

A REVIEW OF CHEMICAL DIFFUSION COEFFICIENT MEASUREMENT TECHNIQUES FOR METALLIC SYSTEMS

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ABSTRACT

Chemical diffusion coefficient measurement techniques have been reviewed for metallic systems. Of the methods reviewed EPMA, mechanical sectioning, XRF, and the electrochemical methods were found to be most suitable for the measurement of the chemical diffusion coefficient. Due to its flexibility, ease of use, speed of measurement and established track record for diffusion coefficient measurements, the EPMA technique is recommended as the candidate method for measuring chemical diffusion coefficients. A summary of the diffusion coefficient measurement ranges for the different methods is also given.

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1 Introduction

Diffusion plays an important role in phase evolution and corrosion in a number of industrial processes ^[1-3]. As our understanding increases, there is an increasing awareness that many diffusion coefficients have a large uncertainty associated with them. This limits the effectiveness of any predictive modelling for diffusion dependent processes such as microstructural evolution in solidification, corrosion rates, heat treatments and other solid state reactions of metals ^[1-3].

In the DTI programme MMPO2, Materials Measurements which Affect Processability, thermodynamic and diffusion data and methods to measure such data, used in such predictive models are being reviewed. The aim of the document is to provide a review of current methods available for measuring diffusion data and establish whether there is a candidate method most suited for measuring the diffusion data required for micro-modelling.

When two materials of different composition are brought together, the resulting composition gradient will tend to the average bulk composition by diffusion. Diffusion is normally measured using a diffusion couple, where two semi-infinite bars of different but homogeneous compositions are joined and annealed for a given time at the temperature of interest ^[4].

For an isotropic material, the diffusive flux J , through a plane perpendicular to the direction of diffusion is given by Fick's First Law ^[4]

$$J = -\tilde{D} \frac{\partial C_A}{\partial x} \quad (1)$$

where C_A is the molar volume of species A in moles m^{-3} , $\tilde{D}$ is the chemical diffusion coefficient in m^2s^{-1} and $\partial C_A / \partial x$ is the concentration gradient with units moles m^{-2} . Strictly speaking, it should be the chemical potential gradient not the concentration gradient used in Equation 1, as it is the chemical potential gradient and not the concentration gradient that provides the driving force for the bulk movement of a species. In most circumstances the concentration gradient can be assumed to equal that of the chemical potential gradient. In the following text it is assumed that the concentration gradient is equal to chemical potential gradient ^[4].

Fick's Second Law (Equation 2) describing the rate of change of composition with time can be derived by the use of Equation 1 and a mass balance of mass fluxes in and out of a control volume.

$$\frac{\partial C_A}{\partial t} = \frac{\partial}{\partial x} \left(\tilde{D} \frac{\partial C_A}{\partial x} \right) \quad (2)$$

Equation 2 permits $\tilde{D}$ to vary with composition. Where $\tilde{D}$ is known to be independent of composition then the Fick's Second Law can be simplified to Equation 3 ^[4].

$$\frac{\partial C_A}{\partial t} = \tilde{D} \frac{\partial^2 C_A}{\partial x^2} \quad (3)$$

From Equation 2 or 3 and a knowledge of the concentration profile (measured experimentally), $\tilde{D}$ can be calculated using the Boltzmann-Matano analysis^[4].

For a detailed reviews of diffusion, derivation of the above equations and explanation of the Boltzmann-Matano analysis see references by Kirkaldy^[4], Crank^[7] or Schmalzried^[8].

1.1 The Diffusion Coefficient

The foregoing discussion was primarily about measurement of diffusion coefficients in a compositional gradient, but there are a number of other diffusion coefficients, some of which are measured under conditions where there are no composition gradients eg self diffusion coefficient¹. These are seldom equal to diffusion coefficients measured under a composition gradient where there is a driving force to minimize the composition gradients in the sample. It is therefore important when modelling diffusion to use diffusion coefficients that represent the physical phenomena you are trying to model and that are appropriate for the constitution of the model. There is a lack of consistency in the nomenclature and terminology used for diffusion coefficients found the literature. This can lead to uncertainty over the physical meaning of the quoted diffusion coefficients. In general the nomenclature and definitions used in this report are those found in the Landolt-Börnstein^[5] compendium and are outlined in the following text.

1.1.1. Diffusion with no Concentration Gradient

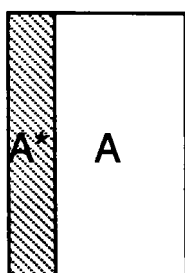
Pure Metals

Self diffusion^[4]

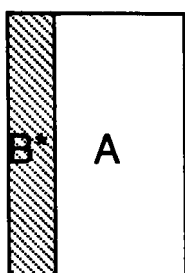
Atoms of A diffusing in solid A, where A is a pure metal. The diffusion coefficient under such conditions is called the **self diffusion coefficient**. It is normally measured using tracers (tagged atoms, usually radioactive isotopes) of A and denoted D_A^{A*} , where the superscript is the diffusing species, the * signifying the species is tagged and the subscript the diffusion medium.

It corresponds to the experimental situation given in Figure 1a, where a thin layer of tracer atoms of A* are deposited on solid A. It is assumed that the different isotope has

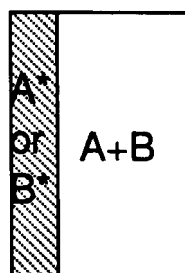
¹ Although self- diffusion coefficients are usually measured where there is an isotopic or radioactivity gradient in a specimen the effects of these gradients are assumed to be negligible on the diffusive flux and the material can be considered homogeneous with respect to composition.



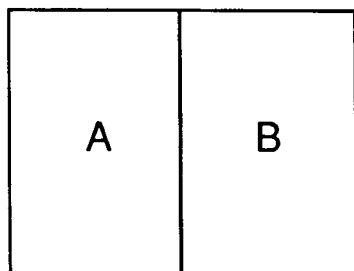
(a)



(b)



(c)



(d)

Figure 1. Schematic representations of different diffusion coefficients

no effect on the mobility of A. It is possible to calculate self diffusion coefficients using Equation 4.

$$D_A^{A*} = \frac{f l^2}{6 \tau} \quad (4)$$

where l is the jump length, τ is the residence time of atoms on a site and f is a constant based on the crystal structure and diffusion mechanism [4].

In general, calculated values of D_A^{A*} are greater than measured values of D_A^{A*} as there is a higher probability of an untagged atom meeting a vacancy than there is tagged atom.

Impurity diffusion [4]

Atoms of B diffusing into a solid A, where A is a pure metal and the concentration of B very small i.e. $B \sim 0$. The diffusion coefficient under such conditions is called the **impurity diffusion coefficient**. It is also measured using tracers (radioactive isotopes) of B and denoted D_A^{B*} , where the superscript and superscripts are as before for self diffusion coefficients. It corresponds to the experimental situation given in Figure 1b, where a thin layer of tracer atoms of B^* are deposited on solid A.

Homogeneous Alloy [4]

Atoms of A or B diffusing into an homogeneous alloy of A+B, where the concentration of A in the alloy is greater than B. Diffusion coefficients in homogeneous alloys are measured using tracers similar to that as previously discussed for self diffusion coefficients. The diffusion coefficient for tracers A^* and B^* under such conditions are called the **solvent self diffusion coefficient** denoted D_{AB}^{A*} and the **solute diffusion coefficient** denoted D_{AB}^{B*} respectively. A physical representation of this experimental situation given in Figure 1c, where a thin layer of tracer atoms of A^* or B^* are deposited on solid AB. These diffusion coefficients are highly dependent on alloy AB's composition and are normally represented as a geometric series of composition.

1.1.2 Diffusion in a Concentration Gradient

Chemical Diffusion [4]

A diffusion coefficient measured in a concentration gradient is a **chemical diffusion coefficient** $\tilde{D}$. Chemical diffusion coefficients measured for interstitial solutes eg hydrogen in iron are referred to as **interstitial diffusion coefficients**. Chemical diffusion coefficients for metals A and B (or alloys of the metals) which form substitutional solid solution are referred to as **interdiffusion coefficients**. A physical representation of this experimental situation given in Figure 1d. Where A can be considered a gas A at constant

pressure as for hydrogen, or a metal A for a typical interdiffusion experiment.

The physical representation and analysis of concentration profiles become increasingly more difficult as the number of diffusion species increase. For single phase ternary systems the Boltzmann-Mantano analysis is still valid although four interdiffusion coefficient are required to describe the diffusion process ^[4].

From Kirkaldy ^[4] the solution to Fick's Second Law for a ternary system A+B+C where A > B and C, ie where A is the solvent, is given by Equations 5 and 6 for species B and C.

$$\frac{\partial C_B}{\partial t} = \frac{\partial \left(D_{BB}^A \frac{\partial C_B}{\partial x} \right)}{\partial x} + \frac{\partial \left(D_{BC}^A \frac{\partial C_C}{\partial x} \right)}{\partial x} \quad (5)$$

and

$$\frac{\partial C_C}{\partial t} = \frac{\partial \left(D_{CC}^A \frac{\partial C_C}{\partial x} \right)}{\partial x} + \frac{\partial \left(D_{CB}^A \frac{\partial C_B}{\partial x} \right)}{\partial x} \quad (6)$$

Diffusion coefficients D_{BB}^A and D_{CC}^A are known as the **major** and D_{BC}^A and D_{CB}^A **cross** terms.

Intrinsic Diffusion ^[4]

Interdiffusion coefficients do not give a complete description of the diffusion process and are only a measure of the aggregate movement of the atoms within a system, not the specific motion of species A and B. **Intrinsic diffusion coefficients** denoted D_A or D_B for a binary alloy A+B, are diffusion coefficients where the diffusion of A (or B) is measured relative to the lattice plane and can be related to the interdiffusion coefficient of an alloy by Equation 7,

$$\tilde{D} = X_B D_A + X_A D_B \quad (7)$$

where X_A and X_B are the molar fractions of A and B. If fine insoluble wires are incorporated into the diffusion couple interface to mark the interface, then the marker shift (Kirkendal velocity)^[4] with respect to the original interface can be measured. A knowledge of the Kirkendal velocity as well as Equation 7 is required to calculate the

intrinsic diffusion coefficients.

Outlined below is Table 1, summarizing the different diffusion coefficients, with the different nomenclature listed in Landolt-Börnstein^[5] and Smithells^[6] data compendia as well as some other common names used in the literature for the different diffusion coefficients.

Type of diffusion coefficient	Landolt-Börnstein ^[5]	Smithells ^[6]	Comments
Chemical diffusion coefficient ie diffusion in a potential gradient			
Interstitial diffusion coefficient	$\tilde{D}$	$\tilde{D}$	also known as chemical diffusion coefficient
Interdiffusivity coefficient (alloy A+B)	$\tilde{D}$	$\tilde{D}$	Also known as mutual diffusion coefficient, chemical diffusion coefficient, diffusion coefficient
Intrinsic diffusion coefficient (alloy A+B)	D_A	D_A	Also known as partial chemical diffusion coefficient, component diffusion coefficient
Chemically homogenous ie no potential gradient [#]			
Tracer self-diffusion coefficient (pure material)	D_A^*	D_A^* at $C_B=0$	Also known as self-diffusion coefficient
Tracer impurity coefficient (B in A) ⁺	D_A^*	D_B^* at $C_B=0$	
Tracer diffusion (alloy A+B)			
Solvent diffusion coefficient (A solvent in A+B)	D_{AB}^*	D_A^*	
Solute diffusion coefficient (B solute in A+B)	D_{AB}^*	D_B^*	

⁺Thin layer of B (very low concentration) on substrate of A

[#] On the assumption that the isotope or the radioactive tracers have negligible effect on the random movement of the atoms/molecules.

2 Methods For Measuring Chemical Diffusion Coefficients

The measurement of diffusion coefficients can be split into two categories, macroscopic methods based on Fick's Laws and microscopic methods^[3]. The distinction being, macroscopic measurements are made over a period of time where a large number of atomic jumps^[3,4], ie an atoms moving from one lattice position to another, have taken place. Microscopic techniques in general measure over timescale where very few such jumps take place, the information being

used to measure the atomic jump frequency (the reciprocal of τ in Equation 4) to calculate self diffusion coefficients ^[3,4]. As this review is primarily about methods for measuring chemical diffusion coefficients only macroscopic measurements shall be discussed.

In general, macroscopic methods measure concentration profiles. These profiles are compared with the appropriate solution of Fick's Laws to obtain the chemical diffusion coefficient ^[4]. This approach is also suitable when measuring parameters that are dependent on the diffusive flux. Except where diffusion coefficients are calculated by some method other than a direct use Fick's First or Second Laws no working equation shall be given in the review of the diffusion measurement method. For a full explanation of how the chemical diffusion coefficient is calculated from a concentration profile see references by Kirkaldy ^[4], Crank ^[7] or Schmalzried ^[8]

Macroscopic techniques can be further subdivided into destructive/non-destructive techniques and steady state/non-steady state techniques ^[3]. Destructive techniques, are sectioned prior to composition analysis. After such a measurement little or no further experimentation can be carried out on the sample. In non-destructive techniques, after diffusion measurement the sample is still intact and can be remeasured or analysed or further diffusion annealed. Where relevant comment will be made on whether or not the measurement method is destructive or not. All non-destructive analysis techniques can be used in conjunction with sectioning (destructive) techniques, although there is little gained by such an approach.

Steady state measurements require a constant composition gradient across a sample for measurement of the diffusion coefficient, where the mass flux into the sample minus mass flux out of the sample is constant value ^[4]. Non-steady state measurements have no such requirement ^[4]. The methods outlined below are divided into steady and non-steady state techniques.

There are a number diffusion measurement techniques in the literature which utilize thin film coating technology ^[3,5], these are principally used in the measurement of self, impurity (or the alloy equivalent) diffusion coefficients. As such thin film techniques will not be discussed except where they are used for measuring chemical diffusion coefficients.

Sectioning

The majority of chemical diffusion coefficient techniques use some form of sectioning (destructive techniques) coupled with composition analysis to obtain a concentration profile ^[5,6]. Often it is the sectioning method that determines the limits of detection of the diffusion measurement technique ^[3]. Therefore it is appropriate to outline the methods for sample sectioning prior to discussing the measurement techniques. Shown in Table 2, are the minimum thickness that a sample can be cut and the smallest diffusion coefficient that can be measured for a given sectioning technique ^[3].

Method	Minimum Slice Thickness/ μm	Minimum Diffusion Coefficient/ m^2s^{-1}
Precision Lathe	10	5×10^{-16}
Microtome	1	5×10^{-18}
Grinder	1	5×10^{-18}
Chemical or Electrochemical Attack	5×10^{-3}	1×10^{-22}
Sputtering	1×10^{-3}	5×10^{-24}

Table 2. Sectioning methods for diffusion measurement techniques ^[3].

Providing the sample is machinable, mechanical sectioning of the sample using the precision lathe, microtome or grinder does not in general hinder the diffusion analysis. Care must be taken when using chemical or electrochemical attack or sputtering to section the diffusion couple as if the material being sectioned is heterogeneous in composition, as all diffusion couples used in chemical diffusion experiments are, there may be preferential removal of a particular species. This would bias the compositional analysis after sectioning and increase the error in any diffusion coefficient calculated from such an analysis^[9].

Once the diffusion couple has been sectioned the sections have to be analysed and the thickness measured to obtain the composition profile.

Wet Chemistry

It is not appropriate for this review to detail the numerous wet chemical methods available for analysing the different elements of a sectioned diffusion couple. Reference should be made to classical wet chemical analysis texts for such details ^[10,11]. It is sufficient to say that wet chemical methods give representative bulk analysis, the errors involved are dependent on the techniques used and the species analysed. In the case of metals most can be analysed by standard atomic adsorption techniques^[10] and the errors involved are likely to be less than the repeatability of the diffusion experiment.

2.1 Steady State Methods ^[12,13]

Steady state techniques use Fick's First Law (Equation 1) to obtain the diffusion coefficient. The principle of the measurement is as follows:

The concentration of the diffusion species is kept constant on either side of the diffusion medium, eg thin sheet or tube. The concentrations C , should be such that $C_1 > C_2$, where subscripts 1 and 2 denote opposite sides of the diffusing medium. After a period of time,

this composition difference results in a constant flux J of the diffusing species and constant composition gradient across the sample of the diffusant.

Under such conditions the diffusion coefficient can be obtained in three ways.

1. An average diffusion coefficient for the boundary concentrations C_1 and C_2 can be obtained from Equation 8

$$\bar{D} = \frac{J t}{(C_1 - C_2)} \quad (8)$$

where t is time.

2. If the concentration profile across the sample is measured then the diffusion coefficient can be determined directly using Equation 1.

3. The time taken to reach steady state conditions.

Steady state techniques are limited to diffusing species that can be delivered to and removed from the diffusing medium in the gas phase and has been most commonly used for hydrogen diffusion measurements^[5,6]. Also these techniques are often limited to high temperatures to achieve the high permeation rates needed to overcome problems of measuring the low flowrates on the gas outlet side.

In order to overcome the problem of measuring low outgas flowrates Saitoh et al^[14] performed permeation experiments on hydrogen in aluminium using a plasma driver. This gives a greater rate of throughput of the gas through the aluminium (presumably by increasing the activity of hydrogen on the "in" side of the aluminium) and enabled measurements to be made at temperatures as low as 25°C. Whilst these measurements were not made in the steady-state mode they demonstrate a method of increasing your outgas flowrate to increase the measurement range of such techniques. The measurement range for steady state measurement techniques is between 10^{-13} and $10^{-9} \text{m}^2 \text{s}^{-1}$ ^[6].

2.2 Non-Steady State Techniques

Most chemical diffusion coefficients are measured under non-steady state conditions^[5,6] and use solutions to Fick's Second Law to obtain the chemical diffusion coefficient.

Radiation Assay Techniques^[15,16]

The concentration profile of a sectioned diffusion couple in a radiation assay technique is obtained by measuring the specific activity of the section. For strong gamma radiation a scintillating counter is most convenient^[15]. It has primarily been used for measuring impurity or self diffusion coefficients^[5,6] but is suitable for use in measurement of all types of diffusion coefficient providing a radioactive isotope can be obtained for the

diffusing species of interest. The range of diffusion coefficient measurement capability for this technique extends from $10^{-23} \text{ m}^2\text{s}^{-1}$ to $10^{-16} \text{ m}^2\text{s}^{-1}$ [5].

In order to minimize the number of sections needed from a sample an autoradiographic technique can be used [15]. Here the diffusion sample can be sectioned at a very small oblique angle which magnifies the penetration distance. The oblique surface is then exposed to photographic film. The density of the image on the film is directly proportional to the intensity of the radiation and hence composition.

Radioactive techniques are limited by the availability of a suitable radioactive isotope for the diffusing species and the health and safety precautions required for working with radioactive material. The health and safety issues cannot be underestimated and would cause great problems for any laboratory using this technique that was not fully conversant with dealing with radioactive materials.

Adsorption/Desorption Methods [14,17-19]

In adsorption/desorption methods, the experiment is set up to allow the diffusant to diffuse into or out of an homogeneous material of known composition, such that the composition of the diffusant at the surface of the sample is maintained at a constant value, and that the sample can be considered a semi-infinite sink over the timespan of the diffusion anneal. This constant surface concentration is usually achieved by fixing the gas composition the sample experiences. The profiles are normally obtained via sectioning and therefore these techniques are destructive.

It is possible to obtain the diffusion coefficient from this method by monitoring the weight loss or gain of a sample with time. For a given time t , Equation 9 gives the expected mass increase/decrease of a sample,

$$M = 2 |C_o - C_s| A \left(\frac{\tilde{D} t}{\pi} \right)^{0.5} \quad (9)$$

where M is the mass of the sample, the subscripts o and s denote initial and surface concentration respectively and A is the surface area through which diffusion is taking place. This has the advantage of being a non-destructive technique.

These methods are only suitable for diffusants that can be supplied or removed in the gas phase and in general only used for elements that diffuse interstitially [5,6]. The measurement range for these measurement techniques is between 10^{-13} and $10^{-9} \text{ m}^2\text{s}^{-1}$ [6].

The Electron Microprobe Analyser (EPMA) ^[3,5,20,21,25,26]

The EPMA, also known as the Castang probe utilizes an electron beam to measure the concentration. In the EPMA high energy electrons (10-30 keV) are focused onto the diffusion couple. The electron beam ($\leq 0.2 \mu\text{m}$ in diameter) stimulates characteristic x-rays which can be analysed by wavelength dispersive spectrometry (WDS) or energy dispersive spectrometry (EDS) or both, depending on what analysers are fitted to the probe. All EPMA's are fitted with WDS and most with EDS ^[20]. The concentration profile is obtained by analysing along the diffusion direction. It is a non-destructive technique therefore further analysis or diffusion annealing can be carried out on the sample. A schematic of the EPMA system is given in Figure 2^[21]. This technique is convenient for studying chemical diffusion and has a composition sensitivity of the order of 10^{-3} ^[3]. The smallest diffusion coefficient measurable is $10^{-15} \text{ m}^2 \text{ s}^{-1}$ ^[3].

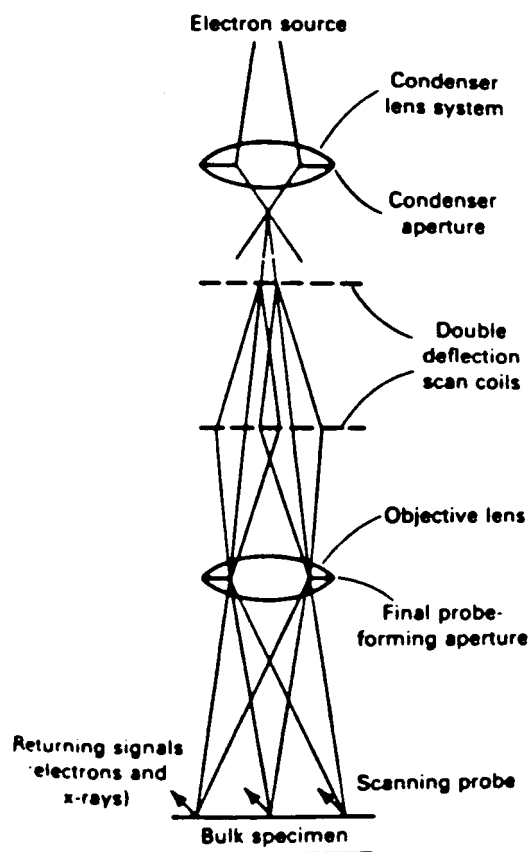


Figure 2. Schematic of an EPMA system ^[21].

The general characteristics of the WDS and EDS are outlined below. It is the limitations of these analysis systems that define the capability of the EPMA.

WDS analysis ^[27]

The working principle of the WDS system is based on Bragg's Law, where the characteristic x-rays are separated using x-ray diffracting crystals. The diffracted x-rays are collected by a proportional counter and processed electronically.

- a. Can detect elements of atomic number greater than 3.
- b. Can discriminate between similar x-ray lines due to high resolution, ~5eV.
- c. Detectability limits of 100ppm.

EDS analysis ^[27]

The EDS system measures the energy of the characteristic x-rays.

- a. Can routinely detect elements of atomic number greater than 11, although with a windowless detector elements with atomic numbers as low as 3 may be detected.
- b. X-ray resolution of 150 keV.
- c. Detectability limits of 1000ppm

Analytical Electron Microscopy (AEM) ^[5,20,21,25]

The AEM also known as the Scanning Transmission Electron Microscope (STEM), focuses a high energy electron beam (80-100keV) on electron transparent thin foils. Characteristic x-rays generated by the interaction between the beam and the sample, as the beam passes through the sample, are collected on the sample side opposite the focused beam and are analysed using an EDS. A schematic of the AEM process is given in Figure 3^[21].

The AEM's limitations are in general that given for the EDS (above). Elemental sensitivity is of the order 0.1-0.8wt%. The chemical composition of volumes as small as 5 nm in diameter and thickness of the order 20-200 nm can be measured ^[20]. In principle the AEM is used to analyse a sample in a destructive or non-destructive manner. For thin films it analyses across a diffusion interface, parallel to the diffusion direction. This is it's normal mode of operation and could be considered non-destructive, although in reality the high energy beam has caused some damage to the sample. The AEM is most suitable for thin film diffusion studies, diffusion systems with very low diffusion coefficients and diffusion studies at low temperatures.

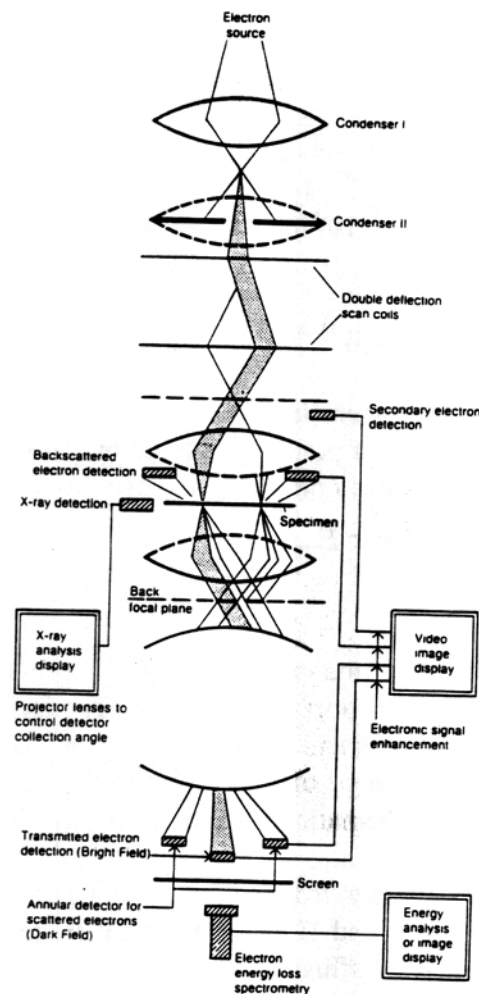


Figure 3.A schematic of the AEM system 3^[21].

Auger Electron Spectroscopy (AES) ^[5,20,28]

Concentration depth profiles in the AES are obtained by Auger analysis and ion (typically Ar^+) sputtering. The sputtering exposes a new surface which can then be analysed using a focused low voltage electron probe (beam). Depth profiles of up to $0.5\mu\text{m}$ can be achieved ^[20] with a spacial resolution of 5nm at best ^[28]. As such this technique is limited to thin film diffusion measurements and measuring relatively small diffusion coefficients. The range of diffusion coefficient measurement capability for this technique extends from $10^{-24} \text{m}^2\text{s}^{-1}$ to $10^{-16} \text{m}^2\text{s}^{-1}$ ^[5].

Secondary Ion Mass Spectroscopy (SIMS) ^[9,20,28]

As with AES the SIMS technique uses ion sputtering (typically Ar^+) to section the sample. Unlike the AES technique though, the SIMS analyses the sputtered off material in a mass spectrometer (usually a quadrapole) to obtain the concentration levels of each sputtered section. It has a spacial resolution between 1 and 50 μm , an elemental sensitivity of between 0.01 at% and 1 ppm and a depth penetration of the order of 50 nm depending on the particular system used ^[28]. It is most suitable for measuring diffusion coefficients in the range 10^{-24} to $10^{-14} \text{ m}^2\text{s}^{-1}$ and has been used extensively in the semiconductor industry ^[20].

Rutherford Backscattering (RBS) ^[3,28-33]

For RBS a high energy ion (incident) beam, usually a helium or hydrogen ions, is fired at the sample. The incident beam is scattered by the sample nuclei and the energies of the scattered ions are proportional to the incident ions energy as given in Equation 10,

$$E_I = k E_S \quad (10)$$

where E is the energy of the ions, subscripts I and S denote incident and scattered beam respectively and k is a proportionality factor. The factor k is dependent on the scattering angle, incident ion mass and sample nuclei mass. Therefore by measuring the angular distribution and the energy of the ions one can obtain the composition of the sample scattering atoms. A schematic diagram of the RBS is shown in Figure 4 ^[29].

Depth information comes from the continuous energy loss of the probing ions, with depths of up to 1 μm and 10 μm and spacial resolution of 1 μm at best ^[20]. The RBS technique can measure diffusion coefficients in the range 10^{-16} and $10^{-23} \text{ m}^2\text{s}^{-1}$ ^[5] and is most suitable for measuring thin films where the diffusion species is highly contrasted with the matrix, i.e. a heavy element in a light matrix ^[3].

X-ray Fluorescence Spectroscopy (XRF) ^[20,34,35]

In XRF x-rays are fired at the sample. The sample atoms are excited by these x-rays and emit characteristic x-rays (fluoresce). The intensity of these x-rays can be related to composition in much the same way as was discussed for the EPMA i.e WDS or EDS. A schematic diagram of the method is given in Figure 5 ^[9].

As can be seen in Figure 5 the x-ray beam is fired at an oblique angle to the specimen which travels parallel to the diffusion flux obtain the concentration profile.

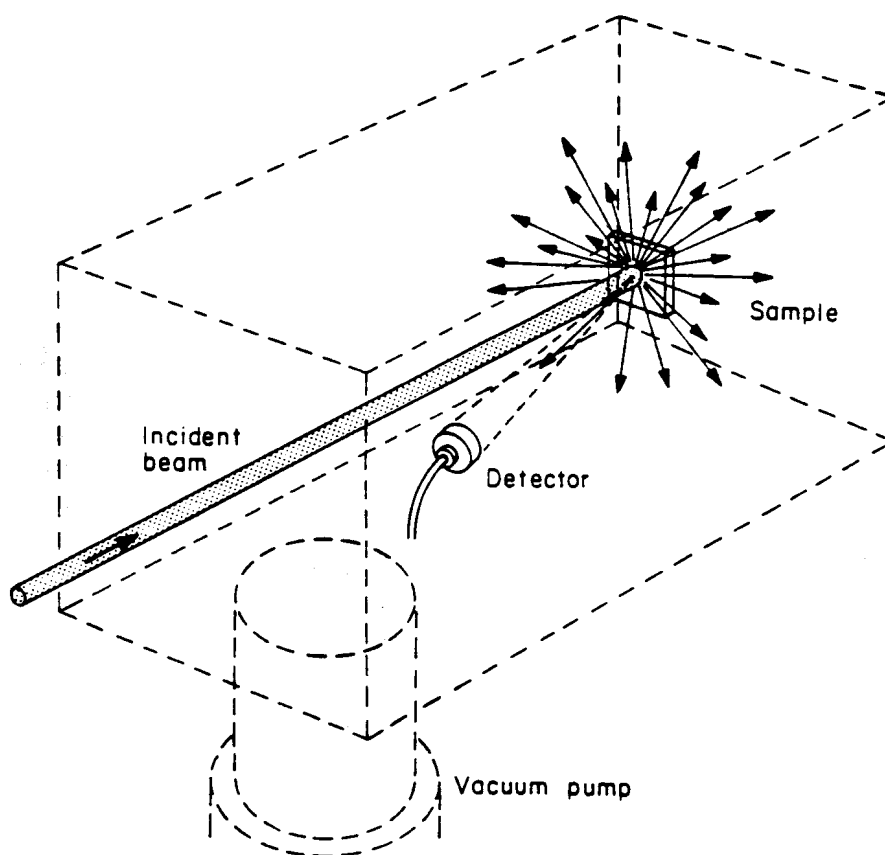


Figure 4. A schematic diagram of the RBS system ^[29].

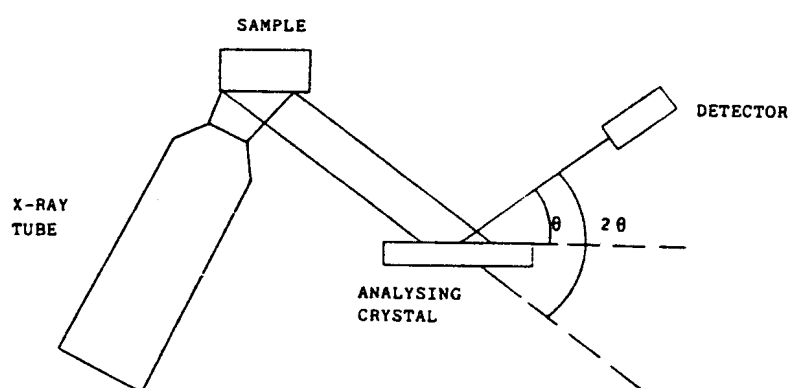


Figure 5. A schematic diagram of the XRF system ^[9].

It is a non-destructive technique with elemental sensitivity of approximately 0.1 at% and the spacial resolution of the order 0.5 mm. With modifications that allow the x-ray beam angle to be varied the spacial resolution can be improved to 20 nm^[20]. In this mode its limitations are as with EPMA dependent on the elemental analysis constraints which are principally defined by the attached analysis units ie WDS or EDS.

In the low resolution method only large diffusion coefficients ($>1 \times 10^{-15} \text{ m}^2\text{s}^{-1}$) can be measured^[20]. In the high resolution method diffusion coefficients as small as $1 \times 10^{-20} \text{ m}^2\text{s}^{-1}$ can be measured^[20].

2.1.1 Other Methods

In principle any measurable parameter that changes with composition can be used to measure the chemical diffusion coefficient. $\tilde{D}$'s have been measured using, the Gorsky effect^[3,5], electrochemistry^[36-40,55], the kinetics of precipitation or sintering^[8,41,42], electrical resistivity^[43,44], x-ray evolution^[45], thermionic emission^[46-48], photoelectric emission^[56,57], lattice distortion diffraction measurements^[34,49,50], and microhardness tests^[51,52]. A difficulty with these techniques can be obtaining a relation between the measured parameter and the composition evolution^[40] and it is unlikely that they would be used for diffusion coefficient measurements where other techniques (such as those outlined above) were available^[8]. The more important 'other' methods are outlined below.

Gorsky Effect^[3,5]

When a metallic sample is bent there is a distortion of the lattice in the sample i.e. the lattice is expanded on one side and contracted on the other. Any solute that distorts the metal lattice will then diffuse in a bent sample towards the expanded side. Thus setting up a concentration gradient. This diffusion leads to an additional time dependent anelastic strain, or a damping in an oscillating sample and can be characterized by a relaxation time τ . The chemical diffusion coefficient under such conditions can be calculated using Equation 11.

$$\tilde{D} = \left(\frac{d}{\pi} \right)^2 \tau^{-1} \quad (11)$$

where τ is measured by either anelastic strain or damping and d is the length of the diffusion zone (sample size). This technique is suitable for measuring very high diffusion coefficients $>10^{-13} \text{ m}^2\text{s}^{-1}$ and so far has only been used for hydrogen diffusion in metals^[3].

Electrochemical Method (Chronopotentiometry)^[36-40,55]

The electrical properties of a material may change as diffusion takes place. This can be utilized to make diffusion measurements.

Consider an electrochemical cell,



where M^1 and M^2 are different metals and the electrolyte is M^1X , by applying an EMF, across such a cell a solid solution between M^1 and M^2 can be formed. The EMF would start to increase as diffusion takes place. The activity of the diffusant remains constant on the surface of the electrode that it is being deposited onto, as for every atom of diffusant that diffuses into the interior of the electrode another is deposited on the surface from the electrolyte. The electrolyte must be a pure ionic conductor and electrochemical transfer must be very much greater than chemical diffusion for this method to be valid.

For such a system the diffusion coefficient is obtained from Equation 12 ^[36]

$$i = FA(C_t - C_o) \left(\frac{\bar{D}}{\pi t} \right)^{\frac{1}{2}} \quad (12)$$

where i is the diffusion current, A is the electrode area, F is Faradays constant, t is time, C is the molar concentration of the electromotive species and subscripts t and o are time t and zero respectively.

This type of measurement has been most successfully used on liquid metals ^[37-39,55] and has been developed to measure diffusion coefficients in oxide couples ^[40].

In principle this method can also be used for solids but it is more difficult to bond an electrolyte to two metals ensuring good electrical contact than it is to make a metal-metal diffusion couple. An obvious solution would be to use a liquid electrolyte but this creates a different set of material handling properties. A suitable electrolyte must also be available for the diffusing species. It is likely to be for these reasons that it is not the preferred method for measuring diffusion coefficients in solid solution systems.

Growth Kinetics of Precipitation ^[8,41,42]

Measurement of the growth rate of a new phase ie precipitation of particles from a supersaturated medium. The growth rate of the new phase must be controlled by diffusion for this method to be valid. The solution to Fick's Second Law for long annealing times and a constant $\bar{D}$ in cylindrical coordinates is given in Equation 13 ^[8],

$$\tau = \frac{r_{avg}^2}{3\bar{D}} \left(\frac{C_p}{C_o - C_e} \right)^{\frac{1}{3}} \quad (13)$$

where the τ is the relaxation time, r_{avg} is the average radius of the precipitating particles, $\bar{D}$ is the interdiffusion coefficient, subscript "o, p and e" denote concentration at time

zero, concentration of precipitating particle and particle equilibrium concentration.

Whilst this is a useful technique for measuring diffusion coefficients with the constraints outlined above, it is of no use in single phase systems or two phase systems where the rate controlling mechanism of precipitation is not diffusion.

Electrical Resistivity ^[3,43,44]

A diffusion couple of periodic composition, usually made by alternate sputtering or chemical deposition of two different compositions, is homogenized. The kinetics of the homogenization are followed by its change in resistivity, ρ . The diffusion couple compositions can be considered a Fourier series with periodicity λ . From such an experiment the diffusion coefficient can be obtained by fitting to Equation 14^[43]

$$R_0 \left[1 - \exp\left(\frac{-t}{\tau}\right) \right] = \frac{A}{N-1} \frac{1}{\left(\frac{2}{\lambda}\right) \int_0^{2\lambda} \frac{dx}{\rho(x; \tilde{D}, t_0)}} \quad (14)$$

where R_0 is a fit parameter, N is the number of layers and A is a geometrical factor. Chemical diffusion coefficients as small as $10^{-27} \text{m}^2 \text{s}^{-1}$ can be measured using this technique ^[3]. This a low temperature technique is most suitable for measuring small diffusion coefficients.

X-ray Evolution ^[45]

Using a similar approach to the resistivity technique above, the kinetics of the homogenization can be followed by x-rays. The diffusion coefficient is obtained from Equation 15 ^[45],

$$\tilde{D} = -\frac{\lambda^2}{8\pi^2} \frac{d}{dt} \left(\ln \frac{I(t)}{I_0} \right)$$

where I is the intensity of the x-ray. Again as with resistivity this is a low temperature technique most suitable for measuring small diffusion coefficients ^[4].

3 Summary of Method for Measuring Chemical Diffusion Coefficients

Figure 6 shows the diffusion coefficient measurement ranges of the different chemical diffusion measurement techniques reviewed in this report. The dotted boxes represent estimated working ranges from references used in the review of the method. The shaded blocks represent ranges obtained from Landolt-Börnstein^[5], Smithells^[6] or Physical Metallurgy^[3]. If the dotted boxes are open ended then no definitive limit could be found.

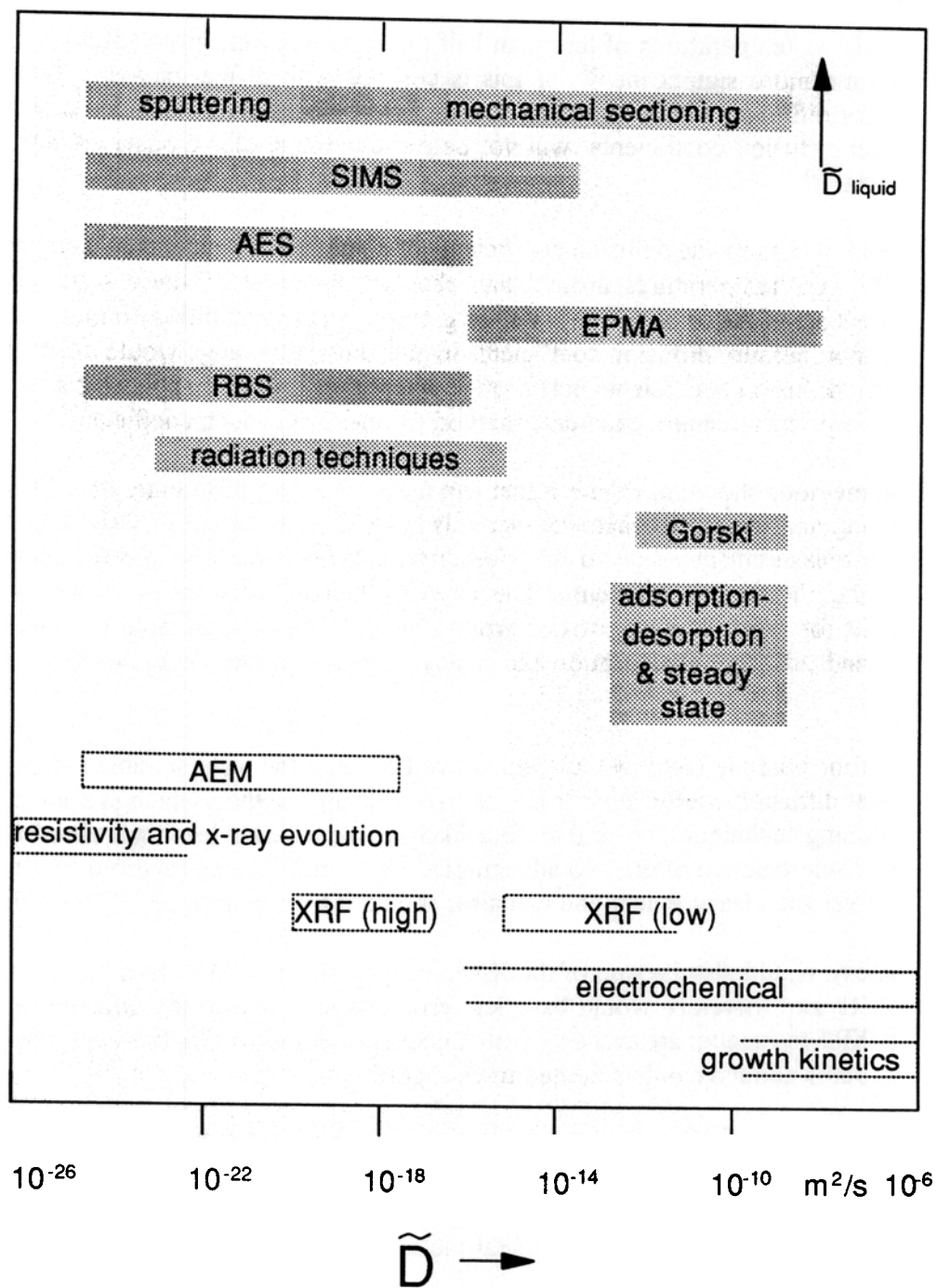


Figure 6. Approximate measurement ranges of various diffusion measurement techniques

In metals, at temperatures of less than half the melting point, grain boundary diffusion begins to become more significant^[53]. If this is coupled with a fine microstructure then the grain boundary diffusion will be the dominant diffusion mechanism^[53]. Under such conditions bulk chemical diffusion coefficients will not be representative of the observed diffusion behaviour of a metal^[53].

Figure 7 and 8 show the diffusion coefficients of a number of elements in aluminium, copper and iron^[54]. At temperatures around half the melting point of these materials, the diffusion coefficient are of the order of $10^{-16} \text{ m}^2\text{s}^{-1}$ or greater. A chemical diffusion measurement technique that cannot measure diffusion coefficients in and above this range would not be able to measure chemical diffusion coefficients in the range where they are most applicable and therefore would not be recommended as a candidate method for measuring such coefficients.

Of the methods shown in Figure 6 that can measure above this range, only EPMA, mechanical sectioning and the electrochemical methods have or in the case of XRF likely to have, a wide enough measurement range to be considered a general purpose measurement technique for measuring diffusion coefficients. The other techniques that measure above $10^{-16} \text{ m}^2\text{s}^{-1}$ are excluded for the following reasons: growth kinetics are only suitable for two phase systems; Gorski and adsorption/desorption and steady state techniques have too narrow a measurement range.

Of the four possible methods outlined above EPMA is the most suitable method for measuring chemical diffusion coefficients. It is a relatively simple method which is non-destructive unlike a sectioning technique and is therefore likely to be a faster less time consuming method. In being non-destructive offers two advantages. The sample can be revisited should there be some doubt over the measurement and can also, should it be required, be further diffusion annealed.

The above would also be true of the XRF, but in general EPMA has a better spacial resolution than XRF and therefore would have less error associated with the diffusion measurement^[20]. Whilst XRF techniques are available with higher spacial resolution, these are not standard pieces of apparatus and have only a limited track record.

Electrochemical methods need a suitable electrolyte for the diffusing species which may not be available, limiting its applicability. Also, sample preparation is difficult as the electrochemical cell used for the measurement has to have good metal-ceramic-metal bonding. This is a much more difficult procedure than the metal-metal bonding required for standard diffusion couple measurements as used by EPMA.

4 Recommendation of a Candidate Technique

The EPMA technique is most suitable method for measuring chemical diffusion coefficients in the range greater than $10^{-16} \text{ m}^2\text{s}^{-1}$ and is recommended as the candidate method for the measurement of such coefficients.

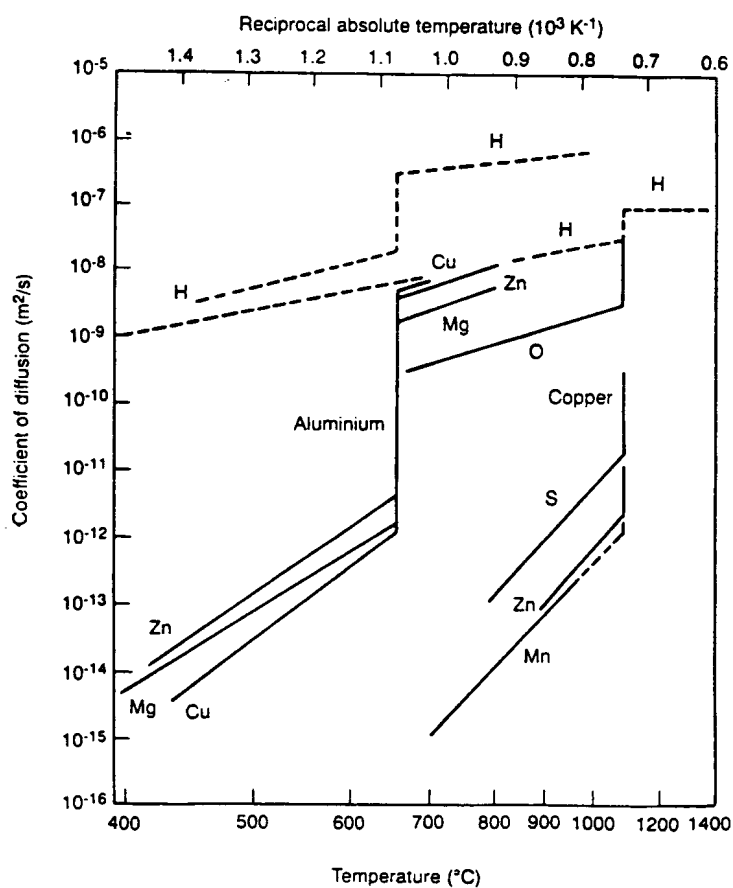


Figure 7. Diffusion coefficients for elements in Al and Cu ^[54].

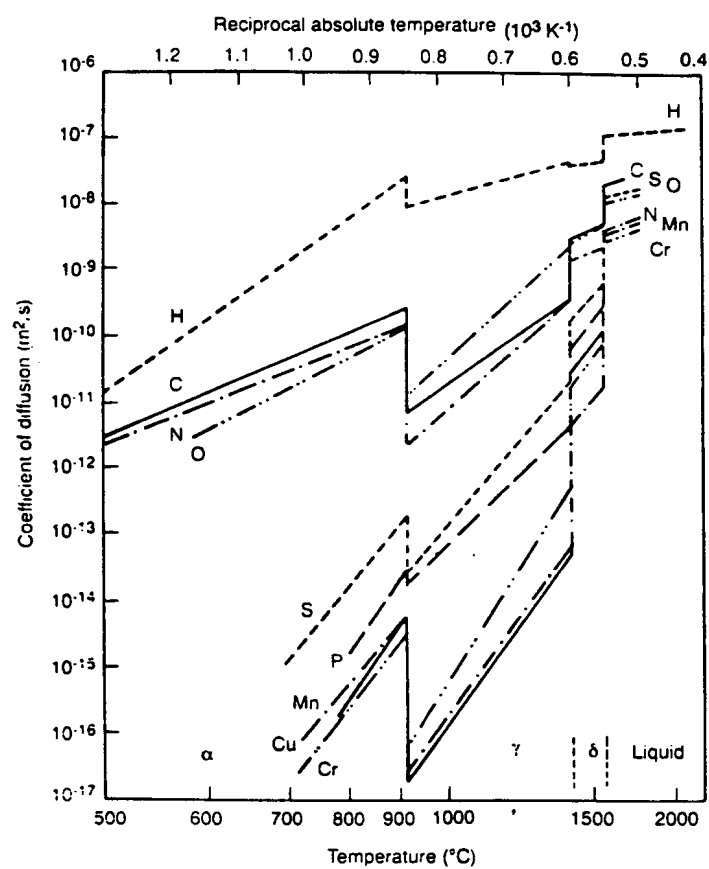


Figure 8. Diffusion coefficients for elements in Fe ^[54].

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