

assignment 1 - solns.

1. Consider the first-order reversible reaction involving two steps : $A_1 \xrightleftharpoons[k_{-1}]{k_1} A_2 \xrightleftharpoons[k_{-2}]{k_2} A_3$. Assuming that initially at time $t = 0$, $[A_1] = [A_1]_0$ and $[A_2]_0 = [A_3]_0 = 0$, obtain expressions for $[A_1]$, $[A_2]$ and $[A_3]$ and the equilibrium constant for the overall reaction $A_1 \rightleftharpoons A_3$

Ans. Write the rate equations for $\frac{d[A_i]}{dt}$; $i = 1, 2, 3$ using the stoichiometry of the elementary steps

$$\frac{d[A_1]}{dt} = k_{-1} [A_2] - k_1 A_1$$

$$\frac{d[A_2]}{dt} = k_1 A_1 - k_{-1} [A_2] - k_2 [A_2] + k_{-2} [A_3]$$

$$\frac{d[A_3]}{dt} = k_2 [A_2] - k_{-2} [A_3]$$

$\therefore [A_1] = [A_1]_0$ and $[A_2]_0 = [A_3]_0 = 0$, note that $[A_1]_0 = [A_1] + [A_2] + [A_3]$

use equilibrium constants to relate equilibrium concentrations with the rate constants :

$$\frac{k_1}{k_{-1}} = \frac{[A_2]_{eq}}{[A_1]_{eq}}, \quad \frac{k_2}{k_{-2}} = \frac{[A_3]_{eq}}{[A_2]_{eq}}$$

$$[A_1]_0 = [A_1]_{eq} + [A_2]_{eq} + [A_3]_{eq} = \left(\frac{k_{-1}}{k_1} + 1 + \frac{k_{-2}}{k_2} \right) [A_2]_{eq}$$

$$\text{or, } [A_2]_{eq} = \frac{k_1 k_{-2}}{k_{-1} k_{-2} + k_1 k_2 + k_1 k_{-2}} [A_1]_0$$

assume that A_2 reaches equilibrium very fast and in the rate equations, we can write $A_2 \approx [A_2]_{eq}$

Substitute for $[A_2]$ in the first eqn. and get a new differential equation for $[A_1]$:

$$\therefore \frac{d[A_1]}{dt} = \frac{k_{-1} k_1 k_{-2}}{k_{-1} k_{-2} + k_1 k_2 + k_1 k_{-2}} [A_1]_0 - k_1 A_1$$

Solve this using the integration factor method :

$$[y = a - by \implies y = \frac{a}{b} (1 - e^{-bt}) + y_0 e^{-bt}]$$

$$[A_1] = \frac{[A_1]_0}{k_{-1} k_{-2} + k_1 k_2 + k_1 k_{-2}} [k_{-1} k_{-2} + (k_1 k_2 + k_1 k_{-2}) e^{-k_1 t}]$$

From this, get

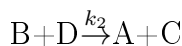
$$[A_3] = [A_1]_0 - [A_1] - [A_2] = \frac{[A_1]_0}{k_{-1} k_{-2} + k_1 k_2 + k_1 k_{-2}} [k_1 k_2 - (k_1 k_2 + k_1 k_{-2}) e^{-k_1 t}]$$

$$\text{At } t \rightarrow \infty, [A_1] = \frac{k_{-1} k_{-2} [A_1]_0}{k_{-1} k_{-2} + k_1 k_2 + k_1 k_{-2}}; \quad [A_3] = \frac{k_1 k_2 [A_1]_0}{k_{-1} k_{-2} + k_1 k_2 + k_1 k_{-2}}$$

\therefore equilibrium constant for the overall reaction,

$$K = \frac{[A_3]_{eq}}{[A_1]_{eq}} = \frac{k_1 k_2}{k_{-1} k_{-2}}$$

2. The reaction $A+B \rightarrow C+D$ takes place in two steps, by the following mechanism :



The first step comes to a rapid equilibrium (constant K_1). Obtain rate of formation of C in terms of K_1 , k_2 and $[A]$ and $[B]$.

Ans.

Ans. As the first step come to an equilibrium, we write the equilibrium constant, $K = \frac{[D]}{[A]^2}$

$$\text{rate} = \frac{d[C]}{dt} = k_2 [B] [D] = k_2 K [A]^2 [B]$$

3. A reaction has the stoichiometry $2A + 2B \rightarrow Y + 2Z$; rate of reaction, $v = k [A]^\alpha [B]^\beta$

Some results for the rate of consumption of A are shown below:

$[A]/\text{mol dm}^{-3}$	$[B]/\text{mol dm}^{-3}$	$v/\text{mol dm}^{-3}\text{s}^{-1}$
1.4×10^{-2}	2.3×10^{-2}	7.4×10^{-9}
2.8×10^{-2}	4.6×10^{-2}	5.92×10^{-8}
2.8×10^{-1}	4.6×10^{-2}	5.92×10^{-6}

Deduce α and β and the rate constant k .

Ans. Comparing the second and third rows as $[A]$ increases 10-fold with $[B]$ constant, the rate increases 100-fold.

\therefore the reaction is second order w.r.t. A and $\alpha = 2$

$$\text{or, } v = k [A]^2 [B]^\beta$$

Comparing the first and second rows as $[A]$ increases to twice its value, and $[B]$ to twice its value, the rate increases by a factor of $\frac{5.92 \times 10^{-8}}{7.4 \times 10^{-9}} = 8$

$$\text{or, } 2^2 \times 2^\beta = 8 \implies \beta = 1$$

4. (a) Integrate the rate equation for an autocatalytic reaction of the form $A \rightarrow P$, with rate law $v = k[A][P]$, and show that

$$\text{or, } \frac{[P]}{[P]_0} = \frac{(1+b)e^{at}}{1+be^{at}}, \text{ where } a = ([A]_0 + [P]_0)k \text{ and } b = \frac{[P]_0}{[A]_0}$$

$$\text{Ans. } A \longrightarrow P \quad v = k[A][P]$$

$$[A]_0 - x \quad x$$

$$\frac{dx}{dt} = k([A]_0 - x)([P]_0 + x)$$

integrating:

$$\frac{1}{[A]_0 + [P]_0} \ln \frac{([P]_0 + x)[A]_0}{[P]_0([A]_0 - x)} = kt$$

$$\text{or, } \ln \frac{([P]_0 + x)[A]_0}{[P]_0([A]_0 - x)} = ([A]_0 + [P]_0)kt = at$$

$$\text{or, } \frac{([P]_0+x)[A]_0}{[P]_0([A]_0-x)} = e^{at}$$

$$\text{or, } \frac{[P]_0+x}{[A]_0-x} = \frac{[P]_0}{[A]_0} e^{at} = b e^{at}$$

$$\text{or, } 1 + b e^{at} = \frac{[P]_0+[A]_0}{[A]_0-x} = \frac{a}{k([A]_0-x)}$$

$$\text{and } e^{at} - 1 = \frac{([P]_0+x)[A]_0}{[P]_0([A]_0-x)} - 1 = \frac{x([P]_0+[A]_0)}{[P]_0([A]_0-x)} = \frac{xa}{k[P]_0([A]_0-x)}$$

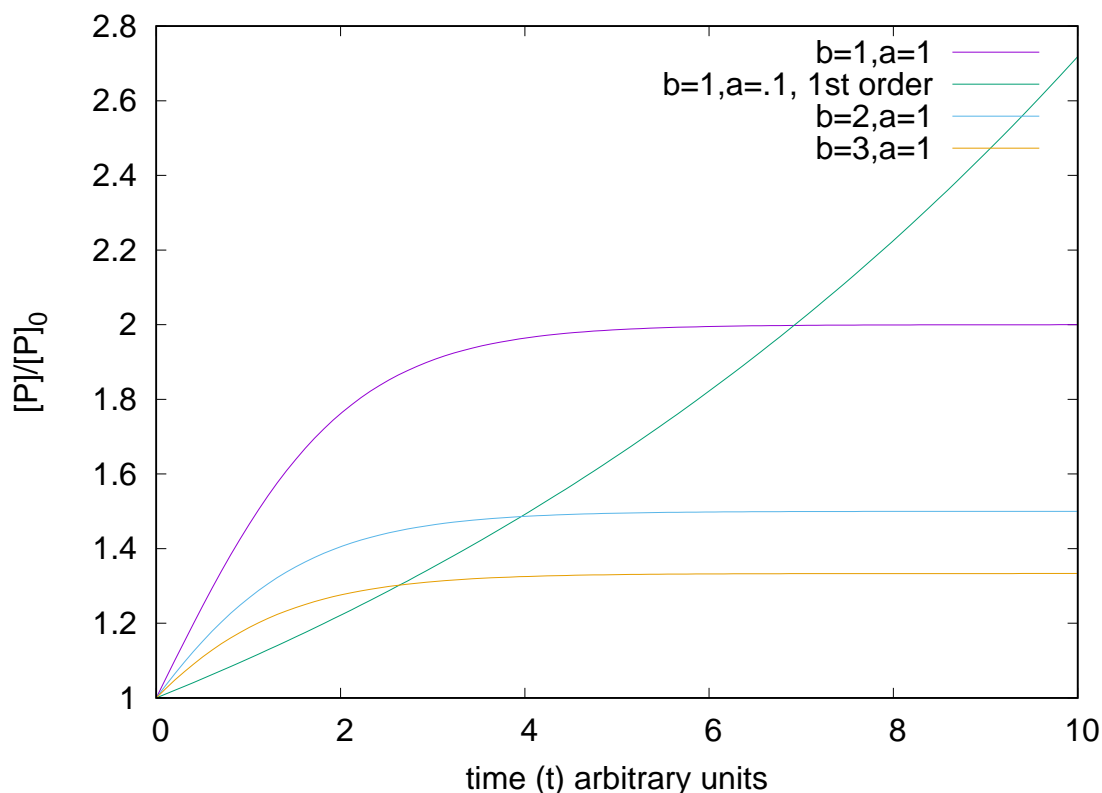
$$\text{or, } \frac{x}{[P]_0} = \frac{e^{at}-1}{1+b e^{at}}$$

$$\text{or, } \frac{[P]_0+x}{[P]_0} = \frac{[P]}{[P]_0} = \frac{e^{at}+b e^{at}}{1+b e^{at}} = \frac{(1+b)e^{at}}{1+b e^{at}}$$

(b) Plot $\frac{[P]}{[P]_0}$ against $a.t$ for several values of b . Discuss the effect of autocatalysis on the shape of a plot of $\frac{[P]}{[P]_0}$ against t by comparing your results with those for a first-order process

Ans. Three results for $a=1$, and $b=1, 2, 3$ are shown. The comparison with a first order $A \rightarrow P$ process is done for $a=.1$ and $b=1$.

The first order concentration keeps increasing exponentially, while for the autocatalytic process, soon the product concentration reaches a maximum value.



Notice that, the autocatalytic process has a faster rate in the beginning. Eventaully, the first

order process has to stop as it reaches a saturation point.

(c) Show that the reaction rate reaches a maximum at $t_{\max} = -\frac{1}{a} \ln b$.

$$\text{Ans. rate, } v = \frac{dx}{dt} = k([A]_0 - x)([P]_0 + x)$$

$$\text{or, } \dot{v} = k[-\dot{x}([P]_0 + x) + \dot{x}([A]_0 - x)] = k\dot{x}([A]_0 - [P]_0 - 2x)$$

$$\text{for rate to be maximum, } \dot{v} = 0$$

$$\text{or, } \dot{x}([A]_0 - [P]_0 - 2x) = 0$$

$$\text{or, } \dot{x} \text{ cannot be zero at maximum,}$$

$$\therefore 2x = [A]_0 - [P]_0$$

$$\text{or, } \frac{2x}{[P]_0} = \frac{2(e^{at_{\max}} - 1)}{1 + be^{at_{\max}}} = \frac{[A]_0}{[P]_0} - 1 = \frac{1}{b} - 1$$

$$\text{or, } \frac{be^{at_{\max}} - b}{1 + be^{at_{\max}}} = \frac{1 - b}{2}$$

By componendo and dividendo,

$$2be^{at_{\max}} + 1 - b = 3 - b$$

$$\text{or, } be^{at_{\max}} = 1$$

$$\text{or, } e^{at_{\max}} = \frac{1}{b} \implies at_{\max} = -\ln b \quad \text{or, } t_{\max} = -\frac{1}{a} \ln b.$$