Course: Chemical Engineering Thermodynamics		
Language: English		
Lecturer: Prof. dr. sc. Marko Rogošić		
TEACHING	**WEEKLY**	**SEMESTER**
Lectures	3	45
Laboratory	1	15
Seminar	1	15
		Overall: 75
		ECTS: 7.0

PURPOSE:

Within the framework of this course the students will master the application of fundamental laws of thermodynamics as well as mathematical methods for solving the chemical engineering problems of: estimation of thermodynamic functions of pure substances, mixtures and solutions, phase equilibria calculation, chemical equilibria calculation. In addition, the student will get acquainted with the fundamentals of the non-equilibrium and irreversible thermodynamics.

THE CONTENTS OF THE COURSE:

Week 1

Introduction to thermodynamics of real systems – what is thermodynamics, what does it deal with, classification of thermodynamics, course contents, prerequisites, basic definitions: thermodynamic systems, functions, parameters, phases, states, processes, laws of thermodynamics,

Volumetric properties of real fluids – *pT*-diagram, Gibbs phase rule, ideal gas equation, deviations from ideality, compressibility coefficient, Joule-Thomson coefficient, liquefaction of real fluid

Volumetric properties of real fluids – gas particles interaction, Lennard-Jones potential, virial equation, Boyle temperature, BWR equation

Seminar: getting acquainted with the seminar numeric problems program, laboratory program as well as with the seminar individual problems program (Rogošić, Zagajski-Kučan)

Seminar – numeric problems: Volumetric properties of real fluids (Zagajski-Kučan)

Week 2

Volumetric properties of real fluids – van der Waals equation, parameters, liquefaction work, equilibrium pressure, corresponding states principle, thermodynamic similarity principle, critical compressibility coefficient, Pitzer acentric coefficient, Lee-Kesler correlation

Volumetric properties of real fluids – third order polynomial equation of states, Redlich-Kwong, Soave-Redlich-Kwong, Peng-Robinson, calculation of *pvT*-properties, comparison of equations, gas mixtures

Thermodynamic properties of real fluids – steam (heat) tables and diagrams, construction of *ph* and *sT*-diagrams, departure functions, corresponding states principle, thermodynamic similarity principle, Yen-Alexander and Lee-Kesler correlation for enthalpy and entropy

Seminar – numeric problems: Volumetric properties of real fluids (Zagajski-Kučan)

Seminar – numeric problems: Volumetric properties of real fluids, preparation for the seminar individual problem 1 (Rogošić, Zagajski-Kučan)

Week 3

Thermodynamic properties of real fluids – fugacity and fugacity coefficient, fugacity as a departure function, calculating Gibbs energy using fugacity, fugacity vs. pressure and fugacity vs. temperature correlations, fugacity and the corresponding states principle, fugacity and the thermodynamic similarity principle

Thermodynamics of real solutions – ideal solution definition, volume, enthalpy and entropy of mixing, the causes of non-ideality of real solutions

Thermodynamics of real solutions – partial molar functions in two- and multicomponent real systems, Gibbs-Duhem equation, partial fugacity and partial fugacity coefficient, mixing functions, excess functions

Seminar – numeric problems: Thermodynamic properties of real fluids (Zagajski-Kučan)

Seminar – individual problems: equation of states of real gases (Rogošić, Zagajski-Kučan)

Week 4

Thermodynamics of real solutions – activity and activity coefficient, standard states of pure gas, liquid and solid as well as of gas and liquid mixture components, Poynting factor, Lewis-Randall rule, infinitely dilute solution, Henry law for real solutions

Thermodynamics of real solutions – determination of partial molar functions using the methods of intercept, tangent, apparent molar functions, as well as by the Gibbs-Duhem equation, Gibbs energy vs. activity and activity coefficient correlation

Activity coefficient models – Activity coefficient models: Margules, power series, Van Laar, Wohl, regular and athermal solutions, Scatchard-Hildebrand; Flory-Huggins interaction parameter, solubility parameter, determination of model parameters

Seminar – numeric problems: Thermodynamic properties of real fluids (Zagajski-Kučan)

Seminar – individual problems: equation of states of real gases (Rogošić, Zagajski-Kučan)

Week 5

Activity coefficient models – activity coefficient models: Wilson, Tsuboka-

Katayama, Hiranuma, NRTL, UNIQUAC; structural group contribution models: ASOG, UNIFAC

Recapitulation – thermodynamics of real solutions and activity coefficient models, preparation for partial exam

Seminar – numeric problems: Thermodynamics of real solutions (Zagajski-Kučan)

Seminar – individual problems: equation of states of real gases (Rogošić)

Week 6

Partial exam 1 – volumetric properties of real fluids, thermodynamic properties of real fluids, thermodynamics of real solutions, activity coefficient models

Thermodynamic equilibrium – equilibrium criteria in isolated and closed systems, system stability criteria, reacting systems, thermodynamic interpretation of Le Chatelier principle

Vapor–liquid equilibria – equilibrium criteria using chemical potentials and partial fugacities, phase non-ideality description using equation of states and activity coefficient models, equilibrium criteria for ideal vapor and liquid phase, respectively

Laboratory: partial molar volumes (Zagajski-Kučan)

Laboratory: partial molar volumes (Zagajski-Kučan)

Week 7

Vapor–liquid equilibria – phase diagrams, *Txy*-diagram, *pxy*-diagram, *xy*-diagram, systems of regular behavior, azeotropic systems, consistency tests

Vapor–liquid equilibria – phase equilibrium calculations in chemical engineering: bubble point, dew point, flash, numerical methods in vapor–liquid equilibrium calculations

Vapor–liquid equilibria – high pressure range: retrograde condensation, equilibrium calculations; solubility of gases in liquids, Prausnitz and Shair procedure

Laboratory: Vapor–liquid equilibria (Zagajski-Kučan)

Laboratory: Vapor–liquid equilibria (Zagajski-Kučan)

Week 8

Liquid–liquid equilibria – equilibrium criteria using chemical potentials, phase diagrams, vapor pressure vs. composition, Gibbs energy of mixing vs. composition, miscibility as influenced by temperature and pressure, determination of model parameters using experimental data, ternary diagrams, lever rule, calculation of equilibrium composition in two- and three-component systems

Liquid–liquid equilibria – breaking azeotropes by changing pressure or by adding the third component, Liquid–liquid–vapor equilibria, phase diagrams, phase equilibrium calculations

Solid–liquid equilibria – equilibrium criteria using chemical potentials and partial fugacities, phase diagrams, eutectics, intermolecular compounds, peritectics, calculation of solubility of a solid in a liquid, Schroeder equations, ternary eutectics, eutectic troughs

Laboratory: Liquid–liquid equilibria (Zagajski-Kučan)

Laboratory: Liquid–liquid equilibria (Zagajski-Kučan)

Week 9

Solid–gas equilibria – equilibrium criteria using chemical potentials and partial fugacities, supercritical fluids as solvents, calculation of solubility of a solid in a fluid (gas)

Recapitulation – thermodynamic equilibrium, vapor–liquid equilibria, liquid–liquid equilibria, solid–liquid equilibria, solid–gas equilibria

Seminar – numeric problems: Thermodynamics of real solutions (Zagajski-Kučan)

Seminar: laboratory data analysis (Zagajski-Kučan)

Week 10

Partial exam 2 – thermodynamic equilibrium, vapor–liquid equilibria, liquid–liquid equilibria, solid–liquid equilibria

Chemical equilibria – chemical equilibrium criterion: minimum Gibbs energy, stoichiometric sum of chemical potentials, homogeneous chemical reactions, standard Gibbs energy of reaction, standard Gibbs energy of reaction vs. temperature correlation

Chemical equilibria – examples of solving homogeneous chemical equilibria problems, chemical equilibria at multireaction systems, determination of minimum number of reaction, Denbigh method, matrix elimination method

Seminar – numeric problems: Vapor–liquid equilibria (Zagajski-Kučan)

Seminar: preparation for the seminar individual problem 2 (Rogošić, Zagajski-Kučan)

Week 11

Chemical equilibria – determination of global minimum Gibbs energy of a systems, heterogeneous chemical equilibria

Thermodynamics of irreversible processes – external and internal entropy change, example of irreversible processes, heat and mass transfer, thermodynamic potentials and flows, entropy production, examples: thermal and mass diffusion

Thermodynamics of irreversible processes – examples: simultaneous thermal and mass diffusion, irreversible expansion of ideal gas, chemical reaction, affinity

Seminar – numeric problems: Liquid–liquid equilibria (Zagajski-Kučan)

Seminar – individual problems: Vapor–liquid equilibria (Rogošić, Zagajski-Kučan)

Week 12

Thermodynamics of irreversible processes – phenomenological equations, flow vs. potential relationship, Onsager phenomenological coefficients, examples: electric current in electrolytes and metals, Ohm law, mass diffusion, Fick law, simultaneous diffusion of two substances

Thermodynamics of irreversible processes – examples: thermal diffusion, Fourier law, thermoelectric effects, cross phenomenological coefficients, chemical reactions, simple and complex

Thermodynamics of irreversible processes – stationary and non-stationary states examples, thermal diffusion, Prigogine principle and its consequences: chemical potential gradient, sequential chemical reactions, stability of a stationary state, Lyapunov stability theory

Seminar – numeric problems: Liquid–liquid equilibria (Zagajski-Kučan)

Seminar – individual problems: Vapor–liquid equilibria (Rogošić, Zagajski-Kučan)

Week 13

Partial exam 3 – chemical equilibria, thermodynamics of irreversible processes

Recapitulation – discussion on the course content, lectures, seminars, laboratory and individual seminar problems, questions and answers, preparation of final written and oral exam

Seminar – numeric problems: Solid–liquid equilibria (Zagajski-Kučan)

Seminar – individual problems: Vapor–liquid equilibria (Rogošić, Zagajski-Kučan)

GENERAL AND SPECIFIC COMPETENCE:

General competences:

Application of fundamental laws of thermodynamics in combination with literature or own experimental data for solving the chemical engineering problems of: 1. estimation of thermodynamic functions of gases and liquids depending on the given pressure, temperature and composition, 2. characterization of vapor–liquid and liquid–liquid equilibria and 3. characterization of chemical equilibria

Understanding of the basic principles of irreversible thermodynamics

Special competences:

Calculation of thermodynamic functions of real fluids using equations of state: virial, vdW, RK, SRK, PR, Lee-Kesler

Calculation of thermodynamic functions of real solutions using activity coefficient models: Margules, Van Laar, Wilson, NRTL, UNIQUAC, UNIFAC, ASOG

Calculation of activity coefficient model parameters using experimental data

Calculation of equilibrium temperature, pressure and phase composition for the vapor–liquid equilibria: bubble point, dew point, flash calculations

Calculation of equilibrium phase composition for the liquid–liquid equilibria

Calculation of equilibrium composition in reacting systems as dependent on pressure and temperature: gas phase reactions, multiple gas phase reactions, heterogeneous reactions

KNOWLEDGE TESTING AND EVALUATION:

Laboratory entrance exam

Laboratory final oral exam

Written exams for two individual seminar problems

3 compulsory partial exams during the semester (if failed – final oral exam)

Final written exam for numeric seminar problems Final oral exam
MONITORING OF THE COURSE QUALITY AND SUCCESSFULNESS: Student inquiry
LITERATURE: Compulsory: M. Rogošić, Internal textbook, www.fkit.unizg.hr, 2013. S.I. Sandler, Chemical, Biochemical and Engineering Thermodynamics, 4th Ed., Wiley, New York, 2006. D. Kondepudi, I. Prigogine, Modern Thermodynamics, Wiley, New York, 1998. Additional: J.M. Smith, H.C. Van Ness, M.M. Abbott, Introduction to Chemical Engineering Thermodynamics, 5th Ed., McGraw-Hill, New York, 1996. J.M. Prausnitz, R.N. Lichtenthaler, E.G. de Azevedo, Molecular Thermodynamics of Fluid Phase Equilibria, 3rd Ed., Prentice Hall, Englewood Cliffs, 1999. B.E. Poling, J.M. Prausnitz, J.P. O'Connell, The Properties of Gases and Liquids, 5th Ed., McGraw-Hill, New York, 2000.