UNIVERSITÀ
DEGLI STUDI DI MILANO-BICOCCA

COURSE SYLLABUS

Physical Chemistry

2021-2-E2701Q013

Aims

The student will learn the basic concepts of classical equilibrium thermodynamics and of chemical kinetics and will develop abilities to solve simple problems of relevance in materials science.

Knowledge and understanding

- Methods for the analysis of isolated and closed thermodynamic systems (including reactive systems)
- Procedures for the computation of the main thermodynamic quantities
- Techniques to evaluate thermodynamically admissible tranformations between equilibrium states
- Methods to describe relevant chemical-physical systems in materials science

Applying knowledge and understanding

- Computation of the equations of state and of the thermodynamic potentials in systems of relevance in materials science
- Evaluation of the limit of applicability of elemental thermodynamic models in systems of relevance in

materials science

Making judgments

- Evaluation of the appropriateness of thermodynamic models used in the analysis of real systems
- Capability to model real systems using thermodynamics

Communication skills
Rigorous use of natural language in science

Learning skills
Activation of critical skills in the analysis of scientific models

Contents

Math Refresher. Zeroth, first and second laws of thermodynamics. Auxiliary thermodynamic potentials. Gas thermodynamics and reaction equilibria in the gaseous phase. States of matter and phases. Elements of chemical kinetics.

Detailed program

Mathematical refresher: Exact differentials, partial derivatives, differential forms. Notation.

The zeroth, first, and second laws of thermodynamics: thermodynamic systems and variables. The temperature and the zeroth principle. Work. Internal energy and the first law. The concept of thermodynamic potential. Impossible, natural, and adiabatically reversible processes. Entropy and the second law. Provisional formulation of an equilibrium criterion.

Auxiliary potentials: enthalpy, Helmholtz, and Gibbs free energies. Properties and use of auxiliary potentials. Fundamental equations for a closed system. The chemical potential. Equilibrium criterion. Auxiliary thermodynamic quantities. Determination of changes in thermodynamic functions with pressure and temperature. Molar quantities and partial molar quantities. The Gibbs-Duhem equation.

Gas thermodynamics and reaction equilibria in the gaseous phase: Perfect gas: chemical potential and equation of state. Real gases: fugacity. Numerical examples of the determination of changes in thermodynamic functions with pressure, volume, and temperature. Perfect gas mixtures. The equilibrium constant for gas-phase reactions and its dependence upon temperature and pressure. Degree of advancement of a chemical reaction.

States of matter and phases: the phase rule for reactive and non-reactive components. Clausius-Clapeyron equation. Latent heat. Notes on phase diagrams for single-component systems. Polymorphism. Phase transitions.

Chemical kinetics: reaction rates. Order and molecularity of reactions. Kinetic equations. Effect of temperature on the kinetic constant. Integration of kinetic equations: integration of the zeroth-order, first-order, and second-order equation. Kinetics and chemical equilibrium: direct and reverse rates, transition state theory. Sequential reactions.

Approximation of the rate-determining step. Steady-state approximation. Parallel reactions.

Prerequisites

Calculus of multi-variable functions

Physics I (Mechanics)

Teaching form

Lectures and numerical exercises will be partially held in the classroom (if COVID emergency allows it) and partially by streaming, using WebEx. Recordings will be made available for all lectures. In addition, students will be offered the possibility of using automated tests and self-assessment tools (available online).

Textbook and teaching resource

K. Denbigh, The principles of chemical equilibrium, Cambridge University Press

Handouts

Students will also have access to automated numerical exercises, self-evaluation tests, and additional educational material available online.

As an alternate textbook, should the main book be inaccessible, students may use Jean-Philippe Ansermet, Sylvain D. Brechet. *Principles of thermodynamics*, available as an ebook: https://search.ebscohost.com/login.aspx?direct=true&db=cat05403a&AN=ebk.CR9781108620932&lang=it&site=eds-live&scope=site

Semester

First semester of the second year

Assessment method

Until the end of the COVID emergency, the exam will be carried out online (through WebEx). The written test will be replaced by the solution of a numerical problem concerning the fundamental aspects of classical thermodynamics (1st and 2nd law, calculation of work and heat exchanged, etc.), physical equilibria (phase transitions, latent heats, melting and boiling points, etc.) or the analysis of chemical equilibria (calculation of equilibrium constants, reaction free energies, etc.); followed by an oral part on the thermodynamic theory and the elements of chemical kinetics. Technical details about the way the exam is organized may be found in this eLearning site.

After the end of the COVID emergency, s

The written test encompasses the solution of three numerical exercises. Typically, the first exercise focuses on the fundamental aspects of classical thermodynamics (1st and 2nd law, calculation of work and heat exchanged, etc.); The second exercise is about physical equilibria (phase transitions, latent heats, melting and boiling points, etc.) while the third one requires the analysis of chemical equilibria (calculation of equilibrium constants, reaction free energies, etc.).

For each exactly solved exercise, 10 points are assigned. Admission to the oral test requires an overall score in the written test of 15 points or more.

The oral test focuses on theory but may include the solution of exercises not correctly solved by the student.

Written and oral tests must be given in the same examination session.

Office hours

By appointment