CML101: Tutorial 2 - Chemical Kinetics
UG Semester - I (2023-24)

1 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?

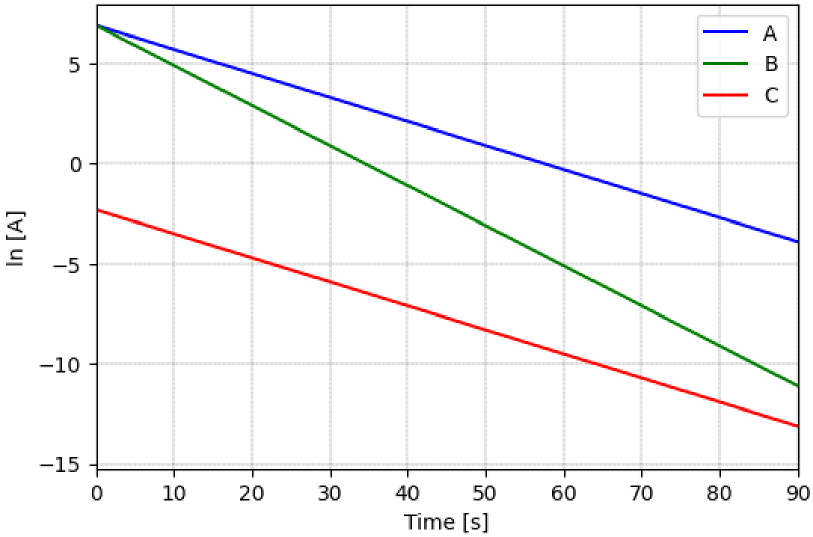
Q16: The thermal decomposition of ethylene oxide follows first order kinetics with a half-life of 363 minutes at 378.5 ^{o}C. The activation energy of this reaction is 52 kcal/mol. Calculate the time required to decompose 75 % of ethylene oxide at 450 ^{o}C.

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

$$\ln k = 11.899 - \frac{3169}{T} \tag{1}$$

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 ^oC the half-life of this reaction changes to 3.2×10^4 s. What is the activation energy required for this reaction?

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 $k = BT^m$ exp($-E_b$/RT). Under these circumstances what would be the relationship between E_a and E_b?

2 Catalysis

Q21: For an enzyme substrate reaction,

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

The slope and the intercept of the plot between $1/\nu$ and 1/[S] are 10^{-2} s and 10^2 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 1×10^{-6} M respectively. Find the rate of reaction when the substrate concentration is 1×10^{-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 μM, 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: $|\Delta E| = 42$ kJ/mol]