1. What is the unit of the rate constant of a zero order reaction? Derive the expression for the half life.

Unit=moles/s

\[ t_{1/2} = \frac{[A]_0}{2k} \]

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

\[ 2A \rightleftharpoons I \]

\[ I + B \rightarrow P \]

\[ \frac{dP}{dt} = k_b[I][B] \]
\[ \frac{d[I]}{dt} = k_1[A]^2 - k_2[I] - k_b[I][B] = 0 \]
\[ [I] = \frac{k_1[A]^2}{k_2 + k_b[B]} \]
\[ \therefore \frac{dP}{dt} = k_b[I][B] = k_b \frac{k_1[A]^2[B]}{k_2 + k_b[B]} \]

Applying the condition for preequilibria

\[ \frac{dP}{dt} = k_b[I][B] = k_b \frac{k_1[A]^2[B]}{k_2} = k_bK[A]^2[B] \]
3. The half-life of radium is 1600 years. How much disintegration per second would be undergone by 1 g of radium?

The half life in seconds will be

\[ 1600 \times 325.25 \times 24 \times 60 \times 60 = 5.049 \times 10^{10} \text{s} \]

\[ k = \frac{0.693}{t_{1/2}} = 1.37 \times 10^{-11} \text{s}^{-1} \]

the number of nuclei present in 1 g of radium is

\[ \frac{6.023 \times 10^{23} \text{mol}^{-1}}{226 \text{ g/mol}} = 2.666 \times 10^{21} \text{g}^{-1} \]

the number of disintegration, is therefore;

\[ 1.37 \times 10^{-11} \text{s}^{-1} \times 2.67 \times 10^{21} \text{g}^{-1} = 3.66 \times 10^{10} \text{g}^{-1} \text{s}^{-1} \]

4. Calculate the bimolecular rate constant at 298 K for the reaction of two different small radicals with a reduced mass of 4.98 \times 10^{-26} \text{kg} and a collision diameter of 500 pm

According to collision theory,

\[ k = N_A \pi d^2 \left( \frac{8k_B T}{\pi \mu} \right)^{\frac{3}{2}} \]

Ans: \(2.17 \times 10^{11} \text{M}^{-1} \text{s}^{-1}\)

5. \(\text{N}_2\text{O}_5\) 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 \(\frac{\text{d}[\text{N}_2\text{O}_5]}{\text{dt}}, \frac{\text{d}[\text{NO}_2]}{\text{dt}}, \frac{\text{d}[\text{O}_2]}{\text{dt}}\) ?

\[ \frac{\text{d}[\text{N}_2\text{O}_5]}{\text{dt}} = 1.5 \times 10^{-4} \text{mol L}^{-1} \text{s}^{-1}, \quad \frac{\text{d}[\text{O}_2]}{\text{dt}} = 0.75 \times 10^{-4} \text{mol L}^{-1} \text{s}^{-1}, \quad \frac{\text{d}[\text{N}_2]}{\text{dt}} = 3 \times 10^{-4} \text{mol L}^{-1} \text{s}^{-1}. \]
6. A first order reaction has activation energy of 104,600 J mol\(^{-1}\) and a pre-exponential factor \(A = 5 \times 10^{13}\) s\(^{-1}\), at what temperature will the reaction have a half-life of 30 days?

\[
\frac{\ln 2}{t_{1/2}} = A \exp^{\frac{E_a}{RT}}
\]

\(T = 269.5\) K

7. What is the kinetic energy of the photoelectron ejected from an electronic energy level whose orbital energy is -13 eV? Assume that the photoionization used HeI radiation of 21.2 eV.

\(\text{IP} = 13\) eV
\(\text{KE} = 21.2 - 13 = 8.2\) eV

8. Freundlich adsorption isotherm is \(x/m = y = kP^n\) or \(\ln y = \ln k + \ln P\). Suggesting a straight line relation between \(\ln y\) and \(\ln P\). When will Langmuir adsorption become this?

Rate of desorption = \(k_d\theta\)
Rate of adsorption = \(k_a(1-\theta)P\)

At equilibrium, \(k_d\theta = k_a(1-\theta)P\)
\(\theta = KP/[1 + KP]\)
\(K = k_a/k_d\)

When \(KP<<1\), or when \(P\) is small,
\(\theta = KP\) or proportional to \(P\)
When \(KP>>1\)
\(\theta = 1\) or reaches a maximum value

For all pressures in between, which is the physical reality, \(\theta\) is proportional to \(P^n\), \(n\) is a value between 0 and 1. So, Langmuir adsorption isotherm will become Freundlich kind in the intermediate pressures.
9. Write down the expression for the $t_{1/2}$ of an $n^{th}$ order reaction.

$$ t_{1/2} = \frac{2^{n-1} - 1}{(n-1)k[A]_0^{n-1}} $$

10. The mechanism for the iodination reaction of acetone is given below:

Mechanism:

$$ \text{CH}_3\text{C-CH}_3 + \text{H}^+ \xrightleftharpoons[k_1]{k_{-1}} \text{CH}_3\text{C-CH}_3 \hspace{1cm} \text{CH}_3\text{C-CH}_3 \hspace{1cm} \text{CH}_2\text{C-CH}_3 + \text{H}^+ \hspace{1cm} \text{CH}_2\text{C-CH}_3 + \text{I}_2 \hspace{1cm} \text{I}(\text{fast}) $$

$$ \text{CH}_3\text{C-CH}_3 \xrightarrow{k_2} \text{CH}_2\text{OCH}_3 \hspace{1cm} \text{CH}_2\text{OCH}_3 \hspace{1cm} \text{I}(\text{solw}) $$

$$ \text{CH}_2\text{OCH}_3 + \text{I}_2 \xrightarrow{k_3} \text{I}(\text{fast}) $$

Based on this mechanism, derive the rate law representing the system. What is the rate order of iodine in this reaction?

$$ -\frac{d[I_2]}{dt} = k_3[H_2C = C(OH) - CH_3]I_2 $$

$$ \Rightarrow [H_3C = C(OH) - CH_3] = \frac{k_2}{k_3} \frac{[CH_3-C = (OH)-CH_3]}{[I_2]} $$

$$ = \frac{k_2}{k_3} \frac{(k_1/k_{-1})[CH_3COCH_3][H^+]}{[I_2]} $$

Substitute in rate expression

$$ -\frac{d[I_2]}{dt} = k_2 \frac{k_1}{k_{-1}} [\text{Acetone}][H^+] $$
11. The Arrhenius parameters for the thermal decomposition of NOCl represented by, \(2\text{NOCl} (g) \rightarrow 2\text{NO} (g) + \text{Cl}_2 (g)\) are \(A = 1.00 \times 10^{13} \text{ M}^{-1} \text{s}^{-1}\) and \(E_a = 104 \text{ kJ mol}^{-1}\). Calculate the Entropy (\(\Delta^\#S\)), Enthalpy (\(\Delta^\#H\)), and Free energy of activation (\(\Delta^\#G\)) for the reaction at 300K.

\[ k = Ae^{-E_a/RT} \]

\[ \Rightarrow E_a = RT^2 \frac{d \ln k}{dT} \quad (1) \]

*From TST*

\[ k = \frac{k_BT}{h} \left( \frac{RT}{P^0} \right)^K_p \quad \text{substitute } K \text{ by } e^{\Delta S/RT}e^{-\Delta H/RT} \text{ take } \ln k \text{ and differentiate wrt } T \]

\[ \Rightarrow \frac{d \ln k}{dT} = \frac{2}{T} + \frac{\Delta H}{RT^2} \quad (2) \text{ comparing (1) and (2)} \]

\[ \Rightarrow E_a = \Delta H + 2RT \]

\[ \Delta H^\# = E_a - 2RT = 104\text{kJ mol}^{-1} - 2(8.314\text{ J K}^{-1} \text{ mol}^{-1})(300\text{K}) \]

\[ \Rightarrow \Delta H^\# = 99.0\text{kJ mol}^{-1} \]

\[ \Delta S^\# = R \ln \left( \frac{Ahe}{e^2 k_BT} \right) \]

\[ \Rightarrow \Delta S^\# = (8.314\text{ J K}^{-1} \text{ mol}^{-1}) \ln \left( \frac{(1.00\times10^{13} \text{ M}^{-1} \text{s}^{-1})(6.626\times10^{-34} \text{ Js})(1\text{M})}{e^2(1.38\times10^{-23} \text{ JK}^{-1})(300\text{K})} \right) \]

\[ \Rightarrow \Delta S^\# = -12.7\text{ J K}^{-1} \text{ mol}^{-1} \]

\[ \Delta G^\# = \Delta H^\# - T\Delta S^\# \]

\[ \Rightarrow \Delta G^\# = 99.0\text{kJ mol}^{-1} - (300\text{K}) \times (-12.7\text{ J K}^{-1} \text{ mol}^{-1}) \]

\[ \Rightarrow \Delta G^\# = 102.8\text{kJ mol}^{-1} \]