





# Phase diagrams

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# Definition

- A **Phase Diagram** describes the state of a materials system in thermodynamic equilibrium as a function of temperature, pressure and composition.
- **Phase Diagrams** are maps of the equilibrium phases associated with various combinations of temperature, pressure, and composition.
- A **Phase Diagram** is a type of chart used to show conditions at which thermodynamically distinct phases can occur at equilibrium.







# Components and phases

### • Components:

The elements (or compounds) which are mixed initially

### • Phases:

The physically and chemically distinct material regions that result *in other words:* 

The phase is a homogeneous part of the space and the phase is limited by a phase boundary







# Thermodynamic equilibrium

• Condition for 2 phases to be in equilibrium

$$\mu_{\mathsf{A}}^{\alpha} = \mu_{\mathsf{A}}^{\beta}$$
$$\mu_{\mathsf{B}}^{\alpha} = \mu_{\mathsf{B}}^{\beta}$$

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## Thermodynamic equilibrium









# What do we need phase diagrams for?

For example:

- to understand solidification processes
  - $\rightarrow$  microstructure  $\rightarrow$  properties
- to characterize compounds and phases
  - Cu<sub>5</sub>Zn<sub>8</sub>, InSb, ...
- to understand reactions
  - Soldering, surface layers, ...







# Number of metallic phase diagrams

### (assuming: 80 metallic elements)

No. of components	No. of possible systems	Approx. No. of investigated systems
1	80	80
2	3 160	2500
3	82 160	3000
4	1 581 580	200
5	24 141 016	20
6	300 500 200	-
	•••	

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# Where to look for phase diagrams?

- Collections of phase diagrams (printed):
  - T.B. Massalski et al. (Ed.) Binary Alloy Phase Diagrams, 2nd Edition (3 volumes) (ASM International 1990)
  - P. Villars, A. Prince, H. Okamoto (Ed.): Handbook of Ternary Alloy Phase Diagrams (10 Volumes), ASM International (Materials Park, OH), 1992.
  - ASM Handbook Vol. 3 Alloy Phase Diagrams, ASM International 1992
- Collections of phase diagrams (online):
  - SGTE Free Binary Alloy Phase Diagrams (and many others) http://www.crct.polymtl.ca/fact/documentation/







# Where to look for phase diagrams?

- Journals on phase diagrams:
  - Journal of Phase Equilibria and Diffusion (Springer)
  - CALPHAD Computer Coupling of Phase Diagrams and Thermochemistry (Elsevier)
- Books on phase diagrams:
  - B. Predel, M. Hoch, M. Pool, "Phase Diagrams and Heterogeneous Equilibria" Springer (2004)







# Gibbs phase rule

$$P + F = C + 2$$

- P = number of phases
- C = number of components
- F = degrees of freedom (number of variables that can be varied independently) (T, p, X<sub>i</sub>)

If the pressure is kept constant:

$$P + F' = C + 1$$

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# Lever rule

If we know T and X<sub>B</sub> then we know:

- how many and what phases are present
- the composition of each phase
- the amount of each phase:
  - $F_{\alpha} = a / (a+b)$  $F_{L} = b / (a+b)$









# Definition of composition

• Molar (atomic) fraction 
$$x_A = \frac{n_A}{\sum_i n_i}$$
  $\sum_i x_i = 1$ 

• Atomic percent  $at\% A = x_A \cdot 100$ 

• Mass fraction 
$$w_A = \frac{m_A}{\sum_i m_i} \quad \sum_i w_i = 1$$

• Weight (mass) percent  $wt\% A = w_A \cdot 100$ 

$$wt\% A = \frac{x_A \cdot M_A}{x_A \cdot M_A + x_B \cdot M_B} \cdot 100$$

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# Unary phase diagrams, example: H<sub>2</sub>O



a, b: 
$$C = 1$$
,  $P = 1$   
 $F = 1 - 1 + 2 = 2$   
c:  $C = 1$ ,  $P = 2$   
 $F = 1 - 2 + 2 = 1$   
Triple pt.:  
 $C = 1$ ,  $P = 3$   
 $F = 1 - 3 + 2 = 0$ 

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# Binary Phase Diagrams

- Isomorphous Systems
- Eutectic Systems
- Eutectoid Systems
- Peritectic Systems
- Peritectoid Systems
- Monotectic Systems
- Syntectic Systems
- Congruent transformations

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## Isomorphous systems



#### Information from this diagram:

• Two phases:  $\alpha$  and L, but three phase fields:

L, L+α, α

- Pure Ni melts at 1455°C
- Pure Cu melts at 1085°C
- Pure component melts at a fixed temperature, an alloy melts in a temperature range.
- Cu-80at%Ni starts to melt at 1382°C (solidus), and becomes complete liquid at 1398°C (liquidus)
- Liquid and solid coexist between the liquidus and solidus temperatures

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### Isomorphous systems, Equilibrium solidification









### Isomorphous systems, nonequilibrium solidification



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## Examples of isomorphous systems: Ag-Au



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## Special cases of isomorphous systems: Au-Ni, Au-Cu



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## Eutectic systems



#### Information from this diagram:

- Eutectic reaction occurs at 187°C and 76 at% Sn:  $L \leftrightarrow \alpha + \beta$ .
- Alloy (0.31<x\_{Sn}<98%) starts to melt at eutectic reaction temperature 187°C and becomes complete liquid at liquidus.
- Alloy ( $x_{Sn}$ <0.31 or  $x_{Sn}$ >98%) starts to melt at solidus, and becomes complete liquid at liquidus.
- Solubility limit of Sn in  $\alpha$  phase varies with temperature, maximum solubility of Sn in  $\alpha$  phase is 31 at% at 187 °C.

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#### Microstructure of eutectic alloy L (76%Sn) 400 (76%Sn) a (31%Sn) ß 300 (98%Sn) Temperature[°C] L+a C. (31%Sa) 200-187°C α 0.98 0.31 0,76 (98%Sn) 100- $\alpha + \beta$ 0.2 0.4 0.6 0.8 Pb x(Sn) Sn $L(76 \text{ at \% Sn}) \xrightarrow[heating]{\text{cooling}} \alpha(31 \text{ at \% Sn}) + \beta(98 \text{ at \% Sn})$ Adapted from www.computherm.com Project WND-POWR.03.02.00-00-1043/16







## Microstructure of solid solution $\alpha$









#### Microstructure of an alloy which exceeds solubility limit L (Co) 400 L 300 Temperature[°¢] O. L+a 200 187°C α 0.31 0.76 0.98 CL. (Co) 100 $\alpha + \beta$ 0.2 0.4 0.6 0.8 a Pb x(Sn) Sn β Adapted from www.computherm.com Project WND-POWR.03.02.00-00-1043/16 International interdisciplinary PhD Studies in Materials Science with English as the language of instruction

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## Ag-Cu system



F = C - P + 2 P = const.F' = C - P + 1

a, b: 
$$C = 2$$
,  $P = 1$   
 $F' = 2 - 1 + 1 = 2$   
c:  $C = 2$ ,  $P = 2$   
 $F' = 2 - 2 + 1 = 1$   
e:  $C = 2$ ,  $P = 3$   
 $F = 2 - 3 + 1 = 0$ 

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## Examples of eutectic systems: Ag-Bi, Sn-Zn



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## Examples of eutectic systems: Al-Si, Bi-Cu



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### Examples of eutectic systems: Bi-Cu



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# Eutectoid systems



#### Information from this diagram:

- Fe-C stable phase boundaries are represented by pink dot lines, and Fe-Fe<sub>3</sub>C metastable phase boundaries are represented by blue solid lines.
- Fe<sub>3</sub>C phase is a line compound (6.7 wt% of Carbon) without any solubility.
- Carbon is an interstitial impurity in iron and forms a solid solution with the  $\alpha$ ,  $\gamma$ ,  $\delta$  phases.
- Eutectoid reaction is a solid state reaction
- with no liquid involved:  $\gamma \leftrightarrow \alpha + \mathbf{Fe_3C}$ .

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## Fe-Fe<sub>3</sub>C system, formation of pearlite

Due to the eutectoid reaction:  $\gamma \leftrightarrow \alpha + Fe_3C$ , pearlite structure is formed. Pearlite: alternating layers of  $\alpha$  and  $Fe_3C$  phases, not a single phase.



- Nucleating at  $\gamma$  grain boundaries.
- Growth by diffusion of carbon to achieve the compositions of  $\alpha$  and Fe<sub>3</sub>C (with structure changes).
- According to lever rule, the amount of  $\alpha$  is much larger than that of Fe<sub>3</sub>C, resulting in a much thicker  $\alpha$  lamellae.



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#### Fe-Fe<sub>3</sub>C system proeutectoid Y 1600 microstructure Y 8 1400 ) 1200 emperature γ, Austenite 1000 Cementite α 800 Fe<sub>3</sub>C, $\alpha$ , Ferrite 600 Proeutectoid $\alpha$ 400 6 2 5 3 Fe Composition (w% C) Fe<sub>3</sub>C Adapted from Eutectoid a www.computherm.com Project WND-POWR.03.02.00-00-1043/16 International interdisciplinary PhD Studies in Materials Science with English as the language of instruction

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#### Fe-Fe<sub>3</sub>C system, hypereutectoid Y microstructure 1600 8 1400 Fe<sub>3</sub>C emperaturel°C Austenite 1000 Cementite Fe<sub>3</sub>C 800 Fe<sub>3</sub>C, a, Ferrite 600 400 -Pearlite 6 5 3 Fe Composition (w% C) Adapted from Fe<sub>3</sub>C www.computherm.com Project WND-POWR.03.02.00-00-1043/16 International interdisciplinary PhD Studies in Materials Science with English as the language of instruction

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## Peritectic systems



#### Information from this diagram:

• Peritectic reaction occurs at 1186°C, Liquid containing 80 at% Ag reacts with  $\gamma_1$  containing 22 at% Ag:

#### $\mathbf{L} + \boldsymbol{\gamma}_1 \leftrightarrow \boldsymbol{\gamma}_2.$

- Alloy (22%<x<sub>Ag</sub><59%) starts to melt at peritectic reaction temperature 1186°C and becomes complete liquid at liquidus.
- Alloy (x<sub>Ag</sub><22% or x<sub>Ag</sub>>59%) starts to melt at solidus, and becomes complete liquid at liquidus.

# Adapted from www.computherm.com

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#### Microstructure in a peritectic system, L 0.22 < x(Ag) < 0.592000 L emperature<sup>[°</sup>C] 1500 71 1186°C 0.80 0.59 000 YI $\gamma_2$ 71 72 500-0.4 0.6 0.2 0.8 0 Pt x(Ag) Ag 71 72

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## Bi-Ni system (another example)



#### Information from this diagram:

- Two peritectic reactions and eutectic reaction
- Peritectic reaction L + FCC ↔ BINI occurs at 645.9°C.
- Peritectic reaction L + BINI  $\leftrightarrow$  BI3NI occurs at 464.8°C.
- Eutectic reaction  $L \leftrightarrow BINI + RHOMBO$ ocurs at 269°C.
- Incongruent melting of phases Bi3Ni and BiNi.

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## Peritectoid systems



#### Information from this diagram:

- Peritectoid reaction is a solid • state reaction without any liquid involved.
- Peritectoid reaction occurs at • 358°C and 18.6 - 24.8 at% Al:  $\alpha + \xi \leftrightarrow \mu$ .

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## Monotectic systems



#### Information from this diagram:

- Monotectic reaction occurs at 663°C and 6 at% In:  $L_1 \leftrightarrow \alpha + L_2$ .
- Alloys of all compositions start to melt at eutectic temperature 156°C:  $L \leftrightarrow \alpha + \beta$ .
- Alloy (x<sub>In</sub><6at% or x<sub>In</sub>>88at%) becomes complete liquid at liquidus.
- Alloy (6at%<x<sub>In</sub><88at%) becomes complete liquid mixture (two liquids with different compositions) at 663°C.

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### Examples of monotectic systems: Cu-Pb, Ag-Ni



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## Monotectoid sytems



#### Information from this diagram:

- Monotectoid reaction occurs at 277.2 °C and 59 at% Zn: FCC\_#2 ↔ FCC\_#1 + HCP
- Solubility limit of Zn in FCC phase varies with temperature, solubility of Zn in FCC phase is 14 at% at 277.2 °C.
- Eutectic reaction occurs at 380.9°C and 88 at% Zn: L ↔ FCC + HCP.

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## Synthetic systems



#### Information from this diagram:

- Syntectic reaction occurs at 557°C:  $L_1 + L_2 \leftrightarrow NaZn_{13}$ .
- Alloys ( $x_{Zn}$ <92.3at%) start to melt at eutectic temperature 98°C: L  $\leftrightarrow \alpha$ +NaZn<sub>13</sub>.
- Alloys (x<sub>Zn</sub>>92.3at%) start to melt at eutectic temperature 419°C: L ↔ β+NaZn<sub>13</sub>.
- Alloy (x<sub>Zn</sub><9.4at% or x<sub>Zn</sub>>94.4at%) becomes complete liquid at liquidus.
- Alloy (9.4at%<x<sub>Zn</sub><94.4at%) becomes complete liquid mixture (two liquids with different compositions) at 557°C.

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### Summary of invariant reactions in binary systems

Reaction	Symbolic equation	Schematic presentation	Example
Eutectic	$L \leftrightarrow \alpha + \beta$	$\alpha \rightarrow \beta$	Cu-Ag, Pb-Sn, Al-Si
Eutectoid	$\alpha \leftrightarrow \beta + \gamma$	$\beta \rightarrow \gamma$	Fe-C
Peritectic	$L+\alpha \leftrightarrow \beta$	$\alpha / \beta / \ell$	Cu-Fe, Pb-In
Peritectoid	$\alpha$ + $\beta$ $\leftrightarrow$ $\gamma$	$\alpha \rightarrow \gamma \qquad \beta$	Al-Cu
Monotectic	$L_1 \leftrightarrow L_2 + \alpha$	$\alpha$	Cu-Pb, Al-In
Monotectoid	$\alpha_1 \leftrightarrow \alpha_2 + \beta$	$\beta \rightarrow \alpha_2 \qquad \alpha_2$	Al-Zn
Syntectic	$L_1 + L_2 \leftrightarrow \alpha$	$L_1/$	Na-Zn

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## Congruent transformations, example: Mg-Si



Congruent transformation - when one phase changes directly into another without change in composition. L  $\leftrightarrow \beta$ 

 $\alpha$  = (Mg)  $\beta$  = Mg<sub>2</sub>Si  $\gamma$  = Si

System can be divided into two independent eutectic systems.

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### Congruent Transformations, examples: In-Sb, Cu-Mg



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## Intermetallic compounds (Phases) - nomenclature

Frequently designated by Greek letters:  $\alpha$ ,  $\beta$ ,  $\gamma$ ,  $\delta$ , ...

- Sometimes:  $\rightarrow \beta$  for bcc phases
  - $\rightarrow \gamma$  for compounds with g-brass structure (Cu<sub>5</sub>Zn<sub>8</sub>)
  - → σ for compounds with a certain tetragonal structure (as in Fe-Cr system)
- Sometimes designated as compound, like:

 $\rightarrow$  Mg<sub>2</sub>Si, Cu<sub>3</sub>Sn, Cu<sub>5</sub>Zn<sub>8</sub>, ...

• Sometimes non-stoichiometry is indicated, for example:

$$\rightarrow$$
 Fe<sub>1-x</sub>S, Ni<sub>1±x</sub>Sb, ...







### Congruent Transformations, example: Fe-Cr



a: melting point minimum

b: congruent transformation  $\gamma \leftrightarrow \alpha$  at minimum

c: congruent transformation  $\alpha \leftrightarrow \sigma$  at maximum

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### A case of Ag-Pt system



Karakaya & Thomson, Bull. Alloy Phase Diagr. 1987 (reproduced in ASM Handbooks)



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### A case of Ag-Pt system



Durussel & Feschotte, J. Alloy Compd. 1996

#### Microstructure of 53 at% Pt Ag-Pt alloy



#### Hart et al., Acta Mater. 2017

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## Experimental detemination of phase diagrams

- Isothermal techniques
  - Metallography
  - X-rays
  - Quantitative determination of phase compositions in multi-phase fields
  - Diffusion couples
- Non-isothermal techniques
  - Thermal analysis techniques (TA, DTA, DSC)
  - Chemical potential techniques
  - Magnetic susceptibility techniques
  - Resistivity, dilatometric methods







## Main phase diagram software and database sellers







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### Commercial database example: PanMo

Table 1.3: Modeling status for all the constituent binary systems





#### Table 1.4: Modeling status for all the constituent ternary systems

· Full description	Al-C-Mo	Al-Cr-Mo	Al-Fe-Mn	Al-Fe-Si	Al-Mn-Si	B-C-Mo	B-Hf-Mo	B-Mo-Re
	B-Mo-Si	B-Mo-Zr	B-Si-Ti	C-Cr-Mo	C-Fe-Mo	C-Hf-Mo	C-Mn-Mo	C-Mo-Re
: Full description for major phases	C-Mo-Si	C-Mo-Ti	C-Mo-Zr	Cr-Fe-Ti	Cr-Mo-Ti	Cr-Mo-Zr	Fe-Mo-Si	Hf-Mo-Si
: Extrapolation	Mo-Re-Si	Mo-Si-Ti	Mo-Si-Zr					

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### Own database example: Li-Mg-Sc system



J. Dutkiewicz, Ł. Rogal, D. Kalita, P. Fima, J. Alloy Compd. 784 (2019) 686-696

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## Ternary phase diagrams – how to read them

- Isothermal Section
- Isopleth
- Liquidus Projection
- Lever Rule in Ternary Field

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### Reading composition in a ternary phase diagram **Isothermal Section:**

- **Fixed Temperature**
- Composition represented on equilateral Triangle
- For low concentration of one component, use a right-angled triangle (e.g. Fe-Cr-C)





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## Reading a ternary phase diagram

- Isothermal Section:
- Phase boundary (Blue)
- Tie-line (Green)
- Tie-triangle (Red)









## Reading a ternary phase diagram

- Isopleth:
- Y-axis: temperature
- X-axis: composition
- Tie-line may not lie on the section



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## Reading a ternary phase diagram

- Liquidus Projection: •
- Univariant line (Blue)
- Isothermal line (Green)
- Primary phase region









### **Isothermal Section:**

Lever rule on tie-line 

### Reading a ternary phase diagram



In Alloy P, two phases are in equilibrium: Fraction of  $\alpha$  = Length(PN) / Length(MN) Fraction of  $\gamma$  = Length(MP) / Length(MN)

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### **Isothermal Section:**

Lever rule on tie-triangle 

### Reading a ternary phase diagram



In Alloy P, three phases are in equilibrium: Fraction of  $\alpha$  = Area(PON) / Area(MNO) Fraction of  $\beta$  = Area(PMN) / Area(MNO) Fraction of  $\gamma$  = Area(POM) / Area(MNO)



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## Types of Ternary Phase Diagrams

- Isomorphous System
- Ternary Three-phase Equilibrium
- Ternary Four-phase Equilibrium
  - Class I Reaction
  - Class II Reaction
  - Class III Reaction
- Congruent Transformation
- A Complex System

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### Isomorphous system

Case: Three binaries are all isomorphous with 2 cigar shape phase boundaries and 1 maximum.



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#### Case: Isothermal sections in decreasing T order.



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#### Case: Isopleths parallel to the B-C binary



## Adapted from www.computherm.com







#### Case: Liquidus projection has no univariant line.



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## Ternary Three-Phase Equilibrium

Case I: Two eutectic binary systems and one isomorphous with Cigar shape phase boundary.



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#### Case I: Isothermal sections in decreasing T order.









Liquidus has one univariant line starting from A-B binary and ending at B-C binary, which separates 2 primary phase fields, Fcc and Bcc.









Liquidus looks similar for:

Case II: Two peritectic binary systems and one Case III: One peritectic binary, one eutectic isomorphous with cigar shape phase boundary. binary and one isomorphous with cigar shape phase boundary. binary and one isomorphous with cigar shape phase boundary.

А Α Liquidus Liquidus 900°C 850°C 0.8<sub>→</sub>/ψ 0.8 950° 800° Adapted from www.computherm.com 0.6 tal a E E 750°C Fcc 0.4 0.4 7100°C Fcc 700°C Bcc 150°C 0.2 0.2. Bcc 850°C 650°C 1050°C 100°C 000°C 000°C 800°C 750°C 700°C 950°C 150°( 600°C 550°C 0.4 0.6 0.8 0.8 0.2 0.2 0.6 0.4 В x(C)С x(C) В

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# Case IV: One eutectic binary and Two isomorphous with Cigar shape phase boundary.



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#### Case IV: Isothermal sections in decreasing T order.









Liquidus has one univariant line starting from A-B binary and ending at a minimum in the ternary field, and only one primary phase field, Fcc.








Liquidus has one univariant line starting from a maximum in the ternary field and ending at A-C binary, and only one primary phase field, Fcc.









# Case VI: Two eutectic binary systems and one isomorphous with Cigar shape phase boundary.



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### Case VI: Isothermal sections in decreasing T order.









Liquidus lines start from a maximum in the ternary field, go separately in opposite directions and end at the two eutectic reactions in the binaries. Two primary phase fields, Fcc and Bcc.









### Ternary four-phase equilibria – class l

Class I: Three eutectic binary systems.



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### Class I: Isothermal sections in decreasing T order.









Liquidus lines start from the three eutectic reactions in the binaries, join together at one point in the ternary field. Three primary phase fields, Fcc, Bcc and Hcp.









### Isopleths through B-A<sub>0.6</sub>C<sub>0.4</sub> and B-A<sub>0.415</sub>C<sub>0.585</sub>



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Characteristics to determine whether it is a Class I four-phase equilibrium:

### Before Reaction: 3 three-phase triangles After Reaction: 1 three-phase triangle









### Ternary Four-Phase Equilibrium – Class II

Class II: Two eutectic binary and one peritectic binary systems.



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### Class II: Isothermal sections in decreasing T order.









Liquidus lines start from the peritectic reaction in A-B binary and the eutectic reaction in A-C binary, join together at one point in the ternary field and then go to the eutectic reaction in B-C binary. Three primary phase fields, Fcc, Bcc and Hcp.









### Isopleths through 25 at.% A and 20 at.% A



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Characteristics to determine whether it is a Class II four-phase equilibrium:

Before Reaction: 2 three-phase triangles

After Reaction: 2 three-phase triangles









### Ternary Four-Phase Equilibrium – Class III

Class III: One eutectic binary and two peritectic binary systems.



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### Class III: Isothermal sections in decreasing T order.









Liquidus lines start from the eutectic reaction in A-B binary, split into two directions in the ternary field and end at the peritectic reactions in A-C and B-C binaries. Three primary phase fields, Fcc, Bcc and Hcp.









### Isopleths through 65 at.% C and 72 at.% C



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Characteristics to determine whether it is a Class III four-phase equilibrium: Before Reaction: 1 three-phase triangle

After Reaction: 3 three-phase triangles









### Congruent Transformation

Case I: Congruent melting in one binary and form a pseudobinary in the ternary field.



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### Case I: Isothermal sections in decreasing T order.









### Case I: Isothermal sections in decreasing T order.









### The isopleth through $A_{0.5}B_{0.5}$ -C is a pseudo-binary system.



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The isopleth through  $A_{0.5}B_{0.5}$ -C cuts the liquidus projection into two parts and each one contains a class I four-phase equilibrium. The red point is a maximum in the liquidus surface.









### The isopleth through $A_{0.5}B_{0.5}$ -C is not a pseudo-binary system.









The liquidus projection contains one class I four-phase equilibrium and one class II four-phase equilibrium.









# Case III: Binaries are all eutectic systems, and there is a ternary compound which melts congruently in the ternary field.



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### Adapted from www.computherm.com







### Case III: Isothermal sections in decreasing T order.









### Case III: Isothermal sections in decreasing T order.



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The delta primary phase appears as an island in the ternary field and there are three class I four-phase equilibria. The red points are three maximums in the liquidus surface.









### A complex ternary system

A complex ternary system involving all three classes of four-phase equilibrium.

Binaries contain three solid solution phases: Fcc, Bcc, and Hcp, and three intermetallic compounds: Delta, Gamma and Epsilon.









#### Isothermal sections showing the invariant reaction 1 in detail.



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#### Isothermal sections showing the invariant reaction 2 in detail.



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#### Isothermal sections showing the invariant reaction 3 in detail.



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Isothermal sections showing the invariant reaction 4 in detail. This reaction occurs in the solid state.





#### Adapted from www.computherm.com







There are three four-phase equilibria on the liquidus surface, two Class I reactions and one Class II reaction.








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## Ag-Au-Cu system



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