MACHAKOS UNIVERSITY

SCHOOL OF PURE AND APPLIED SCIENCES

UNIVERSITY EXAMINATIONS 2018/2019

SECOND YEAR SECOND SEMESTER EXAMINATION FOR THE DEGREE OF BACHELOR OF EDUCATION SCIENCE (SCHOOL BASED)

SCH 101: PHYSICAL CHEMISTRY

TIME: 2 HOURS

INSTRUCTIONS:

ANSWER QUESTION ONE [COMPULSORY] AND ANY OTHER TWO QUESTIONS.

USEFUL CONSTANTS:

$N_o = 6.023 \times 10^{23}\ mol^{-1}$

$1\ eV = 1.602 \times 10^{-19}\ J$

h = Planck's constant = 6.626×10^{-34} J.s

QUESTION ONE (THIRTY MARKS)

a) What is the difference between fractional order reactions and zero order reactions (2 marks)

b) Deduce the rate constant and $t_{1/2}$ for the nth reaction (4 marks)

c) State the 1st, 2nd and 3rd laws of thermodynamics (3 marks)

d) A reaction of the type A ↔ B + C has a rate constant k = 3.6×10^{-5} M/s.

  a. What is the molarity of A after a reaction time of 30.0 min if the initial concentration of A is 0.096 M?

  b. Calculate the half-life (in minutes) of the reaction in part (a) (5 marks)

e) Write the rate law for each of the following elementary reactions: (3 marks)

  (a) $O_3(g) + O(g) \rightarrow 2\,O_2(g)$

  (b) $Br(g) + Br(g) + Ar(g) \rightarrow Br_2(g) + Ar(g)$

  (c) $Co(CN)_5(H_2O)^{2-}(aq) \rightarrow Co(CN)_5{}^{2-}(aq) + H_2O(l)$

f) Derive an expression for the half-life of a zero-order reaction and clearly state the characteristics corresponding to these type of reactions (4 marks)

g) Derive the Clausius–Clapeyron equation (3 marks)

h) The vapor pressure of ethanol at 34.7°C is 100.0 mm Hg, and the heat of vaporization of ethanol is 38.6 kJ/mol. What is the vapor pressure of ethanol (in millimetres of mercury) at 65.0°C? (3 marks)

i) The vapor pressure of water at 25°C is 0.0313 atm. Calculate the values of K_p and K_c at 25°C for the equilibrium $H_2O(l) \leftrightarrow H_2O(g)$. (3 marks)

QUESTION TWO (TWENTY MARKS)

j) The Arrhenius reaction rates increase with increase in temperature

i. Write down the Arrhenius equation (4 marks)

ii. The values of the Arrhenius factor and Activation Energy are 4×10^{12} s^{-1} and 98.6 $KJmol^{-1}$, respectively. Calculate the temperature at which its half-life is 10 seconds. (4 marks)

k) Describe, using equations and appropriate diagrams, how each of the following approach is used to determine the order of reaction. 12 marks

i. Van't Hoff's differential approach

ii. Graphical approach

iii. Substitution methods

QUESTION THREE (TWENTY MARKS)

a) Thermodynamics is a precise quantitative subject whose concepts must be defined clearly. Define and explain each of the following: (8 marks)

(a) System (b) Enthalpy (c) Entropy (d) Phase changes

b) Show that at constant temperature and pressure;

$$\Delta G_{system} = -T\Delta S_{universe}$$ (6 marks)

c) An instant pack contains 75 g of NH_4NO_3 and ¼ kg of water. Compute the temperature changes if the two are mixed together. Cp_{H20} = 75.3 J/mol and RMM of NH_4NO_3 = 80.05g (6 marks)

QUESTION FOUR (TWENTY MARKS)

a) Consider the reaction $H_2(g) + I_2(g) \leftrightarrow 2\ HI(g)$. Suppose that we have a mixture of $H_2(g)$, $I_2(g)$ and HI (*g*) at 700 K with concentrations and $[H_2]_t = 0.10$ M, $[I_2]_t = 0.20$ M, $[HI]_t = 0.40$ M. (The subscript *t* on the concentration symbols means that the concentrations were measured at some arbitrary time *t*, not necessarily at equilibrium.) Calculate reaction quotient and show how the resulting generalizations can be used to predict the direction of the reaction. (6 marks)

b) The equilibrium constant, K_c for the reaction in a) above is 57.0 at 700 K. If the initial concentrations are [H2] = 0.100 M [I2] = 0.200 M at 700K, what are the concentrations of and HI at equilibrium? What is the composition of the equilibrium mixture in moles? (6 marks)

c) Discuss the key factors that alter the composition of an equilibrium mixture (8 marks)

QUESTION FIVE (TWENTY MARKS)

a) For a lead storage battery:

(a) Sketch one cell that shows the anode, cathode, electrolyte, direction of electron and ion flow, and sign of the electrodes. (2 marks)

(b) Write the anode, cathode, and overall cell reactions. (2 marks)

(c) Calculate the equilibrium constant for the cell reaction (E° = 1.924 V). (2 marks)

(d) What is the cell voltage when the cell reaction reaches equilibrium? (2 marks)

b) Consider the following table of standard reduction potentials:

Reduction Half-Reaction	$E°$ (V)
$A^{3+} + 2e^- \rightarrow A^+$	1.47
$B^{2+} + 2e^- \rightarrow B$	0.60
$C^{2+} + 2e^- \rightarrow C$	−0.21
$D^+ + e^- \rightarrow D$	−1.38

i. Which substance is the strongest reducing agent? Which is the strongest oxidizing agent? (2 marks)

ii. Which substances can be oxidized by B^{2+}? Which can be reduced by C? (2 marks)

iii. Write a balanced equation for the overall cell reaction that delivers the highest voltage and calculate $E°$ for the reaction. (2 marks)

c) What is rust? What causes it to form? What can be done to prevent its formation? (6 marks)