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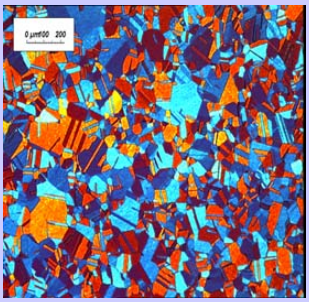
" Fundamentals of Thermodynamic Modelling of Materials "

November 15-19, 2010
INSTN – CEA Saclay, France



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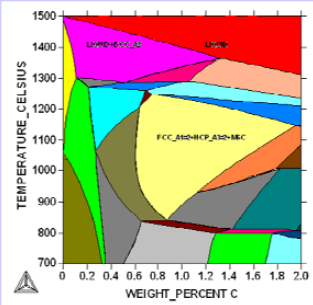
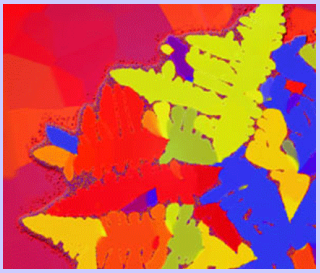


Multicomponent diffusion simulation

[04002]



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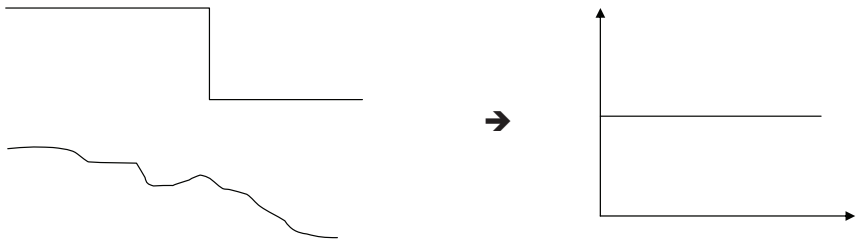
Multicomponent diffusion

Basis and application

Physical basis

- Diffusion from latin ”spread out”
- Irreversible process → no such thing as reversed diffusion, i.e. time has a certain direction!



Information is lost, entropy created during diffusion

Flux and concentration:

Fick´s (first) law :

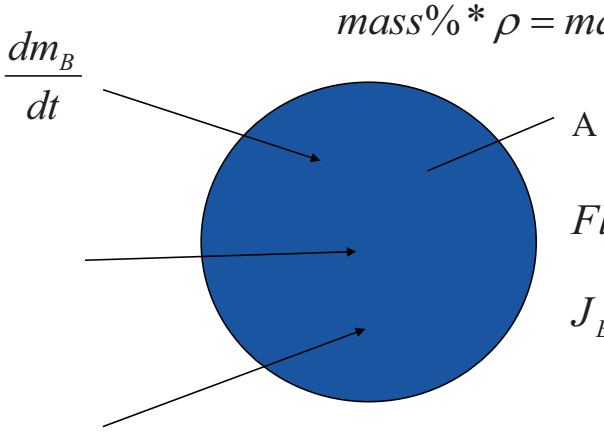
$$J_B = -D_B \frac{\partial c_B}{\partial z}$$

Concentration :

$$c_B = \frac{m_B}{V} = \frac{x_B}{V_m} = mole / volume$$

or

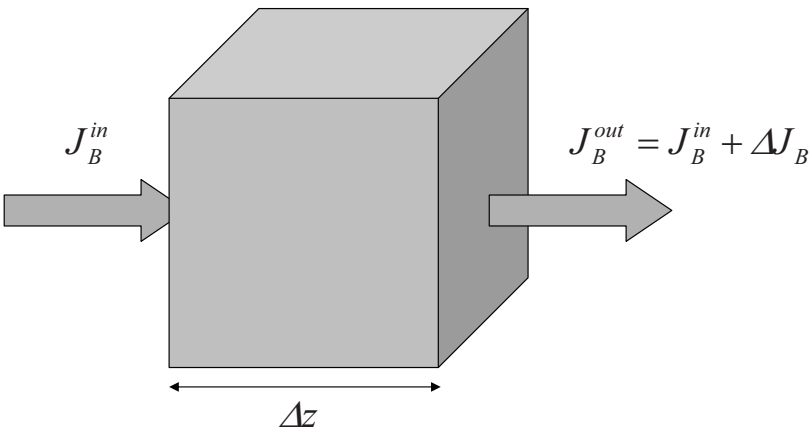
$$mass\% * \rho = mass / volume$$



Flux :

$$J_B = \frac{d\, m_B}{dt} \frac{1}{A}$$

$\frac{dn_B}{dt}$ is not necessarily constant
consider a planar case



$$\Delta J_B = J_B^{out} - J_B^{in}$$

Fick's second law

$$\frac{dn_B}{dt} = A(J_B^{in} - J_B^{out}) = -A\Delta J_B$$

$$n_B = c_B \Delta z A$$

$$\frac{dn_B}{dt} = \frac{dc_B}{dt} A\Delta z$$

Diffusion equations:

Fourier law: $J_Q = -\lambda \frac{\partial T}{\partial z}$

where J_Q is the heat flux, T the temperature and λ the heat conductivity.
Introduce the concentration of enthalpy as H_m / V_m, where H_m is the molar enthalpy:

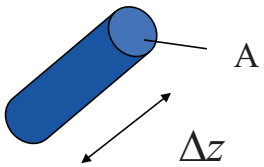
$$J_Q = -D_Q \frac{\partial (H_m / V_m)}{\partial z}$$

The heat diffusivity:

$$D_Q = \lambda V_m / c_p$$

$c_P = (\partial H_m / \partial T)_P$ is the heat capacity under constant pressure.

Ohm's law



$$I = U / R$$

I is the electric current, U the voltage and R the resistance, may be rewritten in a similar form as Fourier's law

$$J_e = -(\Delta z / RA)\frac{\partial u}{\partial z}$$

where $J_e = I / A$ is the electric charge flux, A the cross sectional area of the electric conductor and Δz the distance over which the voltage is U. u is the electric potential. By introducing the electrical conductivity σ as

$$\sigma = \Delta z / (RA)$$

we have a form completely analogous with Fourier's law.

Introduce chemical potential:

$$\mu_B = f(c_B)$$

$$J_B = -D_B \frac{\partial c_B}{\partial z} = -L_B \frac{\partial \mu_B}{\partial z} = -L_B \frac{d\mu_B}{dc_B}\frac{\partial c_B}{\partial z}$$

$$D_B = L_B \frac{d\,\mu_B}{d\,c_B}$$

Flux is proportional to force

$$v_B = M_B F_B = -M_B \frac{\partial \mu_B}{\partial z}, \quad J_B = c_B v_B$$

$$J_B = -c_B M_B \frac{\partial \mu_B}{\partial z} = -c_B M_B \frac{d\mu_B}{dc_B} \frac{\partial c_B}{\partial z} = -D_B \frac{\partial c_B}{\partial z}$$

$$D_B = c_B M_B \frac{d\mu_B}{dc_B}$$

$$\mu_B = \mu_B^0 + RT \ln a_B = \mu_B^0 + RT \ln f_B + RT \ln c_B$$

$$\frac{d\mu_B}{dc_B} = \frac{RT}{c_B}\left(1 + \frac{d \ln f_B}{d \ln c_B}\right)$$

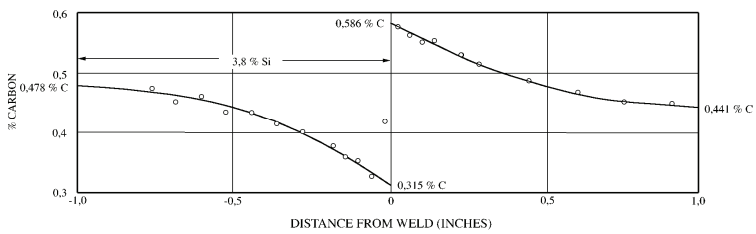
$$D_B = RT\ M_B\left(1 + \frac{d \ln f_B}{d \ln c_B}\right)$$

Ternary system A-B-C: $\mu_B = f(c_B, c_C)$

$$J_B = -M_B c_B \frac{\partial \mu_B}{\partial z} = -M_B c_B \left\{ \frac{\partial \mu_B}{\partial c_B}\frac{\partial c_B}{\partial z} + \frac{\partial \mu_B}{\partial c_C}\frac{\partial c_C}{\partial z} \right\} \Rightarrow$$

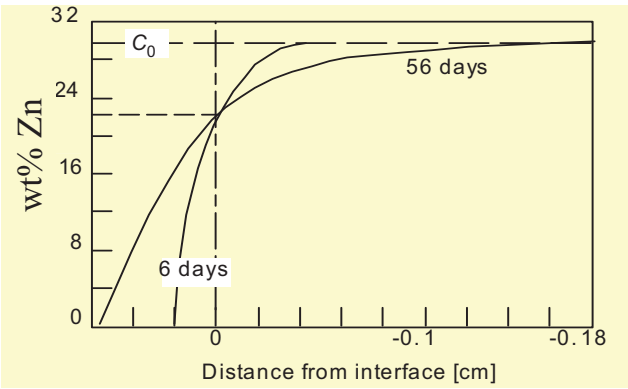
$$J_B = -D_{BB}\frac{\partial c_B}{\partial z} - D_{BC}\frac{\partial c_C}{\partial z}$$

Example:
Fe-Si-C Darken effect:



Frames of reference

- We have to measure flux relative something!
- Many choices possible!
- Example: Consider a composite of Cu and Cu-32% Zn:



If we are only interested in the mixing of Cu and Zn we may regard diffusion as if Cu and Zn exchange place: *JCu=-JZn.* We then have:

$$J_{Cu} = -D_{Cu}\frac{\partial c_{Cu}}{\partial z} = -J_{Zn} = -\left(-D_{Zn}\frac{\partial c_{Zn}}{\partial z}\right)$$

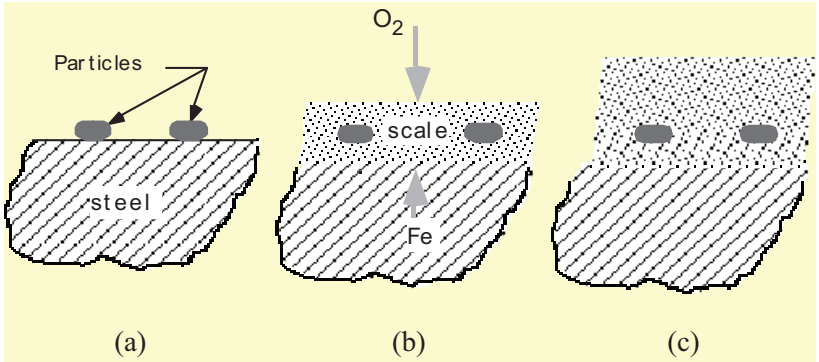
$$c_{Cu} + c_{Zn} = \frac{x_{Cu}}{V_m} + \frac{x_{Zn}}{V_m} = \frac{1}{V_m} \cong \text{const} \quad : \quad \frac{\partial c_{Cu}}{\partial z} + \frac{\partial c_{Zn}}{\partial z} \cong 0$$

$$J_{Cu} = -D_{Cu}\frac{\partial c_{Cu}}{\partial z} \quad \text{and } J_{Zn} = D_{Zn}\frac{\partial c_{Cu}}{\partial z}$$

$$\text{If } \; J_{Cu} = -J_{Zn} \quad : \quad D_{Cu} = D_{Zn} = \tilde{D}_{CuZn}$$

D is called, for example:
chemical diffusion coefficient
interdiffusion coefficient.
The corresponding frame of reference is usually called number fixed frame of reference because there is no net-flow of atoms:
$J_{Cu} + J_{Zn} = 0$

Pfeil's (1929) observations of the diffusion-controlled overgrowth of an oxide scale

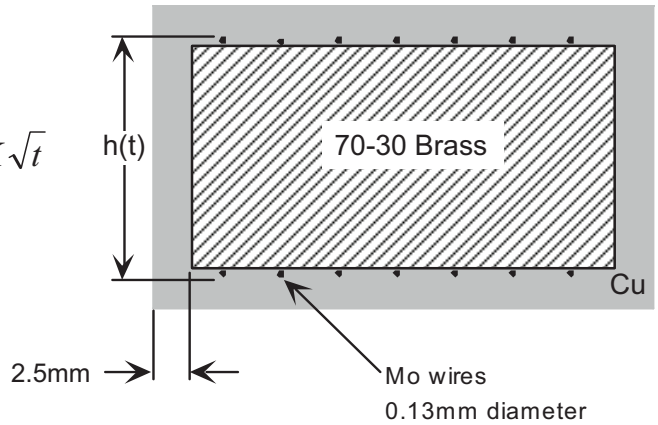


It seems as the particles have moved!

Kirkendall's Diffusion Couple

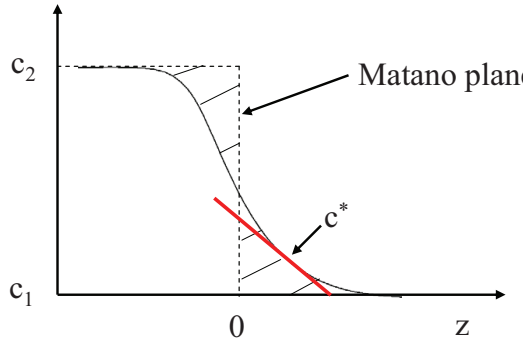
Schematic of the Smigelskas–Kirkendall diffusion couple

$$h(t) - h(0) = -K\sqrt{t}$$



It seems as the Mo-wire has moved!

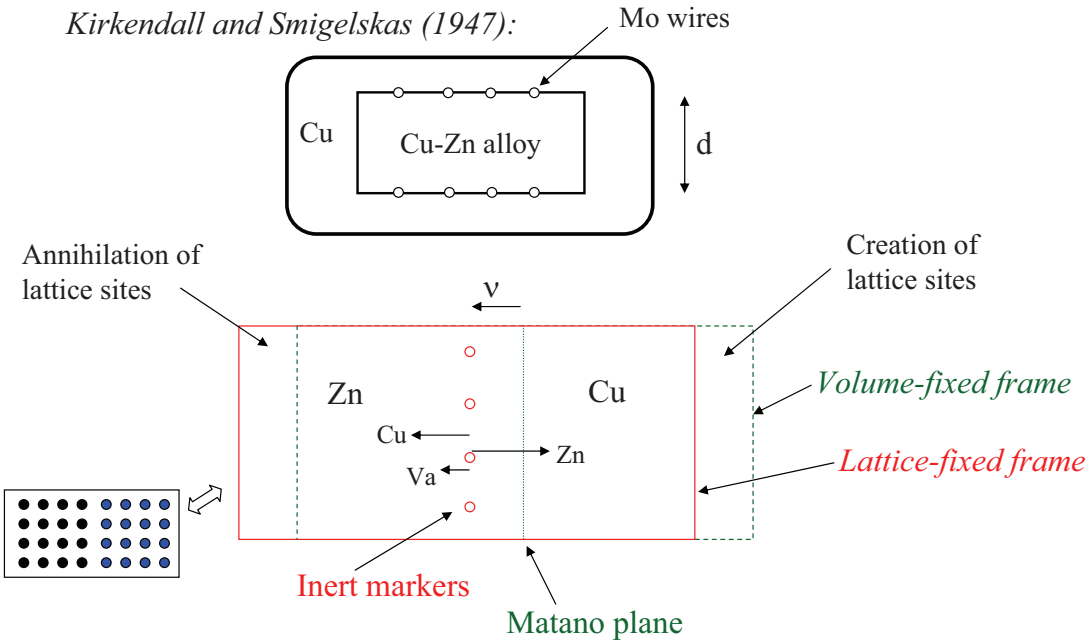
Determining D with diffusion couple technique:



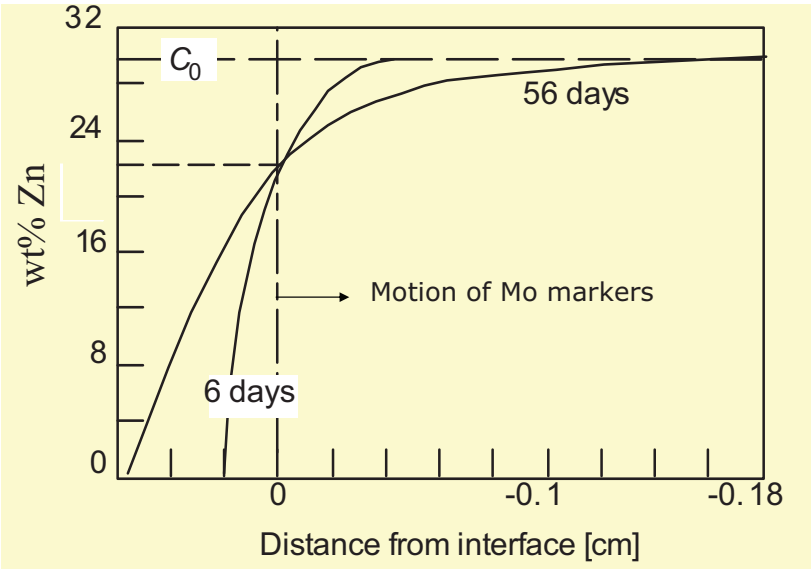
$$\int_{c_1}^{c_2} z\,dc = 0$$

$$\tilde{D}(c^*) = -\left(\int_{c_1}^{c^*} z\,dc\right) \Big/ \left(2t\,\partial c/\partial z\right)$$

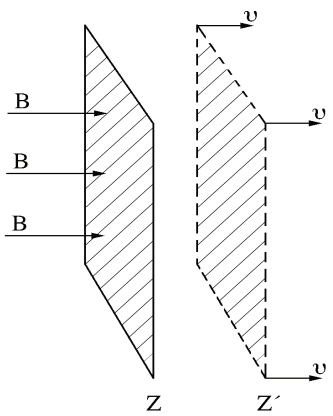
Kirkendall and Smigelskas (1947):



Zn concentration profile



If we express the fluxes relative the markers (fixed to the lattice) we may evaluate one flux for Cu and one for Zn and in general $J'_{Cu} + J'_{Zn} \neq 0$. This is called the lattice-fixed frame of reference and we denote it with J'.



We may transform the number-fixed frame by means of:

$$J_{Cu} = J'_{Cu} - x_{Cu}(J'_{Cu} + J'_{Zn})$$
$$J_{Zn} = J'_{Zn} - x_{Zn}(J'_{Cu} + J'_{Zn})$$

$$J_{Cu} + J_{Zn} = J'_{Cu} + J'_{Zn} - (J'_{Cu} + J'_{Zn}) = 0$$

Fick´s (first) law,
lattice-fixed frame of reference:

$$J'_A = -D'_A \frac{\partial c_A}{\partial z}$$

$$J'_B = -D'_B \frac{\partial c_B}{\partial z}$$

Usually we prefer to write:

$$J'_A = -D'^{A}_{AB} \frac{\partial c_B}{\partial z}$$

$$J'_B = -D'^{A}_{BB} \frac{\partial c_B}{\partial z}$$

Fick´s (first) law,
number-fixed frame of reference:

$$J_A = -D^{A}_{AB} \frac{\partial c_B}{\partial z}$$

$$J_B = -D^{A}_{BB} \frac{\partial c_B}{\partial z}$$

We thus find:

$$D^{Cu}_{CuZn} = D'^{Cu}_{CuZn} - x_{Cu}(D'^{Cu}_{CuZn} + D'^{Cu}_{ZnZn})$$
$$= (1 - x_{Cu})D'^{Cu}_{CuZn} - x_{Cu}D'^{Cu}_{ZnZn}$$

$$D^{Cu}_{ZnZn} = D'^{Cu}_{ZnZn} - x_{Zn}(D'^{Cu}_{CuZn} + D'^{Cu}_{ZnZn})$$
$$= (1 - x_{zn})D'^{Cu}_{ZnZn} - x_{Zn}D'^{Cu}_{CuZn}$$

Observe that we have:

$$D_{Zn} = D^{Cu}_{ZnZn} \quad \text{and } D_{Cu} = -D^{Cu}_{CuZn} \Rightarrow$$
$$D_{Zn} = (1 - x_{zn})D'_{Zn} + x_{Zn}D'_{Cu}$$
$$= \tilde{D}_{CuZn}$$

The D´ coefficients are called individual diffusion coefficients.

Atomistic treatment of diffusion

For crystalline phases it's usually believed that diffusion occurs through A vacancy exchange mechanism.

Assuming that there is a random distribution of vacant sites and that the number of vacncies is everywhere adjusted to equilibrium, it is possible to derive the following expression for the flux of k in a lattice-fixed frame of reference.

$$J^L_k = c_k y_{va} M_{kva} \nabla \mu_k$$

where M_{kva} is some kinetic factor which gives the rate of exchange if there is a vacancy adjacent to a k atom.

Phenomenological equations

$$J_k^L = -\sum_{i=1}^{n} L_{ki} \frac{\partial \mu_i}{\partial z} - L_{1T} \frac{\partial T}{\partial z} - L_{1P} \frac{\partial P}{\partial z} - L_{1\phi} \frac{\partial \phi}{\partial z}$$

They are called phenomenological since they stem from no model, but from the observed conditions of equilibrium.

If we choose to consider an isothermal, isobaric and isopotential system we have:

$$J_k^L = -\sum_{i=1}^{n} L_{ki} \frac{\partial \mu_i}{\partial z} \qquad \left(J_k^L = -L_{kk} \frac{\partial \mu_k}{\partial z} \right)$$

Identification

Assuming that the vacancy exchange mechanism is predominant, and by comparing to the expression derived earlier under this assumption, we may identify:

$$L_{kk} = c_k y_{va} M_{kva}$$

We have now established a relation between M and L.

Transformation to a volume-fixed frame

$$J_k = J_k^L - c_k v = J_k^L - c_k \sum_{k=1}^{n} V_k J_k^L$$

$$= -\sum_{i=1}^{n} L_{ki} \frac{\partial \mu_i}{\partial z} - c_k \sum_{k=1}^{n} V_k \sum_{i=1}^{n} L_{ki} \frac{\partial \mu_i}{\partial z}$$

or,

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

where,

$$L'_{ki} = -\sum_{j=1}^{n} (\delta_{jk} - c_k V_j) L_{ji}$$

Transformation to concentration gradients

Applying the chain-rule of derivation on the previous equation:

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

Or equally if the unreduced diffusivities, D_{kj} are introduced:

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

where,

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

Independent set of driving forces

There is a relation between the n concentration gradients, and it's possible to eliminate one of them:

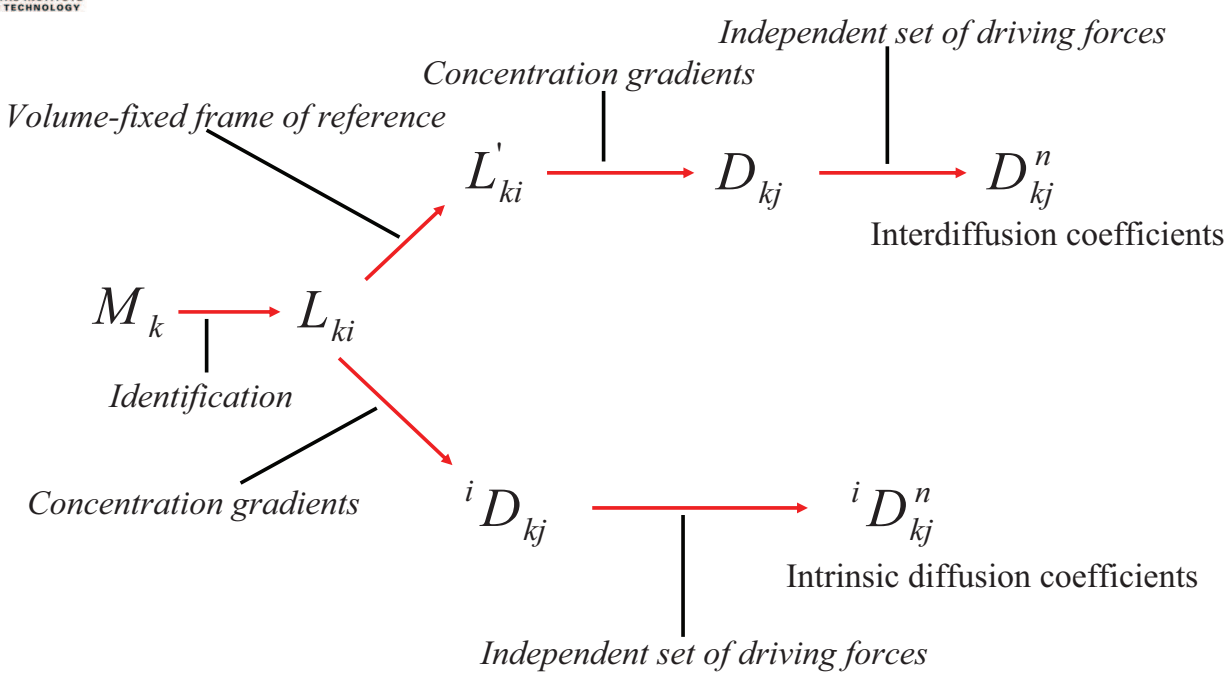
$$\frac{\partial c_n}{\partial z} = -\frac{\partial c_1}{\partial z} - \frac{\partial c_2}{\partial z} - \ldots\ldots\ldots\ldots - \frac{\partial c_{n-1}}{\partial z}$$

and thus, the flux is now expressed: $$J_k = -\sum_{j=1}^{n-1} (D_{kj} - D_{kn}) \frac{\partial c_j}{\partial z}$$

we may identify: $$D_{kj}^n = D_{kj} - D_{kn}$$

and finally obtain: $$J_k = -\sum_{j=1}^{n-1} D_{kj}^n \frac{\partial c_j}{\partial z}$$

Summary of steps taken when transforming from M's to D's



Modeling of the atomic mobility

From absolute reaction rate theory arguments the mobility coefficient for an element B, M_B, may be divided into a frequency factor, M_B^0 and an activation enthalpy Q_B, i.e.

$$M_B = M_B^0 \exp\left(\frac{-Q_B}{RT}\right)\frac{1}{RT}\,{}^{mg}\Gamma$$

Where ${}^{mg}\Gamma$ is a factor taking into account the effect of the ferromagnetic transition. ${}^{mg}\Gamma$ is a function of alloy composition and is represented by:

$${}^{mg}\Gamma = \exp(6\alpha\xi)\exp\left(\frac{-\alpha Q_B}{RT}\right)$$

Frames of reference

Lattice-fixed frame of reference:

- Defined by the inert markers, or that There is no net flow of lattice sites.

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

Volume-fixed frame of reference:

- Defined in such a way that there is no net flow of volume.

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

DICTRA frame of reference:

-Volume-fixed frame, however only the substitutional components are Assumed to contribute to the volume.

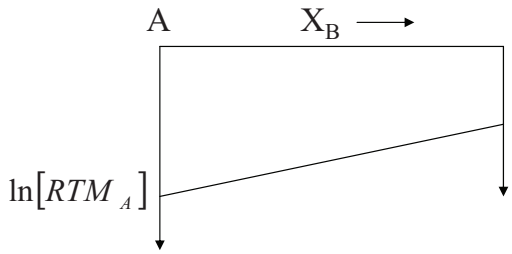
$$\sum_{K\in S}^{n} J_k = 0$$

Modeling of the atomic mobility

When treating the composition dependency of the mobility it has been found superior to expand the logarithm of the mobility rather than the value itself, i.e.

$$RT\ln\left[RTM_B\right] = RT\ln M_B^0 - Q_B + RT\ln {}^{mg}\Gamma$$

Because $\ln\left[RTM_i\right]$ is often found to have a fairly linear composition dependency



Modeling of the atomic mobility

Both $RT\ln M_B^0$ and $-Q_B$ will in general depend upon the composition, the temperature and pressure.

In the spirit of the CALPHAD approach, the composition dependency of these two factors is represented with a linear combination of the values at each end-point of the composition space, and a Redlich-Kister expansion.

$$\Phi_B = \sum_i x_i \Phi_B^i + \sum_i \sum_{j>i} x_i x_j \left[\sum_{r=0}^{m} {}^r\Phi_B^{i,j} (x_i - x_j)^r \right]$$

where Φ_B represents $RT\ln M_B^0$ or $-Q_B$.

Modeling of the atomic mobility

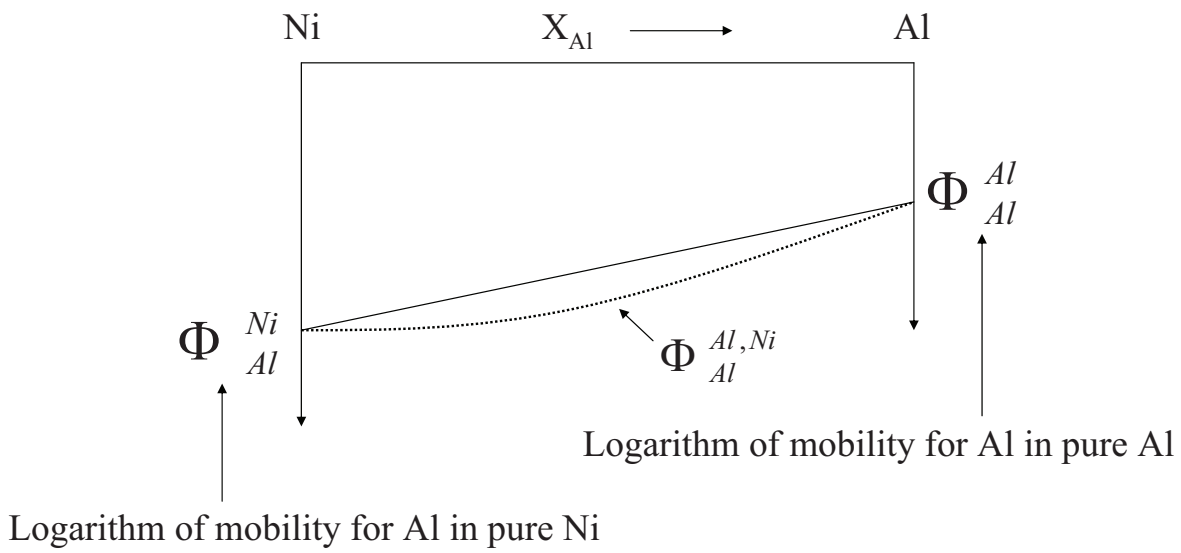
Example: Expression for the mobility of Al in a binary system Ni-Al.

$$RT\ln\left[RTM_{Al}\right] = \underbrace{RT\ln M_{Al}^{0} - Q_{Al}}_{\Phi_{Al}}$$

Where,

$$\Phi_{Al} = x_{Al}\Phi_{Al}^{Al} + x_{Ni}\Phi_{Al}^{Ni} + x_{Al}x_{Ni}\Phi_{Al}^{Al,Ni}$$

Modeling of the atomic mobility



Building a kinetic database

- Collect experimental information

Different levels of ambition!

In a database for A-base alloys:

1. Find Tracer or Dilute diffusivities of the elements (B,C,D…) in A. These can be entered directly in the database, assuming that the mobilities are concentration independent.

Example

Tracer diffusion coefficient of Al and Ni in pure Ni:

$$D^*_{Ni} = 2.26 \cdot 10^{-4} \cdot \exp(\frac{-287000}{RT})$$

$$D^*_{Al} = 7.5 \cdot 10^{-4} \cdot \exp(\frac{-284000}{RT})$$

The tracer diffusion coefficient is directly related to the mobility:

$$RT \ln(D^*_i) = RT \ln(RTM_i)$$

In the database:

PARAM MQ(FCC_A1&NI,NI:VA),, -287000+R*T*LN(2.26E-4)

PARAM MQ(FCC_A1&AL,NI:VA),, -284000+R*T*LN(7.5E-4)

Building a kinetic database

Next level of ambition:

2. Find Tracer, Dilute and self diffusivities of the elements (A,B,C,D…) in the elements (A,B,C,D). These can be entered directly in the database, assuming that the mobilities are linear functions of composition.

Example

Tracer diffusion coefficient of Al and Ni in pure Al:

$$D^*_{Al} = 1.71 \cdot 10^{-4} \cdot \exp(\frac{-142000}{RT})$$

$$D^*_{Ni} = 4.4 \cdot 10^{-4} \cdot \exp(\frac{-145900}{RT})$$

<u>In the database:</u>

PARAM MQ(FCC_A1&AL,AL:VA),, -142000+R*T*LN(1.71E-4)

PARAM MQ(FCC_A1&NI,AL:VA),, -145900+R*T*LN(4.4E-4)

Building a kinetic database

High level of ambition:

3. Assess important systems A-B, A-C, B-C, A-B-C using ALL experimental information.

Possible experimental information

$^{i}D_{kj}^{n}$ **Intrinsic diffusion coefficient**

DI(phase,k,j,n)
LOGDI(phase,k,j,n)

D_{A}^{*} **Tracer diffusion coefficient**

DT(phase,A)
LOGDT(phase,A)

$\tilde{D}_{kj}^{n}$ **Interdiffusion coefficient**

DC(phase,k,j,n)
LOGDC(phase,k,j,n)

Example of data

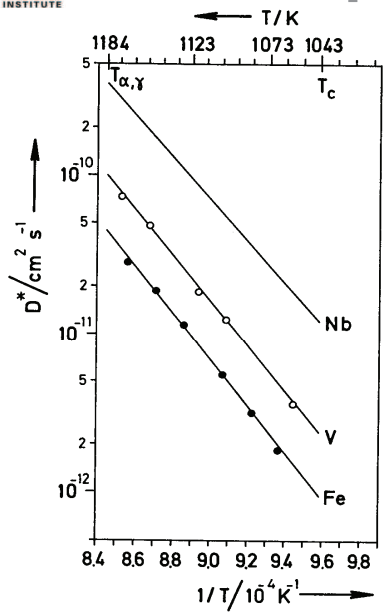


Fig. 2. Arrhenius plots of impurity diffusion of ^{48}V (○) and self-diffusion (●) in α-iron. Impurity diffusion of ^{95}Nb is shown for comparison[20]).

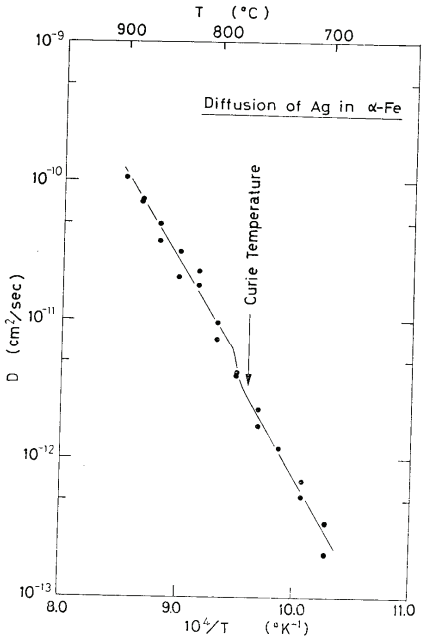


FIG. 5. Temperature dependence of diffusivities of Ag^{110m} in α-Fe.

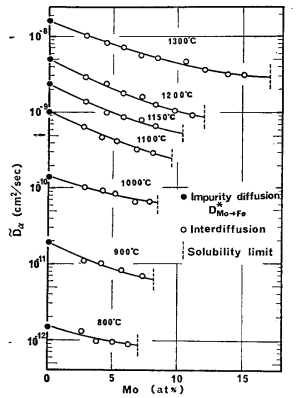


Fig. 3. Concentration dependence of interdiffusion coefficient in α phase of Fe-Mo system.

Assessment of data: Binary Ni-Al system

Let us start by considering the Ni-rich side of the system and assume that the mobilities are independent of composition, i.e.

$$\Phi_{Al} = \Phi^{Al}_{Al} = \Phi^{Ni}_{Al}$$

Then we need only two parameters for the database, i.e.

$$\Phi^{Ni}_{Al} \quad and \quad \Phi^{Ni}_{Ni}$$

Assessment of data: Binary Ni-Al system

These two parameters we can determine from the tracer diffusion coefficients of Al and Ni in Ni, i.e.

$$\Phi_{Al}^{Ni} = RT \ln D_{Al}^{*} = -284000 + RT \ln 7.5 \bullet 10^{-4}$$

$$\Phi_{Ni}^{Ni} = RT \ln D_{Ni}^{*} = -287000 + RT \ln 2.26 \bullet 10^{-4}$$

Assessment of data: Binary Ni-Al system

Next step to improve the description would be to assume a linear concentration dependence for the mobilities of Al and Ni.

We then need the mobilities in pure Al as well, e.g.

$$\Phi_{Al}^{Al} = RT \ln D_{Al}^{*} = -142000 + RT \ln 1.71 \bullet 10^{-4}$$

$$\Phi_{Ni}^{Al} = RT \ln D_{Ni}^{*} = -145900 + RT \ln 4.4 \bullet 10^{-4}$$

Assessment of data: Binary Ni-Al system

Finally, in order to reach a good agreement with our experimental data we would like to introduce two interaction parameters.

$$\Phi_{Al}^{Al,Ni} \quad and \quad \Phi_{Ni}^{Al,Ni}$$

These will be fitted in an optimisation procedure in order to give the best possible agreement with our experimental data points.

Optimization software needed !!!

The Software

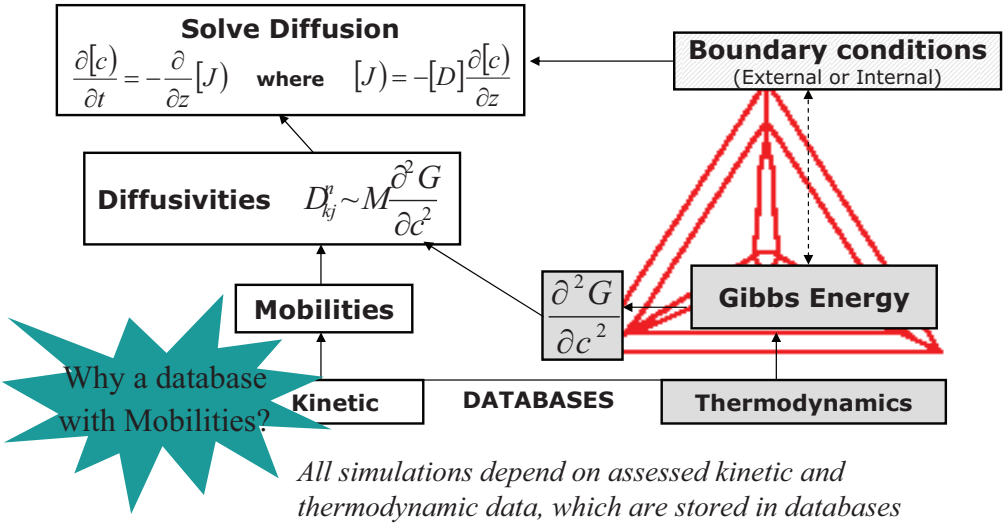
- Software package for simulation of diffusion controlled reactions in multi-component alloys.
- Simulation on geometries, which may be reduced to one dimension (e.g. planar, cylindrical, spherical)
- Linked to Thermo-Calc, which provides all necessary thermodynamic properties.
- The result of more than 20 years and 60 man-years R&D at:

  Royal Institute of Technology in Stockholm, Sweden

  Max-Planck Institute für Eisenforschung in Düsseldorf, Germany

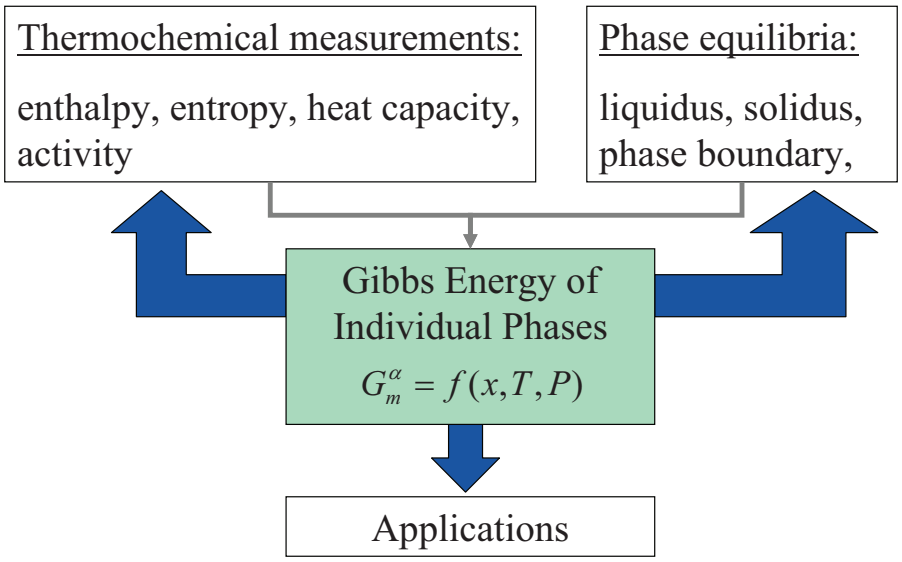
Basic calculation procedure

A numerical finite difference scheme is used for solving a system of coupled parabolic partial differential equations

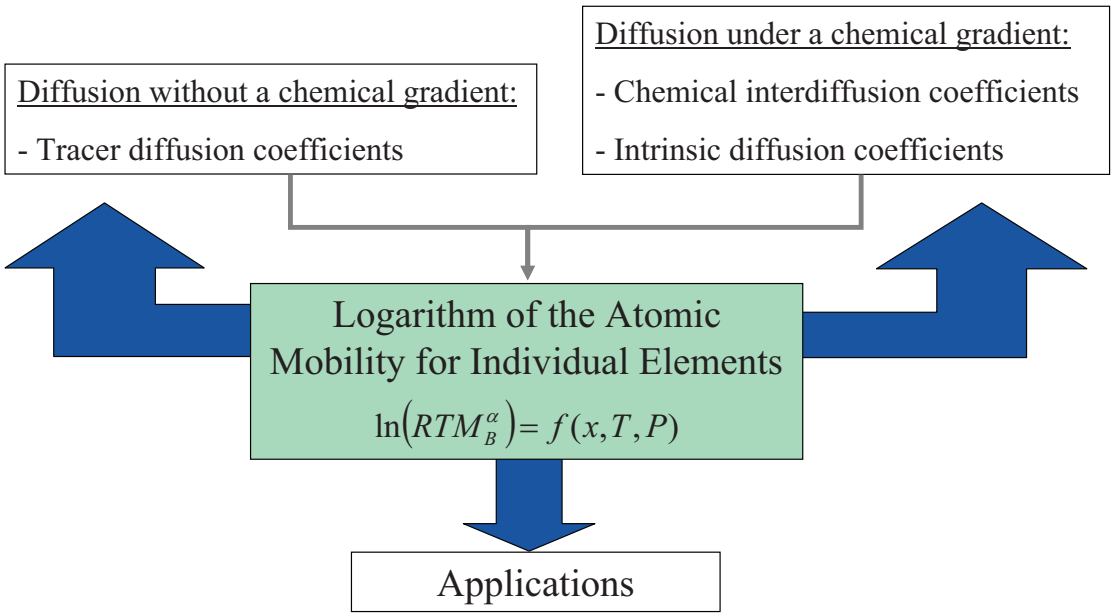


All simulations depend on assessed kinetic and thermodynamic data, which are stored in databases

Thermodynamic Databases (*The CALPHAD approach*)



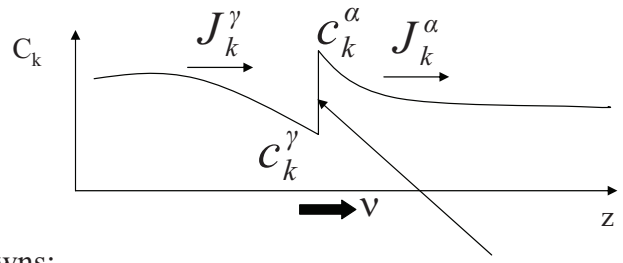
Kinetic Databases
(*in a CALPHAD spirit*)



Several application types

- Diffusion in single-phase systems
- Diffusion with moving interfaces (growth, dissolution of particles etc.)
- Cell calculations (particle distributions, immobile interfaces etc.)
- Diffusion in dispersed systems
- Coarsening or Oswald ripening

Diffusion with a moving interface



Sharp interface with assumption of local equilibrium

<u>n-1 unknowns:</u>

n-2 chemical potentials.

Velocity of phase boundary, ν

<u>n-1 Flux Balance Equations:</u>

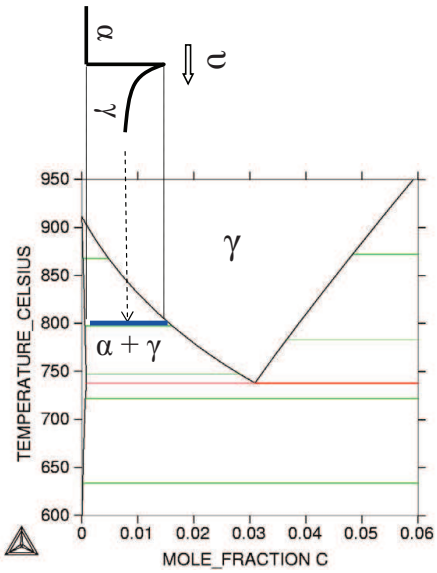
$$\nu(c_k^\alpha - c_k^\gamma) = J_k^\alpha - J_k^\gamma$$

<u>F-B Equations solved as:</u>

$$\sum_k^{n-1}\left(\nu(c_k^\alpha - c_k^\gamma) - (J_k^\alpha - J_k^\gamma)\right)^2 < \varepsilon$$

Diffusion with a moving interface

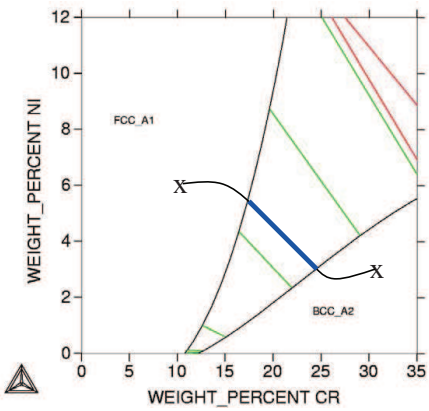
<u>Binary example: Fe-C</u>



<u>Ternary example: Fe-Cr-Ni</u>

n = 3 ⇒ two unknowns!

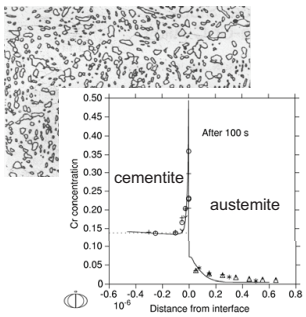
- One a_i or μ_i (i.e. one tie-line)
- The velocity



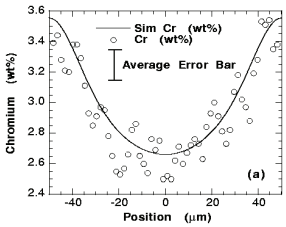
Some application examples

- γ to α transformations in steel
- Growth or dissolution of carbides
- Microsegregation during solidification
- Nitriding of steels
- Nitrocarburising of steels
- σ-phase precipitation in stainless steels
- Transient Liquid-Phase bonding of alloys
- Sintering of cemented carbides
- *and much more …*

Carbide dissolution



Microsegregation during solidification



Purpose of DICTRA

Have a possibility to *Teach*, i.e. bring new insight into problems.

…by linking fundamental models to critically assessed thermodynamic and kinetic data.

Purpose of DICTRA

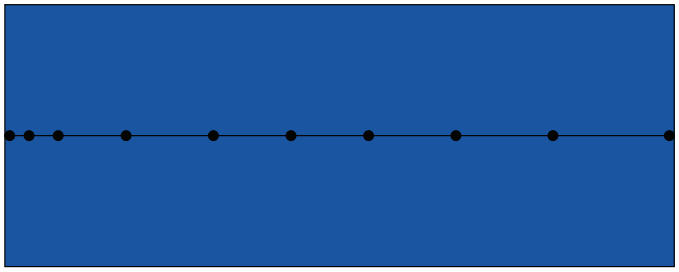
Provide an *engineering tool* for materials and process design.

…by allowing simulations to be performed with realistic conditions and data on alloys of practical importance.

Region

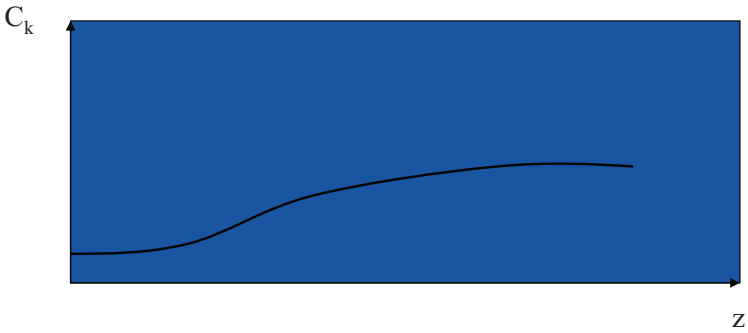
A ”box” with an arbitrary name

Grid



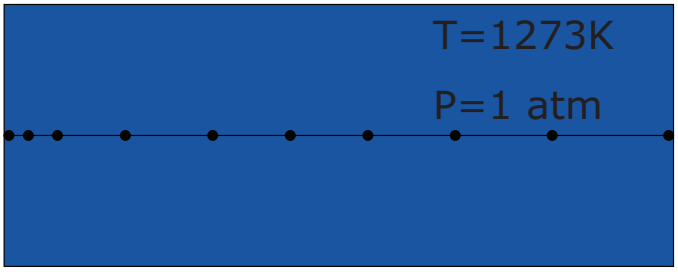
Distribution of node points for numerical calculations

Concentration Profile



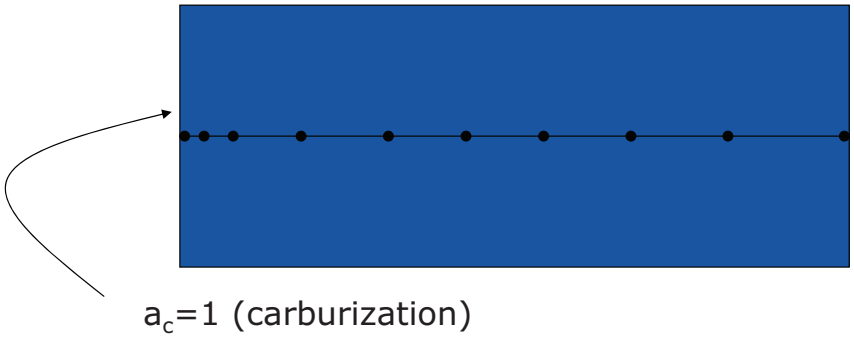
Concentration, C_k of an element as a function of distance z

Global Conditions



Conditions valid for entire system, T and P

Boundary Conditions



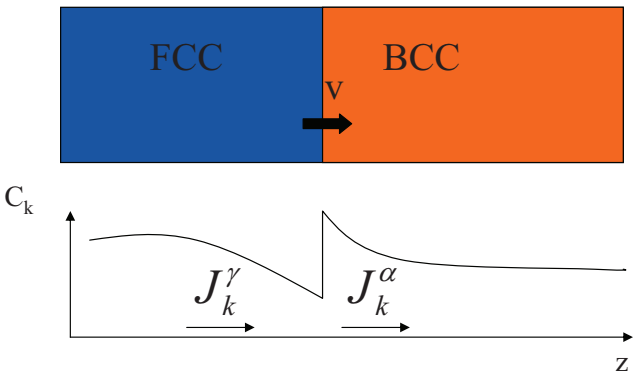
a_c=1 (carburization)

Conditions that apply to region boundaries (could be functions of time and temperature)

Moving Phase Boundary Calculations

- Used for calculating growth or dissolution of a phase.
- Assumptions:
  - Local equilibrium holds at the phase boundary, i.e. concentrations at the boundary can be calculated from an equilibrium calculation in T-C.
  - Diffusion controls the movement of the phase boundary
- Application examples:
  - ✓Carbide dissolution
  - ✓Solidification
  - ✓Growth of σ–phase in a stainless steel

Moving phase boundary simulation



Solve diffusion equation in each phase

Calculate displacement of phase boundary

Use Thermo-Calc to find tie-lines

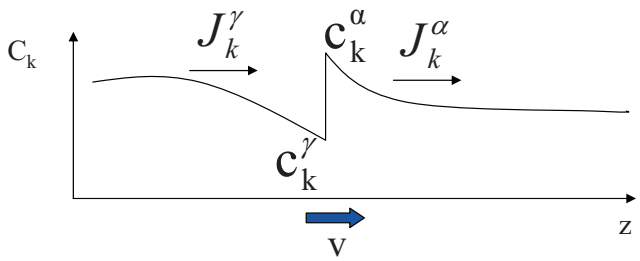
M-P-B theory

Unknowns: Tie-line, specified by n-2 a_i or μ_i

Velocity of phase boundary, v

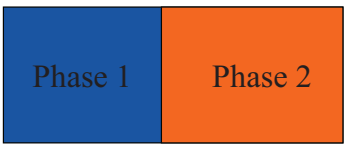
Equations: n-1 flux-balance equations, $v(c_k^\alpha - c_k^\gamma) = J_k^\alpha - J_k^\gamma$

Solved as: $v(c_k^\alpha - c_k^\gamma) - (J_k^\alpha - J_k^\gamma) = 0$

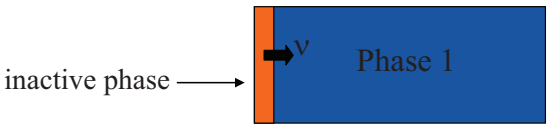


Moving Phase Boundary

- Moving phase boundaries simulations may be setup in DICTRA in two different ways:
  - Introducing two or more adjacent regions containing different phases



  - Entering an inactive phase (formed when thermodynamically stable)



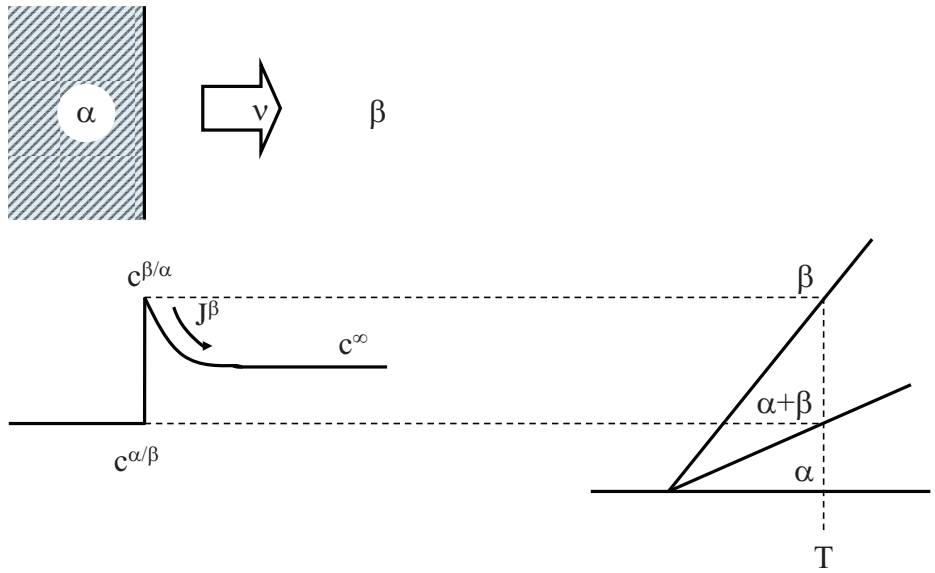
Assumptions – Sharp interface model

- local equilibrium
- profiles as piecewise linear functions
- volume is independent of composition
- volume fixed frame of reference

Calculation scheme - binary case

- determine tieline
- solve PDE
- solve flux balance equation
- update grid

LE – Tieline in Binary system



PDE

$$\frac{\partial c_k}{\partial t} = \frac{\partial}{\partial z}\left(D_k \frac{\partial c_k}{\partial z} \right)$$

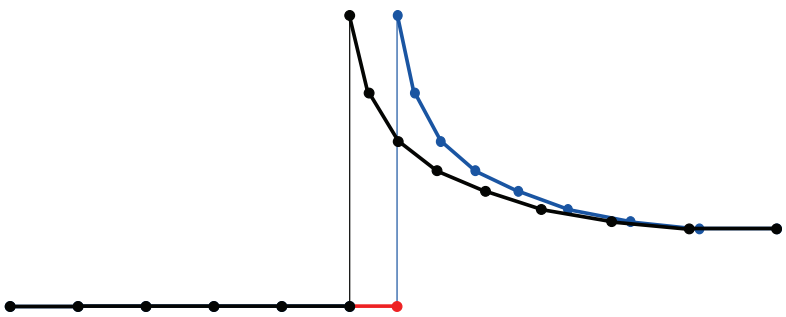
Solved by FDM / FEM

Flux balance equation

$$\nu^{\alpha} c_k^{\alpha} - \nu^{\beta} c_k^{\beta} = J_k^{\alpha} - J_k^{\beta} \qquad k=1,2\ldots.n-1$$

$$c_k^{\alpha}, c_k^{\beta} \text{ from LE}$$
$$J_k^{\alpha}, J_k^{\beta} \text{ from PDE (and LE)}$$
$$\Rightarrow \nu^{p}(\nu^{\alpha}, \nu^{\beta})$$

Grid update



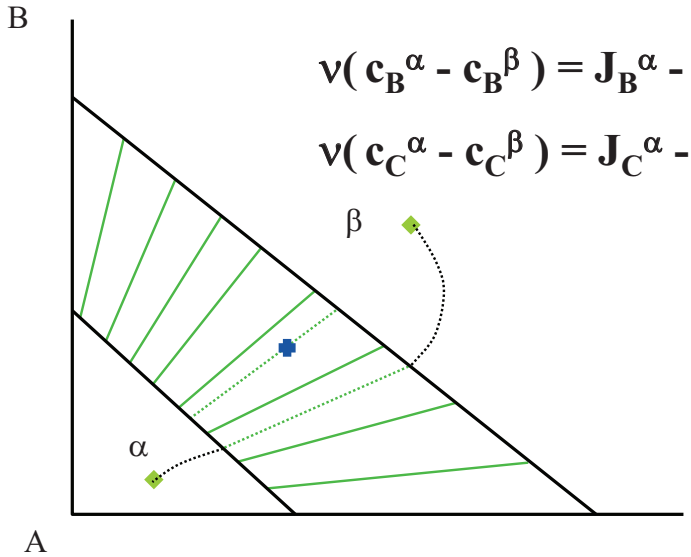
u-fraction

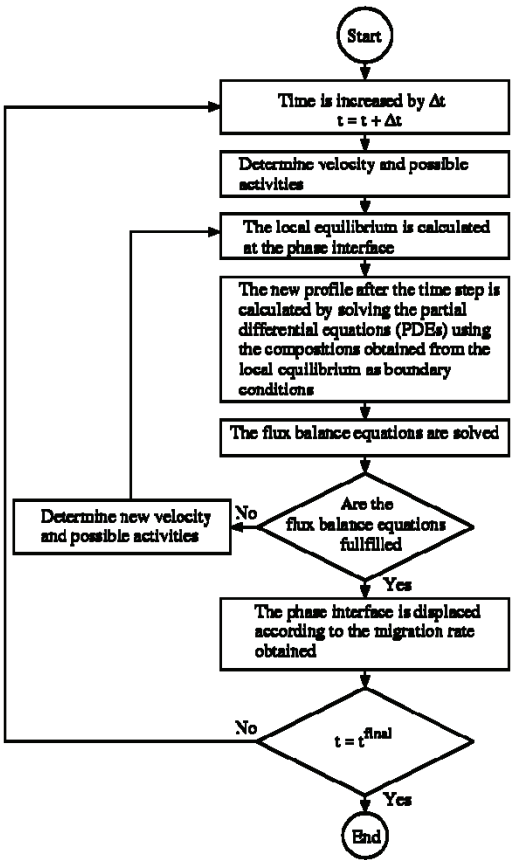
- mole fraction: $$x_k = \frac{N_k}{\sum_i N_i}$$
- mass fraction: $$w_k = \frac{N_k m_k}{\sum_i N_i m_i}$$
- u-fraction: $$u_k = \frac{N_k}{\sum_{i \in s} N_i}$$

Calculation scheme - multicomponent case

- fix activities/potentials
- determine tieline
- solve PDE
- solve flux balance equations
- guess new activities/potentials until
- flux balance equations are fulfilled
- update grid

LE in ternary systems



$$\nu(c_B^{\alpha} - c_B^{\beta}) = J_B^{\alpha} - J_B^{\beta}$$

$$\nu(c_C^{\alpha} - c_C^{\beta}) = J_C^{\alpha} - J_C^{\beta}$$