9 Isotope Effect of Diffusion

In this chapter, we consider the diffusion of two chemically identical atoms that differ in their atomic masses. Their diffusivities are different and this difference is denoted as *isotope effect*. The isotope effect, sometimes also called the mass effect, is of considerable interest. It provides an important experimental means of gaining access to correlation effects. Correlation factors of self- and solute diffusion are treated in Chap.7 and values for correlation factors of self-diffusion in several lattices and for various diffusion mechanisms are listed in Table 7.2. Correlation factors of solute diffusion are the subject of Sect. 7.5. We shall see below that the isotope effect is closely related to the correlation factor. Since correlation factors of self-diffusion often take values characteristic for the diffusion mechanism, isotope effects experiments can throw light on the mechanism.

9.1 Single-jump Mechanisms

Let us consider two isotopes α and β of the same element labelled by their isotopic masses m_α and m_β. Because of their different masses, the two isotopes have different diffusion coefficients in the same host lattice. For self- and impurity-diffusion in coordination lattices the tracer diffusivities can be written as:

$$D^*_\alpha = A\omega_\alpha f_\alpha, \quad \text{and} \quad D^*_\beta = A\omega_\beta f_\beta \,. \tag{9.1}$$

The quantity A contains a geometrical factor, the lattice parameter squared, and for a defect mechanism also the equilibrium fraction of defects or the defect availability next to the solute. The atom-defect exchange rates ω_α or ω_β are factors in Eq. (9.1). The correlation factors for vacancy-mediated diffusion in fcc, bcc, and diamond lattices according to Eq. (7.46) have the same mathematical form, sometimes called the *'impurity form'*:

$$f_\alpha = \frac{u}{\omega_\alpha + u}, \quad \text{and} \quad f_\beta = \frac{u}{\omega_\beta + u} \,. \tag{9.2}$$

The quantity u in Eq. (9.2) depends on the exchange rates between vacancy and solvent atoms *but not* on the vacancy-tracer exchange rate (see Chap. 7). Correlation factors of self- and impurity diffusion have the 'impurity form' because tracer isotopes of the same element as the matrix itself are formally ‘solutes’, whose jump rates differ slightly from those of the host atoms due to the different masses. When the small differences between vacancy-tracer and vacancy-host atom exchange rates are neglected the correlation factor of self-diffusion is reduced to one of the values listed in Table 7.2.

After taking the ratio D^*_α / D^*_β and eliminating u and f_β using Eqs. (9.1) and (9.2), we find

$$\frac{D^*_\alpha - D^*_\beta}{D^*_\beta} = f_\alpha \frac{\omega_\alpha - \omega_\beta}{\omega_\beta} \,. \tag{9.3}$$

The tracer-defect exchange rates can be written as

$$\omega_{\alpha,\beta} = \nu^0_{\alpha,\beta} \exp\left(-\frac{G^M_{\alpha,\beta}}{k_\mathrm{B} T} \right) \tag{9.4}$$

where $\nu^0_{\alpha,\beta}$ denote the attempt frequencies of the isotopes α and β, and $G^M_{\alpha,\beta}$ the Gibbs free migration energies of their jumps. In the following discussion we assume

$$G^M_\alpha = G^M_\beta = G^M \,. \tag{9.5}$$

In other words, the activation enthalpies and entropies of the jump are independent of the isotopic masses of the tracers. This is usually well justified, since the barrier for an atomic jump is determined by the electronic interaction, which is identical for two isotopes of the same element, and not by the masses of the nuclei[1]. Because of Eq. (9.5) the ratio of the jump rates reduces to the ratio of the attempt frequencies:

$$\frac{\omega_\alpha}{\omega_\beta} = \frac{\nu^0_\alpha}{\nu^0_\beta} \,. \tag{9.6}$$

In what follows, we first mention a simple approximation to this frequency ratio: Einstein’s model for the vibration frequencies of atoms in a solid describes a crystal as a set of independent harmonic oscillators. WERT [1] has shown in 1950 that in the classical rate theory, ν^0 is the vibration frequency of an atom in its jump direction. Harmonic oscillator theory tells us that the vibration frequencies are inversely proportional to the square-root of their isotopic masses:

$$\frac{\nu^0_\alpha}{\nu^0_\beta} \approx \sqrt{\frac{m_\beta}{m_\alpha}} \,. \tag{9.7}$$

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[1] Hydrogen diffusion is an exception. For hydrogen isotopes quantum effects (see Sect. 18.2), such as zero-point vibrations and tunnelling are relevant. Both effects are mass-dependent. For atoms heavier than Li, quantum effects are usually negligible.

Inserting Eq. (9.7) into Eq. (9.3) and making use of Eq. (9.6) yields

$$\frac{(D_\alpha^* - D_\beta^*)/D_\beta^*}{\sqrt{m_\beta/m_\alpha} - 1} \approx f_\alpha\,. \tag{9.8}$$

This result was derived by SCHOEN in 1958 [2]. It suggests that a measurement of the isotope effect permits a determination of the correlation factor.

Unfortunately the derivation of Eq. (9.8) is based on the Einstein approximation, which assumes that all atoms in the crystal vibrate independently. In other words, the Einstein model neglects many-body effects. Lattice dynamics shows that the coupling between atomic vibrations is important and manifests itself, among other effects, in a spectrum of phonon frequencies. Based on VINEYARD'S [3] classical statistical mechanics treatment of the atomic jump process (see Chap. 4), MULLEN [4] and LE CLAIRE [5, 6] took into account the influence of many-body effects. They obtain the relation

$$\frac{\omega_\alpha - \omega_\beta}{\omega_\beta} = \Delta K \left(\sqrt{\frac{m_\beta}{m_\alpha}} - 1 \right), \tag{9.9}$$

where ΔK is denoted as the *kinetic energy factor*. It is a dimensionless parameter and denotes the fraction of the kinetic energy of the jumping atom at the saddle-point with respect to the total kinetic energy, associated with the motion of all atoms in the jump direction. From Eqs. (9.3) and (9.9) we find

$$\frac{(D_\alpha^* - D_\beta^*)/D_\beta^*}{\sqrt{m_\beta/m_\alpha} - 1} = f_\alpha \Delta K \equiv E_{\alpha,\beta}, \tag{9.10}$$

which replaces the approximation of Eq. (9.8). The abbreviation $E_{\alpha,\beta}$ introduced in Eq. (9.10) is denoted as the *isotope-effect parameter*. In an analogous way, we arrive at

$$\frac{(D_\beta^* - D_\alpha^*)/D_\alpha^*}{\sqrt{m_\alpha/m_\beta} - 1} = f_\beta \Delta K \equiv E_{\beta,\alpha}. \tag{9.11}$$

In principle, the two isotope-effect parameters, $E_{\alpha,\beta}$ and $E_{\beta,\alpha}$, are different because f_α and f_β are also slightly different. However, the relative mass differences between two isotope pairs are often small. Then, the differences between $E_{\beta,\alpha}$ and $E_{\alpha,\beta}$ are usually of the order of a few percent and often smaller than the errors in a typical isotope effect experiment. Therefore, it is common practice in the literature to use the following approximation:

$$f_\alpha \approx f_\beta \approx f\,. \tag{9.12}$$

Equation (9.12) drops the distinction between f_α and f_β. f is sometimes called the *geometric correlation factor*. f refers to a 'hypothetical' tracer isotope with the same jump rate as the isotopes of the solvent. Then, we may drop the distinction between the two isotope effect parameters (i.e. $E_{\alpha,\beta} \approx E_{\beta,\alpha} \approx E$) and get

$$E = f\Delta K\,. \tag{9.13}$$

Because both f and ΔK are positive and not larger than unity we have the following limits for the isotope effect parameter

$$0 < E \ \leq 1\,. \tag{9.14}$$

Equation (9.13) expresses in compact form the relation between isotope effect and correlation factor mentioned at the beginning of this chapter. If the tracer jump is completely decoupled from the motion of other atoms, we have $\Delta K = 1$. This represents the upper limit for the kinetic energy factor. Since a certain amount of coupling between the diffusing atom and the surrounding atoms always exists, we expect $\Delta K < 1$.

For the interstitial mechanism we have

$$E = \Delta K \tag{9.15}$$

since $f = 1$. If several mechanisms with tracer diffusivities $D_I^*, D_{II}^*, \ldots$ operate simultaneously (see Eq. 8.9), measurements of the isotope-effect give an effective isotope-effect parameter, which corresponds to a weighted average

$$E_{eff} = E_I \frac{D_I^*}{D_I^* + D_{II}^* + \ldots} + E_{II} \frac{D_{II}^*}{D_I^* + D_{II}^* + \ldots} + \ldots\ , \tag{9.16}$$

of the isotope effect parameters $E_I, E_{II}, \ldots$ of the individual mechanisms [7].

A measurement of the isotope effect parameter may not uniquely determine f and hence the diffusion mechanism. Nevertheless, it is definitely useful to identify mechanisms, which are consistent with an experimental value of E, and to reject ones, which are not acceptable.

We remind the reader that in the derivation of Eq. (9.13) we have made use of the mathematical form of Eq. (9.2). Chap. 7 has shown that there are indeed important mechanisms for which the correlation factor has this form. This is the case for the monovacancy mechanisms in cubic coordination lattices and also for the divacancy mechanism in an fcc lattice [8]. There are, however, mechanisms where the correlation factor does not have the impurity form (9.2). Examples are mechanisms which have several jump rates such as diffusion in non-cubic crystals and diffusion mechanisms in cubic crystals, which involve more than one tracer jump rate (e.g., for nearest-neighbour and next-nearest neighbour jumps). Sometimes it is possible to derive equations equivalent to Eq. (9.10) [6]. An example is divacancy diffusion in bcc crystals involving several configurations of a divacancy and transitions between these configurations [9, 10]. For a more detailed discussion of the validity of Eq. (9.13) we refer the reader to a review on isotope effects in diffusion by PETERSON [11].

9.2 Collective Mechanisms

Equation (9.10) has been derived for single-jump mechanisms, where in a jump event only the tracer atom changes permanently its site. A more general jump process involves the simultaneous (or collective) jumping of more than one atom. A simple example is the colinear interstitialcy mechanism (see Fig. 6.7), where two atoms jump simultaneously. For a dumbbell-interstitialcy mechanism even three atoms are displaced permanently. Other examples are direct exchange, ring mechanism an chain-like motion of several atoms. All these mechanisms involve the collective motion of several atoms (see Chap. 6).

For a mechanism in which n atoms move collectively during one jump event, the masses in Eq. (9.7) must be replaced by $(n-1)m + m_{\alpha,\beta}$, where m denotes the average mass of the host atoms [5]. Then,

$$\frac{\nu_\alpha^0}{\nu_\beta^0} = \sqrt{\frac{(n-1)m + m_\beta}{(n-1)m + m_\alpha}} \tag{9.17}$$

and the isotope effect parameter is given by [6]

$$E = \frac{(D_\alpha^* - D_\beta^*)/D_\beta^*}{\sqrt{[m_\beta + (n-1)m])/[m_\alpha + (n-1)m]} - 1} \,. \tag{9.18}$$

As a consequence, the isotope effect is reduced. For a highly collective mechanism, a very small isotope effect is plausible, due to the 'dilution' of the mass effect by the participation of many solvent atoms in the jump event. For example, in metallic glasses, collective jump events of chains of atoms dominate, which typically involve ten to twenty atoms. Indeed the isotope effect parameter is close to zero (see [15, 16] and Chap. 29).

9.3 Isotope Effect Experiments

Isotope effects in diffusion are usually small effects. An exception is diffusion of hydrogen isotopes, which is considered later in Sect. 18.2. Depending on the isotope pair (see Table 9.1), the quantity $(D_\alpha^* - D_\beta^*)/D_\beta^*$ is typically of the order of a few percent. For example, for the isotope pair ^{105}Ag and ^{110m}Ag the term in brackets of Eq. (9.9) is about 0.024. Thus, resolving the effects of a relatively small mass difference on the diffusion coefficient is a challenging task. Since the errors in tracer measurements are typically a few percent, it is not feasible to deduce the isotope effect parameter from determinations of D_α^* and D_β^* in separate experiments.

Typical experimental situations for isotope effect studies are illustrated in Fig. 9.1. Two isotopes of one element are diffused simultaneously into the same sample [11–13]. In this way, errors arising from temperature and time

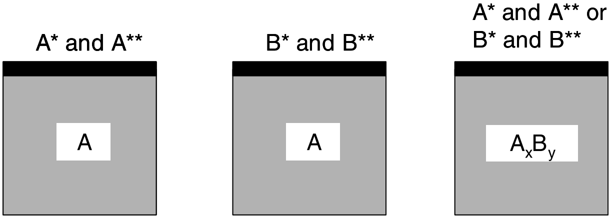

Fig. 9.1. Schematic illustration of various isotope effect experiments. *Left*: isotope pair A^*/A^{**} in a solid element A. *Middle*: isotope pair B^*/B^{**} in a pure solid A. *Right*: isotope pairs A^*/A^{**} or B^*/B^{**} in a binary A_xB_y compound

measurements and from the profiling procedure drop out, since these errors affect both isotopes in the same way. If the isotopes α and β are co-deposited in a very thin layer, the diffusion penetration curves of both isotopes (see also Chap. 13) are given by

$$C_{\alpha,\beta} = C^0_{\alpha,\beta} \exp\left(-\frac{x^2}{4D^*_{\alpha,\beta}t}\right) , \tag{9.19}$$

where $C_{\alpha,\beta}$ denote their concentrations in depth x after a diffusion anneal during time t. For a given time the quantities $C^0_{\alpha,\beta}$ are constants. By taking the logarithm of the ratio C_α/C_β, we get from Eq. (9.19)

$$\begin{aligned} \ln\frac{C_\alpha}{C_\beta} &= \ln\frac{C^0_\alpha}{C^0_\beta} - \frac{x^2}{4D^*_\alpha t} + \frac{x^2}{4D^*_\beta t} \\ &= \ln\frac{C^0_\alpha}{C^0_\beta} + \frac{x^2}{4D^*_\alpha t}\left(\frac{D^*_\alpha}{D^*_\beta} - 1\right) . \end{aligned} \tag{9.20}$$

Using Eq. (9.19) to eliminate x^2, we obtain

$$\ln\frac{C_\alpha}{C_\beta} = \text{const} - \left(\frac{D^*_\alpha}{D^*_\beta} - 1\right)\ln C_\alpha . \tag{9.21}$$

Equation (9.21) shows that from the slope of a plot of $\ln(C_\alpha/C_\beta)$ *versus* $\ln C_\alpha$ the quantity $(D^*_\alpha - D^*_\beta)/D^*_\beta$ can be deduced.

Isotope effect experiments are usually performed with radioisotope pairs. Examples of such pairs suitable for isotope effect studies are listed in Table 9.1. Suppose, for example, that the radioisotopes ^{195}Au and ^{199}Au are diffused into a single crystal of gold. Then, the isotope effect of self-diffusion in gold is studied. With the radioisotopes ^{65}Zn and ^{69}Zn diffusing in gold, the isotope effect of Zn solute diffusion is accessible. In an isotope effect experiment the specific activities (proportional to the concentrations) of both isotopes must be determined separately. Separation techniques can be based

Table 9.1. Examples for pairs of radioisotopes suitable for isotope experiments in diffusion studies

^{12}C	^{22}Na	^{55}Fe	^{57}Co	^{65}Zn	^{64}Cu	^{105}Ag	^{195}Au
^{13}C	^{24}Na	^{59}Fe	^{60}Co	^{69}Zn	^{67}Cu	^{110}Ag	^{198}Au

on the different half-lives of the isotopes, on the differences in the emitted γ- or β-radiation using γ-spectroscopy, or on a combination of γ- and β-counting. Half-life separation requires a short-lived and a long-lived isotope. Scintillation spectroscopy can be used, if the γ spectra are favourable. High-resolution intrinsic Ge or Ge(Li) detectors are recommended for separation and corrections for the Compton-scattered radiation must be made. All methods require careful monitoring of radioactive impurities by either half-life measurements or by spectroscopy. Very good counting statistics is necessary to resolve the small differences between the diffusivities of the two isotopes.

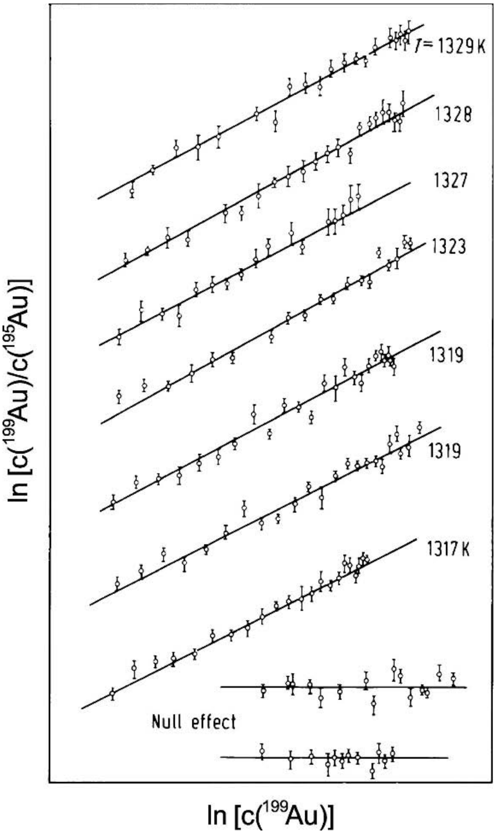

Fig. 9.2. Simultaneous diffusion of the radioisotope pair ^{199}Au and ^{195}Au in monocrystalline Au according to Herzig et al. [14]

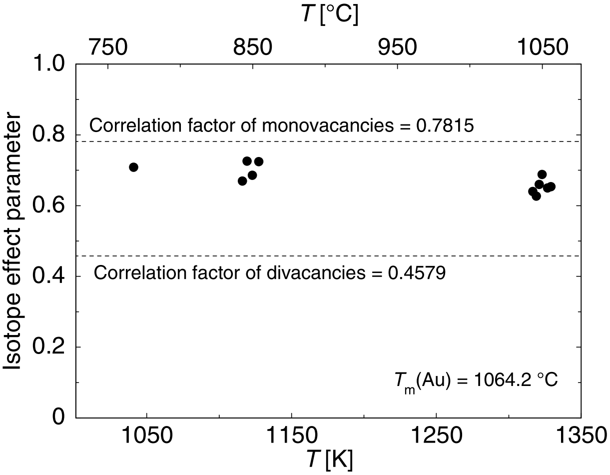

Fig. 9.3. Isotope effect parameters of self-diffusion in Au according to Herzig et al. [14]

Further details about the experimental techniques in isotope effect experiments can be found in the review of Rothman [12]. In a few experiments, stable isotope pairs were utilised as diffusers. Then, the separation is achieved by secondary ion mass spectroscopy (SIMS), which requires good mass resolution and careful background corrections.

Figure 9.2 shows isotope effect measurements for self-diffusion in single crystals of gold according to Herzig et al. [14]. In this experiment the isotope pair ^{199}Au and ^{195}Au was used. The profile measurement was achieved by serial sectioning on a microtome. The isotope concentrations C_α and C_β in each section were separated by combining γ spectroscopy and half-life separation. The logarithm of the ratio C(^{199}Au)/C(^{195}Au) is plotted *versus* the logarithm of C(^{199}Au), as suggested by Eq. (9.21). Isotope effect parameters deduced therefrom are shown in Fig. 9.3. The correlation factor for self-diffusion via monovacancies in an fcc crystal is $f_{1V} = 0.78146$ (see Table 7.2). The experimental results demonstrate that self-diffusion in gold is dominated by the monovacancy mechanism with a kinetic energy factor of $\Delta K \approx 0.9$, which is close to its upper limit 1. The slight decrease of the isotope effect parameter with increasing temperature has been attributed to a small contribution of divacancies according to Eq. (9.16). The divacancy correlation factor ($f_{2V} = 0.458$, see Table 7.2) is smaller than that of monovacanices. Near the melting temperature T_m, the divacancy contribution in Au is, however, not more than 20 % of the total diffusivity [14].

Reviews of isotope effects in diffusion were given by Le Claire [6] and by Peterson [11]. A comprehensive collection of isotope effect data, which were available until 1990, can be found in Chap. 10 of [13]. Diffusion and isotope effects in metallic glasses have been reviewed by Faupel et al. [15, 16].

In metallic glasses, isotope effects parameters are usually small and indicate a collective mechanism, which involve the simultaneous chain- or ring-like motion of several (10 to 20) atoms. As an example, isotope effect measurements involving the isotopes ^{57}Co and ^{60}Co were carried out in the deeply supercooled liquid state of bulk metallic glasses. The isotope effect parameter is very small (around 0.1) over the whole temperature range and exhibits no significant temperature dependence (see Chap. 29) . The magnitude of the isotope effect is similar to that of the isotope effect found in the glassy state of conventional metallic glasses [15, 16]. This lends support to the view that the diffusion mechanism in metallic glasses does not change at the calorimetric glass transition temperature. Highly collective hopping processes occurring in the glassy state still determine long-range diffusion in a deeply undercooled melt.

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