UNIT III : PROBLEM SET - PART B **NAME :** _____

1. (a) The Law of Mass Action States _____

_____.

(b) Does this law apply to reactions that involve more than one step? Explain.

_____

_____.

2. The following are one step reactions.
(1) $N_2O_5 \rightarrow 2NO_2 + 1/2\ O_2$ (2) $H_2 + I_2 \rightarrow 2HI$ (3) $2A + B \rightarrow C + D$ (all gases)

Complete the following table.

REACTION	RATE EQUATION	OVERALL ORDER	UNITS OF k
1			
2			
3			

3. The reaction: $HI + CH_3I \rightarrow CH_4 + I_2$ (all gases)
is known to be first order with respect to both reactants. The rate constant at 50°C is 2.3×10^{-3} litre/mol-min. Starting with equal concentrations of HI and CH_3I, each being 0.200 mol/litre, calculate :
(a) the concentration of HI remaining after 100 min, assuming that the reaction rate is constant over that period of time. (ANS : 0.1908 m/l)

(b) the concentration of I_2 produced after 200 min. (ANS : 0.0184 m/l)

4. For the following reaction : $3A + B \rightarrow D + F$

(a) What is the rate equation as predicted by the Law of Mass Action?

(b) What is the overall order? _____

(c) What is the probability that this reaction has a mechanism? Explain.

(d) Here is the experimental data for this reaction.

EXPT. #	CONC A (m/l) initial	CONC B (m/l) initial	RATE (moles/litre-min)
1	constant	1	4
2	constant	3	12
3	constant	5	20
4	2	constant	3
5	4	constant	12
6	6	constant	27

Using the rate law data, write the rate equation : _____

What is the order? _____ Why is the order different from the overall order? _____

_____

_____

What is the rate of the reaction in terms of B? _____

(e)When do the coefficients of the balanced overall equation equal the exponents of the rate equation.

(f) The following mechanisms are proposed as possible mechanisms for the overall equation. Show your evaluation of each mechanism briefly and summarize by acceptance or rejection of each mechanism with reasoning.

MECHANISM	EVALUATION
(I) (1) A + B = C (slow) (2) C + 2A = D + E (fast) (3) E = F (fast)	
(II) (1) 2A + B = 2E (slow) (2) 2E + A = D + S (fast) (3) S = F (fast)	
(III) (1) 2A + B = P (slow) (2) P + A = S + D (slow (3) 2S = F (fast)	
(IV) (1) 2A + B = D + G (slow) (2) G + A = H (fast) (3) H = F (fast)	
(v) (1) 2A + B = H + F (fast) (2) H + A = D (slow)	

5. (a) Heterogeneous catalysis is _____

_____

(b) Give an example with explanation of the catalysis of $H_2 + O_2$ to form H_2O or the decomposition H_2O_2 into water and oxygen. Your have to find the catalysts!

UNIT III
REMEDIAL PROBLEM SET - PART B

1. Hydrogen peroxide reacts with iodide according to the equatio

$$2H^+ + 2I^- + H_2O_2 = 2H_2O + I_2$$

The mechanism suggested for this reaction is

(1) $H^+ + I^- + H_2O_2 = HOI + H_2O$ (slow)

(2) $H^+ + I^- + HOI = I_2 + H_2O$ (fast)

(a) Do the elementary processes add up to the overall equation? Show this.

(b) According to the mechanism, which elementary process is the rate determining step? Explain.

(c) What is the rate law expression for this reaction? _____

(d) How would you expect the rate to be affected if the I^- concentration is doubled?

2. For the reaction between gaseous chlorine and nitric oxide

$$2NO + Cl_2 = 2NOCl \text{ (all gases)}$$

it is found that doubling the concentration of BOTH reactants increases the rate by a factor of eight, but by doubling the chlorine concentration alone the rate only doubles.
(a) What is the rate law expression <u>with respect to chlorine gas</u> .

(b) What is the overall order of the reaction?

3. The reaction between nitrogen dioxide and fluorine is :

$$2NO_2 + F_2 = 2NO_2F \text{ (all gases)}$$

The rate law data is tabulated as follows :

EXPT #	CONC NO_2 (m/l)	CONC F_2 m/l	RATE (m/l-sec)
1	1	1	2
2	1	2	4
3	1	3	6
4	3	1	6
5	5	1	10
6	6	1	12

(a) Determine the rate law expression. Give reasoning.

3. (b) The overall order is _____.
   (c) The units of k are _____.
   (d) Evaluate the following mechanisms for this reaction. Give reasons for acceptance or rejection of each.

MECHANISM STEPS	EVALUATION
(I)	
(1) $NO_2 + F_2 \rightarrow NO_2F + F$ (slow)	
(2) $F + NO_2 \rightarrow NO_2F$ (fast)	
(II)	
(1) $NO_2 + NO_2 \rightarrow NO + NO_3$ (slow)	
(2) $NO_3 + F_2 \rightarrow NO_2F + OF$ (fast)	
(3) $NO + OF \rightarrow NO_2F$ (fast)	

4. $(CH_3)_3CCl + OH^- \rightarrow (CH_3)_3COH + Cl^-$

   A suggested mechanism which agrees with the rate law data is

   (1) $(CH_3)_3 CCl \rightarrow (CH_3)_3C^+ + Cl^-$ (slow)

   (2) $(CH_3)_3C^+ + OH^- \rightarrow (CH_3)_3COH$ (fast)

   (a) Which step is the rate determining step? Explain.

   (b) What is the rate law expression? _____

   (c) What is the effect on the rate of the reaction if :

   (1) the concentration of $(CH_3)_3CCl$ is tripled?

   (2) the concentration of OH^- is doubled?

5. What advantage is there to the tabulation of specific rate constants for a group of reactions at a common temperature? Why is the temperature important?