

CHEM 3060

Course Topics & Learning Objectives

LM&S: K.J. Laidler, J.H. Meiser and B.C. Sanctuary, *Physical Chemistry*, 4th Edition, Houghton Mifflin, 2003.
E&R: T. Engel, P. Reid, *Physical Chemistry*, 3th Edition, Pearson, 2013.

Section 1: Chemical Equilibrium (5 fifty-minute lectures)

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

(Read the chapters of Thermochemistry, Chemical Equilibrium, Entropy and Gibbs free energy from any first-year Chemistry textbook)

Additional readings:

(LM&S, sections: 2.5, 3.3, 3.5-3.7, 4.1-4.6; pp. 62-74, 106-109, 117-126, 153-166)

(E&R, sections: 1.1, 1.3, 4.1-4.5, 5.7-5.10, 6.1, 6.7, 6.14; pp. 1-2, 6-7, 67-77, 98-106, 125-130, 138-139, 148-153)

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, ΔH° . Meaning. Characteristics. Determination.

Standard enthalpies of formation, ΔH_f° .

Calculation of ΔH° using the ΔH_f° of reactants and products.

Standard entropy of reaction, ΔS° . Meaning.

The Third Law of Thermodynamics.

Calculation of ΔS° 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 ΔG .

Standard Gibbs free energy of reaction, ΔG° : Meaning and interpretation.

Relationship between ΔG and ΔG° : $\Delta G = \Delta G^\circ + RT \ln Q$

Standard Gibbs free energy of formation, ΔG_f° . Meaning.

Calculation of ΔG° (using the ΔG_f° of reactants and products, from K values and from ΔH° and ΔS° values).

Interpreting the sign of ΔG and ΔG° for a system.

Effect of temperature on spontaneity.

The Le Chatelier Principle

Questions you should be able to answer:

- Why is the chemical equilibrium dynamic in nature?
- What happens at the microscopic level when the system reaches the equilibrium state?
- What is the equation that relates kinetics and thermodynamics? Be able to derive it from any concrete example.
- Given a chemical equilibrium, be able to obtain the expression of its equilibrium constant with respect to concentrations (K_c) and partial pressures (K_p).
- Interpret the magnitude of K .
- Understand the relationships involving equilibrium constants and be able to apply them in calculations ((inverting a reaction, multiplying it by a number, and combining reactions).
- Know the conditions for equilibrium and spontaneity at constant temperature and pressure.
- What is a state function? Provide examples
- Derive the expression $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$ from the thermodynamic definition of G .
- Determine if a particular reaction mixture (in concentrations or pressures) is at equilibrium, and if not, be able to determine the direction it will proceed spontaneously (calculating ΔG or comparing Q with K).
- Derive the expression $\Delta G^\circ = -RT \ln K$ from $\Delta G = \Delta G^\circ + RT \ln Q$.
- Distinguish between ΔG and ΔG° , know how to calculate them and interpret their value/sign.
- Explain the meaning and characteristics of ΔH_f° , ΔG_f° , S° , ΔH° , ΔS° and ΔG° .
- Given ΔH_f° , ΔG_f° and S° (from tables at 1 bar and 298.15 K) for the reactant and product species of a reaction, calculate ΔH° , $\Delta G^\circ_{1 \text{ bar}}$, ΔS° , K_p , K_c and $\Delta G^\circ_{1 \text{ M}}$ for the reaction.
- Given the values of ΔH° and ΔS° for a reaction, determine if it is thermodynamically spontaneous (favourable) or not, after calculating ΔG° . If it is not thermodynamically favourable, calculate the temperature at which it will be.
- Apply the Le Chatelier principle to interpret shifts of the equilibrium state after changes in concentration, pressure, volume (for gases and solutions) and temperature.
Explain how dilution affects the dissociation of weak electrolytes.
- Determine (qualitatively) how the equilibrium constant would change if the temperature of a system at equilibrium is changed.
- Determine the best conditions of temperature and pressure (high or low) to increase the concentration of a particular species involved in a system at equilibrium.

1.2. The reference state in thermodynamics

Obtaining the expression for calculating K_p from K_c .

Different types of ΔG° values depending on the standard state chosen at a given temperature (1 M or 1 bar).

Questions you should be able to answer:

- Derive the expression that relates K_p with K_c and be able to apply it in calculations
- Calculate ΔG° values for the 1 mol/L and 1 bar standard states using the corresponding K value.
- Know what type of ΔG° value is calculated with each possible approach.

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

(LM&S, section 4.8; pp. 169-172)

(E&R, section: 6.10; pp. 142-145)

Derivation and interpretation of the van't Hoff equation.

Derivation of the expression that relates K_p with ΔH° and ΔS° for a reaction at a given temperature.

Applications.

Questions you should be able to answer:

- Derive the van't Hoff equation from the Gibbs-Helmholtz equation.
- Use the van't Hoff equation to calculate equilibrium constants at different temperatures, or to calculate ΔH° and ΔS° for a given reaction.
- Derive the expression that relates K_p with ΔH° and ΔS° for a reaction at a given temperature.
- Given the graph of $\ln K_p$ versus $1/T$ and the equation of the graph, be able to:
 - Determine if ΔH° is temperature dependent or no, and its value and sign at a given temperature.
 - Explain the sign of ΔH° applying the Le Chatelier principle.
 - Calculate ΔS° for the reaction considered.
- Draft the van't Hoff plot ($\ln K_p$ vs $1/T$) of a reaction for a particular temperature range given enough information (K_p at two temperatures or details about ΔH° of a reaction).

Section 2: Chemical Kinetics (15 fifty-minute lectures)

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

(LM&S, sections 9.1-9.3, 9.6, 9.7; pp. 363-367, 379-385)

(E&R, sections 35.1-35.3, 35.4, 35.9; pp. 909-912, 917-918, 931-933)

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 .

Questions you should be able to answer:

- Express the rate of a reaction with respect to any of the reactant and product species.
- Given an elementary reaction be able to obtain its rate law.
- Determine the units of the rate constant, and the overall and partial orders of reaction from a rate law.
- Explain the difference between elementary and complex reactions.
- Given the mechanism of a complex reaction be able to determine intermediates and the overall reaction.
- Determine the molecularity of an elementary reaction and classify it accordingly.
- Know the Arrhenius equation in either its exponential or logarithmic form.
- Apply this equation to determine rate constants, pre-exponential factors (A) and activation energies (E_a).
- Know what an Arrhenius plot is and the information that can be obtained from it.
- Determine the units of the pre-exponential factor of a reaction from its rate law or the units of a rate constant.
- Know the graphical characteristics of the Arrhenius plot of a reaction that follows Arrhenius kinetic behavior and what these characteristics mean from a kinetic point of view.
- Explain how A and E_a can be determined for a given reaction experimentally.

2.2. Kinetic theories: Collision theory

(LM&S, section 9.9; pp. 388-390)

(E&R, section 33.6; pp. 868-871)

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.

Questions you should be able to answer:

- Explain the postulates of Collision theory.
- Use this kinetic theory to explain:
 - the meaning of A and E_a .
 - the general trend between experimental and calculated pre-exponential values.
 - the deficiencies of this theory and what could be done *a posteriori* to improve the calculation of A (steric factor).

the factors that make a collision effective from a chemical point of view.
why the rate of an elementary reaction increases when temperature or the concentration of the reactant species increase.

2.3. Transition state theory (TST)

(LM&S, section 9.9; pp. 390-394)

(E&R, section 35.14; pp. 942-946)

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 $\Delta^\ddagger G^\circ$, $\Delta^\ddagger H^\circ$ and $\Delta^\ddagger S^\circ$, respectively, for different types of reactions

Questions you should be able to answer:

- Explain the main postulate of TST and its implication in deriving the thermodynamic formulation of this theory.
- Understand what a TS is and its characteristics.
- Sketch the TS of any elementary reaction knowing what the reactants and products are.
- Indicate the main geometrical characteristics of the TS with respect to the structure of the reactants and products of the reaction.
- Derive the thermodynamic formulation of TST from the expression $R = (k_B T/h) [TS]$.
- Use this kinetic theory to explain the meaning of A and E_a .
- Understand the meaning of the standard Gibbs energy, entropy and enthalpy of activation ($\Delta^\ddagger G^\circ$, $\Delta^\ddagger S^\circ$, $\Delta^\ddagger H^\circ$) of any reaction and know how to calculate them from thermodynamic values of the reactants and the TS.
- Compare the A values of reactions by comparing $\Delta^\ddagger S^\circ$ values.
- Derive the operational definition of E_a .
- Derive the mathematical relationship between k and $\Delta^\ddagger G^\circ$, A and $\Delta^\ddagger S^\circ$, and E_a and $\Delta^\ddagger H^\circ$, for unimolecular and bimolecular gas-phase reactions and reactions in solution.
Use these expressions in calculations.
- Solve problems that relate thermodynamic quantities of a system at equilibrium (K , ΔG° , ΔS° , ΔH°) and kinetic magnitudes (k , A , E_a) of the forward and reverse reactions.

2.4. Kinetic behaviors: Arrhenius, non-Arrhenius and anti-Arrhenius.

Characteristics. Recognition.

Questions you should be able to answer:

- Identify the type of kinetic behaviour of a reaction (Arrhenius, non-Arrhenius, anti-Arrhenius) from its Arrhenius plot.
- Know the graphical characteristics of the three types of kinetic behaviours studied and the kinetic implications of these characteristics.
- Know how to calculate E_a and A at a given temperature for a reaction that follows non-Arrhenius kinetic behaviour.

2.5. The tunneling effect

(LM&S, section 9.9; p. 395)

(E&R, section 16.6-16.8; pp. 367-374)

Questions you should be able to answer:

- What is the tunneling effect?
- Requirements for tunneling to be significant in a given physical or chemical process.
- Provide examples of physical or chemical process in which tunneling is significant.
- Describe the general procedure for calculating a tunneling factor.
- Experimental evidence for tunneling.
- What can be inferred from a non-linear Arrhenius plot at low temperatures due to tunneling?
- Identify chemical reactions in which the tunneling effect would be significant and know how tunneling affects the k , A and E_a of a reaction at a given temperature.

Extra reading: R.P. Bell, "The Tunnel Effect in Chemistry", 1980; pp. 1-5, 12-30, 60-68, 75-76, 107-127.

2.6. Kinetic isotope effects (KIE)

(LM&S, section 9.9; pp. 395-396)

Questions you should be able to answer:

- Explain what a KIE experiment is, why they are used for, and what possible outcomes from this type of experiment are.
- Explain in detail why the rate constant of a reaction decreases when an atom (or atoms) in a reactant species is (are) replaced by a heavier isotope(s) (μ , ν , z_{pe} , D_0 , E_a , k).
- Recognize the different types of KIE from the knowledge of a reaction mechanism.
- Elucidate reaction mechanisms from the results of KIE experiments (and *vice versa*).

2.7. Complex reactions

(LM&S, sections 10.1-10.3; pp. 418-426)

(E&R, sections 35.7.3, 36.1; pp. 927-929, 955-957)

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.

Questions you should be able to answer:

- Identify a complex reaction by inspection of its rate law, the detection of intermediates, and the sign of E_a .
- Classify a set of complex reactions according to the three types studied (opposing, consecutive and parallel reactions).
- Recognize a pair of these reactions given a reaction mechanism.
- Explain the main ideas behind the application of the pre-equilibrium approximation
- Apply the SSA or the pre-equilibrium approximation to obtain rate law expressions and test the validity of reaction mechanisms.
- Explain what a rate controlling (or determining) step is.

2.8. Radical chain reactions

(LM&S, section 10.5; p. 431-437)

(E&R, section 36.5, 36.6; pp. 972-976)

Main steps of a radical chain reaction

Application of the SSA to derive or verify a rate law.

Questions you should be able to answer:

- Identify and obtain the main steps of free-radical chain reactions.
- Obtain the rate law of a radical chain reaction given the reaction mechanism.

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

(LM&S, section 10.3; pp. 426-429)

Question you should be able to answer:

- Explain what a rate controlling (or determining) step is.

Section 3. Elements of Physical Organic Chemistry (7 fifty-minute lectures)

3.1. The electrophilic aromatic substitution reaction

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

Questions you should be able to answer:

- Describe the general mechanism of the EAS reaction.
- Be able to apply the ideas of the general mechanism to concrete EAS reactions.
- Be able to draft possible TSs for these reactions.
- Explain what activating and deactivating substituents are.
- Explain what makes a substituent activating or deactivating. Provide examples.
- Explain how activating and deactivating groups affect the kinetics of EAS reactions relative to the reactions of benzene.
- Be able to classify a given substituent in activating or deactivating. Explain your choice.
- Explain what are the orientation effects of activating and deactivating substituents in benzene towards the electrophilic aromatic substitution reaction (include the special case of halogens). Use concrete examples in your answer and explain.
- Given a mono-substituted benzene, be able to identify and explain the orientation effects of the substituent.
- Explain the orientation effects of activating and deactivating substituents in benzene.

3.2. Molecular Orbital Theory and Frontier Orbitals

Basic elements of Molecular Orbital (MO) theory

Frontier orbitals (HOMO and LUMO) and chemical reactions

Questions you should be able to answer:

- Explain what MOs are and how they are calculated
- Explain what frontier orbitals are and why they are important in chemical reactions
- Explain what is the most important frontier orbital interaction during an EAS reaction.

3.3. The equation for estimating chemical reactivity

Electrostatic criteria of reactivity

Electronic criteria of reactivity

Questions you should be able to answer:

- Explain what an electrostatically-controlled reaction is.
- Explain what an electronically-controlled reaction is.
- Explain how the electrostatic criteria of reactivity applies to the EAS reaction taking activation/deactivation and orientation effects into account.
- Explain how the electronic criteria of reactivity applies to the EAS reaction taking activation/deactivation and orientation effects into account.

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.

Questions you should be able to answer:

- Explain what an acid and a base are according to Lewis theory. Provide examples.
- Mention some of the characteristics that are associated with hard acids and bases. Provide examples.
- Mention some of the characteristics that are associated with soft acids and bases. Provide examples.
- Explain the main idea behind the HSAB theory and relate this with the electronic and electrostatic criteria of reactivity.