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Q1) Given reaction: $A_1 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} A_2 \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} A_3$

also given: at $t=0$; $[A_1] = [A_1]_0$

& $[A_2]_0 = [A_3]_0 = 0$

sol) writing equations.

for $[A_1]$ $\Rightarrow$ $\frac{d[A_1]}{dt} = -k_1[A_1] + k_{-1}[A_2] \rightarrow$ i)

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

for $[A_3]$ $\rightarrow$ $\frac{d[A_3]}{dt} = -k_{-2}[A_3] + k_2[A_2] \rightarrow$ iii)

solving for steady state conc of A_1, A_2, A_3. $\left[\frac{dA_i}{dt} = 0\right]$

from eqn i) $\frac{d[A_1]}{dt} = 0$ $\therefore$ $+k_1[A_1]_{st} = k_{-1}[A_2]_{st}$

or $\boxed{[A_1]_{st} = \frac{k_{-1}}{k_1}[A_2]_{st}} \rightarrow$ 1

from eqn ii) $\frac{d[A_2]}{dt} = 0$ $\therefore$ $-k_2[A_2]_{st} + k_{-1}[A_2]_{st} = k_1[A_1]_{st} + k_{-2}[A_3]_{st}$

substituting $[A_1]_{st}$ from 1 $\Rightarrow (k_2 + k_{-1})[A_2]_{st} = [k_{-1}][A_2]_{st} + k_{-2}[A_3]_{st}$

$\Rightarrow (k_2 + \cancel{k_{-1}} - \cancel{k_{-1}})[A_2]_{st} = k_{-2}[A_3]_{st}$

$\boxed{[A_3]_{st} = \frac{k_2}{k_{-2}}[A_2]_{st}} \longrightarrow$ 2

from eqn iii) $\frac{d[A_3]}{dt} = 0$ $\therefore$ $k_{-2}[A_3]_{st} = k_2[A_2]_{st}$

$\hookrightarrow$ no new result

$\hookrightarrow$ using law of conservation of matter, the total amount of 3 products wont change

$\therefore$ $[A_1]_0 + [A_2]_0 + [A_3]_0 = [A_1]_{st} + [A_2]_{st} + [A_3]_{st}$

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$\therefore [A_1]_0 = \frac{k_{-1}}{k_1}[A_2]_{st} + [A_2]_{st} + \frac{k_2}{k_{-2}}[A_2]_{st}$

$\therefore [A]_0 = [A_2]_{st}\left[\frac{k_{-1}}{k_1} + 1 + \frac{k_2}{k_{-2}}\right]$

$$\therefore \boxed{[A_2]_{st} = [A_1]_0\left[\frac{(k_1)(k_{-2})}{k_{-2}k_{-1} + k_1k_{-2} + k_2k_1}\right]} \rightarrow (3)$$

substituting (3) in (1)

$$[A_1]_{st} = [A_1]_0\left[\frac{(\cancel{k_1})(k_{-2})}{k_{-2}k_{-1} + k_1k_{-2} + k_2k_1}\right] \times \frac{k_{-1}}{\cancel{k_1}}$$

$$\boxed{[A_1]_{st} = [A_1]_0\left[\frac{(k_{-1})(k_{-2})}{k_{-1}k_{-2} + k_1k_{-2} + k_2k_1}\right]} \rightarrow (4).$$

substituting (3) in (2)

$$\boxed{[A_3]_{st} = [A_1]_0\left[\frac{k_2 k_1}{k_{-2}k_1 + k_1k_{-2} + k_2k_1}\right]} \rightarrow (5)$$

↳ Now to find time dependence on $[A_1]$, $[A_2]$ & $[A_3]$
i.e. start by assuming that $[A_2]$ being the intermediate reaches it steady state very quickly, i.e., $[A_2] = [A_2]_{st}$ for all further calc.

i) Finding eqn for A_1 from i)

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

$$\int_{[A_1]_0}^{[A_1]} \frac{d[A_1]}{-k_1[A_1] + k_{-1}[A_2]_{st}} = \int_0^t dt$$

taking $-k_1[A_1] + k_{-1}[A_2]_{st} = b$ (limits b_1, b_2)

$\therefore -k_1\, d[A_1] = db.$

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$$\Rightarrow \int_{b_1}^{b_2} \frac{-db}{k_1(b)} = \int_0^t dt$$

$$\Rightarrow \ln(b_2/b_1) = -k_1 t$$

$$\Rightarrow b_2 = b_1 e^{-k_1 t}$$

$$b_1 \Rightarrow -k_1[A_1]_0 + k_{-1}[A_2]_{st}$$

$$b_2 = -k_1[A_1] + k_{-1}[A_2]_{st}$$

$$\therefore -k_1[A_1] + k_{-1}[A_2]_{st} = (-k_1[A_1]_0 + k_{-1}[A_2]_{st})(e^{-k_1 t})$$

$$\Rightarrow -k_1[A_1] = -k_1[A_1]_0 e^{-k_1 t} + (k_{-1})(e^{-k_1 t} - 1)[A_2]_{st}$$

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

Ans 1

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

iii) finding eqn for A_3 from iii)

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

~~solving using the same technique and k_2 instead of k_{-2} (write k_{-2} instead of k_1 also $[A_2]_{st}$)~~

$$\int_0^{[A_3]} \frac{d[A_3]}{-k_{-2}[A_3] + k_2[A_2]_{st}} = \int_0^t dt$$

taking $-k_{-2}[A_3] + k_2[A_{st}] = b$ (limits b_1, b_2)

$$\int_{b_1}^{b_2} \frac{-db}{(k_{-2})(b)} = \int_0^t dt$$

$$\ln(b_2/b_1) = -k_{-2}t \quad \Rightarrow \underline{b_2 = b_1 e^{-k_{-2} t}}$$

$$b_1 = -k_2(0) + k_2[A_2]_{st}$$

$$b_2 = -k_{-2}[A_3] + k_2[A_2]_{st}$$

$$-k_{-2}[A_3] + k_2[A_2]_{st} = k_2[A_2]_{st}\, e^{-k_{-2}t}$$

$$\Rightarrow [A_3] = [A_2]_{st}\left(\frac{k_2}{k_{-2}} - \frac{k_2}{k_{-2}} e^{-k_{-2}t}\right)$$

$$\Rightarrow [A_3] = \frac{k_2}{\cancel{(k_{-2})}}\left(\frac{k_1 \cancel{k_{-2}}}{k_1k_{-2} + k_1k_2 + k_{-1}k_{-2}}\right)\left([A_1]_0\right)\left(1 - e^{-k_{-2}t}\right)$$

Ans 2

$$\Rightarrow \boxed{[A_3] = [A_1]_0\left(1 - e^{-k_{-2}t}\right)\left(\frac{k_1 k_2}{k_1k_{-2} + k_1k_2 + k_{-1}k_{-2}}\right)}$$

$$\boxed{[A_2] = [A_1]_0\left(\frac{k_1 . k_{-2}}{k_1k_{-2} + k_1k_2 + k_{-1}k_{-2}}\right)}$$ Ans 3

To get keq for the reaction.

keq for $A \rightleftarrows B$ is $\frac{[B]eq}{[A]eq}$

$\therefore$ keq for $A_1 \rightleftarrows A_3$ is

$$keq = \frac{[A_3]_{st}}{[A_1]_{st}}$$

$$keq = \frac{\dfrac{\cancel{[A_1]_0}\,(k_2\, k_1)}{\cancel{k_{-2}k_{-1} + k_1k_{-2} + k_1k_2}}}{\dfrac{\cancel{[A_1]_0}\,[k_{-1}\, k_{-2}]}{\cancel{k_{-2}k_{-1} + k_1k_{-2} + k_1k_2}}}$$

$$\boxed{keq = \frac{k_1\, k_2}{k_{-1}\, k_{-2}}}$$

Ans 4

Q2) $A + B \rightarrow C + D$

$2A \rightleftharpoons D$ (k_1) fast

$B + D \xrightarrow[k_2]{} A + C$.

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sol) as $2A \rightleftharpoons D$ reaches equilibrium very early.

$$k_1 = \frac{[D]_{eq}}{[A]^2_{eq}} \longrightarrow (1).$$

now for $B + D \xrightarrow[k_2]{} A + C$

$$\frac{dC}{dt} = k_2 [B][D] \qquad \text{(fast)}$$

but we just found out that $[D] = [D]_{eq}$

$$\therefore [D] = k_1 [A]^2_{eq}.$$

also $[A]_{eq} = [A]$

$$\therefore [D] = k_1 [A_0]^2$$

$$\therefore \frac{dc}{dt} = k_2 [B]\, k_1 [A_0]^2$$

$$\boxed{\frac{dc}{dt} = k_1 k_2 [A_0]^2 [B]}$$

Q3) $\nu = k[A]^\alpha [B]^\beta$. units for conc → $mol\,dm^{-3}$; units for rate → $mol\,dm^{-3}s^{-1}$

i) $[A] = 1.4 \times 10^{-2}$ $[B] = 2.3 \times 10^{-2}$ $\nu = 7.4 \times 10^{-9}$

$$\therefore 7.4 \times 10^{-9} = k[1.4 \times 10^{-2}]^\alpha [2.3 \times 10^{-2}]^\beta \longrightarrow (1)$$

ii) $[A] = 2.8 \times 10^{-2}$ $[B] = 4.6 \times 10^{-2}$ $\nu = 5.92 \times 10^{-8}$

$$5.92 \times 10^{-8} = k[2.8 \times 10^{-2}]^\alpha [4.6 \times 10^{-2}]^\beta \longrightarrow (2)$$

substituting k from (1) in (2)

$$5.\cancel{92 \times 10^{-8}} = \frac{\cancel{7.4 \times 10^{-9}}}{[\cancel{1.4 \times 10^{-2}}]^\alpha [2.\cancel{3 \times 10^{-2}}]^\beta} [\overset{2}{\cancel{2.8 \times 10^{-2}}}]^\alpha [\overset{2}{4.\cancel{6 \times 10^{-2}}}]^\beta$$

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$\therefore 8 = 2^{\alpha} 2^{\beta}$

or $2^3 = 2^{\alpha+\beta} \Rightarrow \boxed{\alpha+\beta = 3} \rightarrow$ I)

iii) $[A] = 2.8\times10^{-1}$ $[B] = 4.6\times10^{-2}$ $r = 5.92\times10^{-6}$

$$5.92\times10^{-6} = k\,[2.8\times10^{-1}]^{\alpha}\,[4.6\times10^{-2}]^{\beta} \rightarrow (3)$$

substituting k from (2) in (3)

$$\overset{100}{5.\cancel{92\times10^{-6}}} = \frac{\cancel{5.92\times10^{-8}}\,[\overset{10}{\cancel{2.8\times10^{-1}}}]^{\alpha}\,[\cancel{4.6\times10^{-2}}]^{\beta}}{[\cancel{2.8\times10^{-2}}]^{\alpha}\,[\cancel{4.6\times10^{-2}}]^{\beta}}$$

$\Rightarrow 100 = 10^{\alpha} \Rightarrow 10^2 = 10^{\alpha}$

$\therefore \boxed{\alpha = 2}$

from I) if $\alpha = 2$ then $\boxed{\beta = 1}$

substituting $\alpha = 2$ & $\beta = 1$ in iii)

$$(5.92\times10^{-6}) = (k)(2.8\times10^{-1})^2(4.6\times10^{-2})^1$$

$$k = \frac{5.92}{2.8\times2.8\times4.6} \times \frac{10^{-6}}{10^{-2}\times10^{-2}} \; \frac{\cancel{mol\ dm^{-3}}\ s^{-1}}{mol^2\,dm^{-6}\times\cancel{mol\ dm^{-3}}}$$

$$\boxed{k = 1.6415\times10^{-3}\ mol^{-2}\,dm^{6}\,s^{-1}}$$

$A \xrightarrow{b} P$

Q4) $r = k[A][P]$

$$\frac{[P]}{[P]_0} = \frac{(1+b)e^{at}}{1+be^{at}} \qquad a = ([A]_0 + [P]_0)k$$

$$b = [P]_0 / [A]_0$$

show rate maximises at $t_{max} = -\frac{\ln b}{a}$

Plot, $[P]/[P]_0$ against at.

(a) $t=0$ we have $[A]_0$ & $[P]_0$

using law of conservation of matter

at any time t $[A] = [A]_0 + [P]_0 - [P]$

given $\frac{dP}{dt} = r = k[A][P]$

$$\frac{dP}{dt} = k[[A]_0 + [P]_0 - [P]][P]$$

$$\Rightarrow \int_{P_0}^{P} \frac{dP}{k(A_0+P_0-P)(P)} = \int_0^t dt$$

$$\Rightarrow \frac{1}{k}\int_{P_0}^{P} \frac{A_0+P_0-P+P}{(A_0+P_0)} \frac{dP}{(A_0+P_0-P)(P)} \quad \int_0^t dt$$

$$\Rightarrow \frac{1}{(k)(A_0+P_0)}\left(\int_{P_0}^{P} \frac{dP}{P} + \int_{P_0}^{P} \frac{dP}{A_0+P_0-P}\right) = \int_0^t dt$$

$\Rightarrow$ solving $\int_{P_0}^{P} \frac{dP}{A_0+P_0-P}$

taking $A_0+P_0-P = b$ (limits b_1, b_2)

$$-dP = db$$

$$\int_{b_1}^{b_2} \frac{-db}{b} = -\ln(b_2/b_1) = \ln(b_1/b_2)$$

$b_1 = A_0 + \cancel{P_0} - \cancel{P_0}$

$b_2 = A_0 + P_0 - P$

$= \ln(A_0/A_0+P_0-P)$

$$\ln(P/P_0) + \ln(A_0/A_0+P_0-P) = (k)(A_0+P_0)t$$

$$\Rightarrow \frac{P A_0}{(P_0)(A_0+P_0-P)} = e^{k(A_0+P_0)t}$$

take as a

$$P A_0 = (P_0)(A_0+P_0-P)\, e^{at}$$

$$P A_0 = P_0 A_0 e^{at} + P_0^2 e^{at} - P_0 P e^{at}$$

$$P(A_0 + P_0 e^{at}) = P_0 e^{at}(A_0+P_0)$$

$$\frac{P}{\cancel{P_0}} = \frac{P_0 \cancel{P_0}\,(A_0+P_0)\, e^{at}}{(A_0+P_0\, e^{at})}$$

taking $P_0/A_0 = b$.

$$\frac{P}{P_0} = \frac{\left(1+\frac{P_0}{A_0}\right)\cancel{A_0}\, e^{at}}{\left(1+\frac{P_0}{A_0}e^{at}\right)\cancel{A_0}}$$

$$\boxed{\frac{P}{P_0} = \frac{(1+b)e^{at}}{(1+be^{at})}}$$ proved

$a = k(A_0+P_0)$ $\quad b = P_0/A_0$

Part b) taking $P/P_0 = y$

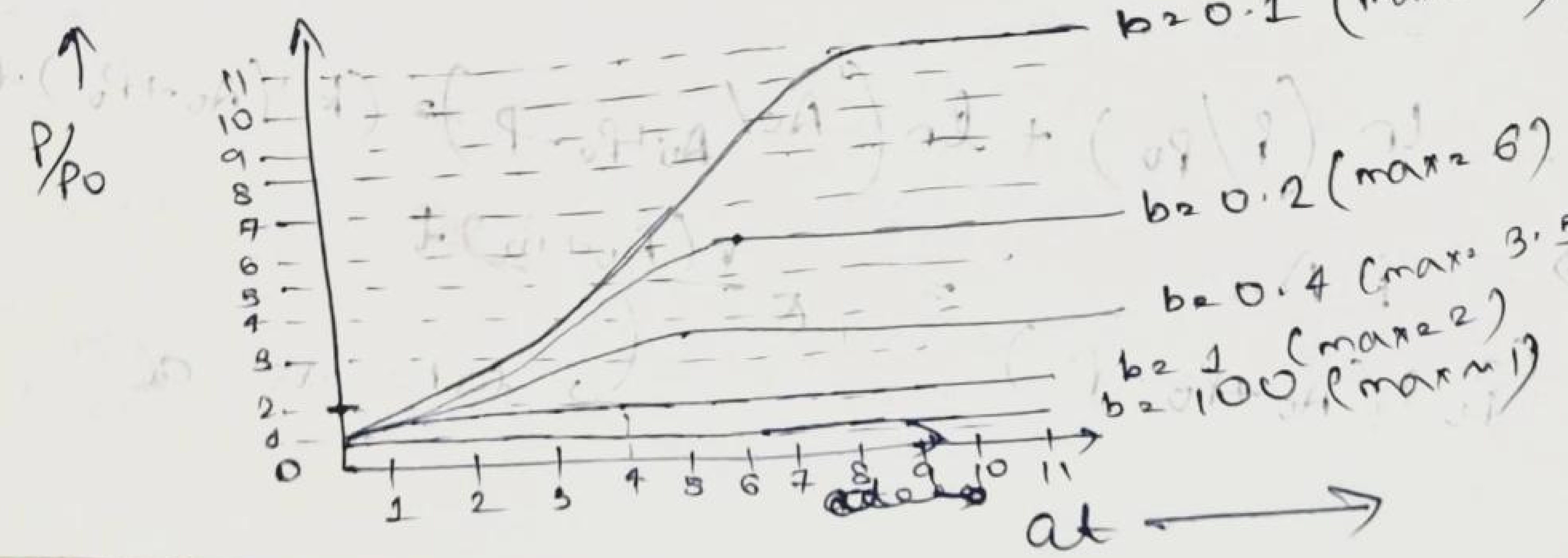
and $at = x$

plotted $y = \dfrac{(1+b)e^{x}}{1+be^{x}}$ for diff b

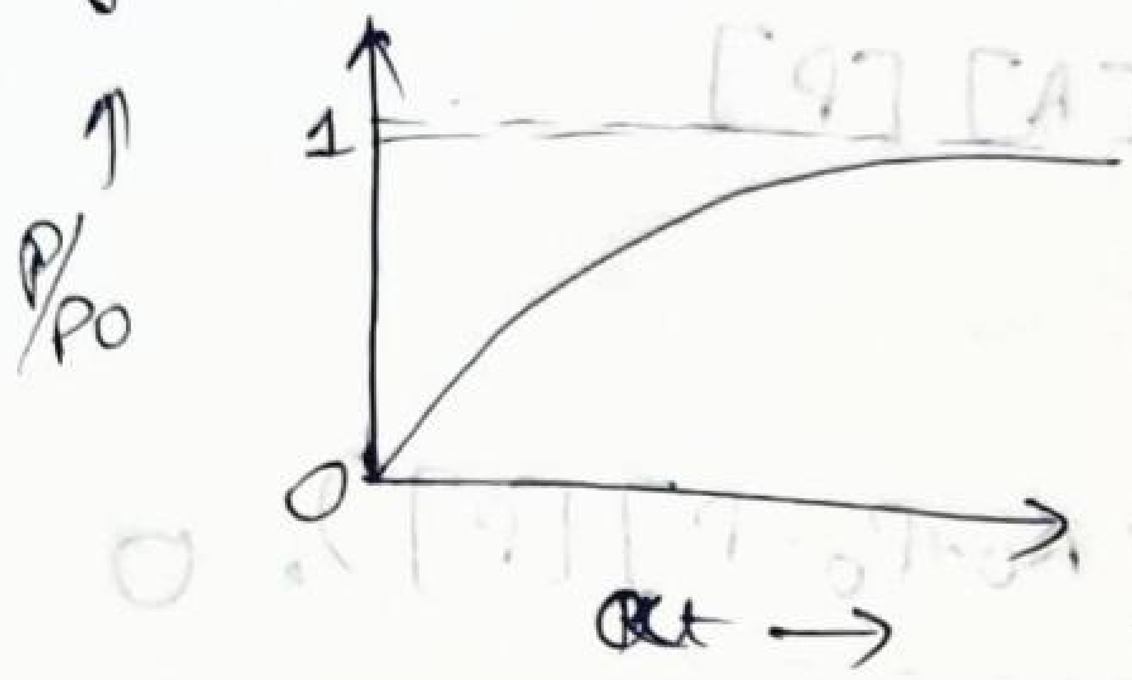
$at = x = k[A_0+P_0]t$

$k \to \geq 0$, $[A_0+P_0] \to \geq 0$, $t \to \geq 0$

$\therefore$ we only consider for $x \geq 0$.



for first order reactions.



$$P = P_0 e^{-at}$$

1) comparing maximums.

o) for first order $\max[P] = P_0$ at $t = \infty$.

o) for autocatalytic

at $t = \infty$ $\quad P = P_0 \dfrac{(1+b)e^{at}}{(1+be^{at})} \approx \dfrac{P_0(1+b)\cancel{e^{at}}}{b\cancel{e^{at}}}$

$$\max[P] = P_0\left(\frac{1+b}{b}\right) \text{ at } t = \infty.$$

2) comparing $t_{1/2}$ (response times)

o) for ~~first order~~ $t_{1/2} = \dfrac{\log_e 2}{a}$

for autocatalytic:

$$\frac{\cancel{P_0}\cancel{(1+b)}}{2b} = \cancel{P_0}\frac{\cancel{(1+b)}e^{at}}{(1+be^{at})}$$

$$\Rightarrow 1 + b\cancel{e^{at}} = \cancel{2}be^{at_{1/2}}$$

$$t_{1/2} = \ln(1/b) \times \frac{1}{a} = -\frac{\ln b}{a}$$

$t_{1/2} = \dfrac{\log_e(1/b)}{a}$

$\therefore$ for $1/b > 2$ ~~respon~~ or $b < 1/2$

response time for autocatalytic is more

for $b > 1/2$ $t_{1/2}$ (response time) for first order reaction is more

3) Comparing nature of curve

o) for first order reaction the curve is convex

o) for autocatalytic the curve is initially concave and then becomes convex.

Part C) Finding t_{max} for reaction rate

rate of the reaction $v = k[A][P]$

for t_{max} $\frac{dv}{dt} = 0$.

$$\frac{d(k[A][P])}{dt} = 0 = \frac{d(k[A_0+P_0-P][P])}{dt} = 0$$

$$\Rightarrow \frac{d(k(A_0+P_0)P - kP^2)}{dt} = 0$$

$$= (k)(A_0+P_0)\frac{dp}{dt} - (k)\left(\frac{dp^2}{dt}\right) = 0$$

$$= (k)(A_0+P_0)\frac{dp}{dt} - (k)(2p)\left(\frac{dp}{dt}\right) = 0.$$

$$\Rightarrow (\cancel{k})(A_0+P_0)\cancel{\frac{dp}{dt}} = (\cancel{k})(2p)\cancel{\frac{dp}{dt}}$$

as $k>0$ & $dp/dt \neq 0$ (P isn't produced no reaction otherwise)

$$\therefore [P] = ([A]_0+[P]_0)/2$$

$$\Rightarrow \frac{A_0+P_0}{2} = P_0\frac{(1+b)e^{at}}{1+be^{at}}$$

$$\Rightarrow \left(\frac{A_0}{P_0}+1\right) = 2(1+b)e^{at}/(1+be^{at})$$

$$\Rightarrow \frac{\cancel{(1+b)}}{b} = \frac{2\cancel{(1+b)}e^{at}}{(1+be^{at})}$$

$$\Rightarrow 1+be^{at} = 2be^{at}$$

$$\Rightarrow t = \frac{\log_e(1/b)}{a}$$

$$\therefore \boxed{t_{max} = -\frac{\ln(b)}{a}}$$ proved

makes sense as this is the time when curve changes from concave to convex.