Diffusion Review

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High Throughput Analysis of Multicomponent Multiphase Diffusion Data

Definitions

- Diffusion under a chemical gradient
  - Interdiffusion of two metals which form a substitutional solid solution
    - In the volume fixed frame of reference, chemical interdiffusion coefficient, $\widetilde{D}_{ij}^{n}$.   (Matano frame)
    - In the lattice fixed plane, intrinsic or partial chemical diffusion coefficient, $^{i}D_{kj}$. (needs inert markers, Kirkendall frame)

- Diffusion in a chemical homogenous system (use of radioactive tracers)
  - Diffusion into a pure metal: Self diffusion coefficient, $D_{i.}^{i}$
  - Diffusion of extremely small concentrations A into pure B: Tracer Impurity diffusion coefficient of A in B
  - Diffusion into an alloy: Tracer diffusivity. D^{*}

Definitions

Coefficient	General Notation	DICTRA notation
Tracer Diffusivity	$D_i^* = \widetilde{v}\beta a^2 f \exp\left(\dfrac{\Delta S_{Va}^f + \Delta S_{Va}^m}{k}\right)\exp\left(-\dfrac{\Delta H_{Va}^f + \Delta H_{Va}^m}{kT}\right)$ $\widetilde{v}$ = vibration frequency a = lattice parameter $\beta = 1$ for FCC and BCC and 1/8 for diamond cubic f = correlation factor $D = D_0 \exp\left(\dfrac{-Q}{RT}\right)$	$D_k^* = RTM_k$ $M_k = \delta^2 v \ \exp\left(-\dfrac{\Delta G_{kVa}^*}{RT}\right)\dfrac{1}{RT}$
Intrinsic Diffusivity (partial chemical)	$D_i = D_i^*\left[1 + \dfrac{\partial \log \gamma}{\partial \log N}\right]$	$^i D_{kj} = c_k M_{kVa}\dfrac{\partial \mu_k}{\partial c_j}$
Chemical Diffusivity (Interdiffusion)	$\widetilde{D} = x_A D_B + x_B D_A$ (binary) D_i and $\widetilde{D}$ are related by the velocity of Kirkendall frame, $v = -J_{Va}V_M$	$D_{kj} = \sum_{i=1}^{n}(\delta_{ik} - x_k)x_i M_i \dfrac{\partial \mu_i}{\partial x_j}V_m$

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DICTRA Notation/Background*

- **Background/Assumptions**
  - Absolute Reaction Rate Theory
  - Vacancy mechanism
  - Probability of constituent *k* to jump to a neighboring lattice site:
    - $$y_{Va} \exp\left(-\frac{\Delta G_{kVa}}{kT}\right)$$

      where y_{Va} = site fraction of vacancies and ΔG_{kVa} = Gibbs energy barrier

    - In the presence of driving force (composition gradient)
      - In the forward direction $\quad \Delta G_{kVa}^{+} \approx \Delta G_{kVa}^{*} - \frac{1}{2}\frac{\partial(\mu_k - \mu_{Va})}{\partial z}\delta$

      - In the backwards direction $\quad \Delta G_{kVa}^{-} \approx \Delta G_{kVa}^{*} + \frac{1}{2}\frac{\partial(\mu_k - \mu_{Va})}{\partial z}\delta$

        » Where ΔG_{kVa}^{*} is the Gibbs energy barrier in the absence of a driving force and δ is the jump distance

  - Velocity as a result of the probability to jump forward and backwards:

    $$\upsilon_k = \delta \nu y_{Va}\left[\exp\left(-\frac{\Delta G_{kVa}^{+}}{kT}\right) - \exp\left(-\frac{\Delta G_{kVa}^{-}}{kT}\right)\right] \quad \text{where } \nu = \text{attempt frequency}$$

  - Net flux:

    $$J_k = c_k \upsilon_k = c_k \delta^2 \nu y_{Va} \exp\left(-\frac{\Delta G_{kVa}^{*}}{kT}\right)\left[\exp\left(\delta\frac{\partial(\mu_k - \mu_{Va})/\partial z}{2kT}\right) - \exp\left(-\delta\frac{\partial(\mu_k - \mu_{Va})/\partial z}{2kT}\right)\right]$$

*References: Borgenstam et. al., *J. Phase Equilibria,* **21** (2000) 269.
Andersson and Ågren, *J. Appl. Phys.* **72** (1992) 1350.
Ågren, *J. Phys. Chem. Solids*, **43** (1982) 421.
Ågren, *J. Phys. Chem. Solids*, **43** (1982) 385.

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DICTRA Notation/Backgroud (2)

$$J_k = c_k \upsilon_k = c_k \delta v y_{Va} \exp\left(-\frac{\Delta G^*_{kVa}}{kT}\right)\left[\exp\left(\delta \frac{\partial(\mu_k - \mu_{Va})/\partial z}{2kT}\right) - \exp\left(-\delta \frac{\partial(\mu_k - \mu_{Va})/\partial z}{2kT}\right)\right]$$

Expanding exponentials to the first order using a Taylor series expansion

$$\exp(x) = \sum_{n=0}^{\infty} \frac{x^n}{n!} = 1 + x + \frac{x^2}{2!} + \frac{x^3}{3!} + \cdots$$

$$\exp\left(\delta \frac{\partial(\mu_k - \mu_{Va})/\partial z}{2kT}\right) = 1 + \delta \frac{\partial(\mu_k - \mu_{Va})/\partial z}{2kT} \qquad \exp\left(-\delta \frac{\partial(\mu_k - \mu_{Va})/\partial z}{2kT}\right) = 1 - \delta \frac{\partial(\mu_k - \mu_{Va})/\partial z}{2kT}$$

$$J_k = c_k \upsilon_k = -c_k \delta^2 v y_{Va} \exp\left(-\frac{\Delta G^*_{kVa}}{kT}\right)\frac{\partial(\mu_k - \mu_{Va})/\partial z}{kT}$$

If the vacancy concentration is assumed to be in thermodynamic equilibrium

$$\frac{\partial G}{\partial n_{Va}} = \mu_{Va} = 0$$

$$J_k = c_k \upsilon_k = -c_k \delta^2 v y_{Va} \exp\left(-\frac{\Delta G^*_{kVa}}{kT}\right)\frac{\partial \mu_k/\partial z}{kT} = -L_{kk}\frac{\partial \mu_k}{\partial z}$$

DICTRA Notation:
Mobility Defined

$$J_k = c_k \upsilon_k = -c_k \delta^2 \nu y_{Va} \exp\left(-\frac{\Delta G^*_{kVa}}{kT}\right) \frac{\partial \mu_k / \partial z}{kT} = -c_k y_{Va} M_{kVa} \frac{\partial \mu_k}{\partial z}$$

$$M_{kVa} = \delta^2 \nu \ \exp\left(-\frac{\Delta G^*_{kVa}}{kT}\right) \frac{1}{kT}$$

$$M_{kVa} = M_k^0 \exp\left(\frac{-\Delta G_{kVa}}{RT}\right) \frac{1}{RT} \quad M_k^0 = \delta^2 \nu$$

$$L_{kk} = c_k y_{Va} M_{kVa}$$

For a pure component that is substitutional then $y_{Va} = 1$ and $\boxed{D_k^* = RTM_k}$

Tracer diffusivity is not dependent on the thermodynamics.

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Intrinsic Diffusivity and the Lattice Fixed-Frame of Reference

In the lattice-fixed frame, assuming the number of lattice sites are conserved:

$$\sum_{k=1}^{n} J_k = -J_{Va}$$

$$J_k = -\sum_{j=1}^{n} {}^{i}D_{kj} \frac{\partial c_j}{\partial z} = -\sum_{j=1}^{n-1} L_{kk} \frac{\partial \mu_k}{\partial c_j} \frac{\partial c_j}{\partial z}$$

where ${}^{i}D_{kj}^{n}$ is the intrinsic diffusivity and *z* is distance

$${}^{i}D_{kj} = L_{kk} \frac{\partial \mu_k}{\partial c_j} = c_k y_{Va} M_{kVa} \frac{\partial \mu_k}{\partial c_j}$$

Assuming y_{Va} = 1, then $\boxed{{}^{i}D_{kj} = c_k M_{kVa} \frac{\partial \mu_k}{\partial c_j}}$

Interdiffusion Coefficient and the Volume-Fixed Frame

In the volume-fixed frame, assuming the volume is conserved:

$$\sum_{k=1}^{n} J_k V_k = 0$$

$$V_m = \sum_{k=1}^{n} x_k V_k \qquad V_k = \left(\frac{\partial V}{\partial N_k} \right)_{P,T,N_j}$$

where V_m is the molar volume, x_k is the mole fraction, N_k is the number of moles of component k.

Assuming all substitutional components, then assume $\qquad V_k = V_s \qquad c_i = \dfrac{x_i}{V_m}$

$$J_k = -\sum_{j=1}^{n} L'_{ki} \nabla \mu_j \qquad L'_{kj} = \sum_{i=1}^{n} \left[\delta_{ik} - x_k \left(\frac{V_i}{V_m} \right) \right] L_{ij}$$

$$\boxed{D_{kj} = \sum_{i=1}^{n} \left(\delta_{ik} - x_k \right) x_i M_i \frac{\partial \mu_i}{\partial x_j} V_m}$$

$Note: \quad x_k \dfrac{V_i}{V_m} = x_k \dfrac{V_s}{V_s \sum\limits_{i=1}^{n} x_i} = x_k \quad as \quad \sum\limits_{i=1}^{n} x_i = 1$

Assuming $y_{Va} = 1$ the $M_i = M_{kVa:}$ $\quad M_i = M_{kVa} = \delta^2 \nu \, \exp\left(-\frac{\Delta G^*_{kVa}}{kT} \right) \frac{1}{kT}$

Reduce diffusivities when $V_k = V_s$: $\quad D^n_{kj} = D_{kj} - D_{kn}$

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Ternary A-B-C System

In the lattice fixed frame of reference, assuming a substitutional solid solution for a given phase:

$$M_{kVa} = M_k^0 \exp\left(\frac{-\Delta G_{kVa}}{RT}\right)\frac{1}{RT}$$

Assume: $M_k^0 = 1$

Then the activation energy, Q_k:

$$\Delta G_{AVa}^* = x_A y_{Va}\Delta G_A^{A:Va} + x_B y_{Va}\Delta G_A^{B:Va} + x_C y_{Va}\Delta G_A^{C:Va} + \Delta G^{excess}$$

$$\Delta G_{BVa}^* = x_A y_{Va}\Delta G_B^{A:Va} + x_B y_{Va}\Delta G_B^{B:Va} + x_C y_{Va}\Delta G_B^{C:Va} + \Delta G^{excess}$$

$$\Delta G_{CVa}^* = x_A y_{Va}\Delta G_C^{A:Va} + x_B y_{Va}\Delta G_C^{B:Va} + x_C y_{Va}\Delta G_C^{C:Va} + \Delta G^{excess}$$

Note x_i = mole fraction of component i
y_i = site fraction of component i
on a given sublattice

Since this is a substitutional solid solution with no interstitials, $y_{Va} = 1$:

Concentration variables: $c_k = \dfrac{x_k}{V_m} = \dfrac{x_k}{\displaystyle\sum_{j=1}^{n} x_j V_j}$ *and* $V_j = \left(\dfrac{\partial V}{\partial N_j}\right)_{P,T,N_k}$

Where x_k is the mole fraction of component k, V_j is the partial molar volume and N_j is the number of moles of component k.

Assume all the substitutional components have the same partial molar volume: $V_j = V_s$ then for the A-B-C system: $V_m = x_A V_s + x_B V_s + x_C V_s$

Ternary A-B-C System

In the lattice fixed frame of reference:
$$\sum_{k=1}^{n} J_k = -J_{Va} = J_A + J_B + J_C$$

$$J_k = -\sum_{j=1}^{n} {}^i D_{kj} \frac{\partial c_j}{\partial z} = -\sum_{j=1}^{n-1} L_{kk} \frac{\partial \mu_k}{\partial c_j} \frac{\partial c_j}{\partial z}$$

$${}^i D_{kj} = L_{kk} \frac{\partial \mu_k}{\partial c_j} = c_k y_{Va} M_{kVa} \frac{\partial \mu_k}{\partial c_j}$$

Note y_{Va} =1 and for simplicity drop the Va from $M_{kVa} = M_k$

$$L_{AA} = x_A M_A$$
$$L_{BB} = x_B M_B$$
$$L_{CC} = x_C M_C$$

$$c_i = \frac{x_i}{V_m}$$

$${}^i D_{AA} = L_{AA} \frac{\partial \mu_A}{\partial c_A} \qquad {}^i D_{AB} = L_{AA} \frac{\partial \mu_A}{\partial c_B} \qquad {}^i D_{AC} = L_{AA} \frac{\partial \mu_A}{\partial c_C}$$

$${}^i D_{BA} = L_{BB} \frac{\partial \mu_B}{\partial c_A} \qquad {}^i D_{BB} = L_{BB} \frac{\partial \mu_B}{\partial c_B} \qquad {}^i D_{BC} = L_{BB} \frac{\partial \mu_B}{\partial c_C}$$

$${}^i D_{CA} = L_{CC} \frac{\partial \mu_C}{\partial c_A} \qquad {}^i D_{CB} = L_{CC} \frac{\partial \mu_C}{\partial c_B} \qquad {}^i D_{CC} = L_{CC} \frac{\partial \mu_C}{\partial c_C}$$

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Ternary A-B-C System

In the volume-fixed frame of reference:
$$\sum_{k=1}^{n} J_k V_k = 0 = \left(J_A + J_B + J_C \right) \cdot V_s$$

$$J_k = -\sum_{i=1}^{n} L'_{ki} \frac{\partial \mu_i}{\partial z} = -\sum_{i=1}^{n} L'_{ki} \sum_{j=1}^{n} \frac{\partial \mu_i}{\partial c_j} \frac{\partial c_j}{\partial z} = -\sum_{j=1}^{n} D_{kj} \frac{\partial c_j}{\partial z}$$

$$D_{kj} = -\sum_{i=1}^{n} L'_{ki} \frac{\partial \mu_i}{\partial c_j} = \sum_{i=1}^{n} \left(\delta_{ik} - x_k \right) x_i M_i \frac{\partial \mu_i}{\partial x_j} V_m$$

See next page for expansion

$$L'_{kj} = \sum_{i=1}^{n} \left[\delta_{ik} - x_k \left(\frac{V_i}{V_m} \right) \right] L_{ij} \qquad L_{kk} = c_k y_{Va} M_{kVa}$$

Equivalent forms

Or
$$J_k = -\sum_{i=1}^{n} L''_{ki} \left[\nabla \mu_i - \left(\frac{V_i}{V_m} \right) \nabla \mu_n \right]$$

$$L''_{ki} = \sum_{j=1}^{n} \left[\delta_{ij} - x_i \left(\frac{V_i}{V_m} \right) \right] L'_{kj} = \sum_{j=1}^{n} \sum_{r=1}^{n} \left[\delta_{ir} - x_i \left(\frac{V_r}{V_m} \right) \right] \left[\delta_{jk} - x_k \left(\frac{V_j}{V_m} \right) \right] L_{jr}$$

$$D_{kj} = \sum_{i=1}^{n} L''_{ki} \frac{\partial \left[\mu_i - (V_i/V_m)\mu_n \right]}{\partial c_j} = \sum_{i=1}^{n} L'_{ki} \frac{\partial \mu_i}{\partial c_j} - \sum_{i=1}^{n} x_i \frac{\partial \mu_i}{\partial c_j} \sum_{r=1}^{n} \left(\frac{V_r}{V_m} \right) L'_{kr}$$

Recall that the Gibbs–Duhem equations provides that: $\sum_{i=1}^{n} x_i \frac{\partial \mu_i}{\partial c_j} = 0$ thus, $D_{kj} = \sum_{i=1}^{n} L'_{ki} \frac{\partial \mu_i}{\partial c_j}$

Reduce diffusivities when $V_k = V_s$: $\quad D_{kj}^n = D_{kj} - D_{kn} \quad J_k = -\sum_{j=1}^{n-1} D_{kj}^n \frac{\partial c_j}{\partial z}$

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Ternary A-B-C

$$D_{kj} = -\sum_{i=1}^{n} L'_{ki} \frac{\partial \mu_i}{\partial c_j} = \sum_{i=1}^{n} (\delta_{ik} - x_k) x_i M_i \frac{\partial \mu_i}{\partial x_j} V_m$$

$$D_{AA} = (1-x_A)x_A M_A \frac{\partial \mu_A}{\partial x_A} V_m + (0-x_A)x_B M_B \frac{\partial \mu_B}{\partial x_A} V_m + (0-x_A)x_C M_C \frac{\partial \mu_C}{\partial x_A} V_m$$

$$D_{AB} = (1-x_A)x_A M_A \frac{\partial \mu_A}{\partial x_B} V_m + (0-x_A)x_B M_B \frac{\partial \mu_B}{\partial x_B} V_m + (0-x_A)x_C M_C \frac{\partial \mu_C}{\partial x_B} V_m$$

$$D_{AC} = (1-x_A)x_A M_A \frac{\partial \mu_A}{\partial x_C} V_m + (0-x_A)x_B M_B \frac{\partial \mu_B}{\partial x_C} V_m + (0-x_A)x_C M_C \frac{\partial \mu_C}{\partial x_C} V_m$$

$$D_{BA} = (0-x_B)x_A M_A \frac{\partial \mu_A}{\partial x_A} V_m + (1-x_B)x_B M_B \frac{\partial \mu_B}{\partial x_A} V_m + (0-x_B)x_C M_C \frac{\partial \mu_C}{\partial x_A} V_m$$

$$D_{BB} = (0-x_B)x_A M_A \frac{\partial \mu_A}{\partial x_B} V_m + (1-x_B)x_B M_B \frac{\partial \mu_B}{\partial x_B} V_m + (0-x_B)x_C M_C \frac{\partial \mu_C}{\partial x_B} V_m$$

$$D_{BC} = (0-x_B)x_A M_A \frac{\partial \mu_A}{\partial x_C} V_m + (1-x_B)x_B M_B \frac{\partial \mu_B}{\partial x_C} V_m + (0-x_B)x_C M_C \frac{\partial \mu_C}{\partial x_C} V_m$$

$$D_{CA} = (0-x_C)x_A M_A \frac{\partial \mu_A}{\partial x_A} V_m + (0-x_C)x_B M_B \frac{\partial \mu_B}{\partial x_A} V_m + (1-x_C)x_C M_C \frac{\partial \mu_C}{\partial x_A} V_m$$

$$D_{CB} = (1-x_C)x_A M_A \frac{\partial \mu_A}{\partial x_B} V_m + (0-x_C)x_B M_B \frac{\partial \mu_B}{\partial x_B} V_m + (1-x_C)x_C M_C \frac{\partial \mu_C}{\partial x_B} V_m$$

$$D_{CC} = (1-x_C)x_A M_A \frac{\partial \mu_A}{\partial x_C} V_m + (0-x_C)x_B M_B \frac{\partial \mu_B}{\partial x_C} V_m + (1-x_C)x_C M_C \frac{\partial \mu_C}{\partial x_C} V_m$$

Relation between Intrinsic and Interdiffusion Coefficients

From Sohn and Dayananda (*Met. Mat. Trans* **33A** (2002) 3375)

Published notation:
$$\widetilde{D}_{ij}^n = D_{ij}^n - N_i \sum_{k=1}^{n} D_{kj}^n$$

$\widetilde{D}_{ij}^n =$ interdiffusion coefficient

$D_{ij}^n =$ intrinsic diffusion coefficient (reduced)

$N_i =$ atom fraction

DICTRA notation:
$$\widetilde{D}_{ij}^n = {}^i D_{ij}^n - x_i \sum_{k=1}^{n} {}^i D_{kj}^n$$

Example: $\widetilde{D}_{AA}^C = {}^i D_{AA}^C - x_A \left({}^i D_{AA}^C + {}^i D_{BA}^C + {}^i D_{CA}^C \right)$

$\widetilde{D}_{AA}^C = D_{AA} - D_{AC}$ (see previous slide for expansion of D_{AA} and D_{AC})

$$\widetilde{D}_{AA}^C = x_A V_m \left[(1-x_A) M_A \frac{\partial \mu_A}{\partial x_A} - x_B M_B \frac{\partial \mu_B}{\partial x_A} - x_C M_C \frac{\partial \mu_C}{\partial x_A} \right] - x_A V_m \left[(1-x_A) M_A \frac{\partial \mu_A}{\partial x_C} - x_B M_B \frac{\partial \mu_B}{\partial x_C} - x_C M_C \frac{\partial \mu_C}{\partial x_C} \right]$$

Note $\quad {}^i D_{kj} = x_k M_k \dfrac{\partial \mu_k}{\partial x_j}$

$$\widetilde{D}_{AA}^C = x_A V_m \left[M_A \frac{\partial \mu_A}{\partial x_A} - {}^i D_{AA} - {}^i D_{BA} - {}^i D_{CA} \right] - x_A V_m \left[M_A \frac{\partial \mu_A}{\partial x_C} - {}^i D_{AC} - {}^i D_{BC} - {}^i D_{CC} \right]$$

$$\widetilde{D}_{AA}^C = x_A V_m M_A \frac{\partial \mu_A}{\partial x_A} - x_A V_m M_A \frac{\partial \mu_A}{\partial x_C} - x_A V_m \left[\left({}^i D_{AA} - {}^i D_{AC} \right) + \left({}^i D_{BA} - {}^i D_{BC} \right) + \left({}^i D_{CA} - {}^i D_{CC} \right) \right]$$

$$\widetilde{D}_{AA}^C = \left({}^i D_{AA} - {}^i D_{AC} \right) - x_A V_m \left[\left({}^i D_{AA} - {}^i D_{AC} \right) + \left({}^i D_{BA} - {}^i D_{BC} \right) + \left({}^i D_{CA} - {}^i D_{CC} \right) \right]$$

Rewrite in terms of reduce diffusivities

$$\widetilde{D}_{AA}^C = {}^i D_{AA}^C - x_A V_m \left[{}^i D_{AA}^C + {}^i D_{BA}^C + {}^i D_{CA}^C \right]$$

Note:

$${}^i D_{kj}^n = {}^i D_{kj} - {}^i D_{kn}$$
$${}^i D_{AA}^C = {}^i D_{AA} - {}^i D_{AC}$$
$${}^i D_{BA}^C = {}^i D_{BA} - {}^i D_{BC}$$
$${}^i D_{CA}^C = {}^i D_{CA} - {}^i D_{CC}$$

Diffusion Data Sources

1. Smithells and similar sources

2. Landolt & Bornstein series (http://link.springer.de/link/service/series/0284/tocs/t003.htm)
   - Atomic Defects III/25
     The presence and the interaction of atomic or point defects in metals and alloys are of great importance for their macroscopic behaviour under irradiation. Volume III/25 is the first critical and comprehensive data collection in the field described above. It includes a chapter on He as an important alloying element, produced under most relevant irradiation conditions. Editor: H. Ullmaier
   - Diffusion in Solid Metals and Alloys III/26
     Volume III/26 presents a comprehensive and critically evaluated collection of diffusion data for solid metals and alloys. The following properties are covered: Self- and impurity diffusion in metallic elements, self-diffusion in homogeneous binary alloys, chemical diffusion in binary and ternary alloys, diffusion in amorphous alloys, diffusion of interstitial foreign atoms in metallic elements, mass and pressure dependence of diffusion, diffusion along dislocations, grain and interphase boundary diffusion and diffusion on surfaces. Editor: H. Mehrer
   - Diffusion in Semiconductors and Non-Metallic Solids III/33

3. NIST Diffusion Data Center
   - Diffusion references up to 1980
   - Catalog: Author, System, Card number
   - Includes translations of various international references and copies of government reports.

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Types of Diffusion Experiments

- Methods based on diffusion over a long distance
- Methods based on the measurement of jump frequencies

Method	Δx	D $(cm^2 s^{-1})$
Lathe sectioning, grinding	0.1 – 250 μm	10^{-15} 10^{-6}
Microtome	1 – 10 μm	$10^{-13} - 10^{-8}$
Chemical	10 μm	$10^{-11} - 10^{-8}$
Electrochemical	50 nm	$10^{-16} - 10^{-13}$
Sputtering	5 – 100 nm	$10^{-18} - 10^{-13}$
Modulated Structures	0.5 – 5 nm	$> 10^{-22}$
Ion Microprobe (SIMS)	1 – 100 nm	$10^{-19} - 10^{-13}$
Electron microprobe	> 2 μm	$10^{-12} - 10^{-8}$
Rutherford backscattering	50 nm	$10^{-16} - 10^{-13}$
Nuclear Reaction analysis	20 – 100 nm	$5 \times 10^{-17} - 10^{-12}$

Jean Philibert. *Atom Movements: Diffusion and Mass Transport in Solids*, Cedex, France:Les Editions de Physique, 1991 p. 362.

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Types of Diffusion Experiments

- Methods based on diffusion over a long distance

- Methods based on the measurement of jump frequencies

Method	D (cm^{2}s^{-1})
Nuclear Magnetic Resonance (NMR)	10^{-16} – 10^{-5}
Neutron inelastic scattering	10^{-7} – 10^{-5}
Mössbauer Effect	10^{-11} – 10^{-7}
Conductivity (ionic crystals)	10^{-13} – 10^{-6}
Resistivity (semiconductors	10^{-16} – 10^{-8}
Elastic after-effect	10^{-21} – 10^{-17}
Internal friction	10^{-16} – 10^{-11}
Magnetic anisotropy	10^{-21} – 10^{-17}

Jean Philibert. *Atom Movements: Diffusion and Mass Transport in Solids*, Cedex, France:Les Editions de Physique, 1991 p. 362.

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Methods for determining concentration profiles

- Non-destructive:
  - Deconvolution procedures:
    - Photoelectron spectroscopy, Auger electron spectroscopy, Rutherford backscattering, Nuclear reaction analysis
  - **Microanalysis on a transverse section**
    - **Electron probe microanalysis**
    - Ion probe and microprobe (SIMS)
  - Diffusion of a gas across a membrane at steady state
- Destructive methods
  - Sectioning Methods
    - Mechanical methods (lathe sectioning, grinding)
    - Chemical or electrochemical peeling
    - Cathodic sputtering
- Indirect methods
  - Radiotracers: decrease of surface activity
  - Gas-Solid Diffusion couples (Thermogravimetry, Isotopic exchange)
  - **Micrographic methods (Precipitate formation and dissolution)**
  - Autoradiography
  - Synthetic modulated structures (Interdiffusion)
  - Transmission electron microscopy (dislocation climb)
  - Electrical Resistivity (semiconductors, non-stoichiometric oxides, ionic crystals)

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Obtaining Interdiffusion Coefficients from Profiles

- Inverse methods
  - **Composition independent** interdiffusion coefficients:
    - Error Function Fits (Fujita & Josting)
    - Flux through Matano interface
    - Square Root Diffusivity Method
      - Inverse Square Root Diffusivity Matrix (Krishtal et. al.)
      - Square Root Diffusivity Matrix (Morral)
    - Method of Moments (Ghez et al.)
  - Composition-dependent interdiffusion coefficients
    - Only average values for narrow phases (Intermetallics)
    - Requires intersecting diffusion paths for ternary alloy
    - Methods
      - Boltzman/Matano (assume constant molar volume)
      - Sauer & Fries/DenBroeder/Wagner
  - Locally composition-independent diffusion coefficients
    - Local average coefficients (Dayananda and Sohn) from single path (ternary system)

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Obtaining Interdiffusion Coefficients from Profiles

- Direct methods:
  - Composition independent diffusivities
  - Composition dependent diffusivities
    - Finite difference solution and optimization of D's to fit experimental data (Bouchet & Mervil, 2002)
    - Use of DICTRA and optimization for dispersed phase systems
    - Others

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