INSTITUTO POLITÉCNICO DE BRAGANÇA

Course Unit	Chemical Thermodynamics II	Field of study	Thermodynamics and Transport Phenomena
Bachelor in	Chemical Engineering	School	School of Technology and Management
Academic Year	2023/2024	Year of study	2
Level	1-2	ECTS credits	6.0
Type	Semestral	Semester	2
Code	9125-755-2205-00-23		

Workload (hours)	Contact hours	T	TP	PL	TC	S	E	OT	O
162		30	-	30	-	-	-	-	-

T - Lectures; TP - Lectures and problem-solving; PL - Problem-solving, project or laboratory; TC - Fieldwork; S - Seminar; E - Placement; OT - Tutorial; O - Other

Name(s) of lecturer(s): Maria Olga de Amorim Sá Ferreira

Learning outcomes and competences

At the end of the course unit the learner is expected to be able to:
1. Recognize the formalism for the thermodynamic description of multicomponent system.
2. Learn the concepts of partial molar properties, chemical potential, fugacity, fugacity coefficient and activity coefficient.
3. Develop phase equilibria calculations: liquid-vapor, liquid-liquid, liquid-liquid-vapor, solid-liquid and solid-vapor.
4. Know and understand the main types of phase diagrams.
5. Analyse graphically and numerically system stability.
6. Develop chemical equilibrium calculations in simple systems and with multiple reactions.
7. Know and apply experimental methods for the measurement of thermodynamic properties of mixtures as well as phase equilibria.
8. Apply experimental information for the thermodynamic description of a mixture in conditions not available experimentally. Use databases and estimation methods to evaluate thermodynamic properties.

Prerequisites

Before the course unit the learner is expected to be able to:
1. Apply mathematical concepts, particularly from differential and integral calculus.
2. Use of informatics tools such as MATLAB or MS Excel.

Course contents

Solution Thermodynamics Theory. Applications of Solution Thermodynamics Theory. Vapour-Liquid Equilibrium (VLE) at Moderate Pressures. Equations of State in the Calculation of Thermodynamic Properties and VLE. Topics in the Study of Phase Equilibria. Chemical Equilibrium.

Course contents (extended version)

1. Solution Thermodynamics Theory
   - Fundamental equations of solution thermodynamics.
   - Chemical potential and its relation with equilibrium states. Partial molar properties.
   - Change of chemical potential with temperature and pressure. Gibbs-Duhem equation.
   - Ideal gas mixture and Gibbs theorem. Fugacity and fugacity coefficient of a pure species.
   - Calculation of the fugacity coefficient of a pure species and the fugacity of a saturated liquid.
   - Fugacity coefficient of a species in solution. Fugacity as an equilibrium criteria.
   - Generalized correlations for the fugacity coefficient: Lee-Kesler and Pitzer.
   - Ideal solution. Lewis-Randall model. Excess properties.
   - The activity coefficient of a species in solution and its change with pressure and temperature.
2. Applications of Solution Thermodynamics Theory
   - Gibbs phase rule and Duhem theorem. VLE equations. Raoult's law.
   - Lewis-Randall model and Henry's law. Positive and negative deviations to ideality.
   - Infinite dilution activity coefficients and Henry's constant.
   - Excess Gibbs energy models. Redlich-Kister and inverse Redlich-Kister expansions.
   - Margules and van Laar equations. Regular solution theory by Scatchard-Hildebrand.
   - Local composition models: Wilson, NRTL and UNIQUAC. The UNIFAC group-contribution method.
   - Model parameters from fitting excess Gibbs energy.
   - Infinite dilution activity coefficients and azeotropic behaviour. Mixture properties.
3. Vapor-Liquid Equilibrium (VLE) at Moderate Pressures
   - Qualitative behaviour of VLE.
   - VLE diagrams for a binary system: P-composition, T-composition and composition-composition.
   - Positive and negative deviation to Raoult's law. Positive and negative azeotropic systems.
   - VLE calculations: vapour pressures (Antoine equation), fugacity and activity coefficients.
   - Different VLE calculations.
   - Dew point (pressure or temperature), bubble point (pressure or temperature) and flash calculations.
4. Equations of State in the Calculation of Thermodynamic Properties and VLE
   - Fundamental equations for the calculation of residual properties by EoS.
   - Virial and Redlich-Kwong equations.
   - Cubic EoS in the calculation of VLE: vapour pressure of a pure substance.
   - Fugacity coefficient of a pure substance and a species in solution using SRK and Peng-Robinson EoS.
   - VLE by equilibrium constants. DePriester diagrams for light hydrocarbons.
5. Topics in the Study of Phase Equilibria
   - Equilibrium and stability. Minimizing the total Gibbs energy of a system.
   - Graphical interpretation of stability. Different stability criteria.
   - LLE. Different equilibrium diagrams for binary systems: critical mixture temperatures.
   - Representation of LLE by triangular diagrams. Distribution coefficient. ELL criteria.
   - VLLE: different graphical representations and their interpretation.
   - Thermodynamic equations for the representation of VLLE. Totally immiscible liquids.
   - SLE: equilibrium equation in terms of thermodynamic properties of the solid.
   - Regular solution theory and UNIFAC. SVE.
6. Chemical Equilibrium
   - Reaction coordinate.
   - Equilibrium in chemical reactions: minimizing total Gibbs energy and the chemical potential.
   - Equilibrium constants and standard Gibbs energy of reaction change.
   - Temperature effect on the equilibrium constant.
   - Standard Gibbs energy of reaction change with temperature.
   - Relation between equilibrium constants and composition. Gas and liquid phase reactions.
   - Different aggregation states and its relation with standard states.
   - Phase rule and Duhem theorem for reactive systems. Methodology for multiple reactions.

Recommended reading

1. J. M. Smith; H. C. Van Ness; M. M. Abbott; M. T. Swihart, Introduction to Chemical Engineering Thermodynamics, 9th Edition, McGraw-Hill, 2022.
2. S. P. Pinho, Manual da Disciplina de Termodinâmica Química II, Escola Superior de Tecnologia e de Gestão, Bragança, 2016.
3. J. M. Prausnitz; R. N Lichtenthaler e E. G. Azevedo, Molecular Thermodynamics of Fluid-Phase Equilibria, 3rd edition, Prentice-Hall, 1999.
4. E. G. Azevedo, Termodinâmica Aplicada, 4ª Edição, Escolar Editora, 2018.
5. S. I. Sandler, Chemical, Biochemical and Engineering Thermodynamics, 5th edition, John Wiley & Sons, 2017.

Teaching and learning methods

Theoretical analysis of fundamental tools and concepts for the compreension, application and calculations in the thermodynamics area. Presentation of practical examples and exercices. Problem solving and critical analysis of the results. Evaluation of homework. Development of application projects.

Assessment methods

1. Alternative 1 - (Regular, Student Worker) (Final)
   - Intermediate Written Test - 25% (Test covering the first part of the course (Chapter 1).)
   - Intermediate Written Test - 30% (Test covering the second part of the course (Chapter 2 to 4).)
   - Intermediate Written Test - 30% (Test covering the third part of the course (Chapter 5 and 6).)
   - Case Studies - 15% (Development and critical analysis of selected problems.)
2. Alternative 2 - (Regular, Student Worker) (Final, Supplementary, Special)
   - Final Written Exam - 100% (Global written exam.)

Language of instruction

English

Electronic validation

Maria Olga de Amorim Sá Ferreira	Hélder Teixeira Gomes	António Manuel Esteves Ribeiro	José Carlos Rufino Amaro
28-02-2024	13-03-2024	13-03-2024	16-03-2024