Department of Chemistry, IIT Madras
CY 102 – Physical Chemistry Quiz II

Useful data: 1 atm = 1.013×10^5 N m^{-2}; R = 8.314 JK^{-1}mol^{-1}; 1 Joule = 1 N m

1. A reactor contains NH_3 at a pressure 200 torr and 856°C. When a tungsten catalyst is introduced resulting in the decomposition of NH_3, the following observations were made. The pressure change was (a) 56 torr in 500 sec, (b) it was 90 torr in 800 sec and (c) it was 112 torr in 1000 sec. Find the order for the decomposition of NH_3. Explain your result. Calculate the rate constant of the reaction expressing concentration in moles per dm^3 and time in seconds.

   Ans: dp/dt = 0.1125 torr sec^{-1} = k
   Rate is independent of pressure change
   $\Rightarrow$ zero order --------- 3
   k = 0.1125 x 1.013 x 10^5/ 760 RT x 1000 = 1.597 x 10^{-6} mol dm^{-3} s^{-1} ----------- 2

2. The following data are given for a first order consecutive reaction,
   $A \xrightarrow{k_1} B \xrightarrow{k_2} C$: (i) initial concentration of A is 1.0 M and that of B and C are zero. (ii) The concentration of A at 10 min of reaction is 0.67 M. If the rate constant k_2 is 6.0 x 10^{-3} min^{-1}, calculate the $[B]_{max}$ and the corresponding t_{max} for the reaction.
   Ans: A = $[A]_0 e^{-k_1 t}$) to be derived --------- 2
   k_1 = 0.040 min^{-1}, k_2 = 0.006 min^{-1}
   t_{max} = ln k_1/k_2 / $k_1 - k_2$ = 55.8 min ----------- 2
   $[B]_{max}$ = $k_1[A]_0/k_2 - k_1 (e^{-k_1 t} - e^{-k_2 t})$
   = 0.716 M ------------- 2

3. For a reversible first order reaction $A \underset{k_2}{\overset{k_1}{\rightleftharpoons}} B$, the initial concentration of A is 18.23 M and the concentration of B at infinite time is determined to be 13.28 M. If the time required for reaching half the equilibrium concentration of B is 73.1 min, calculate k_1 and k_2.
   Ans: k_{eq} = $[B]_{eq}/[A]_{eq}$ = 13.28 / 18.23 – 13.28 = 2.68 = k_1/k_2 ---------- 2
   $[B]_{eq}/2$ = ln 2 / k_1+k_2 = 73.1 min
   $\therefore$ k_1 = 0.00690 min^{-1} -------------- 2
   k_2 = 0.002576 min^{-1} ------------- 2

   Alternate route for Q.3:
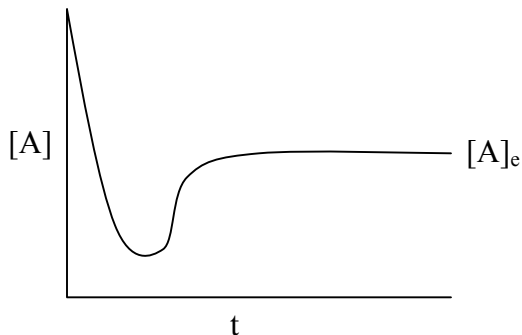   Let the question be as it is
   k_{eq} = 2.68 = k_1/k_2 ------------- 2
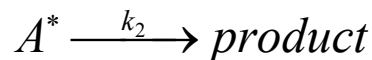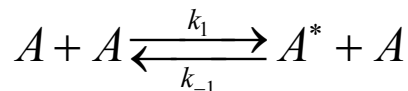 $[A]_{eq}$ = 18.23 – 13.28 = 4.95

$[A]_{eq}$ = 2.475
k_1 = 1/73.1 ln 18.23/2.475 = 0.0273 min^{-1} ------------2
k_2 = k_1/2.683 = 0.0102 min^{-1} --------- 2
Note: But there is a problem [A] goes to less than $[A]_{eq}$ at a definite time.

4. Derive a rate expression for a gas phase reaction involving the following steps using steady state approximation.

$$A + A \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} A^* + A$$

$$A^* \xrightarrow{k_2} product$$

If the effective rate constants for this reaction are 2.50×10^{-4} s^{-1} at 1.30 kPa and 2.10×10^{-5} s^{-1} at 12 Pa, calculate k_1 in appropriate units.

Ans: Lindemann mechanism.
dp/dt = $k_2k_1[A]^2$ / $k_2+k_{-1}[A]$

k_{eff} = k_1k_2 [A]/$k_2+k_{-1}[A]$ $\Rightarrow$ 1/k = 1/$k_1[A]$ + k_{-1} / k_1k_2
For k_{eff}. At two different pressures,

K_1 = 1/12 – 1/1300 / 1/2.1 x 10^{-5} – 1/2.5 x 10^{-4} = 0.082564 Pa^{-1}/43619.055
$\therefore k_1$ = 1.89 x 10^{-6} / 1   Pa^{-1} s^{-1} / 1 -------------- 2

5. (a) If $k_{obs} = \left(\dfrac{k_1 k_2}{k_3} \right)^{\frac{1}{2}}$, express E_{obs} in terms of individual activation energies.

Ans: k_{obs} = A e$^{-Ea/RT}$ = [A_1 e$^{-E1/RT}$. A_2 e$^{-E2/RT}$ / A_3 e$^{-E3/RT}$]$^{1/2}$ - 1
=$(A_1A_2/A_3)^{1/2}$ e$^{1/2(-E1/RT – E2/Rt + E3/RT)}$

$E_{obs} = E_1 + E_2 - E_3 / 2$ --------- 2
There are other possible steps.

(b) Evaluate the number of half lives for 99.9% conversion of a first order
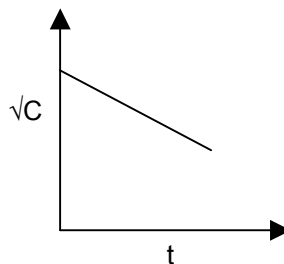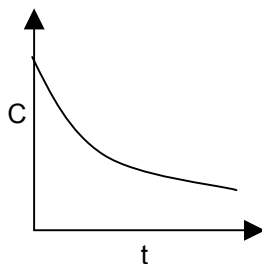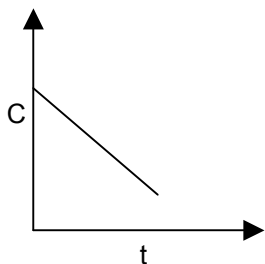reaction.
Ans: $t_{1/2} = \ln 2/k$ ----------- 1
For 99.9 u/u conversion, $[A]/[A_0] = 100 - 99.9 / 100 = 0.1/100$
$k\, t_{99.9} = \ln 10,000$ $t_{99.9} = \ln 10,000/k$ ----------- 1
No. of half lives $= t_{99.9}/t_{1/2} = \ln 10,000 / \ln 2 = 9.966 \approx 10$ half lives
There are other ways too.   -------------- 1

(c) Find the order for the following cases and evaluate the slope: (4 marks)

Ans: $-d[C]/dt = k$ zero order -----1 $-d[C]/dt = k[C] = k[C]_0\, e^{-kt}$ $-d\sqrt{C}/dt = k$ ----- 1
                                         First order ------ 1 $-1/2\sqrt{C}\, d[C]/dt = k$
                                                                   $-d[C]/dt = 2k\sqrt{C}$
                                                                   order = ½ ------- 1

6.   The Michaelis constant for an enzyme catalysed reaction at 25°C is 0.035 mol dm^{-3}. The rate
      of the reaction is 1.15×10^{-3} mol dm^{-3}s^{-1} when the substrate concentration is 0.110 mol dm^{-3}.
      (i) Calculate the maximum rate of this reaction. (ii) Find the substrate concentration for which
      the enzyme shows one quarter of its maximum rate.

      Ans: rate $= V_{max}[S] / k_m + [S]$ -------------- 2
      $1.15 \times 10^{-3} = V_{max} \times 0.110/0.035 + 0.110$
      $V_{max} = 1.52 \times 10^{-3}$ mol dm^{-3} s^{-1} --------- 1
      $V_{max}/4 = V_{max}[S] / K_m + [S]$
      $\therefore 3[S] = 0.035 \Rightarrow [S] = 0.01166$ 2mol dm^{-3}