Thermo-Calc Software

DICTRA On-line Training

Åke Jansson, John Ågren, Carl-Magnus Lancelot, André Schneider, Johan Bratberg

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www.thermocalc.com

Thermo-Calc Software

Diffusion Module (DICTRA)

Day 1

9:00	Introduction to DICTRA (= Diffusion Module)
9:40	**Example** - Up-hill diffusion in the Fe-Si-C system
10:25	Q&A
10:40	**Example** – Carburisation and de-carburisation
11:10	**Example –** Particle growth
11:45	Q&A
12:00	Home assignment 1

Download material for today:
https://download.thermocalc.com/courses/Diff-Day1/

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Diffusion Module (DICTRA)

Day 2

9:00	Home assignment 1
9:10	**Example** - Solidification using Scheil
9:30	**Example** - Scheil with real back-diffusion in the solid.
9:50	**Example** – DICTRA solidification (Moving phase boundary)
10:30	Q&A
10:45	Diffusion theory and numerics
11:15	**Example** – Homogenisation model: Diffusion couple
11:45	Q&A
12:00	Home assignment 2

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Diffusion Module (DICTRA)

Day 3

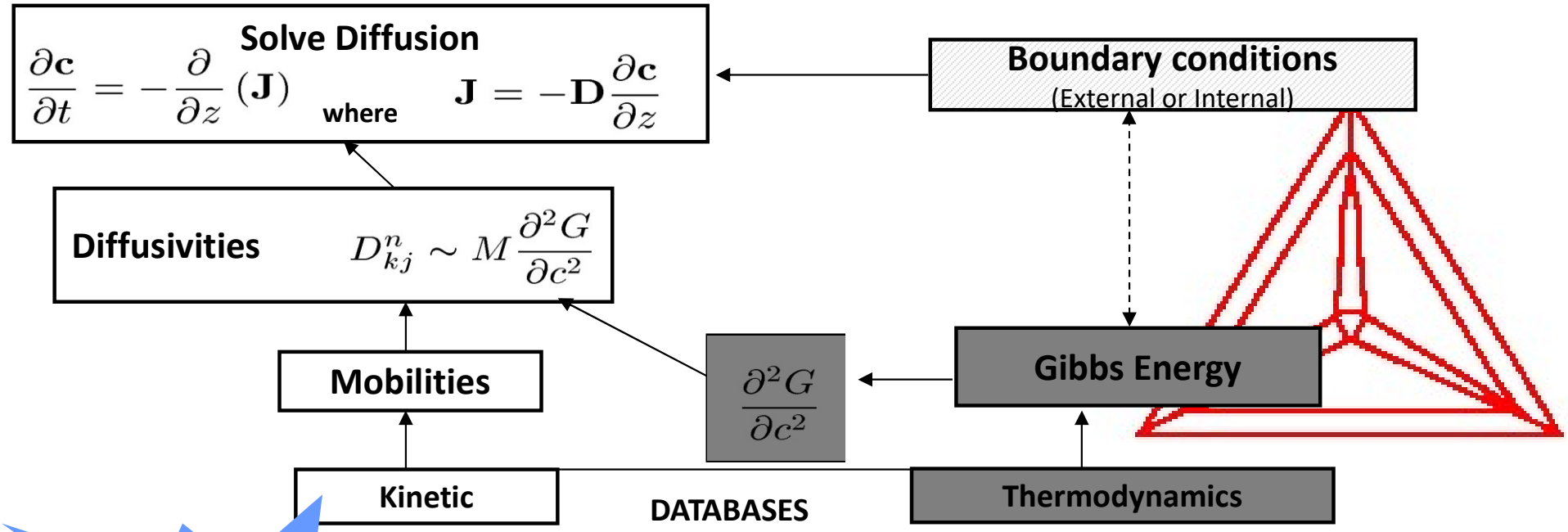
9:00	Home assignment 2
9:10	**Example** – Dissolution of cementite particles (moving phase boundary calculation)
10:10	Console mode and macro files.
10:30	Q&A
10:45	**Example** – Gradient sintering in Cemented carbide
11:30	Trouble shooting
11:45	Q&A
12:00	End

The Software

- Software package for simulation of diffusion controlled reactions in multi-component alloys.
- Simulation on geometries, which may be reduced to one spatial coordinate (planar, cylindrical or spherical)
- Linked to Thermo-Calc, which provides all necessary thermodynamic properties.
- Development started over 35 years ago at:
  - Royal Institute of Technology in Stockholm, Sweden
  - MPI für Eisenforschung in Düsseldorf, Germany (only very early)
  - Thermo-Calc Software AB (from 1997 and on)

Basic calculation procedure

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



Why a database with Mobilities?

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

Thermodynamic Databases (*The CALPHAD approach)*

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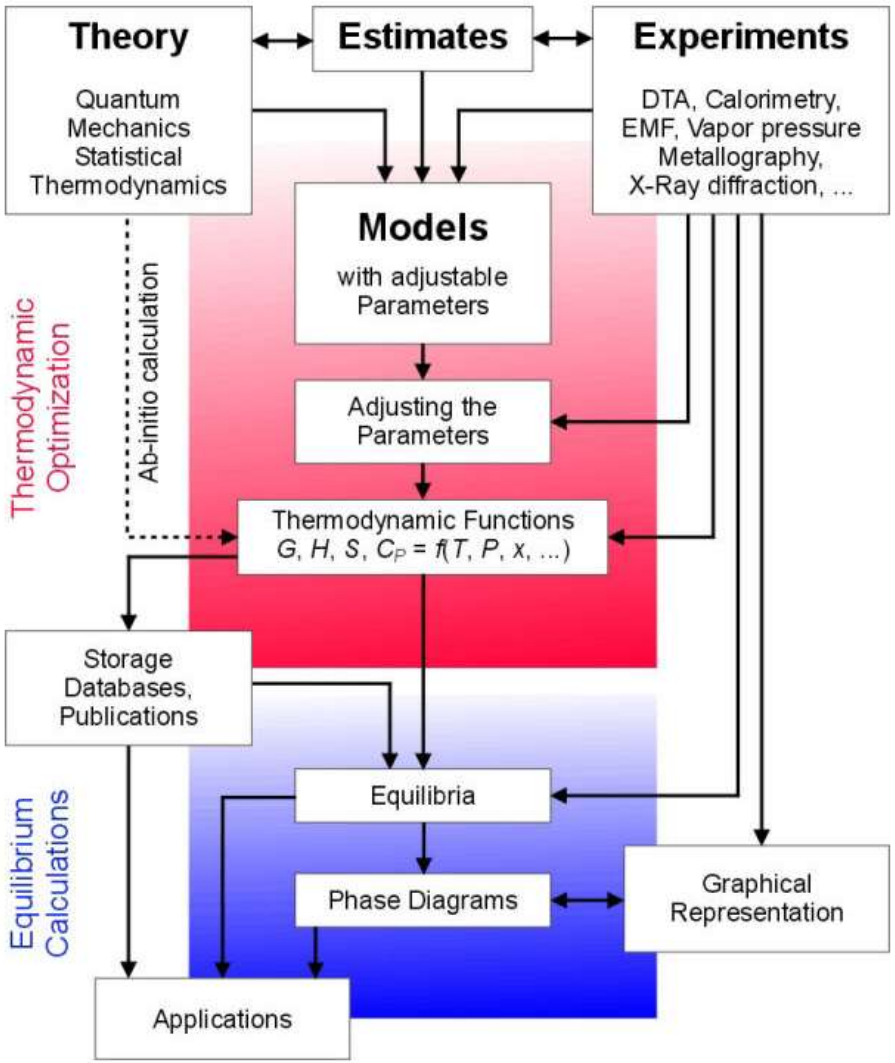
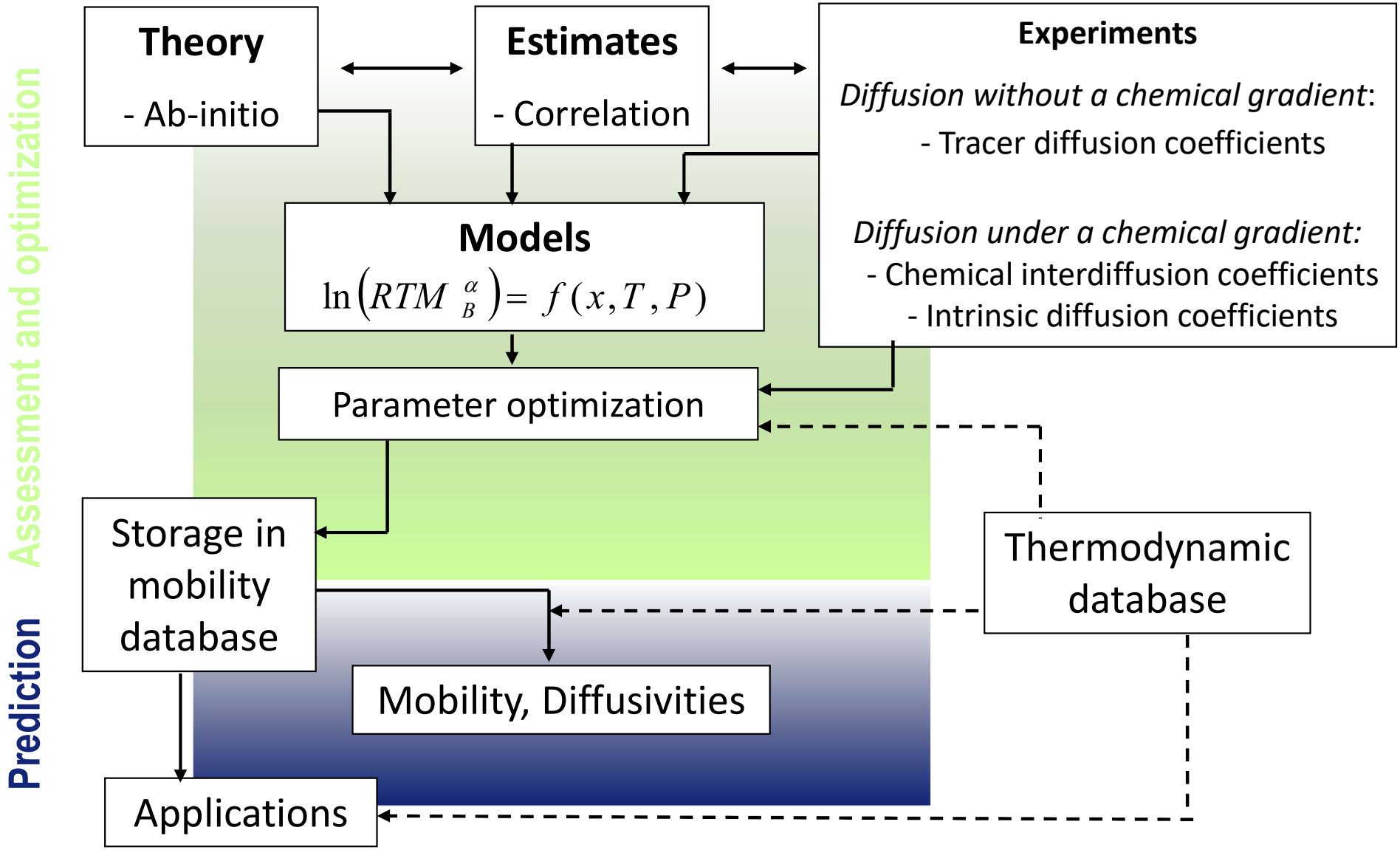


Kinetic Databases (*in a CALPHAD spirit*)



Modelling of the atomic mobility

From absolute reaction-rate theory arguments Andersson and Ågren[1] suggested:

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

M_B Mobility for element B
M_B^0 Frequency factor
Q_B Activation energy

When treating the composition dependency of the mobility, Jönsson[2] found it superior to expand the logarithm of the mobility rather than the value itself, i.e.

$$RT\ln\left[RTM_B\right] = RT\ln M_B^0 - Q_B$$

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

1. Andersson, Ågren, J Appl Phys 72(1992)1350
2. Jönsson, Scand J Metall 24(1995)21

Composition dependency

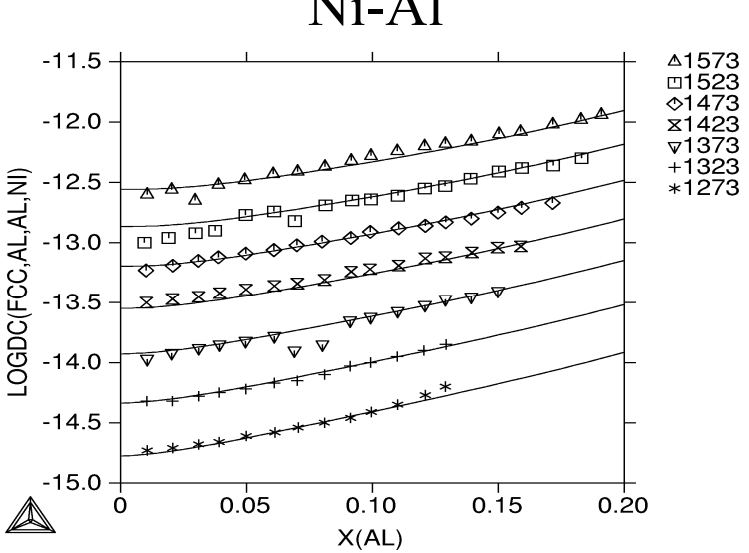
In a CALPHAD spirit the composition dependency is represented with a linear combination of the values at each endpoint of the composition space, and a Redlich-Kister expansion, i.e.

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

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

Example: FCC Ni-Al

Ni	Al
Φ_{Ni}^{Ni}	Φ_{Al}^{Ni}
Φ_{Ni}^{Al}	Φ_{Al}^{Al}
$\Phi_{Ni}^{Al,Ni}$	$\Phi_{Al}^{Al,Ni}$

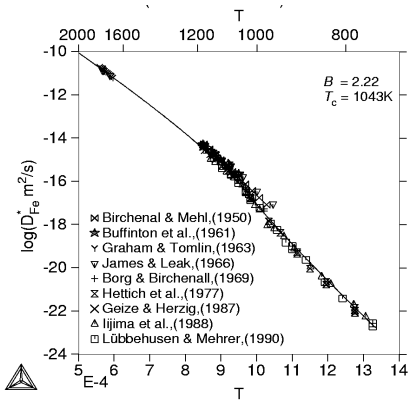


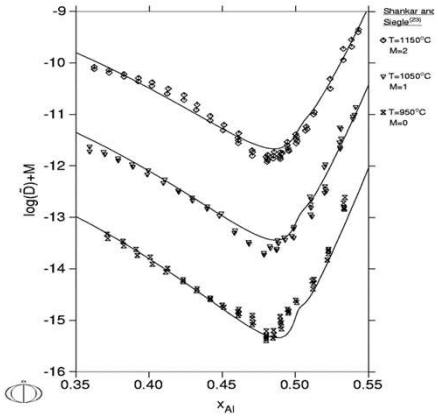
Engström , Ågren, Z Metallkd 87(1996)92

Other effects on mobility

- ✓ Ferromagnetic ordering
- ✓ Chemical ordering

can have very strong effects on the mobility and are described by a separate term each in the mobility expression.





Mobility enhancement in grain boundaries or dislocations are not taken into account in the mobility databases. It can be handled in the software by entering cross sectional area fractions and a factor reducing the activation energy compared to the bulk (console mode only).

DICTRA application types

Thermo-Calc Software

- Diffusion in single-phase systems
- Diffusion with moving interfaces
- Cell calculations (particle distributions, immobile interfaces etc.) – only in Console mode or *use TC-PRISMA*
- Diffusion in dispersed systems – only in Console mode, *use*
- Homogenization model
- Coarsening or Ostwald ripening – *use TC-PRISMA*
- Growth of pearlite – Console mode, very little used.

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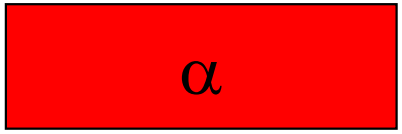
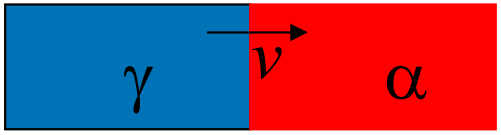
DICTRA application types

Thermo-Calc Software

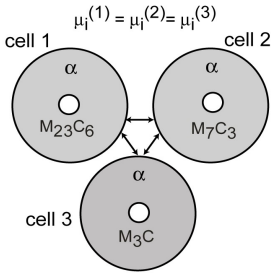
Single phase



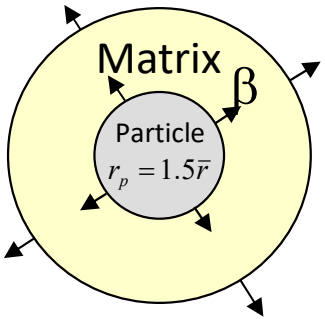
Moving boundary



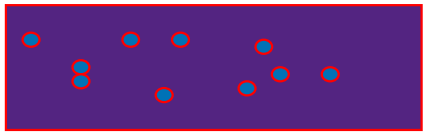
Cell



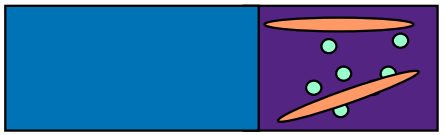
Coarsening



Disperse system

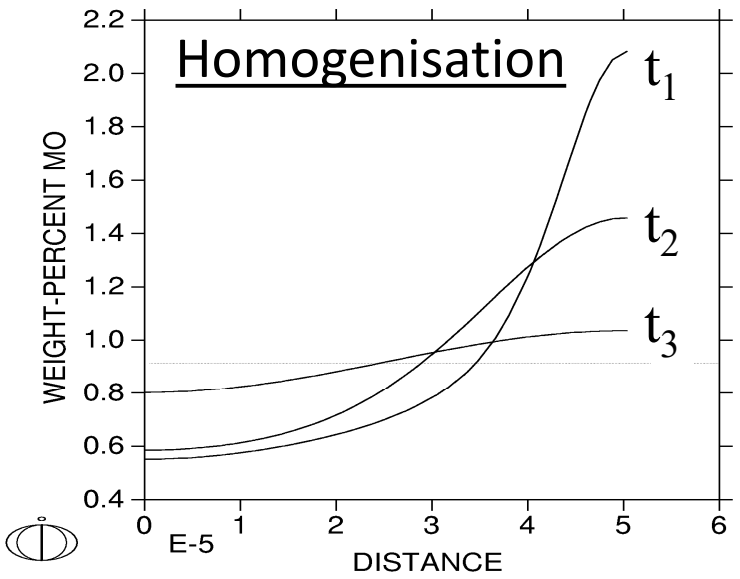


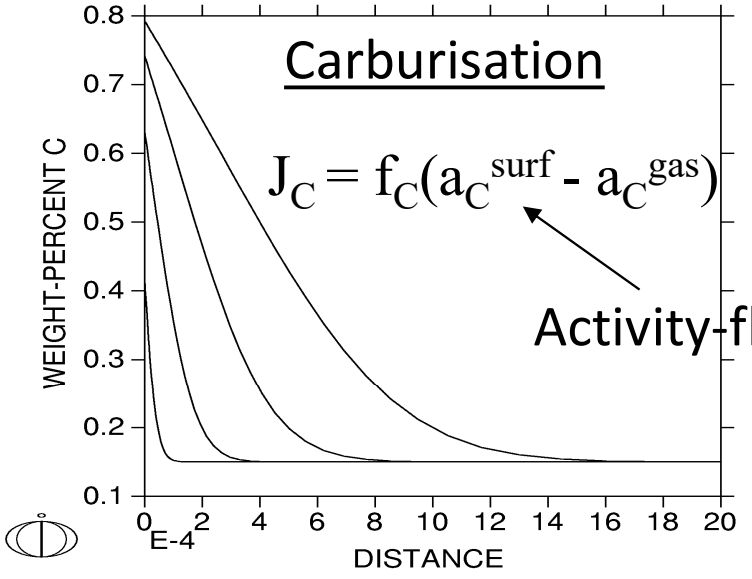
Homogenization



Diffusion in single-phase systems

Straight-forward non-complex simulations, usually on homogenisation or carburisation treatments



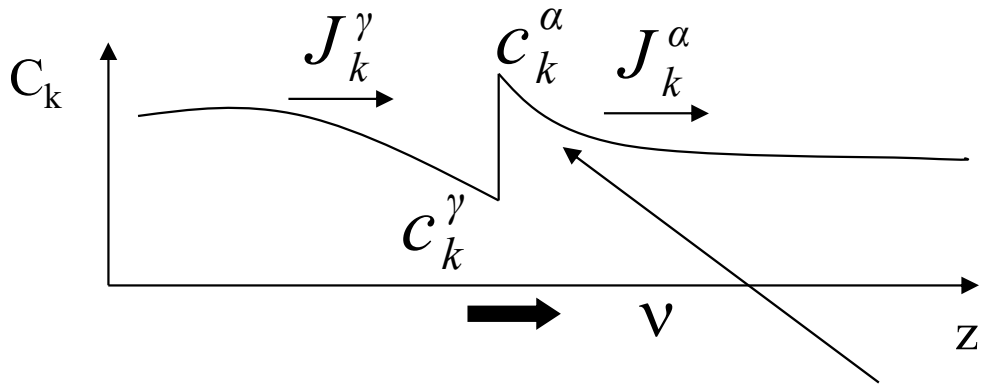


Boundary conditions can be specified as functions of time, temperature and pressure.

Different functions may be used in different time intervals.

Also: Spatially non-isothermal simulations

Diffusion with a moving interface



n-1 unknowns:

n-2 chemical potentials.

Velocity of phase boundary, v

Sharp interface with assumption of local equilibrium (also para-equilibrium possible)

n-1 Flux Balance Equations:

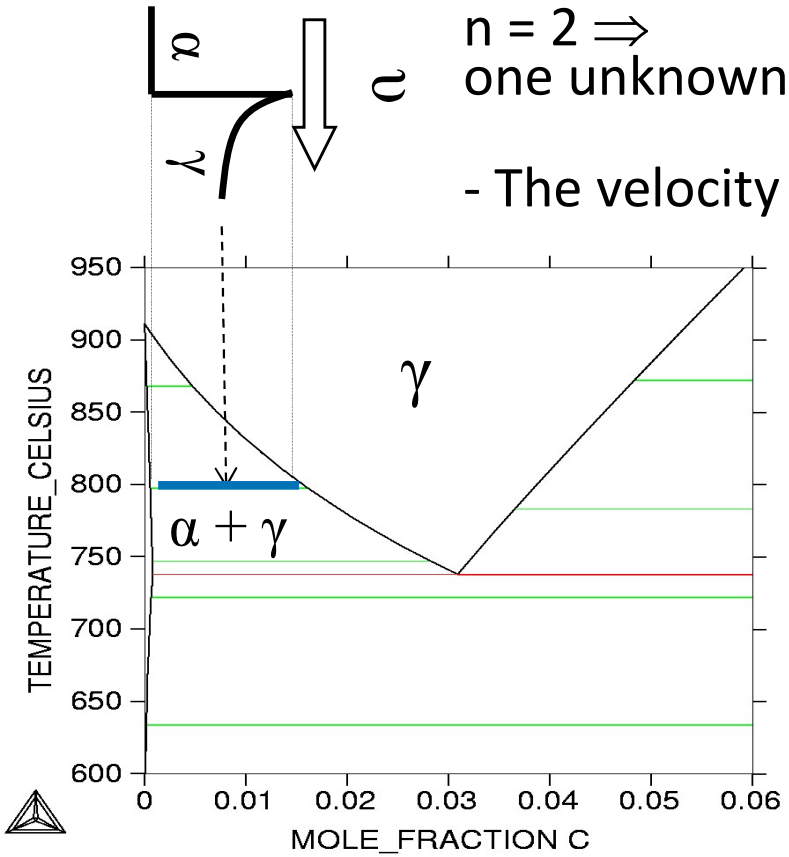
$$v\left(c_k^\alpha - c_k^\gamma\right) = J_k^\alpha - J_k^\gamma$$

F-B Equations solved as:

$$\sum_{k=1}^{n-1}\left[v\left(c_k^\alpha - c_k^\gamma\right) - \left(J_k^\alpha - J_k^\gamma\right)\right]^2 < \varepsilon$$

Diffusion with a moving interface

Binary example: Fe-C



n = 2 ⇒ one unknown

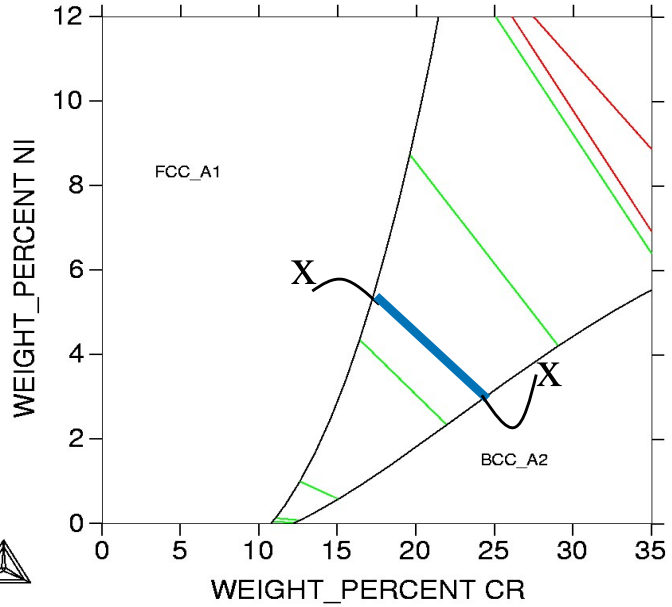
- The velocity

P, T const.

Ternary example: Fe-Cr-Ni

n = 3 ⇒ two unknowns!

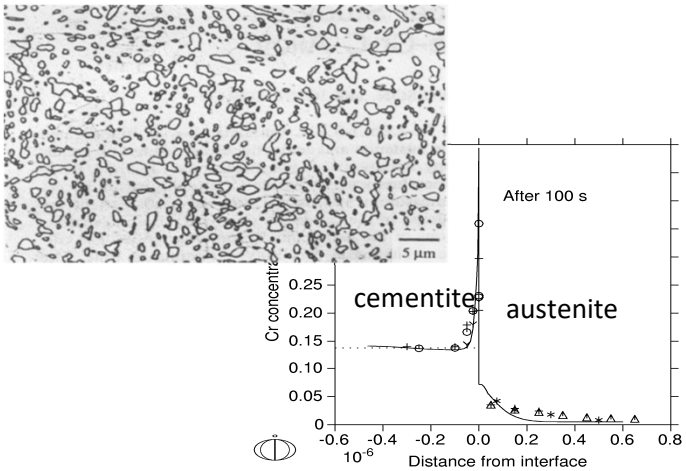
- One a_i or μ_i (i.e. one tie-line)
- The velocity



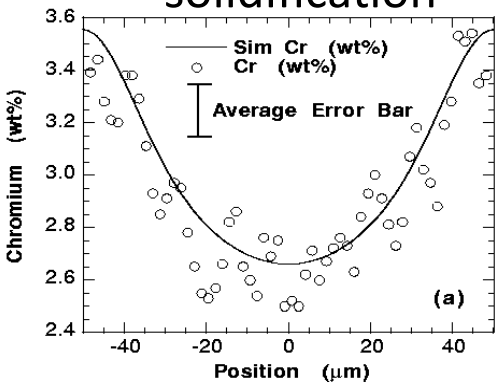
Some application examples

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

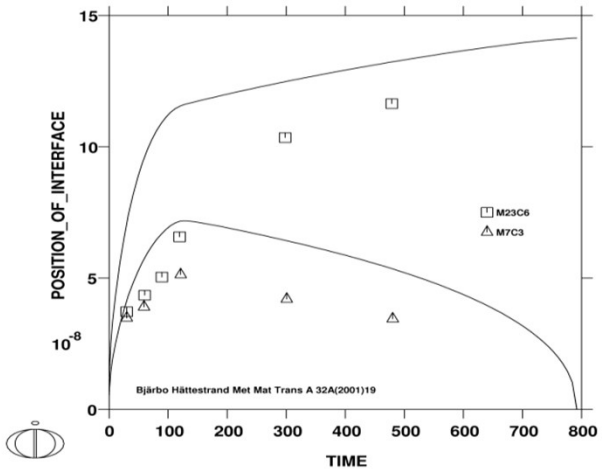
Carbide dissolution



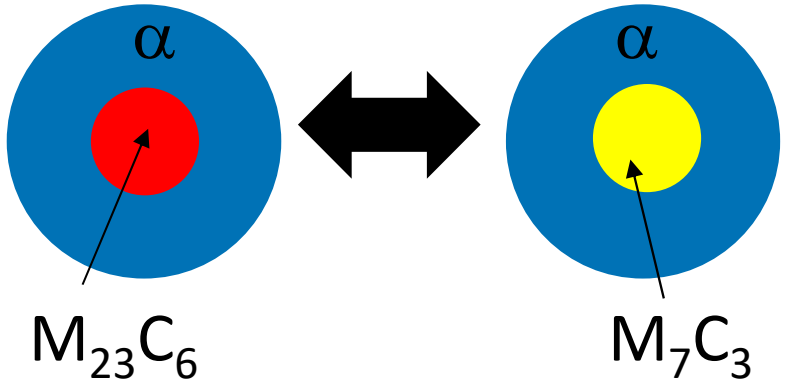
Microsegregation during solidification



Cell calculations



- Growth or dissolution of particle distributions
- Competing growth or dissolution
- Interdiffusion across an immobile interface



Conditions for cell boundaries:

✓ Equal diffusion potentials Φ_i for the elements

$$\Phi_i = \mu_i - \mu_n$$ for subst. elements

$$\Phi_i = \mu_i$$ for interstitial elements

✓ Flux balances to conserve the mass of the elements

$$\frac{J_i^{\text{cell}\#1}}{n^{\text{cell}\#1}} = \frac{J_i^{\text{cell}\#2}}{n^{\text{cell}\#2}}$$ n, cell distribution factors

Diffusion in dispersed systems

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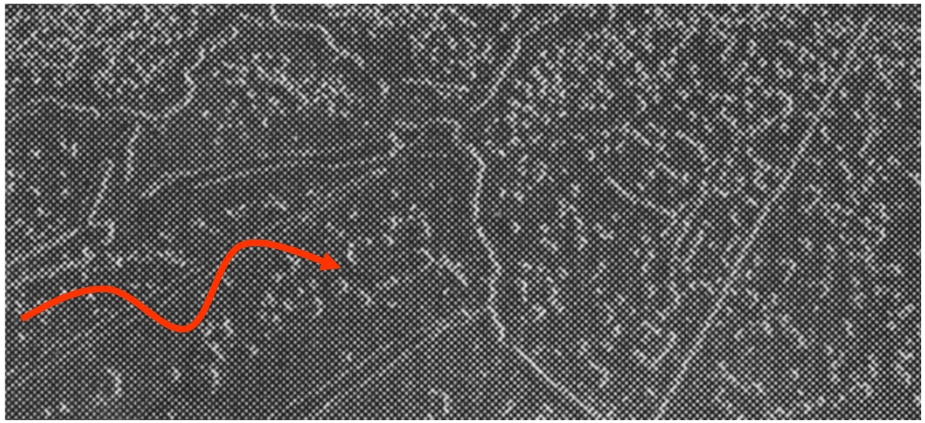
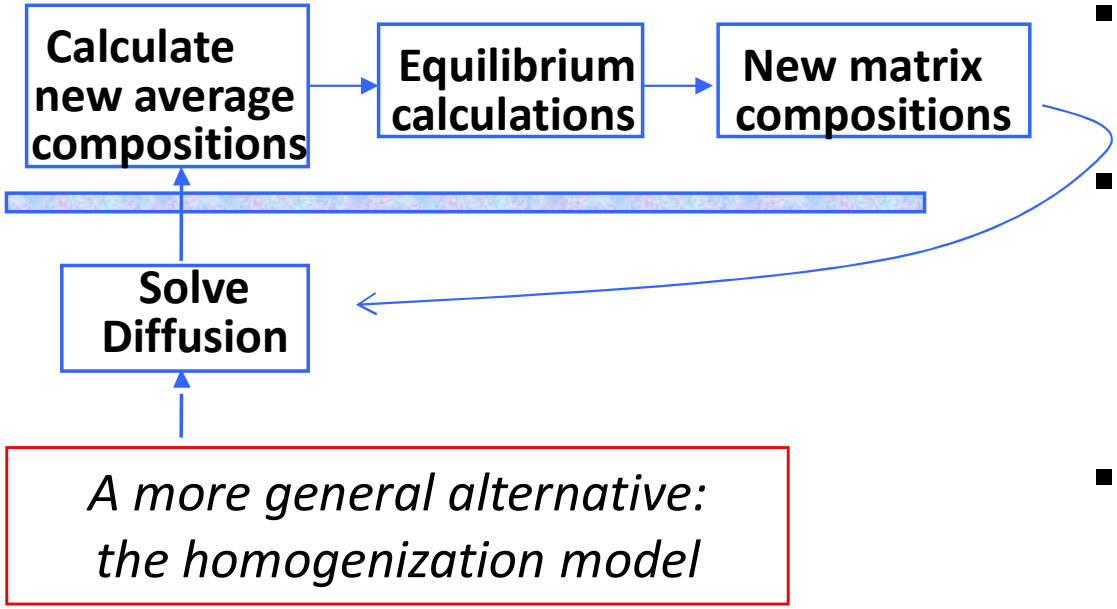
Assumptions:

- Diffusion takes place in the matrix phase only.
- Equilibrium holds locally in each node.





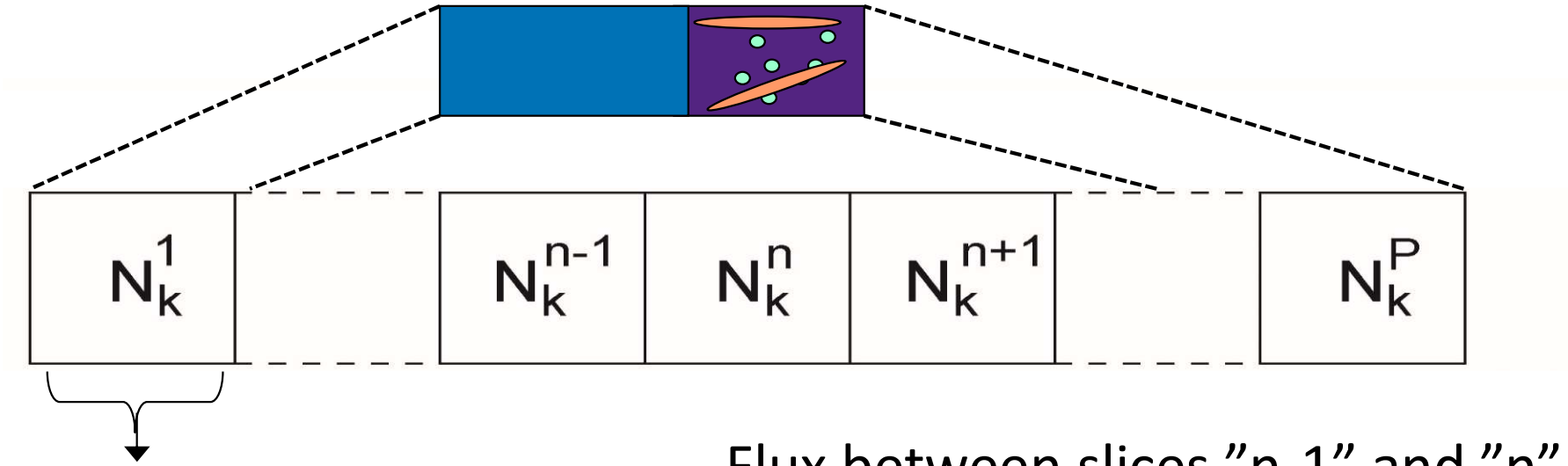
A more general alternative: the homogenization model

- Carburisation of high-temperature alloys
- Interdiffusion in composite materials
  - coating/substrate systems
  - weldments between steels
  - joints of dissimilar steels
- Gradient sintering of cemented carbide work-tool pices

Engström et al, Met Mat Trans A 25A(1994)1127

Homogenization model

This approach allow us to account for diffusion in more than one phase



Equilibrium calculation for each slice

↓

Phase fractions
Phase compositions
Chemical potentials
Mobilities

Flux between slices ”n-1” and ”n”

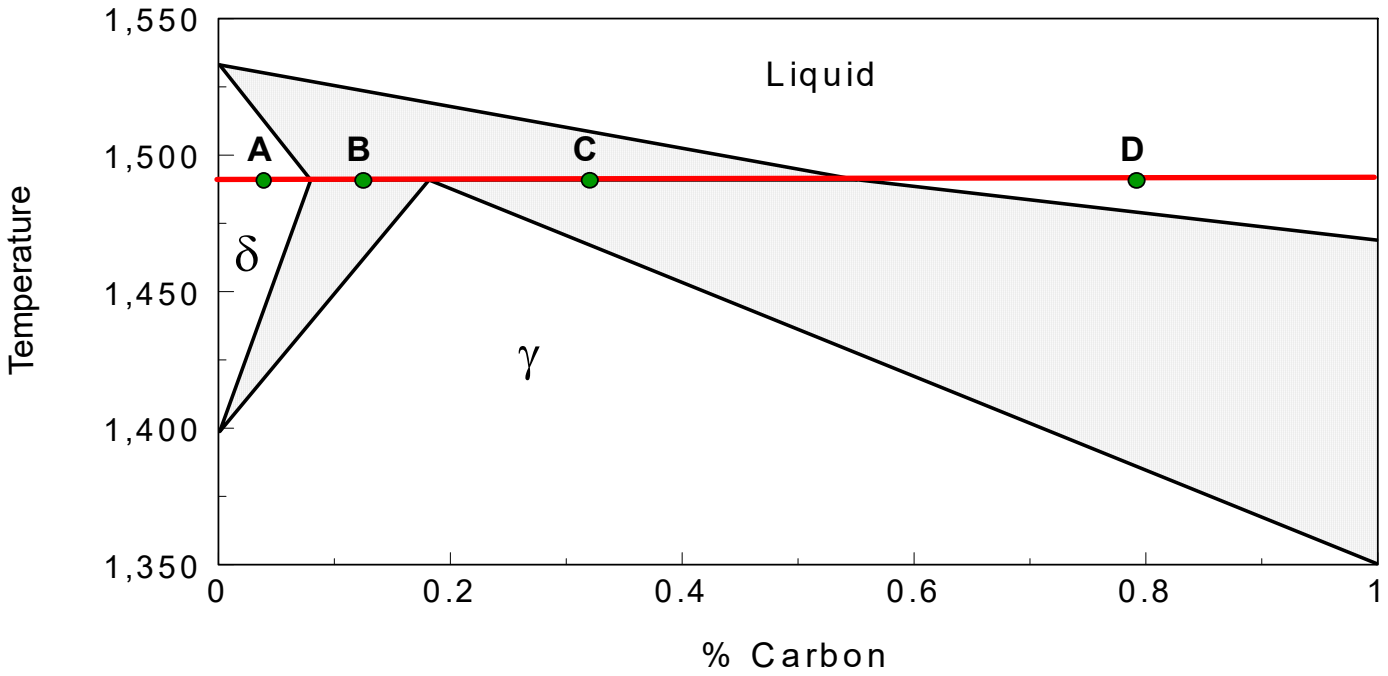
$$J_k = \frac{-1}{V_m}\sqrt{[M_k x_k]_{n-1}^{eff}\,[M_k x_k]_n^{eff}}\,\frac{\Delta\mu_k}{\Delta z}$$

”Effective” $[M_k x_k]$ from combining rules

Larsson, Engström, Acta Mater 54(2006)2431
Larsson, Höglund, Calphad 33(2009)495

Case study: Micro-segregation during solidification

- VESPISM (Virtual Experiments to Solve Problems In Steel Metallurgy).
- Development of phase-field code (MICRESS) linked to Thermo-Calc.
- Solidification experiments were performed for alloys A – D below as one assignment in this project.

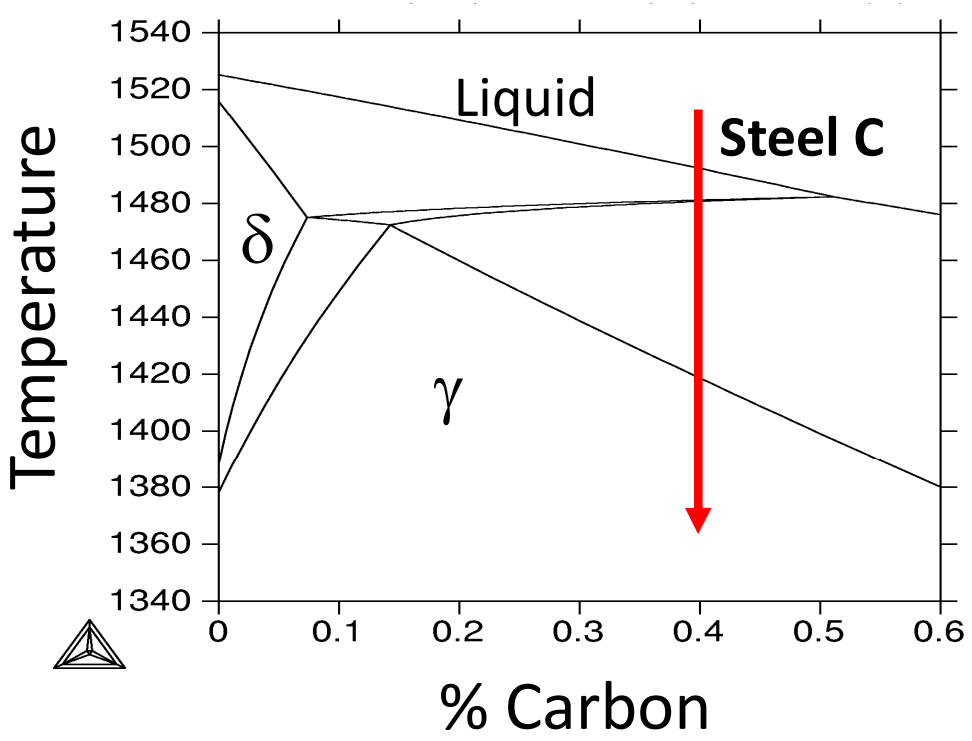


Observed micro-segregation in Steel C

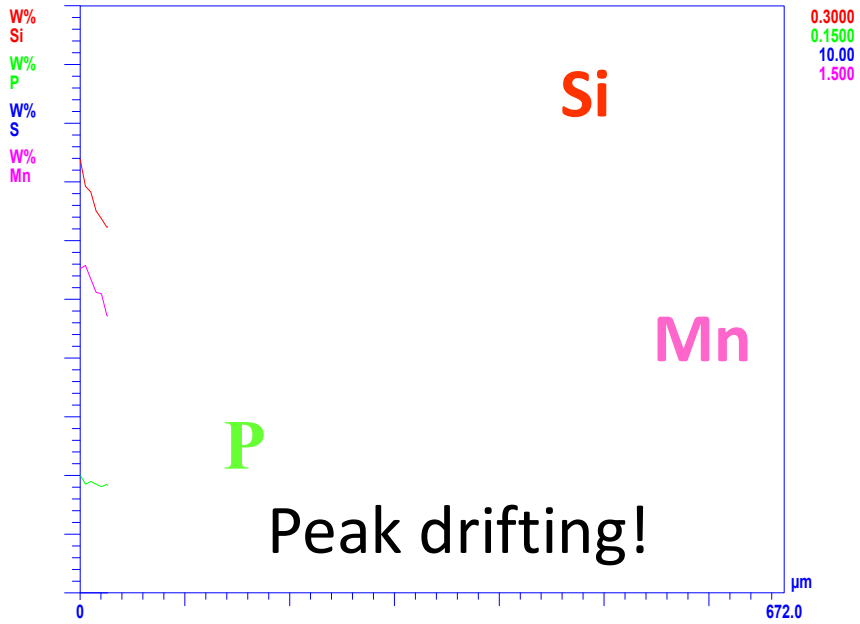
Thermo-Calc Software

Steel C:

Fe - 0.8% Mn – 0.7%Si – 0.03%P – 0.4% C

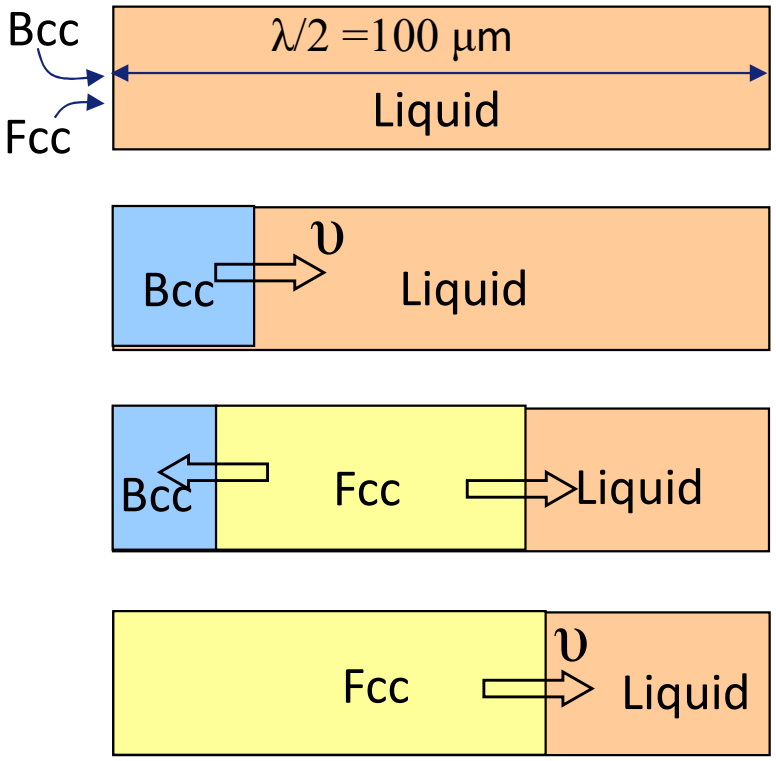


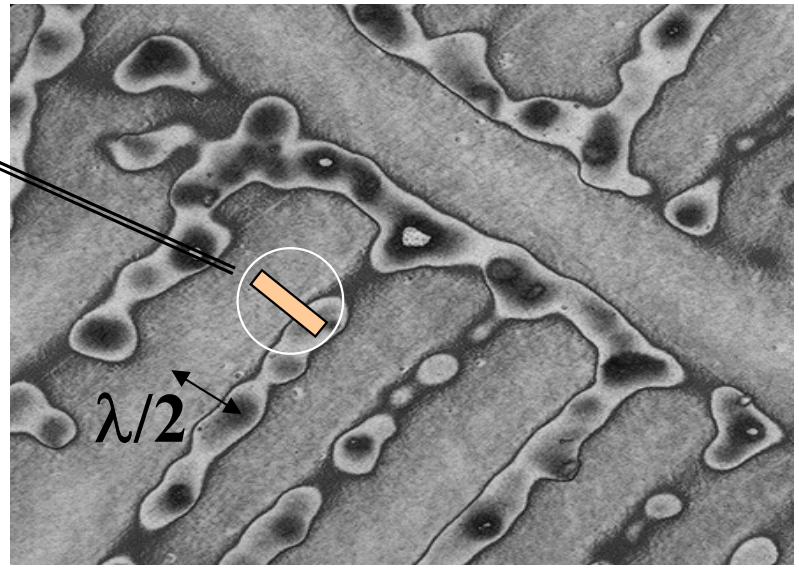
Line-scans across the dendrite arms (performed by Corus-UK)



Question: Why does the P peak drift away from the Mn and Si peaks?

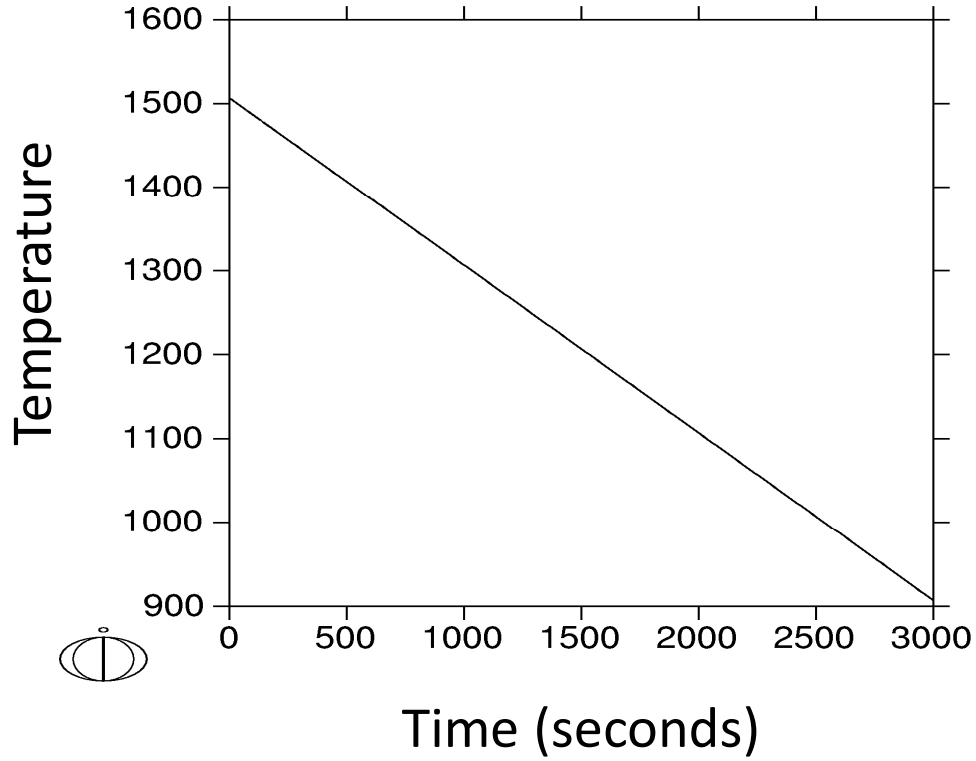
Analysis using DICTRA





- Secondary dendrite arm spacing assumed to be 200 μm.

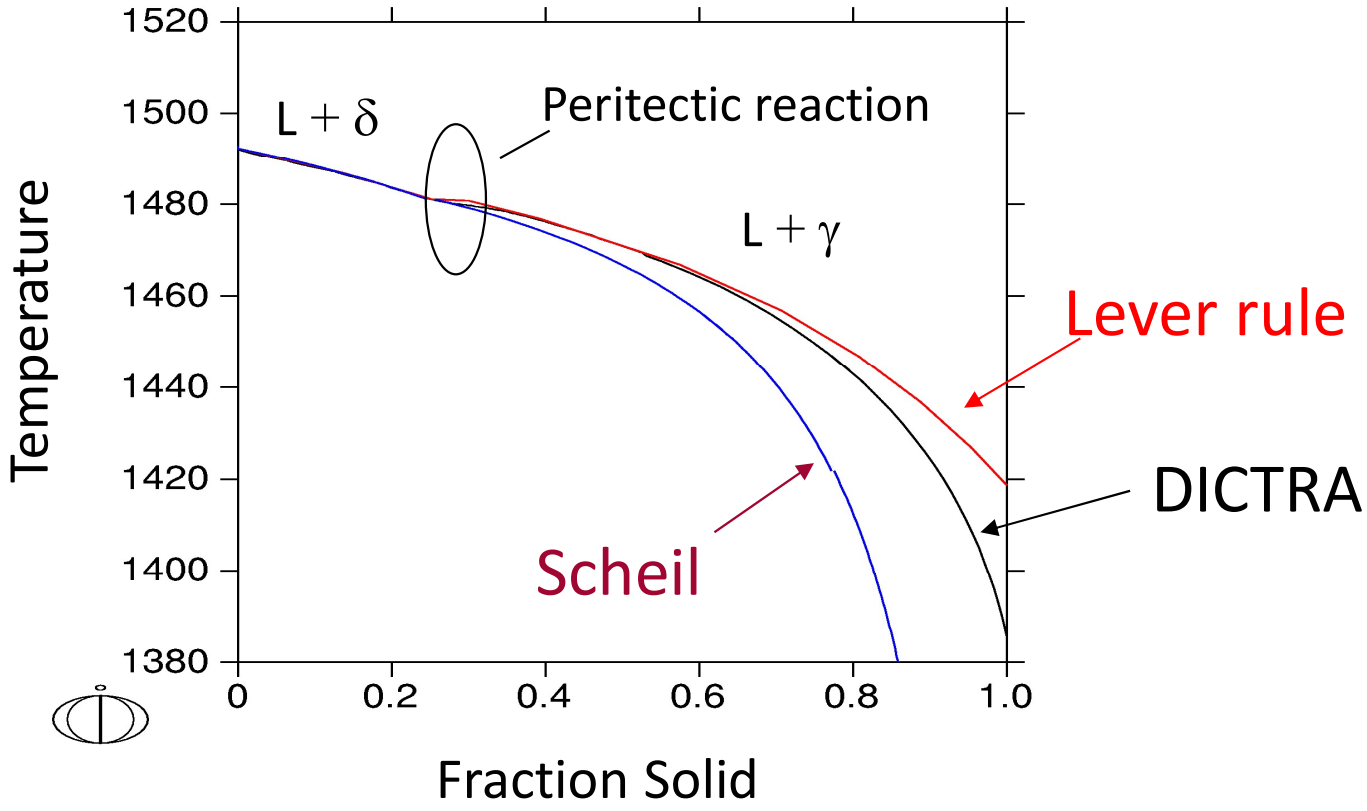
Cooling function



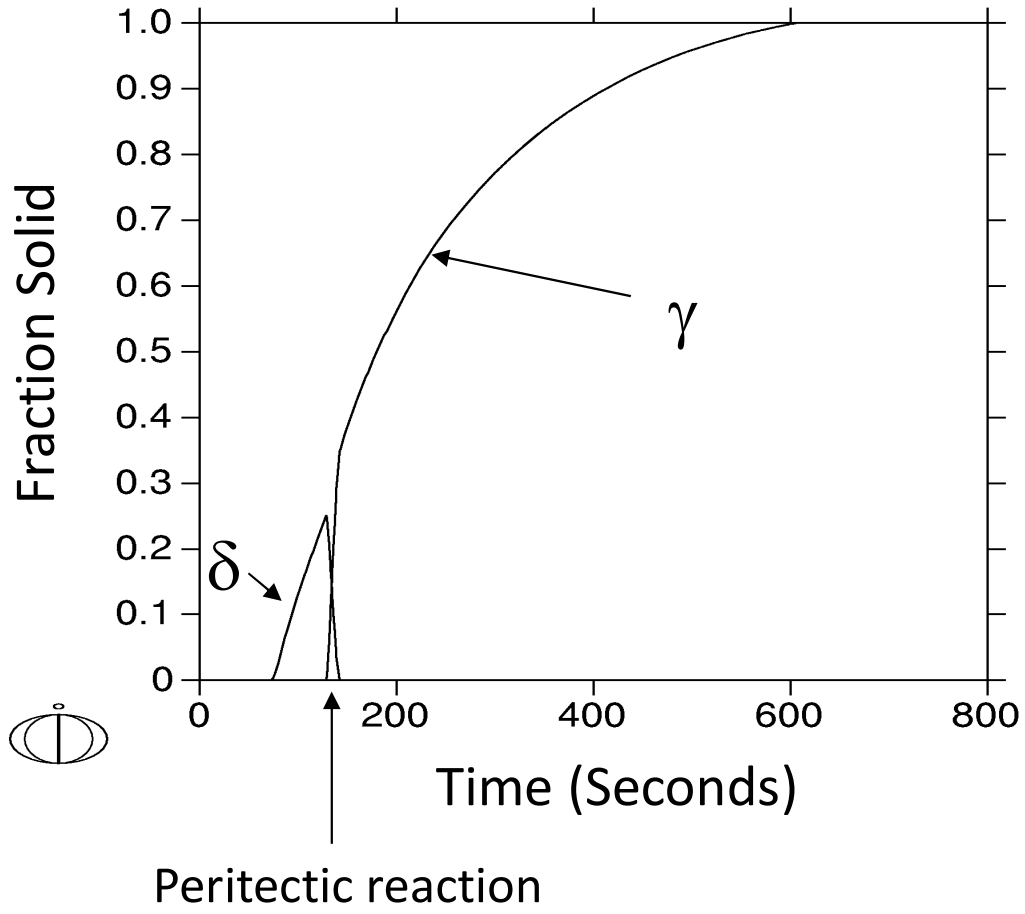
Cooling rate assumed to be 0.2 ºC/s

- More advanced cooling functions may of course also be imposed.
- Also possible to instead define a condition on the rate of latent heat removal from the system.

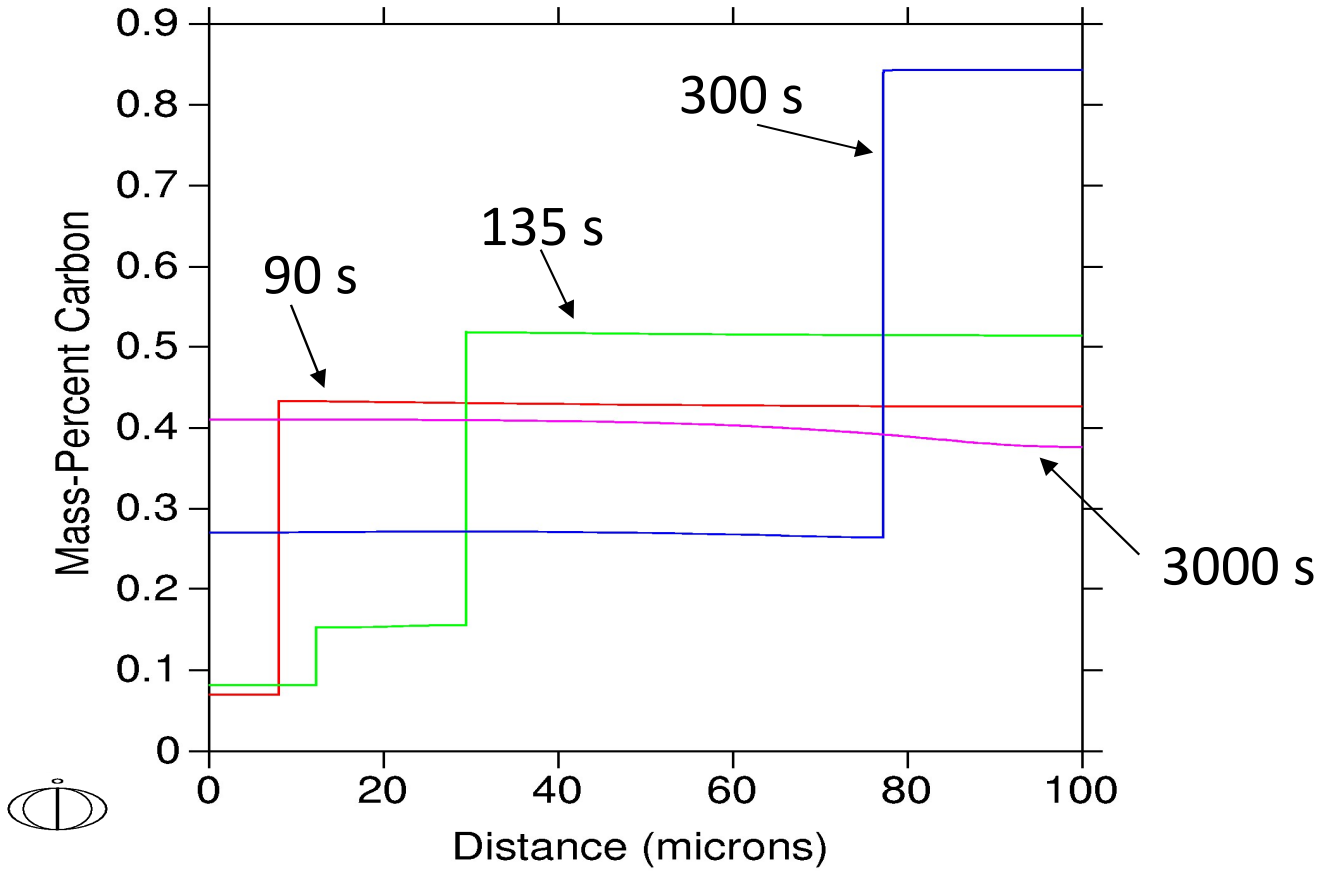
Solidification range



Fraction of solid phases

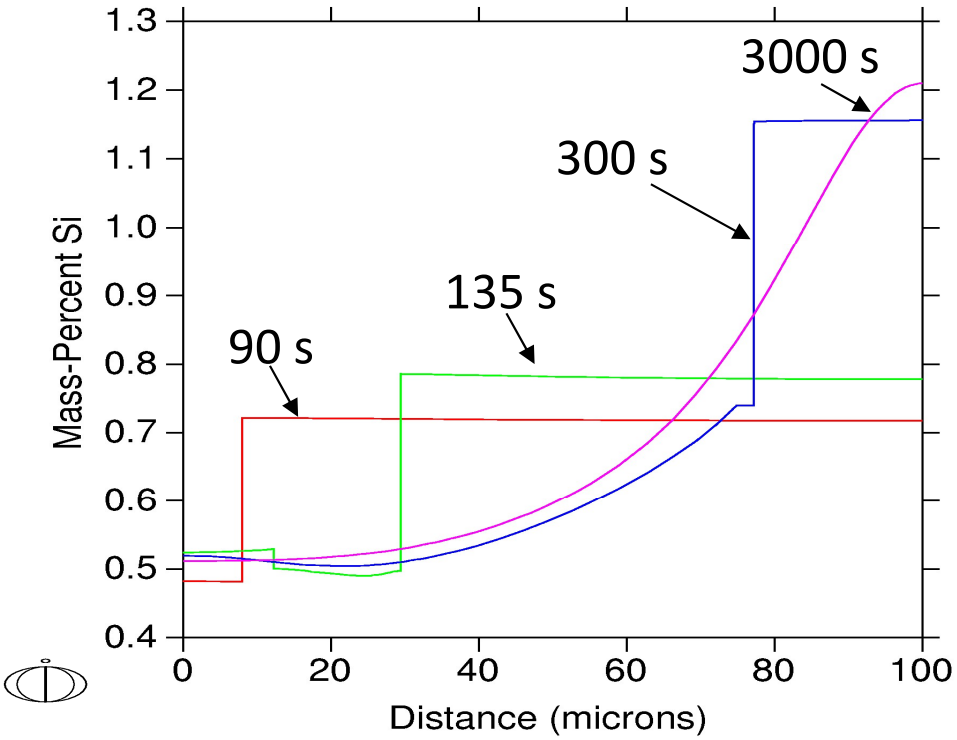


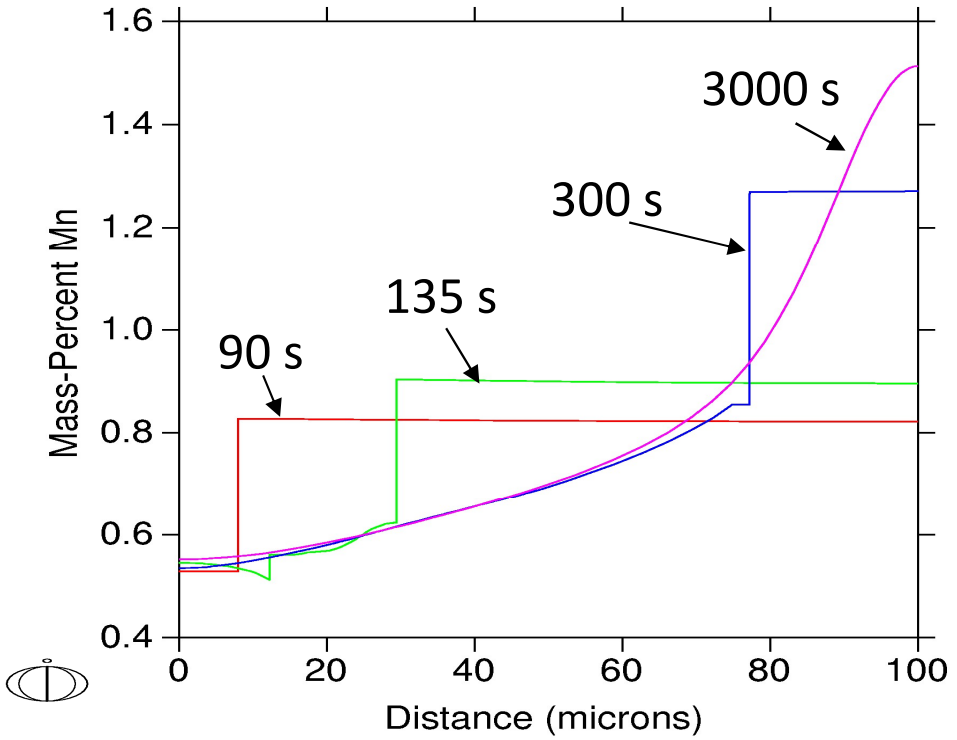
Carbon profiles during solidification



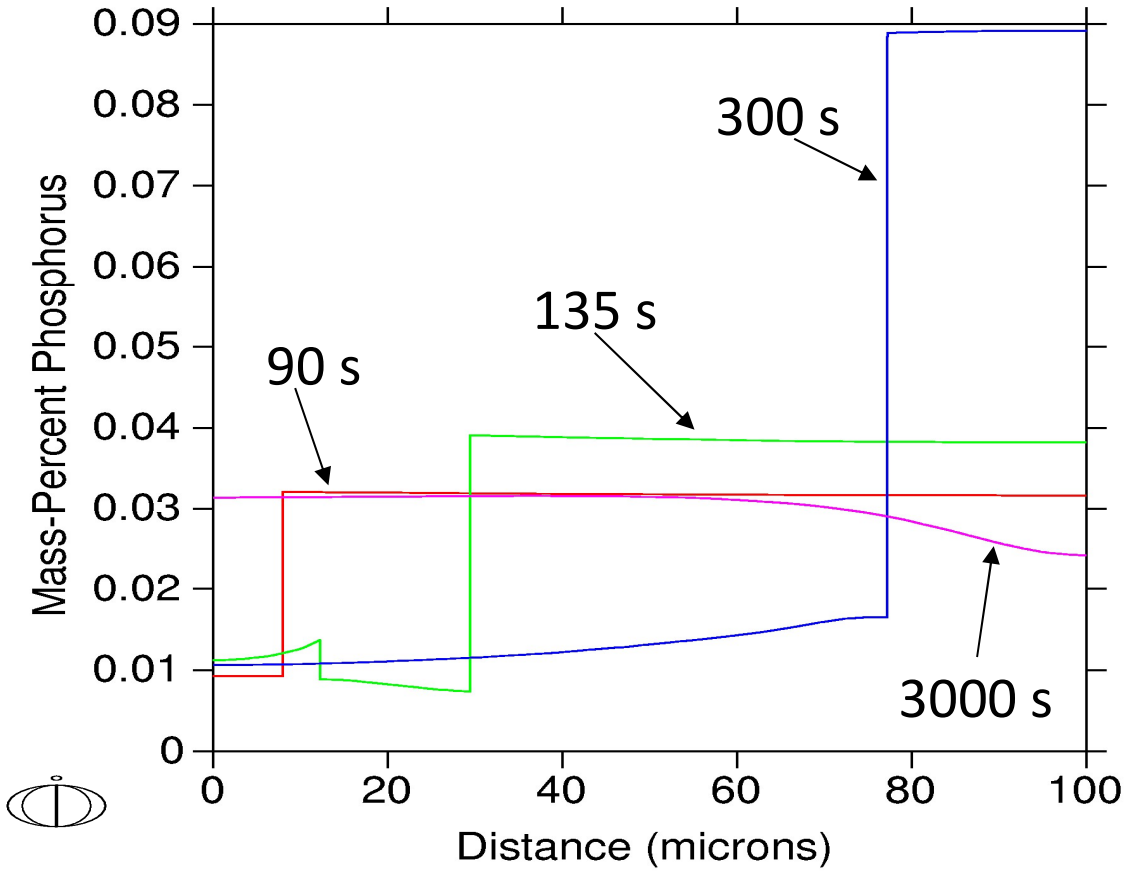
Silicon and Manganese

Thermo-Calc Software



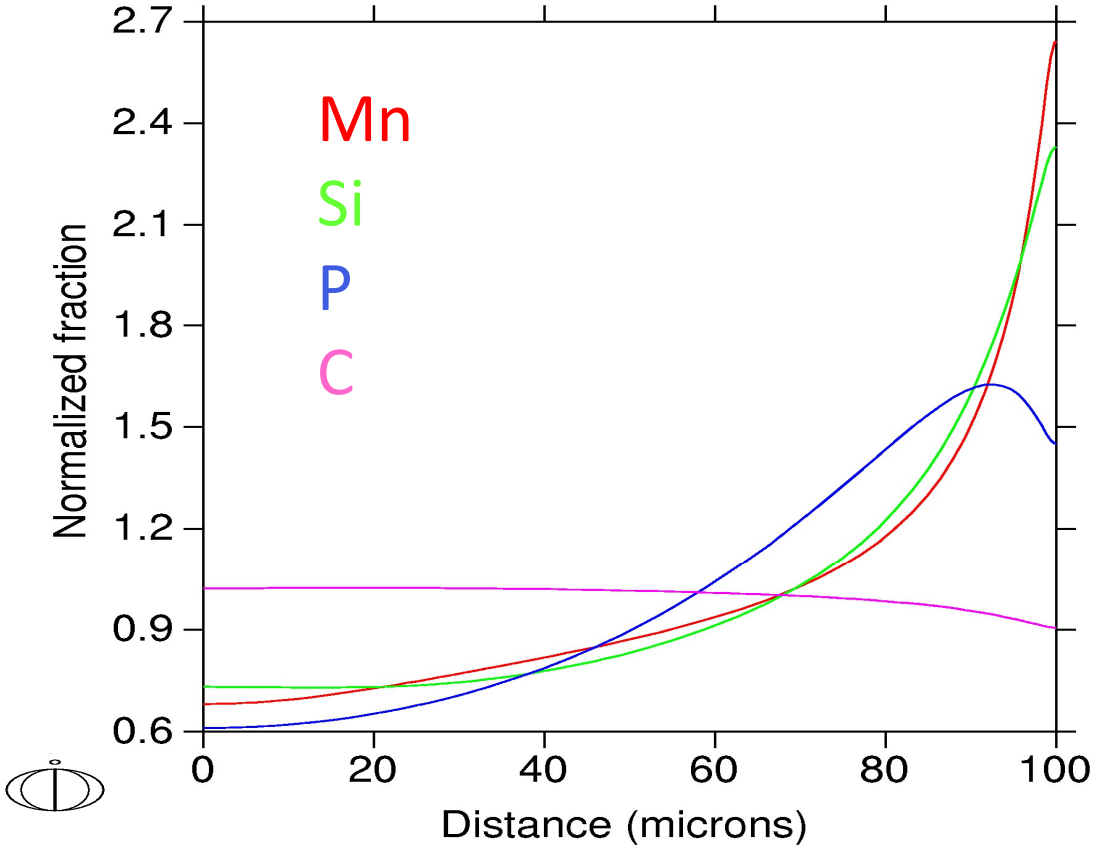


Phosphorus


0.09
0.08
0.07
0.06
0.05
0.04
0.03
0.02
0.01
0
Mass-Percent Phosphorus
0
20
40
60
80
100
Distance (microns)
300 s
135 s
90 s
3000 s

Segregation profiles after 610 s
(when the last melt disappears)

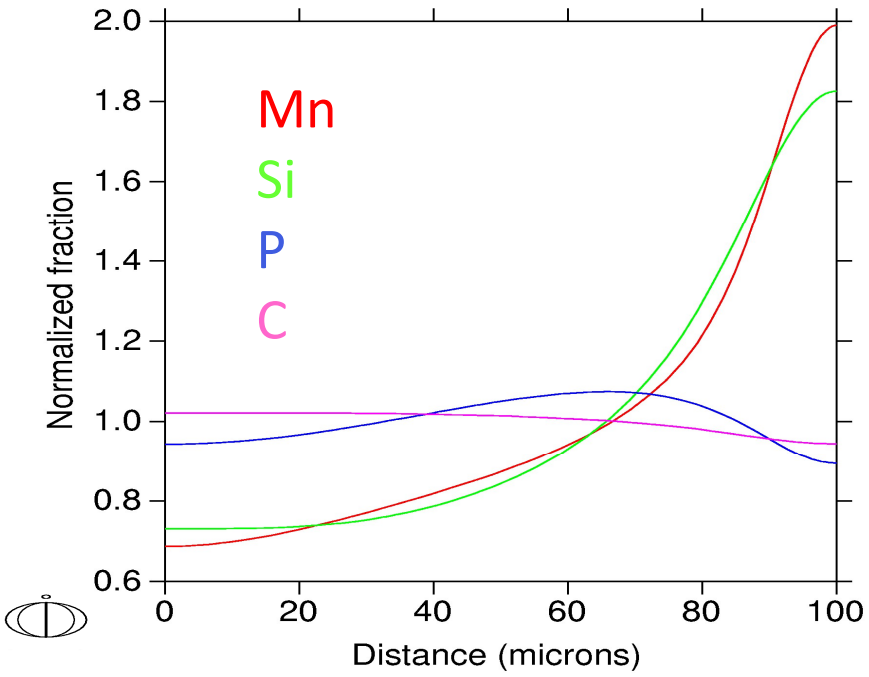
Thermo-Calc Software



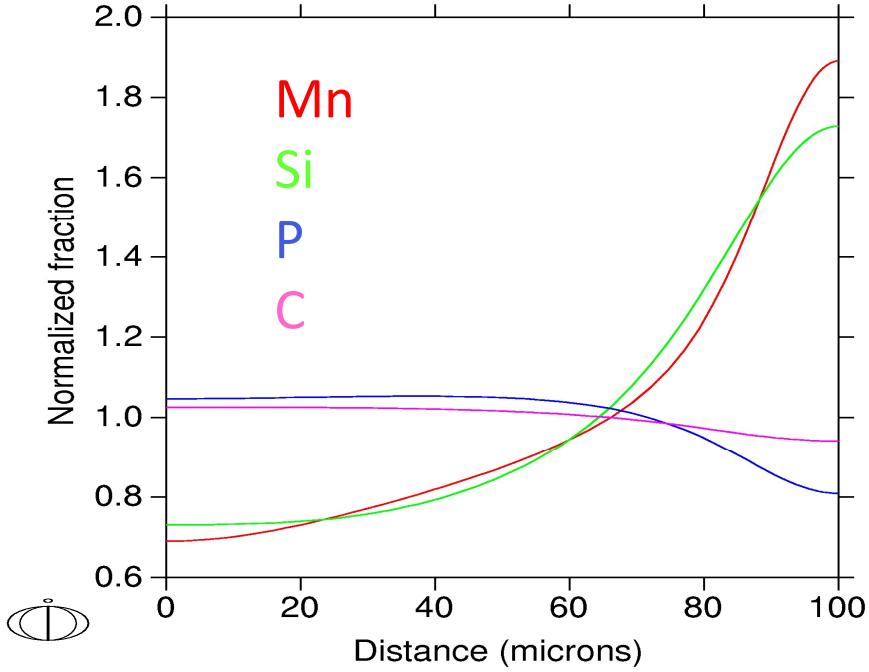
Segregation profiles after 1000 and 3000 s

Thermo-Calc Software

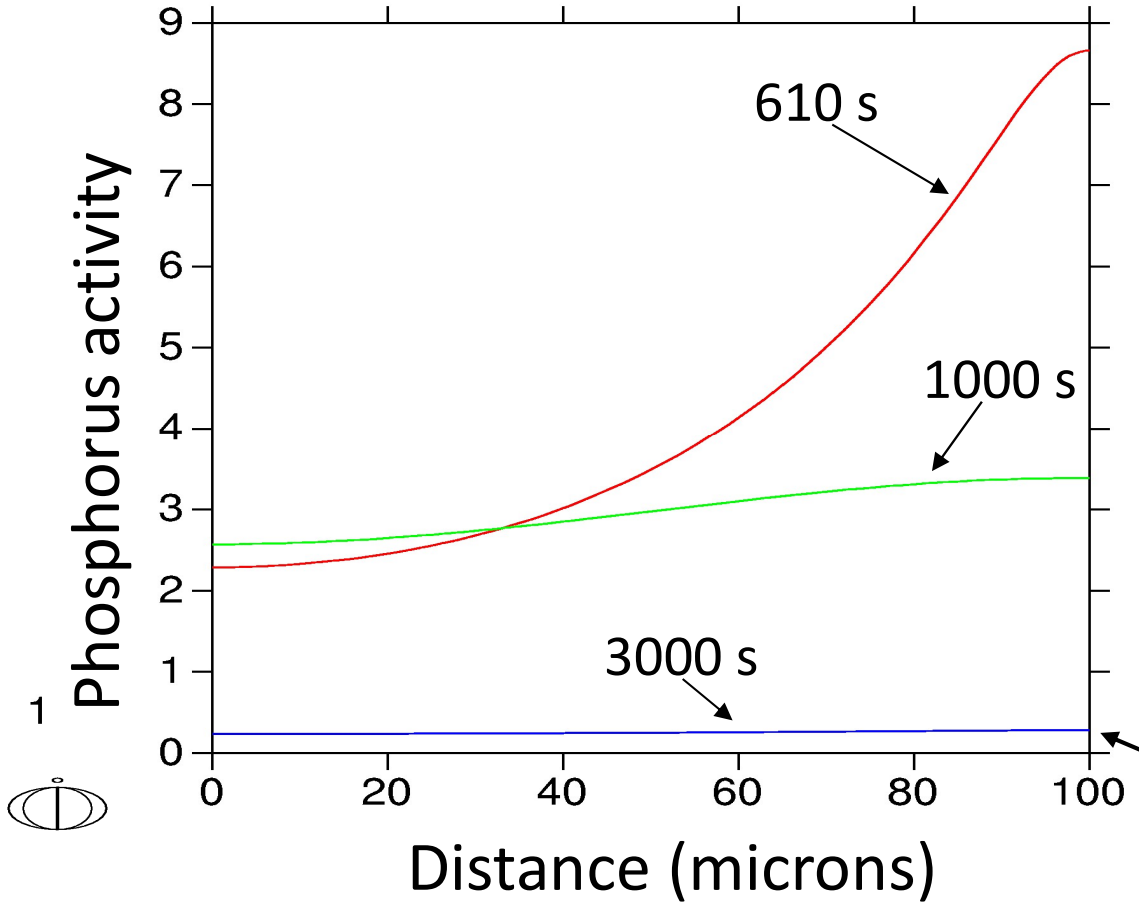
after 1000 s



after 3000 s



The solution



- ✓ Mn and Si increase the phosphorus activity.
- ✓ Phosphorus diffusion much faster compared to Mn and Si diffusion.

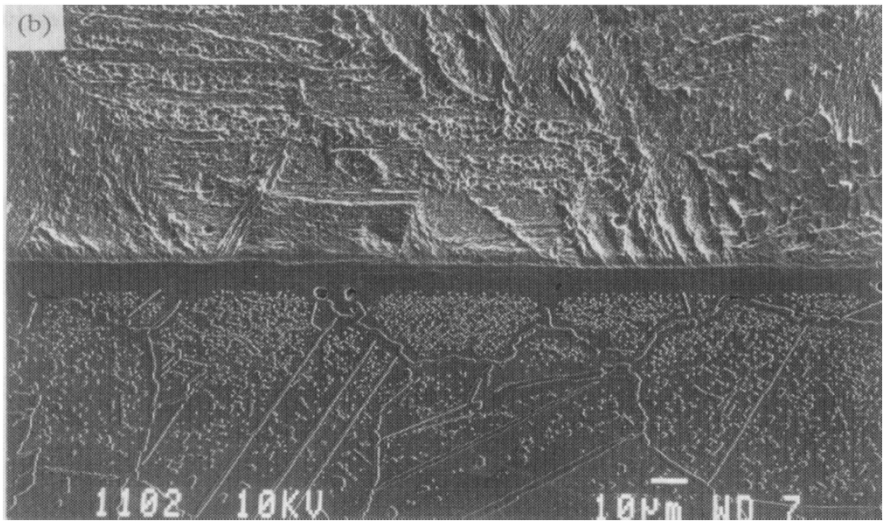
At the late stage further phosphorus redistribution is controlled by slow Mn and Si diffusion.

Compound tubes for waste incinerators

Thermo-Calc Software

After 4 h at 1100 ºC

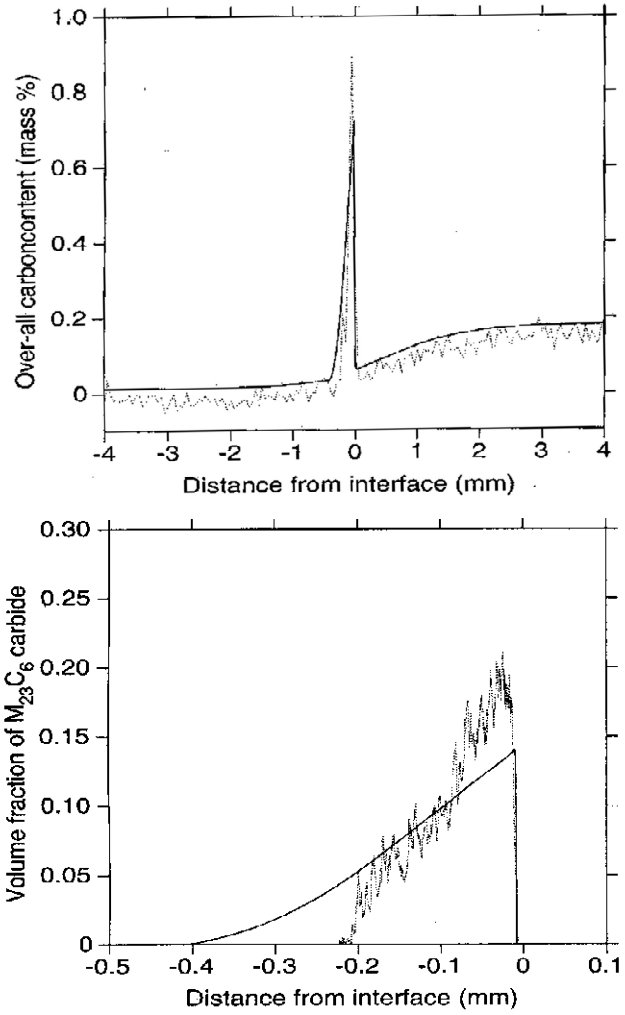
4L7 (0.18% C)



Sanicro28

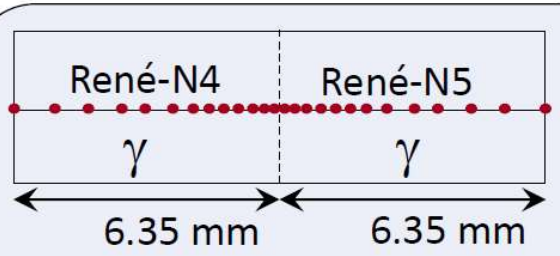
(30.5% Ni, 27% Cr, 3.3% Mo, 1.8% Mn, 0.014% C)

Helander, Ågren, Nilsson, ISIJ Int 37(1997)1139



Interdiffusion in Ni-superalloys

Thermo-Calc Software



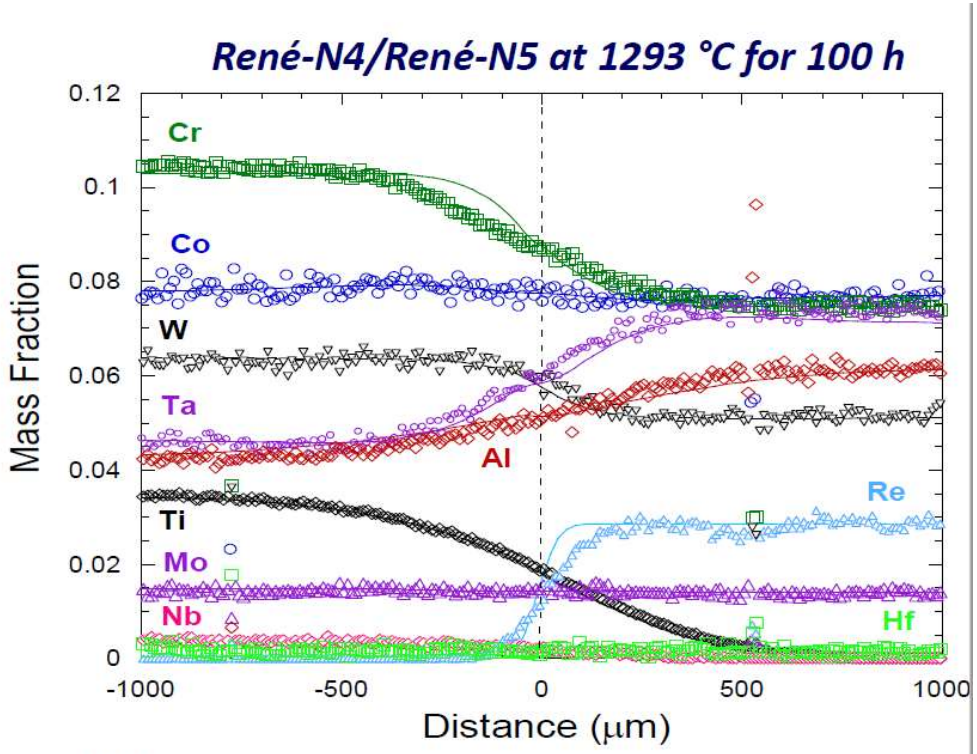
Double geometric grid: 200 points

Databases used

Thermodynamics: ThermoTech

Kinetics: NIST Ni-mob

$\tilde{D}$ is a 10×10 matrix where all coefficients depend on concentration



From: C. E. Campbell, Metallurgy Division, NIST

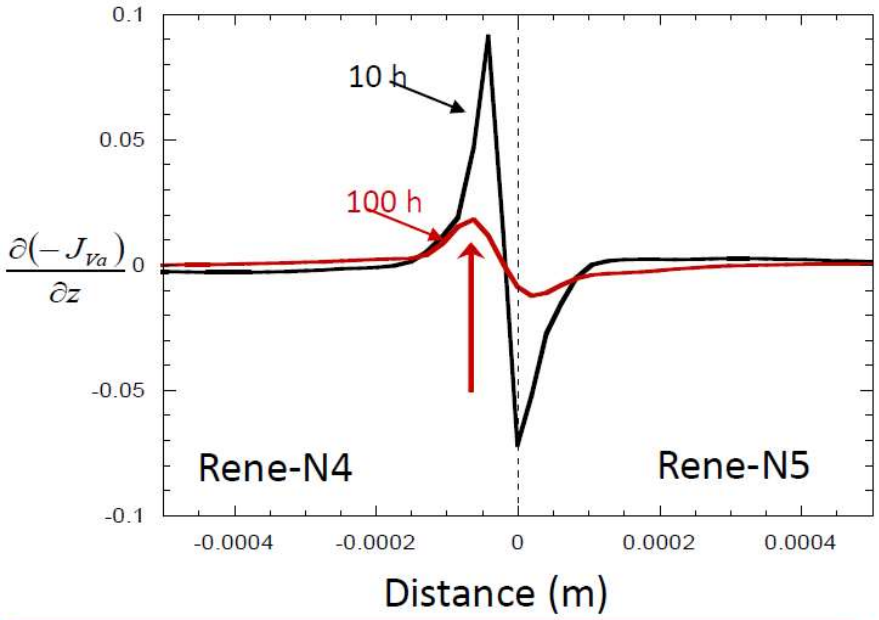
See also: Campbell et al, Mat Sci Eng A 407(2005)135

Experimental work performed by T. Hansen, P. Merewether, B. Mueller, Howmet Corporation, Whitehall, MI.

Interdiffusion in Ni-superalloys

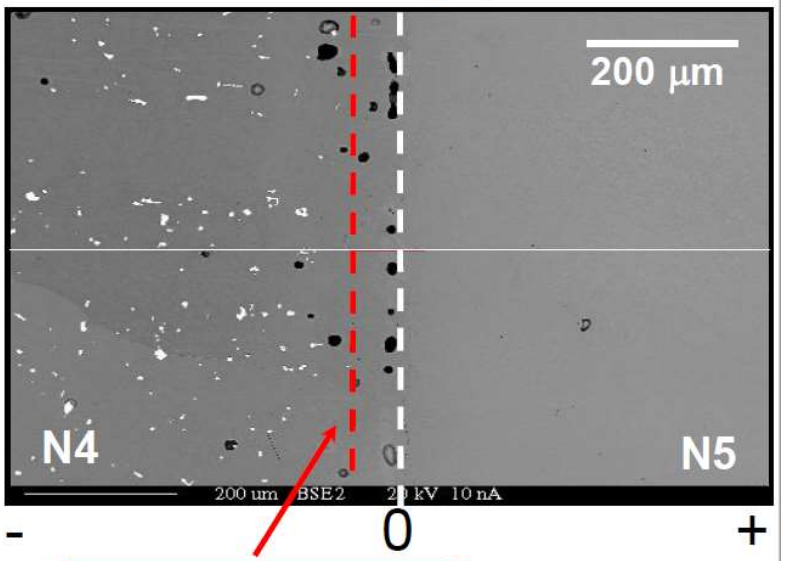
Thermo-Calc Software

Kirkendall porosity prediction



Maximum gives location of pore formation.

Back scatter image; 100 h



Predicted position for maximum pore formation

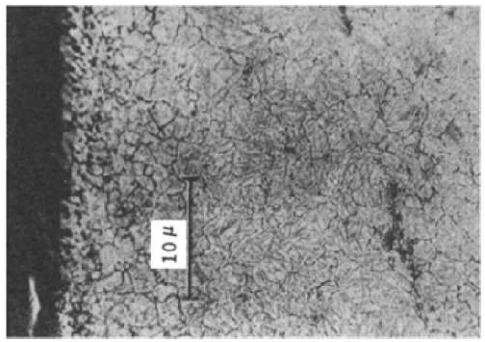
From: C. E. Campbell, Metallurgy Division, NIST

See also: Campbell et al, Mat Sci Eng A 407(2005)135

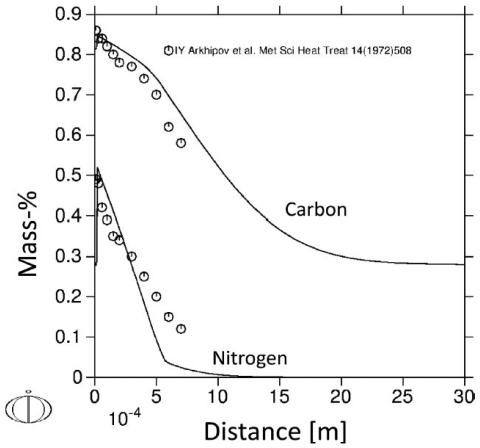
Coupled carbonitriding and internal oxidation

Thermo-Calc Software

Fe-0.28C-1.15Cr-0.95Mn-0.27Si
850°C, 24 h

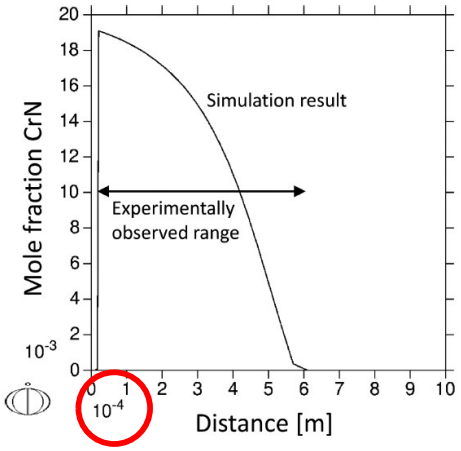


Concentrations

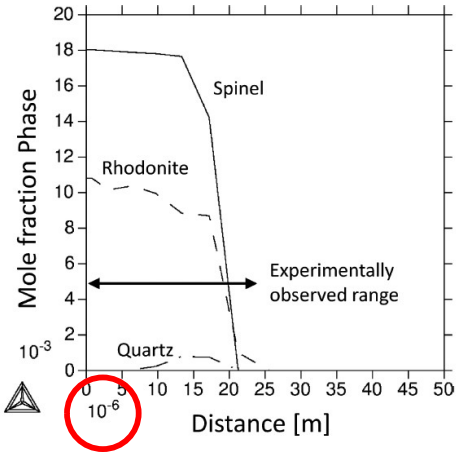


Micrograph and experimental data
Arkhipov et al Met Sci Heat Treat 14(1972)508

Fraction nitride



Fraction oxides



Larsson, Ågren, HTM J Heat Treatm Mat 72(2017)19

Compatibility of Databases

Thermo-Calc Software

Thermodynamic Database	Kinetic Database
SSOL2, SSOL4, SSOL5, SSOL6, SSOL7, SSOL8	MOB2
TCFE5 and earlier versions	MOB2
TCHEA2, TCHEA3+4+5, TCHEA6+7	MOBHEA1, MOBHEA2, MOBHEA3
TCFE6, 7, 8, TCFE9, TCFE10, TCFE11, TCFE12, TCFE13	MOBFE1, 2, 3, 4, 5, 6, 7, MOBFE8
TTNI8 and earlier versions	MOBNI1
TCNI4, TCNI5, TCNI6*	MOBNI2*
TCNI7, TCNI8	MOBNI3, MOBNI4
TCNI9+TCNI10+TCNI11, TCNI12	MOBNI5, MOBNI6
TTAL8 and earlier versions	MOBAL1 and BISHOP
TCTI4, TCTI5	MOBTI4
TCAL1+2+3, TCAL4,TCAL5, TCAL6+7, TCAL8, TCAL9	MOBAL3,4,5, MOBAL6, MOBAL7, MOBAL8
TCMG1+2+3+TCMG4+TCMG5, TCMG6	MOBMG1, MOBMG2
TCCU1, TCCU2, TCCU3, TCCU4, TCCU5 + TCCU6	MOBCU1, 2, 3, 4, MOBCU5

* Pairing of TCNI6 and MOBNI2 is not possible for the LIQUID phase.

Some DICTRA specific concepts.

Terminology needed mostly for Console Mode

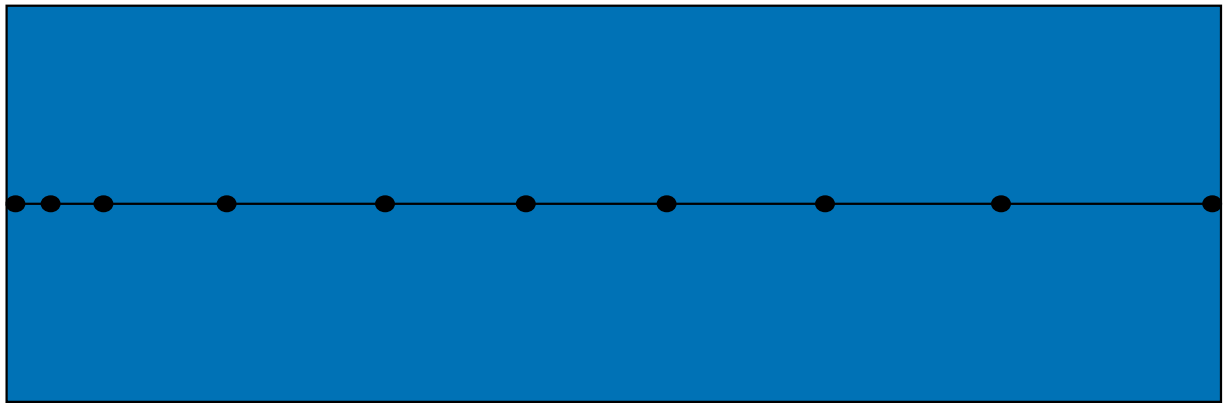
Region

A ”box” filled with the phase(s) where diffusion takes place. Can be given any name.

The region has two boundaries, left and right.

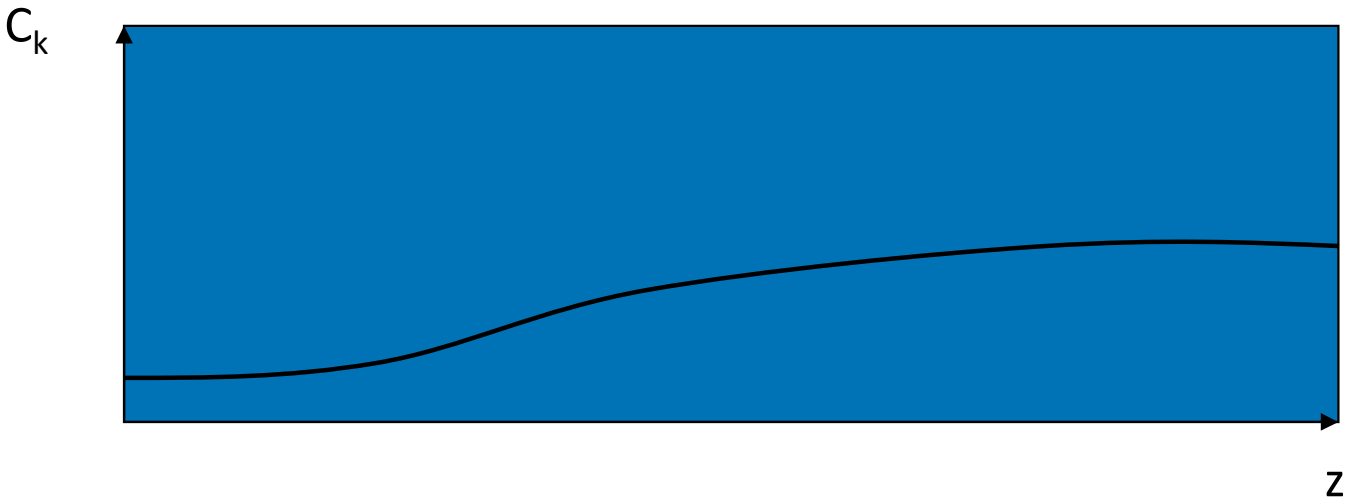
Grid

Thermo-Calc Software



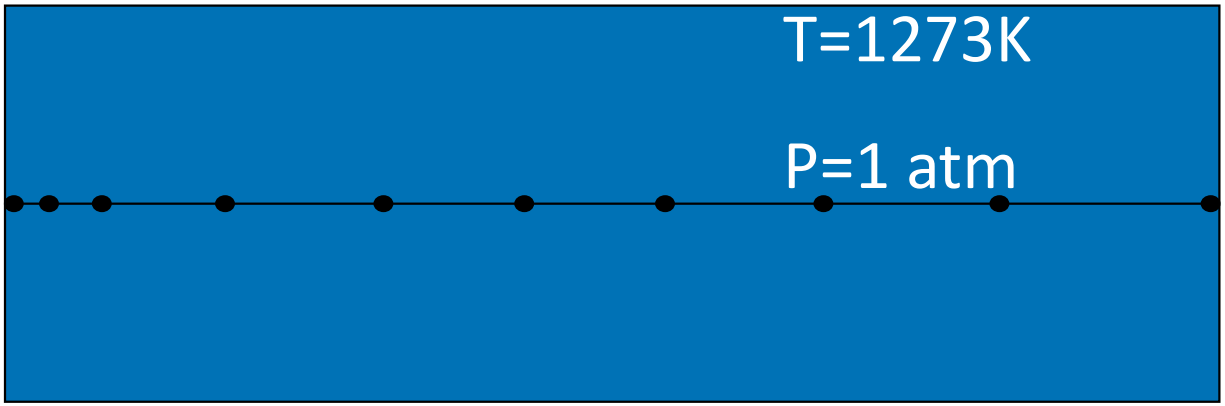
Distribution of node points for numerical calculations (inside the region).

Concentration Profile



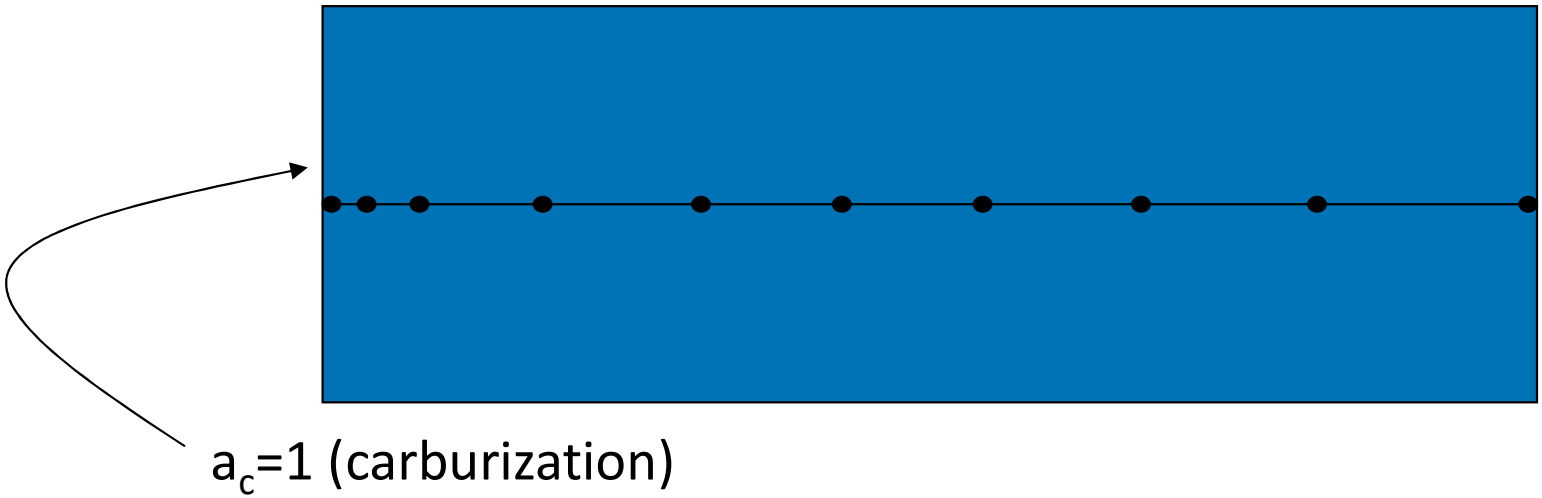
Concentration, C_k of an element as a function of distance z.

Global Conditions



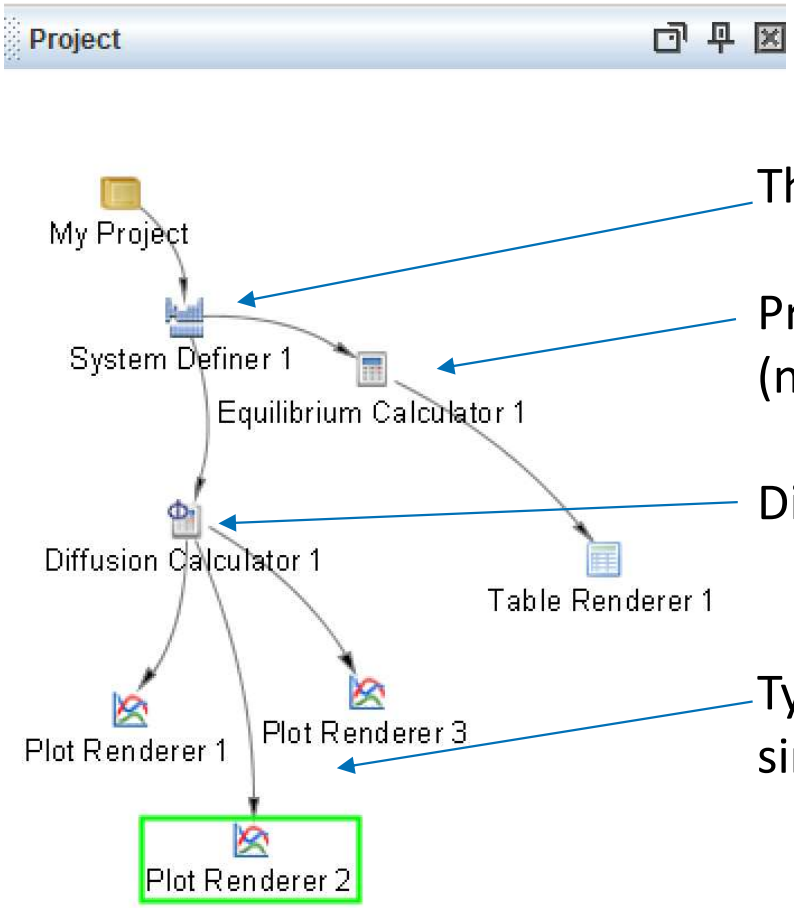
Conditions valid for entire system, T and P.

Boundary Conditions



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

DICTRA Project in Graphical mode



Thermodynamic + Mobility data!

Preliminary Thermo-Calc calculation. (not included in template)

Diffusion simulation setup & run.

Typically many different plots from a single simulation (only 1 in template).

Typical calculation setup - Graphical

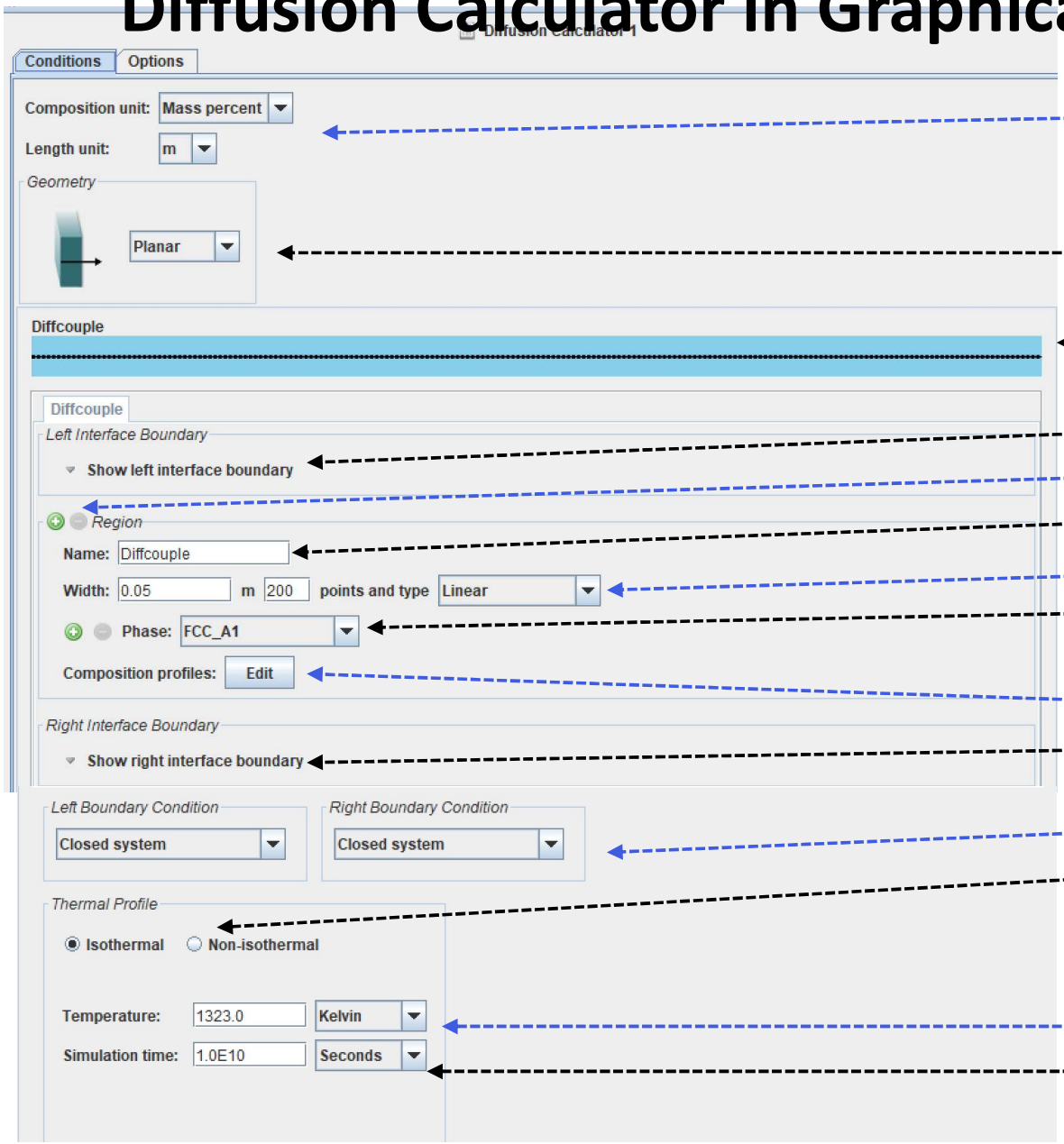
Thermo-Calc Software

1. Select thermodynamic and kinetic data
2. Choose units for composition and distance
3. Enter geometry
4. Enter region(s)
5. Enter grid(s) in region(s)
6. Enter phase(s) in region(s)
7. Enter composition(s) for the phases

(8. Set boundary conditions)

9. Set condition for temperature
10. Set simulation time
11. Perform simulation

Diffusion Calculator in Graphical mode



Set composition unit & length unit

Set geometry

Visual of the region with its grid.

Click to set phase to form on the left.

Click plus to add more regions.

Name the predefined 1st region.

Set region size, grid points and type.

Set matrix phase in region. Click plus to add more phases.

Set the composition for matrix phase.

Click to set phase to form on the right.

Set boundary conditions.

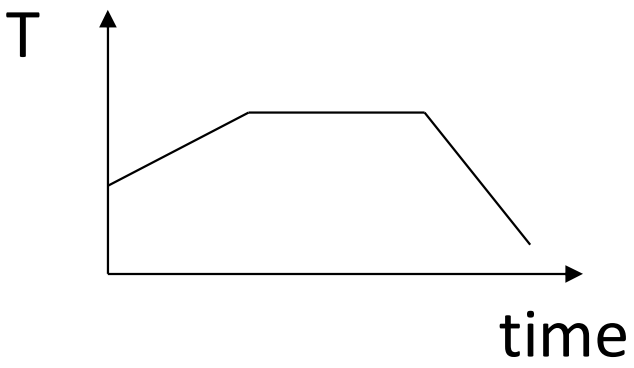
Select isothermal or not. If not, a box for editing T-profile will open.

Set iso-thermal temperature.

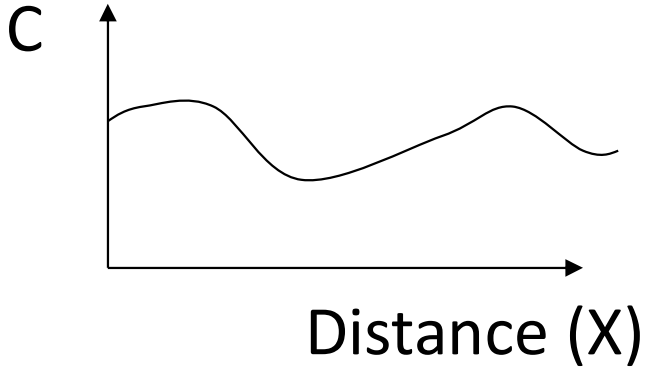
Set simulation time.

Input of T and c – Console mode

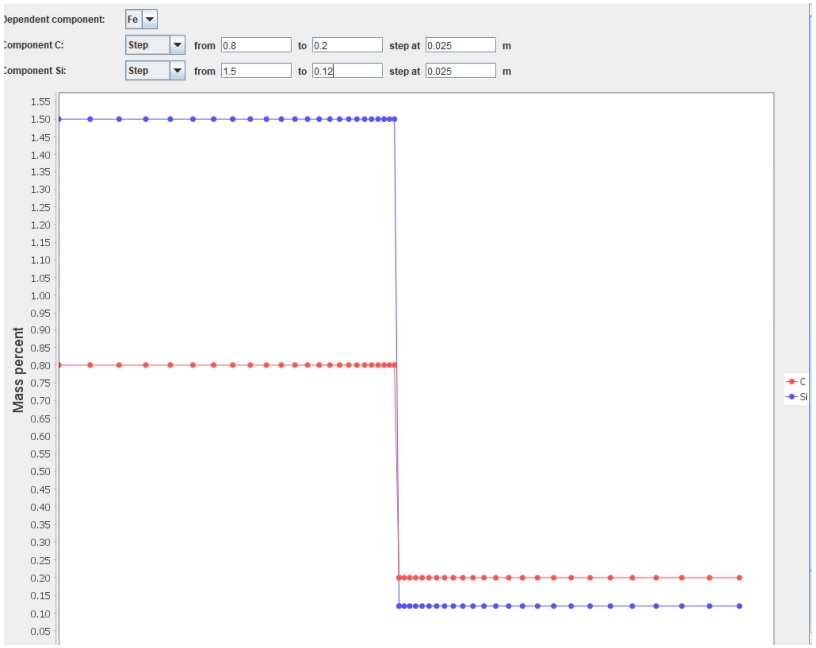
- Temperature (T) can be entered as a function of time (and distance)
- Many different functions can be used (+, -, *, **, SQRT(X), EXP(X),LOG(X),SIN(X))



- Initial concentration can be entered as a function of distance or read from a file
- Special functions e.g. error-functions (erf(x)) and heaviside step functions (hs(x)) can be used.

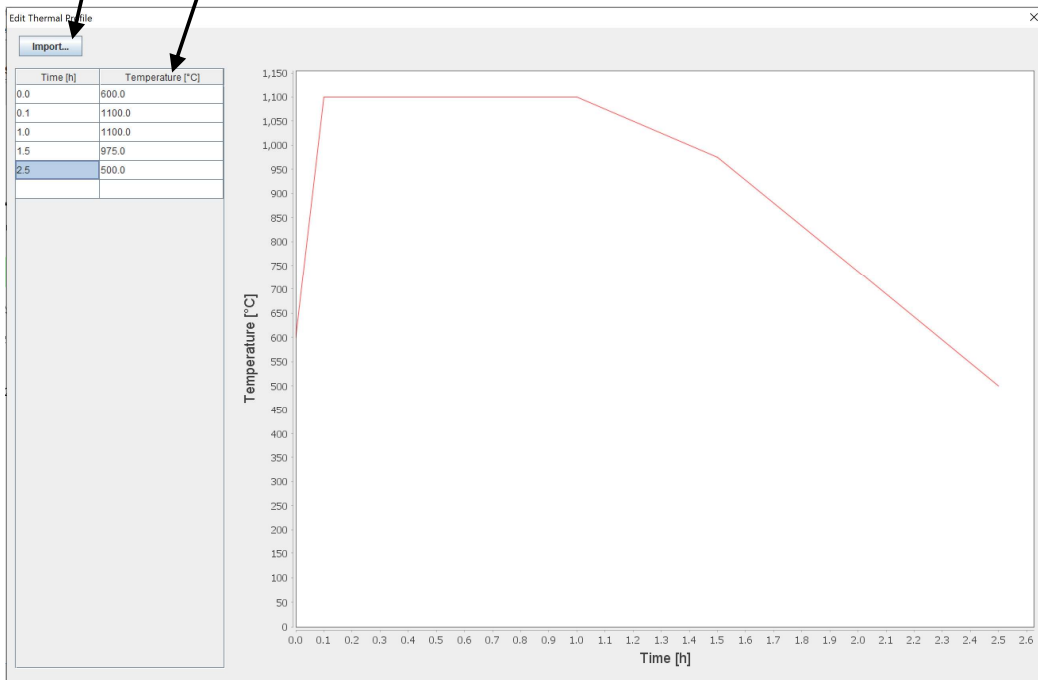


Input of c and T – Graphical mode



Input of composition profile:
- Linear
- Step (shown above)
- Function

Input of Temperature profile:
- isothermal
- import from file (e.g. Excel)
- edit by hand



One phase Example

- Uphill diffusion

Uphill diffusion in a Fe-Si-C alloy

Thermo-Calc Software

- In a classic experiment (published 1949), L.S. Darken welded together two steels having similar C-contents, but with different Si-contents.

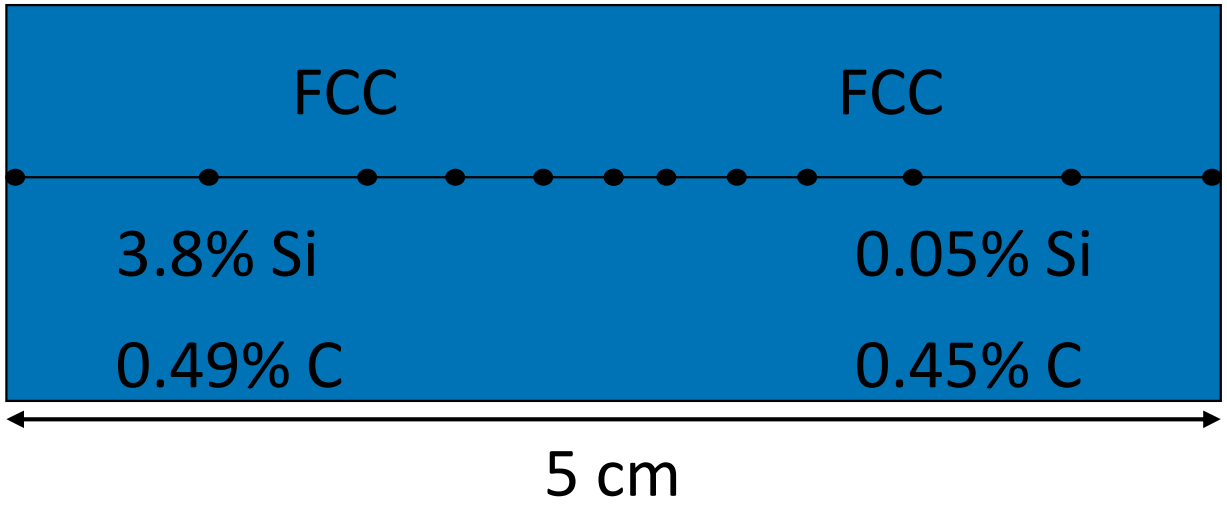
Steel 1	Steel 2
3.8 %Si	0.05 %Si
0.49 %C	0.45 %C

- After annealing Darken was able to conclude that C had diffused up its own concentration gradient, so-called "uphill diffusion". Darken thereby proved that it is the difference in C-activity rather than the difference in C-concentration that is the driving force for diffusion.

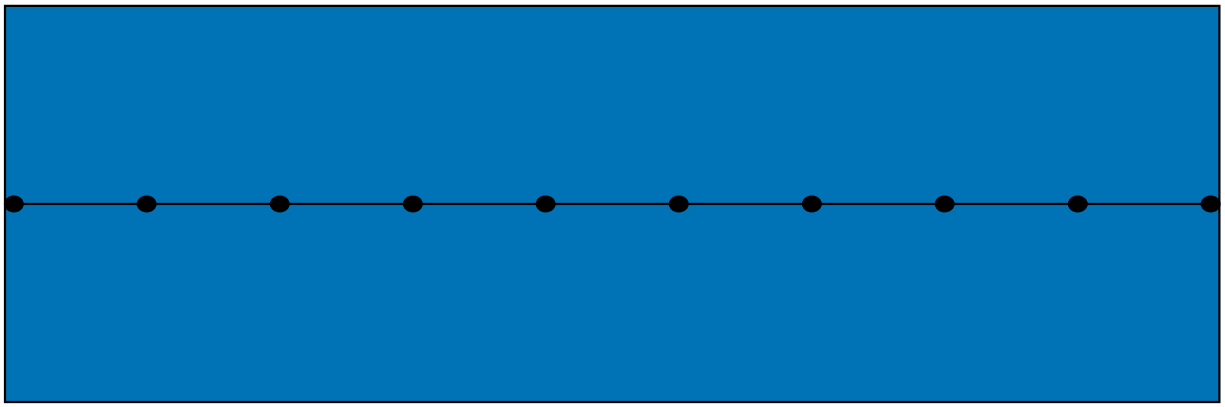
Darken, Trans AIME 180(1949)430

DICTRA Setup

- One single region entered.
- Only FCC entered into this region, i.e. single-phase.
- Composition profiles entered with a step in center.
- Closer spacing between grid points towards the center.
- Global conditions: Constant temperature, T=1050 C.
- Boundary conditions: Zero-flux (= closed system).

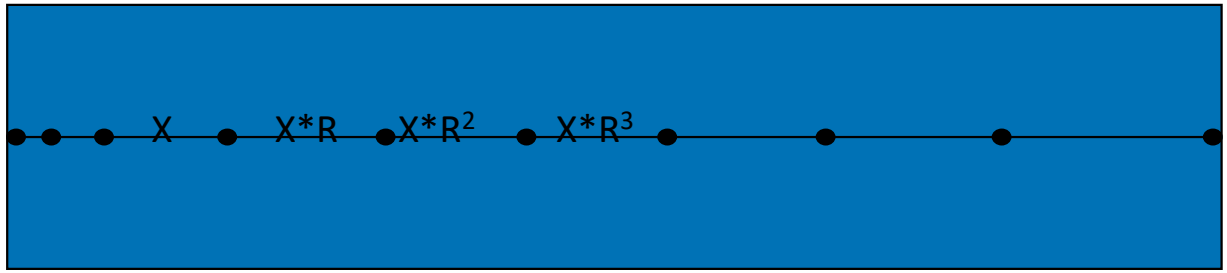


Linear grid

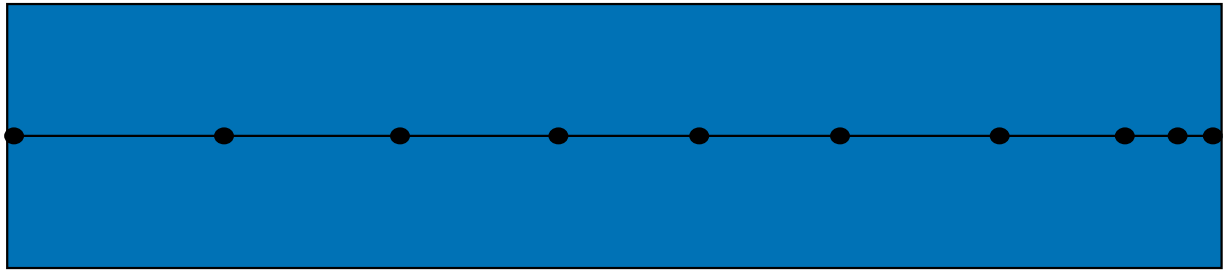


Equidistant distribution of node points.

Geometric Grid



R>1

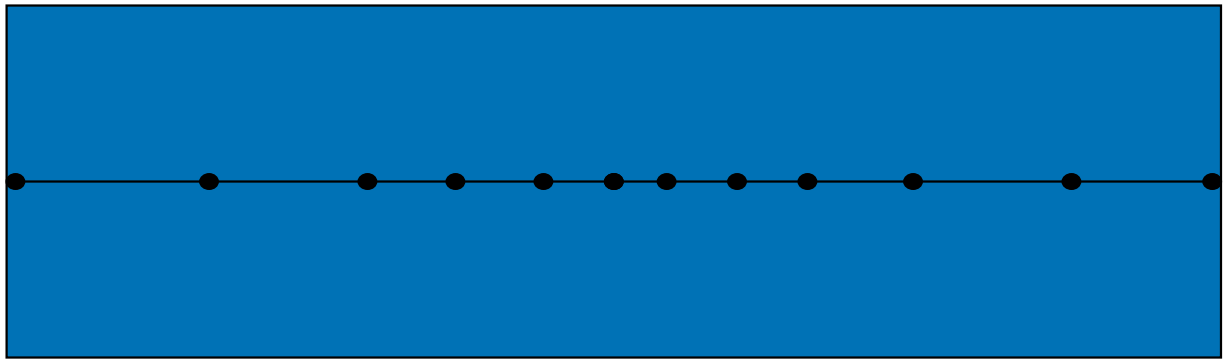


R<1

Node points represents geometric series

Double Geometric Grid

Thermo-Calc Software



R<1 R>1

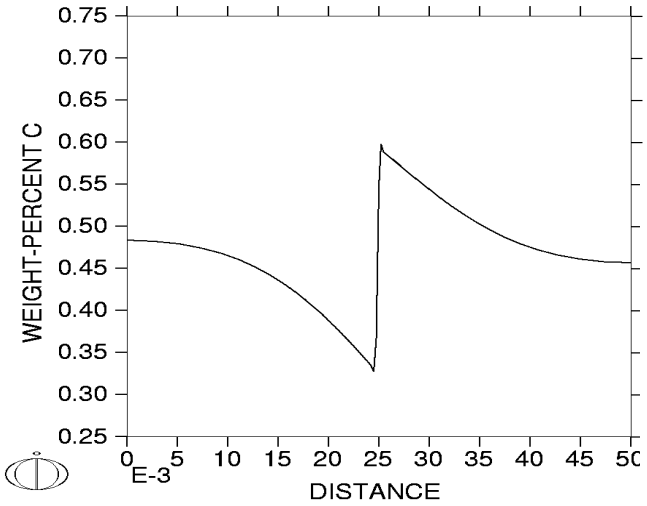
Uphill diffusion

$$J_k = -\sum_{j=1}^{n-1} D_{kj}^{n} \frac{\partial c_j}{\partial z} \quad \Rightarrow \quad J_C = -D_{CC}^{Fe} \frac{\partial c_C}{\partial z} - D_{CSi}^{Fe} \frac{\partial c_{Si}}{\partial z}$$

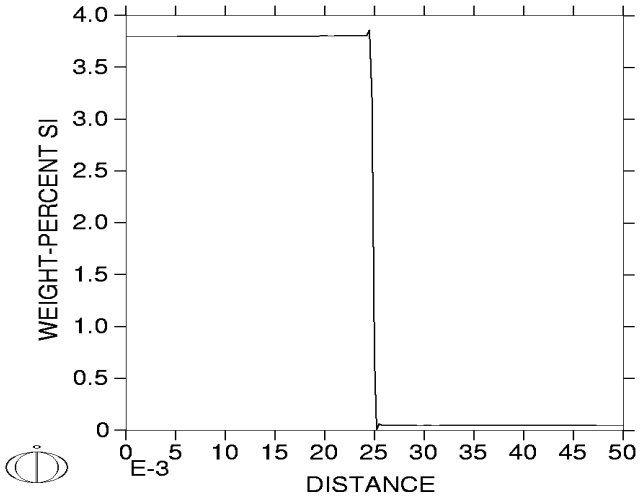
"Off-diagonal" term

Can cause uphill diffusion

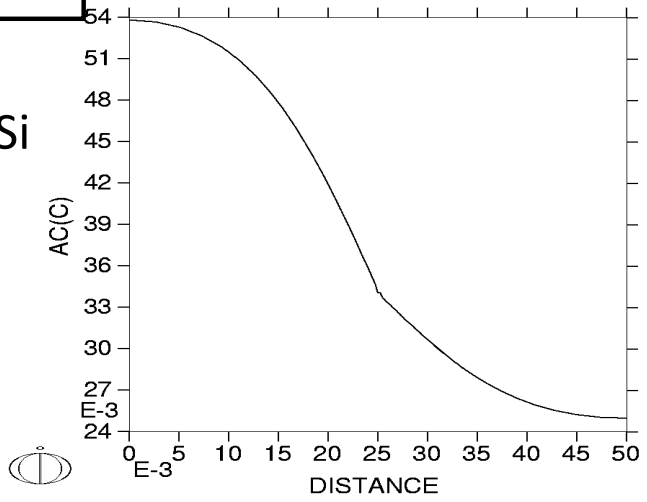
Concentration-profile for C



Concentration-profile for Si



Activity-profile for C



Darken, Trans AIME 180(1949)430

Uphill diffusion

Thermo-Calc Software

Diagonal term.

Off-diagonal term.

$$J_C = -D_{CC}^{Fe}\frac{\partial c_C}{\partial z} - D_{C\,Si}^{Fe}\frac{\partial c_{Si}}{\partial z}$$

Flux of carbon.

Diffusivity of C with respect to the gradient in C. Fe = ref. element.

Conc. gradient for C.

Diffusivity of C with respect to the gradient in Si. Fe = ref. element.

Conc. gradient for Si.

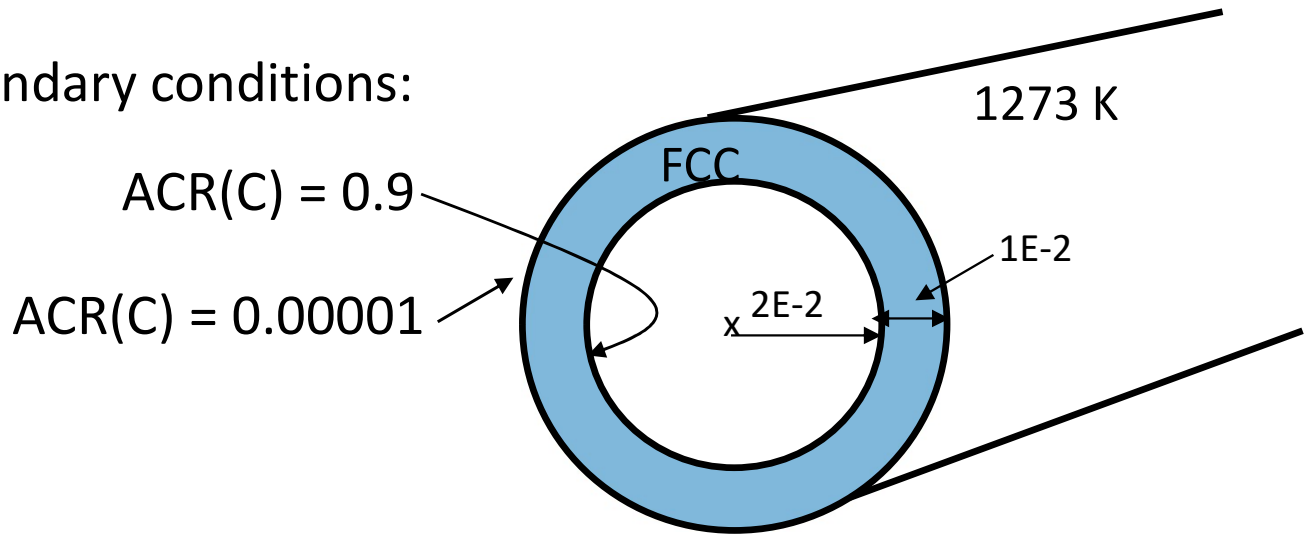
Thermo-Calc Software

Q & A

One phase Example
- Carburisation

Example – diffusion through a tube wall

Boundary conditions:



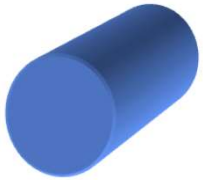
Demonstrates the use of:

- Geometries
- Boundary conditions
- Reference states

Alloy composition:
Fe – 0.6Mn – 0.7Si – 0.05C (wt-%)

DICTRA Geometries

Infinitely wide plate of a certain thickness.



Infinitely long cylinder of a certain radius.

Sphere with a certain radius.

Boundary conditions

Thermo-Calc Software

In Graphical Mode:

Closed System (this is default)
Mixed zero flux and activity (Very useful!)
Composition

There are some more possible boundary condtions in Console Mode:

Fix flux value (very theorethical)
Potential/Activity flux function (for real specialists)
Iterative activity flux function (for real specialists)
Gas (allows for growing/shrinking region)

U-fraction

The composition variable used internally in DICTRA

”Mole fraction with respect to substitutional elements only”

Natural choice if it is assumed that

- The partial molar volume is the same for all substitutional elements (V_S)
- The partial molar volume is zero for all interstitial elements

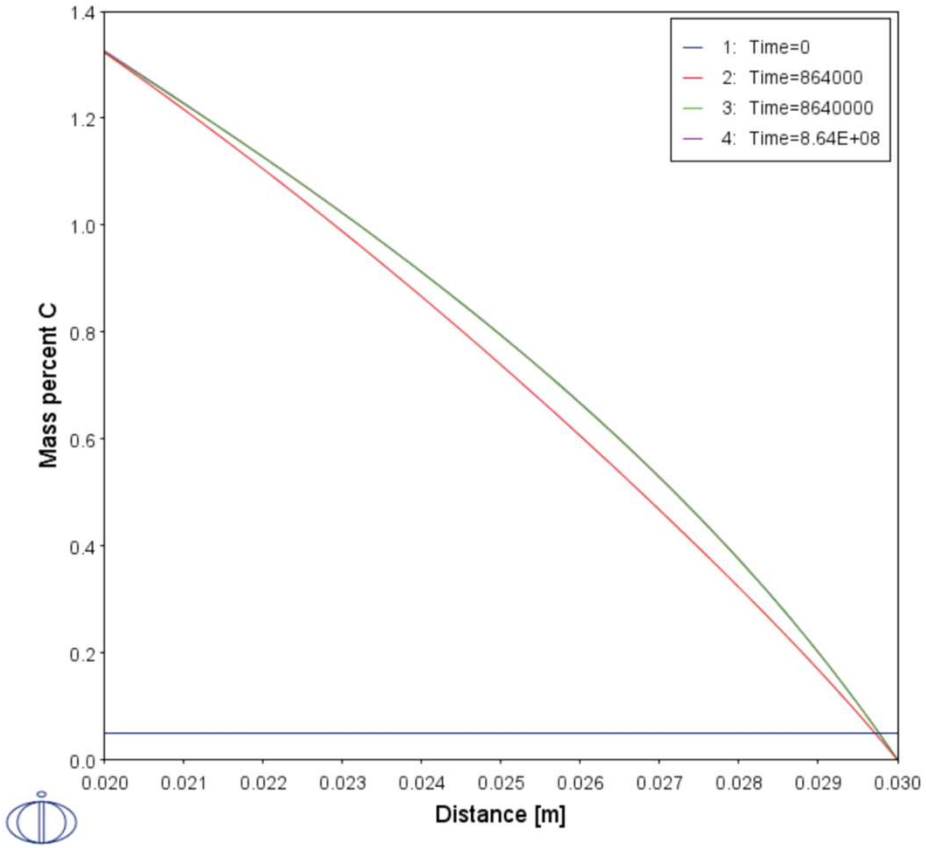
Example: System Fe-Cr-C, u_k is u-fraction, x_k is mole fraction

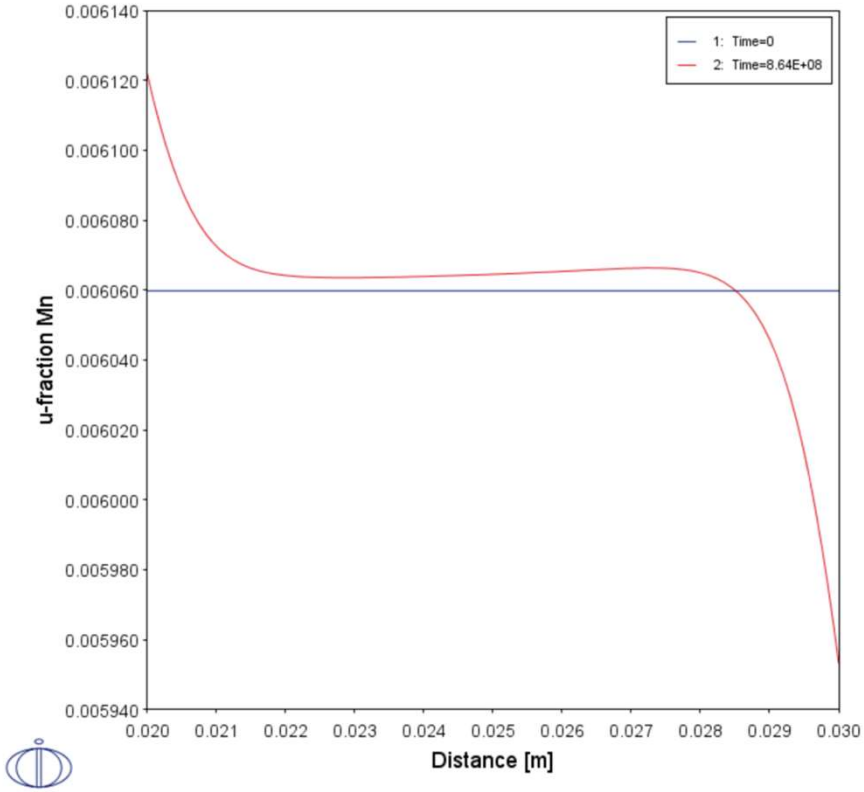
$$u_{Cr} = \frac{x_{Cr}}{x_{Cr} + x_{Fe}} = \frac{x_{Cr}}{1 - x_C} \qquad u_{Fe} = \frac{x_{Fe}}{x_{Cr} + x_{Fe}} \qquad u_C = \frac{x_C}{x_{Cr} + x_{Fe}}$$

$$u_{Cr} + u_{Fe} = 1$$

$$c_k = u_k / V_S \qquad [\mathrm{mol/m^3}]$$

Results – diffusion through a tube wall





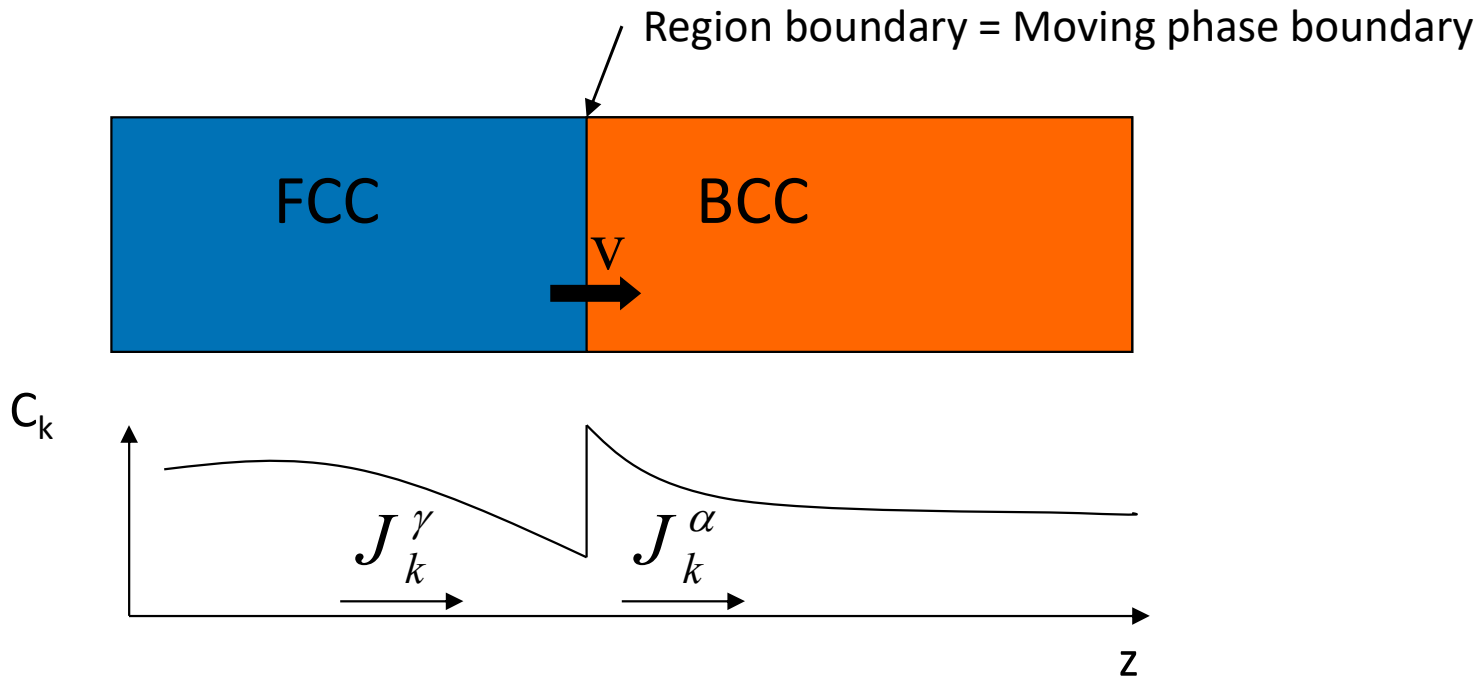
Moving Phase boundary Example

- Growth of a particle

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 Thermo-Calc.
  - ✓ 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



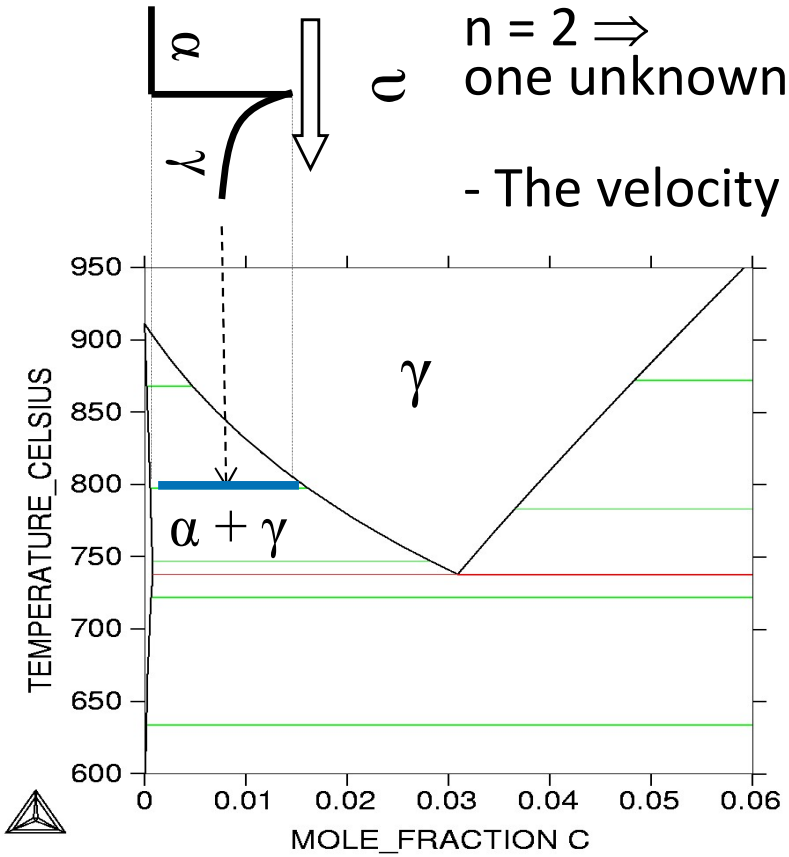
Solve diffusion equation in each phase

Calculate displacement of phase boundary

Thermo-Calc is used to find tie-lines

Diffusion with a moving interface

Binary example: Fe-C



n = 2 ⇒ one unknown

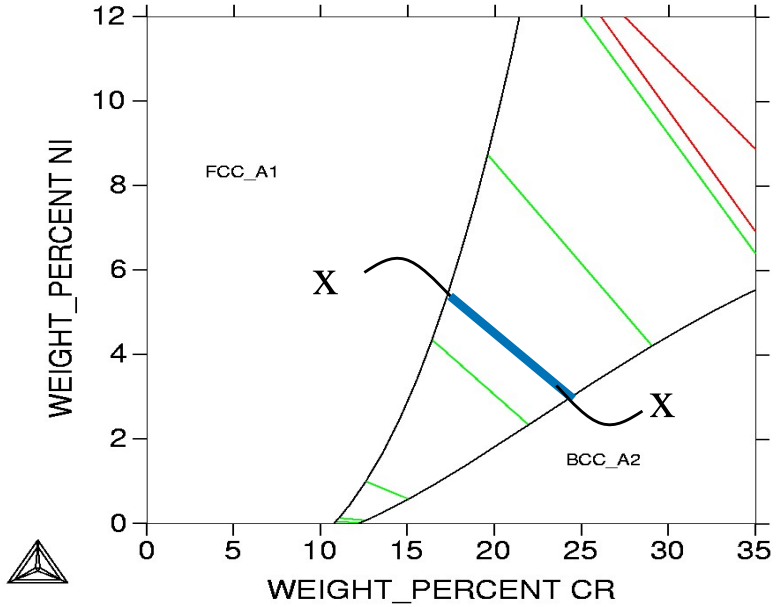
- The velocity

P, T const.

Ternary example: Fe-Cr-Ni

n = 3 ⇒ two unknowns!

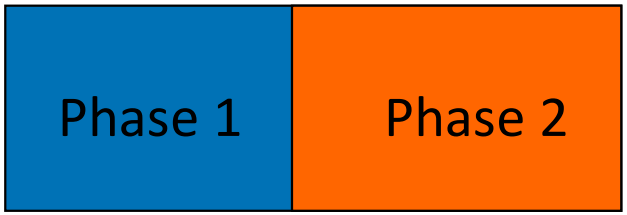
- One a_i or μ_i (i.e. one tie-line)
- The velocity



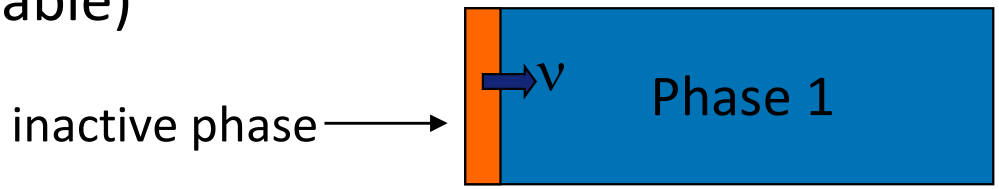
Moving Phase Boundary

- Moving phase boundary simulations may be set up in DICTRA in two different ways:

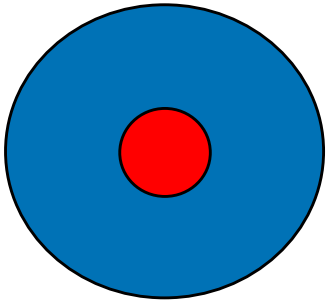
1) Introducing two or more adjacent regions containing different phases



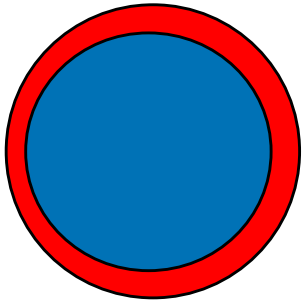
2) Entering an inactive phase (formed when thermodynamically stable)



Some possible geometries

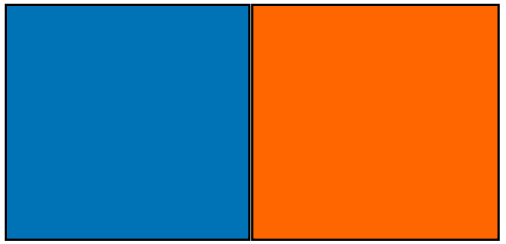


Growth or dissolution of a spherical precipitate

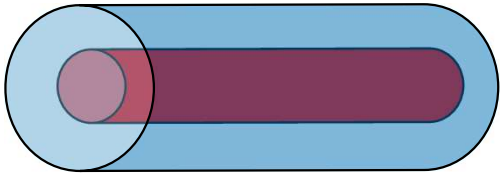


Growth of spherical film

(Grain-boundary film)



Planar growth

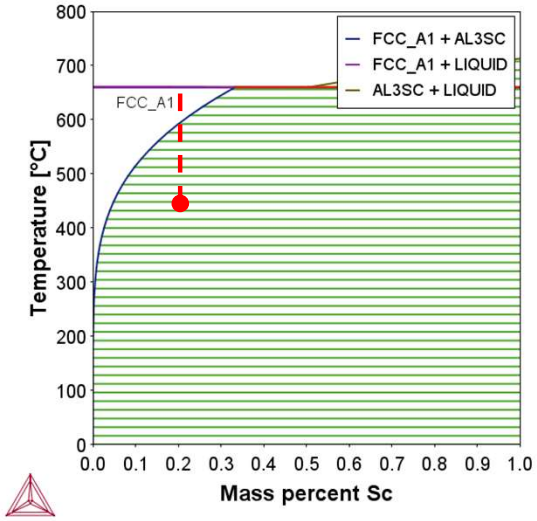


Growth of cylindrical precipitate

Example: Particle growth

Thermo-Calc Software

Al – 0.2 wt-% Sc

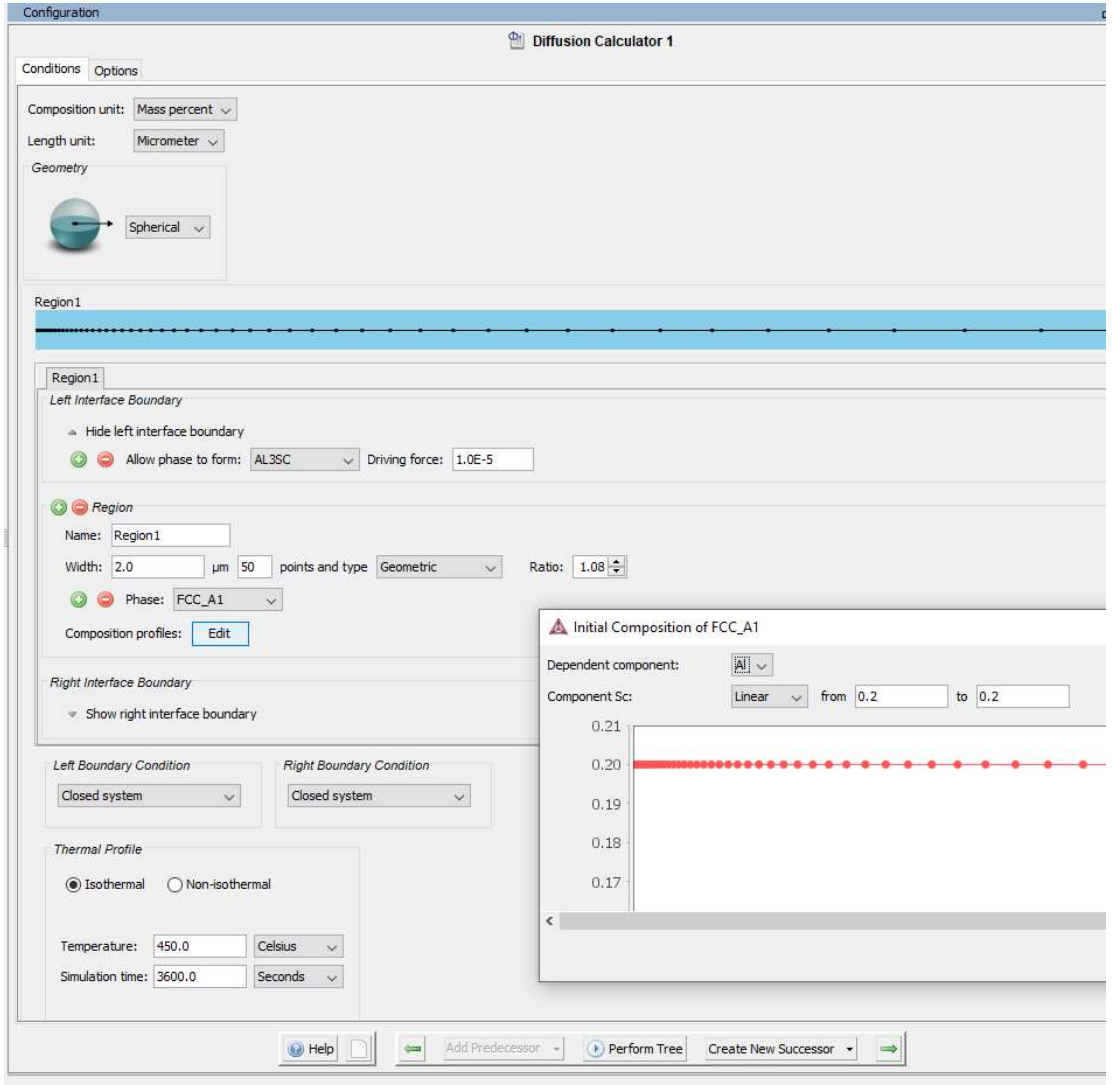


Quench to 450°C.

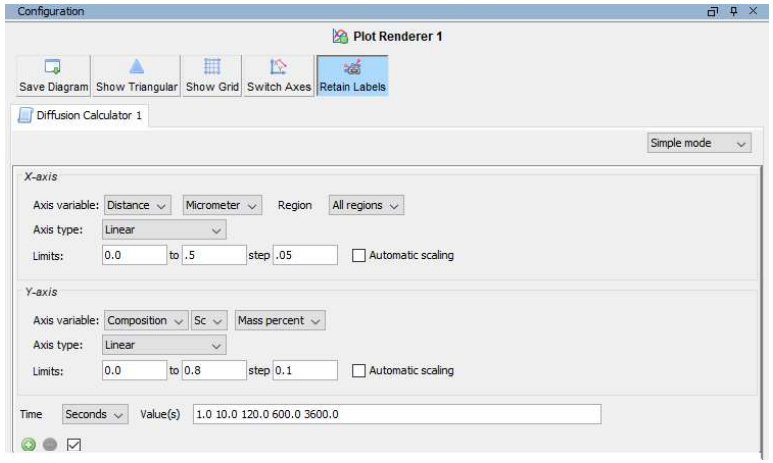
→ Supersaturated FCC

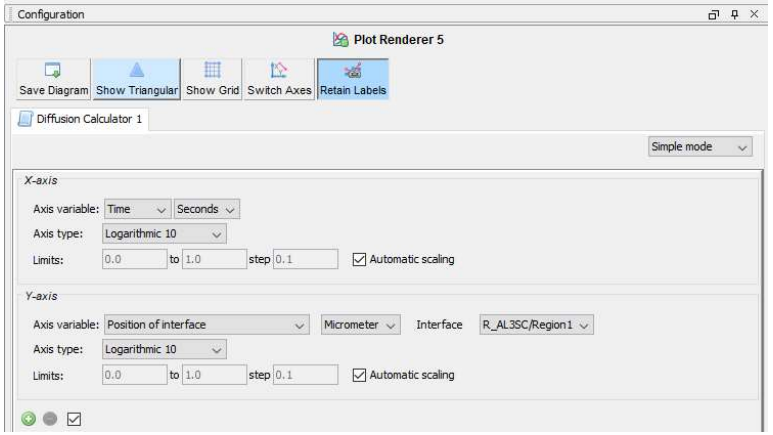
→ Driving force for the precipitation of Al_3Sc

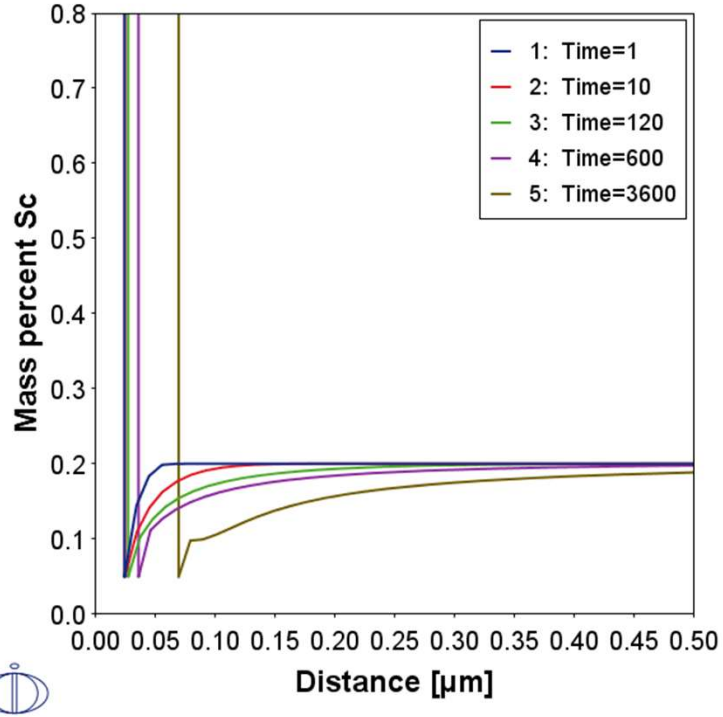
→ Diffusion controlled growth of Al_3Sc

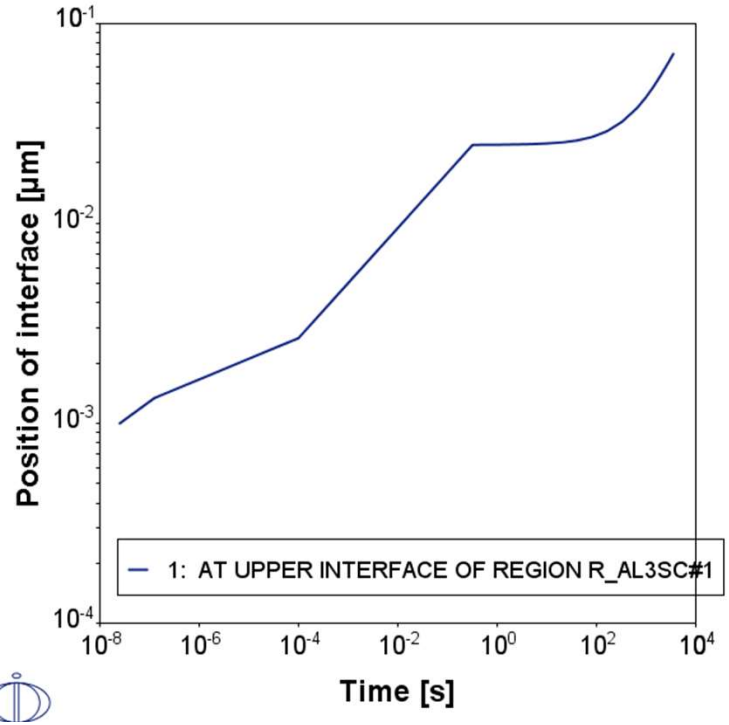


Results: Particle growth









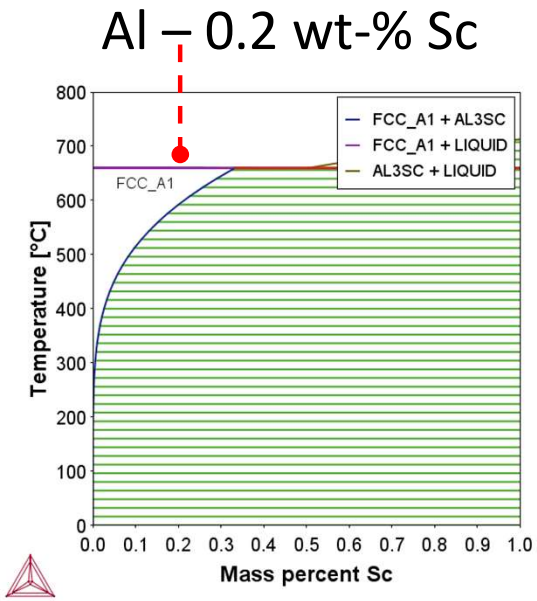
Thermo-Calc Software

Q & A

Home assignment 1

Home assignment 1: Particle growth

Thermo-Calc Software



Try to make the Al-Sc simulation we just performed more realistic by adding the cooling from single-phase FCC at 600 °C to 450 °C.
Let's assume this cooling takes 2 seconds.

Does this change how much the phase interface has moved after 1 hour?

1) You have to change the setting to non-isothermal.
2) Also consider how you can compare the two results after time=3600 s.