390: Materials Design

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Contents

1 Catalog Description 2
2 Course Outcomes 2
3 CHiMaD Case Studies 3
   3.1 Materials for Additive Manufacturing 3
   3.2 Printable Cobalt-Based Superalloys 3
   3.3 Structural Composites for Extreme Environments 3
   3.4 Thermoelectric Materials 3
   3.5 Electronic Material Inks 3
4 Laboratories 3
   4.1 Lab 1: Materials Selection 4
   4.2 Lab 2: Thermocalc 9
   4.3 Lab 3: DICTRA 46
   4.4 Lab 4: PrecipiCalc/TC-PRISMA 55
5 Problems 66
   5.1 Materials Selection in Mechanical Design 67
   5.2 Thermo-Calc 70
   5.3 DICTRA and PrecipiCalc/TC-PRISMA 72
      5.3.1 DICTRA 72
      5.3.2 TC-PRISMA 73
1 Catalog Description

Analysis and control of microstructures. Quantitative process/structure/property/performance relations, with case studies. Computer lab for modeling multicomponent thermodynamics and transformation kinetics. Prerequisites: 315, 316 1,2, or consent of instructor.

2 Course Outcomes

At the conclusion of the course students will be able to:

1. Apply a systems approach to complex problem identification and formulation.

2. Apply property/performance relations to materials selection, and to the specification of property objectives to meet user performance needs in evolving environments.

3. Apply mechanistic models in design integration of process/structure and structure/property relations in dynamic multilevel-structured materials systems

4. Synthesize results of interdisciplinary design research.

5. Apply computational skills in materials selection (CMS Selector), multicomponent thermodynamics (THERMOCALC) and diffusion (DICTRA), and integrate them in the theoretical conceptual design of materials.

6. Perform in cross-functional teams.

7. Communicate effectively in oral, written and graphical form.
3 CHiMaD Case Studies

3.1 Materials for Additive Manufacturing

3.2 Printable Cobalt-Based Superalloys

3.3 Structural Composites for Extreme Environments

3.4 Thermoelectric Materials

3.5 Electronic Material Inks

4 Laboratories
4.1 Lab 1: Materials Selection

1. What is CES/CMS?
   - Cambridge Engineering/Materials Selector
   - Database/Software comes from Cambridge University, UK.

2. Why CMS?
   - Allows off-the-shelf selection of materials (not a software to design new material(s)).
   - There are more than 50,000 materials available to the engineers
     - Q1: "...how one is to find one’s way through the enormous catalog, narrowing it down to a single, sensible choice?"
     - Q2: "Can one devise a rational procedure for material selection?"
   - Requires minimal knowledge of Materials Science i.e., it can also be used by non-materials scientists/engineers and other professionals.

3. Objectives of Today’s Lab. Exercise
   - Demonstration of performance-property link.
   - Demonstration of cross-property plots.
   - Demonstration of multi-level materials selection process.

4. Quantification of Performance and the Performance Index
   In the context of mechanical design, the performance of a component is governed by three factors: the functional requirement (e.g., the need to carry load, transfer heat, withstand shock etc.), the geometry, and the material properties. Then, the performance of component can be expressed by the following relationship:

\[ p = f(F, G, M) \]

where:
\( F \) = specified functional requirements,
\( G \) = geometric parameters,
\( M \) = material properties,

and \( p \) is the aspect of the performance to be optimized. The three sets of parameters are assumed to be separable, so the above equation can be written as:

\[ p = f_1(F), f_2(G), f_3(M) \]
where $f_1(F)$, $f_2(G)$, $f_3(M)$ are functions. Since the functions are separable, the optimum material can be chosen without solving the entire design problem. Thus, $f_3(M)$ is called the "performance index". The optimum material is the same regardless of the geometry and functional requirements.

5. Classification of Materials (after M. F. Ashby):

6. Classification of Properties in CMS

- **Continuous**: General, Mechanical, Thermal, Electrical, Shape Factor
- **Discrete**: Environment
- **Logical**: Forming, Joining, Surface Treatment, Available Forms
- **Identifier**: Metal, Ceramic, Natural, Polymer, Composite

7. Databases in CMS

- Generic (will be used for lab and homework)
- Light Alloys Database (purchased)
- Polymers Database (purchased)
- Copper Alloys Database (not purchased)
- Conductors Database (not purchased)
- Metal Matrix Composites Database (not purchased)
- Ferrous Alloys Database (not purchased)
- Foams Database (not purchased)

8. Materials Data and Design Process (after M. F. Ashby)
9. Why Log-Log Plots?

- When property cross-plots are done, it is found that data for a given class of materials cluster together; they can be enclosed in a single 'balloon'. The wide range of properties for a given class of material is the manifestation of processing-structure-property links.

- Balloons can be constructed for different kinds of materials representing different properties. Thus, property cross-plot balloons can be displayed in a convenient and accessible way (ease of visualization!).

10. How does it work?

- Application of set theory and relational algebra

11. System Architecture:
Case Study: Materials for Flywheels (Adapted from CES Background Reading and Tutorial)

Background: The applications of flywheels to store energy range from children’s toys, to old steam engines to the power storage and regenerative braking systems for vehicles.

Advanced flywheel designs have achieved energy densities in the range of 100-250 kJ/kg. Although these energy densities are much less than those in gasoline (44,000 kJ/kg) a sudden release due to failure can be disastrous. Thus, the disk must be surrounded by a burst-shield.

Using CES, we will determine the materials best suited for these advanced flywheel designs. Our selection will be based on maximizing the strength, while minimizing the weight and cost, and maximizing the fracture toughness.
An efficient flywheel stores as much energy per unit weight as possible without failing. The amount of kinetic energy the flywheel can store is limited by its strength. The energy $U$ stored in the flywheel is:

$$U = \frac{J\omega^2}{2}$$ (4.1)

where $J$ is the polar moment of inertia for the disk:

$$J = \frac{\pi}{4}\rho R^4 t^2$$ (4.2)

The mass of the disk, $m$, is:

$$m = \pi \rho R^2 t$$ (4.3)

The quantity to be maximized is the energy per unit mass, which we obtain from the combination of the previous 3 equations:

$$\frac{U}{m} = \frac{R^2\omega^2}{4}$$ (4.4)

Spinning the flywheel not only increases the stored energy, but also increases the centrifugal stress. The maximum principal stress in a spinning disk of uniform thickness is

where $\nu$ is Poisson’s ratio, equal to about 1/3 for most solids.

The stress must not exceed the failure stress, $\sigma_f$, with an appropriate safety factor, $S$. These restrictions place an upper bound on the angular velocity, $\omega,$
and the disk radius, $R$. Now $(U/m)$ can be rewritten in terms of the failure stress.

Assuming Poisson’s ratio to be constant, the performance index $(M)$ is given as

$$M = \ldots$$

Thus, the best materials for a flywheel are those with high strength and low density. Additionally, we would like to determine which materials provide the most strength per dollar. Good fracture toughness is also important.

We can now use CES to determine which materials meet these requirements.

Start CES EduPack 2019

### 4.2 Lab 2: Thermocalc
Northwestern University
Materials Science and Engineering
MatSci 390: Materials Design (Spring 2019)
Laboratory#2: Calculation of Phase Diagrams and Driving Force Using Thermo-Calc 2017b GUI

I. ThermoCalc Overview
a. What is Thermo-Calc?
- Software/Database package for thermodynamic calculations
- Originated from Royal Institute of Technology, Stockholm (www.thermocalc.com)
b. What Thermo-Calc does?
- Stable and meta-stable heterogeneous phase equilibria
- Amounts of phases and their compositions
- Thermochemical data such as enthalpies, heat capacity and activities
- Transformation temperatures, such as liquidus and solidus
- Driving force for phase transformations
- Phase diagrams (binary, ternary and multi-component)
- Solidification applying the Scheil-Gulliver model
- Thermodynamic properties of chemical reactions
- Consider constrained equilibrium, such as effect of stress, interfacial energy etc.
c. Applications
- Materials processing
- Materials design

II. Objectives
- How to use Thermo-Calc 2017b (Graphical Mode)
- How to interpret the results of a single equilibrium calculation
- Calculation of multi-component systems
- Calculation of driving force for precipitation

III. Thermo-Calc is Modular
The organization of Thermo-Calc modules is schematically shown below:

IV. Definitions Relevant to Thermo-Calc
System: A region (defined in terms of composition, temperature and pressure) of interest that can be closed or open to the exchange of matter, heat and work to its surroundings. In ThermoCalc all equilibrium calculations are performed with the assumption that the system is closed.
Phases: A region in the system that is homogeneous (uniform) and physically distinct and has the same structure and property everywhere.

Equilibrium State: A stable state against internal fluctuations in a number of variables.

Gibbs Phase Rule: States the number of degrees of freedom in a system is equal to the number of components in the system minus the number of stable phases plus 2 (temperature and pressure).

Components: The smallest possible division of matter required to describe a given phase.

Constituents: Determine the composition dependence of the properties of the phase and can reflect additional internal degrees of freedom.

Species: The collection of all constituents for the phases in a given system and can be elements, molecular aggregates, charged or neutral.

V. Thermo-Calc 2017b Graphical User Interface

TC2017b has a Graphical User Interface as well as an optional Console Mode. The software allows for calculations of multicomponent phase diagrams and property diagrams through the use of menus, buttons, and entering a few values e.g. compositions. In this lab, only Graphical Mode will be used. TC2017b-GUI uses the same thermodynamic databases as previous versions of Thermo-Calc and Console Mode.

The GUI Interface

The figure below is an example of the default GUI layout for Graphical Mode.

Project: Create, manipulate and navigate between the activities that make up a project.

Configuration: Shows the settings that can be configured for the currently selected activity.

Results: Shows the results of a calculation, either plotted as a diagram or displayed in table format.

Scheduler: Displays information about jobs, such as calculations, that are being performed or are scheduled to be performed. You can cancel scheduled jobs and if a job has failed, then you can view information about the error.

Event log: By default, this window is closed but it displays during calculation processes. You can always open it to view progress of calculations and to troubleshoot.

VI. Basic Steps in ThermoCalc 2017b (Graphical Mode) Calculations

Step 1 Create a Project: Select the desired application module in the main window.
Step 2 System Definer: Define the database and system
Step 3 Equilibrium Calculator: Define the conditions for the initial equilibrium
Step 4 Perform: Calculate the equilibrium and extrapolate it by stepping/mapping in 1 or 2 directions
Step 5. Plot/Table Renderer: Define the axes to plot

VII. Important Concepts in Thermo-Calc

a. The Concept of Status

Entered: The phase, component, or species can freely participate in the energy minimization procedure.
Dormant: The phase is allowed to participate in the energy minimization but not allowed to have any mass (i.e. driving force).
Fixed: The phase is forced to be present in a given quantity
Suspended: The phase, component, or species is ignored.

b. The Conditions of Equilibrium

• The system must be constrained by intensive or extensive state variables in order to reduce the degrees of freedom in the system to zero.
• The degrees of freedom in the system are equal to the number of components plus 2 (temperature and pressure).
• Any phase that is forced to be present by a FIXED status reduces the degrees of freedom by 1.
• Typically the size of the overall system must be constrained by setting the number of moles in the system equal to 1.
• Functions of state variables can also be used as conditions, but must be posed such that the function equals 0.

c. State Variables

Intensive:
T = Temperature in K
P = Pressure in Pascal
ACR(component) = Activity
MUR(component) = Chemical potential

Extensive:
S, S(phase) = Entropy of the system or phase
V, V(phase) = Volume of the system or phase
G, G(phase) = Gibbs energy of the system or phase
H, H(phase) = Enthalpy of the of the system or phase
A, A(phase) = Helmholtz energy of the system or phase
DGM(phase) = Driving force per mole of the phase/RT
N(comp), N(phase, comp) = Number of moles of the component in the system or phase
B(comp), B(phase, comp) = Mass of the component in the system or phase
N = Total number of moles in the system
B = Total mass in the system.

All extensive variables can be normalized to the moles in the system by appending an M to the descriptor. The same is true for the mass with W and the volume with V. As a convenience X and W can be used to denote mole fraction and mass fraction respectively.
VIII. Types of Calculations in POLY3 Module

I. Single Equilibrium (Single Point Calculation): Nothing is varied
II. Step Calculation (Property Diagram): One state variable is varied
III. Map Calculation (Phase Diagram): Two state variables are varied

IX. EXAMPLES:

EXAMPLE 1: Single Point Calculation of Fe-0.02C (wt%) at T=800°C
You can use the Single Point Calculation to determine phase fraction and composition. Its results should match what you could calculate from Lever Rule.

Step 1: Open TC2017b and enter GUI mode. Select ‘Single Point Equilibrium’

Step 2: System Definer 1 - Pick Database and Elements in System
Step 3: System Definer 1 - Identify Phases and Phase Constitution in System

Click [Phases and Phase Constitution] Tab.
Uncheck all phases except: BCC_A2, CEMENTITE, FCC_A1, GRAPHITE
Only the checked phases are “Entered” and are allowed in the calculation.
Unchecked phases are “Suspended”

In the Configuration Window, pick ‘TCFE9’ from the Database Dropdown menu.
Add ‘Fe’ and ‘C’ to the system by clicking on them.
Choose Mass Percent and Type 0.02 for C

Step 4: Equilibrium Definer 1-Set Temperature and Composition. Then Perform calculation. The calculation would take a few seconds.
Step 5: Table Renderer Results and Save as a Text, HTML or XLS file

EXAMPLE 2: Step Calculation for a Dilute Al-Mn-Ge-Si Alloy

In the Configuration Window, set:
Temperature (Celsius) = 800.0
Composition (C) = 0.02
**Make sure the composition unit says “Mass Percent”**

Right-Click on [Table Renderer] or [Equilibrium Calculator] and then Left-Click [Perform Now] or “Perform Tree”

Highlight and Right-Click the Table Renderer Results. Click ‘Save As’
You can Save the result as a .TXT, .XLS, or .HTML file

You can return to any previous part of the calculation by clicking on the appropriate section of the Project Tree.

The Stable Phases are listed with Mole, Mass and Volume Fractions and Compositions
Property Diagram starts a “Step” calculation. This involves “Stepping” through a single variable after initiating a point equilibrium. Step Calculations can result in graphs or tables of the calculated properties. For example, to determine the optimum temperature for processing for a given alloy we can use one of the compositions as variable for STEPping.

In this example, we will use an Al-0.7Mn-0.5Si-0.3Ge (wt%) alloy. We want to find out what is its solution treatment temperature (i.e., the temperature at which all solutes are dissolved in Al). We also want to know what the equilibrium phase(s) are at various aging temperatures.

**Step 1: Open TC2017b and enter GUI mode. Select ‘Property Diagram’**

Click [Property Diagram] to begin the calculation.
Step 2: Change the database, add the correct elements, go to the Phases tab.

Change the Database in the dropdown menu to "TCAL2". Add the elements Al, Si, Mn Ge and their content.

Step 3: Choose Phases

Click "Check/Uncheck All" to remove all phases. Check the following phases:
Al11Mn4_HT
Al12Mn
Al4Mn_R
Al6Mn
Al8Mn5
DIAMOND_A4
FCC_L12
LIQUID
Step 4: Set Conditions (Temperature and Composition). Then Perform calculation.

- Temperature: 700.00K
- Pressure: 100000.0 Pa
- System Size: 1 Mole
- Comp. Mn: 0.7 wt%
- Comp. Ge: 0.3 wt%
- Comp. Si: 0.5 wt%

Under "Axis Definitions" (This defines the step calculation):
- Quantity: Temperature; Min = 500; Max = 1000
- Step Division = 10; Type = "Linear-max step size"
- Method = "Normal"

Step 5: Plot Renderer Results and Save the Diagram or Data Table

This is commonly called a Step Diagram. It shows equilibrium phase fractions of phases present in the system at a given temperature. It is best to plot phase fraction in Log base 10.

- **X-Axis**: Put Temperature in Celsius. Adjust Limits to Min: 250, Max: 700, Step: 50
- **Y-Axis**: Make Axis Type “Logarithmic 10”. Adjust Limits to Min: 0.001, Max: 1.0, Step: 1

To execute these changes, use Perform button or Perform Now from the Project tree.

A table with the data calculated can be created using “Table Renderer”.

EXAMPLE 3: Map Calculation for a Fe-C Metastable Phase Diagram

Mapping Calculations allow variation of two variables. These enable the calculation of phase diagrams (varying Temperature and Composition). For this example, we’ll calculate a metastable equilibrium diagram of Fe-C.

Right-Click “Equilibrium Calculator” in the Project Tree. Right-Click “Create New Successor>Table Renderer”. Right-Click “Perform” to generate the corresponding table. You can copy all data or save all as a text, xls, or html file.
Step 1: Open TC2017b and enter GUI mode. Select ‘Phase Diagram’
Binary Calculator or Ternary Calculator are quick templates for Binary and Ternary Diagrams but
feature less customizability.

Step 2: Choose the Correct Database and add Elements

Click [Phase Diagram] to begin the calculation

In the Configuration Window, pick ‘TCFE9’ from the Database Dropdown menu.
Add ‘Fe’ and ‘C’ to the system by clicking on them.
Step 3: Add Phases and Make Graphite Dormant

Uncheck all phases and then Check to add: BCC_A2, CEMENTITE, GRAPHITE, FCC_A1, LIQUID

Change GRAPHITE to “DORMANT” with the dropdown menu

Step 4: Set Mapping Conditions, Then Perform calculation

Composition Unit: Mass Percent
Temperature: 1000 K
Pressure: 100000 Pa
System Size: 1 Mole
Comp. C: 1.0

Set these conditions under Axis Definitions:
- Mass Percent C: Min=0.0; Max=10; Step division=1000; Type=Linear min No. of steps
- Temperature: Min=700; Max=1900; Step division=10; Type=Linear max Step Size

Step 5: Change Axis Limits. Insert Labels
Step 6: Labeling Phase fields.
This is a metastable equilibrium diagram due to Graphite. The only ¡®accurate¡¯ section is that of less than 10 wt% C.

EXAMPLE 4: Calculate an Isothermal Section of Fe-Ni-Cr system at 600°C
An isothermal section of the ternary system provides us the composition-phase roadmap at a particular temperature. This information is very useful in selecting alloy compositions, knowing the equilibrium phases present, their amounts and compositions for a given alloy composition etc. The phase equilibria of Fe-Ni-Cr system is the basis for designing various types of stainless steels. For example, if one wants to design an austenitic stainless steel, the alloy composition should be in the FCC phase field. Or, if one wants to design a duplex stainless steel, the alloy composition should be in the BCC+FCC phase field. Calculation of an isothermal section at 600ºC is a demonstration of such alloy selection process.

Step 1: Open TC2017b and enter GUI mode. Select ‘Phase Diagram’

Step 2: Choose the Correct Database and add Elements

Click [Phase Diagram] to begin the calculation
Step 3: Add Phases

In the Configuration Window, pick ‘TCFE9’ from the Database Dropdown menu. Add ‘Fe’, ‘Ni’ and ‘Cr’ to the system by clicking on them.

Only Check LIQUID, FCC_A1, BCC_A2, and SIGMA phases in the calculation as “Entered”

Step 4: Set Conditions, Then Perform calculation
Step 5: Finish the plot as a Triangular Diagram.

Adjust Calculation Conditions:
- Comp. Unit = Mass Percent
- Temp. = 600 C
- Pressure = 100000 Pa
- System Size = 1 mole
- Comp Ni = 10
- Comp Cr = 10

Adjust Limits on Axis Definitions:
- Quantity: Mass Percent Cr; Min = 0; Max = 100; Step Division = 10.0; Type = Linear Max Step Size
- Quantity: Mass Percent Ni; Min = 0; Max = 100; Step Division = 10.0; Type = Linear Max Step Size.

Set Plot to “Show Triangular” and “Perform” to show Ternary Phase Diagram.

This is an Isothermal Section of a Ternary diagram. Next, a Vertical Section of this system will be calculated using the Project Tree.

Step 6: Create a new Branch of the Project
Step 7: Set Conditions and Perform Equilibrium Calculations

Go to the Project Window: Right-Click on “System Definer”, “Create New Successor>Equilibrium Calculator” This creates a branched calculation using the same initial system, elements and phases.

Change Mass Percent Cr and Temp.
Vary Mass percent of Cr from 10 to 30 by 100 steps
Vary Temperature in C from 300 to 1200 by steps of 10
**Perform** only this tree

Step 8: Create a new Plot Renderer
Step 9: Create a new Plot Renderer, Set Plot Axis and Perform

Go to the Project Window:
Right-Click on “Equilibrium Calculator”, “Create New Successor>Plot Renderer”

The new plot appears in Plot Renderer 2. Set your axis limits to:
Cr: Min=10.0, Max=30.0, Step=2.0
Temp(C): Min=300, Max=1200, Step=100
Calculation of Driving Forces

Graphical Illustration of Driving Force for Nucleation

Step I: A line is drawn tangent to Gibbs energy-composition curve of the matrix phase $\beta$ at the bulk composition of the alloy ($X_{B, \beta}^0$). This line will be automatically tangent to the capillarity-increased Gibbs energy-composition curve of the critical nucleus, $\alpha'$. 

Step II: A line is drawn tangent to Gibbs energy-composition curve of the precipitate phase $\alpha$ so that the ratio of the distance between the intercepts on both sides of the Gibbs energy-composition diagram is equal to $\frac{V_{A, \alpha}'}{V_{B, \alpha}}$, the ratio of the partial molar volume of $A$ to that of the solute $B$ in the $\alpha$ phase.

$\Delta G^E = $ nucleation driving force with nucleus composition same as that of equilibrium composition
$\Delta G^N = $ nucleation driving force in the presence of capillarity
$\Delta G^M = $ maximum nucleation driving force (in the absence of capillarity).
Driving Force for Nucleation

I. Why Driving Force?
- The microstructure of most engineering materials are derived by controlling the kinetics of first-order phase transformation.
- The driving force is an important scaling parameter in understanding and controlling the kinetics of phase transformations in general.
- Classical Nucleation Theory: The time-dependent nucleation rate $J^*$ is

$$J^* = N \beta^* Z \exp \left( \frac{-\Delta G^*}{kT} \right) \exp \left( -\frac{t}{\tau} \right)$$

$N$ is the density of viable nucleation sites, $\beta^*$ is the frequency factor, $Z$ is the Zeldovich nonequilibrium factor, $\Delta G^*$ is the activation energy for formation of the nucleus, $\tau$ is the incubation time, $t$ is the isothermal reaction time. For spherical nuclei:

$$\Delta G^* = \frac{16 \pi \sigma^3}{3 (\Delta G_M^2)}$$

and

$$r^* = -2 \sigma \Delta G_M^M.$$

II. Calculation of Driving Force for Nucleation (neglecting capillarity)
- Binary Alloy: $\Delta G_M = (\mu_{A,\alpha}^M \times A_{\alpha} + \mu_{B,\alpha}^M \times B_{\alpha}) - (\mu_{A,\beta}^M \times A_{\alpha} + \mu_{B,\beta}^M \times B_{\alpha})$ (per mole of $\alpha$ formed) (per mole of $\alpha$ removed)

- Multicomponent Alloy: $\Delta G_M = (\mu_{A,\alpha}^M - \mu_{B,\beta}^M) \times M_{\alpha}$

where $\mu = (\mu_1, \mu_2, ..., \mu_n)$ and $\mathbf{X} = (X_1, X_2, ..., X_n)$ are vectors.

Graphical Illustration of Driving Force for Transformation

Diffusional Transformation:
When an alloy of composition $\left( X_{\beta,\alpha}^M \right)$ transforms to $\alpha$ and $\beta$ phases having equilibrium compositions $X_{\alpha,\alpha}^E$ and $X_{\beta,\beta}^E$, respectively, the Gibbs energy of the system will have decreased by an amount $\Delta G^{fr}$, as graphically shown below. This is called the driving force for transformation which is very different from driving force for nucleation. This is due to the fact that the formation of first nuclei does not change of initial composition of $\beta$ $\left( X_{\beta,\beta}^E \right)$. 
Driving Forces for Nucleation and Transformation

I. Diffusional Transformation:

- \( \Delta G^M = f(X_{B, \beta}^i, T, t) \) and \( \Delta G^{Tr} = f(X_{B, \beta}^i, T, t) \), but \( \Delta G^M \neq \Delta G^{Tr} \)
  
  where \( \Delta G^M \) is the maximum driving force for nucleation, \( \Delta G^{Tr} \) is the driving for transformation, \( X_{B, \beta}^i \) is the instantaneous composition of the matrix, \( T \) is temperature, and \( t \) is the isothermal time.

- Time dependency:
  
  All nuclei do not form and reach critical size at the same time. Due to various reasons some nuclei reach critical size earlier than others. The nuclei which reach critical size at time \( t_1 \) will subsequently undergo growth or coarsening (classical vs Langer-Schwartz). As a result the degree of supersaturation in the matrix will be reduced. It is also possible that the precipitation process is not complete at time \( t_2 (> t_1) \), and nucleation might still be occurring. In that case the driving force for nucleation at time \( t_2 \) will be less than that at time \( t_1 \).

- At Equilibrium:
  
  When \( X_{B, \beta}^i = X_{B, \beta}^E \), \( \Delta G^M = \Delta G^{Tr} = 0 \)
**II. Partitionless Transformation (massive, martensite, congruent solidification/melting etc.):**

\[
\Delta G^M = \Delta G^T = f(X^o_{B, \beta}, T)
\]

**III. Sign Convention for Driving Force for Nucleation**

- If \(-\Delta G^M\) is +ve, the phase is stable and it has the tendency to precipitate
- If \(-\Delta G^M\) is –ve, the phase is not stable

In ThermoCalc, the driving force for nucleation is expressed as a dimensionless quantity.

\[
\Delta G^T = \frac{\Delta G^M}{RT}
\]

Thus,

\[
\Delta G^T (J/mol) = \Delta G^T C . R . T
\]

where \(\Delta G^T\) is the driving force for nucleation in ThermoCalc, \(T\) is the temperature in K, and \(R\) is universal gas constant.

**EXAMPLE 5: Composition-Variant Transformation**

Consider a Fe-1.5wt%C alloy quenched (rapidly enough to suppress any transformation during cooling) form high temperature to room temperature. The supersaturated alloy will be subjected to aging in the temperature range of 300 to 800 K. Let us assume that any of the three phases, Cementite, Diamond and Graphite can precipitate. We want to know how the driving forces for precipitation of these phases vary with temperature.
Step 1: Open TC2017b and enter GUI mode. Select ‘Property Diagram’

Click [Property Diagram] to begin the calculation

Step 2: Change the database, add the correct elements, go to the Phases tab.

Change the Database in the dropdown menu to “TCFe9”
Add the elements Fe, C and their content
Step 3: Choose Phases

Only Check FCC_A1, CEMENTITE, DIAMOND_A4, GRAPHITE phases.

Make the Cementite, Diamond_A4, and Graphite Phases “Dormant” for a driving force calculation.

Step 4: Set Conditions (Temperature and Composition).

In the Conditions tab, set Temperature = 500 K, w(C)=1.5 wt%

Min(T)=300 K, Max(T)=800 K, step=10, Linear max step size, Normal
Step 5: Enter Driving Force Functions
In ThermoCalc, the driving force is expressed as a dimensionless quantity, \(dgm(\text{phase})\). To calculate the driving force in J/mol, we have to multiply this quantity with \(R\) and \(T\), where \(R\) is the universal gas constant and \(T\) is the temperature in K.

In the Functions tab, enter the following as a Function:
- Function 1 = 8.314 * \(T\) * DGM(CEMENTITE)
- Function 2 = 8.314 * \(T\) * DGM(DIAMOND)
- Function 3 = 8.314 * \(T\) * DGM(GRAPHITE)

Step 6: Define the diagram axis variables

Set Y axis as Function and Function 1.
Click on green “+” to generate 2 new sets of diagram.
Set the Y axis as Function and Function 2 and Function 3, respectively.
Click Perform to perform the calculations.
Step 7: Adjust the Y axis scale

Which phase has the highest driving force for precipitation?
In general, what is the effect of temperature on the driving force for precipitation?

EXAMPLE 6: Composition-Invariant Transformation

There are many examples of phase transformations where the compositions of the parent and product phase are exactly the same. These are called composition-invariant transformations. Examples include massive transformation, martensitic transformation, congruent ordering, congruent melting (or solidification) etc. Then, the driving force for such a transformation (ΔGm) is given by the difference in molar Gibbs energy i.e., \[ ΔG_m = ΔG_m(\text{product}) - ΔG_m(\text{parent}) \]. Let us consider a Fe-10Ni-0.5C wt% alloy being cooled continuously from 727°C to 27°C. This alloy may undergo a martensitic transformation. For the sake of simplicity, we will approximate martensite as the BCC phase given in ThermoCalc.
Step 1: Open TC2017b and enter GUI mode. Select ‘Property Diagram’

Step 2: Change the database, add the correct elements, go to the Phases tab.

Click [Property Diagram] to begin the calculation

Change the Database in the dropdown menu to “TCFE9”
Add the elements Fe, Ni, C and their content
Step 3: Choose Phases

Change the Database in the dropdown menu to "TCFe9". Add the elements Fe, Ni, C and their content.

Check BCC_A2 and FCC_A1 phase in the calculation as "Entered".

Step 4: Set Conditions (Temperature and Composition).

In the Conditions tab, set Temperature = 1000 K, w(Ni)=10 wt%, w(C)=0.5 wt%

Min(T)=300 K, Max(T)=1000 K, step size=50 K, Linear max step size, “Separate Phases”
Step 5: Enter Driving Force Functions

In the Functions tab, enter the following as a Function:
Function 1 = GM(BCC) - GM(FCC)
Then “Perform”

Step 6: Adjust Y axis variable & scale

Set Y axis as Function and Function 1.
Click Perform to perform the calculations.
Step 7: Make a New Plot with Gibbs Energy of all phases

What is the $T_o$ temperature of the alloy, where $T_o$ is the temperature where $G_m(bcc) - G_m(fcc) = 0$, using the plot of Driving Force versus Temperature? Does this correspond to the plot of Gibbs energy versus temperature?

Assuming that the martensitic transformation starts at a Driving Force of $-1000$ J/mol, what is the $M_s$ temperature of the above alloy?
The process of materials design involves a large amount of calculations using different models in order to study trade-offs and to perform optimization of design strategies. It is a tedious and time-consuming task to manually operate all models without an easy to use operational environment. This lab will introduce an improved interface for accessing Thermo-Calc. This new interface should greatly simplify all calculations that you will need to do. Currently, the interface will calculate basic thermodynamic quantities, martensite start temperature, solution temperature, carbide driving force, carbide coarsening rate, solidification segregation and more.

To Login
1. Run x-win32 in the background from Start>Programs
   Right click on the header bar and choose reset.
   (Icon “X” in the connection-bar at the bottom right corner of screen shows that x-win32 is running)
2. Run PuTTY from Start>Programs>PuTTY>PuTTY
   To connect to Wiglaf:
   Type in the following host name
   wiglaf.ms.northwestern.edu
   Enable X11 Tunneling in PuTTY:
   Go to Category → SSH>X11 in the tree on the left
   Check the box Enable X11 forwarding
   Click Open
   Click Yes to the PuTTY Security Alert
   Type your User Name when prompted with ‘login as’ and then press Enter
   Type your Password when prompted and press Enter
3. To access the interface, type in made & at the prompt in the SSH Window.

Once MADE is open, drag the left side of the panel (vertical line) to the middle of the window to view the “Composition/Model Input” window.

Using MADE:

Inputs:
Models
Under the input tab, MADE has three major panels. On the top right hand side is the Model Manager Panel. The model manager panel contains a set of facilities to manage model executables. The user can select the model of interest by highlighting the program and then double clicking with the left mouse button. When a model is selected, the name of the program appears within the “[]” of the panel title, and the model input parameters are shown in the Composition/Model Input Panel. The “Info” button in the “Model Actions” button is used to display detailed information of the highlighted model.

Composition/Model Input
The left hand side panel is the window for the compositions and model inputs. You may choose to step through one or two composition ranges in the interface. To do this, click on the box next to the number. This will highlight the box in red. A second composition box will appear which will represent the high value of the composition range. If you want to customize the elements or add new elements into your calculation, click on the “Input Actions” button and then click “Change Element List”. Then enter a list containing all elements of interest such as “Al Mg Cu Si”, where the first element is the base element.

TDBs
The TDB Manager Panel allows the user to select the appropriate database for the model. For multi-component steel systems you should use the “ssol+m2c” database for all of your calculations EXCEPT Ms (Martensite Start Temperature) calculations. For Ms calculations, use the “mart5” database.

Northwestern University
Materials Science and Engineering
Mat Sci 390: Materials Design (Spring 2019)
Laboratory#3 & 4: MADE (MAterials DESign)
Models and Examples

1. Basic Model

The Basic model is a general-purpose program to retrieve thermodynamic/mobility quantities after the equilibrium calculation for a closed system (fixed mass). It needs temperature as an additional model input beside material composition. Basic relies on the extra input to configure the calculation. It requires at least one extra input name. The first extra input name (ENT PH) has to be a list of interested phase name(s) that go into (enter) the equilibrium calculation. The optional 2nd extra input name (Dor PH) represents a name list of dormant phases. The optional 3rd entry (P3 MADE) is used to put in special POLY3 commands before every equilibrium calculation. As this entry is one line in a whole, the user has to use "$" to combine different lines of commands into one line.

Example 1: Calculation of driving force for precipitation as a function of temperature using the Basic Model (Same as Example 5 in the Thermo-Calc Lab)

Problem Definition:
Consider an Fe-1.5wt%C alloy quenched (rapidly enough to suppress any transformation during cooling) from high temperature to room temperature. The supersaturated alloy will be subjected to aging in the temperature range of 300 to 800 K. Let us assume that any of the three phases: cementite, diamond, and graphite, can precipitate. We want to know how the driving forces for precipitation of these phases vary with temperature.

Steps:
1. In Model Manager select the Basic model
2. In TDB Manager select the ssol+m2c database
3. In the Composition Panel set wt% C=1.5 (note: you may have to change the selected element list to Fe C). Check the box next to T and input the temperature range from 27 to 527 C.
4. Click on the Compute tab. Set grid for T equal to 15 (these are the number of calculations it will carry out within the range)
5. Click on Compute button
6. It will now ask for additional inputs. Enter FCC as the entered phase (line 1). Enter cem dia gra as the dormant phases (line 2). We want the program to output the driving force for precipitation as J/mol. To do that enter the following command in line 3 of the Extra Input box:

   en-sym function df1=8.314*T*dgm(cem);$en-sym function df2=8.314*T*dgm(dia);en-sym function df3=8.314*T*dgm(gra);$  

7. Click on OK
8. It will now ask for additional outputs. By default the outputs are G, H and S. Specify df1, df2 and df3 in lines 1, 2 and 3 as additional outputs. Click on OK.
9. The program will run calculations. If everything goes ok it should say “15 out of 15 calculations are successful”
10. Click on Create Plot Tab: Plot title and Plot subtitles are shown at the top. You can modify them if you wish.
11. The quantities to be plotted are shown in the lower panel. When you click on the Plot button, MADE launches the PlotMTV program (which is a separate program from MADE) to view the results. Within the PlotMTV program, the user can zoom in/out, toggle log scale, print to selected printer ("Print" button) or save as a PostScript file ("Print to File" button: by default it saves it as cmd.ps in your home folder). Open another terminal and type "gs cmd.ps" to see the plot. The generated PlotMTV plot may contain multiple pages. The number of pages is exactly the number of model outputs plus the user specified extra output. In the PlotMTV window, the arrow buttons at the bottom left corner are designed to flip up or down through the pages. You can flip down to see how the driving forces for precipitation for Cementite, Diamond and Graphite vary with temperature.

Additional Processing:
12. To view all three driving force curves on the same plot we need to merge the plots together. To do that we need to save the results. Click on the Save Result button on the MADE interface. Give the file a name and save (note: the file name cannot contain spaces). Click on Yes when it asks “Add Saved Data for Merging Plots”.
13. Click on the Merge Plots tab. There are two options for merging the plots: Combine and Overlay. The Combine option allows us to combine the curves according to an equation such as “df1-(df2+df3)”. The Overlay option simply plots all the curves on the same window. For the current example we need the Overlay option. Select Overlay from the drop down menu at the top.
14. Remove any lists in the functions or items list. Select the three functions: df1, df2, and df3 that you want to graph together. Double click df1, df2, and df3 in the available results list (bottom left). Click on the Plot button
15. It will now plot all the functions on the same window.

Note: To learn more about PlotMTV and its options, please refer to the manual in the Design Studio or Tech D145.
2. bccfcc-ms and bccfcc-t0 Models

The bccfcc-Ms model calculates the Martensite start temperature i.e. the temperature at which austenite (fcc) starts transforming to martensite (bcc) upon cooling. The bccfcc-T0 model calculates the T0 temperature i.e. the temperature at which the bcc phase and the fcc phase have the same free energy.

Example 2: Calculation of Martensite Start Temperature (Ms) of Fe-9Cr-15Co-1.5Ni-xMo-yV-0.24C Alloys

Problem Definition:
Calculation of Ms temperature is a very crucial step in designing ultra-high strength, secondary hardening martensitic steels. Such calculation allows us to select the alloy(s) whose Ms temperature is sufficiently high so that upon quenching (from solution treatment temperature) to room temperature a fully (≥ 95%) martensitic microstructure is obtained. If the Ms temperature is not high enough, then we may get incomplete transformation at room temperature and the alloy is to be quenched to sub-ambient temperature(s). Typically, in the alloy design procedure we select alloy(s) having Ms temperature between 200 to 300°C.

Clear your result of last example first: go to Merge Plots and Results Action and select Clear.

Steps:
1. In Model Manager select the bccfcc-ms model
2. In TDB Manager select the mart5 database
3. In the Composition Panel change the element list to: Fe C Cr Co Ni Mo V
4. In the Composition Panel set wt% C=0.24, wt% Cr=9, wt% Co=15, wt% Ni=1.5, wt% Mo=0.5 and wt% V=0.5
5. In all calculations leave “G^el Cor(J/mole)” as 0.
6. Click on the Compute tab. Notice that there is no grid bar this time. That is because we are doing calculation at a single point
7. Click on Compute button
8. The program will run the calculations. If everything goes ok it should say “Successful Calculation”
9. The output is the calculated Ms temperature (in Celsius) and the error associated with the Ms.

To calculate Ms with composition variation
10. We will now calculate the Ms with Mo and V variation. Click on the Input tab to go back
11. Check the box next to Mo and specify the range from 0 to 4 wt %
12. Check the box next to V and specify the range from 0 to 1 wt%
13. Click on the Compute tab. Set grids for Mo and V: total number of calculations =(Mo grid)*(V grid)
14. Click on Compute button
15. The program will run the calculations. If everything goes ok it should say that the calculations are successful
16. Click on the Create Plot Tab. The Plot title and Plot subtitles are shown at the top.
17. Click on Plot to view the Ms temperature as a function of composition. Notice that it is plotted in the form of a contour plot with Mo on one axis and V on the other. Each of the curves then corresponds to a unique Ms value.
18. MADE gives the option of specifying the iso-contour values. To do that, go back to the Create Plot interface on MADE. On the field next to Ms(C) specify the iso-contour values separated by a blank space e.g. 266 276 286. Click on Plot again to view the contour lines on the plot.
19. Click Save Result button on the MADE interface. Give the file a name and save. Click Yes when it asks “Add Saved Data for Merging Plots”.

4.2 Lab 2: Thermocalc
Example 3:  
Calculation of T0 Temperature of Fe-9Cr-15Co-1.5Ni-xMo-yV-0.24C Alloys

1. Go back to the Input tab and select bccfcc-t0 in the Model Manager Panel.
2. In TDB Manager select the ssol+m2c database.
3. Repeat steps 3-15 from above example (Example 3-2). In this example the model calculates the T0 temperature instead of the Ms temperature.
4. Click on the Create Plot tab. The plot title and plot subtitles are shown at the top.
5. Click on Plot to view the T0 temperature as a function of composition. Each curve corresponds to a unique T0 value.
6. Click Save Result button on the MADE interface. Give the file name and save. Click Yes when it asks “Add Saved Data for Merging Plots”.
7. Click on the Merge Plots tab.
8. Click on the Show Options button.
9. Select Overlay in the drop-down menu.
10. On the bottom left of the screen, you should see an Available Results window which lists the calculations from the Ms and T0 calculations.
11. Double click on [1](1) Ms and [2](1) T0. You should see the functions that you picked in the Function or Items window.
12. Click on Lines under Contour Settings.
13. Click on Plot. You should see the Ms plot overlaid on the T0 plot.
14. Close the plot and return to the main MADE window.
15. Type \{278\} \{729\} in the Iso-Contour Values menu. This allows you to isolate the 278 C line in the Ms calculation and the 729 C line in the T0 calculation.
16. Click Plot. You should see the range of Mo and V compositions that satisfy both conditions: Ms=278 C and T0=729 C.

3. carb-dg and carb-np Models

The carb-dg model calculates the driving force for precipitation of the M2C, MC, M6C, M3C2, M7C3 and M23C6 carbides from a bcc matrix at a given temperature. The carb-np model calculates the equilibrium phase fractions of the carbides present at a given temperature.

Example 4:  Calculation of Driving Force for Nucleation of Incoherent Carbides in Fe-9Cr-15Co-1.5Ni-xMo-yV-0.24C Alloys at 510°C. (Same as Example 2-6)

Problem Definition:
The calculation of driving force for nucleation is very important for precipitation hardening alloys. In secondary hardening steels, a substantial strength contribution comes from very fine dispersion of M2C carbide precipitates. To ensure very fine dispersion of precipitates, it is necessary to maximize the driving force for nucleation, because the size of the critical nucleus is inversely proportional to the driving force (see one of my earlier notes!). The purpose of this example is to demonstrate the calculation of driving force for nucleation of M2C carbide and other carbides in secondary hardening steels.

Steps:
1. In Model Manager select the carb-dg model.
2. In TDB Manager select the ssol+m2e database.
3. In the Composition Panel set wt% C=0.24, wt% Cr=9, wt% Co=15, wt% Ni=1.5 and wt% Mo from 0 to 4 and wt% V from 0 to 0.5. Set T=510°C (note: you may have to change the selected element list).
4. Notice that there are a few extra inputs. Specify the bcc input to be 0 (Fe). As we want Incoherent M2C, specify the M2C input as 0 (incoherent). Specify the M2C APR value as 1 and M2C beta value as 0.3.
5. Click on the Compute tab. Set the grids for Mo and V.
6. Click on Compute button.
7. The program will ask for Extra Output Names. We don’t want any extra output so just click on OK.
8. The program will run the calculations. If everything goes ok it should say that the calculations are successful.
9. Click on the Create Plot Tab. The Plot title and Plot subtitles are shown at the top.
10. Click on Plot to view the Driving Forces for precipitation as a function of composition. Notice that it is plotted in the form of a contour plot with Mo on one axis and V on the other. Each of the curves then corresponds to a unique Driving Force Value. The first window is for the M2C Driving Force. Compare the values and the trend to your answer for Lab 2 Example 6. It should be similar.
11. Scroll down to view the Driving Force for precipitation for the other carbides. Overall, which carbide has the maximum driving force for precipitation?

Example 5: Calculation of Equilibrium Phase Fraction of Incoherent M2C in Fe-9Cr-15Co-1.5Ni-5Mo-0.5V-0.24C Alloy between 500-1000°C.

Problem Definition:
Using a similar composition as in the above example, we want to see how the M2C phase fraction varies with temperature

Steps:
1. In Model Manager select the carb-np model
2. In TDB Manager select the ssol+m2c database
3. In the Composition Panel set wt% C=0.24, wt% Cr=9, wt% Co=15, wt% Ni=1.5, wt% Mo=5, wt% V= 0.5 and vary T from 500-1000°C (note: you may have to change the selected element list)
4. As we want Incoherent M2C, specify the M2C input as 0 (incoherent). Specify the M2C APR value as 1 and M2C beta value as 0.3
5. Click on the Compute tab. Set the grid for T
6. Click on Compute button
7. The program will ask for Extra Output Names. We don’t want any extra output so just click on OK
8. Click to the Create Plot tab and view the plots as before.
9. Notice that as we increase the tempering temperature, the BCC phase fraction increases and the M2C phase fraction decreases (as expected)

3. Coarsen Model
In precipitation hardening systems, it is not only desirable to have very fine precipitates to begin with (at nucleation) it is equally desirable to maintain fine size scale of the precipitates for long periods of time. After the completion of precipitation, the average size of the precipitates increases with time by the process called coarsening. Using the LSW theory K is defined as

\[ F^2 - F_0^2 = \frac{4}{9} K (t - t_0) \]  \hspace{1cm} (1) 

\[ K = \frac{2\sigma V_{\beta}^B}{RT} K' \]  \hspace{1cm} (2) 

where \( r \) and \( r_0 \) are the average particle size at time \( t \) and \( t_0 \), respectively, \( \sigma \) is the interfacial energy, \( V_{\beta}^B \) is the molar volume of the \( \beta \) phase, \( R \) is the universal gas constant and \( T \) is the temperature in K.

As an example, if \( M = (Cr, Mo) \) then \( K' \) can be expressed as:

\[ \frac{1}{K'} = \frac{1}{K_{Cr}} + \frac{1}{K_{Mo}} \]  \hspace{1cm} (3) 

\[ \frac{1}{K_M} = \frac{D_{\beta}^\alpha}{(k_M - k_{Cr} \ell (k_M - 1))X_M^o} \]  \hspace{1cm} (4)
where $\beta = \text{M}_2\text{C}$ carbide phase (HCP), $\alpha = \text{matrix}$ (BCC) phase, $X_M^{\alpha}$ is the mole fraction of element M in the matrix phase, $k_M$ is the partitioning coefficient of element M, and $D_M^{\alpha}$ is the diffusivity of element M in the matrix phase. The partitioning coefficient is defined by $X_M^{\beta}/X_M^{\alpha}$, where $X_M^{\beta}$ is the mole fraction of element M in the $\beta$ phase as given by the tie-line. The *coarsen* model offers a general tool to calculate the normalized coarsening rate $K/(\sigma V_m)$ using both Lee and Morrall and Purdy (MP) models. *Coarsen* is general as it doesn’t specify the matrix and the precipitate phase names until run time. For a detailed explanation of the models used refer to the MADE manual Page 60.

Example 6: Calculation of Coarsening Rate Constant of M2C Carbide in Fe-3Cr-14Co-15Ni-1.5W-xMo-yV-0.25C Alloys at 510°C

**Problem Definition:**
The purpose of this exercise is to demonstrate the calculation of coarsening rate constant of M2C carbide phase in multi-component steels

**Steps:**
1. In Model Manager select the *coarsen* model
2. In TDB Manager select the *ssol+m2c* database
3. In the Composition Panel set wt% C=0.25, wt% Cr=3, wt% Co=14, wt% Ni=15, wt% W=1.5, wt% Mo from 1 to 5, wt% V from 0 to 0.2 and T=510°C (note: you may have to change the selected element list)
4. Notice that there are a few extra inputs. The Form Ratio is the stage of formation at which we want to calculate the coarsening rate constant. The form ratio of 0.5 represents half completion, and the corresponding coarsening rate is usually a more representative quantity for the overall kinetics. Set the Form Ratio equal to 0.5. Set the D-off dia scale to be 1.
5. Click on the Compute tab. Set the grids for Mo and V
6. Click on Compute button
7. The program will ask for Extra Input Names. We want the matrix phase to be bcc and the precipitating phase to be M$_2$C. Specify bcc in line 1 and m2c in line 2 and click on OK
8. The program will ask for Extra Output Names. We don't want any extra output so just click on OK
9. The program will run the calculations. If everything goes ok it should say that the calculations are successful
10. Click on the Create Plot Tab. The Plot title and Plot subtitles are shown at the top.
11. Click on Plot to view the Coarsening Rate Constants as a function of composition.

**4. Other Models**
carb-dg: Calculates the cementite driving force from bcc matrix
fe-dtsol: Calculates the liquidus line in Fe based system
fe-segreg: Calculates the compositional segregation during the solidification of multicomponent Fe based alloys in ingots.
fe-ts: Calculates the Solution temperature in multicomponent Fe alloys
liquidus: A general model which calculates the liquidus/single phase region in multicomponent alloys (doesn’t have to be Fe based)

**Note:** You are encouraged to familiarize yourself with the above models by using the compositions given in the exercises.

**Important:** In order to save your results in the form of a table you should click on the Save Results button under the Create Plot tab. The program saves the results in a text file in a tabular form.

**Note:** To save plots in Black and White:
1. When you have a plot open click the “print to file” button
2. In the SSH Window type: gs cmd.ps to open the saved plots in ghost viewer.
3. The files that were saved to file should appear on the screen. Copy plots and insert into homework.
4.3 Lab 3: DICTRA
In this lab you will learn how to simulate the diffusional processes in multicomponent systems using DICTRA (Diffusion Controlled TRAnsformation). DICTRA is a very convenient tool for solving multicomponent diffusion problems with systems having simple geometry, particularly for problems involving a moving boundary. DICTRA combines ThermoCalc with a procedure to solve the diffusion problem and a Newton-Raphson iteration technique to determine the migration rate of the interface and the equilibrium at phase interfaces.

- **Fick’s 2nd Law:**

  \[
  \frac{\partial c_k}{\partial t} = \nabla \cdot (D_k \nabla c_k) \quad \text{and} \quad \frac{\partial c_k}{\partial t} = \nabla \cdot (c_k M_k \nabla \mu_k) = c_k M_k \nabla^2 \mu_k
  \]

  - Reduce parameters by using mobility term
  - Separates kinetic and thermodynamic terms
  - Diffusion controlled transformations (DICTRA) solves Fick’s 2nd Law at each grid point.

For non steady state diffusion, Fick’s 2nd law is used where the change in composition of an element versus a change in time is given by the gradient of the flux (the flux is in parenthesis in the above figure). Because diffusivities are usually a function of composition it cannot be taken out to the front of this del operator. However, if we write the flux in terms of mobility, which is NOT a function of composition we can take that to the front of the del operator. This also reduces the parameters stored in the database and separates the kinetic and thermodynamic terms.

The diffusion database holds the mobility terms and the chemical potential is extracted from the thermodynamic database.

DICTRA solves Fick’s 2nd law at every grid point in the model using Thermocalc to calculate the chemical potentials needed.
Example: \( \gamma \) to \( \alpha \) transformation in a binary Fe – C alloy

This example deals with the kinetics of phase transformation from austenite (\( \gamma \)-fcc) to ferrite (\( \alpha \)-bcc) in a binary Fe-C alloy upon cooling and isothermal holding. We will start the simulation at a high temperature at 1173 K (900C) and we assume a gradual cooling down to 1050 K (777C). When we reach 1050 K we keep the temperature constant and thus have an isothermal transformation. We will assume the ferrite (\( \alpha \)-bcc) to be an inactive phase adjacent to the initial austenite (\( \gamma \)-fcc), and the cooling rate is 10 K/minute (0.1667 K/sec) down to 1050 K (777C) starting from 1173 K (900C). The composition of the alloy is Fe – 0.15wt% C.
Step 1: Open TC2017b and select “Diffusion Simulation”

Step 2: Define the system

1. Select databases
   “SSOL2” as thermodynamic database
   “MOB1” as mobility database
   (By clicking green plus button, you can add another database)

2. Choose Fe and C as elements of the system
Step 3: Define calculation conditions

1. Click on “Diffusion Calculator 1”

2. Define region 1
   - Set width = 2 * 10^{-3} [mm]
   - Set number of grid-points = 50
   - Set grid type as “Geometric” with ratio = 1.05
     (Geometric grid provides more grid-points on the left-hand side region)
   - Set Phase = “FCC_A1”

3. Click on “Edit” button for composition profiles

Select “Phases and Phase Constitution” tab
Select phases below for both SSOL2 and MOB1 databases
- BCC_A2 (Entered)
- FCC_A1 (Entered)
4. Set composition of C in austenite as “Linear” from 0.15 to 0.15 \[\text{wt}\%\] (Constant composition inside austenite region)

5. Click on “Apply” button

6. Assign ferrite phase on the left interface of austenite
   - Click on “Show left interface boundary” button
   - Select “BCC_A2” phase as a phase allowed to form
   - Set “Driving force” = $1 \times 10^{-5}$

(From these procedures, ferrite is selected as inactive phase adjacent to left interface of austenite. Driving force for ferrite nucleation will be continuously monitored during calculation, and allowed to form when the driving force exceeds $1 \times 10^{-5}$)
7. Define thermal profile
   Select “Non-isothermal”
   Click on “Edit thermal profile” button

8. Input thermal profile as shown left
   0 sec => 1173 K (900 C)
   728 sec => 1050 K (777 C)
   107 sec => 1050 K (777 C)
   
   (Cooling starts from 1173 K down to 1050 K, with the cooling rate of 10 K/minutes. Thus, cooling takes 738 sec. After the cooling, system will be kept at the constant temperature of 1050 K, until the total heat-treatment time reaches 107 seconds)

9. Click “OK”
4.3 Lab 3: DICTRA

Step 4: Define plot conditions

1. Click “Plot Renderer 1”

2. Choose X-axis as Distance
   Axis variable => Distance, μm, All regions
   Axis type   => Linear
   Limits      => Automatic scaling

3. Choose Y-axis as Composition of C
   Axis variable => Composition, C, Mass percent
   Axis type   => Linear
   Limits      => 0.0 to 0.6, step 0.1
   (Unclick “Automatic scaling”)

4. Designate which time step you would like to plot
   Input “1000 100000 1e7”
   (Please note you put space between numbers)
   (This gives you three different plots of
time = 1,000 sec
time = 100,000 sec
time = 10,000,000 sec)

10. Click “Options”

11. Choose “potential” for finding tie-line at phase interface
Step 5: Execute calculation

From the figure above, you can see that as time goes, ferrite grows, and carbon becomes homogenized in austenite phase. Please note left-hand side is ferrite, and right-hand side is austenite.

※ After 1000 sec, ferrite has already nucleated but carbon concentration in austenite is mostly unchanged from the initial value of 0.15 wt%. Only the near-interface region is enriched with carbon in austenite

※ After $10^7$ sec, ferrite has grown further, and carbon in austenite has nearly been homogenized

Step 6: Interpret the result

From the figure above, you can see that as time goes, ferrite grows, and carbon becomes homogenized in austenite phase. Please note left-hand side is ferrite, and right-hand side is austenite.

※ After 1000 sec, ferrite has already nucleated but carbon concentration in austenite is mostly unchanged from the initial value of 0.15 wt%. Only the near-interface region is enriched with carbon in austenite

※ After $10^7$ sec, ferrite has grown further, and carbon in austenite has nearly been homogenized
4.4 Lab 4: PrecipiCalc/TC-PRISMA
I. PrecipiCalc Overview
I.a. What is PrecipiCalc?
- Sophisticated software for calculating the precipitation kinetics of second phase transformations.
- Developed by Questek Innovations LLC.
- Platform: UNIX, MS Windows.

I.b. What PrecipiCalc does?
- Realistic and mechanistic modeling of nucleation, growth and coarsening without resorting to ad hoc treatments
- Relies on DICTRA (Diffusion Controlled TRAnsformation) to perform fundamental thermodynamics and mobility calculations

I.c. Applications
- Materials processing & Materials design

II. PrecipiCalc Architecture
- Layered Architecture Pattern.
- Five layers where each layer may provide services to all the layers above
  - Layer I: PrecipiCalc class, the top layer – calculating core particle size distribution evolution
  - Layer II: pcNucleation, pcTemperature, pcEnd – nucleation model, temperature profile and termination model
  - Layer III: pcGrowth – growth model based on multi-component thermodynamics and kinetics
  - Layer IV: pcLP, pcSurfEng – lattice parameter (molar volume) and surface energy
  - Layer V: pcStore class, the bottom layer – storage of particle size distribution and its associated quantities (e.g. volume fraction, mean size)

III. TC-PRISMA
The Precipitation module (TC-PRISMA) is an add-on module in Thermo-Calc which treats concurrent nucleation, growth/dissolution and coarsening under arbitrary heat treatment conditions in multi-component and multi-phase systems using Langer-Schwartz theory and the Kampmann-Wagner numerical approach. The Precipitation module (TC-PRISMA) extends the functionality available through Thermo-Calc and the Diffusion module (DICTRA) and can be used for calculations of:
- Concurrent nucleation, growth/dissolution and coarsening of precipitates
- Temporal evolution of particle size distribution
- Average particle radius and number density
- Volume fraction and composition of precipitate
- Nucleation rate and coarsening rate
- Isothermal transformation/Time-Temperature-Transformation (TTT) diagrams
- Continuous-Cooling-Transformation (CCT) diagrams
- Estimation of multi-component interfacial energy
Example 1. Isothermal Precipitation of Al$_3$Sc in Al-0.18Sc (wt%) binary alloy

This example simulates the kinetics of precipitation of Al$_3$Sc from an FCC_A1 solution phase.

**Step 1: Open TC2017b and enter GUI. Select ‘TC-PRISMA’**

![Image of TC2017b GUI with highlighted instructions]

- Click [Precipitation Simulation Demo] to begin the calculation

**Step 2: Pick Database and Elements in System**

![Image of TC2017b GUI with highlighted instructions]

- Change the database package in the dropdown menu to “Al based alloys”
- Add the elements Al, Sc and their content
Step 3: Identify Phases in System

Step 4: Set Simulation Conditions. Then Perform calculation. The calculation would take a few minutes.

Click “Check/Uncheck All” to remove all phases. Check the following phases in both databases:
- Al3Sc
- FCC_A1

Set These Conditions:
- Composition: Sc 0.18 wt%
- Matrix Phase: FCC_A1
- Precipitation Phase: Al3Sc
- Nucleation Sites: Bulk
- Interfacial Energy: Calculated

Under “Calculation Type”
- Temperature = 350 C
- Simulation Time = 1e7 s
Step 5: Plot Renderer Results

Change your plotting conditions
Y-Axis: Mean Radius, Al3Sc, Axis
Type “Logarithmic 10”.
X-Axis: Time in seconds, Axis Type
“Logarithmic 10”.
Perform To execute these changes

Other plot options
Example 2. Stable and Metastable Carbides in Fe-0.1C-12Cr (wt%) Steel - TTT Diagram

This example simulates the kinetics of precipitation of both stable and metastable carbides from ferrite phase. It demonstrates that metastable carbides may first emerge and then disappear, and the stable phase prevails.

Step 1: Open TC2017b and enter GUI. Select ‘TC-PRISMA’

Click [Precipitation Simulation Demo] to begin the calculation

Step 2: Pick Database and Elements in System

Change the database package in the dropdown menu to “Steel and Fe alloys”
Add the elements Fe, C, Cr and their content
Step 3: Identify Phases in System

Click “Check/Uncheck All” to remove all phases. Check the following phases in both databases:

- BCC_A2
- Cementite
- M23C6
- M7C3

Step 4: Set Simulation Conditions for TTT diagram. Then Perform calculation. The calculation would take a few minutes.

Under “Calculation Type”

**Temperature**: min 500°C, max 800°C, step 25°C

**Simulation Time**: 1e8 s

**Volume Fraction**: 0.0001

Set These Conditions:

- **Composition**: C 0.1 wt%, Cr 12 wt%
- **Matrix Phase**: BCC_A2
- **Precipitation Phase**:
  - Cementite, Grain Boundaries, User Defined 0.167 J/m²
  - M23C6, Grain Boundaries, User Defined 0.252 J/m²
  - M7C3, Grain Boundaries, User Defined 0.282 J/m²

Simulation Time: 1e8 s
Step 5: Plot Renderer Results

Example 3. Cooling Rate Diagram of $\gamma$-$\gamma'$ Ni-10Al-10Cr (at%) superalloy – CCT diagram

In this example, a CCT diagram for a Ni-10Al-10Cr $\gamma$-$\gamma'$ alloy is calculated and plotted with superimposition of the cooling rate values.

Step 1: Open TC2017b and enter GUI. Select ‘TC-PRISMA’
Step 2: Pick Database and Elements in System

Change the database package in the dropdown menu to “Demo Ni based superalloys”
Add the elements Ni, Al, Cr and their content

Step 3: Identify Phases in System

Click “Check/Uncheck All” to remove all phases.
Check the following phases in both databases:
DIS_FCC_A1
FCC_L12#2
Step 4: Set Simulation Conditions for CCT diagram. Then Perform calculation. The calculation would take a few minutes.

Set These Conditions:
- **Composition**: Al 10 at%, Ni 10 at%
- **Matrix Phase**: DIS_FCC_A1
- **Precipitation Phase**: FCC_L12#2
- **Nucleation Sites**: Bulk
- **Interfacial Energy**: 0.023 J/m²

Under “Calculation Type”
- **Temperature**: 500K – 1200K
- **Cooling Rate**: 0.01, 0.1, 1, 10, 100 K/s
- **Volume Fraction**: 1e-4

Step 5: Plot/Table Renderer Results
Click the ‘Temperature’ or ‘FCC_L12#2’
The results can be shown in ascending or descending sort.
5 Problems
5.1 Materials Selection in Mechanical Design

Note: In order to receive credit for the CES materials selection problems, you must:

- answer the questions
- explain the process used to get your answers
- include ALL relevant CES plots with explanations of the information given on each plot in all problems. CES plots should be properly enlarged in specific regions if needed, and failed records of materials (materials that do not satisfy the criteria shown in gray) should be hidden.

There is no unique answer to the questions. Therefore, your grade will not be determined by the particular materials you choose. You can select any materials that satisfy the criteria and as long as you explain the process used to get your answer.

Start from “Level 3” database and “All bulk materials” for all problems.

To change units go to: tools → settings → units → <automatic-metric> or <metric>

1) General use of the CES database: Answer the following using CES database:

(a) A component is currently made of soft commercially pure Gold. Due to high cost of gold, please use CES to suggest two other materials that have greater thermal conductivity.

(b) Find a material with $250 < E < 350$ GPa and density $7,000 < \rho < 8,000$ kg/m$^3$.

(c) Which have higher specific stiffness, $E/\rho$: titanium alloys or tungsten carbides?

(Hint: use ‘Tree’ in the selection stage to select titanium alloys and tungsten carbides only)

(d) Is the fracture toughness, $K_{IC}$, of common engineering polymers like PVC elastomer (Shore A60) higher or lower than those of engineering ceramics like silicon carbide (HIP)?
2) **Multi-stage materials selection using CES database**  You are employed by a company that manufactures various sports goods except tennis rackets. Even though the company is doing well, in an effort to expand company’s market the management decided to introduce a new product: tennis rackets. Being the only Materials Engineer in the company your new assignment is to select four different materials that would be suitable for manufacturing tennis rackets.

Since you have already used CES, you should not have any problem in getting started. First, let us examine the essential functions of a body of a tennis racket: structural support for the string, transfer of force, absorption of energy (damping) etc. Often, the tennis rackets are also subjected to mechanical abuse (due to bad temper or frustration of the players). Thus, the optimal materials must be light, stiff, strong, and should have reasonably good fracture toughness. In conjunction with the CES database, the following multi-stage criteria may be applied to select off-the-shelf materials suitable for manufacturing tennis rackets.

**Stage I:** Assume that due to the complex shape of the body of the tennis racket the maximum stiffness at minimum weight is given by the following performance index:

\[ M_1 = \frac{\sqrt{E}}{\rho} \]  \hspace{1cm} (5.1)

where \( E \) is the Young’s Modulus, and \( \rho \) is the density.

**Stage II:** The maximum ductile strength of rods at minimum weight is given by the following performance index:

\[ M_2 = \frac{\sigma_{y}^{0.8}}{\rho} \]  \hspace{1cm} (5.2)

where \( \sigma_{y} \) is the yield stress (Elastic Limit in CES).

**Stage III:** The maximum fracture toughness of rods at minimum weight is given by the following performance index:

\[ M_3 = \frac{K_{IC}}{\rho} \]  \hspace{1cm} (5.3)

where \( K_{IC} \) is the fracture toughness.

**Stage IV:** Selection of materials that will give minimum density and maximum damping capacity. In CES, the damping behavior is represented by the Mechanical Loss Coefficient under Optical, aesthetic and acoustic properties. A higher mechanical loss coefficient implies a better damping capacity. Use Box Method for selecting a subset of materials (with \( \rho < 2,000 \text{ kg/m}^3 \) and mechanical loss coefficient greater than 0.008) in this stage.
Use the above four stages of selection to determine the optimal materials for tennis racquets. The materials must also satisfy the following:

- \( M_1 > (0.001 \text{ GPa})^{0.5}/(\text{kg/m}^3) \)
- \( M_2 > (0.01 \text{ MPa})^{0.8}/(\text{kg/m}^3) \)
- \( M_3 > (0.02 \text{ MPa}\sqrt{\text{m}})/(\text{kg/m}^3) \)

Turn in the following:

(a) Graphical output for each stage showing the selection line/box. In the report, you must explain how you have drawn the selection line in each stage;

(b) Table for Materials passing 4 of the 4 stages

(c) Select four different materials that passed all the stages for manufacturing tennis racquets. At this stage you may consider cost (listed in CES) so that racquets will have a wide range of price. List the Young’s modulus, the yield stress, the fracture toughness, the loss coefficient, and price of the materials you selected, in a table like the one outlined below:

<table>
<thead>
<tr>
<th>Material</th>
<th>( E ) (Pa)</th>
<th>( \sigma_y ) (Pa)</th>
<th>( K_{IC} ) (MPa(\sqrt{\text{m}}) )</th>
<th>Mech. Loss Coeff.</th>
<th>Price</th>
</tr>
</thead>
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3) **Multi-stage materials selection using CES database:** As an engineer at a minor aircraft company, you have been given the task of determining the proper material for use as an aircraft door. After research you have determined nine properties that the material must possess. They are as follow:

- Fracture toughness, \( K_{IC} > 40 \text{ MPa}\sqrt{\text{m}} \)
- Young’s Modulus, \( E > 100 \text{ GPa} \)
- Density, \( \rho < 5,000 \text{ kg/m}^3 \)
- Thermal Expansion \(< 20\times10^{-6}/\degree\text{C} \)
- Elongation \( > 10 \% \)
- Cost \(< 20 \text{ USD/kg} \)
- Recycle fraction in current supply \( > 20 \% \)
• Flammability = {non-flammable}
• Durability in fresh water = {excellent}

Determine a suitable material for this application

5.2 Thermo-Calc

Requirements for Thermo-Calc questions:

• Your answers to all of questions must be substantiated by calculated diagrams and I should be able to make out as to what you have to plot in the figure(s)

• Everyone must submit his/her own calculated diagram(s)

• The title of the phase diagrams MUST be your name

• All phase fields must be labeled; and (v) a copy of the equilibrium results obtained from the TC 2017b window must accompany the answers that require equilibrium calculations

• You will receive an automatic zero if it is found that you have submitted someone else’s phase diagram or graph.

• Warning: The phase labeling function of TC2017b occasionally gives you obviously wrong results. You may try removing all labels and adding them again, or adjusting window/graph sizes. If you can’t get it right from the software, clarify the situation and give your answers in your homework.

4) Pb-Sn solders are widely used in electronic packaging (chip-to-chip and chip-to-carrier interconnections) and various other applications related to soldering. However, due to toxicity of Pb and environmental concerns, Pb-Sn solders have been banned in many applications, such as, food packaging (e.g., beverage cans), certain plumbing applications etc. The Sn-In phase diagram is important for designing multicomponent Pb-free solders.

Hints: (i) Use SSOL2 database; (ii) For both the Pb-Sn and In-Sn systems, consider the following phases only: LIQUID, FCC_A1 and BCT_A5; (iii) temperature limits for mapping: 0 – 400°C for both alloys. In the SSOL database, the Sn-phase is defined by BCT_A5, because its structure is body centered tetragonal, the In-phase and Pb-phase are defined by FCC_A1, because both of their structures are face centered cubic.
5.2 Thermo-Calc

(a) Calculate Pb-Sn and In-Sn equilibrium phase diagrams. You have to submit the calculated phase diagrams with all phase fields labeled.

(b) What are the calculated eutectic temperatures in Pb-Sn and In-Sn systems?

(c) What are the calculated solid solubilities of Pb in Sn and In in Sn at their respective eutectic temperatures? Answer this question both in weight and atomic percents of Pb and In.

(d) Despite toxicity/environmental concerns, Pb-Sn solders are widely used in all microelectronic packages. In particular, the Pb-Sn eutectic alloy. For a Sn-38 wt.% Pb alloy, answer the following:
   i What are the phases present at 50°C and 130°C? (Note: many devices, such as computers operate in this temperature range)
   ii What are the amounts and composition (in wt%) of the phases present at 50 and 130°C?
   iii What are the important differences you notice between the calculated results at these two temperatures?

5) Calculation of the Ms temperature (temperature when martensite starts to form) is a very crucial step in designing ultra-high strength, secondary hardening martensitic steels. Such a calculation allows us to select the alloy(s) whose Ms is sufficiently high so that upon quenching (from solution treatment temperature) to room temperature a fully martensitic microstructure is obtained. If the Ms is not high enough, then we may get incomplete transformation at room temperature and the alloy will need to be quenched at subambient temperatures. Therefore, an alloy with an Ms>300°C would be desirable.

Hints: (i) Use the SSOL2 database; (ii) consider the following phases for 2.1-2.4: BCC_A2 and FCC_A1, consider the following phases for 2.5: LIQUID, BCC_A2, FCC_A1, HCP_A3, SIGMA, CEMENTITE, M23C6, and M7C3 (iii) stepping ranges for 2.1-2.4: 200 to 1000°C for temperature; mapping ranges for 2.5: 750 to 1250°C for temperature (iv) A solution treatment temperature is defined as the temperature at which all solutes will be in solid solution in one phase.

Given the alloy Fe – X wt. % C – 14 wt. % Co – 8 wt. % Cr – 6 wt% Ni – 0.5 wt. % Mo – 0.3 wt. % V

(a) What is the T0 temperature of the above alloy as a function of C content at 0.1 wt%, 0.3 wt%, 0.5 wt%, 0.7wt% and 0.9 wt%?

(b) Comment of the effect of C on the T0 temperature.
(c) Assuming that the martensitic transformation starts at a Driving Force of -1500 J/mol, what is the Ms temperature of the above alloy as a function of C content at 0.1 wt%, 0.3 wt%, 0.5 wt%, 0.7 wt% and 0.9 wt%?

(d) Comment on the compositional dependence of Ms temperatures and determine which alloy(s) would be appropriate for the application stated in the above question.

(e) Calculate the vertical section of this alloy. For a solution treatment temperature of 1000°C, what is the maximum amount of C that can be put in the alloy? Show this point of the phase diagram.

5.3 DICTRA and PrecipiCalc/TC-PRISMA

To receive credit:

- Your answers to all of questions must be substantiated by calculated diagrams or table renderer results
- everyone must submit his/her own calculated diagram(s)
- the title of the phase diagrams MUST be your name

5.3.1 DICTRA

6) \( \gamma \) to \( \alpha \) transformation in a ternary Fe-0.15wt%C-0.50wt%Si steel, when cooled from 1173K down to 1050K with the cooling rate of 10K/minute, and then isothermally held at 1050K until total heat-treatment time reaches 107 sec.

(a) Provide a plot of carbon concentration vs distance at t=1000, 100000, 107 sec.

(b) Provide a plot of silicon concentration vs distance at t=1000, 100000, 107 sec. Compare with the plot of the carbon concentration. Which element do you think is more mobile in this steel at this temperature, C or Si?

Hints:

- Use the SSOL2 database as thermodynamics database, and MOB1 database as mobility database
- Consider the following phases: FCC_A1 (\( \gamma \), austenite) and BCC_A2 (\( \alpha \), ferrite)
• assume fully homogenized austenite (FCC_A1) at the beginning of the heat-treatment
• apply 50 grid-points of geometric grid with ratio = 1.05 in the initial austenite region
• assume ferrite starts to form when the driving force exceeds 10^-5 (vi) use potential (not activity) for finding tie-line at the phase interface

5.3.2 TC-PRISMA

7) Isothermal precipitation calculation of $\gamma$-$\gamma'$ Ni-12Al (at%) alloy at 450 °C for 1e15 s

Hints:
• Use the Demo Ni alloys database package
• Consider the following phases: DIS_FCC_A1 (matrix) and FCC_L12#2 (precipitate)
• Precipitate nucleation sites: bulk, interfacial energy 0.035 J/m²

(a) What is the maximum number density of precipitate? How long does it take to reach the maximum number density of precipitates (in hours)?
(b) What is the volume fraction of precipitate phase and matrix composition (Al concentration in at%) at 1e15 s?

8) 3. Isothermal precipitation calculation of metastable and stable carbides in Fe-0.1C-12Cr (wt%) at 750 °C for 1e6 s

(a) From the volume fraction vs. time figure, can you tell the sequence of precipitation?

Hints:
• Use the Steel and Fe alloys database package;
• consider the following phases: BCC_A2 (matrix), CEMENTITE (precipitate), M23C6 (precipitate), and M7C3 (precipitate)
• precipitate nucleation sites: grain boundaries
• interfacial energy: CEMENTITE (0.167 J/m²), M23C6 (0.252 J/m²), M7C3 (0.282 J/m²)
• plot volume fraction of all three carbides (linear) vs. time (log 10)

(b) Can you obtain this precipitation sequence without doing this isothermal calculation?
Hint: Example 2 in Lab 5b tutorial

(c) What the volume fraction of the stable precipitate phase at 1e6 s? How about its equilibrium volume fraction?

Hint: TC single point equilibrium calculation using TCFE9 database with BCC_A2, CEMENTITE, M23C6, and M7C3 entered