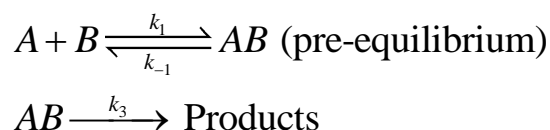


Department of Chemistry, IIT Madras
CY1001 (Chemistry: Structure, Bonding and Reactivity)
Semester: Aug – Nov 2014
Assignment 3: Chemical Kinetics (20/09/2014)
(Teachers : AKM / GRR / EP / RG)

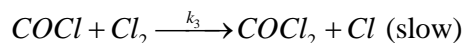
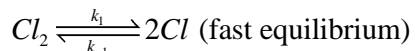
1. The reaction $2\text{NO}_2 + \text{F}_2 \rightarrow 2\text{NO}_2\text{F}$, is first order wrt NO_2 as well as F_2 . Rationalize using a suitable mechanism.
2. $\text{NO}_2 + \text{CO} \rightarrow \text{NO} + \text{CO}_2$, Rate = $k[\text{NO}_2]^2$. Suggest a suitable mechanism and rationalize.
3. For a general reaction mechanism



Compare the rate expressions using the concepts of pre-equilibrium and SSA.

4. For the reaction $\text{CO} + \text{Cl}_2 \rightarrow \text{COCl}_2$, the following mechanism is proposed. Show that the mechanism conforms to the experimental rate law:

$$\frac{d[\text{COCl}_2]}{dt} = k[\text{CO}][\text{Cl}_2]^{3/2}$$



5. The overall reaction $2\text{NO} + \text{O}_2 = 2\text{NO}_2$ is exothermic. 'k' of the reaction decreases with 'T'. How to rationalize using the following mechanism?
6. The temperature coefficient of a reaction is the ratio of rate constants at two temperatures differing by 10K. Find this value for the same reaction carried out at 300 K and 310 K. (2.8)
7. A dimerization reaction at 300 K follows Arrhenius equation, with $A = 10^{5.61}$ and $E_a = 65.4 \text{ kJ}$. Calculate the thermodynamic parameters of activation.

$$\Delta S^{0\#} = -154.25 \text{ JK}^{-1} \text{ mol}^{-1}$$

$$\Delta H^{0\#} = 60.412 \text{ kJ mol}^{-1}$$

$$\Delta G^{0\#} = 106.692 \text{ kJ mol}^{-1}$$

8. For a first order reaction, $A \xrightarrow{k_1} B \xrightarrow{k_2} C$, show that the optimization of B leads to

$$t = \left(\frac{1}{k_2 - k_1} \right) \ln \frac{k_2}{k_1}.$$

9. For the opposing reactions, $A \xrightleftharpoons[k_b]{k_f} B$, show that when [A] and [B] are halfway to their equilibrium values, $t = \frac{\ln 2}{k_f + k_b}$.

10. Consider a reaction, $A \longrightarrow \text{products}$. If this reaction is one-half order with respect to A, integrate the rate expression and decide what function should be plotted from the data to determine the rate constant.

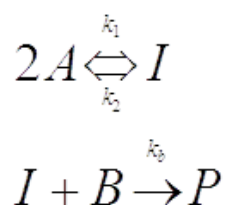
11. A reaction follows a complex mechanism involving multiple elementary steps with rate constant, $k = \frac{k_1 k_2 k_3}{k_4}$. What should be the activation energy of the overall reaction? Hint: Use Arrhenius expression.

12. Explain why the value of ΔS^\ddagger for the unimolecular decomposition of isopropyl nitrite in the gas phase is small and positive.

13. What is the unit of the rate constant of a zero order reaction? Derive the expression

$$\text{for the half life. (unit = sec}^{-1} \quad t_{1/2} = \frac{[A]_0}{2k} \text{)}$$

14. Show that the following reaction is a third order reaction when pre-equilibrium assumption is valid.



15. The half-life of radium is 1600 years. How much disintegration per second would be undergone by 1 g of radium? ($k=1.37 \times 10^{-11} \text{ s}^{-1}$)

16. N_2O_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

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

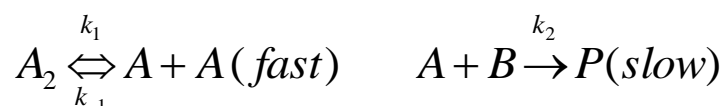
$$\frac{d[\text{N}_2\text{O}_5]}{dt} = 1.5 \times 10^{-4} \text{ mol L}^{-1}\text{s}^{-1}.$$

$$\frac{d[\text{O}_2]}{dt} = 0.75 \times 10^{-4} \text{ mol L}^{-1}\text{s}^{-1}.$$

$$\frac{d[\text{N}_2]}{dt} = 3 \times 10^{-4} \text{ mol L}^{-1}\text{s}^{-1}.$$

17. A first order reaction has 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? ($T = 269.5 \text{ K}$)

18. The following reaction mechanism involves an intermediate A. Deduce the rate law for the reaction.



19. For a first order consecutive reaction, write down the rate expressions and obtain concentrations [A], [B] and [C] at time t in terms of $[\text{A}]_0$, k_1 and k_2 . Obtain the same for B and C under steady state conditions. If $[\text{A}]_0 = 100 \text{ M}$, $k_1 = 0.04 \text{ min}^{-1}$, $k_2 = 0.006 \text{ min}^{-1}$, Calculate the concentrations of A, B and C at 5 min. ($[\text{A}] = 81.87$, $[\text{B}] = 17.85$, $[\text{C}] = 0.278$)

20. N_2O_5 decomposes according to 1st order kinetics, and 10% of it decomposed in 30 s. Estimate k , $t_{1/2}$ and percent decomposed in 500 s. ($k=0.00351 \text{ s}^{-1}$, $t_{1/2} = 197 \text{ s}$, **82.7 %**)

21. The decomposition of A is first order, and [A] is monitored. The following data are recorded:

t / min	0	2	4	8
[A]/[M]	0.100	0.0905	0.0819	0.0670

Calculate k , *half-life*, t when $[A] = 0.010$ and $[A]$ when $t = 5$ min. ($k = 0.0499$, *Half life* = 13.89)

22. Dimerization of butadiene is second order: $2 \text{C}_4\text{H}_6(\text{g}) = \text{C}_8\text{H}_{12}(\text{g})$

The *rate constant* k at some temperature is 0.100. The initial concentration of butadiene [B] is 2.0 M. Calculate the time required for [B] = 1.0 and 0.5 M, and calculate concentration of butadiene when $t = 1, 5, 10$, and 30 min.

$t =$	1	5	10	15	30	35
[B] =	1.67	1.0	0.67	0.50	0.29	0.25

23. For the reaction: $2 \text{NO}_2(\text{g}) \rightarrow 2 \text{NO}(\text{g}) + \text{O}_2(\text{g})$

The *rate constant* $k = 1.0 \times 10^{-10} \text{ s}^{-1}$ at 300 K and the *activation energy* $E_a = 111 \text{ kJ mol}^{-1}$. What are A , k at 273 K and T when $k = 1 \times 10^{-11}$? ($A = 2.13 \times 10^9 \text{ s}^{-1}$, $k = 1.23 \times 10^{-12} \text{ s}^{-1}$, $T = 285 \text{ K}$)

24. The *rate constant* for the first-order decomposition of a compound A in the reaction $2 \text{A} \rightarrow \text{P}$ is $k = 2.78 \times 10^{-7} \text{ s}^{-1}$ at 25°C. What is the *half-life* of A?

25. A reaction $2 \text{A} \rightarrow \text{P}$ has a third-order rate law with $k = 3.50 \times 10^{-4} \text{ dm}^6 \text{ mol}^{-2} \text{ s}^{-1}$. Calculate the time required for the concentration of A to change from $0.077 \text{ mol dm}^{-3}$ to $0.021 \text{ mol dm}^{-3}$. ($t = 1.5 \times 10^6 \text{ s}$)

26. Deduce an expression for the time it takes for the concentration of a substance to fall to one-third its initial value in an n^{th} order reaction.

$$t_{1/3} = \frac{3^{n-1} - 1}{k(n-1)} [A]_0^{1-n}$$

27. The reaction $\text{A}^- + \text{H}^+ \rightarrow \text{P}$ has a *rate constant* given by the empirical expression $k_2 = (8.72 \times 10^{12}) e^{-(6134 \text{ K}/T)} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$. Evaluate the *energy* and *entropy* of *activation* at 25°C. (*Enthalpy of activation* = 48.52 kJ mol⁻¹, *Entropy of activation* = -32.2 kJ mol⁻¹).