

**CY 102: Assignment III(Chemical Kinetics)**  
**8<sup>th</sup> March 2004**

1. The Half of uranium -235 is  $7.1 \times 10^6$  years while that of the much shorter-lived isotope sodium-24 is only 15.0 hours. Calculate the first order rate constants for the radioactive decay of these isotopes in appropriate, and identical, units.

$$\text{Ans: } K_{\text{U-235}} = 0.693/2.24 \times 10^{16} \text{ s} = 3.09 \times 10^{-17} \text{ s}^{-1}$$

$$K_{\text{Na-24}} = 0.693/5.4 \times 10^4 \text{ s} = 1.28 \times 10^{-5} \text{ s}^{-1}.$$

2. The pseudo-first-order rate constant for the decomposition of NO Cl (g) to NO and Cl<sub>2</sub> is measured and found to be  $1.96 \times 10^6 \text{ m}^3 \text{ mol}^{-1} \text{ s}^{-1}$ . The actual rate limiting step is  $\text{Cl} + \text{NOCl} \rightarrow \text{Cl}_2 + \text{NO}$  which has rate constant  $k_2$ . The reaction is pseudo-first-order in chlorine atoms because the concentration of chlorine atoms is so much less than the concentration of NOCl.
- Calculate the value of the rate constant  $k_2$ , with units, when  $p(\text{NOCl}) = 10.0 \text{ mol/m}^3$ .
  - Calculate the value of the reaction rate, with units, when  $p(\text{NOCl}) = 10.0 \text{ mol/m}^3$  and  $p(\text{Cl}) = 1.0 \times 10^3 \text{ mol/m}^3$ .

$$\text{Ans: Rate} = k_2 [\text{Cl.}] [\text{NOCl}]$$

$$k_2 = 1.96 \times 10^6 \text{ m}^3 \text{ mol}^{-1} \text{ s}^{-1} \times 10 \text{ mol m}^3$$

$$= 1.96 \times 10^7 \text{ s}^{-1} \text{ (apparent 1<sup>st</sup> order)}$$

$$\text{Rate} = 1.96 \times 10^6 \times 10^3 \times 10 = 1.96 \times 10^4 \text{ mol m}^{-3} \text{ s}^{-1}.$$

3. For  $\text{N}_2(\text{g}) + 3\text{H}_2(\text{g}) \rightarrow 2\text{NH}_3(\text{g})$ , determine the rate expression using the given data. Find  $k$  with units.

[N <sub>2</sub> ] (M)	[H <sub>2</sub> ] (M)	Initial rate (M/min)
0.10	0.10	0.0021
0.10	0.20	0.0084
0.20	0.40	0.0672

$$\text{Ans: Rate} = k[\text{N}_2]^a [\text{H}_2]^b$$

$$(0.0084/0.0021) = (0.20/0.10)^b$$

$$\therefore b = 2$$

$$(0.0672/0.0084) = (0.20/0.10)^a (0.40/0.20)^2$$

$$\therefore a = 1$$

$$\text{Rate} = k[\text{N}_2] [\text{H}_2]^2$$

$$K = 2.1 \text{ r}^{-2} \text{ min}^{-1}.$$

4. The halogen astatine can only be obtained artificially through bombardment. It has been found to be useful for the treatment of certain types of cancer of the thyroid gland. One form of radioactive astatine is a particle emitter with a half-life of 7.21 hr.

If a sample containing 0.100 mg of astatine is given to a person at 9 a.m. one morning, how much astatine will remain after about 14 hours?

$$\begin{aligned} \text{Ans: } \ln 2 &= k t_{1/2} \\ k &= 0.0961 \text{ h}^{-1} \\ \ln ([\text{At}]/0.100) &= -0.0961 \text{ h}^{-1} \times 14 \text{ hr} = -1.35 \\ \therefore [\text{At}] &= 0.026 \text{ mg remaining.} \end{aligned}$$

5.  $\text{N}_2\text{O}_5$  gas decomposes according to the reaction  $2\text{N}_2\text{O}_5 \rightarrow 4\text{NO}_2 + \text{O}_2$ . The rate of reaction at 328 K is found to be  $0.75 \times 10^{-4} \text{ mol L}^{-1} \text{ s}^{-1}$ . What are the values of

$$\frac{d[\text{N}_2\text{O}_5]}{dt}, \quad \frac{d[\text{NO}_2]}{dt} \quad \text{and} \quad \frac{d[\text{O}_2]}{dt}?$$

$$\begin{aligned} \text{Ans: } 2\text{N}_2\text{O}_5 &\rightarrow 4 \text{NO}_2 + \text{O}_2 \\ d[\text{N}_2\text{O}_5]/dt &= -1.5 \times 10^{-4} \text{ mol l}^{-1} \text{ s}^{-1}. \\ d[\text{NO}_2]/dt &= 3 \times 10^{-4} \text{ mol l}^{-1} \text{ s}^{-1}. \\ d[\text{O}_2]/dt &= 0.75 \times 10^{-4} \text{ mol l}^{-1} \text{ s}^{-1}. \end{aligned}$$

6. The decomposition of ozone  $2\text{O}_3(\text{g}) \rightarrow 3\text{O}_2(\text{g})$  is studied in a 2 L reaction vessel and found  $\frac{d[\text{O}_3]}{dt} = -1.5 \times 10^{-2} \text{ mol L}^{-1} \text{ s}^{-1}$ .

- (a) What is the rate of reaction?  
 (b) What is the rate of conversion?  
 (c) What is the value of  $\frac{d[\text{O}_2]}{dt}$ ?

$$\begin{aligned} \text{Ans: (a) rate of reaction} &= 0.75 \times 10^{-2} \text{ mol L}^{-1} \text{ s}^{-1} \\ \text{(b) Rate of conversion} &= 1.5 \times 10^{-2} \text{ mol L}^{-1} \text{ s}^{-1} \\ \text{(c) } \frac{d[\text{O}_2]}{dt} &= 2.25 \times 10^{-2} \text{ mol L}^{-1} \text{ s}^{-1}. \end{aligned}$$

7. A first order reaction has an activation energy of  $104,600 \text{ J mol}^{-1}$  and a pre-exponential factor  $A = 5 \times 10^{13} \text{ s}^{-1}$ , at what temperature will the reaction have a half-life of 30 days?

$$\begin{aligned} \text{Ans: } \ln 2/t_{1/2} &= A \exp^{-E_a/RT} \\ \therefore T &= 269.5 \text{ k.} \end{aligned}$$

8. Find the order and the value of the rate constant from the following kinetic data obtained for a certain reaction.

C(M)	8	6	4.5	3.4
t(s)	0	42	97	169

Ans: Data fits into second order expression,

$$1/[A] = 1/[A]_0 + kt$$

$$k = 1.004 \times 10^{-3} \text{ m}^{-1} \text{ s}^{-1}.$$

9. For an  $n^{\text{th}}$  order reaction  $nA \rightarrow P$  which goes to completion, derive the integrated rate law and half life expressions.

Ans:  $A \rightarrow \text{product}$   $n^{\text{th}}$  order in A.

$$\text{Rate} = d[A]/dt = -k[A]^n$$

$$\int_1^2 [A]^{-n} d[A] = -k \int_1^2 dt$$

$$[A]^{-n+1} - [A]_0^{-n+1} / -n+1 = -kt \text{ for } n \neq 1$$

$$\text{or } [[A]/[A]_0]^{1-n} = 1 + [A]_0^{n-1} (n-1) kt$$

$$\text{and } t_{1/2} = 2^{n-1} - 1 / (n-1) [A]_0^{n-1} k$$

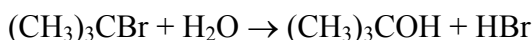
10. A reaction follows the rate law  $\sqrt{[A]} - \sqrt{[A]_0} = -\frac{kt}{2}$ . Find the order and units for k.

Ans: Substitute  $n = 1/2$  in the solution of prob. 9

$$\text{Which gives } \sqrt{[A]} - \sqrt{[A]_0} = -\frac{kt}{2}$$

$$\text{Units for } k = \text{mol}^{1/2} \text{ litre}^{-1/2} \text{ sec}^{-1}.$$

11. T- butyl bromide is converted into t-butyl alcohol in a solvent containing 90% acetone and 10% water. The reaction is



The data for the concentration of t-butyl bromide versus time is given below

T(MIN)	(CH <sub>3</sub> ) <sub>3</sub> CBR (MOL L <sup>-1</sup> )
0	0.1056
9	0.0961
18	0.0856
24	0.0767
40	0.0645
54	0.0536
72	0.0432
105	0.0270

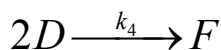
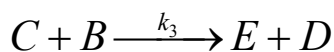
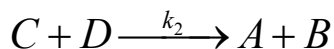
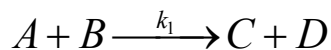
Find the order, rate constant and half-life of the reaction?

Ans: Data fits into 1<sup>st</sup> order integrated rate expression.

$$K = 0.0125 \text{ min}^{-1}$$

$$t_{1/2} = 55.5 \text{ min.}$$

12. Write down the differential rate equations for the removal of A, B, C and D species in the following reaction scheme:



Ans:  $-d[A]/dt = k_1 [A][B] - k_2 [C][D]$   
 $-d[B]/dt = k_1 [A][B] - k_2 [C][D] + k_3 [C][B]$   
 $-d[C]/dt = k_2 [C][D] + k_3 [C][B] - k_1 [A][B]$   
 $-d[D]/dt = k_2 [C][D] - k_1 [A][B] - k_3 [C][B] + 2k_4 [D]^2$

13. For a parallel first order reactions  $A \xrightarrow{k_1} B$  and  $A \xrightarrow{k_2} C$ , find the half-life of A. Show that the observed activation energy for the disappearance of A is given by

$$E_a = \frac{k_1 E_1 + k_2 E_2}{k_1 + k_2}$$

Ans:  $[A] = [A]_0 e^{-(k_1+k_2)t}$   
 $[A] = [A]_0/2$  at  $t_{1/2}$   
 $\therefore 2 = e^{(k_1+k_2)t_{1/2}}$   
 $t_{1/2} = \ln 2 / (k_1 + k_2)$   
 $d[C]/dt = (k_1 + k_2) [A]$   
 $\ln k = \ln A - E_a/RT$   
 $E_a = RT^2 d \ln k / dT = RT^2 d \ln (k_1 + k_2) / dT$   
 $\therefore E_{obs} = RT^2 / (k_1 + k_2) (k_1 E_1 / RT^2 + k_2 E_2 / RT^2)$   
 $= k_1 E_1 + k_2 E_2 / k_1 + k_2$

14. For a reversible reaction  $A \xrightleftharpoons[k_2]{k_1} B$ , obtain expressions for  $[A]$  and  $[B]$  at time  $t$  and also for the time required to reach half of  $[A]_{eq}$  and  $[B]_{eq}$ .

Ans:  $A \xrightleftharpoons[k_2]{k_1} B$  initially only A is present. i.e  $[A] = [A]_0$  &  $[B] = 0$  at  $t=0$ .

$$d[A]/dt = k_2 [A]_0 - (k_1 + k_2) [A]$$

$$= -(k_1 + k_2) ([A] - [A]_{eq})$$

$$\therefore [A]_{eq} = k_2 / k_1 + k_2 [A]_0$$

Integration

$$\ln [A]_0 - [A]_{eq} / [A] - [A]_{eq} = (k_1 + k_2)t$$

$$\therefore [A] = k_2 [A]_0 / k_1 + k_2 (1 + k_1 / k_2 e^{-(k_1 + k_2)t})$$

$$\text{Illy } [B] = k_1 [A]_0 / k_1 + k_2 (1 - e^{-(k_1 + k_2)t})$$

and time for half  $[A]_{\text{eq}}$  or  $[B]_{\text{eq}} = \ln^2/k_1+k_2$

15. For a first order consecutive reaction  $A \xrightarrow{k_1} B \xrightarrow{k_2} C$ , write down the rate expressions and obtain concentrations  $[A]$ ,  $[B]$  and  $[C]$  at time  $t$  in terms of  $[A]_0$ ,  $k_1$  and  $k_2$ . Obtain the same for B and C under steady state conditions. If  $[A]_0 = 100 \text{ M}$ ,  $k_1 = 0.04 \text{ min}^{-1}$ , calculate the concentrations of A, B and C at 5 min.

Ans: See notes/text for the 1<sup>st</sup> part.

$$[A] = 81.87$$

$$[B] = 17.85$$

$$[C] = 0.278$$

16. For a reaction  $A + B \xrightleftharpoons[k_2]{k_1} C \xrightarrow{k_3} D$ , find rate expression for the formation of D applying steady state approximation. C is a reactive intermediate.

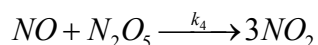
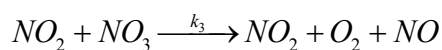
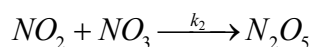
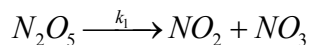
Ans: Using SSA

$$d[C]/dt = k_1[A][B] - k_2[C] - k_3[C] = 0$$

$$[C] = k_1[A][B]/k_2+k_3$$

$$d[D]/dt = k_3[C] = k_1k_3[A][B]/k_2+k_3.$$

17. The following mechanism is suggested for the decomposition of  $N_2O_5$   
 $2N_2O_5(g) \rightarrow 4NO_2(g) + O_2(g)$ :



Find the rate law consistent with this mechanism.

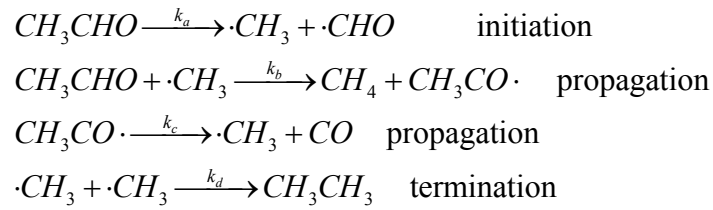
$$\text{Ans: } d[NO]/dt = k_1[NO_2][NO_3] - k_4[NO][N_2O_5] = 0$$

$$d[NO_3]/dt = k_1[N_2O_5] - k_2[NO_2][NO_3] - k_3[NO_2][NO_3] = 0$$

$$d[N_2O_5]/dt = -k_1[N_2O_5] + k_2[NO_2][NO_3] - k_4[NO][N_2O_5]$$

$$\therefore d[N_2O_5]/dt = -2k_1k_3[N_2O_5]/k_2+k_3$$

18. Pyrolysis (thermal decomposition in the absence of air) of acetaldehyde  $CH_3CHO(g) \xrightarrow{\Delta} CH_4(g) + CO(g)$  is a chain reaction. The proposed Rice Herzfeld mechanism is given below:



Show that this mechanism is consistent with the experimental rate law

$$\frac{d[\text{CH}_4]}{dt} = k[\text{CH}_3\text{CHO}]^{3/2}.$$

Ans: intermediates:  $\text{CH}_3$  &  $\text{CH}_3\text{CO}$

$$d[\text{CH}_3]/dt = k_a[\text{CH}_3\text{CHO}] - k_b[\text{CH}_3][\text{CH}_3\text{CHO}] + k_c[\text{CH}_3\text{CO}] - 2k_d[\text{CH}_3]^2 = 0$$

SSA

$$d[\text{CH}_3\text{CO}]/dt = k_b[\text{CH}_3][\text{CH}_3\text{CHO}] - k_c[\text{CH}_3\text{CO}] = 0$$

$$\therefore [\text{CH}_3] = [k_a/2k_d]^{1/2} [\text{CH}_3\text{CHO}]^{1/2}$$

$$d[\text{CH}_4]/dt = k_b[\text{CH}_3][\text{CH}_3\text{CHO}]$$

$$= k_b (k_a/2k_d)^{1/2} [\text{CH}_3\text{CHO}]^{3/2}$$

$$d[\text{CH}_4]/dt = k_{\text{obs}}[\text{CH}_3\text{CHO}]^{3/2}$$