1) A reacção reversível A ⇄ B é conduzida numa bateria de dois reactores CSTR associados em série, sabendo-se que o segundo reactor tem o dobro do volume do primeiro. O reagente A é alimentado à bateria de reactores numa concentração de 0.5 M, a um caudal volumétrico de 20 L/min. As reacções directa e inversa são elementares e os valores da constante cinética da reacção directa e da constante de equilíbrio são respectivamente 0.15 min^{-1} e 28. *The reversible reaction A ⇄ B is carried out in a battery of two CSTR reactors arranged in series, it being known that the second reactor is double the volume of the first reactor. Reagent A is fed to the reactor battery in a concentration of 0.5 M at a volumetric flow rate of 20 L / min. The direct and reverse reactions are elementary and the values of the direct reaction kinetic constant and the equilibrium constant are 0.15* min^{-1} *and 28, respectively.*

a) Deduza a expressão da lei cinética. *Derive the expression of the rate law.*

b) Para cada um dos reactores deduza as expressões que relacionam o volume do reactor com a conversão. *For each of the reactors, derive the expressions that relate the volume of the reactor to the conversion.*

c) Determine o valor da conversão de equilíbrio. *Determine the value of the equilibrium conversion.*

d) Sabendo que a conversão à saída do 2º reactor corresponde a 99% da conversão de equilíbrio, determine a conversão à saída do 1º reactor. *Knowing that the conversion at the exit of the 2nd reactor corresponds to 99% of the equilibrium conversion, determine the conversion at the exit of the 1st reactor.*

e) Determine os volumes dos reactores. *Determine the volumes of the reactors.*

2) A figura mostra a curva cinética obtida em reactor batch correspondente à reacção elementar em fase líquida 2A→B. A reacção é conduzida em reactores batch com o volume de 5 m^3 cada, que são carregados com A puro. *The figure shows the kinetic curve obtained in a batch reactor, corresponding to the elemental liquid phase reaction 2A→B. The reaction is carried out in batch reactors of 5* m^3, *which are loaded with pure A.*

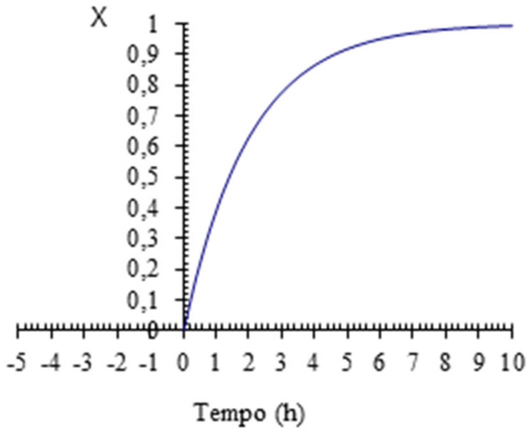
a) Escreva a expressão da lei cinética. *Write the expression of the rate law.*

b) Escreva a equação da curva mostrada no gráfico. *Write the equation of the curve shown in the graphic.*

c) Usando o gráfico, calcule o valor da constante cinética da reacção. *Evaluate the value of the kinetic constant. Use the graphic.*

d) Determine a conversão óptima e o tempo de reacção óptimo. *Calculate the optimal conversion and the optimal reaction time.*

e) Supondo que a fábrica funciona 24 h por dia e 330 dias por ano, calcule o número de reactores necessário a uma produção anual de B de 1500 TON. Utilize a conversão calculada em d), mas se não resolveu a alínea d) arbitre um valor. *If the plant works 24 h day and 330 days year, determine the number of reactors needed for an annual production of B of 1500 TON. Use the conversion calculated in d) but if you were not able to, use any value at your choice.*



Dados: Tempos mortos: 120 min. Peso molecular de A: 58. Peso molecular de B: 116. Densidade de A: 0.791. Se não resolveu a alínea b), use k = 0,074 $dm^3\ mol^{-1}\ h^{-1}$. *Data:* t_d*: 120 min. Molecular weight of A: 58. Molecular weight of B: 116. Density of A: 0.791. If you were not able to solve b) use* $k = 0{,}074\ dm^3\ mol^{-1}\ h^{-1}$.

Resolução:

Prob 1a

Lei cinética *kinetic law*:

$$-r_A = k\left(C_A - \frac{C_B}{Ke}\right) = kC_{A0}\left(1 - X - \frac{X}{Ke}\right)$$

Prob 1b

Balanços molares *mole balances*:

Reactor 1:

$$\tau_1 = \frac{C_{A0}\,X_1}{-r_{A1}} = \frac{C_{A0}\,X_1}{kC_{A0}\left(1 - X_1 - \frac{X_1}{Ke}\right)} = \frac{X_1}{k\left(1 - X_1 - \frac{X_1}{Ke}\right)}$$

Reactor 2:

$$\tau_2 = \frac{C_{A0}\,(X_2 - X_1)}{-r_{A2}} = \frac{C_{A0}\,(X_2 - X_1)}{kC_{A0}\left(1 - X_2 - \frac{X_2}{Ke}\right)} = \frac{X_2 - X_1}{k\left(1 - X_2 - \frac{X_2}{Ke}\right)}$$

Prob 1c

$$Ke = \frac{C_{Be}}{C_{Ae}} = \frac{C_{A0}\,X_e}{C_{A0}\,(1 - X_e)} = \frac{X_e}{1 - X_e}$$

$$Ke = \frac{X_e}{1 - X_e} \qquad \therefore Ke - KeX_e = X_e \qquad \therefore Ke = (1 + Ke)X_e$$

$$\therefore X_e = \frac{Ke}{1 + Ke} = \frac{28}{1 + 28} = 0{,}966$$

Prob 1d

$$\tau_2 = 2\,\tau_1$$

$$\therefore\ \frac{X_2 - X_1}{k\left(1 - X_2 - \frac{X_2}{Ke}\right)} = 2\,\frac{X_1}{k\left(1 - X_1 - \frac{X_1}{Ke}\right)}$$

$$\therefore\ \frac{X_2 - X_1}{1 - X_2 - \frac{X_2}{Ke}} = \frac{2\,X_1}{1 - X_1 - \frac{X_1}{Ke}}$$

$$X_2 = 0{,}99\, X_e = 0.99 \times 0.966 = 0.956$$

$$\therefore \frac{0.956 - X_1}{1 - 0.956 - \frac{0.956}{28}} = \frac{2\, X_1}{1 - X_1 - \frac{X_1}{28}}$$

$$\therefore \frac{0.956 - X_1}{0.009857} = \frac{2\, X_1}{1 - X_1 - \frac{X_1}{28}}$$

$$\therefore (0.956 - X_1)\left(1 - X_1 - \frac{X_1}{28}\right) = \ 2\, X_1 0.009857$$

$$\therefore \left(0.956 - 0.956X_1 - 0.956\frac{X_1}{28} - X_1 + {X_1}^2 + \frac{{X_1}^2}{28}\right) = \ 0.019714\, X_1$$

$$\therefore (1 + 0.03571){X_1}^2 - (0.956 + 0.03414 + 1 + 0.019714\,)X_1 + 0.956 = 0$$

$$\therefore 1.03571{X_1}^2 - 2.009854X_1 + 0.956 = 0$$

$$\therefore X_1 = \frac{2.009854 \pm \sqrt{2.009854^2 - 4 * 1.03571 * 0.956}}{2 * 1.03571} = \begin{cases} \mathbf{1.1059} \\ \mathbf{0.8346} \end{cases}$$

Prob 1e

$$\tau_1 = \frac{X_1}{k\left(1 - X_1 - \frac{X_1}{Ke}\right)} = \frac{0.8346}{0.15 \times \left(1 - 0.8346 - \frac{0.8346}{28}\right)} = 41.03\ min$$

$$\tau_1 = \frac{V_1}{v} \quad \therefore \frac{V_1}{v} = 41.03 \quad \therefore V_1 = 41.03 \times 20 = 820.6\ L \quad \therefore V_2 = 1641.2\ L$$

Prob 2a

$$2A \longrightarrow B$$

$$-r_A = k\, {C_A}^2$$

Prob 2b

Balanço molar *Mole balance*:

$$r_A V = \frac{dN_A}{dt} \quad \therefore -r_A V = N_{A0}\frac{dX}{dt} \quad \therefore \frac{dX}{dt} = \frac{-r_A V}{N_{A0}}$$

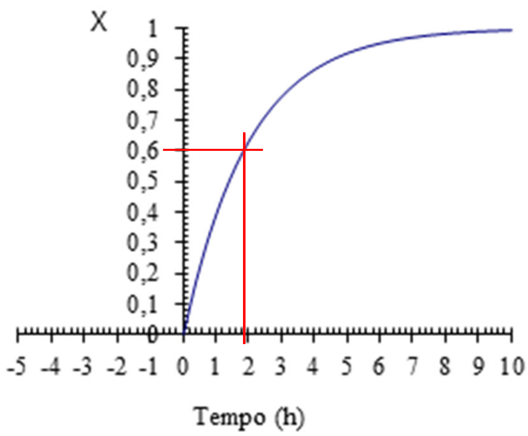
$$\therefore\ \frac{dX}{dt} = \frac{k\ C_A{}^2 V}{N_{A0}} = \frac{k\ C_A{}^2}{\frac{N_{A0}}{V}} = \frac{k\ C_A{}^2}{C_{A0}} \qquad \therefore\ \frac{dX}{dt} = \frac{k\ C_{A0}{}^2 (1-X)^2}{C_{A0}} \qquad \therefore\ \frac{dX}{dt} = k\ C_{A0}(1-X)^2$$

$$\therefore\ \int_0^X \frac{dX}{(1-X)^2} = k\ C_{A0} \int_0^t dt \qquad \therefore\ \left.\frac{1}{1-X}\right|_0^X = k\ C_{A0}t \qquad \therefore \frac{1}{1-X} - 1 = k\ C_{A0}t$$

$$\therefore \frac{1}{1-X} = 1 + k\ C_{A0}t \qquad \therefore X = 1 - \frac{1}{1+k\ C_{A0}t} \qquad \therefore X = \frac{k\ C_{A0}t}{1+k\ C_{A0}t}$$

Prob 2c

$$\frac{1}{1-X} - 1 = k\ C_{A0}t \qquad \therefore k = \frac{X}{C_{A0}t(1-X)}$$



$$t = 1{,}9\ h \qquad X = 0{,}6$$

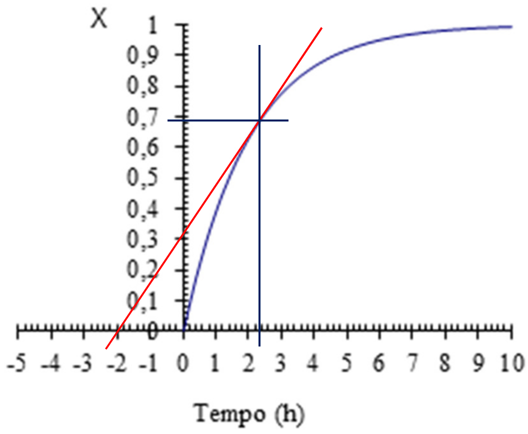
Base da alimentação *feed base*: 1 L

$$m_{A0} = 791\ g \qquad \therefore N_{A0} = \frac{791}{58} = 13{,}638\ mol \qquad \therefore C_{A0} = 13{,}638\ M$$

$$\therefore k = \frac{0{,}6}{13{,}638 \times 1{,}9 \times (1-0{,}6)} = 0{,}0579\ L/(mol\ h)$$

Prob 2d

Tempo morto: t_d = 120 min



$$X_{opt} = 0{,}68 \quad t_{opt} = 2{,}3\ h$$

Prob 2e

Tempo de operação *operating time – time of 1 batch*:

$$t = t_{opt} + t_d = 2{,}3 + 2 = 4{,}3\ h$$

Número de operações por ano *number of batch/year*:

$$N_{batch} = \frac{24 \times 330}{4{,}3} = 1841$$

Produção por operação *production/batch*:

$$N_B = \frac{1{,}5 \times 10^9}{1841 \times 116} = 7024\ mol$$

Quantidade de A a carregar num reactor único *Amount of A to be loaded into a single reactor*:

$$A \longrightarrow \frac{1}{2}B$$

$$N_B = \frac{1}{2}N_{A0}X \qquad \therefore N_{A0} = \frac{2N_B}{X} = \frac{2 \times 7024}{0.68} = 20659\ mol$$

Volume dum reactor único *volume of a single reactor*:

$$V = \frac{N_B}{C_{A0}} = \frac{20659}{13{,}638} = 1514{,}8\ L$$

$$V_R = 1{,}15V = 1{,}15 \times 1514{,}8 = 1742\ L$$

Número de reactores *number of reactors*:

$$N_R = \frac{1742}{5000} = 0.35$$

Basta, portanto, um reactor de 5 m^3.