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**Assignment – I**

1. Express the rate of the following reaction in terms of different reactants and products :

4 NH3 (g) + 5 O2 (g) → 4 NO (g) + 6 H2O (g)

If the rate of formation of NO is 3.6 x 10 – 3 mol L – 1 s – 1, calculate (i) rate of disappearance of NH3

(ii) rate of formation of H2O.

1. The reaction , 2 N2O5 (g) ⇌ 4 NO2 (g) + O2 (g) was studied in a closed vessel. It was found that the concentration of NO2 increases by 2 x 10 – 2 mol/L in five seconds. Calculate : (i) rate of reaction (ii) the rate of change of concentration of N2O5.
2. For an elementary reaction : 2 A + B → 3 C ; the rate of appearance of ‘C’ at time ‘t’ is 1.3 x 10 – 4 mol L – 1 s – 1, Calculate at this time : (i) rate of the reaction (ii) rate of disappearance of A.
3. For the decomposition of dinitrogen pentoxide at 200˚C , N2O5 (g) N2O4 (g) + O2 (g), if the initial pressure is 114 mm and after 25 minutes of the reaction, total pressure of the gaseous mixture is 133 mm, calculate the average rate of reaction in (a) atm min– 1 (b) mol L – 1 s – 1
4. The decomposition of N2O5 in CCl4 solution at 318 K has been studied by monitoring the concentration of N2O5 in the solution. Initially the concentration of N2O5 is 2.33 M and after 184 minutes, it is reduced to 2.08 M. The reaction takes place according to the equation : 2 N2O5 → 4 NO2 + O2

Calculate the average rate of this reaction in terms of hours, minutes and seconds. What is the rate of production of NO2 during this period ?

1. Nitrogen dioxide (NO2) reacts with fluorine (F2) to form nitryl fluoride (NO2F).

2 NO2 (g) + F2 (g) → 2 NO2F (g)

Write the rate of reaction in terms of : (i) rate of formation of NO2F (ii) rate of disappearance of NO2 (iii) rate of disappearance of F2.

1. Express the relationship between the rate of production of water and the rate of disappearance of oxygen in the reaction : 2 H2 + O2 → 2 H2O.
2. For the reaction , 4 NH3 (g) + 5 O2 (g) → 4 NO (g) + 6 H2O (g) , if the rate expression in terms of disappearance of NH3 is – , write the rate expression in terms of concentrations of O2 and H2O.
3. A reaction ; 2 X → Y + 3 Z (e.g. 2 NH3 → N2 + 3 H2) is being carried out in a closed vessel. The rate of disappearance of X, – is found to be 0.066 mol L – 1 s – 1. Calculate and
4. A chemical reaction, 2 A → 4 B + C, in gas phase occurs in a closed vessel. The concentration of B is found to be increased by 5 x 10 - 3 mol/L in 10 seconds. Calculate : the rate of disappearance of A.

CHEMICAL KINETICS Page No. 1

1. A + 2 B → 3 C + 2 D . The rate of disappearance of B is 1 x 10 – 2 mol L – 1 s – 1. What will be (i) Rate of the reaction (ii) Rate of change in concentration of A and C ?
2. For the reaction , R → P, the concentration of a reactant changes form 0.03 M to 0.02 M in 25 minutes. Calculate the average rate of reaction using units of time both in minutes and seconds.
3. In a reaction, 2 A → Products, the concentration of A decreases from 0.5 mol/L to 0.4 mol/L in 10 minutes. Calculate the rate during this interval.
4. Which of the following statements is correct?
5. The rate of a reaction decreases with passage of time as the concentration of reactants decreases
6. The rate of a reaction is same at any time during the reaction.
7. The rate of a reaction is independent of temperature change.
8. The rate of a reaction decreases with increase in concentration of reactant(s).
9. Which of the following expressions is correct for the rate of reaction given below ?

5 Br – (aq) + (aq) + 6 H+ (aq) 3 Br2 (aq) + 3 H2O (l)

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| a) = 5 | b) = |
| c) = | d) = 6 |

1. For a reaction, A → B, the rate of reaction can be denoted by or + , state the significance of plus and minus signs in this case.
2. Write expression for rate of reaction in terms of each reactant and product for the reaction

N2 + 3 H2 2 NH3

1. Express the rate of the following reaction in terms of disappearance of hydrogen in the reaction

3 H2 (g) + N2 (g) 2 NH3 (g)

1. For the reaction, N2 (g) + 3 H2 (g) 2 NH3 (g), if [NH3]/t = 4 x 10 – 8 mol L – 1 s – 1, what is the value of [H2]/t?
2. Show graphically the average and instantaneous rate of a reaction.
3. In a catalytic experiment involving Haber’s processes, N2 (g) + 3 H2 (g) 2 NH3 (g), the rate of reaction was measured as : rate = [NH3]/t = 2 x 10 – 4 Ms – 1. If there were no side reactions, what was the rate of reaction expressed in terms of N2?

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| a) 1 x 10 – 4 Ms – 1 | b) 4 x 10 – 4 Ms – 1 | c) 5 x 10 – 3 Ms – 1 | d) 1 x 10 – 3 Ms – 1 |

1. In the synthesis of ammonia from nitrogen and hydrogen gases, if 6 x 10 – 2 mole of hydrogen disappears in 10 minutes, the number of moles of ammonia formed in 0.3 minutes is

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| a) 1.8 x 10 – 2 | b) 1.2 x 10 – 3 | c) 4 x 10 – 2 | d) 3.6 x 10 – 2 |

1. For the reaction , N2O5 (g) 2 NO2 (g) + O2 (g), the value of rate of disappearance of N2O5 is given as 6.25 x 10 – 3 mol L – 1 s – 1 . The rate of formation of NO2 and O2 is given respectively as :

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| --- | --- |
| a) 1.25 x 10 – 2 molL – 1 s – 1 & 6.25 x 10 – 3 molL – 1s – 1 | b) 6.25 x 10 – 3 molL – 1 s – 1 & 6.25 x 10 – 3 molL – 1s – 1 |
| c) 1.25 x 10 – 2 molL – 1 s – 1 & 3.125 x 10 – 3 molL – 1s – 1 | d) 6.25 x 10 – 3 molL – 1 s – 1 & 3.125 x 10 – 3 molL – 1s – 1 |

1. For the reaction, A + 3 B → 2 C + 2 D , the concentration of A changes from 0.0150 M to 0.0135 M in 1 minute. What is the rate of formation of C in Ms – 1.

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| a) 5 x 10 – 5 | b) 2.5 x 10 – 5 | c) 3 x 10 – 5 | d) 5 x 10 – 4 |

CHEMICAL KINETICS Page No. 2

**Karan Arora** **M: 9416974837**

1. For the reaction : 2 N2O5 → 4 NO2 + O2 : Select the correct statement
2. Rate of formation of O2 is same as rate of formation of NO2.
3. Rate of disappearance of N2O5 is two times the rate of formation of NO2.
4. Rate of formation of O2 is 0.5 times rate of disappearance of N2O5 .
5. Rate of formation of NO2 is equal to rate of disappearance of N2O5
6. In a certain reaction shown below ; 4 A + 2 B → 3 C, If rate of formation of C is 9.6 x 10 – 2 mol/L s. What will be rate of reaction ?

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| --- | --- | --- | --- |
| a) 9.6 x 10 – 2 mol/L s | b) 3.2 x 10 – 2 mol/L s | c) 2.4 x 10 – 2 mol/L s | d) 4.8 x 10 – 2 mol/L s |

1. For the reaction, H2O2 + 2 H+ + 3 → + 2 H2O, Select the correct statement
2. Rate of disappearance of H2O2 will be three times the rate of disappearance of I – .
3. Rate of disappearance of H2O2 is 1/3 of rate of formation of
4. Rate of disappearance of I – ions will be three times the rate of formation ions.
5. Rate of formation of H2O is ½ of rate of formation of
6. For the hypothetical reaction : 2 A → 3 C, the reaction rate ‘r’ in terms of the rate of change of the concentration is given by :

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| a) r = | b) r = | c) r = | d) r = |

1. For the reaction N2 + 3 H2 → 2 NH3, the rate of change of concentration for hydrogen is – 0.3 x 10 – 4 Ms – 1. The rate of change of concentration of ammonia is

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| a) – 0.2 x 10 4 Ms – 1 | b) 0.2 x 10 – 4 Ms – 1 | c) 0.1 x 10 – 4 Ms – 1 | d) 0.3 x 10 – 4 Ms – 1 |

1. For the chemical reaction N2 (g) + 3 H2 (g) 2 NH3 (g), The correct option is :

|  |  |
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| a) = | b) = 2 |
| c) = | d) 3 = 2 |

1. For the reaction : N2 + 3 H2 → 2 NH3, if = 2 x 10 – 4 mol L – 1 s – 1 , the value of would be

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| a) 4 x 10 – 4 mol L – 1 s – 1 | b) 6 x 10 – 4 mol L – 1 s – 1 | c) 1 x 10 – 4 mol L – 1 s – 1 | d) 3 x 10 – 4 mol L – 1 s – 1 |

1. For the reaction, 2 A + B → 3 C + D, which of the following does not express the reaction rate?

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| a) | b) | c) | d) |

1. Considered the reaction, N2 (g) + 3 H2 (g) 2 NH3 (g). The equality relationship between and is

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| a) = | b) + = |
| c) + = | d) = |

CHEMICAL KINETICS Page No. 3

**Answers**

1. (i) 3.6 x 10 – 3 mol L – 1 s – 1 (ii) 5.4 x 10 – 3 mol L – 1 s – 1 2. 10 – 3 mol L – 1 s – 1 (ii) 2 x 10 – 3 mol L – 1 s – 1

3. (i) 4.33 x 10 – 5 mol L – 1 s – 1 (ii) 8.66 x 10 – 5 mol L – 1 s – 1 4. (i) 0.002 atm min – 1 (ii) 8.58 x 10 – 7 mol L – 1 s – 1

5. 6.79 x 10 – 4 mol L – 1 min – 1, 1.13 x 10 – 5 mol L – 1 s – 1, 4.07 x 10 – 2 mol L – 1 hr – 1, 2.72 x 10 – 3 mol L – 1 min – 1

6. (i) (ii) (iii) 7. =

8. Rate = = 9. = 0.033 mol L – 1 s – 1 , = 0.099 mol L – 1 s – 1

10. 2.5 x 10 – 4 mol L – 1 s – 1

11. (i) 0.5 x 10 – 2 mol L – 1 s – 1 (ii) = 0.5 x 10 – 2 mol L – 1 s – 1 , + = 1.5 x 10 – 2 mol L – 1 s – 1

12. 4 x 10 – 4 M/min , 6.66 x 10 – 6 M/sec 13. 5 x 10 – 3 M/min 14. a 15. c

17. = = 18. 19. 6 x 10 – 8 mol L – 1 s – 1

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| 21. a | 22. b | 23. c | 24. a | 25. c | 26. b |
| 27. c | 28. b | 29. b | 30. c | 31. d | 32. a |
| 33. b |  |  |  |  |  |

CHEMICAL KINETICS Page No. 4

**Karan Arora** **M: 9416974837**

**Assignment – II**

1. For a homogeneous decomposition of N2O5 into NO2 and O2 : 2 N2O5 (g) → 4 NO2 (g) + O2 (g),

Rate = = k [N2O5], Find out the order with respect to N2O5 .

1. Calculate the overall order of a reaction which has the rate expression :

a) Rate = k b) Rate = k

1. The rate law for a reaction is found to be : Rate = k [] [ I – ] [H+]2 . How would the rate of reaction change when

(i) Concentration of H+ is doubled (ii) Concentration of I – is halved (iii) Concentration of each of , I –  and H+ are tripled ?

1. The rate of a gaseous reaction is halved when the volume of the vessel is doubled. What is the order of the reaction ?
2. For the reaction ; 2 X → X2 , the rate of reaction becomes 27 times when the concentration of X is increased three times. What is the order of the reaction ?
3. A reaction is of first order in reactant A and of second order in reactant B. How it the rate of reaction affected when (i) concentration of B alone is increased to three times (ii) the concentration of A as well as B is doubled ?
4. Identify the reaction order from each of the following rate constant : (i) k = 2.3 x 10 – 5 litre mol – 1 sec – 1  (ii) k = 3.1 x 10 – 4 sec – 1  (iii) k = 9.3 x 10 – 4 mol litre – 1 sec – 1
5. The rate constant of a reaction is 3 x 102 h – 1 . What is the order of reaction ?
6. In the reaction ; A → B, the value of the rate constant was found to be 1 x 10 – 2  mol – 1 L sec – 1 . What is the order of the reaction? How will the catalyst affect the value of the rate constant ?
7. The rate of reaction; A + B → Products is given by Rate = k . What are the units of the rate constant?
8. A reaction is of second order with respect to a reactant. How is the rate of reaction affected if the concentration of the reactant is reduced to half? What is the unit of rate constant of such a reaction ?
9. What are the units of rate constant for zero order and first order reactions ?
10. What is the order of reaction whose rate constant has the same units as the rate of reaction ?
11. For a reaction, A + B → Product, the rate law is given by : r = k . What is the order of the reaction?
12. The conversion of the molecules X to Y follows second order kinetics. If the concentration X is increased to three times, how will it affect the rate of formation of Y?
13. From the rate expressions for the following reactions, determine their order of reaction and the dimensions of the rate constant :
14. 3 NO (g) → N2O (g) + NO2 (g) ; Rate = k
15. H2O2 (aq) + 3 I – (aq) + 2 H+ → 2 H2O (l) + ; Rate = k
16. CH3CHO (g) → CH4 (g) + CO (g) ; Rate = k
17. C2H5Cl (g) → C2H4 (g) + HCl (g) ; Rate = k

CHEMICAL KINETICS Page No. 5

1. Define specific reaction rate or rate constant.
2. Define: Rate of reaction and rate constant.
3. The rate law for the reaction : Ester + H+ → Acid + Alcohol is : dx/dt = k . What would be the effect on the rate if (i) Concentration of the ester is doubled? (ii) concentration of H+ is doubled?
4. How does the value of rate constant vary with reactant concentration?
5. What is the effect of temperature on rate constant of a reaction?
6. Define the term ‘order of reaction’ for chemical reactions.
7. Rate of a reaction is given by the equation : Rate = k . What are the units for the rate and the rate constant for this reaction?
8. The rate of a gaseous reaction is given by the expression k . If the volume of the reaction vessel is suddenly reduced to 1/4th of the initial volume, the reaction rate relating to original rate will be

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| a) 1/10 | b) 1/8 | c) 8 | d) 16 |

1. In a reaction, A → B, the rate of reaction increases two times on increasing concentration of the reactant four times, then order of reaction is

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| a) 0 | b) 2 | c) 1/2 | d) 4 |

1. The rate of the reaction 2 NO + Cl2 → 2 NOCl is given by the rate equation : rate = k . The value of the rate constant can be increased by

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| --- | --- |
| a) Increasing the temperature | b) Increasing the concentration of NO |
| c) Increasing the concentration of Cl2 | d) Doing all of these |

1. The unit of rate constant for a zero order reaction is

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| --- | --- | --- | --- |
| a) mol L – 1 s – 1 | b) L mol – 1 s – 1 | c) L2 mol – 2 s – 1 | d) s – 1 |

1. Rate constant of a reaction (k) is 175 L2 mol – 2 s – 1 . What is the order of the reaction?

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| --- | --- | --- | --- |
| a) First | b) Second | c) Third | d) Zero |

1. Which one of the following statements for the order of a reaction is incorrect?
2. Order of reaction is always whole number
3. Order can be determined only experimentally
4. Order is not influenced by stoichiometric coefficients of the reactants
5. Order of reaction is sum of powers to the concentration terms of reactants to express the rate of reaction.
6. Rate law for the reaction A + 2 B → C is found to be : rate = k . Concentration of reactant ‘B’ is doubled , keeping the concentration of ‘A’ constant, the value of rate constant will be …………………

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| a) the same | b) doubled | c) quadrupled | d) halved |

1. For the reaction, A + B → C + D, doubling the concentration of both the reactants increases the reaction rate by 8 times and doubling the concentration of only B simply doubles the reaction rate. The rate law is given as

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| a) r = k | b) r = k | c) r = k | d) r = k |

1. The value of rate constant depends upon

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| a) Temperature | b) Concentration | c) Catalyst | d) Both (a) & (c) |

1. For the reaction, 2 NO (g) + O2 (g) → 2 NO (g), the volume is suddenly reduced to half its value by increasing pressure on it. If reaction is of first order w.r.t O2 and second order w.r.t NO, the rate of reaction will

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| --- | --- |
| a) Decrease to 8 times of the initial value | b) Increase to 8 times of the initial value |
| c) Increase to 4 times of the initial value | d) Decrease to 4 times of the initial value |

CHEMICAL KINETICS Page No. 6

**Karan Arora** **M: 9416974837**

1. The rate of the reaction, 2 A + B → Products is given by the rate expression, rate = k . If [A] is 2 molar and [B] is 100 molar, then the order of reaction will be

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| a) 2 | b) 0.5 | c) 1.5 | d) 1 |

1. The unit of rate constant and rate of reaction are same for

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| --- | --- | --- | --- |
| a) First order | b) Zero order | c) Second order | d) Third order |

1. For the reaction A + B → Products, it is observed that :
2. On doubling the initial concentration of A only, the rate of reaction is also doubled and
3. On doubling the initial concentrations of both A and B, there is a change by a factor of 8 in the rate of the reaction.

The rate of this reaction is given by :

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| a) r = k | b) r = k | c) r = k | d) r = k |

1. 3 A → B + C It would be a zero order reaction, when
2. The rate of reaction is proportional to square of concentration of A
3. The rate of reaction remains same at any concentration of A
4. The rate remains unchanged at any concentration of B and C
5. The rate of reaction doubles if concentration of B is increased to doubled

**Answers**

1. 1 2. (a) 2 (b) 1/2 3. (i) 4 times (ii) halved (iii) 81 times 4. Order of reaction = 1

5. 3 6. (i) 9 times (ii) 8 times 7. (i) 2nd order (ii) Ist order (iii) zero order 8. 1st order

9. 2nd order, catalyst increases the value of the rate constant 10. Mol – 3/2 L 3/2 s – 1

11. Rate reduces to 1/4th , units of k = L mol – 1 s – 1  12. mol L – 1 s – 1 , s – 1 13. Zero order

14. 2.5 15. increase 9 times 16. 2 , L mol – 1 s – 1  **;** 2 , L mol – 1 s – 1  **;**  3/2 , L1/2 mol – 1/2 s – 1 **;**  1 , s – 1

19. (i) doubled (ii) No effect 23. mol L – 1 s – 1 , L2 mol – 2 s – 1  24. d 25. c 26. a

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| --- | --- | --- | --- | --- | --- |
| 27. a | 28. c | 29. a | 30. a | 31. c | 32. d |
| 33. b | 34. c | 35. b | 36. a | 37. b |  |

CHEMICAL KINETICS Page No. 7

**Karan Arora** **M: 9416974837**

**Assignment – III**

1. At 373 K, the half-life period for the thermal decomposition of N2O5 is 4.6 sec and is independent of the initial pressure N2O5. Calculate the specific rate constant at this temperature.
2. A first order reaction is found to have a rate constant, k = 5.5 x 10 – 14 s – 1. Find the half-life of the reaction.
3. A first order reaction is 40 % complete in 50 minutes. Calculate the value of rate constant. In what time will the reaction be 80 % complete?
4. Show that in case of a first order reaction, the time required for 99.9 % of the reaction to be take place is about 10 times than that required for half the reaction.
5. The initial concentration of N2O5 in the first order reaction, N2O5 (g) → 2 NO2 (g) + ½ O2 (g), was 1.24 x 10 – 2 mol/L at 318 K. The concentration of N2O5 after 60 minutes was 0.2 x 10 – 2 mol/L. Calculate the rate constant of the reaction at 318 K.
6. A first order reaction has a specific rate of 10 – 3 s – 1. How much time will it take for 10 g of the reactant to reduce 2.5 g?
7. The following data were obtained during the first order thermal decomposition of N2O5 (g) at constant volume : 2 N2O5 (g) → 2 N2O4 (g) + O2 (g)

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| --- | --- | --- |
| Sr. No. | Time/s | Total pressure (atm) |
| 1 | 0 | 0.5 |
| 2 | 100 | 0.512 |

Calculate the rate constant.

1. A first order reaction is found to have a rate constant k = 7.39 x 10 – 5 s – 1. Find the half-life of this reaction.
2. Time for half change for a first order reaction is 25 minutes. What time will be required for 99 % reaction?
3. The half-life period for a first order reaction is 60 minutes. What percentage of the reactant will be left behind after 120 minutes?
4. It was found that the solution of cane sugar in water was hydrolyzed to the extent of 25 % in 60 minutes. Calculate the time taken for the sugar to be 50 % hydrolyzed, assuming that the reaction is of first order.
5. Decomposition of a gas is of first order. It takes 80 minutes for 80 % of the gas to be decomposed when its initial concentration is 8 x 10 – 2 mol/L. Calculate the specific reaction rate.
6. Find the two-third life () of a first order reaction in which k = 5.48 x 10 – 14 s – 1.
7. A first order reaction has rate constant of k = 1.15 x 10 – 3 s – 1. How long will it take for 6 g of reactant to reduce to 3 g?
8. For a first order reaction, calculate the ratio between the time taken to complete three fourth of the reaction and the time taken to complete half of the reaction.
9. For a first order reaction, it takes 5 minutes for the initial concentration of 0.6 mol/L to become 0.4 mol/L. How long in all will it take for the initial concentration to become 0.3 mol/L?
10. A first order reaction is 75 % complete in 60 minutes. Find the life half of this reaction.
11. In a reaction, 5 g ethyl acetate is hydrolysed per litre in the presence of dil. HCl in 300 minutes. If the reaction is of first order and the initial concentration of ethyl acetate is 22 g/L, Calculate the rate constant of the reaction.
12. A first order decomposition reaction takes 40 minutes for 30 % decomposition. Calculate its value.

CHEMICAL KINETICS Page No. 8

1. In a particular reduction process, the concentration of a solution that is initially 0.24 M is reduced to 0.12 M in 10 hours and 0.06 M in 20 hours. What is the rate constant of this reaction?
2. The following rate data were obtained for the thermal decomposition of N2O5 (g)

2 N2O5 (g) → 2 N2O4 (g) + O2 (g)

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| --- | --- | --- |
| Time (sec) | 0 | 50 |
| Total pressure (atm) | 0.2 | 0.25 |

Calculate the reaction rate when the total pressure is 0.28 atm.

1. The half life period of a first order reaction is 600 sec. What percent of A remains after 30 minutes?
2. 50 % of a reaction of first order is completed in 16 minutes. What fraction of the reaction would occur in 32 minutes?
3. The decomposition of a compound is found to follow a first order rate law. If it take 15 minutes for 20 % of original material to react, Calculate :
4. Specific rate constant
5. The time at which 10 % of the original material remains unreacted
6. The time it takes for the next 20 % of the reactant left to react after the first 15 minutes.
7. A first order reaction is 15 % complete in 20 minutes. How long will it take to be 60 % complete.
8. The rate constant for a first order reaction is 60 s – 1. How much time will it take to reduce the concentration of the reactant to 1/10th of its initial value?
9. A first order reaction has a rate constant of 0.0051 min – 1. If we begin with 0.1 M concentration of the reactant, what concentration of the reactant will remain in the solution after 3 hours.?
10. A first order reaction, k = 1.5 x 10 – 6 per second at 240˚C. If the reaction is allowed to run for 10 hours, what percentage of initial concentration would have changed to products? What is the half-life period of this reaction?
11. The thermal decomposition HCO2H is a first order reaction with a rate constant of 2.4 x 10 – 3 s – 1 at a certain temperature. Calculate how long will it take for three-fourths of initial quantity of HCO2H to decompose. (log 0.25 = 0.6021)
12. The thermal decomposition of a compound is of first order. If 50 % of the compound is decomposed in 120 minutes, how long will it take for 90 % of the compound to be decomposed?

**Answers**

1. 0.1507 s – 1 2. 1.26 x 10 13 sec 3. 0.010216 min – 1 , 157.58 min 4. 10 5. 0.0304 min – 1

6. 1386.6 sec 7. 4.98 x 10 – 4 s – 1 8. 9.38 x 10 3 sec 9. 166.16 min 10. 25 %

11. 145 minutes 12. 0.02012 min – 1 13. 2 x 10 13 sec 14. 602.7 sec 15. 2

16. 8.54 min 17. 30 minutes 18. 8.6 x 10 – 4 min – 1 19 . 77.86 min

20. 6.93 x 10 – 2 hr – 1 , 1.9 x 10 – 5 s – 1 21. 5.54 x 10 – 4 atm s – 1 22. 12.5 % 23. 3/4 or 75 %

24. (i) 0.01488 min – 1 (ii) 154.77 min (iii) 15 minutes 25. 112.7 min 26. 0.0384 s 27. 0.04 M

28. 5.2 % , 128.3 hrs 29. 9 min 38 sec 30. 398.8 min

CHEMICAL KINETICS Page No. 9

**Karan Arora** **M: 9416974837**

**Assignment – IV**

1. Nitric oxide, NO reacts with oxygen to produce nitrogen dioxide : 2 NO (g) + O2 (g) 2 NO2 (g).

What is the predicted rate law, if the mechanism is :

(i) NO + O2 NO3 (fast) (ii) NO3 + NO NO2  + NO2 (slow)

1. For the reaction, NO2 (g) + CO (g) CO2 (g) + NO (g), the experimentally determined rate expression below 400 K is : Rate = k [NO2]2. What mechanism can be proposed for this reaction?
2. For the chemical reaction, 4 HBr + O2 2 H2O + 2 Br2, Rate = k [HBr] [O2] .

What is the probable mechanism of the reaction?

1. Nitric oxide reacts with hydrogen to give nitrogen and water (2 NO + 2 H2 N2 + 2 H2O). The kinetics of this reaction is explained by the following steps:

(i) 2 NO + H2 N2 + H2O2 (slow) (ii) H2O2 + H2 2 H2O (fast).

What is the predicted rate law?

1. For the reaction at 500 K, NO2 (g) + CO (g) CO2 (g) + NO (g), the proposed mechanism is as below: (i) NO2 + NO2 NO + NO3 (slow) (ii) NO3 + CO CO2 + NO2 (fast). What is the rate law for the reaction?
2. The possible mechanism for the reaction : 2 H2 + 2 NO N2 + 2 H2O is

(i) 2 NO N2O2 (fast) (ii) N2O2 + H2 N2O + H2O (slow)

(iii) N2O + H2 N2 + H2O (fast)

What is (i) The rate law for the reaction (ii) The order of the reaction?

1. Consider the decomposition of hydrogen peroxide in alkaline medium which is catalyzed by iodide ions :

2 H2O2 2 H2O + O2

This reaction takes place in two steps as given below :

Step I : H2O2 + I –  H2O + IO – (slow) ; Step II : H2O2 + IO – H2O + I –  + O2 (fast)

1. Write the rate law expression and determine the order of reaction with respect to H2O2.
2. What is the molecularity of each individuality step?
3. Write the overall order of reaction.
4. Out of step I and II, which one is the rate determining step?

CHEMICAL KINETICS Page No. 10

**Answers**

1. Rate = k [NO]2 [O2]

2. **Step I** : NO2 + NO2 NO + NO3 ; **Step II** : NO3 + CO CO2 + NO2

3. HBr + O2 HOOBr ; HOOBr + HBr 2 HOBr ; HOBr + HBr H2O + Br2] x 2

4. Rate = k [NO]2 [H2] 5. Rate = k [NO2]2 6. Rate = k [NO2]2 [H2] ; order = 3

7. (a) Rate = k [H2O2] [I –] , order with respect to H­2O2 = 1. (b) Molecularity : **Step I** = 2 ; **Step II** = 2

(c) Overall order = 2 (d) Step I is rate determining step

CHEMICAL KINETICS Page No. 11

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**Assignment – V**

1. The rate constant of a reaction is 1.2 x 10 – 3 sec – 1 at 30 and 2.1 x 10 – 3 sec – 1 at 40. Calculate the energy of activation of the reaction.
2. The rate of a particular reaction doubles when temperature changes from 27 to 37. Calculate the energy of activation of such a reaction.
3. The activation energy of a reaction is 94.14 kJ/mol and the value of rate constant at 313 K is 1.8 x 10 – 5 sec– 1 . Calculate the frequency factor A.
4. The first order rate constant for the decomposition of ethyl iodide by the reaction :

C2H5I (g) C2H4 (g) + HI (g)

at 600 K is 1.6 x 10 – 5 s – 1 . Its energy of activation is 209 kJ/mol. Calculate the rate constant of the reaction at 700 K.

1. rate constant K of a reaction varies with temperature according to the equation.

Log K = constant –

where Ea is the energy of activation of the reaction. When a graph is plotted for log k versus 1/T, a straight line with a slope – 6670 K is obtained. Calculate the energy of activation for this reaction. State the units

(R = 8.314 J K – 1 mol – 1 ).

1. The rate constant of a reaction increases by 5 % when the temperature of the reaction is increased from 300 to 301 K whereas equilibrium constant increases only by 2 %. Calculate the activation energy for the forward as well as backward reaction.
2. At 27 in the presence of a catalyst, the activation energy of a reaction is lowered by 2 Kcal. Calculate by how much the rate of reaction will increase?
3. A hydrogenation reaction is carried out at 500 K. If the same reaction is carried out in the presence of a catalyst at the same rate, the temperature required is 400 K. Calculate the activation energy of the reaction if the catalyst lowers the activation energy by 20 kJ/mol.
4. The rate constant of a reaction at 500 K and 700 K are 0.02 s – 1 and 0.07 sec – 1 respectively. Calculate the values of Ea and A.
5. Two reactions of the same order have equal pre exponential factors but their activation energies differ by 24.9 kJ/mol. Calculate the ratio between the rate constants of these reactions at 27.
6. The rate constant of a reaction is 1 x 10 – 3 sec – 1 at 27 and 2 x 10 – 3 sec – 1 at 37. Calculate the activation energy of the reaction.
7. The rate of a particular reaction quadruples when the temperature changes form 293 K to 313 K. Calculate energy of activation for such a reaction assuming that it does not change with temperature.
8. The rate of a reaction triples when temperature changes from 50 to 100. Calculate the energy of activation for such a reaction. (R = 8.314 J K – 1 mol – 1 )
9. For a reaction, the energy of activation is zero. What is the value of rate constant at 300 K, if k = 1.6 x 106 sec – 1 at 280 K? (R = 8.31 J K – 1 mol – 1 )

CHEMICAL KINETICS Page No. 12

1. The activation energy of a first order reaction at 300 K is 60 KJ/mol. In the presence of a catalyst, the activation energy is lowered to 50 KJ/mol at the same temperature. How many times the arte of reaction will change?
2. Given that the temperature coefficient for saponification of ethyl acetate by NaOH is 1.75. Calculate the activation energy of the reaction.
3. The activation energy of a reaction is 75.2 KJ/mol in the absence of a catalyst and 50.14 KJ/mol with a catalyst. How many times will the rate of grow in the presence of the catalyst if the reaction proceeds at 25? (R = 8.314 J K – 1 mol – 1 )
4. The rate constant of a reaction at 700 K and 760 K are 0.011 M – 1  s – 1 and 0.105 M – 1  s – 1 respectively. Calculate the values of Arrhenius parameters.
5. A 1st order reaction is 50 % complete in 30 minutes at 27 and 10 minutes at 47. Calculate
6. Rate constant for the reaction at 27 and 37
7. Energy of activation for the reaction.
8. A first order reaction is 50 % complete in 50 minutes at 300 K and the same reaction is again 50 % complete in 25 minutes at 350 K. Calculate the activation energy of the reaction.

**Answers**

1. 44.13 kJ/mol 2. 53.6 kJ/mol 3. 9.194 x 1010 sec – 1  4. 6.353 x 10 – 3 sec – 1

5. 127711.4 J/mol 6. 36.65 kJ/mol , 21.78 kJ/mol

7. k’ = 28 k, the rate of reaction will increases 28 times.

8. 100 kJ/mol 9. 18.23 kJ/mol , 1.603 10. 2.162 x 104 11. 53.6 kJ/mol

12. 52.86 kJ/mol 13. 22.01 kJ/mol 14. 1.6 x 106 s – 1  15. it will increases 55 times

16. 42.70 kJ/mol 17. 24660 times 18. Ea = 166.3 kJ/mol , A = 2.824 x 1010

19. = 2.31 x 10 – 2 min – 1 , = 6.93 x 10 – 2 min – 1 , Ea = 43.85 kJ/mol 20. 12.104 kJ/mol

CHEMICAL KINETICS Page No. 13

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**Assignment – VI**

1. For a gaseous reaction , 2A + B2 2AB, the following rate data were obtained at 300 K

|  |  |  |
| --- | --- | --- |
| Rate of disappearance of B2 | Concentration | |
| (mol L – 1 min – 1 ) | [A] | [B] |
| 1. 1.8 x 10 – 3 | 0.015 | 0.15 |
| 1. 1.08 x 10 – 2 | 0.09 | 0.15 |
| 1. 5.4 x 10 – 3 | 0.015 | 0.45 |

Calculate the rate constant for the reaction and rate of formation of AB when [A] is 0.02 and [B2] is 0.04 mol/lit at 300 K.

1. For the reaction , 2 N2O5 (g) 4 NO2 (g) + O2 (g), the following results have been obtained :

|  |  |  |
| --- | --- | --- |
| S.No. | [N2O5] mol/L | Rate of disappearance of N2O5  (mol L – 1 min – 1 ) |
| 1 | 1.13 x 10 – 2 | 34 x 10 – 5 |
| 2 | 0.84 x 10 – 2 | 25 x 10 – 5 |
| 3 | 0.62 x 10 – 2 | 18 x 10 – 5 |

1. calculate the order of reaction (b) Write rate law (c) Calculate rate constant of the reaction
2. For the thermal decomposition of acetaldehyde, CH3CHO (g) CH4 (g) + CO (g) , the following data were obtained: Predict the order of reaction by following data.

|  |  |  |
| --- | --- | --- |
| Experiment | Initial Pressure (torr) | Initial rate of increase in total pressure (torr) |
| 1 | 300 | 0.61 (r1) |
| 2 | 200 | 0.27 (r2) |

1. The initial rate of reaction A + 5 B + 6 C 3 L + 3 M has been determined by measuring the rate of disappearance of A under the following conditions :

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| Expt. No. | [A]0/M | [B]0/M | [C]0/M | Initial rate/M min – 1 |
| 1 | 0.02 | 0.02 | 0.02 | 2.08 x 10 – 3 |
| 2 | 0.01 | 0.02 | 0.02 | 1.04 x 10 – 3 |
| 3 | 0.02 | 0.04 | 0.02 | 4.16 x 10 – 3 |
| 4 | 0.02 | 0.02 | 0.04 | 8.32 x 10 – 3 |

Determine the order of reaction with respect to each reactant and overall order of reaction. What is the rate constant? Calculate the initial rate of change in concentration of B and L.

1. For the reaction ; A + B Products, the following initial rates were obtained at various given initial concentrations :

|  |  |  |  |
| --- | --- | --- | --- |
| S. No. | [A] mol/L | [B] mol/L | Initial rate M/s |
| 1 | 0.1 | 0.1 | 0.05 |
| 2 | 0.2 | 0.1 | 0.10 |
| 3 | 0.2 | 0.2 | 0.05 |

Determine the half life period.

CHEMICAL KINETICS Page No. 14

**Answers**

1. (i) k = 0.8 L mol – 1 min – 1  (ii) required rate of formation = 1.28 x 10 – 3 mol L – 1 min – 1

2. (i) Order = 1 (ii) Rate = k [N2O5] (iii) k = 1.5 x 10 – 2 min – 1

3. 2

4. (i) Rate = k [A0] [B0] [C0]2 (ii) Overall order = 1 + 1 + 2 = 4 (iii) k = 1.3 x 104 M – 2 min – 1

(iv) d[B]/dt = 1.04 x 10 – 2 M/min , d[L]/dt = 6.24 x 10 – 3 M/min

5. 1.386 s

CHEMICAL KINETICS Page No. 15