# THOMPSON RIVERS UNIVERSITY

## Department of Physical Sciences (Chemistry)

## CHEM 3060 – 3 Credits
### Physical Chemistry 1 (3,0,0)
### Fall 2023

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| **Instructor:** | Dr. Nelaine Mora-Diez |
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| **Office Hours:** | Mon, Thur (11:30 - 12:00 PM) & Wed (10:00 - 10:30 AM) |
| | Additional office hours are available by appointment |

## Description

Assuming prior basic knowledge of thermodynamics and chemical kinetics, this course deals with various topics in the areas of chemical equilibrium, kinetics, and some aspects of physical organic chemistry, after studying the kinetics of the electrophilic aromatic substitution reaction.

## Prerequisites

CHEM 2250 (C- minimum). See the TRU Calendar for details.

## Lectures

The official scheduled time for this class is:

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|---|---|---|
| Monday | 8:30 – 9:45 AM | S-266 |
| Wednesday | 8:30 – 9:45 AM | S-266 |

This course will have blended components, in which recorded lectures will be made available for some sections before solving exercises about them.

## Moodle

Electronic course-related materials will be available through Moodle.
Moodle course: CHEM 3060 - Physical Chemistry 1 (Mora-Diez)
To access Moodle on the Internet, use the Moodle quick link from the TRU homepage (www.tru.ca).

## Assessment

Grades will be assigned on the following basis:

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| Moodle Quizzes | 15% | (One attempt allowed before the closing date) |
| Test 1 | 20% | (Wed, Oct 4) |
| Test 2 | 20% | (Wed, Nov 1) |
| Test 3 | 30% | (Wed, Nov 15) |
| Test 4 | 15% | (Wed, Nov 29) |

Test 1 will evaluate <u>all</u> the topics covered (and review materials) until Sept 28.

Test 2 will evaluate <u>all</u> the topics covered (and review materials) until Oct 26, with emphasis on topics not yet evaluated.

Test 3 will evaluate <u>all</u> the topics covered in Sections 1 and 2 (except complex systems).

Test 4 will evaluate complex systems (Section 2) and Section 3.

If you miss Test 1 or Test 2 for a valid reason, their value will be added to Test 3.

To receive a passing grade, students must achieve at least 50% (42.5/85) in the sum of Tests 1 to 4.
A letter grade will be awarded using the TRU Grading System (Policy ED-3-5) on p. 24 of the TRU Calendar. This one-semester course is worth 3 credits.

## Reference Texts

K.J. Laidler, J.H. Meiser and B.C. Sanctuary, *Physical Chemistry*, 4th Edition, Houghton Mifflin, 2003.

T. Engel and P. Reid, *Physical Chemistry*, 3th Edition, Pearson, 2013.

## Academic Policy

It is the responsibility of all students to be aware of TRU Student Academic Policies, Regulations and Procedures found in the TRU Calendar (www.tru.ca/calendar/current/). These include Academic Honesty Policy ED-5-0 (p. 24), Appeals Policy ED-4-0 (p. 25), Students Attendance ED-3-1 (p. 24), and Exams Policy ED-3-9 (p. 24). Forms of Academic Dishonesty are summarized and described on the TRU Calendar, and include cheating, misconduct, fabrication, and plagiarism.

**Course Content** (may change as the course progresses)

## Section 1: Chemical Equilibrium

**1.1. Review of basic topics** (Self-study from notes and references provided)

Characteristics of the equilibrium state in chemistry.
Relationship between the rate constants of the forward and reverse reactions and the equilibrium constant $K_c$ at the same temperature.
Equilibrium constants relative to concentrations ($K_c$) and pressures ($K_p$) at equilibrium.
Calculating $K_p$ from $K_c$ and *vice versa*.
Relationships involving equilibrium constants.
Interpreting the magnitude of K.
Determining if a reaction mixture is at equilibrium or not. Direction of spontaneous reaction. The reaction quotient (Q).
Standard enthalpy of reaction, $\Delta H°$. Meaning. Characteristics. Determination.
Standard enthalpies of formation, $\Delta H_f°$.
Calculation of $\Delta H°$ using the $\Delta H_f°$ of reactants and products.
Standard entropy of reaction, $\Delta S°$. Meaning.
The Third Law of Thermodynamics.
Calculation of $\Delta S°$ using the absolute entropies of reactants and products.
The Second Law of Thermodynamics and the thermodynamic criteria for equilibrium and spontaneity at constant temperature and pressure.
The Gibbs free energy (G).
State functions.
Interpreting the sign of $\Delta G$.
Standard Gibbs free energy of reaction, $\Delta G°$: Meaning and interpretation.
Relationship between $\Delta G$ and $\Delta G°$: $\Delta G = \Delta G° + RT\ln Q$
Standard Gibbs free energy of formation, $\Delta G_f°$. Meaning.
Calculation of $\Delta G°$ (using the $\Delta G_f°$ of reactants and products, from K values and from $\Delta H°$ and $\Delta S°$ values).
Interpreting the sign of $\Delta G$ and $\Delta G°$ for a system.
Effect of temperature on spontaneity.
The Le Chatelier Principle

**1.2. The reference state in thermodynamics**

Obtaining the expression for calculating $K_p$ from $K_c$.
Different types of $\Delta G°$ values depending on the standard state chosen at a given temperature (1 M or 1 bar).

**1.3. Temperature dependence of equilibrium constants: The van't Hoff equation**

Derivation and interpretation of the van't Hoff equation.
Derivation of the expression that relates $K_p$ with $\Delta H°$ and $\Delta S°$ for a reaction at a given temperature.
Applications.

## Section 2:   Chemical Kinetics

### 2.1. Review of basic concepts (Self-study from notes and references provided)

Rate of reaction; Rate law; Order of reaction; Partial orders of reaction.
Rate constant (determination of units).
Elementary reactions; Complex reactions.
Intermediates.
Rate law of elementary reactions; Molecularity.
The temperature dependence of rate constants.
The Arrhenius equation. Arrhenius plot. Interpretation of A and $E_a$.

### 2.2. Kinetic theories: Collision theory

Collision theory: postulates.
Main equations; steric factor.
Meaning of A and $E_a$.
Factors that determine the effectiveness of a collision.
Deficiencies of the theory.

### 2.3. Transition state theory (TST)

The postulates of TST.
The transition state (TS) of an elementary kinetic step.
The thermodynamic formulation of TST.
Relating k, $E_a$ and A with $\Delta G^{\neq}$, $\Delta H^{\neq}$ and $\Delta S^{\neq}$, respectively, for different types of reactions

### 2.4. Kinetic behaviors: Arrhenius, non-Arrhenius and anti-Arrhenius. Characteristics. Recognition.

### 2.5. The tunneling effect

### 2.6. Kinetic isotope effects (KIE)

### 2.7. Complex reactions

Evidence for a composite mechanism.
Types of complex reactions.
Elucidation of rate laws from a reaction mechanism.
Review of the steady state approximation (SSA). Application to more complex systems.

### 2.8. Radical chain reactions

Main steps of a radical chain reaction
Application of the SSA to derive or verify a rate law.

### 2.9. Rate determining steps (Reading material, not covered in class)

# Section 3.    Elements of Physical Organic Chemistry

## 3.1. Electrophilic aromatic substitution reactions

Mechanism of the electrophilic aromatic substitution (EAS) reaction.
Main examples of EAS reactions in benzene.
Activating and deactivating substituents: effects on the kinetics of EAS reactions
Orientation effects of substituents

## 3.2. Frontier orbitals and organic chemical reactions

Basic elements of Molecular Orbital (MO) theory
Frontier orbitals (HOMO and LUMO) and chemical reactions

## 3.3. The equation for estimating chemical reactivity

Electrostatic criteria of reactivity
Electronic criteria of reactivity

## 3.4. The principle of hard and soft acids and bases (HSAB)

Lewis theory of acids and bases
The HSAB theory: General characteristics of hard and soft acids and bases
Relating the HSAB theory with the electronic and electrostatic criteria of reactivity.