



# **MATERIALS EQUILIBRIA**

MSc Courses on materials engineering or metallurgical engineering  
(full time students)

by prof. dr. Geoprge KAPTAY

Course sheet

**University of Miskolc**  
**Faculty of Materials Science and Engineering**  
**Institute of Physical Metallurgy and Nanotechnology**

Miskolc, Spring Semester, Academic year of 2017/18 AC

## 1. Course description

<b>Name of the course:</b> <b>MATERIALS EQUILIBRIUM</b>	<b>Neptun code:</b> MAKFKT345M <i>University of Miskolc, Faculty of Materials Science and Engineering, Institute of Physical Metallurgy and Nanotechnology</i>
	Basic subjects, MSc
<b>professor:</b> <i>Dr. George Kaptay</i>	
<b>Semester:</b> 2nd	<b>preconditions:</b> -
<b>Classes per week:</b> 2 hours of lectures	<b>Requirements:</b> <i>homework + test + oral exam</i>
<b>Credits:</b> 4	full time MSc students

### **The goal of the course:**

To teach both theoretically and technically how to calculate phase equilibria in one- and two-component materials systems and how to read the characteristics of equilibrium from them.

### **Short description in key-words:**

System, phase, component, mole fraction, phase fraction, materials balance, characteristics of the equilibrium state, state parameters, Gibbs energy, laws of thermodynamics, condition of global and heterogeneous equilibria, phase rule, one-component phase diagrams (construction and interpretation), Gibbs energy of two-component mixtures and solutions, ideal solution and their phase diagrams (their derivation and interpretation), solutions models and the 4th law, compound phases, two-component phase diagrams (their derivation, interpretation and classification).

**How to apply:** see NEPTUN.

**Way of teaching:** oral, with a green board.

### **Requirements during the semester:**

Personalized house works for maximum of 50 points (creation of phase diagrams via excel) + test for max. 50 points + additional points during classes for performance. Less than 10 points: can repeat the course any time in the future; below 50 points: can repeat homeworks or test at the end of semester; more than 50 point: allowed to oral exam.

### **Final evaluation on oral exam:**

2 questions from the list of subjects delivered during the course for additional 100 points, altogether maximum of 200 points. Points 100 – 119: satisfactory (2); points 120 – 139: medium (3); points 140 – 159: good (4); above 160 points: excellent (5).

### **Compulsary Literature:**

1. Kaufman L, Bernstein H: Computer Calculation of phase diagrams (with special reference to refractory metals) - Academic Press, NY, USA, 1970, 334 pp.
2. N.Saunders, AP Miodownik: CALPHAD, a Comprehensive Guide, Pergamon, 1998, 479 p
3. Lukas HL, Fries SG, Sundman B: Computational Thermodynamics. The Calphad method. Cambridge University Press, 2007, Cambridge, UK, 313 pp.

**Suggested further reading:**

- G.Kaptay: On the tendency of solutions to tend toward ideal solutions at high temperatures – Metall Mater Trans A, 2012, vol.43, pp. 531-543.
- G.Kaptay: Nano-Calphad: extension of the Calphad method to systems with nano-phases and complexions - J Mater Sci, 2012, vol.47, pp.8320-833
- J188. G.Kaptay. The exponential excess Gibbs energy model revisited. Calphad, 2017, vol.56, pp.169-184. doi: 10.1016/j.calphad.2017.01.002.

**2. Classes per week**

<b>Week</b>	<b>Subject</b>
<b>1</b>	1. The hierarchy of matter: system, phases, components, mole fraction and phase fractions and relations between them. 2. State parameters and their connections to the characteristics of equilibrium state, properties of the system and satisfaction of customers. 3. The initial state, the equilibrium state and states in-between (thermodynamics vs kinetics) 4. The number of stable elements. The number of combinations of state parameters and the time needed to perform all experiments. Why a method to calculate equilibrium of materials is needed.
<b>2</b>	5. The Gibbs energy the system. The general condition of equilibrium. 6. The integral Gibbs energy of phases and the partial Gibbs energy of the components. 7. The condition of heterogeneous equilibrium. 8. Constituents of the Gibbs energy: the inner energy, the volume work and the entropy term.
<b>3</b>	9. Experimental methods and model description of the standard Gibbs energy of pure components as function of temperature and pressure. 10. Graphical derivation of one-component phase diagrams. 11. An Excel algorithm to calculate one-component phase diagrams.
<b>4</b>	12. Graphical derivation of one component phase diagrams with allotropes 13. Derivation of the phase rule 1: the maximum number of equilibrium phases 14. Derivation of the phase rule 2: fixed and free state parameters, and their meaning for one-component phase diagrams 15. The number of phase combinations.
<b>5</b>	16. The pressure dependence of the melting point 17. The critical point and the difference between vapors and gases. 18. The four types of one-component phase diagrams for “solid”, “liquid”, “vapor” and “gaseous” phases at standard conditions 19. General issues on constructing phase diagrams for two-component systems. 20. The average integral Gibbs energy of mixtures and the integral Gibbs energy of solutions.
<b>6</b>	21. The connection between partial and integral Gibbs energies (the tangent method) 22. The Gibbs energy of an ideal solution. 23. Construction of a binary phase diagram if a liquid solution is ideal, and if the solid phases have no mutual solubility (no allotropes, no compounds, different solid structures).
<b>7</b>	24. Interpretation of the eutectic phase diagram: construction of the phase composition diagrams.

	<p>25. Interpretation of the eutectic phase diagram: construction of the phase ratio diagrams.</p> <p>26. The equation for the liquidus line, which keeps equilibrium between pure solid phase alpha (and betha) and the ideal liquid A-B solution.</p> <p>27. The excel algorithm to construct the eutectic phase diagram: if a liquid solution is ideal, and if the solid phases have no mutual solubility (no allotropes, no compounds, different solid structures).</p>
<b>8</b>	<p>28. Construction of a binary phase diagram if both solid and liquid solutions are ideal (no allotropes, no compounds, identical solid structures): the solid solution type phase diagram.</p> <p>29. Equations for the equilibrium solidus and liquidus lines for a solid ideal A-B solution and a liquid ideal A-B solution. The excel algorithm to construct the solid solution type phase diagram (if both solid and liquid solutions are ideal (no allotropes, no compounds, identical solid structures)).</p> <p>31. Interpretation of the solid solution phase diagram: construction of the phase ratio diagrams and the phase composition diagrams.</p>
<b>9</b>	<p>34. Concentration dependence of the excess Gibbs energy of solutions.</p> <p>35. Temperature dependence of the excess Gibbs energy of solutions (the 4<sup>th</sup> law).</p> <p>36. Construction of solid phase separation line on phase diagrams, due to the repulsion of components within a solid solution phase.</p> <p>37. The equations for the equilibrium separation line and the critical temperature for two solid solutions of the same structure but different compositions (the components repulse each other in the solid solution).</p>
<b>10</b>	<p>38. The equilibrium between a real solid solution and the ideal liquid solution.</p> <p>39. The excel algorithm to calculate solidus and liquidus lines for the equilibrium of a real solid solution and an ideal liquid solution.</p> <p>40. The graphical construction of the diagram with a minimum azeotropic point.</p> <p>41. The condition when a minimum azeotropic point appears.</p> <p>42. The equations to find the coordinates of the azeotropic point.</p>
<b>11</b>	Test
<b>12</b>	<p>43. The graphical construction of the eutectic phase diagram (same crystal structures, repulsion between components).</p> <p>45. The peritectic phase diagram with and without the minimum azeotrope.</p> <p>46. The topological diagram of possible phase diagrams as function of melting point difference between the components and their interaction energy in the solid state if the liquid solution is ideal (no compounds, no allotropes, crystal structures equal).</p>

### 3. Sample homeworks

**General conditions.** The task is sent via e-mail. To be sent back via e-mail: a report, with author / title / date / task / equations needed / data needed / results, including a calculated phase diagram (by EXCEL). If you have a question: send an e-mail and will get my respond within 24 hours. First 3 good solutions: extra points. Being late after deadline: minus 1 point / day.

**Homework 1.** You use the first of your selected elements (see another file). Calculate its phase diagram below 100 bar. Attached help: standard Gibbs energies of solid and liquid phases of Dinsdale + standard Gibbs energies of vapors (Barin).

**Homework 2.** Same as 1, but use your second selected element and calculate its phase diagram till 100,000 bar of pressure. Additional data: molar volumes of solid and liquid phases as function of temperature.

**Homework 3.** Calculate a solid solution phase diagram using your two elements. Suppose they form ideal solutions in both solid and liquid states. Indicate a special point at the phase diagram at  $T =$  average of the two melting points, composition: 50 mol % and describe the equilibrium state of matter in this point.

**Homework 4.** Calculate an eutectic phase diagram using your two elements. Suppose they form an ideal solution in liquid state, and are mutually insoluble in solid state. Indicate a special point at the phase diagram at  $T =$  average of the two melting points, composition: 35 mol % of component B and describe the equilibrium state of matter in this point.

**Homework 5.** Calculate a solid solution phase diagram with phase separation in solid state using your two elements. Suppose they form an ideal solution in liquid state, and are mutually soluble in solid state, with an interaction energy of  $\Omega(s) = R \cdot T_m$ , where  $R = 8.3145 \text{ J/molK}$ ,  $T_m$  the melting point of the elements with a lower melting point (K). Indicate a special point in the phase diagram at  $T =$  average of the two melting points, composition: 35 mol % of component B and describe the equilibrium state of matter in this point.

**Homework 6.** Calculate a solid solution phase diagram with phase separation in solid state using your two elements. Suppose they form an ideal solution in liquid state, and are mutually soluble in solid state, with an interaction energy of +10 kJ/mol. Indicate a special point at the phase diagram at  $T =$  average of the two melting points, composition: 35 mol % of component B and describe the equilibrium state of matter in this point.

#### 4. Questions on oral exam

1. The hierarchy of matter: system, phases, components, mole fraction and phase fractions and relations between them.
2. State parameters and their connections to the characteristics of equilibrium state, properties of the system and satisfaction of customers.
3. The initial state, the equilibrium state and states in-between (thermodynamics vs kinetics)

4. The number of stable elements. The number of combinations of state parameters and the time needed to perform all experiments. Why a method to calculate equilibrium of materials is needed.
5. The Gibbs energy of the system. The general condition of equilibrium.
6. The integral Gibbs energy of phases and the partial Gibbs energy of the components.
7. The condition of heterogeneous equilibrium. The essence of the phase rule.
8. Constituents of the Gibbs energy: the inner energy, the volume work and the entropy term.
9. Experimental methods and model description of the standard Gibbs energy of pure components as function of temperature and pressure.
10. Graphical derivation of one-component phase diagrams.
11. An Excel algorithm to calculate one-component phase diagrams.
12. Graphical derivation of one component phase diagrams with allotropes
13. Derivation of the phase rule 1: the maximum number of equilibrium phases
14. Derivation of the phase rule 2: fixed and free state parameters, and their meaning for one-component phase diagrams
15. The number of phase combinations.
16. The pressure dependence of the melting point
17. The critical point and the difference between vapors and gases.
18. The four types of one-component phase diagrams for “solid”, “liquid”, “vapor” and “gaseous” phases at standard conditions
19. General issues on constructing phase diagrams for two-component systems.
20. The average integral Gibbs energy of mixtures and the integral Gibbs energy of solutions.
21. The connection between partial and integral Gibbs energies (the tangent method)
22. The Gibbs energy of an ideal solution.
23. Construction of a binary phase diagram if a liquid solution is ideal, and if the solid phases have no mutual solubility (no allotropes, no compounds, different solid structures).
24. Interpretation of the eutectic phase diagram: construction of the phase composition diagrams.
25. Interpretation of the eutectic phase diagram: construction of the phase ratio diagrams.
26. The equation for the liquidus line, which keeps equilibrium between pure solid phase alpha (and betha) and the ideal liquid A-B solution.
27. The excel algorithm to construct the eutectic phase diagram: if a liquid solution is ideal, and if the solid phases have no mutual solubility (no allotropes, no compounds, different solid structures).
28. Construction of a binary phase diagram if both solid and liquid solutions are ideal (no allotropes, no compounds, identical solid structures): the solid solution type phase diagram.
29. Equations for the equilibrium solidus and liquidus lines for a solid ideal A-B solution and a liquid ideal A-B solution. The excel algorithm to construct the solid solution type phase diagram (if both solid and liquid solutions are ideal (no allotropes, no compounds, identical solid structures).
31. Interpretation of the solid solution phase diagram: construction of the phase ratio diagrams and the phase composition diagrams.
34. Concentration dependence of the excess Gibbs energy of solutions.
35. Temperature dependence of the excess Gibbs energy of solutions (the 4<sup>th</sup> law).
36. Construction of solid phase separation line on phase diagrams, due to the repulsion of components within a solid solution phase.

37. The equations for the equilibrium separation line and the critical temperature for two solid solutions of the same structure but different compositions (the components repulse each other in the solid solution).
38. The equilibrium between a real solid solution and the ideal liquid solution.
39. The excel algorithm to calculate solidus and liquidus lines for the equilibrium of a real solid solution and an ideal liquid solution.
40. The graphical construction of the diagram with a minimum azeotropic point.
41. The condition when a minimum azeotropic point appears.
42. The equations to find the coordinates of the azeotropic point.
43. The graphical construction of the eutectic phase diagram (same crystal structures, repulsion between components).
45. The peritectic phase diagram with and without the minimum azeotrope.
46. The topological diagram of possible phase diagrams as function of melting point difference between the components and their interaction energy in the solid state if the liquid solution is ideal (no compounds, no allotropes, crystal structures equal).

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