

8 Dependence of Diffusion on Temperature and Pressure

So far, nothing has been said about the dependence of diffusion upon thermodynamic variables such as temperature, pressure, and composition. Diffusion in solids generally depends rather strongly on temperature, being low at low temperatures but appreciable at high temperatures. In an *Arrhenius diagram* the logarithm of the diffusivity is plotted *versus* the reciprocal absolute temperature. The wide range of diffusivities and activation parameters, which can occur in a solid is illustrated in the Arrhenius diagram of Fig. 8.1, where diffusion coefficients for various elements in lead are displayed. The ‘spectrum’ of diffusivities covers many orders of magnitude from the very fast diffusion of copper to the rather slow self-diffusion of lead. For semiconductors, an even wider spectrum of foreign atom diffusivities has been reported (see Chap. 24).

The variation of the diffusion coefficient with pressure, at least for pressures accessible in laboratory devices, is far less striking than that with temperature. Usually, the diffusivity decreases with pressure not more than a factor of ten for pressures of 1 GPa (10^4 bar). The variation of the diffusivity with composition can range from the very slight to significant. Examples of the influence of composition on diffusion can be found in Parts III to VI of this book. In this chapter, we concentrate on the dependence of the diffusivity on temperature and pressure.

8.1 Temperature Dependence

8.1.1 The Arrhenius Relation

The temperature dependence of diffusion coefficients is frequently, but by no means always, found to obey the Arrhenius formula

$$D = D^0 \exp\left(-\frac{\Delta H}{k_B T}\right). \quad (8.1)$$

In Eq. (8.1) D^0 denotes the *pre-exponential factor* also called the *frequency factor*, ΔH the *activation enthalpy* of diffusion¹, T the absolute temperature,

¹ In the literature the symbol Q is also used instead of ΔH .

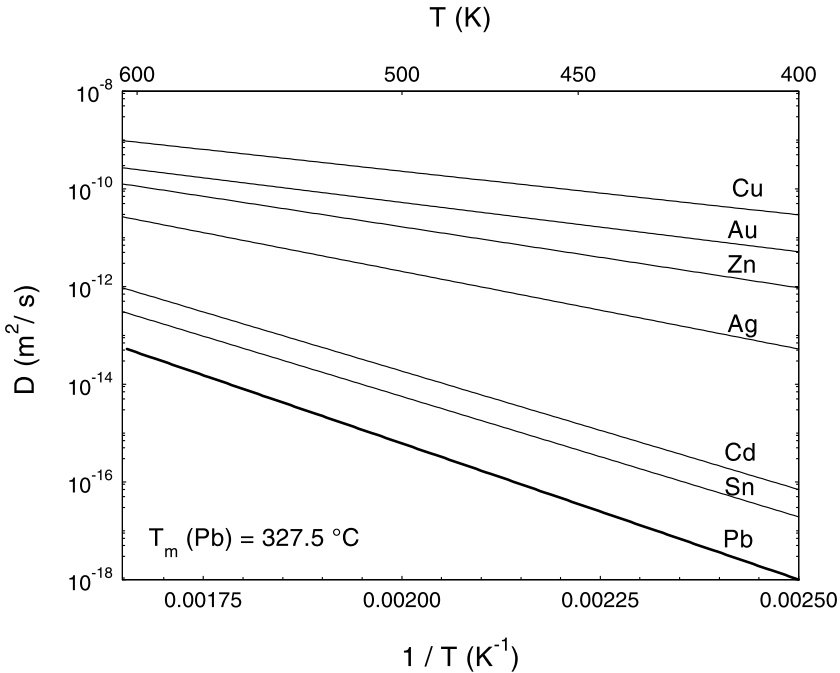


Fig. 8.1. Arrhenius plot of diffusion for various elements in Pb; activation parameters from [1]

and k_B the Boltzmann constant. Both ΔH and D^0 , are called the *activation parameters* of diffusion². The activation enthalpy of a diffusion process

$$\Delta H = -k_B \frac{\partial \ln D}{\partial (1/T)} \quad (8.4)$$

corresponds to the negative slope of the Arrhenius diagram. For a temperature-independent activation enthalpy, the Arrhenius diagram is a straight line with slope $-\Delta H/k_B$. The intercept of the extrapolated Arrhenius line

² Equation (8.1) is also written as

$$D = D^0 \exp\left(-\frac{\Delta H}{RT}\right), \quad (8.2)$$

where R denotes the gas constant. Then,

$$R = N_A k_B = 8.3145 \times 10^{-3} \text{ kJ mol}^{-1} \text{ K}^{-1} \quad (8.3)$$

with N_A denoting the Avogadro number. The activation enthalpy ΔH is either measured in SI units $\text{kJ mol}^{-1} \text{ K}^{-1}$ or in eV per atom. Note that 1 eV per atom = $96.472 \text{ kJ mol}^{-1}$.

for $T^{-1} \Rightarrow 0$ yields the pre-exponential factor D^0 . It can usually be written as

$$D^0 = gf\nu^0 a^2 \exp\left(\frac{\Delta S}{k_B}\right), \quad (8.5)$$

where ΔS is called the *diffusion entropy*, g is a geometrical factor, f is the correlation factor, ν^0 is the attempt frequency, and a some lattice parameter. Combining Eqs. (8.1) and (8.5) we can write

$$D = gf\nu^0 a^2 \exp\left(\frac{\Delta S}{k_B}\right) \exp\left(-\frac{\Delta H}{k_B T}\right) = gf\nu^0 a^2 \exp\left(-\frac{\Delta G}{k_B T}\right). \quad (8.6)$$

On the right-hand side of Eq. (8.6), the *Gibbs free energy of activation*

$$\Delta G = \Delta H - T\Delta S \quad (8.7)$$

has been introduced to combine the activation enthalpy and entropy. Thermodynamics tells us that

$$\frac{\partial \Delta H}{\partial T} = T \frac{\partial \Delta S}{\partial T}. \quad (8.8)$$

Thus, the temperature variations of enthalpy and entropy are coupled. If ΔH is temperature independent, this must hold for ΔS as well and vice versa.

Activation parameters for diffusion in metals and alloys can be found in the data collection edited by the present author [1] and for semiconductors and other non-metallic materials in a collection edited by BEKE [2].

The physical interpretation of the activation parameters ΔH and of D^0 depends on the diffusion mechanism, on the type of diffusion process, and on the lattice geometry. Simple Arrhenius behaviour should not, however, be assumed to be universal. Departures from it may arise for reasons which range from fundamental aspects of the mechanisms of atomic migration (multiple mechanisms, multiple jump vectors, ...) to effects associated with impurities and/or with microstructural features such as grain boundaries or dislocations. In this chapter, we consider lattice diffusion. Diffusion along high-diffusivity paths is the subject of Chaps. 31 and 32.

If several diffusion mechanisms with diffusion coefficients D_I, D_{II}, \dots and activation parameters $\Delta H_I, \Delta H_{II}, \dots$ and D_I^0, D_{II}^0, \dots contribute to the total lattice diffusivity, D , we have

$$D = D_I + D_{II} + \dots = D_I^0 \exp\left(-\frac{\Delta H_I}{k_B T}\right) + D_{II}^0 \exp\left(-\frac{\Delta H_{II}}{k_B T}\right) + \dots \quad (8.9)$$

In such cases, the Arrhenius diagram will show an upward curvature. With increasing (decreasing) temperature the contribution of the process with the highest (lowest) activation enthalpy becomes more and more important. The activation enthalpy defined by Eq. (8.4) is then an effective (or apparent) value

$$\Delta H_{eff} = \Delta H_I \frac{D_I}{D_I + D_{II} + \dots} + \Delta H_{II} \frac{D_{II}}{D_I + D_{II} + \dots} + \dots, \quad (8.10)$$

which represents a weighted average of the individual activation enthalpies. A well-studied example is self-diffusion in metals. Compared with divacancies (index: 2V), usually the monovacancy mechanism (index: 1V) is the dominating contribution to self-diffusion in fcc metals at temperatures below about 2/3 of the melting temperature since $\Delta H_{1V} < \Delta H_{2V}$. At higher temperatures divacancies contribute with a magnitude that varies from metal to metal (see [3, 4] and Chap. 17).

8.1.2 Activation Parameters – Examples

In what follows, we consider explicitly the physical interpretation of the activation parameters for three examples, all concerning cubic lattices: interstitial diffusion, self-diffusion via vacancies, and solute diffusion in a dilute substitutional alloy.

For **direct interstitial diffusion** (see Chap. 6) in a dilute interstitial alloy an unoccupied interstice is available next to the jumping atom. Random walk theory of Chap. 4 tells us that the diffusivity of solute interstitials can be written as

$$D = ga^2\omega = ga^2\nu^0 \exp\left(-\frac{G^M}{k_B T}\right), \quad (8.11)$$

where g is a geometrical factor, a the lattice parameter, and ω the jump rate to a neighbouring interstitial site. For octahedral interstitials in the fcc lattice we have $g = 1$ and in the bcc lattice $g = 1/6$.

As discussed in Chap. 5, the Gibbs free energy of migration G^M – the major parameter in the jump rate ω – can be separated according to

$$G^M = H^M - TS^M, \quad (8.12)$$

where H^M denotes the enthalpy and S^M the entropy of migration of the interstitial solute. Comparing Eqs. (8.1) and (8.11), the activation parameters of interstitial diffusion have the following meaning:

$$\Delta H \Rightarrow H^M \quad \text{and} \quad \Delta S \Rightarrow S^M. \quad (8.13)$$

Direct interstitial diffusion is the simplest diffusion process. The enthalpy and entropy of diffusion are identical with the pertinent migration quantities of the interstitial. Activation enthalpies of interstitial diffusers, such as H, C, N, and O in metals, tend to be fairly low since no defect formation enthalpy is required. For the same reason, interstitial diffusion is a much faster process than self- or substitutional solute diffusion.

Self-diffusion and diffusion of substitutional solutes (impurities) are defect-mediated. The diffusivity is, in essence, a product of geometrical

terms ga^2 , a correlation factor (f for self-diffusion or f_2 for impurity diffusion) and of the atomic jump rate (Γ for self-diffusion or Γ_2 for impurity diffusion):

$$D = fga^2\Gamma \quad (\text{self-diffusion}), \quad D_2 = f_2ga^2\Gamma_2 \quad (\text{impurity diffusion}). \quad (8.14)$$

In the case of self-diffusion, the defect availability equals the equilibrium site fraction of the defect, C_D^{eq} , discussed in Chap. 5. For a monovacancy mechanism in an elemental crystal, we have $C_D^{eq} \equiv C_{1V}^{eq}$. The *jump rate of a self-atom* can be written as

$$\Gamma = C_D^{eq}\omega = g_D \exp\left(-\frac{G_D^F}{k_B T}\right)\omega, \quad (8.15)$$

where ω denotes the *defect jump rate*. On the right-hand side of Eq. (8.15), the expression for the equilibrium fraction of defects from Chap. 5 has been inserted with the Gibbs free energy of defect formation G_D^F . g_D is a geometric factor depending on the lattice geometry and the type of the defect. For monovacancies in a monoatomic solid $g_D = 1$. For self-interstitials in $\langle 100 \rangle$ -dumbbell configuration in an fcc crystal $g_D = 3$.

For solute diffusion in a very dilute substitutional alloy (often denoted as impurity diffusion) the Lomer relation Eq. (5.31) from Chap. 5 describes the defect-availability, p , on a site adjacent to a solute. We then find for the *jump rate of a substitutional impurity*:

$$\Gamma_2 = p\omega_2 = C_D^{eq} \exp\left(\frac{G^B}{k_B T}\right)\omega_2 = g_D \exp\left(-\frac{G_D^F - G^B}{k_B T}\right)\omega_2. \quad (8.16)$$

G^B denotes the Gibbs free energy of binding between defect and solute and ω_2 the defect-solute exchange rate. The quantity $G_D^F - G^B$ is the Gibbs free energy of defect formation on a site adjacent to the solute. For an attractive interaction ($G^B > 0$) the defect availability p is enhanced whereas for a repulsive interaction ($G^B < 0$) it is reduced compared to the equilibrium defect concentration in the pure host lattice. As usual, G^B can be decomposed according to $G^B = H^B - TS^B$, where H^B is the binding enthalpy and S^B the binding entropy (see Chap. 5).

The Gibbs free energies of the defect-mediated jumps can be separated into the enthalpic and entropic terms according to:

$$G^M = H^M - TS^M \quad (\text{self-atom}), \quad G_2^M = H_2^M - TS_2^M \quad (\text{impurity}). \quad (8.17)$$

G^M is the Gibbs free energy of motion for an exchange of the self-atom with the defect in a pure solvent. G_2^M is the barrier for an exchange-jump between impurity and defect (e.g., a vacancy). Then, the exchange jump rates read either

$$\omega = \nu^0 \exp\left(-\frac{G^M}{k_B T}\right) = \nu^0 \exp\left(\frac{S^M}{k_B}\right) \exp\left(-\frac{H^M}{k_B T}\right), \quad (8.18)$$

or

$$\omega_2 = \nu_2^0 \exp\left(-\frac{G_2^M}{k_B T}\right) = \nu_2^0 \exp\left(\frac{S_2^M}{k_B}\right) \exp\left(-\frac{H_2^M}{k_B T}\right), \quad (8.19)$$

where ν^0, ν_2^0 denote the corresponding *attempt frequencies*. Usually, the Debye frequency of the lattice is an adequate approximation for the attempt frequencies. Of course, values of the Gibbs energies, enthalpies, and entropies of motion depend on the defect involved and on the material considered.

Inserting the expressions of f and Γ or f_2 and Γ_2 into Eq. (8.14), we arrive at the following activation parameters:

- For self-diffusion via one type of defect (subscript D) we get

$$\Delta H \Rightarrow H_D^F + H_D^M \quad \text{and} \quad \Delta S \Rightarrow S_D^F + S_D^M. \quad (8.20)$$

The activation enthalpy (entropy) of self-diffusion equals the sum of the formation and migration enthalpies (entropies) of the diffusion-mediating defect. For a monovacancy we have $\Delta H = H_{1V}^F + H_{1V}^M$.

- For solute diffusion in a dilute substitutional alloy the activation enthalpy is a more slightly complex quantity. Combining Eqs. (8.4), (8.14), and (8.16) we get

$$\Delta H_2 \Rightarrow H_D^F - H^B + H_2^M + C. \quad (8.21)$$

The correlation term

$$C = -k_B \frac{\partial \ln f_2}{\partial(1/T)} \quad (8.22)$$

arises from the temperature dependence of the correlation factor f_2 of impurity diffusion (see Chap. 7). The quantity $H_D^F - H^B$ is the formation enthalpy of the defect-impurity complex and H_2^M the barrier for a impurity-defect exchange. Depending on the various contributions, the activation enthalpy of substitutional impurity diffusion, ΔH_2 , can be higher or lower than the activation enthalpy of self-diffusion (see Chap. 19).

8.2 Pressure Dependence

The effect of hydrostatic pressure p on diffusion can easily be recognised from the Arrhenius expression Eq. (8.6). A variation of the diffusivity with pressure is largely due to the fact that the Gibbs free energy of activation varies with pressure according to

$$\Delta G = \Delta H - T\Delta S = \Delta E - T\Delta S + p\Delta V. \quad (8.23)$$

Here ΔE denotes the *activation energy* (ΔE is the change in internal energy) and ΔV the *activation volume* of diffusion. Thermodynamic tells us that

$$\Delta V = \left(\frac{\partial \Delta G}{\partial p}\right)_T. \quad (8.24)$$

Equation (8.24) can be considered as the definition of the activation volume.

A comprehensive characterisation of a diffusion process requires information about three activation parameters, namely:

$$\Delta E, \Delta S, \text{ and } \Delta V.$$

The activation energy ΔE and the entropy ΔS are usually well appreciated in the diffusion literature, whereas the activation volume ΔV is often a ‘forgotten’ parameter. Activation enthalpy and activation energy are related via

$$\Delta H = \Delta E + p\Delta V. \quad (8.25)$$

The term $p\Delta V$ can be significant at high pressures. At ambient pressure, it is almost negligible for solids. Then $\Delta E \approx \Delta H$ and activation energy and activation enthalpy are synonymous.

Equations (8.6) and (8.24) show that the activation volume can be obtained from measurements of the pressure dependence of the diffusion coefficient at constant temperature via

$$\Delta V = -k_{\text{B}}T \cdot \left(\frac{\partial \ln D}{\partial p} \right)_T + \underbrace{k_{\text{B}}T \cdot \frac{\partial \ln (fa^2\nu^0)}{\partial p}}_{\text{corr. term}}. \quad (8.26)$$

As an example, Fig. 8.2 shows the self-diffusion coefficient of gold as a function of pressure at constant temperature. The slope of the logarithm of D as a function of p corresponds to the first term of Eq. (8.26). The second term on the right-hand side of Eq. (8.26) is a correction term. It can be estimated from the isothermal compressibility κ_T and the Grüneisen constant γ_G [5–7]:

$$\text{corr. term} \approx k_{\text{B}}T\kappa_T\gamma_G. \quad (8.27)$$

Estimates for the correction terms on the basis of Eq. (8.27) lead to small corrections in the range of 0.01 to 0.03 Ω , where Ω denotes the atomic volume. Often the correction term can be neglected within the experimental accuracy. In the case of Fig. 8.2, the activation volume is $\Delta V = 0.76 \Omega$.

If several mechanisms with diffusivities D_I, D_{II}, \dots operate simultaneously (see Eq. 8.9), measurements of the pressure dependence give an effective activation volume

$$\Delta V_{\text{eff}} = \Delta V_I \frac{D_I}{D_I + D_{II} + \dots} + \Delta V_{II} \frac{D_{II}}{D_I + D_{II} + \dots} + \dots, \quad (8.28)$$

which is a weighted average of the activation volumes of the individual activation volumes $\Delta V_I, \Delta V_{II}, \dots$. Since the relative contributions of several mechanisms vary with temperature (and pressure) the effective activation volume is temperature (and pressure) dependent.

Activation volumes of ionic conduction (see Chaps. 26 and 27) can be determined from the pressure dependence of the dc conductivity, σ_{dc} , according to

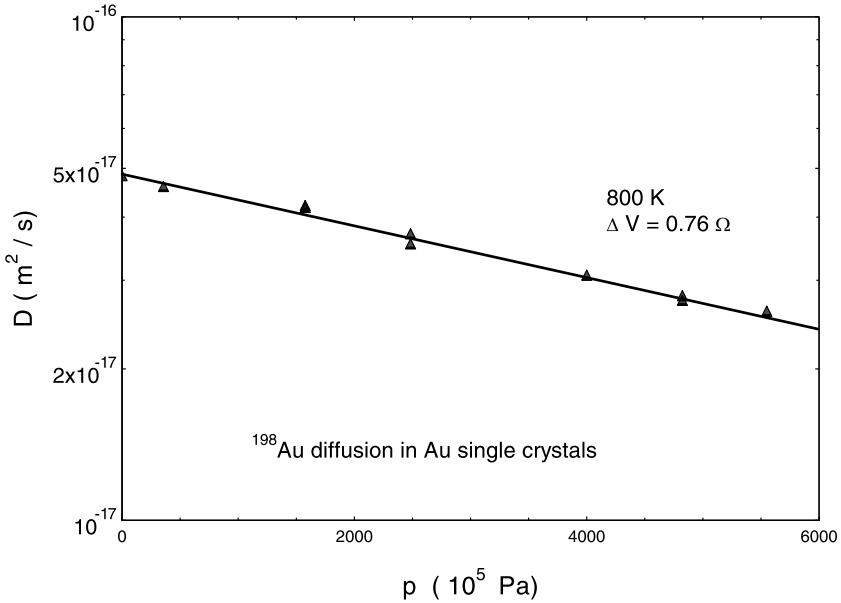


Fig. 8.2. Pressure dependence of ^{198}Au diffusion in Au single crystals at constant temperature according to WERNER AND MEHRER [11]. Ω denotes the atomic volume of Au

$$\Delta V_{\sigma} \approx -k_{\text{B}}T \frac{\partial \ln \sigma_{dc}}{\partial p}. \quad (8.29)$$

The atomistic meaning of ΔV_{σ} depends on the type of the ion-conducting material, on the type of disorder (Frenkel or Schottky disorder), and on the temperature region studied (intrinsic or extrinsic region). Examples are discussed below.

There are good reasons why the study of pressure effects has consumed energies of many researcher in the past. First, a thorough understanding of diffusion requires knowledge about the influence of pressure on the diffusivity. Second, in favourable cases the value of ΔV itself, its magnitude and sign, can throw light on the mechanism(s) of diffusion that is (are) operating (see below). Some selected values for activation volumes are listed in Table 8.1. For elemental crystals the unit is the atomic volume Ω ; for compounds the unit is the molar volume V_m . For a comprehensive collection of activation volumes for metals and alloys available until 1990 the reader is referred to Chap. 10 in [1]. A more recent review about the effects of pressure on self- and solute diffusion in metals and semiconductors is given in [6].

The microscopic interpretation of the activation volume ΔV depends on the mechanism of diffusion as it also does for ΔH and ΔS . As discussed in Chap. 6, self-diffusion in crystalline solids is mediated by defects. In metals, monovacancies dominate self-diffusion at low and moderate temperatures,

Table 8.1. Activation volumes of diffusion and ionic conduction; in units of the atomic volume Ω for elements; in units of the molar volume V_m for compounds.

Diffusion process	$\Delta V/\Omega$ or $\Delta V/V_m$	Reference
Cu self-diffusion	+0.93 to +1.09	Beyeler and Adda [8]
Ag self-diffusion	+0.66 to +0.88	Beyeler and Adda [8], Rein and Mehrer [9]
Au self-diffusion	+0.72 to +0.75	Dickerson et al. [10], Beyeler and Adda [8] Werner and Mehrer [11], Rein and Mehrer [9]
Na self-diffusion	+0.4 to +0.75	Mundy [12]
Ge diffusion in silicon	-0.68 to -0.28	Södervall et al. [15], Aziz et al. [16]
N in α -iron	+0.05	Bosman et al. [13]
C in α -iron	-0.08 to -0.02	Bosman et al. [14]
Al self-diffusion	+1.29	Beyeler and Adda [8]
Ge in Al	+1.16 to + 1.24	Thürer et al. [17]
Zn in Al	+0.74 to +1.09	Erdelyi et al. [18]
Mn in Al	+1.67	Rummel et al. [19]
Co in Al	+1.64 to 1.93	Rummel et al. [19]
Schottky pair formation: V_{SP}^F	1.63 for KBr 2.04 for NaCl 1.23 for KBr 1.37 for NaBr	Yoon and Lazarus [22]
Cation migration: V_{VC}^M	0.21 for KCl 0.26 for NaCl 0.25 for KBr 0.25 for NaBr	Yoon and Lazarus [22]
Intrinsic conduction: $V_{VC}^M + V_{SP}^F/2$	1.03 for KCl 1.28 for NaCl 0.87 for KBr 0.93 for NaBr	Yoon and Lazarus [22]
Ag ion conduction α -AgI	≈ 0	Mellander [23]

whereas divacancies contribute to some extent as temperatures approach the melting temperature. Self-interstitials are important, for example, in silicon. In what follows, we illustrate the activation volumes for various mechanisms.

8.2.1 Activation Volumes of Self-diffusion

For a defect mechanism of self-diffusion the Gibbs free energy of activation is composed of a formation (superscript F) and a migration (superscript M) term (see Sect. 8.1):

$$\Delta G = G_D^F + G_D^M. \quad (8.30)$$

Considering Eq. (8.24) it is obvious that the activation volume is also composed of a formation volume, V_D^F , and a migration volume, V_D^M , of the diffusion-mediating defect according to

$$\Delta V = V_D^F + V_D^M. \quad (8.31)$$

The **formation volume of a monovacancy** is illustrated in Fig. 8.3. The left-hand side of the figure indicates a vacancy in a ‘rigid’ lattice. Without relaxation the volume of the crystal would increase by one atomic volume Ω . The situation illustrated on the right-hand side corresponds to a vacancy with some relaxation of the neighbouring atoms. This picture indicates for the formation volume of a monovacancy:

$$V_{1V}^F = +\Omega - V_{rel,1V}. \quad (8.32)$$

Usually, inward relaxation is found, which implies that the formation volume of the vacancy V_{1V}^F is somewhat smaller than Ω as the relaxation volume $V_{rel,1V}$ is positive. The amount and sign of relaxation depend on the material.

The **formation volume of a divacancy** encompasses the increase of the crystal volume due to the creation of two new lattice sites minus the relaxation volume $V_{rel,2V}$:

$$V_{2V}^F = +2\Omega - V_{rel,2V}. \quad (8.33)$$

The formation volume of the divacancy is larger than that of a monovacancy, i.e. $V_{2V}^F > V_{1V}^F$. For a material in which diffusion is mediated by mono- and divacancies the total activation volume increases as the relative divacancy contribution to the total diffusivity increases with temperature (see Chap. 17).

The **formation volume of a self-interstitial** is illustrated in Fig. 8.4. Without relaxation the formation of a self-interstitial would decrease the crystal volume by one atomic volume. On the other hand, the formation of a self-interstitial causes (considerable) outward relaxation of the surrounding lattice.

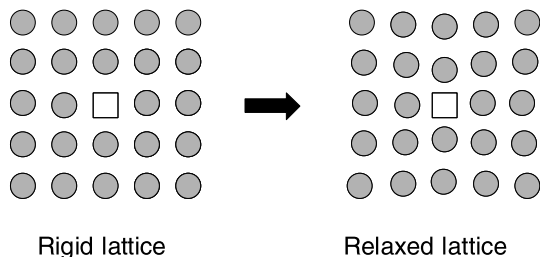


Fig. 8.3. Schematic illustration of the formation volume of a vacancy

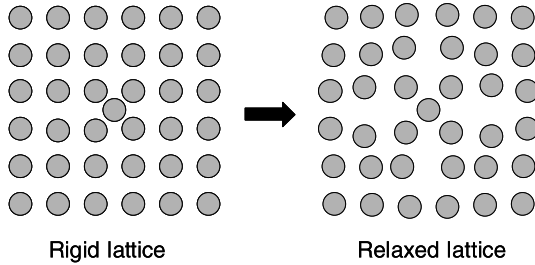


Fig. 8.4. Illustration of the formation volume of a self-interstitial

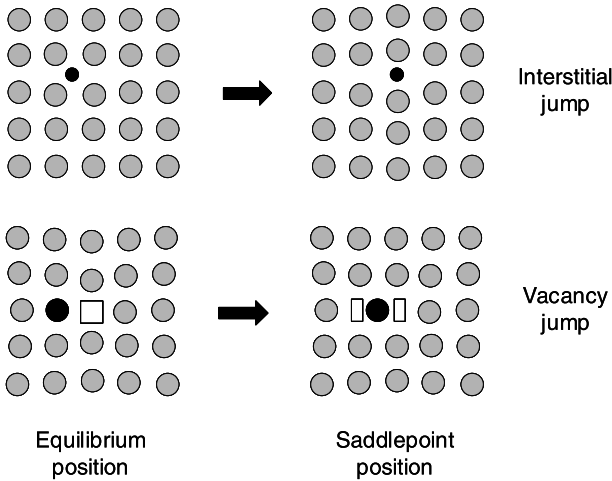


Fig. 8.5. Illustration of the migration volume. *Upper part*: interstitial migration. *Lower part*: vacancy migration

$$V_I^F = -\Omega + V_{rel,I}. \quad (8.34)$$

Whether V_I^F is positive or negative depends on the amount of outward relaxation. If the relaxation volume $V_{rel,I}$ is positive and larger than one atomic volume – as is the case for close-packed metals [20] – the formation volume is positive. For a less densely packed structure such as silicon, a negative formation volume of a self-interstitial can be expected.

The **migration volume** of an atom (or of a defect) refers to the volume change when the jumping atom is transferred from its equilibrium position to the saddle-point position. Its illustration is a somewhat ‘dangerous’ procedure. The jump event occurs in a short time interval of about 10^{-12} s. During this short period a complete relaxation of the saddle-point configuration cannot occur because atomic displacements in a solid proceed by the velocity of sound. Nevertheless, with some precaution Fig. 8.5 may serve as an illustration of the migration volume.

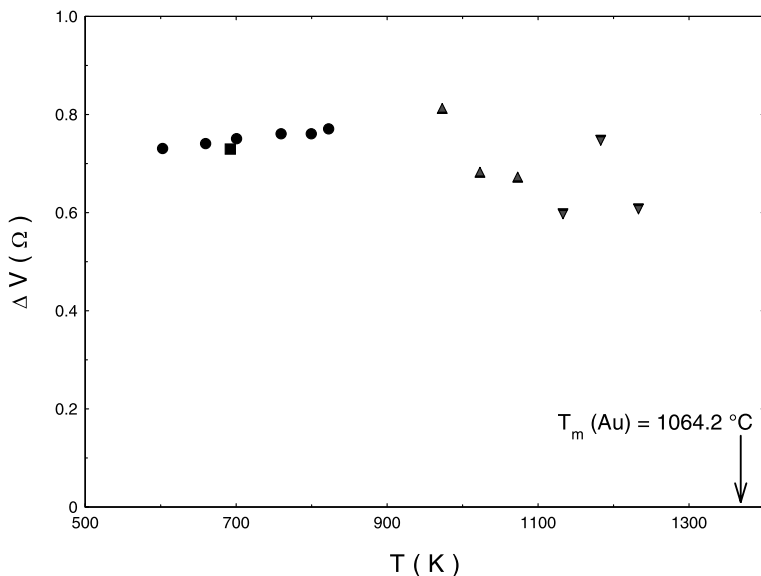


Fig. 8.6. Activation volumes for self-diffusion in Au *versus* temperature: triangles [8], square [9], full circles [11]

The migration volume of a vacancy in close-packed metals is fairly small. Experimental values around $V^M = 0.15 \Omega$ have been reported for Au. These values were determined by studying the effect of hydrostatic pressure on the annealing rate of vacancies, which had been produced by quenching Au wires from high temperatures [21]. Similar numbers are reported for Pt. These values suggest that the major part of the activation volume of vacancy-mediated self-diffusion in metallic elements (see Table 8.1) must be attributed to the formation volume.

Figure 8.6 shows the activation volumes ΔV for self-diffusion of Au between about 600 K and the melting temperature T_M . ΔV is almost independent of temperature indicating that a single mechanism dominates in the whole temperature range. For Au this is the monovacancy mechanism. Values between 0.6 and 0.9 Ω are typical for vacancy-mediated diffusion in close-packed metals such as Cu, Ag, and Au (see Table 8.1). For silver, an increase of the activation volume from about 0.6 to 0.9 Ω has been reported [6, 9] and taken as evidence for the simultaneous action of mono- and divacancies (see Chap. 17).

A comparison between the activation volumes of self-diffusion of noble metals and of sodium indicates (see Table 8.1) that the relaxation around a vacancy is more pronounced for bcc metal. Negative activation volumes between about -0.6Ω and -0.3Ω have been reported for the diffusion of Ge in silicon (see Table 8.1). Solute diffusion of Ge in silicon is very similar to Si self-diffusion and Ge diffuses by the same mechanism as Si. Negative acti-

vation volumes are considered as evidence (among others) for self-interstitial mediated diffusion in silicon (see [6, 15] and Chap. 23).

8.2.2 Activation Volumes of Solute Diffusion

For diffusion of **interstitial solutes** no defect formation term is required. Then, from Eqs. (8.11) and (8.24) the activation volume is

$$\Delta V = V^M, \quad (8.35)$$

where V^M is the migration volume of the interstitial solute. As already mentioned, ‘small’ atoms such as C, N, and O in metals diffuse by this mechanism. The effect of pressure was studied for C and N in α -Fe, for C in Co and for C in Ni and for N and O diffusion in V (for references see Chap. 10 in [1]). Interstitial diffusion is characterised by small values of the activation volume. For example, for C and N diffusion in α -iron small values between -0.08 and +0.05 Ω were reported (see Table 8.1). This implies that interstitial diffusion is only very weakly pressure dependent.

Diffusion of **substitutional impurities** is mediated by vacancies. According to Sect. 8.1 the diffusivity can be written as

$$D_2 = ga^2\nu_0 \exp\left(-\frac{G_{1V}^F - G^B}{k_B T}\right) \exp\left(-\frac{H_2^M}{k_B T}\right) f_2, \quad (8.36)$$

where G^B is the Gibbs energy of binding between solute and vacancy. H_2^M denotes the activation enthalpy for defect-impurity exchange and f_2 the correlation factor of impurity diffusion. Using Eq. (8.24), we get for the activation volume of solute diffusion:

$$\Delta V_2 = V_{1V}^F - V^B + \underbrace{V_2^M - k_B T \frac{\partial \ln f_2}{\partial p}}_{C_2}. \quad (8.37)$$

The term $V_{1V}^F - V^B$ represents the formation volume of the impurity-vacancy pair. It is different from the formation volume of the vacancy in the pure solvent due to the volume change V^B associated with pair formation. V_2^M is the migration volume of the vacancy-solute exchange, which in general is different from the migration volume V_{1V}^M of the vacancy in the pure matrix. Finally, the term C_2 arises from the pressure dependence of the solute correlation factor. $V_2^M + C_2$ can be interpreted as the migration volume of the solute-vacancy complex.

The activation volumes for various solutes in aluminium listed in Table 8.1 show a considerable variation. As we shall see in Chap. 19, transition metal solutes are slow diffusers, whereas non-transition elements are normal diffusers in Al. Self-diffusion in Al has been attributed to the simultaneous action of mono- and divacancies and a similar interpretation is tenable for the

diffusion of non-transition elements such as Zn and Ge. On the other hand, transition elements in Al have high activation enthalpies and entropies of diffusion, which can be attributed to a repulsive interaction between vacancy and solute (see Chapt 19). The high activation volumes for the transition metals diffusers Mn and Co indicate large formation and/or migration volumes of the solute-vacancy complex [6].

8.2.3 Activation Volumes of Ionic Crystals

The pressure dependence of the ionic conductivity has been studied in several alkali halide crystals (KCl, NaCl, NaBr, KBr) with Schottky disorder by YOON AND LAZARUS [22]. These crystals consist of sublattices of cations (index C) and anions (index A). In the intrinsic region, i.e. at high temperatures, cation and anion vacancies, V_C and V_A , are simultaneously present in equal numbers (Schottky pairs). In the extrinsic region of crystals, doped with divalent cations, additional vacancies in the cation sublattice are formed to maintain charge neutrality (see Chaps. 5 and 26):

- (i) In the **intrinsic region** the conductivity is due to Schottky pairs. The formation volume of Schottky pairs is

$$V_{SP}^F = V_C^F + V_A^F, \quad (8.38)$$

where V_C^F and V_A^F denote the formation volumes of cation and anion vacancies, respectively. The following values for the formation volume of Schottky pairs have been reported [22] in units $\text{cm}^3 \text{mol}^{-1}$:

V_{SP}^F : 61 ± 9 for KCl, 55 ± 9 for NaCl, 54 ± 9 for KBr, 44 for NaBr.

- (ii) In the **extrinsic region** the conductivity is dominated by the motion of cation vacancies because anion vacancies are less mobile. Thus, from the pressure dependence of the conductivity one obtains the migration volume of the cation vacancy, V_C^M . The following values have been reported [22]:

V_C^M : 8 ± 1 for KCl, 11 ± 1 for NaCl, 11 ± 1 for KBr, 8 ± 1 for NaBr.

Due to the higher mobility of cation vacancies the activation volume of the ionic conductivity in the intrinsic region, ΔV_σ , is practically given by

$$\Delta V_\sigma = V_{SP}^F/2 + V_C^M. \quad (8.39)$$

In principle, anion vacancies also contribute to the conductivity (see Chap. 26). However, as the anion component of the total conductivity is usually small this contribution has been neglected in Eq. (8.39).

A comparison between activation volumes in metals and ionic crystals with Schottky disorder may be useful. In units of the molar volumes of the crystals, V_m , the activation volumes of the ionic conductivity in the intrinsic region are:

ΔV_{σ} : $1.03 V_m$ for KCl, $1.28 V_m$ for NaCl, $1.23 V_m$ for KBr, $1.37 V_m$ for NaBr.

The activation volumes for intrinsic ionic conduction, which is due to the motion of vacancies, are of the order of one molar volume. These values are similar to activation volumes of self-diffusion in close-packed metals, where the activation volume is also an appreciable fraction of the atomic volume of the material (see above). In contrast, the migration volumes of cation vacancies are smaller:

V_{VC}^M : $0.21 V_m$ for KCl, $0.26 V_m$ for NaCl, $0.25 V_m$ for KBr, $0.25 V_m$ for NaBr.

These values indicate a further similarity between metals and ionic crystals. In both cases, the migration volumes of vacancies are only a small fraction of the atomic (molar) volume.

The α -phase of silver iodide is a typical example of a *fast ion conductor* (see Chap. 27). The immobile I^- ions form a body-centered cubic sublattice, while no definite sites can be assigned to the Ag^+ ions. In the cubic unit cell 42 sites are available for only two Ag^+ ions. Because of these structural features, Ag^+ ions are easily mobile and no intrinsic defect is needed to promote their migration. The pressure dependence of the dc conductivity in α -AgI was studied up to 0.9 GPa by MELLANDER [23]. The activation volume is 0.8 to $0.9 \text{ cm}^3 \text{ mol}^{-1}$. This very low value can be attributed to the migration of Ag^+ ions, confirming the view that migration volumes are small.

8.3 Correlations between Diffusion and Bulk Properties

Thermodynamic properties of solids such as melting points, heats of melting, and elastic moduli reflect different aspects of the lattice stability. It is thus not surprising that the diffusion behaviour correlates with thermodynamic properties. Despite these correlations, diffusion remains a kinetic property and cannot be based solely on thermodynamic considerations. In this section, we survey some correlations between self-diffusion parameters and bulk properties of the material. These relationships, which can be qualified as ‘enlightened empirical guesses’, have contributed significantly to the growth of the field of solid-state diffusion. The most important developments in this area were: (i) the establishment of correlations between diffusion and melting parameters and (ii) Zener’s hypothesis to relate the diffusion entropy with the temperature dependence of elastic constants. These old and useful correlations have been re-examined by BROWN AND ASHBY [24] and by TIWARI ET AL. [25].

8.3.1 Melting Properties and Diffusion

Diffusivities at the Melting Point: The observation that the self-diffusivity of solids at the melting point, $D(T_m)$, roughly equals a constant is an old

one, dating back to the work of VAN LIEMPT from 1935 [27]. But it was not until the mid 1950s that enough data of sufficient precision were available to recognise that $D(T_m)$ is only a constant for a given structure and for a given type of bonding: the bcc structure, the close-packed structures fcc and hcp, and the diamond structured elements all differ significantly. As data became better, additional refinements were added: the bcc metals were subdivided into two groups each with characteristic values of $D(T_m)$ [26]; also alkali halides were seen to have a characteristic value of $D(T_m)$ [31]. Figure 8.7 shows a comparison of self-diffusion coefficients extrapolated to the melting point for various classes of crystalline solids according to BROWN AND ASHBY [24]. The width of the bar is either twice the standard deviation of the geometric mean, or a factor of four, whichever is greater. Data for the solidus diffusivities of bcc and fcc alloys coincide with the range shown for pure metals. It is remarkable that $D(T_m)$ varies over about 6 orders of magnitude, being very small for semiconductors and fairly large for bcc metals.

At the melting temperature T_m according to Eq. (8.6) the self-diffusivity is given by

$$D(T_m) = D^0 \exp\left(-\frac{\Delta H}{k_B T_m}\right) = g f a^2 \nu^0 \exp\left(\frac{\Delta S}{k_B}\right) \exp\left(-\frac{\Delta H}{k_B T_m}\right). \quad (8.40)$$

The constancy of the diffusivity at the melting point reflects the fact that for a given crystal structure and bond type the quantities D^0 and $\Delta H/(k_B T_m)$ are roughly constant:

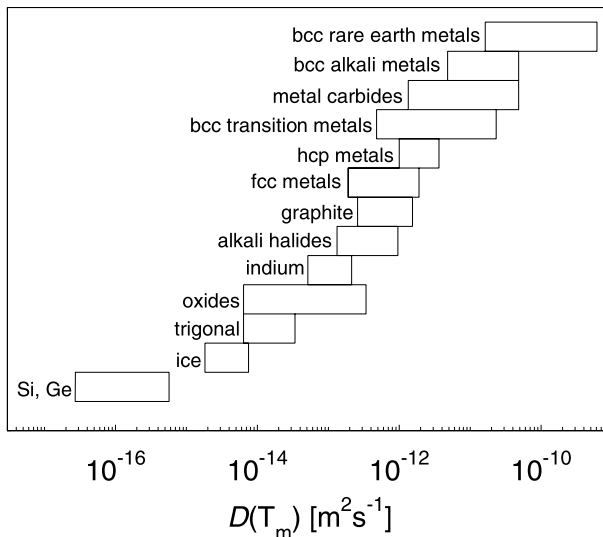


Fig. 8.7. Self-diffusivities at the melting point, $D(T_m)$, for various classes of crystalline solids according to BROWN AND ASHBY [24]

The pre-exponential factor D^0 is indeed almost a constant. According to Eq. (8.5) it contains the attempt frequency ν^0 , the lattice parameter a , geometric and correlation factors, and the diffusion entropy ΔS . Attempt frequencies are typically of the order of the Debye frequency, which lies in the range of 10^{12} to 10^{13} s $^{-1}$ for practically all solids. The diffusion entropy is typically of the order of a few k_B . Correlation factors and geometric terms are not grossly different from unity.

The physical arguments for a constancy of the ratio $\Delta H/(k_B T_m)$ are less clearcut. One helpful line of reasoning is to note that the formation of a vacancy, like the process of sublimation, involves breaking half the bonds that link an atom in the interior of the crystal to its neighbours; the enthalpy required to do so should scale as the heat of sublimation, H_s . The migration of a vacancy involves a temporary loss of positional order – it is somehow like local melting – and involves an energy that scales as the heat of melting (fusion), H_m . One therefore may expect

$$\frac{\Delta H}{k_B T_m} \approx \alpha \frac{H_s}{k_B T_m} + \beta \frac{H_m}{k_B T_m}, \quad (8.41)$$

where α and β are constants. The first term on the right-hand side contains the sublimation entropy at the melting temperature, $S_s = H_s/T_m$; the second term contains the entropy of melting, $S_m = H_m/T_m$. These entropy changes are roughly constant for a given crystal structure and bond type; it follows that $\Delta H/(k_B T_m)$ should be approximately constant, too.

Activation Enthalpy and Melting Properties: From practical considerations, correlations between melting and activation enthalpy are particularly useful. Figure 8.8 shows the ratio $\Delta H/(k_B T_m)$ for various classes of crystalline solids. It is approximately a constant for a given structure and bond type. The constants defined in this way vary over a factor of about 3.5. The activation enthalpy was related to the melting point many years ago [27–29]. These correlations have been reconsidered for metals and alloys by BROWN AND ASHBY [24] and for pure metals recently by TIWARI ET AL. [25]. The activation enthalpy of diffusion is related via

$$\Delta H \approx K_1 T_m \quad (8.42)$$

to the melting temperature (expressed in Kelvin) of the host crystal. This relation is called the *van Liempt rule* or sometimes also the *Bugakov – van Liempt rule* [30].

One may go further by invoking the thermochemical *rule of Trouton*, which relates the melting point of materials to their (nearly) constant entropy of melting, S_m . Trouton's rule, $S_m = H_m/T_m \approx 2.3 \text{ cal/mol} = 9.63 \text{ J/mol}$, allows one to replace the melting temperature in Eq. (8.42) by the enthalpy of melting, H_m . Then, the van Liempt rule may be also expressed as

$$\Delta H \approx \frac{K_1}{S_m} H_m \equiv K_2 H_m. \quad (8.43)$$

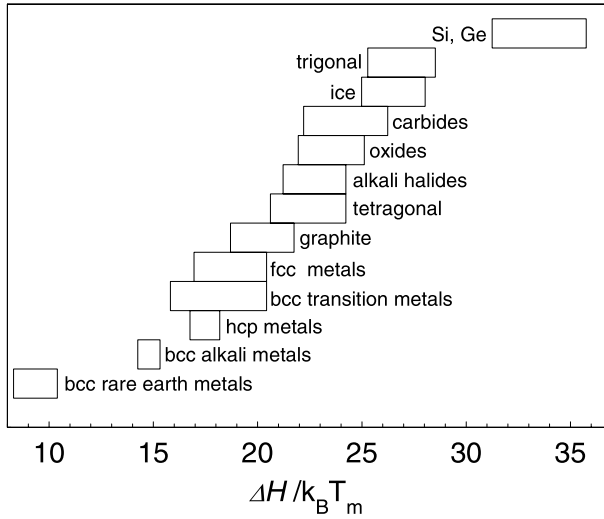


Fig. 8.8. Normalised activation enthalpies of self-diffusion, $\Delta H/(k_B T_m)$, for classes of crystalline solids according to BROWN AND ASHBY [24]

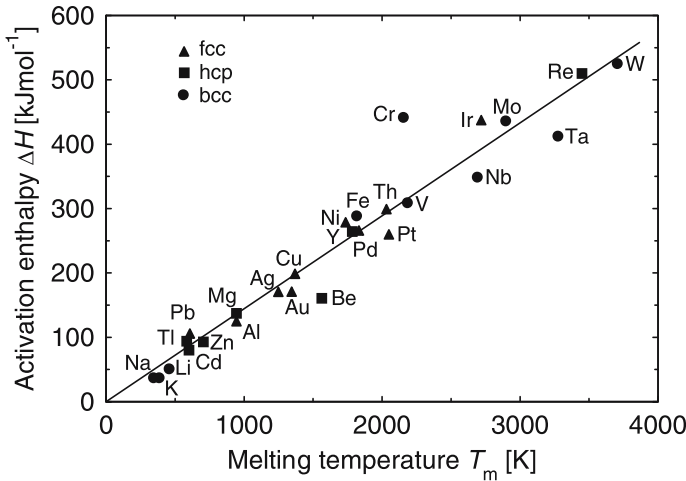


Fig. 8.9. Activation enthalpies of self-diffusion in metals, ΔH , versus melting temperatures, T_m , according to TIWARI ET AL. [25]

K_1 and K_2 are constants for a given class of solids. Plots of Eqs. (8.42) and (8.43) for metals are shown in Figs. 8.9 and 8.10. Values of the slopes for metals are: $K_1 = 146 \text{ Jmol}^{-1} \text{ K}^{-1}$ and $K_2 = 14.8$ [25].

The validity of Eq. (8.42) has been demonstrated for alkali halides by BARR AND LIDIARD [31]. For inert gas solids and molecular organic solids,

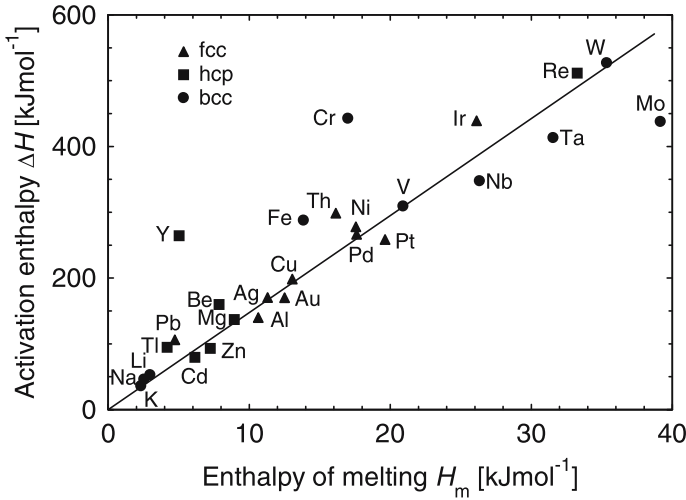


Fig. 8.10. Activation enthalpies of self-diffusion in metals, ΔH , versus melting enthalpies, H_m , according to TIWARI ET AL. [25]

the validity of Eqs. (8.42) and (8.43) has been established by CHADWICK AND SHERWOOD [32].

The correlations above are based on self-diffusion, which is indeed the most basic diffusion process. Diffusion of foreign elements introduces additional complexities such as the interaction between foreign atom and vacancy and temperature-dependent correlation factors (see Chaps. 7 and 19). Correlations between the activation enthalpies of self-diffusion and substitutional impurity diffusion have been proposed by BEKE ET AL. [33].

Activation Volume and Melting Point: The diffusion coefficient is pressure dependent due to the term $p\Delta V$ in the Gibbs free energy of activation. The activation volume of diffusion, ΔV , has been discussed in Sect. 8.2. NACHTRIEB ET AL. [34, 35] observed that the diffusivity at the melting point is practically independent of pressure. For example, in Pb and Sn the lattice diffusivity, as for most metals, decreases with increasing pressure in such a way that the increased melting point resulted in a constant rate of diffusion at the same homologous temperature. If one postulates that $D(T_m)$ is independent of pressure, we have

$$\frac{d[\ln D(T_m)]}{dp} = 0. \quad (8.44)$$

Then, we get from Eq. (8.6)

$$\Delta V = \frac{\Delta H(p=0)}{T_m(p=0)} \frac{dT_m}{dp} \quad (8.45)$$

if the small pressure dependence of the pre-exponential factor is neglected. This equation predicts that ΔV is controlled by the sign and magnitude of dT_m/dp . In fact, BROWN AND ASBY report reasonable agreement of Eq. (8.45) with experimental data [24]. In general, dT_m/dp is positive for most metals and indeed their activation volumes are positive as well. For plutonium dT_m/dp is negative and, as expected from Eq. (8.45), the activation volume of Pu is negative [36].

Later, however, also remarkable exceptions have been reported, which violate Eq. (8.45). For example, dT_m/dp is negative for Ge [37], but the activation volume of Ge self-diffusion is positive [38] (see also Chap. 23). Neither the variation of the activation volume with temperature due to varying contributions of different point defects to self-diffusion nor the differences between the activation volumes of various solute diffusers are reflected by this rule.

8.3.2 Activation Parameters and Elastic Constants

A correlation between the elastic constants and diffusion parameters was already proposed in the pioneering work of WERT AND ZENER [39, 40]. They suggested that the Gibbs free energy for migration (of interstitials), G^M , represents the elastic work to deform the lattice during an atomic jump. Thus, the temperature variation of G^M should be the same as that of an appropriate elastic modulus μ :

$$\frac{\partial(G^M/G_0^M)}{\partial T} = \frac{\partial(\mu/\mu_0)}{\partial T}. \quad (8.46)$$

The subscript 0 refers to values at absolute zero. The migration entropy S^M is obtained from the thermodynamic relation

$$S^M = -\frac{\partial G^M}{\partial T} \quad (8.47)$$

and $H^M = G^M + TS^M$ yields the migration enthalpy. In the Wert-Zener picture both H^M and S^M are independent of T if μ varies linearly with temperature. If this is not the case, both S^M and H^M are temperature dependent. Substituting the thermodynamic relation and $G_0^M \approx H^M$ in Eq. (8.46), we get:

$$S^M \approx -\frac{H^M}{T_m} \cdot \frac{\partial(\mu/\mu_0)}{\partial(T/T_m)} = \Theta \frac{H^M}{T_m}. \quad (8.48)$$

At temperatures well above the Debye temperature, elastic constants usually vary indeed linearly with temperature. The derivative $\Theta \equiv -\partial(\mu/\mu_0)/\partial(T/T_m)$ is then a constant. Its values lie between -0.25 to -0.45 for most metals. Then H^M and S^M are proportional to each other and the model of Zener predicts a positive migration entropy.

For a vacancy mechanism, Zener's idea is strictly applicable only to the migration and not to the formation property of the defect. One can, however,

always deduce a diffusion entropy via $\Delta S = k_{\text{B}} \ln[D^0/(gfa^2\nu^0)]$ from the measured value of D^0 . Experimental observations led Zener to extend his relation to the activation properties of atoms on substitutional sites:

$$\Delta S = \lambda\theta \frac{\Delta H}{T_m}. \quad (8.49)$$

Then the pre-exponential factor can be written as

$$D^0 = fga^2\nu^0 \exp\left(\lambda\theta \frac{\Delta H}{T_m}\right). \quad (8.50)$$

λ is a constant that depends on the structure and on the diffusion mechanism. For self-diffusion in fcc metals $\lambda \approx 0.55$ and for bcc metals $\lambda \approx 1$. The relation Eq. (8.49) is often surprisingly well fulfilled. We note that this relation also suggests that the diffusion entropy $\Delta S = S^M + S^F$ is positive. This conclusion is supported by the well-known fact that the formation entropy for vacancies, S^F , is positive (see Chap. 5).

8.3.3 Use of Correlations

The value of the correlations discussed above is that they allow diffusivities to be estimated for solids for which little or no data are available. For example, when diffusion experiments are planned for a new material, these rules may help in choosing the experimental technique and adequate thermal treatments. The correlations should be used with clear appreciation of the possible errors involved; in some instances, the error is small.

We emphasise that the correlations have been formulated for self-diffusion. Solute diffusion of substitutional solutes in most metals differs by not more than a factor of 100 for many solvent metals and the activation enthalpies by less than 25% from that of the host metal (see Chap. 19).

There are, however, remarkable exceptions: examples are the very slow diffusion of transition metals solutes in Al and the very fast diffusion of noble metals in lead and other ‘open metals’ (see Chap. 19). Also diffusion of interstitial solutes (see Sect. 18.1), hydrogen diffusion (see Sect. 18.2), and fast diffusion of hybrid foreign elements in Si and Ge (see Chap. 25) do not follow these rules.

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