frac{1}{3}, \frac{1}{2} \), for \( z = 2, 3, 4 \) respectively.

For a vacancy mechanism, \( f = f_Q \) and so if Na diffuses by a simple vacancy mechanism the diffusion is along chains of sites with a restricted number of connections between chains.

If Na\(^+\) ions jumped co-linearly in pairs by a vacancy or interstitialcy mechanism then from (37) \( f = 2 f_Q \) so that \( f \) is between 0.4 and 1.0.

The \( f \) values for the interstitialcy or "two-atom" vacancy mechanism lie in this range, so that these are possible mechanisms. Diffusion by cooperative jumps of several ions is also not excluded. Na\(^+\) cannot be diffusing by the exchange mechanism, which does not transport charge and so gives an infinite \( f_Q \).

Thus the work on sodium diffusion suggests that Ag\(^+\) does not diffuse by exchange, but otherwise does not elucidate the situation.

IV.3 The "Near Surface" Effect

Typical penetration profiles obtained for the diffusion of germanium and of silver in vitreous silica are given in Figs.7,10,12,14 and 17.

As remarked earlier three distinct regions can be distinguished denoted by region I, II and III.

In this section we are concerned with region I which in the activity vs. penetration-plot exhibits anomalous behaviour in the form of an
upward "wiggle".

In region I, initially the concentration decreases rapidly with penetration, then shows an upward wiggle before it again continues to decrease rapidly.

Most near surface anomalies reported occur within 1 μ of the surface. However segregation effects have been reported over distances greater than a micron [102].

Mortlock (1967 [81]) in a paper about the near surface anomaly in gold reviewed different explanations for the near surface anomalies.

In our case the penetration profiles were obtained by the residual activity method so that if the absorption is assumed to be negligible the measured activity should decrease monotonically for increasing penetration.

An upward surge of the concentration versus penetration distance profile could be due to radioactive contamination, for example radioactive debris from previous grindings at that particular penetration distance. Such a surge is also possible if an appreciable fraction of the radiation is absorbed.

To find out if absorption could be the cause, the absorption coefficient for the radiation of the germanium tracer used was calculated as follows:

It can be shown that an absorber whose bulk density is ρ and which is made up of a mixture of elements whose mass attenuation coefficients are

\[
\left( \frac{\mu_1}{\rho_1} \right) \cdot \left( \frac{\mu_2}{\rho_2} \right) \ldots \text{etc. will have an overall mass attenuation coefficient given by:}
\]

\[
\frac{\mu}{\rho} = \frac{\mu_1}{\rho_1} w_1 + \frac{\mu_2}{\rho_2} w_2 + \ldots
\]
where \( w_1, w_2, w_3 \ldots \) are the weight fractions of the elements which make up the absorber.

The absorber in question is SiO\(_2\) so that

\[
\frac{\mu}{\rho} (\text{SiO}_2) = \frac{\mu}{\rho} (\text{Si}) \times \text{weight fraction of Si} \\
+ \frac{\mu}{\rho} (\text{O}) \times \text{weight fraction of O} .
\]  

(43)

Tables E143 in the Handbook of Physics and Chemistry (1970) give the value of \( \frac{\mu}{\rho} \) for selected values of \( \lambda^* \).

The energy of the radiation used in our case was 9.2 keV.

\[
E = h\nu = \frac{hc}{\lambda^*}
\]

or

\[
\lambda^* = \frac{hc}{E} .
\]

\( \lambda^* \) therefore can be computed and is found to be 1.35 Å.

Making a graph of \( \frac{\mu}{\rho} (0) \) vs \( \lambda^* \) and interpolating from the graph we get for \( \frac{\mu}{\rho} (0) \) at 1.35 Å the value of 7.5 \( \text{cm}^{-1} \text{gm cm}^{-3} \).

To compute \( \frac{\mu}{\rho} (\text{Si}) \) which is not given in the tables, we make use of elements with atomic number, \( Z \), near to that of Si (\( Z = 14 \)). Those are Al (\( Z = 13 \)) and S (\( Z = 16 \)). Since

\[
\frac{\mu}{\rho} (\text{Si}) = \frac{\mu}{\rho} (\text{Al}) + \frac{1}{3} \left[ \frac{\mu}{\rho} (\text{S}) - \frac{\mu}{\rho} (\text{Al}) \right]
\]

(44)

and with

\[
\frac{\mu}{\rho} (\text{S}) = 63.2 \text{ cm}^2 \text{ gm}^{-1}
\]

and

\[
\frac{\mu}{\rho} (\text{Al}) = 34.0 \text{ cm}^2 \text{ gm}^{-1}
\]

we arrive for \( \frac{\mu}{\rho} (\text{Si}) \) with the aid of equation (44) at the value of 43.6 \( \text{cm}^2 \text{ gm}^{-1} \). Inserting the computed values of \( \frac{\mu}{\rho} (0) \) and \( \frac{\mu}{\rho} (\text{Si}) \) in equation (43) one arrives at \( \frac{\mu}{\rho} (\text{SiO}_2) = 24 \text{ cm}^2 \text{ gm}^{-1} \) and since \( \rho(\text{SiO}_2) = 2.205 \text{ g/cc} \), we finally get \( \mu(\text{SiO}_2) = 53 \text{ cm}^{-1} \).
Accordingly radiation travelling through 30 μm of glass will only lose about 15% of its intensity; since this will be only a small part of the integrated activity measured, the absorption will not affect the residual activity significantly (see also Appendix I).

The question could well be asked why such an involved calculation was used and why the absorption coefficient could not be measured directly instead. The reason for doing the calculation is that since the germanium used emitted γ-rays, the absorption would depend very strongly on the absorber and to measure the coefficient would entail the use of a very thin slab of the same vitreous silica as used in the experiment. This was found to be impossible with the means at our disposal.

In the case of diffusion of silver in vitreous silica the radiation used was γ-radiation with an energy of 0.656 MeV.

From the "Siegbahn" tables [84] we obtain

\[ \frac{\mu}{\rho} (0) = 0.077 \text{ cm}^2/\text{gm} \]

\[ \frac{\mu}{\rho} (\text{Si}) = 0.077 \text{ cm}^2/\text{gm} \]

and therefore

\[ \frac{\mu}{\rho} (\text{SiO}_2) = 0.169 \text{ cm}^{-1} \]

by the same procedure as adopted in the case of germanium diffusion.

We can neglect absorption when

\[ 1.69 \times 10^{-5} \sqrt{\Delta t} < 0.01 \]

or

\[ \sqrt{\Delta t} < \frac{0.01}{1.69 \times 10^{-5}} = 5.9 \times 10^2 \text{ m} \] (see Appendix I) which condition was satisfied for our silver diffusion profiles.

Absorption as the cause of the upward wiggle in the activity vs penetration profile can therefore be discounted.

An alternative explanation as remarked before is that at a certain distance from the surface the structure of the glass changes in such a fashion that activity removed in previous grindings is trapped and that it is extremely difficult to remove the contamination,
even by ultrasonic cleaning (see Fig. 44) as can be seen from a scanning electron microscope photograph of the surface.

Pre-annealing for prolonged periods (three weeks) at 900°C caused this "trapping effect" to disappear [82]. This suggests that the structure of the glass has been changed in such a way by the preliminary heat treatment that identical grinding and polishing procedures make it possible for "trapping features" to develop in specimens which have not been pre-annealed in contrast to the specimens which have been pre-annealed. (See also discussion on electron microscopy of glass surfaces, Ch. III.)

Whereas the "trapping effect" as seen in the upward wiggle in the concentration vs penetration profile does not tell us anything about the process of diffusion itself, it does indicate the need to be aware when comparing diffusion results of different workers of the thermal history of the glass under investigation.

It could be argued that pre-annealing should be done as a routine procedure for all the glass blocks used. In glass however, one does not really know what effects pre-annealing has on the structure. If generally speaking the purpose of pre-annealing is getting rid of inhomogeneities, the question can be asked if pre-annealing while presumably getting rid of micro-cracks, for example, during heating, does not introduce new ones during cooling. Also, if specimens have to be used later on at different temperatures, one must make sure that all specimens had the same pre-treatment. This can be done in one laboratory in a consistent and uniform way, but one does not know what "a consistent and uniform way" in another laboratory means. Other workers might have different regimens for heating and cooling.

To illustrate what we mean by regimen, an example is taken from an article "on the influence of micro-structure on diffusion processes
in glasses" (Frischat (1970 [83]). For a Na$_2$O-SiO$_2$ glass with a 14.8% Na$_2$O content, three steps in the pre-diffusion thermal history were involved. Firstly the glass melt was held for one hour in a Pt crucible at 1500°C and was "stirred for homogenization". Secondly, the resulting homogeneous glass was annealed for half an hour at 480°C and thirdly, to attain "phase-separation" the glass was heat-treated for 8 hours at 600°C. This shows what is sometimes involved in pre-diffusion heat treatment. It is to be noted that no particulars were given on how the preheated specimen was cooled down to room temperature. In the thermal history of glass, cooling is no less important than heating.

Thus the pre-annealing regimen of the glass can be complicated and further pre-annealing might in fact complicate matters more.

We can summarise by saying that the near-surface anomalous behaviour, in our case, is very likely the result of radioactive contamination.

IV.4 Diffusion of Silver and Germanium in Region III

The log D vs $\frac{1}{T}$ plot for the diffusion of germanium in silica glass in region III is shown in Fig. 20 and the corresponding plot for silver is shown in Fig. 22.

In these plots a change of slope takes place at about 570°C.

In contrast to the Arrhenius plots for region II which we have discussed previously, the diffusivity increases with decreasing temperature.

From the plots in Fig. 20 and 22 it is seen that the diffusion mechanism could not be the same as in region II since the slope of the Arrhenius plot is of opposite sign.

Line or surface faults are often thermally unstable and so anneal out at higher temperatures. Thus diffusion controlled by such
defects could become slower as the temperature increased just as region III diffusion does.

It is thus plausible to attribute region III diffusion to diffusion along line or surface faults, acting as "short-circuits".

How could such "short-circuits" arise?

Revesz (1970 [85]) discussed a new model for defects in non-crystalline silicon dioxide.

Revesz observes that gross "bulk" properties of SiO₂ films as revealed by X-ray and electron microscopy, infra-red spectroscopy etc. resemble closely those of vitreous silica and that these in turn exhibit a significant similarity to the properties of the crystalline modifications of SiO₂.

This is due to the fact that the short range order in both crystalline and non-crystalline SiO₂ is in the first approximation the same.

A perfect glass or vitreous material may be defined in the following way: there are no broken bonds, the short range order is maintained everywhere and the mean value of the bridging bond angle as well as its distribution around the mean is the same everywhere. If this mean value and/or the distribution in a given volume element is different from that in the surroundings, then a "defect" has formed. This can happen without breaking bonds or disrupting the short range order, without deforming the Si-O tetrahedra in our case. These "defects" or micro-heterogeneities can, in principle, occur in a random or correlated manner. If the randomly distributed micro-heterogeneities show a larger degree of order than their surroundings, then they approach the "crystallites" of the crystallite theory of glasses [86].

If the micro-heterogeneities occur in a correlated manner along a given direction, then a channel or chain type "defect" arises in the non-crystalline solid.
If some property of the bond is sensitive to relatively small changes in bond angle, then we can expect that these micro-heterogeneities will show different behaviour from their surroundings.

This will be especially noticeable for the case of "channel" formation along a preferred direction.

If the local order within a micro-heterogeneity is similar to that of a crystalline modification, then an increase of the size of the micro-heterogeneity perhaps with the cooperation of point defects may result in a micro-crystallite [86]. This situation corresponds roughly to the degradation of a single crystal to polycrystalline material through the formation of small angle and large angle boundaries.

The flexibility of the non-crystalline structure, as manifested in the large spread of the bridging bond angle (see also discussion of Vukcevich model, Fig. 36a) renders almost impossible a clear distinction among various types of disorder.

This means that in a non-crystalline solid, the transition from relatively small disturbances in the electron distribution (micro-heterogeneity) to gross morphological defects (voids, pinholes etc.) may be continuous. Therefore the treatment of transport processes in non-crystalline solids can be very difficult and can lead to ambiguous results if concepts developed in connection with single crystals are used without paying special attention to the peculiarities of the defect structure of non-crystalline solids.

An especially interesting micro-heterogeneity is the so-called channel. Channels are somewhat similar to edge dislocations in crystals which are also correlated defects.

The significant difference between these two defects is however that because of the spread in the bridging bond angle channels can form without disrupting the short range order of the vitreous solid, whereas dislocations are necessarily associated with deviations from the short
range order characteristic of the perfect crystal.

Other authors have also considered the possibility of channels in glass.

Experimentally it has been found that heat treatment destroys the channels [87] hence there is a decrease in etch rate.

Extended defects have been observed in glass fibres drawn in vacuum and a model was proposed which consists of an array of elementary domains organized in a super-lattice. The elementary "domains" could have different lattice patterns from perfect crystalline to amorphous. The super-lattice in turn would exhibit various degrees of order from completely amorphous to increasingly para-crystalline (Zarzycki and Mezard, 1962 [88]).

Lang and Miuscov [89] in their studies of the growth of synthetic quartz suggested cellular development forming an irregular polygonal network with the congregation of dislocations in or near the fault surfaces at the later stages of growth.

There is evidence from the electron-micrographs that there are faults within the volume of the crystal that could produce fast diffusion paths and that these could anneal out to produce diffusion coefficients that decrease as the temperature increases.

With the Revesz model in mind we can say that if it is accepted that in the SiO₂ matrix there are "channels" present, the diffusion of germanium and silver in region III can be thought of as proceeding predominantly along those channels.

As the temperature rises it is assumed that the number of channels decreases sufficiently fast to overwhelm any increase in diffusion rate in the individual channels so that the net result is that the total rate of material transport along the channels drops off.

Later experiments on the diffusion of germanium in pre-annealed
silica glass by S. Takabayasi [82] did not exhibit a region III in the corresponding penetration profiles. This tends to confirm the idea that the channels can be removed by annealing.

IV.4.1 Electron microscopy of the glass surface

Electron micrographs of surfaces of the left-over specimens are given for blocks annealed at 900°, 600° and 400°C in Figs. 26-32.

Lower magnification (5000x) produced micrographs which accentuated the "rugged" appearance of the surface.

IV.4.1.1 The granular structure

A higher magnification (30,000x) shows granulation characteristic of the whole surface.

Heating at higher temperatures seems to result in finer granulation which is surprising since one would expect smaller grains to coalesce into larger aggregates at higher temperatures.

However the time of annealing could be a factor. The specimen at 400°C had been heated for the order of months, the one at 900° not longer than three weeks, which implies that at 400°C the granules had more time to grow into larger aggregates than at 900°C. The granular size was characteristic for one block. At 400°C, the grain diameter ranged from about 100 Å to about 200 Å.

IV.4.1.2 Previous views on the significance of the granular structure

Oberlies (1956)[90], Haller and Macebo (1968) [91], Warshaw (1959) [92], using electron microscopy of surfaces, all related surface structure with bulk properties. Zarzycki and Mezard (1962) [88] also used the electron microscope but for "transmission" photographs of glass fibres drawn in vacuum. They proposed a "para-crystalline" structure
of the glass.

Russell and Bergeron (1965) [93] used two independent methods: electron microscopy and small angle X-ray scattering. The results obtained by those two methods were in good quantitative agreement.

Vaisfeld (1971) [94] considered transmission electron microscopy questionable because of "inevitable and unforeseen changes which the glass undergoes during preparation".

Seward and Uhlman (1970) [18] pointed out that surface structure as seen by previous authors with the electron microscope could be attributed to the method of preparation of the specimen.

We see from the above that no definite conclusion has been reached concerning the relation of surface structure to bulk structure.

IV.4.1.3 The nature of the granular structure

Assuming that the granular structure is not an artefact, one may obtain useful information by investigating it further.

Warshaw [96] suggested that the existence of a granular structure implies that the glass is inhomogeneous in bulk, and on a micro-scale consists of areas of varying bond strength. A fracture will propagate best in areas of weakest bonding (see Fig. 43) and a surface similar to that in Fig. 44 will be obtained. It should be noted that these ideas are not at variance with the idea of glass as an extended random network (Warren [96]).

We prepared samples for electron-microscopy similar to those used in Warshaw's investigation and as may be seen by comparing Figs. 44 and 45 the structures obtained were similar.

It might be added that "areas of weakest bonding" could well provide short-circuit paths in diffusion similar to "dislocation diffusion" in regular crystals.
FIG. 43. PROBABLE LINE OF WEAKEST BONDING BETWEEN SUB-STRUCTURES ACCORDING TO WARSHAW [92].
FIG. 44. FRACTURED SURFACE OF PYREX-BRAND GLASS. (150,000X) [92] WITH IMAGINARY LINE (A) INDICATING AREA OF WEAKEST BONDING.

FIG. 45. ELECTRON-MICROGRAPH PICTURE OF GLASS SURFACE, (30,000X), AFTER 400°C ANNEAL, FROM SPECIMEN USED IN THIS INVESTIGATION WITH IMAGINARY LINE (A) INDICATING AREA OF WEAKEST BONDING.
IV.4.1.4 The crevices

The most characteristic feature in the lower magnification micrographs are regular crevice-like structures, best described as "staircases". These structures are present in polished surfaces and also in surfaces from fractured glass. They are commonly held to be caused by shock-propagation of stresses caused by the fracturing process in the glass. This fracturing process can be crushing, polishing, scratching or similar mechanical operations. Fig. 46 shows an electron micrograph of the surface of a crushed specimen. The typical tapering steps of the "staircase" structure can be seen in the micrographs in Fig. 26, Fig. 32 and Fig. 46.

As far as the discussion in this thesis is concerned, the importance lies only in the fact that surface irregularities, like the ones shown in Fig. 47 at 10,000x magnification, definitely show the possibility of contamination by radioactive grinding debris. A radioactive particle trapped in a crevice like that shown in Fig. 47 can be hard to dislodge, even with ultrasonic cleaning.

Therefore, while these crevices are only artefacts caused by polishing they are important in the sense that since in the residual method they always form a feature of the surface facing the counter surface (e.g. surface of the scintillation crystal) they can cause false counts by trapping radioactive debris from previous grindings and cause an upward trend in the concentration vs penetration curves.

If an increase in activity with increasing penetration is caused by trapped ground-off particles why do upward "wriggles" in the profiles only occur near the surface? Presumably spurious trappings can take place at any depth or distance from the original surface of the specimen. This is true but trapped debris from layers near the original surface are much more radioactive than that of deeper layers. It might also be argued that the glass block has different
FIG. 46. SCANNING-ELECTRON MICROGRAPH OF SURFACE OF CRUSHED SPECIMEN (900°C) 800X.

FIG. 47. ANOTHER PART OF THE SURFACE SHOWN IN FIG. 46 ALSO TAKEN WITH SCANNING-ELECTRON MICROSCOPE 10,000X.
degrees of homogeneity at different distances from the original surfaces, so that the same kind of polishing procedure does not result in the same amount of corrugation at deeper penetrations.

Speculations about the significance of the basic granulated structure have been controversial (see also Section IV.1.2).

IV.5 Discussion of X-ray Diffraction Analysis on Vitreous Silica

In contrast to the many sharp diffraction peaks from crystalline material, Fig. 4c, No.9, glasses produce only a single broad peak, Fig. 4c No.10, on a strip chart recording. This peak will be referred to as the "diffraction" maximum.

Nash (1963) [95] found in X-ray diffraction analysis of silicate rock glasses that: "

"the 2θ position, the intensity, and the symmetry of glass diffraction maxima, vary systematically with the change in SiO₂ content of the glass".

In a subsequent paper [22], by the same author, a detailed investigation of 96 silicate glass specimens of varying composition confirmed the earlier conclusion that angular position of the diffraction maximum of glass is a function of the silica content of the glass and Fig. 48 illustrates this.

Does devitrification occur? X-ray diffraction analysis can tell us if any devitrification took place. If the glass had recrystallized in any significant measure, one would expect to find a diffractogram more "spiky" than "broad", more like Fig.4c, No.9 than Fig.4c, No.10. This is because glass and other non-crystalline substances only produce broad maxima of X-ray scattering in diffraction patterns.

From the diffractograms in the present investigation (Fig. 4, c, d, e) it can be seen that no devitrification has taken place.
IV.5.1 X-ray parameters of vitreous silica

To furnish a point of reference a small amount of pure Si was mixed with the sample. The spike at the left hand side at $2\theta = 28.5^\circ$ corresponds to the silicon peak. That the pure Si peaks vary in height from picture to picture is due to the fact that the amount of pure Si used for obtaining this peak was not the same for all specimens.

The method adopted to measure the $2\theta$ position, the intensity and the background level of the glass diffraction maximum is shown in Fig. 48. This method is one of many possible and is quite arbitrary. However, it has been proved to be the most simple and reproducible provided the diffraction maximum is adequately resolved [22]. Since the material used in the present investigation was SiO$_2$ with impurities present in only minute quantities (within the order of p.p.m.) one does not expect big changes in $2\theta$ value, and this is what is observed.

For the position of the diffraction maximum, $2\theta = (21.5 \pm 0.2)^\circ$ corresponding to $d = 4.2 \text{ Å}$.

One might well ask what significance the "statistical" spacing $d$ has in a material like glass, which has only short range order.

As early as 1915, Debye [97] and Ehrenfest [98] proved theoretically that diffraction maxima would be produced by glass if there are interatomic distances occurring repeatedly in the structure. The so-called "radial distribution analysis" commonly used in the X-ray study of glass (Grjothium, 1958 [99]) shows that the numerical value of these interatomic distances can be determined from observed scattering intensities. These distances in silicate glass correspond with the known interatomic distances of silica tetrahedrons and of arrays of tetrahedrons.

According to Tilton (1957) [15];

"glass can be thought of as composed of small clusters of definitely arranged but slightly disordered structural units, 'vitrons'," which in turn are composed of smaller more nearly regular units such as the SiO$_4$ tetrahedra. "Vitrons" tend to form in a melt and are capable of
FIG. 48. STRAIGHT LINE METHOD OF FIXING 2θ POSITION, PEAK INTENSITY AND BACKGROUND INTENSITY ACCORDING TO NASH [22].
limited continuous growth. Within this vitron structure there are prominent curved or hybrid "planes" in which numerous atoms are located and which produce coherent scattering of X-rays. There is a wide distribution of interplanar distances. Scattering of X-rays will occur from each of these planes, and the greater the density of planes with a given interplanar distance the more intense will be the X-ray scatter from that set of planes (and at the corresponding Bragg angle). Tilton [15] showed theoretically that a prominent set of planes defined by vitrons can exist in silica glass with a statistical d spacing of 4.2 Å.

The above concept suggests that a change in 2θ angle corresponds to changes in the interplanar distance (between pseudo crystal planes).

In the present investigation Fig. 4c, d, e show small changes in 2θ but not as markedly as in Fig. 49, where according to Nash [22] a definite trend could be seen, i.e. a decrease in SiO₂ content corresponding to increasing value of 2θ angle.

As remarked earlier, our approximately constant 2θ value confirms the constant SiO₂ content of our specimens.

A decrease in scattering intensity with decrease in SiO₂ content indicates that the "reflectivity" of the hybrid planes in the glass decreases, suggesting that the degree of disorder of planes and of the structure as a whole increases as the silica glass structure incorporates foreign atoms or molecules. This is clearly seen in Fig. 49 where there is a marked difference between the intensity for 88% and 40% SiO₂ content, but in our case, no such systematic variation was observed. It is true that the lowest value (at 622°C) and the highest value (for a specimen annealed at 722°C) differ by about 43%, but no definite conclusion can be drawn because the amount of material analysed was not the same.
FIG. 49. VARIATION OF 2θ with SiO₂ CONTENT ACCORDING TO NASH [22].
We can summarize the information given by our X-ray diffractograms as follows:

(1) no devitrification has taken place in the course of the experiment;

(2) the observed 2θ position corresponds to a d value of 4.2 Å characteristic of pure SiO₂;

(3) no definite conclusions can be drawn regarding the increase or decrease of order as a function of temperature.
CHAPTER V

CONCLUSIONS

1. The penetration plots show three regions of interest
   I. the near surface region
   II. the volume diffusion region
   III. the "diffusion-through channels" region.

2. The "upward wiggle" in region I (due to contamination) and the trend in the Arrhenius plot in region III are not evident if the glass specimens have been pre-annealed at about 900°C for a period of some months.

3. In region III which is due to "diffusion through channels" there is a change in slope at 570°C and D decreases as T increases.

4. The region II Arrhenius plot also shows a change in activation energy around 570°C. This is surmised to correspond to a transition from a predominantly β-configuration of the network in the lower temperature range to a predominantly α-configuration of the network in the higher temperature range.

5. The Arrhenius parameters for volume diffusion are:
   for germanium:
   \[ D = 8.2^{+6.7}_{-3.7} \times 10^{-10} \exp\left[-\frac{(0.70\pm0.06)\text{eV}}{kT}\right] \text{cm}^2/\text{sec between 570°C and 956°C} \]
   \[ D = 1.1^{+0.7}_{-0.4} \times 10^{-12} \exp\left[-\frac{(0.21\pm0.03)\text{eV}}{kT}\right] \text{cm}^2/\text{sec between 413°C and 570°C} \]
   for silver:
   \[ D = 6.0^{+4.8}_{-6.0} \times 10^{-2} \exp\left[-\frac{(1.51\pm0.02)\text{eV}}{kT}\right] \text{cm}^2/\text{sec between 570°C and 948°C} \]
   \[ D = 1.0^{+0.3}_{-0.2} \times 10^{-5} \exp\left[-\frac{(0.48\pm0.02)\text{eV}}{kT}\right] \text{cm}^2/\text{sec between 441°C and 570°C} \]
   for the runs made below 570°C; \( k = 8.62 \times 10^{-5} \text{ eV/°C} \).
6. The reason for the big difference in diffusion rate between silver and germanium is that they are located on different sites. The germanium ions are mainly at silicon sites whereas the silver is located between the silicon sites in "network modifying" sites. Tracers diffusing in vitreous silica may in general be divided into two classes:

(1) those with diffusion coefficients between $10^{-2} - 10^{-8}$ cm$^2$/sec including Ag, together with He, Ne, Na, K and Li.

(2) those with diffusion coefficients of the order of $10^{-12}$ cm$^2$/sec, including Ge, together with Al and O.

Ions of the first type are located on network modifying sites whereas ions of the second type are located on silica network sites.

7. For the diffusion of germanium and silver in vitreous silica we can tabulate the $f\Delta K$ values as follows

<table>
<thead>
<tr>
<th>Diffusing ion</th>
<th>$f\Delta K$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>one body mechanism</td>
</tr>
<tr>
<td>Ag</td>
<td>0.6 ± 0.2</td>
</tr>
<tr>
<td>Ge</td>
<td>0.7 ± 0.3</td>
</tr>
</tbody>
</table>

8. Probable diffusion mechanisms are:

<table>
<thead>
<tr>
<th></th>
<th>Diffusion mechanism</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ge</td>
<td>interstitialcy</td>
</tr>
<tr>
<td>Ag</td>
<td>interstitialcy, vacancy.</td>
</tr>
</tbody>
</table>
9. Variation of $Q$ through the transition region for germanium and silver diffusion in vitreous silica can be attributed to the change in network configuration with increasing temperature, from a predominantly $\beta$-configuration to a predominantly $\alpha$-configuration.

Changes in network configuration cause:

1. reduction in interatomic distances (during "squeezing").
   
   There will be changes in the repulsive forces and Coulomb interactions; $Q$ increases

2. decrease of $\pi$-bonding with neighbouring oxygens in the case of germanium, which is located on network sites;
   
   $Q$ decreases

3. reduction in "doorway" size; $Q$ increases.

The resultant variation of the activation energy in the transition region is therefore a balance between factors causing a decrease in activation energy and factors causing an increase in activation energy.

Comparison of diffusion of silver in Homosil in this thesis with diffusion of sodium and potassium in similar glasses by other workers makes it clear that:

(a) silver is located on network modifying sites;

(b) above 570°C the activation energy, $Q$, for Na, K and Ag seems to be a function of ionic size only;

(c) differences in diffusing behaviour between Ag, Na and K show differences in the change in $Q$ in the transition region which are not due to differences in the properties of the glasses used;

(d) the order of increase in $\delta Q(= Q_{\text{above } 570^\circ\text{C}} - Q_{\text{below } 570^\circ\text{C}})$ is also the order of increasing polarizability and this suggests a possible connection between diffusion behaviour and polarizability of the ions.
10. For future research, the analysis of the change of network structure during heating is recommended, since in the diffusion in such materials as glass, tracer diffusion cannot be done without heating the glass with its possible attendant change in network configuration. A post-annealing analysis of the matrix by X-ray diffraction or other means is of limited value since in cooling down to room temperature the network may have changed again.

X-ray analysis during heating is nowadays a distinct possibility.
APPENDIX I

The condition on $\sqrt{Dt}$, so that absorption can be neglected

Assuming that $D$ and the surface concentration are constant, the residual activity profile form will be given by Gruzin's equation without approximation:

$$A(x') = \frac{1}{\mu} \frac{dA(x')}{dx} = C_s \text{erfc} \left( \frac{x'}{2\sqrt{Dt}} \right)$$  \hspace{1cm} (1)

where $A(x') =$ activity remaining after removal of a thickness $x'$ measured from the surface of the solvent phase;

$\mu =$ absorption coefficient of the activity;

$D =$ diffusion coefficient;

$t =$ annealing time;

$C_s =$ a constant.

The formulae of the thesis give us the quantity $D'$ defined by

$$\frac{1}{2\sqrt{D't}} =$ slope of the least-squares fit of

$$(2i\text{erfc})^{-1}(A(x')/.886A(0)) \text{ vs. } x' \text{ to a straight line.}$$

$D' = D$, the diffusion coefficient, only if $\mu = 0$; for a non-zero $\mu$, $D'$ will differ from $D$ and the difference will increase with increasing $\mu$.

For the X-rays emitted by germanium $\mu = 50 \text{ cm}^{-1} = 0.005 \text{ pm}^{-1}$ (p. 131). Since $\sqrt{Dt} < 9 \mu m$ for all germanium profiles, $\mu \sqrt{Dt} < 0.045$ and so the maximum error will be given by the difference between $D$ and $D'$ for $\mu \sqrt{Dt} = 0.045$. We obtain bounds to $D'$ by calculating $(2i\text{erfc})^{-1}(A(x')/.886A(0))$ for various values of $x'$ and considering the bounds to the least-squares slope of

$(2i\text{erfc})^{-1}(A(x')/.886A(0)) \text{ vs. } x'$ which the calculations imply.

First we derive an explicit formula for $A(x')/A(0)$ from (1) above.

After a thickness $x'$ has been removed the activity remaining, $A(x')$, can be expressed as
\[ A(x') = \int_{x'}^{\infty} C_s \text{erfc}\left( \frac{x}{2\sqrt{Dt}} \right) \exp \left( -\mu(x-x') \right) dx \] (2)

\[ = C_s \exp (\mu x') \int_{x'}^{\infty} \text{erfc}\left( \frac{x}{2\sqrt{Dt}} \right) \exp (-\mu x) dx \] (3)

\[ = -\frac{C_s}{\mu} \exp (\mu x') \int_{x'}^{\infty} \text{erfc}\left( \frac{x}{2\sqrt{Dt}} \right) \frac{d}{dx} \exp (-\mu x) dx \] (4)

\[ = -\frac{C_s}{\mu} \exp (\mu x') \left[ \text{erfc}\left( \frac{x}{2\sqrt{Dt}} \right) \exp (-\mu x) \right]_{x'}^{\infty} \]

\[ = -\int_{x'}^{\infty} \frac{2}{\sqrt{\pi}} e^{-x^2/4Dt} \cdot \frac{1}{2\sqrt{Dt}} \exp (-\mu x) dx \] (5)

Integrating by parts gives

\[ = \frac{C_s}{\mu} \text{erfc}\left( \frac{x}{2\sqrt{Dt}} \right) - \frac{C_s}{\mu} \exp (\mu x') \int_{x'}^{\infty} \frac{1}{\sqrt{\pi Dt}} \exp \left( -\frac{x^2}{4Dt} - \mu x \right) dx \] (6)

\[ = \frac{C_s}{\mu} \text{erfc}\left( \frac{x}{2\sqrt{Dt}} \right) - \frac{C_s}{\mu} \exp (\mu x') \frac{\exp (\mu^2 Dt)}{\sqrt{\pi Dt}} \cdot \]

\[ \int_{x'}^{\infty} \exp \left[ -\left( \frac{x}{2\sqrt{Dt}} + \mu \sqrt{Dt} \right)^2 \right] dx \] (7)

If we write \( u = \frac{x}{2\sqrt{Dt}} + \mu \sqrt{Dt} \) we can evaluate the integral,

\[ \int_{x'}^{\infty} \exp \left[ -\left( \frac{x}{2\sqrt{Dt}} + \mu \sqrt{Dt} \right)^2 \right] dx = \int_{x'}^{\infty} e^{-u^2} \cdot 2\sqrt{Dt} du \]

\[ = \frac{\sqrt{\pi}}{2} 2\sqrt{Dt} \text{erfc}\left( \frac{x}{2\sqrt{Dt}} + \mu \sqrt{Dt} \right) \] (9)

so that now writing in terms of \( \frac{x'}{2\sqrt{Dt}} \) and \( \mu \sqrt{Dt} \) only we get for the activity

\[ A(x') = \frac{C_s}{\mu} \left[ \text{erfc}\left( \frac{x}{2\sqrt{Dt}} \right) - \exp \left[ \mu \sqrt{Dt} \left( \frac{2x'}{2\sqrt{Dt}} + \mu \sqrt{Dt} \right) \right] \right] \cdot \text{erfc}\left( \frac{x}{2\sqrt{Dt}} + \mu \sqrt{Dt} \right) \] (10)

in which \( A(x') \) is explicitly expressed as a function of \( \frac{x'}{2\sqrt{Dt}} \) and \( \mu \sqrt{Dt} \) only.

\[ A(x') / 0.886A(0) \] was calculated from (10) for \( \mu \sqrt{Dt} = 0.045 \) and \( x = 0, 0.2\sqrt{Dt}, 1.0\sqrt{Dt}, 2.0\sqrt{Dt}, 3.0\sqrt{Dt} \) and \( (2\text{erfc})^{-1}(A(x')/0.886A(0)) \) was then found.
The values of \((\text{erfc})^{-1}(A(x')/0.886A(0))\) are tabulated below together with the values of \((\text{erfc})^{-1}(A(x')/0.886A(0))\) for \(\mu = 0\) for comparison. It is clear that in the experimental range of \(x'\), the least-squares slope and \(1/2\sqrt{D't'}\) for \(\mu\sqrt{Dt} = 0.045\) will be less than 1\% lower than \(1/2\sqrt{Dt}\) except perhaps for very small \(x'\), so that \(D'\), the measured diffusion coefficient, will be no more than 3\% greater than the true diffusion coefficient \(D\) for any germanium profile.

<table>
<thead>
<tr>
<th>(x'/2\sqrt{Dt})</th>
<th>(\text{(2ierfc)}^{-1}(A(x')/0.886A(0)))</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(\mu = 0) (\mu = 0.045) (\mu = 0.01)</td>
</tr>
<tr>
<td>0</td>
<td>0 (0) (0)</td>
</tr>
<tr>
<td>0.1</td>
<td>0.1 (0.0989) (0.0998)</td>
</tr>
<tr>
<td>0.5</td>
<td>0.5 (0.496) (0.499)</td>
</tr>
<tr>
<td>1.0</td>
<td>1.0 (0.992) (0.998)</td>
</tr>
<tr>
<td>1.5</td>
<td>1.5 (1.495) (1.498)</td>
</tr>
</tbody>
</table>

The table also gives the results for \(\mu\sqrt{Dt} = 0.01\). In this case the error in the diffusion coefficient produced by assuming \(\mu = 0\) will be less than 1\%, i.e., negligible. The absorption coefficient of the silver \(\gamma\)-rays was calculated to be \(0.169 \text{ cm}^{-1} = 1.69 \times 10^{-5} \text{ \mu m}^{-1}\) so that the effect of absorption will be negligible if \(\sqrt{Dt} < 590 \text{ \mu m}\) which was always the case for the silver diffusion profiles.
APPENDIX II

a. Obtaining values of fΔK from the experimental data

\[ f = \frac{1 - \frac{D_\alpha}{D_\beta}}{1 - \frac{W_\alpha}{W_\beta}} \]

(1)

\[ D_\alpha = \text{diffusion coefficient of isotope } \alpha \]

\[ D_\beta = \text{diffusion coefficient of isotope } \beta \]

\[ W_\alpha = \text{jump rate of isotope } \alpha \]

\[ W_\beta = \text{jump rate of isotope } \beta \]

\[ 1 - \frac{W_\alpha}{W_\beta} = \left( 1 - \left[ \frac{(n-1)M + M_\beta}{(n-1)M + M_\alpha} \right]^{1/2} \right) \Delta K \]

(2)

where \( M_\beta = \text{mass of isotope } \beta \)

\( M_\alpha = \text{mass of isotope } \alpha \)

\( M = \text{average mass of the non-tracer atoms involved in the diffusion.} \)

For a mechanism in which two atoms jump simultaneously, such as an exchange or interstitialcy mechanism, \( n = 2 \).

Substituting \( n = 2 \) in equation (2) we get

\[ 1 - \frac{W_\alpha}{W_\beta} = \left( 1 - \left[ \frac{M + M_\beta}{M + M_\alpha} \right]^{1/2} \right) \Delta K \]

(3)

\( M = 28 \text{ atomic units (Si)} \)

\( M_\beta = 71 \text{ atomic units (Ge)} \)

\( M_\alpha = 68 \text{ atomic units (Ge)} \)

which gives

\[ \left( \frac{M + M_\beta}{M + M_\alpha} \right)^{1/2} = \left( \frac{28 + 71}{28 + 68} \right)^{1/2} = 1.0155 \]

(4)
From the isotope experiment data we find

\[
\frac{D_\alpha}{D_\beta} = 1.015.
\]

so that

\[
f\Delta K = \frac{1 - (1.015)}{1 - (1.0155)} = 1.0 \pm 0.5 .
\]  \hspace{1cm} (5)

Similarly for a "one-atom" jump mechanism such as a vacancy or interstitial mechanism we calculate \( f\Delta K = 0.7 \pm 0.3 \).

For the diffusion of germanium and silver in vitreous silica we can tabulate the results as in Table VI.

<table>
<thead>
<tr>
<th>Diffusing Ion</th>
<th>( n = 1 )</th>
<th>( n = 2 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ag</td>
<td>0.6 ± 0.2</td>
<td>0.8 ± 0.2</td>
</tr>
<tr>
<td>Ge</td>
<td>0.7 ± 0.3</td>
<td>1.0 ± 0.5</td>
</tr>
</tbody>
</table>

**Table VI**
The isotope effect

b. The importance of a zero-isotope effect line

The isotope effect is determined by studying the dependence of the ratio $\frac{C_\alpha}{C_\beta}$ of concentrations of two isotopes $\alpha$ and $\beta$ on the concentration $C_\alpha$, of isotope $\alpha$. Because the isotope effect is small, the ratio is not a sensitive function of $C_\alpha$; $\ln(C_\alpha/C_\beta)$ will rarely change by more than 0.1 - 0.2 over a large range of $\ln C_\alpha$. Thus even a small systematic non-isotope effect dependence of $\ln(C_\alpha/C_\beta)$ on $\ln C_\alpha$ will effectively invalidate the results.

Even if precautions are taken e.g. pure isotopes are used, fixed counting geometry etc. minor faults in the counters or in the procedure of extracting isotope ratios from the measured counts could cause $C_\alpha/C_\beta$ to depend on the count rate; if a 100-fold dilution makes a difference of only 10% in $C_\alpha/C_\beta$ a spurious effect of the same magnitude as the true isotope effect will occur and render the experiment meaningless. Thus counts must be taken concurrent with the actual experiments of samples all having the same isotope ratio but with different count rates; these counts are then processed in the same way as the actual sections to obtain $C_\alpha/C_\beta$ and $C_\alpha$. If the $\ln(C_\alpha/C_\beta)$ vs. $\ln C_\alpha$ line so obtained is horizontal no systematic error from a dependence of $C_\alpha/C_\beta$ on count rate will arise in the isotope effect measurements; if this line is not horizontal, the procedure of obtaining $C_\alpha/C_\beta$ must be changed or corrections made.

In Section II.5 (p. 36, 41) a procedure for checking systematic errors was given. In addition zero isotope effect lines for both the
For both Ge and Ag a mixture of the isotopes was dissolved. From this first mixture various dilutions were made and deposited on planchets by decantation and subsequent evaporation. The count rate of the different planchets was then measured using the same method as used for the planchets in the isotope experiment (see Appendix IV).

The resultant slope in the case of the zero isotope effect line for germanium diffusion was $-0.0007 \pm 0.0007$ and for silver diffusion $-0.0002 \pm 0.0007$ by least-squares fitting. The errors here are standard errors based on the scatter of the experimental points. In both cases the slope appears to be close to zero. The slope of the isotope effect line for germanium is $-0.0129 \pm 0.0047$. Thus the ratio of the observed difference between the slopes of the isotope effect line and its corresponding zero isotope effect line to the standard error of this difference is 2.5. The probability of such a value being found by chance alone is of the order of 10%.

For silver the slope of the isotope effect line is $-0.0128 \pm 0.0013$. Hence the ratio of the observed difference between the slopes of the isotope effect line and the corresponding zero isotope effect line to the standard error of this difference is 8.5. The probability of this value being found by chance alone is of the order of $10^{-6}$.

It would appear therefore that both isotope effect experiments are meaningful when judged on the bases of the observational errors involved.
APPENDIX II

The isotope effect

c. Some isotope-effect results in crystalline materials, glass and liquids and their relevance to the present work

1. The isotope effect for crystals

Isotope effect measurements have been made in several classes of crystalline materials. Measurements for self-diffusion in f.c.c. and h.c.p. metals, [117] alkali halides [28] and cesium [130] have given $f\Delta K$ values of 0.5 - 0.8, consistent with the vacancy mechanism believed to be predominant in these materials. They have given values of $\Delta K$ which show that most but not all of the kinetic energy of the motion resides in the migrating atom [28].

For interstitial diffusion, $f\Delta K$ for the heavier isotopes is generally 1 within the limits of error, that is, there is no disturbance of the host lattice during the jump. For the diffusion of H in metals which also proceeds interstitially, the value of $f\Delta K$ is reduced below 1, probably by quantum effects, [28]. These considerations suggest that diffusion in our case is not controlled by a simple interstitial mechanism.

Interstitialcy self-diffusion isotope effects have been measured for only a few cases. For silver in AgBr and AgCl it was found that for a direct interstitialcy jump, $\Delta K = 1$, as is the case for interstitial diffusion, while $\Delta K$ for an indirect interstitialcy jump was small [78]. This indicates that the idealized picture of an indirect interstitialcy jump is not correct as it is a process in which the surrounding atoms play an important part.

B.c.c. metals have a more open structure and so might more closely resemble glass in their diffusion properties. For b.c.c. metals $f\Delta K$ is smaller than for f.c.c. metals so that if a vacancy mechanism holds, the
participation of neighbouring atoms is greater than for f.c.c. materials.

Our results give high values of $f\Delta K$ and so one ought not to draw parallels with these materials.

Measurements of impurity diffusion isotope effects in metals have been done to check the theories giving the impurity diffusion correlation factor and to use those theories to calculate jump-frequencies [118]. The agreement of the calculated correlation factor with experiment can sometimes be used to determine the mechanism of diffusion [119]. The impurity diffusion correlation factor is in general temperature dependent and so to compare theoretical enthalpies with experimental ones, one should subtract out the correlation factor contribution determined by isotope effect measurements [120]. The theory of the correlation factor as developed in the above work would not apply to glass, and so at present impurity diffusion correlation factors can only be used to eliminate some of the possible diffusion mechanisms, or to isolate a contribution to the activation energy.

2. The isotope effect for glass

He and Ne probably diffuse by an interstitial mechanism in SiO$_2$ glass. For Ne, $f\Delta K = 1$ [121] and for He the deviation of $f\Delta K$ from 1 can be explained by quantum effects [122]. Thus the interstitial mechanism $f\Delta K$ is still 1, supporting the argument that $f\Delta K$ values for Ag and Ge diffusion in SiO$_2$ glass make interstitial mechanisms unlikely.

For diffusion of Na in sodium silicate glass, $f\Delta K$ from the isotope effect was found to be about 0.25 in the 350°C - 430°C range [123] and comparison with $f_\sigma$ suggested an interstitialcy-type mechanism.

In our case $f\Delta K$ seems to be larger than for Na diffusion in silicate glass, so that there is apparently some change in diffusion properties in going from sodium silicate glass to SiO$_2$ glass even though it
appears there is no change over a wide range of Na$_2$O content in sodium silicate glass.

3. The isotope effect for liquids

The isotope effect for tracer diffusion is small or negligible for self diffusion in benzene and the diffusion of benzene in other simple hydrocarbons [124] [125], for hydrogen diffusion in liquid nitrogen [126] and for alkali-ion diffusion in alkali halide-water solutions [127]. However, the significance of the alkali-ion results is uncertain because of the doubt as to the number of water molecules which are attached to the ion and make up part of the effective mass of the diffusing particle.

Generally speaking diffusion in liquids does not consist of a series of activated jumps involving the diffusing atom and a few neighbours but involves a large number of atoms at each step of the process. The "jump distances" are smaller than inter-atomic distances and the "jump frequencies" are of the same order as the thermal vibration frequencies [128]. When the isotope tracer used is changed, only a small proportion of the atoms in the liquid is altered. In a typical diffusion step only a few of the atoms participating will be altered so that the rate of diffusion will not be change much i.e. the isotope effect would be expected to be small.

It should be noted however, that the values of $\frac{D(\text{HDO in H}_2\text{O})}{D(\text{HTO in H}_2\text{O})} - 1$ and $\frac{D(\text{HDO in D}_2\text{O})}{D(\text{DTO in D}_2\text{O})} - 1$ are appreciably different from zero. They are about one half of what would be predicted by a proportionality of diffusion rate to the inverse square root of the mass [129]. Water is in many respects an anomalous liquid and it may be that to a considerable extent a fixed structure persists above the melting point so that diffusion is a "single-atom" activated process as in most solids.

In SiO$_2$ glass and sodium-silicate glass the isotope effect is non-negligible (this thesis and [123]). The atoms in a glass will be vibrating
about fixed positions most of the time just as is the case in a crystal and so this non-negligible $f\Delta K$ value is plausible; diffusion in both glasses and crystals is an activated process. As far as diffusion is concerned glass behaves like a crystal without long range order rather than like a liquid.
APPENDIX III

The justification for the use of the "wrong" solution

For Gaussian concentration profiles, the slope of the
\[ \ln(C_\alpha/C_\beta) \text{ vs. } \ln C_\alpha \] plot equals \( 1 - \frac{D_\alpha}{D_\beta} \) exactly (see also p. 50, this thesis).

We shall show that for error function concentration profiles the slope is of
the same order of magnitude at large penetrations and can be used to find
\[ 1 - \frac{D_\alpha}{D_\beta}, \] at least approximately.

Assuming that \( x_s = 0 \), eqn. (16), p. 46 implies that
\[
\ln C_\alpha = \ln C_{\alpha s} + \ln \text{erfc} \left( \frac{x}{2\sqrt{D_\alpha t}} \right)
\]
\[
\ln C_\beta = \ln C_{\beta s} + \ln \text{erfc} \left( \frac{x}{2\sqrt{D_\beta t}} \right).
\]

The slope of the \( \ln(C_\alpha/C_\beta) \) vs. \( \ln C_\alpha \) plot
\[
\frac{d}{d \ln C_\alpha} \frac{d\ln(C_\alpha/C_\beta)}{dx}
= \frac{d\ln(C_\alpha/C_\beta)}{dx} \cdot \frac{dx}{d \ln C_\alpha}
= 1 - \frac{(d \ln C_\beta/dx)}{(d \ln C_\alpha/dx)}
= 1 - \frac{\sqrt{D_\alpha}}{\sqrt{D_\beta}} \frac{\exp(x^2/4D_\alpha t) \text{erfc}(x/2\sqrt{D_\alpha t})}{\exp(x^2/4D_\beta t) \text{erfc}(x/2\sqrt{D_\beta t})}.
\]

One might hope to proceed further by using the asymptotic expansion
of \( \exp(j^2) \text{erfc} j \). Unfortunately in the range of \( x/2\sqrt{D_\alpha t} \), \( x/2\sqrt{D_\beta t} \) of
interest in diffusion experiments several terms of the expansion are
required to obtain a good representation of the function and no simple
mathematical formula for the slope can be found; the slope must be
calculated either from the expansion or from tables.

The slope can be written as \(1 - \frac{D^\alpha}{D^\beta}\) multiplied by a function of \(x/2\sqrt{D^\alpha/\tau}\) and \(D^\alpha/D^\beta\) which we write as \(q(x/2\sqrt{D^\alpha/\tau}, D^\alpha/D^\beta)\). Since we would expect \(0 < f\Delta K < 1\), the value of \(D^\alpha/D^\beta\) for either pair of isotopes used in our experiments will be between 1.0 and 1.025. The count rates used experimentally suggested that calculations could be restricted to \(x/2\sqrt{D^\alpha/\tau} < 2.5\). Accordingly the function \(q\) was calculated from tables [113] for various values of \(x/2\sqrt{D^\alpha/\tau}\) and \(D^\alpha/D^\beta\) in the ranges mentioned above.

### TABLE VII

<table>
<thead>
<tr>
<th>(x/2\sqrt{D^\alpha/\tau})</th>
<th>(q(x/2\sqrt{D^\alpha/\tau}, D^\alpha/D^\beta))*</th>
</tr>
</thead>
<tbody>
<tr>
<td>.25</td>
<td>.62</td>
</tr>
<tr>
<td>.5</td>
<td>.71</td>
</tr>
<tr>
<td>1.0</td>
<td>.82</td>
</tr>
<tr>
<td>1.5</td>
<td>.88</td>
</tr>
<tr>
<td>2.0</td>
<td>.92</td>
</tr>
<tr>
<td>2.5</td>
<td>.95</td>
</tr>
</tbody>
</table>

* for \(\frac{D^\alpha}{D^\beta}\) between 1.001 and 1.025.

It was found that the value of \(q\) at a given \(x/2\sqrt{D^\alpha/\tau}\) varied by less than ±.01 as \(D^\alpha/D^\beta\) varied between 1.001 and 1.025, so that a sufficiently accurate representation of \(q(x/2\sqrt{D^\alpha/\tau}, D^\alpha/D^\beta)\) will be obtained for our purpose by considering \(q\) as a function of \(x/2\sqrt{D^\alpha/\tau}\) only. Table VII gives \(q\) as a function of \(x/2\sqrt{D^\alpha/\tau}\); the values are accurate to ±.01 for any \(D^\alpha/D^\beta\) between
1.001 and 1.025.

It may be seen that the slope does approach \( 1 - \frac{D \alpha}{D \beta} \) at large penetrations, but that for the penetrations found experimentally it is a poor approximation to take the slope as \( 1 - \frac{D \alpha}{D \beta} \).

If we only take sections with \( x > \sqrt{D \alpha} \tau \) the slope obtained by fitting \( \ln(C_\alpha/C_\beta) \) vs. \( \ln C_\alpha \) to a straight line by least-squares will certainly lie between \( 0.7 \left( 1 - \frac{D \alpha}{D \beta} \right) \) and \( 1 - \frac{D \alpha}{D \beta} \), i.e. it will equal \( (0.85 \pm 0.15) \left( 1 - \frac{D \alpha}{D \beta} \right) \) as was assumed in our analysis. If the sections used for the least-squares fit are spread over a range of \( x \) on either side of \( x = 2\sqrt{D \alpha} \tau \) the error in taking the slope as \( 0.85 \left( 1 - \frac{D \alpha}{D \beta} \right) \) will be less than \( \pm 0.15 \left( 1 - \frac{D \alpha}{D \beta} \right) \).
APPENDIX IV

Experimental techniques including error analysis

a. Procedure used for the annealing and sectioning in the diffusion
   of Germanium and Silver in SiO$_2$-glass (Homosil)

(I) The Homosil glass plate as received from the factory was cut into
    blocks approximately 1 x 1 x 0.8 cm, with a diamond slitting wheel
    in a converted lath. The glass plate was clamped on a stage
    travelling in precision machined grooves perpendicular to the
    longitudinal axis of the lath.

(II) The glass blocks were given a preliminary ultrasonic cleaning for
     10 sec. with Freon as a cleaning fluid.

(III) No pre-annealing has been carried out with the specimens investigated
      for this thesis.

(IV) A fixed amount of solution containing NH$_4$OH to prevent clouding and
      some tracer was deposited on the upper surface of the glass block
      (see also II.3, page 28, this thesis).
      The amount of solution was 0.1 ml, deposited with a calibrated
      microsyringe.

(V) The glass block with the drop of diffusant on it was placed
    beneath an infrared lamp for 10 min. for the solution to dry.

(VI) A second glass block was put on top of the first one so that the
     diffusant was sandwiched between the two glass blocks. The blocks
     were then tied together with Pt wire.

(VII) The "sandwich" was placed in a one inch diameter fused silica tube
      and the tube inserted into a Stanton Redcroft furnace (with Kanthal
      strip element; max. temperature: 1300°C) which was thermo-
      statically controlled within one Celsius degree (see Fig. 50).

(VIII) The sample temperature was measured by a Pt/(Pt+10% Rh) thermo-
couple placed inside the fused silica tube with the thermocouple junction placed as close as possible to the interface between the glass blocks.

The cold junction of the thermocouple was connected with compensating leads to a cold junction thermostat, which was connected by copper wires to a Leeds and Northrup K-3 Universal Potentiometer. At intervals the potentiometer voltage was read to the nearest μV, and, the cold junction temperature being known, the temperature of the thermocouple hot junction could be determined from tables. The time at which the reading was taken was recorded to the nearest minute.

The thermocouple hot junction temperatures so obtained were converted to 1968 International Scale temperatures by using a calibration of the thermocouple against a thermocouple calibrated by N.B.S., with both the thermocouple hot joints in close contact with each other. This calibration was repeated every few months in case changes occurred.

The junction temperature was monitored between potentiometer readings by a Leeds and Northrup Speedomax type-W recorder. This allowed corrections to be made in the case of power failures. The temperature during the annealing was taken as the average of the corrected temperature readings.

(IX) After diffusion annealing the "sandwich" was taken out of the fused silica tube and the glass blocks were stored in labelled vials.

(X) As well as diffusing in from the interface, tracer will diffuse over the whole surface and then diffuse into the glass blocks from all sides. The non-interface diffusion was not taken into account in the solutions of the diffusion equation used and so its effects must be eliminated. To do this a layer of a thickness of at least three times the estimated $\sqrt{Dt}$ was removed from each of the block
surfaces except for the interface surface. The layer was ground off with 6 µm diamond paste deposited on a glass microscope slide (see Fig. 51), the amount removed being determined with a micrometer screw gauge. After grinding and polishing the microscope slide was discarded; a new microscope slide was used for every grinding and polishing cycle so that no radioactive contamination of surfaces could take place.

Disposable or rubber gloves were worn during the grinding and in all subsequent handling of the blocks to avoid body contamination.

(XI) The glass specimen as prepared in (X) was weighed on a Mettler H-20 balance reading to $10^{-5}$ g, taking the average ($W_1$) of 10 weighings.

(XII) The radioactivity present in the glass specimen was measured. Care was taken to preserve geometry. Statistical uncertainty was minimized by taking more than $10^4$ counts. The counting set up is showing in Fig. 52, Fig. 53 and Fig. 54.

Before and after a count was taken, a standard consisting of the same tracer as the diffusant was counted.

The counting sequence was therefore as follows:

(a) background (for about 1000 counts)

(b) standard (to better than 0.3%)

(c) sample (to better than 1%)

(d) standard (to better than 0.3%)

(e) background (for about 1000 counts).

The averaged background was subtracted from the sample and average of the standard counts. The ratio of the sample count rate minus the average background count rate to the mean value of the two standard count rates gave the relative activity of the block. This counting sequence reduced the errors from the following causes.
(1) electronic drift in the counting circuits
(2) decay of the radioisotope during sample analysis
(3) effect of temperature fluctuations on noise level and gain of the photomultiplier
(4) variations in background level which occur particularly after falls of rain.

After the count a layer was ground off the interface surface with diamond paste deposited on a glass microscope slide. The grinding was started with 9 μm paste and successively finer grades were used. The final polish was done with 1/4 μm paste.

To obtain absolutely parallel and flat ground surfaces it might be considered to be better to mount the specimen on a grinder and grind on rails as originally proposed by de Bruin and Watson [108]. However a metal grinder of the usual type is so heavy that it will exceed the capacity of the precision balance used, and it was therefore decided not to use this method.

To make sure that the ground surface was flat, the interference fringes in the film between the polished surface and an optical flat were observed. They were almost straight and widely spaced, indicating that the surface was flat to much better than 1 μm.

To make sure that parallel layers were removed, comparator readings were taken at various points on the surface being ground (e.g. at the corners and in the middle) before and after each grinding. The difference between the comparator readings before and after each grinding was the same within the limits of error for different points on the surface and the calculated thickness removed agreed with that calculated from the weight differences so that parallel layers were in fact removed.

After grinding and polishing the block was ultrasonically cleaned
and weighed as before giving an average weight, $W_{II}$.

(XIII) The area of the interface surface was then computed from the mean length and the mean breadth of the specimen measured with a travelling microscope. The difference $(W_I - W_{II})$, the known specific gravity of the material taken off (2.205 g/cm$^3$) together with the calculated surface of the layer taken off gives the thickness removed

$$x_1 = \frac{\text{weight difference}}{\text{specific gravity}} \times \frac{1}{\text{surface}} \text{ in appropriate units.}$$

The first count rate of a sectioning run being quite high, there was only a short interval between obtaining $W_I$ and $W_{II}$ despite the fact that $W_I$ was taken before the count and $W_{II}$ after, so that no error in the weight arose from this cause.

(XIV) A count was taken as before with the following sequence:
(a) background
(b) standard (using the same standard as the previous count)
(c) sample
(d) standard
(e) background.

The ratio

$$A(x_1) = \frac{\text{sample count rate} - \text{av. background count rate}}{\text{av. standard count rate} - \text{av. background count rate}}$$

was then calculated. $A(x_1)$ is therefore the relative activity after a thickness $x_1$ has been removed.

(XV) The experimental procedure then proceeded in cycles; the $n$th cycle will be as follows:
(a) weighing ($W_I$)
(b) optical measurement of the area of the surface which is being ground down
(c) weighing \( W_{11} \)

(d) calculating the thickness \( x_n \) removed during (b);

the total thickness removed since sectioning began will be

\[ x_1 + x_2 + \ldots + x_n \]

(e) counting (background, standard, sample, standard, background).

The standard used was the same for all counts for a given block.

(f) \( A(x_n) \) was calculated.

With the long counting times necessary when working at sample count rates approaching background level, counting was interrupted to check on standard and background and the values averaged out. This was found more reliable than a continuous sample count taken over several hours.

(XVI) Determination of the diffusion coefficients from the profiles was not straightforward. For the boundary conditions found experimentally and for a constant diffusion coefficient,

\[ A(x)/A(o) = 0.886 \times \text{erf(c}(x/2\sqrt{Dt}) \] (eqn. (23) p. 48 of the thesis)

where \( A(o) \) is the total activity from the dissolved tracer. This equation implies that a plot of \((\text{erf}(c(\text{A}(x)/.886A(o))) \] vs. \( x \)

will be a straight line whereas the experimental profiles give a plot consisting of two straight lines within experimental error for any reasonable \( A(o) \). This indicates that a block was not a homogeneous medium with respect to diffusion, i.e. diffusion in it could not be described by a single \( D \). If diffusion is a mixture of bulk and "short-circuit" diffusion (see IV.4) the profile can be treated approximately as a superposition of two error function profiles. (See [3], p. 690 et seq. The diffusion coefficient of region II will be approximately equal to the bulk diffusion coefficient and the diffusion coefficient of region III will be relate
Accordingly separate diffusion coefficients were obtained for each profile for regions II and III. 

A(o) for region II was found by extrapolating back to x = 0 on the A(x) vs. x plot from the part of the profile coming from dissolved tracer, A(o) for region III by extrapolating back to x = 0 from region III of the A(x) vs. x plot. If the experimental profile was exactly a superposition of two independent profiles, A(o) for region III should be subtracted from A(o) for region II found as above in order to obtain the correct A(o) for region II; however according to theory the profile is not an exact superposition and this refinement makes little difference to the value of D, so that this was not done.

Having obtained A(o), A(x)/.886A(o) was calculated for each point in the appropriate region, \((2ierfc)^{-1}(A(x)/.886A(o))\) worked out from the tables of Carslaw and Jaeger [107] and the least-squares slope of \((2ierfc)^{-1}(A(x)/.886A(o))\) vs. x found. This gave \(1/2\sqrt{Dt}\) and D could then be found.

(XVII) The value of \(x_s\), the thickness of the surface layer, was estimated by noting that for \(x > x_s\) the slope of A(x) vs. x began to decrease rapidly. The slope of A(x) vs. x at \(x = x_s\) gives \(C_s\), the solubility limit, shown in Fig. 8 and 15. The thickness of the surface layer was small.

**ISOTOPE EFFECT RUNS**

(a) The procedure up to step (XII) above was the same for isotope effect runs, except that the deposited solution contained a mixture of two tracers instead of just one tracer. From then on the procedure was
different because in this case individual sections were counted, not
the residual activity as sections were removed.

(b) A set of sections was prepared for counting as described on p. 35 of
the thesis (see also Fig. 55 and 56).

The weight of the planchet and diamond paste ready for grinding was
found, before grinding, and compared with the weight, after grinding,
of the planchet + grindings + the dried washings from the glass
specimen. The difference will give the weight of the material counted
exactly. This difference may not be equal to the weight of the block
before grinding minus the weight after grinding because of losses
during washing. A correction was made to the observed count rate for
losses of this type.

The sections within a distance of at least $\sqrt{\frac{t}{\Delta t}}$ of the surface were not
counted, in order to reduce the error resulting from the use of
Gaussian equations in our case (see Appendix III).

(c) To minimise the effects of counter drift the sections were counted in
random order. For the germanium isotope effect the order of counts for
each section was: background, standard, section, standard, background.
The standard was a mixture of the tracers being used.

About six months later the count was repeated and for some sections
the count was repeated again later.

For the silver isotope effect, the order of counts for each section was:
with discriminator set to channel 1, background, standard, section,
standard, background

```
" " " " " 2, background
" " " " " 1, standard
" " " " " 2, section
" " " " " 1, standard
" " " " " 2, background.
```

For the description of channel 1 and channel 2, see Fig. 5, p. 37.

(d) After this the isotope ratio for each section was calculated using the
half-life method for germanium (see below) and the energy separation method for silver, (see p. 51).

(e) Correlation factors were then calculated from appropriate plots (see p. 50 et seq. and Appendix III).

THE CALCULATION OF THE RATIO OF TWO ISOTOPES BY THE HALF-LIFE METHOD

We choose an arbitrary time as \( t = 0 \); the same \( t = 0 \) is used for all sections from the same block.

Suppose that for a particular section the count rate from the mixture of isotopes \( \alpha \) and \( \beta \) at

\[
t = t_1 \text{ was } M^* \text{ counts/sec and at } \quad t = t_1 + t_2 \text{ was } N^* \text{ counts/sec.}
\]

The half-lives \( T_{\alpha} \) and \( T_{\beta} \) of isotopes \( \alpha \) and \( \beta \) being known, the decay constants \( \lambda_\alpha \) and \( \lambda_\beta \) are given by

\[
\lambda_\alpha = \frac{\ln 2}{T_\alpha} \quad \lambda_\beta = \frac{\ln 2}{T_\beta}.
\]

Suppose that at \( t = 0 \) the count rates for the two isotopes were \( I_\alpha \) and \( I_\beta \) counts/sec then

\[
M^* = I_\alpha e^{-\lambda_\alpha t_1} + I_\beta e^{-\lambda_\beta t_1} \quad (1)
\]

\[
N^* = I_\alpha e^{-\lambda_\alpha (t_1 + t_2)} + I_\beta e^{-\lambda_\beta (t_1 + t_2)} \quad (2)
\]

Solving (1) and (2) for \( I_\alpha \) and \( I_\beta \) we arrive at the required ratio:

\[
\frac{I_\beta}{I_\alpha} = \frac{e^{-\lambda_\alpha t_1} (N^* - M^* e^{-\lambda_\beta t_2})}{e^{-\lambda_\beta t_1} (M^* e^{-\lambda_\alpha t_2} - N^*)} \quad (3)
\]

All the quantities on the right hand side are known and so the ratio of count rates at \( t = 0 \) can be calculated. This will be equal to the ratio of concentrations times a factor which will be the same for all the sections.
FIG. 50. STANTON REDCROFT ANNEALING FURNACE WITH FUSED SILICA TUBE INSERTED.
FIG. 51. GLASS BLOCK ON MICROSCOPE SLIDE WHICH IS USED AS A GRINDING BASE.
FIG. 52. O.R.T.E.C. MODULAR COUNTING ARRANGEMENT WITH LEAD CASTLE AND SCINTILLATION COUNTER.
FIG. 53. PLANCHET IN ISOTOPE EXPERIMENT IN COUNTING POSITION.
FIG. 54. GLASS BLOCK IN COUNTING RACK WITH CONSTANT HORIZONTAL POSITION AND VARIABLE VERTICAL POSITION.
FIG. 55. MODIFIED PLANCHET USED AS COMBINED GRINDING BASE AND COUNTING PLANCHET.

FIG. 56. GLASS BLOCK BEING GROUND ON CIRCULAR MICROSCOPE COVER GLASS ARALDITE BONDED TO BOTTOM OF PLANCHET.
APPENDIX IV

Experimental techniques including error analysis

b. Error analysis

b.1. Errors in the measurement of the diffusion coefficient

The uncertainty in the diffusion coefficient as a function of temperature is due to the following causes:

I. Uncertainty in the diffusion temperature

II. Uncertainty in the annealing time

III. Uncertainty in the position of the interface between surface solute and the bulk of the system

IV. Uncertainty in the diffusion coefficient caused by uncertainties in the thickness removed

V. Uncertainty in the extrapolation to obtain A(0)

VI. Error due to absorption

VII. Random errors in \((2\text{ierfc})^{-1} \frac{A(x)}{.886 A(0)}\)

VIII. Uncertainty in the diffusion profile caused by non-parallelism to the original surface of sections removed

IX. The possibility that the experimental boundary conditions differ from those which are used to derive the diffusion coefficients from Fick's Laws.
I Uncertainties in the annealing temperature

These are as follows:

(a) The thermocouple calibration is uncertain. The thermocouples used were compared with a thermocouple calibrated by N.B.S. and with each other at temperatures in the range used and variations found suggest an uncertainty in temperature from this cause of ± 3°C. The thermocouples were in close contact at their hot junction during calibration.

(b) The temperature was measured only at isolated instants; not as a continuous function of time. By taking readings at very short intervals during a particular annealing we found the fluctuations in the normal intervals between readings to be less than ± 2°C; this is therefore the maximum error from this cause.

(c) The thermocouple junction is not at the position of the interface in the diffusion sandwich. If there is a temperature gradient in the furnace, the temperatures read off may be in error. Temperature gradients were measured under experimental conditions without the sample being present and the uncertainty from this cause is ± 1°C.

(d) Uncertainty in the potentiometer reading which determines the thermo-E.M.F. This will be less than ± 0.1°C and so is negligible.

Thus the maximum temperature uncertainty for any run will be ± 6°C.

The uncertainty in \( D \) from this cause may be obtained as follows:

At any \( T \), the activation energy \( Q \) can be written as

\[
Q = -\frac{k d(\ln D)}{d(1/T)}
\]

or

\[
\frac{d(\ln D)}{d(1/T)} = -\frac{Q}{k}.
\]

Now
\[
\frac{dD}{dT} = \frac{d(\ln D)}{d(T)} \frac{d(1/T)}{dT} \frac{dD}{d(\ln D)}
\]
\[
= - \frac{Q}{k} \left[ - \frac{1}{T^2} \right] \times D = \frac{QD}{kT^2}.
\]
For small \( T \), \( \frac{\Delta D}{\Delta T} \approx \frac{dD}{dT} = \frac{QD}{kT^2}.

If \( \Delta T \) is taken to be the error in temperature then \( \Delta D \) will be the error in \( D \).

The fractional error in \( D \), \( \frac{\Delta D}{D} \), is equal to \( \frac{Q}{kT^2} \Delta T \).

Thus the error in \( D \) depends very strongly on the activation energy as well as on the actual error in temperature and this may be illustrated by our results. The error in temperature is not much different above and below 840°K, but because the activation energy for Ag and Ge diffusion above 840°K is higher than below 840°K, the percentage error in the diffusion coefficient from this cause will be higher above 840°K.

In Table VIII values of \( \frac{\Delta D}{D} \) are tabulated as a function of \( T \).

TABLE VIII

<table>
<thead>
<tr>
<th>minimum temperature of the region</th>
<th>( \frac{Q}{kT^2} ) (max)</th>
<th>( \frac{\Delta D}{D} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ge 840°K</td>
<td>0.07</td>
<td>&lt; ± 7%</td>
</tr>
<tr>
<td>Ge 690°K</td>
<td>0.03</td>
<td>&lt; ± 3%</td>
</tr>
<tr>
<td>Ag 840°K</td>
<td>0.02</td>
<td>&lt; ± 15%</td>
</tr>
<tr>
<td>Ag 690°K</td>
<td>0.04</td>
<td>&lt; ± 7%</td>
</tr>
</tbody>
</table>

II Uncertainty in the annealing time

For the purpose of calculating the diffusion coefficient, the
annealing time, $t$, was taken as the time from the attainment of the final temperature to the time when the block was pulled out of the furnace. This neglected warming up and cooling down periods, during which some diffusion will occur.

In fact the product of $D_{\text{expt}}$ (experimental diffusion coefficient) $\times$ the time $t$ can be expressed as follows:

$$D_{\text{expt}} \cdot t = \int_{-t_1}^{0} D_0 \exp(-Q/kT(t)) dt + D_0 \cdot \exp(-Q/kT) \cdot t + \int_{t}^{t_2} D_0 \exp(-Q/kT(t)) dt$$

where

- $t_1 =$ warming up period
- $t =$ annealing time
- $t_2 - t =$ cooling down period.

Let us put

$$\Delta D = (D_{\text{expt}} - D_{\text{true}})$$

Therefore

$$\Delta D \cdot t = D_{\text{expt}} \cdot t - D_{\text{true}} \cdot t$$

$$= D_{\text{expt}} \cdot t - D_0 \exp(-Q/kT) \cdot t$$

$$= \int_{-t_1}^{0} D_0 \exp[-Q/kT(t)] dt + \int_{t}^{t_2} D_0 \exp[-Q/kT(t)] dt$$

Therefore

$$\frac{\Delta D \cdot t}{D_{\text{true}} \cdot t} = \frac{\int_{-t_1}^{0} D_0 \exp[-Q/kT(t)] dt + \int_{t}^{t_2} D_0 \exp[-Q/kT(t)] dt}{D_0 \exp[-Q/kT] \cdot t}$$

whence, writing $D$ for $D_{\text{true}}$,

$$\frac{\Delta D}{D} = \frac{\int_{-t_1}^{0} D_0 \exp(-Q/kT(t)) dt + \int_{t}^{t_2} D_0 \exp(-Q/kT(t)) dt}{D_0 \exp(-Q/kT) \cdot t}.$$
\[
\int_{-t_1}^{0} D \exp(-Q/kT(t)) \text{ was evaluated from the diffusion coefficients measured at lower temperatures and the temperature-time relation during warming up. It was not possible to measure the temperature during cooling, so it was assumed that the contribution to diffusion during this time was the same as during warming up.}
\]

The quoted diffusion coefficient was larger than the actual diffusion coefficient certainly by less than 2% in all cases. Though we can give a firm upper bound to the error in general, the accuracy to which we can determine the error in any particular case is only of the same order as the error itself. Thus no correction was made to the quoted diffusion coefficients.

III. Uncertainty in the position of the interface between surface solute and the bulk of the system

This uncertainty was estimated by taking extreme possibilities for the position of the interface, working out \(A(o)\) for the extremes and then carrying out the calculation of \(D\) in the usual way. The total spread of \(D\) values between the two extremes was always less than ± 2% of the central value obtained with the "most reasonable" position of the interface.

One can estimate common-sense extremes without difficulty; we generally took as wide a spread as possible.

IV. Uncertainty in the diffusion profile caused by uncertainty in the thickness removed

If the percentage error in the weight of each section is 0.3%, and the errors are random, then the % error in total weight removed will be, according to standard statistical treatment, \(0.3\sqrt{N}\%\), \(N\) being the number of sections removed. Above twenty sections per block were removed so that the error in cumulative weight removed will always be < 1.4% and will give a percentage error in thickness of the same amount. An error of ± 2% in determining the cross-section with the travelling microscope gave an additional error of ± 2% in the thickness. The total error in the thickness will then be
less than ± 3.5% leading to an error of less than ± 7% in D.

V. Uncertainty in the extrapolation required to obtain $A(o)$

The extrapolation required to obtain $A(o)$ is uncertain. The error from this cause was found by taking the extreme values of $A(o)$ obtainable by reasonable extrapolations and calculating $D$ from them. The error from this cause is small, even if the spread of $A(o)$ is large. The error never exceeded ± 5%.

VI. Uncertainty due to absorption

It was shown in Appendix I that the error from this cause was less than 3% for all the germanium diffusion coefficients and negligible (< 1%) for the silver diffusion coefficients.

Our method of obtaining error bounds could be used to find the error in any particular case and make appropriate corrections. However the accuracy of the error estimate and the error itself appear to be too low to warrant making the corrections in our case.

VII. Random errors in $(2 \text{ierfc})^{-1} \frac{A(x)}{.886 A(o)}$

The random errors would be due mainly to statistical errors in the count rate, but there may be other causes. The random error in $D$ was found from the standard error of the slope of the least-squares fit of $(2 \text{ierfc})^{-1} \frac{A(x)}{.886 A(o)}$ vs. $x$ which was used to find $D$. These uncertainties were given on page 54 (ii) and can be tabulated as follows:

<table>
<thead>
<tr>
<th></th>
<th>Region II</th>
<th>Region III</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ge</td>
<td>± 10 - 50%</td>
<td>± 10 - 40%</td>
</tr>
<tr>
<td>Ag</td>
<td>± 20 - 50%</td>
<td>± 10 - 30%</td>
</tr>
</tbody>
</table>
VIII. Uncertainty in the diffusion profile caused by non-parallelism to the original surface removed

If sections are not parallel to the original surface, different thicknesses will be removed from different parts of the sample cross-section; after an average thickness $x_a$ has been removed, a thickness $x_a + h_1$ will have been removed from a fraction $k_1$ of the cross-section, $x_a + h_2$ from a fraction $k_2$ and so on. Then

$$A(x_a)/0.886A(0) = k_1 \text{erfc}((x_a + h_1)/2\sqrt{Dt}) + k_2 \text{erfc}((x_a + h_2)/2\sqrt{Dt}) + \ldots$$

For any specified amount and type of non-parallelism, $A(x_a)/0.886A(0)$ can be calculated from this equation as a function of $x_a$, the diffusion coefficient found in the usual way, and the error in it deduced.

The error finally quoted should be an upper bound, so a situation must be found for which the error is greater than for any situation encountered in our experiments. By making calculations it was found that:

(a) If $\sqrt{Dt}$ is fixed and the thicknesses removed from different parts of the cross-section lie within a fixed amount $h$ of each other after the removal of any number of sections, then the magnitude of the deviation of $(2\text{erfc})^{-1}(A(x_a)/0.886A(0))$ from its value for parallel sectioning is greater for $k_1 = k_2 = 1/2$, $h_1 = +h/2$, $h_2 = -h/2$ than for any situation encountered in our experiments; the sign of the deviation is the same.

(b) Other things being equal, the error in the diffusion coefficient increases as the range of $x_a$ over which the profile is measured decreases.

(c) If the deviation of the last section from parallelism with the original surface is fixed, the error in the diffusion coefficient is greater when many sections are not parallel to preceding sections than when only one section is not parallel to preceding sections.

The deviation of the last section from parallelism with the original
surface was less than $0.2\sqrt{Dt}$ in all profiles, and the range of $x_a$ over which readings were taken was always greater than $0.5\sqrt{Dt}$. Then in the light of (a), (b) and (c) an upper bound to the error will be obtained if we consider a profile sectioned over the range $x_a = 0-0.5\sqrt{Dt}$ with $k_1, k_2 = 1/2$ and $h_1 = 0.2 x_a$, $h_2 = -0.2 x_a$. The values of $A(x_a)/.886A(0)$ and $(2\text{erfc})^{-1}(A(x_a)/.886A(0))$ for selected $x_a$ are given below in Table IX.

<table>
<thead>
<tr>
<th>$x_a/\sqrt{Dt}$</th>
<th>$A(x_a)/.886A(0)$</th>
<th>$(2\text{erfc})^{-1}(A(x_a)/.886A(0))$</th>
<th>$(2\text{erfc})^{-1}(A(x_a)/.886A(0))$ for parallel sections</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>1.0284</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>0.2</td>
<td>.9401</td>
<td>0.0997</td>
<td>0.1</td>
</tr>
<tr>
<td>0.3</td>
<td>.8456</td>
<td>0.1495</td>
<td>0.15</td>
</tr>
<tr>
<td>0.4</td>
<td>.7750</td>
<td>0.1988</td>
<td>0.2</td>
</tr>
<tr>
<td>0.5</td>
<td>.7008</td>
<td>0.2482</td>
<td>0.25</td>
</tr>
</tbody>
</table>

TABLE IX

The least-squares slope of the $(2\text{erfc})^{-1}(A(x_a)/.886A(0))$ vs. $x_a$ curve for the non-parallel sectioning is $0.496/\sqrt{Dt}$, which is approximately $0.5/1.01\sqrt{Dt}$. Thus non-parallelism will raise the measured diffusion coefficient above its true value by less than 2% in all cases. However with the information available the error in any particular case can not be determined sufficiently accurately to warrant making a correction for non-parallelism.

IX. The possibility that the experimental boundary conditions differ from those which are used to derive the diffusion coefficients from Fick's Laws

a. Homogeneity of the original deposit is not required as long as there is sufficient tracer at all points for the surface layer to cover the whole
surface without any gaps. Inspection with the naked eye did not reveal any gaps, so that any such gaps, if present, must be less than 0.1 mm diameter in typical dimensions and widely spaced.

b. Using the one dimensional diffusion equation assumes that the sample cross section remains constant through the diffusion zone, which requirement was fulfilled to better than 1%. The total error from a and b will be less than 1%.

c. Another way in which boundary conditions could break down is the assumption that the glass block is homogeneous; there is experimental evidence (see Appendix V) that there are microcracks in the bulk of the material and this will affect interpretation of the diffusion results.
b.2. Uncertainties and errors in the isotope effect measurements

The causes of uncertainty and error in the isotope effect measurements can be listed as follows:

I. Uncertainty in the relative weight of different sections

II. Statistical uncertainty in the count rates

III. Errors from drift in the discriminator settings; this is important in the case of the Ag-isotope effect measurements because of the use of two lower level discriminators

IV. Variations in sample geometry

V. Errors arising from non-parallelism of the sections to the original interface

VI. Uncertainties in the published half-life values; this will be important in the case of the Ge-isotope effect measurements

VII. Errors resulting from the use of equations appropriate to Gaussian concentration profiles when the actual profiles were not Gaussian.
Detailed discussion of errors

I. Uncertainty in the relative weight of different sections

II. Uncertainty in the count rate

III. Drift in discriminator settings

IV. Changes in sample geometry

Uncertainties due to I, II, III and IV will be random in nature. Thus the total uncertainty from these causes can be estimated from the standard error of the least-squares slope of the $\ln \frac{C_B}{C_\alpha}$ vs. $\ln C_\alpha$ plot and was found to be about 35% for Ge and 10% for Ag runs.

V. Non-parallelism to the original surface

The percentage error from error (V) will be less than 2% in both the germanium and silver isotope effect experiments; cf. [114]. The actual percentage error in any particular case can not be determined sufficiently accurately to warrant correcting $f\Delta K$ for this source of error.

VI. Errors in the half-life used

This error will be important for the calculation of the Ge-isotope effect. The best published values for the half-life of the Ge-isotopes are given in Table X.

<table>
<thead>
<tr>
<th>Isotope</th>
<th>half-life (days)</th>
<th>uncertainty (days)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^{71}\text{Ge}$</td>
<td>11</td>
<td>± 0.15 [111]</td>
</tr>
<tr>
<td>$^{68}\text{Ge}$</td>
<td>280</td>
<td>± 20 [112]</td>
</tr>
</tbody>
</table>

TABLE X

The uncertainties in the half-lives lead to an uncertainty in the ratio of concentrations, and this will lead to an uncertainty of about ± 7% in the slope and in the value of $f\Delta K$.
VII. Error from use of equations derived for Gaussian profiles

According to Appendix III this error will be less than 15% for any of the sections used for the $\ln \frac{C_B}{C_\alpha}$ vs $\ln C_\alpha$ plot.

In fact, the error in it will be much less, because the sections counted extend over a considerable range of penetration. The actual error can therefore be taken to be less than 10%.
### TABLE XI
Uncertainties in the diffusion coefficient

<table>
<thead>
<tr>
<th>Source of uncertainty or error</th>
<th>max. uncertainty or error in $D$</th>
</tr>
</thead>
</table>
| I Uncertainty in annealing temperature | ± 7% for Ge above 570°C  
| | ± 15% for Ag above 570°C  
| | ± 3% for Ge below 570°C  
| | ± 7% for Ag below 570°C  |
| II Uncertainty in annealing time | + 2%  |
| III Uncertainty in the position of the interface between solute and glass phases | ± 2%  |
| IV Uncertainty in thickness removed | ± 7%  |
| V Uncertainty in $A(0)$ | ± 5%  |
| VI Absorption of radiation in the glass | < 1% for silver diffusion  
| | < 3% for germanium diffusion  |
| VII Uncertainty in $\frac{(2ierfc)^{-1} A(x)}{0.886 A(0)}$ | ± 10-50% for Ge diffusion in region II  
| | ± 10-40% for Ge diffusion in region III  
| | ± 20-50% for Ag diffusion in region II  
| | ± 10-30% for Ag diffusion in region III  |
| VIII Non-parallelism, to the original surface, of sections removed | + 2%  |
| IX Uncertainty in the boundary conditions | ± 1%  |

Major sources of uncertainty are therefore I, VII and in the case of germanium diffusion also VI. On the basis of this Table the maximum error limits for $D$ for Ge diffusion in region II can be rounded (to the nearest 5%) to ± 75%. The corresponding error limits for Ag are ± 85%, taking the maximum value of error VII.
TABLE XII

Uncertainties in $f_{\Delta K}$

<table>
<thead>
<tr>
<th>Source of uncertainty or error</th>
<th>max. uncertainty or error in $f_{\Delta K}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>I uncertainty in the relative weight of different sections</td>
<td>± 35% for Ge and ± 10% for Ag from I, II, III and IV combined</td>
</tr>
<tr>
<td>II uncertainty in the count rate</td>
<td></td>
</tr>
<tr>
<td>III drift in the discriminator settings</td>
<td></td>
</tr>
<tr>
<td>IV changes in sample geometry</td>
<td></td>
</tr>
<tr>
<td>V non-parallelism to the original surface</td>
<td>- 2%</td>
</tr>
<tr>
<td>VI errors in the half-life used</td>
<td>± 7% for Ge</td>
</tr>
<tr>
<td>VII error from use of equations derived for Gaussian profiles</td>
<td>± 10%</td>
</tr>
</tbody>
</table>

The major sources of uncertainty are:


b. VII.

c. VI, for germanium.

The maximum error limits for $f_{\Delta K}$ are therefore approximately ± 50% for Ge and ± 20% for Ag.
APPENDIX V

Experimental evidence for microcracks in the bulk of the structure

The diffusion of silver and germanium in region III as discussed in IV.4 was attributed to enhanced diffusion by some kind of short-circuit mechanism. Subsequent discussion based on electron microscopy of the glass surface, and the discussion of the nature of the granular surface structure make this explanation more plausible, but it was realized that the occurrence of short-circuit paths in the bulk of the material was only inferred from surface structure. An attempt was therefore made to find direct experimental evidence for short-circuit paths in the bulk of the diffused material by taking transmission electron micrographs of very thin sections of the material.

Glass blocks which had been annealed at 948°C, 511°C and 441°C together with a glass block in the "as-received" state were prepared for transmission electron microscopy (T.E.M.) by the ion-bombardment technique. The experimental details of the ion-bombardment technique for preparing specimens for transmission electron microscopy are given by Barber [115] and Gillespie et al. [116]. The technique preserves fine-scale structural features without introducing artifacts. Transmission electron microscopy of the glass so prepared showed in all blocks microcracks a few hundred Å long; see Figs. 57, 58, 59, 60 and 61.

Electron diffraction patterns taken close to the microcracks showed the matrix to be of a crystalline nature, as can be seen from Fig. 62. Electron diffraction patterns of spots far from the microcracks, in the homogeneous part of the matrix showed the typically blurred pattern of amorphous solids (see Fig. 63).
Microcracks seem to fall into two classes as shown in the electronmicrographs.

(a) straight cracks with sometimes some kind of step-structure (see Figs. 57, 58).

(b) wavy cracks (see Fig. 61).

The straight cracks predominate in parts of the matrix free from large amounts of impurities; they consist of a single straight line or set of straight lines running through a clear portion of the matrix (see Fig. 58). The wavy cracks are not unlike the ones inferred from surface structure as shown in Figs. 44 and 45, and are almost always situated in regions containing large amounts of impurities as shown in Fig. 61.

Fig. 64 shows a microcrack in an ion-thinned glass-foil obtained from a glass block in which germanium had been diffused. An X-ray microprobe analysis of a spot exactly on the microcrack revealed the presence of germanium (see Fig. 65).

No counts were registered when the X-ray microprobe analysis was conducted on a spot just outside the microcrack (see Fig. 66). This does not necessarily mean that there is no diffused germanium at all in the bulk of the material outside the microcrack. There might be germanium present but in too low a concentration to be detected. It does show that germanium segregates in microcracks, and makes the assumption of short-circuit path diffusion a reasonable one.

Fig. 67 shows a microcrack in an ion-thinned glass foil obtained from a block in the as-received state. An X-ray microprobe showed that no germanium or silver was present either in the microcrack or in the bulk of the material, see Fig. 68 and 69.

However the dependence of the number, structure and arrangement of the annealing temperature must be studied further before positive statements can be made.
FIG. 57. MICROCRACK IN VITREOUS SILICA
TRANSMISSION ELECTRON MICROSCOPY OF ION-
THINNED FOIL Magn. 200,000X.
FIG. 58. MICROCRACK IN VITREOUS SILICA. TRANSMISSION ELECTRON MICROSCOPY OF ION-THINNED FOIL. Magn. 200,000X.
FIG. 59. MICROCRACKS IN VITREOUS SILICA.
TRANSMISSION ELECTRON MICROSCOPY OF ION-
THINNED FOIL. Magn. 200,000X.
FIG. 60. MICROCRACK IN VITREOUS SILICA
TRANSMISSION ELECTRON MICROSCOPY OF ION-
THINNED FOIL. Magn. 200,000X.
FIG. 61. MICROCRACKS IN VITREOUS SILICA.  
TRANSMISSION ELECTRON MICROCOPY OF ION-THINNED FOIL.  Magn. 200,000X.
FIG. 62. ELECTRON DIFFRACTION PATTERN OF GLASS-FOIL CLOSE TO PRECIPITATED MATERIAL.
FIG. 64. SECONDARY ELECTRON IMAGE OF MICROCRACK IN GLASS FOIL OBTAINED BY THE ION BOMBARDMENT TECHNIQUE [115] [116]. THE GLASS-FOIL WAS OBTAINED FROM A BLOCK IN WHICH GERMANIUM HAD BEEN DIFFUSED. THE MICROGRAPH WAS TAKEN WITH THE SCANNING ELECTRON MICROSCOPE, ACCELERATING VOLTAGE 30 kV. MAGN. 4500 X.
FIG. 65. BAR HISTOGRAM OF X-RAY MICROPROBE ANALYSIS OF A SPOT IN THE MICROCRACK OF FIG. 64. VERTICAL AXIS: NUMBER OF COUNTS. HORIZONTAL AXIS: ENERGY DISTRIBUTION. $\alpha$ CHARACTERISTIC PEAK OF GERMANIUM IS AT 9.885 keV. BEAM DIAMETER = approx. 100Å
FIG. 66. BAR HISTOGRAM OF X-RAY MICROPROBE ANALYSIS OF A SPOT IN THE NEIGHBORHOOD OF THE MICROCRACK SHOWN IN FIG. 64. THE ABSENCE OF THE $K\alpha$ CHARACTERISTIC PEAK OF GERMANIUM AT 9.885 keV IS EVIDENT.
FIG. 67. SECONDARY ELECTRON IMAGE OF MICROCRACK IN GLASS FOIL. THE GLASS FOIL WAS OBTAINED BY ION BOMBARDMENT TECHNIQUE [115] [116] FROM A SLAP OF SiO$_2$ GLASS IN THE "AS-RECEIVED" STATE; TAKEN WITH SCANNING ELECTRON MICROSCOPE. ACCELERATING VOLTAGE 30 kV. MAGN. 4800 X.
FIG. 68. BAR HISTOGRAM OF X-RAY MICROPROBE ANALYSIS OF A SPOT ON THE MICROCRACK DEPICTED IN FIG. 67. NO EVIDENCE OF THE CHARACTERISTIC Kα PEAK OF GERMANIUM CAN BE FOUND AT 9.885 keV.
FIG. 69. BAR HISTOGRAM OF X-RAY MICROPROBE ANALYSIS OF A SPOT IN THE NEIGHBORHOOD OF THE MICROCRACK DEPICTED IN FIG. 67. NO EVIDENCE OF THE CHARACTERISTIC $\text{K}_\alpha$ GERMANIUM PEAK COULD BE FOUND AT 9.885 keV.
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## LIST OF SYMBOLS

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Definition</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>A(x)</td>
<td>relative activity after thickness x removed</td>
<td>45</td>
</tr>
<tr>
<td>A(o)</td>
<td>total activity from dissolved tracer</td>
<td>45</td>
</tr>
<tr>
<td>Å</td>
<td>ångström = 10^{-8} cm</td>
<td>16</td>
</tr>
<tr>
<td>C</td>
<td>concentration of diffusing species</td>
<td>3</td>
</tr>
<tr>
<td>C_s</td>
<td>solubility limit of the diffusing species in the solvent phase</td>
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<td>C_αs</td>
<td>solubility limit of the diffusing species α in the solvent phase</td>
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<td>C_α</td>
<td>concentration of diffusion species α</td>
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<tr>
<td>C_71</td>
<td>concentration of Ge_71</td>
<td>75</td>
</tr>
<tr>
<td>C_68</td>
<td>concentration of Ge_68</td>
<td>75</td>
</tr>
<tr>
<td>C_105</td>
<td>concentration of Ag_105</td>
<td>76</td>
</tr>
<tr>
<td>C_110m</td>
<td>concentration of Ag_110m</td>
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</tr>
<tr>
<td>°C</td>
<td>degree Celsius</td>
<td>ix</td>
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<td>c</td>
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<td>frequency factor in the Arrhenius equation for the diffusion coefficient</td>
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<td>diffusion coefficient of isotope β</td>
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<td>energy required for the barrier atom to have appropriate vibrational amplitude for the jump to take place (in the dynamical theory of diffusion)</td>
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<td>E_0</td>
<td>energy required for the diffusing atom to attain the critical amplitude of motion for the jump (in the dynamical theory of diffusion)</td>
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<td>f_o</td>
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ΔF  free energy for the jump of a diffusing particle  126

F(x)  \( F(x) = \frac{A(x)}{A(0)} \) = fractional activity remaining after a thickness \( x \) has been removed  48

G  modulus of elasticity  102

G*  mobility  5

ΔG  Gibbs free energy of activation per mole  7

ΔH  enthalpy of activation per mole  8

ΔH_v  enthalpy of vacancy formation  8

(h)  force potential  96

I  current of diffusing particles per unit area of section  3

I_α  activity of isotope α  3

I_β  activity of isotope β  3

J  amount of material diffusing per unit area of section per unit time  3

k  Boltzmann constant  5

kp  kilopoise  103

ΔK  fraction of transitional kinetic energy possessed by the solute atom at the saddle point  49

k_1, k_2, ..., k_n  fraction removed from cross-section  3

Kα  X-ray line; emitted when an electron goes from the \( n = 2 \) to the \( n = 1 \) shell  270

L  proportionality constant as in \( I = -L \cdot \frac{∂u}{∂x} \)  3

M  amount of deposit initially on the surface  6

M_2  molecular mass of matrix species  49

M_α  molecular mass of isotope α  49

M_β  molecular mass of isotope β  49

M*  count rate for a particular section at \( t = t_1 \)  49

m_α  mass of isotope α  49

m_β  mass of isotope β  49

N  number of particles (of type A) per cm³  119

N*  count rate for a particular section at \( t = t_1 + t_2 \)  119

n  number of atoms moving simultaneously in a diffusion jump  126
$P$ jump probability in each of $z$ directions 119
$p, p_1$ location of planes perpendicular to x-axis at $x$ and $x + dx$ respectively
$Q$ activation energy 6
$q = \frac{\text{slope}}{1 - \frac{D_\alpha}{D_\beta}} = \frac{1}{\frac{d \ln(C_\alpha/C_\beta)}{d \ln C_\alpha}} \frac{1}{1 - \frac{D_\alpha}{D_\beta}}$
$R$ universal gas constant 6
$r$ radius of diffusing ion 102
$r_D$ "doorway" radius 102
$r_T$ correlated jump distance 120
$r_0$ uncorrelated jump distance 120
$r_0$ Si-O bond length 95
$r_{0\alpha}$ Si-O bond length in the $\alpha$-phase 95
$r_{0\beta}$ Si-O bond length in the $\beta$-phase 95
$r_0^\alpha$ equilibrium Si-O distance for $\alpha$ configuration 95
$r_0^\beta$ equilibrium Si-O distance for $\beta$ configuration 95
$\Delta S$ entropy of activation of the diffusion coefficient 7
$\Delta S_f$ entropy of vacancy formation 8
$T$ absolute temperature ix
$T_m$ melting or liquidus temperature 16
$T_g$ glass transition temperature 16
$T_{gls}$ transition temperature for slow cooling glass 16
$T_{glf}$ transition temperature for fast cooling glass 16
$T_1, T_2, \ldots, T_n$ points of impact of electron-beam on specimen in scanning electron microscope 42
t time 4
$u = \frac{x}{2\sqrt{Dt}}$ 47
$V$ volt 37
$\text{MeV}$ $10^6$ electron volt 37
$W_\alpha$ jump rate of isotope $\alpha$ 125
$W_\beta$ jump rate of isotope $\beta$ 125
$W_2$ jump frequency of diffusing impurity atom 49
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<td>$W_2^\beta$</td>
<td>jump frequency of diffusing impurity atom of isotope $\beta$</td>
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<td>$W_I$</td>
<td>average weight of glass block before grinding</td>
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<td>average weight of glass block after grinding</td>
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<td>number of counts per min of $Ag_{110m}$ in channel I</td>
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<td>$Y_{105}$</td>
<td>number of counts per min of $Ag_{105}$ in channel I</td>
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<td>number of possible jump directions</td>
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<td>$z^*$</td>
<td>number of nearest neighbours in the sublattice</td>
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<td>$Z$</td>
<td>atomic number</td>
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<td>numerical factor in the formula for the diffusion coefficient depending on geometry and mechanism of diffusion</td>
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<td>Si-O-Si angle</td>
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<td>$\mu$</td>
<td>absorption coefficient for the activity in the material</td>
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</table>
\( \mu_1, \mu_2 \)

absorption coefficients of the elements making up the absorber

\( \mu m \)
micron = 10^{-4} \text{ cm}

\( \nu \)
frequency as in \( E = h \nu = \frac{hc}{\lambda} \)

\( \nu^* \)
vibration frequency of diffusing atom

\( \bar{\nu} \)
weighted frequency factor in the formula for the diffusion coefficient in the dynamical theory of diffusion

\( \rho \)
density of matrix

\( \rho_1, \rho_2, \ldots \)
densities of the constituents making up the absorber

\( \sigma_A \)
ionic conductivity involving single particles, A

\( \sigma \)
ionic conductivity involving several particles

\( \eta \)
\( \eta = \mu \sqrt{\text{Dt}} \)

\( \xi \)
\( \xi = \frac{x^t}{2\sqrt{\text{Dt}}} \)