

assignment 3 - solns.

(due before class on 3 Nov 2020)

1. For a reaction $A + BC \rightarrow AB + C$ the reactive cross section,

$$\sigma = \begin{cases} 100 \text{Å}^2 & \text{if } v > 5 \times 10^3 \text{m/s} \\ 0 & \text{if } v < 5 \times 10^3 \text{m/s} \end{cases}$$

What is the rate at 300 K if the reduced mass of the reactants is 1 amu? How long will it take to form a mole of C?

$$\text{Ans. } \varepsilon_a = \frac{1}{2} \mu v^2 = \frac{1}{2} \cdot (5 \times 10^3)^2 \text{J/mol} = 1.25 \times 10^7 \text{J/mol}$$

$$\therefore k = N_A \sigma \sqrt{\frac{8k_B T}{\pi \mu}} e^{-\frac{\varepsilon_a}{k_B T}} = 6.023 \times 10^{23} \times \sqrt{\frac{8 \times 1.38064852 \times 10^{-23} \text{m}^2 \text{kg s}^{-2} \text{K}^{-1} \times 300 \text{K}}{3.1416 \times 1.6605 \times 10^{-27} \text{kg}}} \times e^{-\frac{1.25 \times 10^7}{8.314 \times 300}} = \dots$$

In absence of additional information, we assume unit concentrations of the reactants. Then the rate is equal to the rate constant in magnitude.

$$\text{If we have } [A]_0 = [B]_0 = 1 \text{ mol/l}$$

and we want to convert all of it, that will take Assuming the reaction to be elementary, it is a second order reaction, hence with equal initial concentrations, $[A]_0 = [B]_0$,

$$\frac{1}{[A]} - \frac{1}{[A]_0} = kt$$

$$\text{If we have } [A]_0 = [B]_0 = 1 \text{ mol/l}$$

and we want to convert all of it, that will take infinite time.

$$\therefore \text{for a mole of C to be formed per liter, we need to have } [A]_0 = 1 + \Delta \text{ mol/l}$$

$$\text{then } t = \frac{1}{k} \left(\frac{1}{\Delta} - 1 \right)$$

2. A treatment alternative to the deterministic approach to kinetics is the stochastic approach.

Read the article "Stochastic Approach to Reaction and Physico-Chemical Kinetics" by E. A. Boucher, attached as a supplement to today's (23 Oct 2020) lecture on Moodle. Outline the differences between the two methods and between their applications.

Ans. The major difference is in the use of theory of probability and related tools (statistics). Use of the generating function and master equation approach is basic in the stochastic approach. Unlike the phenomenological kinetics, it helps us to see conversion of molecules ab initio including chance as a scientific problem of exploration.

Your response will be graded according to the details you have mentioned and the insights you show.

3. For the reaction $\text{H}_2 + \text{I}_2 \xrightleftharpoons[k_{-1}]{k_1} 2\text{HI}$, $k_1 = 10^{14} \cdot e^{-\frac{165 \text{ kJ/mol}}{RT}}$ and $k_{-1} = 10^{13} \cdot e^{-\frac{185 \text{ kJ/mol}}{RT}} \text{ cm}^3/\text{mol s}$.

What is the equilibrium constant K for a mixture of H_2 , I_2 and HI at $T = 300 \text{ K}$ and 2000 K ?

$$\text{Ans. } K_{eq} = \frac{k_1}{k_{-1}} = \frac{10^{14} \cdot e^{-\frac{165}{RT}}}{10^{13} \cdot e^{-\frac{185}{RT}}} = 10 \cdot e^{\frac{20}{0.00831T}} = 10 \cdot e^{\frac{2405.6}{T}}$$

$$\therefore T = 300 \implies K_{eq} = 10 \cdot e^{\frac{2405.6}{300}} = 3.04 \times 10^4$$

$$\therefore T = 2000 \implies K_{eq} = 10 \cdot e^{\frac{2405.6}{2000}} = 33.3$$

4. How does increasing the ionic strength affect the rate of the reaction $\text{H}_2\text{O}_2 + 2\text{H}^+ + 2\text{Br}^- \rightarrow 2\text{H}_2\text{O} + \text{Br}_2$?

What ionic strength will cause a change of 25% in rate?

Ans. In absence of any additional information, assume the activated complex to involve all the reactants,

$$\text{then } k = \frac{k^0}{K_\gamma}; K_\gamma = \frac{\gamma^\ddagger}{\gamma_{\text{H}_2\text{O}_2} \cdot \gamma_{\text{H}^+}^2 \cdot \gamma_{\text{Br}^-}^2}$$

The neutral species will have no contribution to the activity coefficient

$$\log k = \log k^0 - 2A \{z_{\text{H}^+}^2 + z_{\text{Br}^-}^2\} \sqrt{I}$$

$$\log k = \log k^0 - 4A\sqrt{I}$$

\therefore with increasing ionic strength, the rate will decrease.

for change of 25% in rate, $\frac{k}{k^0} = 0.75$

$$\text{using } A = 0.509, \log \frac{k}{k^0} = \log(0.75) = -4 \times 0.509 \times \sqrt{I}$$

$$\therefore I = \left(\frac{\log(0.75)}{4 \times 0.509} \right)^2 = 0.02$$