CML101: Tutorial 1 - Chemical Kinetics
UG Semester - I (2023-24)

1 Rate laws

Q1: For a reaction of the following generalized form,

$$\sum_i \nu_i A_i = 0 \tag{1}$$

where, ν_i are the stoichiometric coefficients of the chemical species A_i. Write the rate expression in terms of the extent of reaction, ξ.

How would you monitor the rate ($\frac{d\xi}{dt}$) for the following chemical reactions?
(i) Bromination of $CH_3CH{=}CH_2$ in aqueous solution
(ii) Gas phase reaction: $H_2(g) + O_2(g) = H_2O(g)$
(iii) $C_6H_5N_2(aq) + H_2O(l) \rightarrow C_6H_5OH(aq) + H^+(aq) + N_2(g)$
(iv) radioactive decay of Iodine-131
(v) Sucrose inversion (Wilhelmy's experiment)

Q2: The rate of decomposition of acetaldehyde can be studied by measuring the pressure in a system at constant volume and temperature. Express the rate of reaction in terms of the rate of change of the pressure. The overall reaction is

$$CH_3CHO(g) \rightarrow CH_4(g) + CO(g)$$

Q3: The rate law of the following reaction,

$$CHCl_3(g) + Cl_2(g) \rightarrow CCl_4(g) + HCl(g)$$

$$\text{Rate} = k[CHCl_3][Cl_2]^{1/2}$$

What is the overall order of the reaction? Find out the unit of the (i) rate and (ii) rate constant of the above reaction.

Q4: The decomposition of N_2O_5 involves the following reaction,
$$2N_2O_5 \rightarrow 4NO_2 + O_2$$
(i) How is the rate of N_2O_5 decomposition related to the rate at which NO_2 and O_2 appear in the above reaction?

(ii) If the rate of N_2O_5 decomposition is 4.2×10^{-7} M/s at a particular instant, what is the rate of appearance of (a) NO_2 and (b) O_2 at that instant?

Q5: The rate constant for the hydrolysis of ethyl acetate by sodium hydroxide is 6.36 L mol^{-1} min^{-1}. The initial individual concentration of the ester and the base was 0.02 moles L^{-1}. What proportion of the ester will be hydrolyzed after 30 minutes?

Q6: The catalytic decomposition of H_2O_2 is monitored by titrating the solution with $KMnO_4$ at time intervals, 0, 5, 10, and 20 mins. The amount of $KMnO_4$ required to titrate the solution at each time interval is 46.2, 37.1, 29.8, and 19.6 ml, respectively. Find out the order of the reaction and its half-life.

Q7: Due to an excessive growth of bacteria in the lake water, with bacteria concentration $5.0 \times 10^{-7} g/cm^3$, swimming in the lake has been prohibited. Swimming is only allowed when the bacterial concentration reduces to $3.0 \times 10^{-7} g/cm^3$. Based on the previous years data, the bacterial death has been found to follow first-order kinetics with a death rate of 1.45 day^{-1}, how many days must the inhabitants wait until they can swim in the lake again?

Q8: For the reaction of nitric oxide with hydrogen,

$$2NO(g) + 2H_2(g) \rightarrow N_2(g) + 2H_2O(g)$$

the following data are obtained,

Expt. no.	[NO] (M)	[H2] (M)	Intial Rate (M/s)
1	0.10	0.10	1.23×10^{-3}
2	0.10	0.20	2.46×10^{-3}
3	0.20	0.10	4.92×10^{-3}

(i) Find out the rate law of the above reaction.
(ii) Calculate the rate constant
(iii) What is the rate of the reaction when [NO] = 0.050 and $[H_2]$ = 0.150.

Q9: If the rates of reaction are ν_1 and ν_2 at concentration c_1 and c_2 of a reactant, respectively. The order of reaction is 'n'. Assuming that the concentration of all other reactants remains constant, what would be the order of the reaction with respect to that specific reactant? Now take an example: Assume that you have performed a reaction and you find that doubling the concentration of that reactant doubles the reaction rate. What is the order of the reaction?

2 Complex reactions: Reaction mechanism

Q10: The reaction *cis-2-butene* to *trans-2-butene* is first order in both directions. At 25^oC, the equilibrium constant is 0.406 and the forward rate constant is 4.21×10^{-4} s^{-1}. Starting with a sample of pure *cis* isomer with $[\text{cis}]_o = 0.115$ mol.dm^{-3}, how long would it take for half the equilibrium amount of the *trans* isomer to form?

Q11: For the following consecutive reaction of first order,

$$\text{X} \xrightarrow{k_1} \text{Y} \xrightarrow{k_2} \text{Z}$$

where $k_1 = 2s^{-1}$ and $k_2 = 0.1s^{-1}$. Calculate the time 't' in seconds required for Y to reach its maximum concentration? Assume that only X is present at time, t=0.

Q12: Consider the following chemical reactions,

$$\text{NO(g)} + \text{Br}_2\text{(g)} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \text{NOBr}_2\text{(g)} \qquad \text{(fast)}$$

$$\text{NOBr}_2\text{(g)} + \text{NO(g)} \xrightarrow{k_2} 2\ \text{NOBr(g)} \qquad \text{(slow)}$$

Show that the rate law derived from the above reaction mechanism is consistent with the experimental rate law, Rate $= k[NO]^2[Br_2]$, where the experimental rate constant, $k = k_2k_1/k_{-1}$.

Q13: A proposed mechanism of the N_2O_5 decomposition reaction $N_2O_5 \rightarrow 2NO_2 + \frac{1}{2}O_2$ is as follows,

$$\text{N}_2\text{O}_5 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \text{NO}_2 + \text{NO}_3$$

$$\text{NO}_2 + \text{NO}_3 \xrightarrow{k_2} \text{NO} + \text{O}_2 + \text{NO}_2$$

$$\text{NO} + \text{NO}_3 \xrightarrow{k_3} 2\text{NO}_2$$

Apply steady-state approximation to show that the overall rate of the above reaction is

$$-\frac{\text{d}[\text{N}_2\text{O}_5]}{\text{dt}} = k[N_2O_5]$$

The overall rate constant k can be written in terms of k_1, k_{-1}, k_2, and k_3.

Q14: The mechanism of stratospheric destruction of Ozone (O_3) is given below,

$$\text{O}_3 + \text{M} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \text{O}_2 + \text{O} + \text{M}$$

$$\text{O}_3 + \text{O} \xrightarrow{k_3} 2\text{O}_2$$

Determine the destruction rate of Ozone based on the above reaction mechanism. Simplify the rate equation when the concentration of M is very high.

3 Temperature-dependence on reaction rate

Q15: The rate constant of a chemical reaction varies with temperature as follows,

Temperature (^{o}C)	Rate constant, k (s−1)
189.7	2.52×10^{-5}
198.9	5.25×10^{-5}
230.3	6.30×10^{-4}
251.2	3.16×10^{-3}

(i) From the data given in the table, calculate the activation energy of the reaction, (ii) find out the rate constant when the temperature is raised to 430.0 K, and (iii) can you estimate the reaction rate constant at much higher temperature, say 280 ^{o}C?

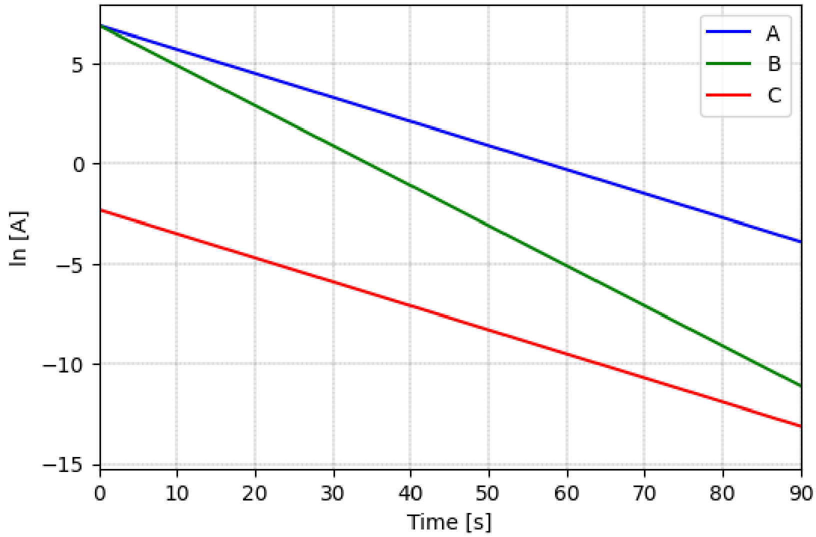
Q16: The thermal decomposition of ethylene oxide follows first order kinetics with a half-life of 363 minutes at 378.5 ^{o}C. The activation energy of this reaction is 52 kcal/mol. Calculate the time required to decompose 75 % of ethylene oxide at 450 ^{o}C.

Q17: The dependence of a rate constant of a second order reaction with temperature can be described by the following equation,

$$\ln k = 11.899 - \frac{3169}{T} \tag{2}$$

If the initial concentration of both the reactants is 0.005 M, (i) calculate the activation energy, and (ii) half-life ($t_{1/2}$) of the reaction at 25 ^{o}C.

Q18: Imagine you studied a first order chemical reaction in the lab and obtained the following plots from three independent experiments -



(i) Which two graphs were obtained from the experiment carried out at the same temperature? Explain the similarities and differences between the two graphs.
(ii) Which two graphs indicate that the experiments were started with the same initial concentration? Why do their slope differ at two different temperature? Explain.

Q19: SO_2Cl_2 decomposes following first order kinetics,

$$SO_2Cl_2(g) \rightarrow SO_2(g) + Cl_2(g)$$

At 600 K the half-life for this process is 2.3×10^5 s. (i) What is the rate constant at this temperature? (ii) At 320 ^{o}C the rate constant is 2.2×10^{-5} s^{-1}. What is the half-life at this temperature?

Q20: The Arrhenius rate expression k = A exp(-E_a/RT) is only an approximation as one finds that the pre-exponential factor (A) is not completely temperature independent. Assure that it weakly depends on temperature as A = BT^m. Then the rate expression becomes k = A BT^m exp(-E_b/RT). Under these circumstances what would be the relationship between E_a and E_b?

4 Catalysis

Q21: For an enzyme substrate reaction,

$$\text{E+S} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \text{ES}$$
$$\text{ES} \xrightarrow{k_2} \text{E+P}$$

The slope and the intercept of the plot between 1/r and 1/[S] are 10^{-2} s and 102 M^{-1}s respectively. If $E_0 = 10^{-6}$ M and $k_{-1}/k_2 = 1000$, the value of k_1 would be?

Q22: V_{max} and K_m for an enzyme catalyzed reaction are 2×10^{-3} M s^{-1} and $1{\times}10^{-6}$ M respectively. Find the rate of reaction when the substrate concentration is $1{\times}10^{-6}$ M is?

Q23: For an enzyme substrate reaction, a plot between 1/V and 1/[S] yield a slope of 40 s. if the enzyme concentration is 2.5 m, then the catalytic efficiency of the enzyme is?

Q24: The enzyme carbonic anhydrase catalyzes the reaction, CO_2(g) + H_2O(l) $\rightarrow$ HCO_3^-(aq) + H^+(aq). In water, without the enzyme, the reaction proceeds with a rate constant of 0.039 s^{-1} at 25 ^{o}C. In the presence of the enzyme in water, the reaction proceeds with a rate constant of 1.0×10^6 s^{-1} at 25 ^{o}C. Assuming the collision factor is the same for both situations, calculate the difference in activation energies for the uncatalyzed versus enzyme catalyzed reaction. [Ans: difference = 42 kJ]