Lead City University, Ibadan
Faculty of Sciences
Department of Biochemistry

COURSE PARTICULARS

Course Title: Chemical Kinetics and Thermodynamics
Course Code: CHM 311
No. of Units: 3
Status: Compulsory

LECTURER DETAILS

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COURSE DESCRIPTION

Chemistry is the science that describes the structure and composition of matter, the changes in structure and composition these matters undergo and the energy relations associated with the changes. Physical Chemistry is, therefore, a branch of chemistry which concerns itself with the study of the structure of matter and its physical properties, and the laws governing the chemical interactions. The study goes further to collect the experimental data needed to define the properties of gases, liquids solids, solutions and colloidal dispersions and to provide them a theoretical foundation in the form of laws.

COURSE OBJECTIVE

At the end of this course, students are expected to;

a. Identify the effects of temperature, concentration and catalysts on reaction rates.
b. Be able to approve the order of a reaction from the experimental data given.
c. Explain concisely collision and kinetic theories as involved in rates of reactions.
d. Describe reversible, chain and consecutive side reactions.

ASSESMENT

Class Attendance	5marks
Test(s) and Assignments	25marks
Final Examination	70marks

LECTURE PLAN

Week	Topic
1	Review of Reaction Rates
2	Effects of temperature, concentration and catalyst on reaction rates
3	Rate of reaction, rate constant and units.
4	Order of reaction and determination of their fractional lives
5	Molecularity of a reaction
6	Experimental methods for studying slow and fast reaction
7	Theories of reaction rates and collision theories of reaction
8	Collision theory in unimolecular reaction
9	Kinetic theory in termolecular reactions and complex reactions
10	Reversible reactions
11	Consecutive reactions
12	Types of chemical equilibria
13	Phase Equilibria

READING LIST

1. Sharma K.K. and Sharma L.K. (2006): A textbook of Physical Chemistry, Vikas Publishing House, 4th Edition.
2. Peter Atkins (2006): Inorganic Chemistry, Oxford University Press, 4th Edition.

TUTORIAL QUESTIONS

1a. The rate constant for a reaction at 110°C is found to be twice the value of that at 100°C. Calculate the activation energy of the reaction. **Given: R = 8.314 JKmol^{-1}**.

b. Write the Arrhenius equation and define all terms.

c. Define the half-life of a reaction. Derive an expression for the half-life of a first-order reaction.

2a. The rate constant of a first-order reaction is 3.46 x 10^{-2} s^{-1} at 298K. What is the rate constant at 350K if the activation energy for the reaction is 50.2 KJ/mol?

b. If the constant of a first order-reaction is 66s^{-1}. What is the rate constant in units of minutes?

c. Write the reaction rate expression for the following reaction in terms of the disappearance of the reactants and appearance of the products.

$H_{2(g)} + I_{2(g)} \rightarrow 2HI_{(g)}$

3a. Complete the various steps for the following chain reaction.

i. $Br_2 \rightarrow 2Br'$

ii. $Cl_2 \rightarrow 2Cl'$

b. Derive an expression for the quarter-life of a first-order reaction.

c. Derive the unit of K_2 in second-order reaction.

4a. Explain the effects of a catalyst as regards reaction rate.

b.i. After 500sec. half of a certain substance has reacted. What fraction of the substance will react after 800sec. if the reaction is of first-order?

ii. Using the following data:

t (sec)	0	900	1800
Conc.	50.8	19.7	7.62

Show that the reaction is of first-order.

5a. Define the following terms:

i. The order of a reaction.

ii. The molecularity of a reaction.

b. Describe the four parameters on which the rate of chemical reactions depends.

c. What is the molecularity of the following reactions?

i. $2NO + O_2 \rightarrow 2NO_2$

ii. $2FeCl_3 + SnCl_2 \rightarrow 2FeCl_2 + SnCl_4$

iii. $CH_3COOC_2H_5 + NaOH \rightarrow CH_3COONa + C_2H_5OH$

6a. Show that the inversion of sucrose is a first-order reaction.

b. Explain briefly what is meant by the following terms:

i. Consecutive reactions.

ii. Chain reactions.

iii. Side reactions.

iv. Reversible reactions

c. Explain the following expression:

$t_{1/2}$; $x = \frac{a}{2}$

7. Consider this elementary step:

$X + 2Y \rightarrow XY_2$

a. Write a rate law for the expression above.

b. If the initial rate of formation of XY_2 is 3.80×10^{-3} m/s and the initial concentrations of X and Y are 0.26M and 0.88M respectively, what is the rate constant of the reaction?

c. i. Define the term 'Activation Energy' (E_a).

d. ii. Of what importance is Activation Energy in Catalysis.

8a.i. Show that a reaction with the following data is of second-order.

Time (s)	0	4	6	10	14	20
(a-x)		8.04	5.30	4.58	3.50	2.70	2.22
X		0	2.74	3.46	4.54	5.34	5.82

ii. find the half-life of the reaction

b. Derive the mathematical expression for a first-order reaction.

c. Discuss and give two examples of enzyme catalysis.

9a. The hydrolysis of ethyl nitrobenzoate ($C_2H_5C_6H_4N$) by aqueous sodium hydroxide was followed at 25°C by titration of the hydroxide against standard acid at different stages in the reaction. From the given data, show that the reaction is of second-order:

Time (s)	0	95	140	222	334	805	1364
ml. of acid	10	9.3	9.0	8.5	7.9	6.1	4.8

b. The following data was obtained on the hydrolysis of methyl acetate at 25°C in the presence of 0.35M hydrochloric acid which was used as a catalyst.

Time (s)	0	1200	4500	7140	∞

ml. of alkali 24.36 25.85 29.32 31.72 47.15

from the data above, show that the hydrolysis of methyl acetate is a first-order reaction.

c. The first order rate constant for the reaction of methyl chloride (CH_3Cl) with H_2O to produce methanol (CH_3OH) and hydrochloric acid (HCl) is 3.32×10^{-10} s^{-1} at 25°C. Calculate the rate constant at 40°C, if the activation energy is 116KJmol^{-1}.

10a. Decomposition of benzene diazonium chloride was studied at a constant temperature by measuring the volume of N_2 evolved at various intervals of time. The following data was obtained:

Time (min.)	0	20	50	70	∞
N_2 (ml.)	0	10	25	33	162

From the data above, show that the decomposition of benzene diazonium chloride is of first-order reaction.

b. Derive the equation for determining rate constant for a second-order reaction in which $a = b$.

c. The thermal decomposition of N_2O_5 obeys first-order kinetics. At 45°C, a plot of $\ln[N_2O_5]$ versus t gives a slope of -6.18×10^{-4} min^{-1}. What is the half-life of the reaction?

11a. It has been determined experimentally that the sequence of steps for a chemical reaction is as follows:

A + B → C (Slow)

C + B → D (Fast)

What is the rate equation and the overall chemical equation for the reaction steps above?

b. Derive the formula for determining the half-life of a first-order reaction?

c. Write the reaction rate expression for the following reaction in terms of the disappearance of reactants and the appearance of the product.

$2H_{2(g)} + O_{2(g)} \rightarrow 2H_2O_{(g)}$

12a. The decomposition of ethane (C_2H_6) to methyl radicals is a first-order reaction with a rate constant of 5.36×10^{-4}s at 700°C. Calculate the half-life of the reaction in minutes.

b. Derive an expression for the quarter-life of a first-order reaction.

c. Show the mathematical relationship between a zero-order reaction and its half-life.

13a. Benzene diazonium chloride decomposes in the presence of water according to first-order kinetics. If the rate constant at 25°C is 2.8×10^{-3} min^{-1}, and the activation energy is 11.9Kcal mol^{-1}. Find the rate constant at 35°C.

b. Trichloroacetic acid in aniline solvent (acting as a catalyst) decomposes to give chloroform and carbon dioxide. The rate constant for this first-order reaction is 4.0×10^5 min^{-1} at 25°C and 8.0×10^4 min^{-1} at 45°C. Calculate the energy of activation for this reaction.

c. The radioactive isotope of an element x has a half-life of 950 days and decays by first order kinetics. (a) What is the rate constant of the decay reaction of x ? (b) How much would a sample of 10g of x be left after 3,000 days?

14a. How does a catalyst increase the rate of a reaction?

b. List eight (8) general characteristics of catalyzed reactions.

c. Distinguish between homogeneous and heterogeneous catalysis.

15a. A first-order reaction is 40% complete at the end of 5min. Calculate its reaction rate in seconds?

b. In the hydrolysis of ethyl acetate using equal concentration of HCl and NaOH the following results were obtained:

t (min.)	0	5	15	25	35

HCl (ml)16.0 10.24 6.13 4.32 3.41

Show that the reaction is of second-order.

i. Find the half-life of the reaction above.

ii. at what time will the concentration of HCl be 7.22ml?