

CHUKA



UNIVERSITY

UNIVERSITY EXAMINATIONS

EXAMINATION FOR THE AWARD OF DEGREE OF BACHELOR OF SCIENCE

CHEM 323: CHEMICAL KINETICS

STREAMS: BSC CHEMISTRY

TIME: 2 HOURS

DAY/DATE: MONDAY 16/12/2024

11.30 A.M – 1.30 P.M.

INSTRUCTIONS:

- *ANSWER QUESTION ONE AND ANY OTHER TWO QUESTIONS.*

General data and fundamental constants

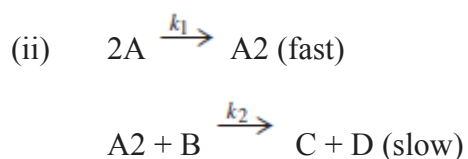
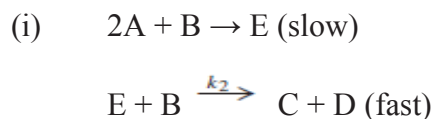
Quantity	Symbol	Value	Power of ten	Units
Speed of light	c	2.997 925 58*	10^8	m s^{-1}
Elementary charge	e	1.602 176	10^{-19}	C
Faraday's constant	$F = N_A e$	9.648 53	10^4	C mol^{-1}
Boltzmann's constant	k	1.380 65	10^{-23}	J K^{-1}
Gas constant	$R = N_A k$	8.314 47		$\text{J K}^{-1} \text{mol}^{-1}$
		8.314 47	10^{-2}	$\text{dm}^3 \text{bar K}^{-1} \text{mol}^{-1}$
		8.205 74	10^{-2}	$\text{dm}^3 \text{atm K}^{-1} \text{mol}^{-1}$
		6.236 37	10	$\text{dm}^3 \text{Torr K}^{-1} \text{mol}^{-1}$
Planck's constant	h	6.626 08	10^{-34}	J s
	$\hbar = h/2\pi$	1.054 57	10^{-34}	J s
Avogadro's constant	N_A	6.022 14	10^{23}	mol^{-1}
Atomic mass constant	m_u	1.660 54	10^{-27}	kg
Mass				
electron	m_e	9.109 38	10^{-31}	kg
proton	m_p	1.672 62	10^{-27}	kg
neutron	m_n	1.674 93	10^{-27}	kg
Vacuum permittivity	$\epsilon_0 = 1/c^2 \mu_0$	8.854 19	10^{-12}	$\text{J}^{-1} \text{C}^2 \text{m}^{-1}$
	$4\pi\epsilon_0$	1.112 65	10^{-10}	$\text{J}^{-1} \text{C}^2 \text{m}^{-1}$
Vacuum permeability	μ_0	4π	10^{-7}	$\text{J s}^2 \text{C}^{-2} \text{m}^{-1} (= \text{T}^2 \text{J}^{-1} \text{m}^3)$
Magneton				
Bohr	$\mu_B = e\hbar/2m_e$	9.274 01	10^{-24}	J T^{-1}
nuclear	$\mu_N = e\hbar/2m_p$	5.050 78	10^{-27}	J T^{-1}
g value	g_e	2.002 32		
Bohr radius	$a_0 = 4\pi\epsilon_0 \hbar^2 / m_e e^2$	5.291 77	10^{-11}	m
Fine-structure constant	$\alpha = \mu_0 e^2 c / 2h$	7.297 35	10^{-3}	
	α^{-1}	1.370 36	10^2	
Second radiation constant	$c_2 = hc/k$	1.438 78	10^{-2}	m K
Stefan–Boltzmann constant	$\sigma = 2\pi^5 k^4 / 15h^3 c^2$	5.670 51	10^{-8}	$\text{W m}^{-2} \text{K}^{-4}$
Rydberg constant	$R = m_e e^4 / 8h^3 c \epsilon_0^2$	1.097 37	10^5	cm^{-1}
Standard acceleration of free fall	g	9.806 65*		m s^{-2}
Gravitational constant	G	6.673	10^{-11}	$\text{N m}^2 \text{kg}^{-2}$

*Exact value

QUESTION ONE (30 MARKS)

a)

- (i) A reaction is 50% complete in 20 min. How much time will be taken to complete 75% reaction? (1 Mark)
- (ii) The kinetics of a reaction was followed by measuring the absorbance due to a reactant at its λ max at 25°C. The log (absorbance) versus time (min) plot was a straight line with a negative slope (0.30×10^{-2}) and a positive intercept. Find the half-life period of reaction. (1 Mark)
- (iii) A radioactive element gives 2000 counts per min at a given time. After one hour, counts were found to be 750 per min. What is half-life of the element? (1 mark)
- (iv) A reactant reacts 30% in 30 min. If the reaction follows a second order kinetics, find rate constant and remaining concentration of reactant after 60 min. (2 Mark)
- (v) A second order reaction with initial concentration of each reactant as 0.5 mol dm^{-3} was carried out in presence of acid as catalyst. At pH 4.0 the half-life of reaction was found to be 60 min. calculate the observed and true rate constant for the reaction. (2 marks)
- (vi) In an experiment consisting of two reactants A and B, the half-life of reaction was measured. The half-life remained same when concentration of B doubled keeping [A] constant. On the other hand, when concentration of B is kept constant and [A] was doubled, the half-life reduced to half of its original value. Find the order of reaction with respect to each A and B. Suggest the rate law and also suggest which of the following mechanism agrees with rate law: (2 marks)



- (vii) Explain the processes of fluorescence and phosphorescence with help of Jablonski-Diagram showing mechanism of the two processes.
(3 marks)

- (viii) The values of rate constants for reaction

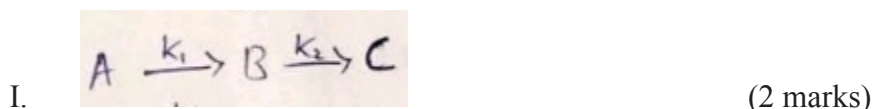


Were observed as $3.0 \times 10^{-5} \text{ mol}^{-1} \text{ dm}^3 \text{ s}^{-1}$ and $2.5 \times 10^{-3} \text{ mol}^{-1} \text{ dm}^3 \text{ s}^{-1}$ at 357°C and 447°C , respectively. Calculate the E_{act} for forward and backward reaction of $\Delta H = 15.5 \text{ kJ mol}^{-1}$.
(1 marks).

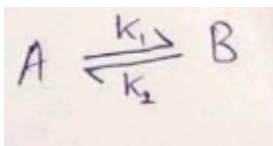
- (ix) Derive Arrhenius equation and explain how the parameters involved in equation can be determined experimentally (3 marks)

b)

- i. Prove that for n^{th} order reaction, the plot of $\ln t_{1/2}$ versus $1/T$ is a straight line and slope of the line is equal to E_{act} . (1 mark)
- ii. Determine the values of rate constant K_1 and K_2 in the following reactions.

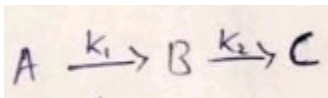


- iii. For a reversible reaction



k_1 is $4.0 \times 10^{-2} \text{ s}^{-1}$ and k_2 is half of k_1 . Initial concentration of A is 2.0 mol dm^{-3} . At what time the concentration of B will be 1.0 mol dm^{-3} . (2 marks)

- iv. If the initial concentration of A is 2.0 mol dm^{-3} and k_1 and k_2 are 0.30 and 0.15 min^{-1} , respectively, at what time the concentration of B in the following reaction will be maximum:



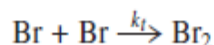
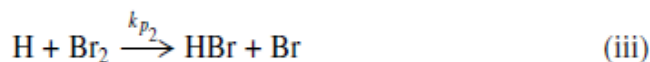
Also calculate the maximum concentration of B. (2 marks)

- v. Discuss the following:
- Steady state treatment (2 marks)
 - Steps involved in chain reaction and provide suitable equations for each step. (2 marks)

QUESTION TWO (20 MARKS)

a)

- i. The possible mechanism for reaction between H_2 and Br_2 is given by



Determine the rate of reaction between $[\text{Br}]$ and $[\text{H}]$ using the steady state approximation method with respect to $[\text{H}]$ and $[\text{Br}]$ respectively (3 Marks)

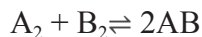
- Discuss transition state theory and partition function using thermodynamic approach. (4 Marks)
- For a first order parallel reaction, the Arrhenius factor for formation of two products are 108 sec^{-1} and their energy of activation are 150 and 75 kJ mol^{-1} , respectively. At what temperature the two products will be formed at the same rate? (3 marks)

For two parallel reactions of the same order, the rate constants are k_1 and k_2 and the energies of activation are E_1 and E_2 , respectively. Prove that apparent overall energy of activation $E = \frac{k_1 E_1 + k_2 E_2}{k_1 + k_2}$

iv. Explain steric factors in terms of partition function (2 Marks)

b)

i. The E act and pre-exponential factor for a reaction



Are 15.5 kJ mol^{-1} and $10.9 \times 10^{10} \text{ dm}^3 \text{ mol}^{-1} \text{ sec}^{-1}$, respectively. Calculate the values of ΔH^\ddagger and ΔS^\ddagger at 1000 K. (2 Marks)

ii. It is assumed that the values of q_t , q_v and q_r for different molecules in reaction

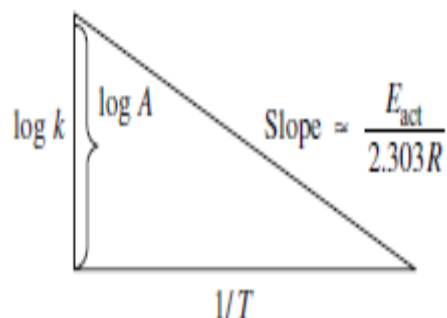


are equal. Calculate the value of Arrhenius factor A at 298°K for above reaction,

if $q_t = 10^8$, $q_r = 10$ and $q_v = 1$. (2 Marks)

iii. Calculate the rate constant for decomposition of HI at 500 K, if energy of activation is $130.0 \text{ kJ mol}^{-1}$ and collision diameter of HI is 3.5 \AA (2 Marks)

iv. The plot of $\log k$ versus $1/T$, i.e. Arrhenius plot was linear with a negative slope 4.50×10^3 and intercept equal to 11.90 for a reaction. Calculate E act, ΔH^* (at 25°C) and ΔS^\ddagger (2 Marks)



QUESTION THREE (20 MARKS)

a)

(i) Comment and justify that the order of a reaction may often be changed by varying the concentration of the reactants. (2.5 marks)

(ii) Zero order reaction must be multistep. Explain. Does such a reaction go to completion? (2.5 marks)

(iii) Comment on elementary reactions with molecularly greater than 3 generally don't occur. (2 marks)

(iv) Justify the statement using Lindemann mechanism. 'Unimolecular reactions are not always of first order' (3 marks)

(b)

(i) The effective rate constant of a first order reaction Lindemann mechanism has the following values $2.5 \times 10^{-3} \text{ sec}^{-1}$ when $C = 5 \times 10^{-2} \text{ gmole.lit}^{-1}$ and $4.2 \times 10^{-3} \text{ sec}^{-1}$ when $c = 9.8 \times 10^{-2} \text{ gm.mole.sec}^{-1}.\text{lit}^{-1}$. Find out the rate coefficient for the activation step. (2 marks)

(ii) Some P_4 is introduced into a flask at 600 degrees containing some inert gas. Phosphine proceeds to decompose into P_4 (g) and H_2 (g) and the reaction goes to completion the total pressure is given below as a function of time

T(sec)	0	60	120	α
P(mm of Hg)	260	270.5	273.14	274

The rate of equation for the backward reaction is given by

$$K_2 p_{\text{P}_4}^a \cdot p_{\text{H}_2}^b$$

Calculate a and b. Let the initial pressure of phosphine be 20 mm of Hg and half-life be 25 sec. Calculate k if the decomposition is first order and of its second order. (4 marks)

(iii) The gas phase reaction $2\text{N}_2\text{O}_5 \rightarrow 4\text{NO}_2 + \text{O}_2$ has $k = 2.05 \times 10^{13} \exp^{-(24.65 \text{ kcal.mol}^{-1}/RT)} \text{ sec}^{-1}$

(I) Give the values of A and E_a . (2 marks)

(II) Find k at 0 degrees (1 mark)

(III) Find $t_{1/2}$ at 0 degrees (1 mark)

QUESTION FOUR (20 MARKS)

a)(i) Derive the rate equation based on the absolute rate theory (4 marks)

(ii) Calculate ΔH^* and ΔS^* for a second order reaction



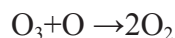
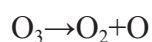
at 500K given $A = 2.0 \times 10^9 \text{ s}^{-1}$ and the energy of activation = 111 KJ mol^{-1} where

A = pre-exponential factor in Arrhenius equation $\{R = 8.31547 \text{ J K}^{-1} \text{ mol}^{-1}$,

$h = 6.62608 \times 10^{-34} \text{ Js}$, $K = 1.38065 \times 10^{-23} \text{ J K}^{-1}$, $N_A = 6.02214 \times 10^{23} \text{ mol}^{-1}\}$

(2 marks)

(iii) For the thermal decomposition of O_3 the following mechanism has been suggested



Assuming that $K^{-1}[\text{O}_2] \gg k_2 [\text{O}_3]$ show that the rate of the overall reaction is

$$-d[\text{O}_3]/dt = k[\text{O}_3]^2/[\text{O}_2].$$

(3 marks)

(iv) A certain substance A is mixed with an equal quantity of a substance B. At the end of 1 hour 75% A reacted. How much A will be left unreacted at the end of 2 hours if the reaction is of

(I) First order in A and independent of B. (1 mark)

(II) First order in A and first order in B (2 marks)

(III) Zero order in A and independent in B (1 mark)

(b) (i) Write short notes on differences between photochemical and thermal chemical reactions

(3 marks)

(ii) Einstein law of photochemical equivalence is always valid comment. (2 marks)

(iii) The quantum yield is always greater than one for any chain reaction comment.

(2 marks)

Table F.2 A selection of derived units

Physical quantity	Derived unit*	Name of derived unit
Force	1 kg m s^{-2}	newton, N
Pressure	$1 \text{ kg m}^{-1} \text{ s}^{-2}$ 1 N m^{-2}	pascal, Pa
Energy	$1 \text{ kg m}^2 \text{ s}^{-2}$ 1 N m 1 Pa m^3	joule, J
Power	$1 \text{ kg m}^2 \text{ s}^{-3}$ 1 J s^{-1}	watt, W

* Equivalent definitions in terms of derived units are given following the definition in terms of base units.

Table F.3 Common SI prefixes

Prefix	y	z	a	f	p	n	μ	m	c	d
Name	yocto	zepto	atto	femto	pico	nano	micro	milli	centi	deci
Factor	10^{-24}	10^{-21}	10^{-18}	10^{-15}	10^{-12}	10^{-9}	10^{-6}	10^{-3}	10^{-2}	10^{-1}
Prefix	da	h	k	M	G	T	P	E	Z	Y
Name	deca	hecto	kilo	mega	giga	tera	peta	exa	zeta	yotta
Factor	10	10^2	10^3	10^6	10^9	10^{12}	10^{15}	10^{18}	10^{21}	10^{24}