MACHAKOS UNIVERSITY

University Examinations 2022/2023 Academic year

SCHOOL OF PURE AND APPLIED SCIENCES

DEPARTMENT OF PHYSICAL SCIENCES

THIRD YEAR SECOND SEMESTER EXAMINATION FOR

BACHELOR OF SCIENCE (ANALYTICAL CHEMISTRY)

SAN 305: PHOTOCHEMISTRY

DATE: 20/4/2023 **TIME: 8:30 – 10:30 AM**

INSTRUCTIONS

- The paper consists of **two** sections.
- Section **A** is **compulsory** (30 marks)
- Answer any **two** questions from section **B** (each 20 marks)
- Check for periodic Table behind the Question paper (page 4)

Useful constants

$c = 3.0 \times 10^{8}$ m/s $h = 6.626 \times 10^{-34}$ Js = 6.624 × 10^{-27} erg-sec, N = 6.02×10^{23}

1 kcal = 4200 J

SECTION A

QUESTION ONE (30 MARKS)

a) State and explain the laws of photochemistry (4 marks)

b) The energy gap between the triplet ground state and the excited singlet state for molecular oxygen is 120 kJ mol^{-1}. Calculate the wavelength of photons given off if an excited singlet state relaxes to the ground state with emission of light (3 marks)

c) (i) Using the Jablonski diagram explain the various photophysical processes (8 marks)

(ii) Use the Jablonski diagram to explain why the wavelength of fluorescence is greater than that of phosphorescence (4 marks)

d) A solution which transmits 12 % of a certain wavelength of light beam is passed through a 1.5 cm cell containing 0.45 molar solution. Calculate the:

(i) Transmittance (1 mark)

(ii) Absorbance (2 marks)

(iii) Molar extinction coefficient (2 marks)

e) (i) Explain why the quantum yield for the photochemical formation of hydrogen chloride is high in the absence of oxygen but low when oxygen is present (2 marks)

(ii) Calculate the quantum yield of gaseous HI when irradiated with a wavelength of 253 nm where 0.018 moles of HI decompose per kcal of radiant energy absorbed (4 marks)

SECTION B

QUESTION TWO (20 MARKS)

a) Using relevant diagrams, explain each of the following phenomenon:

(i) Kasha's rule (3 marks)

(ii) Stokes shift (3 marks)

(iii) Franck-Condon principle (3 marks)

b) State four differences between fluorescence and phosphorescence (4 marks)

c) Explain the mechanism of photosensitization (5 marks)

d) State the conditions for high or low quantum yield (2 marks)

QUESTION THREE (20 MARKS)

a) State four causes of low quantum yield (4 marks)

b) Distinguish between;-

(i) Primary and secondary photochemical process (2 marks)

(ii) Chemiluminescence and photochemical reaction (2 marks)

c) Describe the principle of flash photolysis (5 marks)

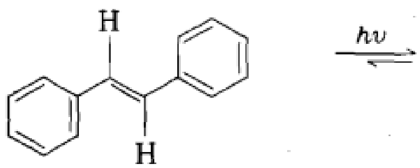
d) The extinction coefficient of $K_3[Fe(CN)_6]$ at 419 nm is 1020 $cm^2\ mol^{-1}$. Determine the percentage of light that is transmitted from a cell of thickness 2.0 cm containing 1×10^{-4} M $K_3[Fe(CN)_6]$ solution (4 marks)

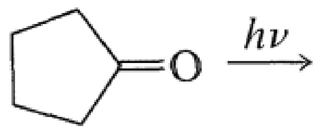
e) A solution containing 5.2 0 ppm $KMnO_4$ had a percentage of 32 % in 1.25 cm cell at 520 nm. Calculate the molar absorptivity of the solution at 520 nm (3 marks)

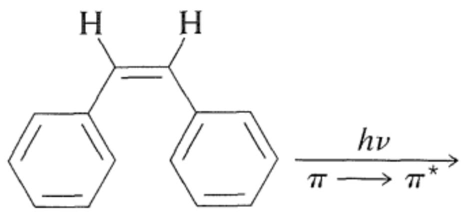
QUESTION FOUR (20 MARKS)

a) State five differences between photochemical reaction and thermal reaction (5 marks)

b) Complete and name the types of photochemical reactions given below

(i)  (2 marks)

(ii)  (2 marks)

(iii)  (2 marks)

c) State four applications of fluorescence (4 marks)

d) Show a photochemical reaction between H_2 and Br_2 and determine the expression for the rate of formation of HBr (5 marks)

QUESTION FIVE (20 MARKS)

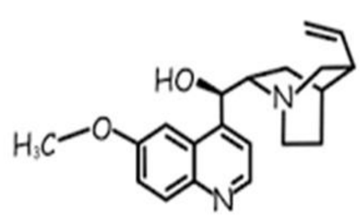
a) (i) What is an actinometer? (2 marks)

(ii) Briefly explain the working principle of any one chemical actinometer (6 marks)

b) Using a schematic diagram, show an experimental set up how you will determine the quantum yield of a solution and state the function of each component in your experimental set up (7 marks)

c) Substitution of carboxylic acid or carbonyl group on an aromatic ring generally inhibits fluorescence. Explain (2 marks)

d) Using the structure of quinine molecule below explain which part will likely behave as a chromophore and as a reaction centre (3 marks)



Periodic Table of the Elements 2006

	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	
1 H 1.01																	2 He 4.00
3 Li 6.94	4 Be 9.01											5 B 10.81	6 C 12.01	7 N 14.01	8 O 15.99	9 F 19.00	10 Ne 20.18
11 Na 22.99	12 Mg 24.31											13 Al 26.98	14 Si 28.09	15 P 30.97	16 S 32.07	17 Cl 35.45	18 Ar 39.95
19 K 39.10	20 Ca 40.08	21 Sc 44.96	22 Ti 47.87	23 V 50.94	24 Cr 52.00	25 Mn 54.94	26 Fe 55.85	27 Co 58.93	28 Ni 58.69	29 Cu 63.55	30 Zn 65.41	31 Ga 69.72	32 Ge 72.64	33 As 74.92	34 Se 78.96	35 Br 79.90	36 Kr 83.80
37 Rb 85.47	38 Sr 87.62	39 Y 88.91	40 Zr 91.22	41 Nb 92.91	42 Mo 95.94	43 Tc (98)	44 Ru 101.07	45 Rh 102.91	46 Pd 106.42	47 Ag 107.87	48 Cd 112.41	49 In 114.82	50 Sn 118.71	51 Sb 121.76	52 Te 127.60	53 I 126.90	54 Xe 131.29
55 Cs 132.91	56 Ba 137.33	57 La 138.91	72 Hf 178.49	73 Ta 180.95	74 W 183.84	75 Re 186.21	76 Os 190.23	77 Ir 192.22	78 Pt 195.08	79 Au 196.97	80 Hg 200.59	81 Tl 204.38	82 Pb 207.2	83 Bi 208.98	84 Po (209)	85 At (210)	86 Rn (222)
87 Fr (223)	88 Ra (226)	89 Ac (227)	104 Rf (261)	105 Db (262)	106 Sg (266)	107 Bh (264)	108 Hs (270)	109 Mt (268)	110 Ds (281)	111 Rg (272)							

58 Ce 140.12	59 Pr 140.91	60 Nd 144.24	61 Pm (145)	62 Sm 150.36	63 Eu 151.97	64 Gd 157.25	65 Tb 158.93	66 Dy 162.50	67 Ho 164.93	68 Er 167.26	69 Tm 168.93	70 Yb 173.04	71 Lu 174.97
90 Th 232.04	91 Pa 231.04	92 U 238.03	93 Np (237)	94 Pu (244)	95 Am (243)	96 Cm (247)	97 Bk (247)	98 Cf (251)	99 Es (252)	100 Fm (257)	101 Md (258)	102 No (259)	103 Lr (262)