School of Mathematics & Applied Statistics

MATH111: Mathematics Applied Mathematical Modelling 1

Assignment Week 8 Solutions

Spring 2004

1. A *batch reactor* has neither inflow nor outflow of reactants or products whilst the reaction is being carried out. Suppose that the reaction

$$A \to B$$

occurs in a batch reactor. For an nth-order reaction the rate of change of reactant concentration in the reactor is given by

$$\frac{\mathrm{d}A}{\mathrm{d}t} = -k_1 A^n, \quad A(0) = A_0,$$

where A_0 is the initial concentration of the reactant.

(a) By solving the appropriate differential equation determine how the concentration of reactant in the reactor depends upon the time since the reactor was started for

(i) a first-order reaction,

(ii) a second-order reaction.

Solution

(i) The differential equation we wish to solve is

$$\frac{\mathrm{d}A}{\mathrm{d}t} = -k_1 A^1, \quad A(0) = A_0.$$

Thus

$$\begin{aligned}
\int_{A_0}^{A} \frac{\mathrm{d}A}{A} &= -k_1 \int_0^t \mathrm{d}t \\
[\ln(A)]_{A_0}^{A} &= -k_1 [t]_0^t \\
\ln\left[\frac{A}{A_0}\right] &= -k_1 t \\
A &= A_0 e^{-k_1 t}.
\end{aligned}$$

(ii) The differential equation we wish to solve is

$$\frac{\mathrm{d}A}{\mathrm{d}t} = -k_1 A^2, \quad A(0) = A_0.$$

Thus

$$\begin{aligned}
\int_{A_0}^{A} \frac{\mathrm{d}A}{A^2} &= -k_1 \int_0^t \mathrm{d}t \\
\left[\frac{-1}{A}\right]_{A_0}^{A} &= -k_1 [t]_0^t \\
\frac{-1}{A} + \frac{1}{A_0} &= -k_1 t \\
A &= \frac{A_0}{1 + A_0 k_1 t}.
\end{aligned}$$

(b) Hence obtain a formula for the time taken (t_R) for the concentration of reactant to decrease to 10% of its initial value for

(i) a first-order reaction,

(ii) a second-order reaction.

Solution. Note that when $t = t_R$ $A = 0.1A_0$.

(i) We use the solution $A = A_0 e^{-k_1 t}$. Then

$$\begin{aligned} 0.1A_0 &= A_0 e^{-k_1 t_R} \\ \ln(0.1) &= -k_1 t_R \\ t_R &= \frac{\ln(10)}{k_1}. \end{aligned}$$

(ii) We use the solution $A = \frac{A_0}{1+A_0 k_1 t}$. Then

$$\begin{aligned} 0.1A_0 &= \frac{A_0}{1 + A_0 k_1 t_R} \\ 0.1\,(1 + A_0 k_1 t_R) &= 1 \\ t_R &= \frac{9}{A_0 k_1}. \end{aligned}$$

(c) (i) For a given first-order reaction $k = 10^{-4}\,\mathrm{s}^{-1}$. Determine t_R.

(ii) For a given second-order reaction the product $kA_0 = 10^{-3}\,\mathrm{s}^{-1}$. Determine t_R.

Solution.

(i) Using the formula

$$t_R = \frac{\ln(10)}{k_1}$$

we have

$$\begin{aligned} t_R &= \frac{\ln(10)}{10^{-4}} \\ &= 10^4 \ln(10) \\ &= 23025.9\,\mathrm{s} \quad \text{or } 6.4\,\text{hr}. \end{aligned}$$

(ii) Using the formula

$$t_R = \frac{9}{A_0 k_1}.$$

we have

$$\begin{aligned} t_R &= \frac{9}{10^{-3}} \\ &= 9 \times 10^3 \\ &= 9000\,\mathrm{s} \quad \text{or } 2.5\,\text{hr}. \end{aligned}$$

2. A company is discharging a herbicide into a river that flows into a marsh, where it is degraded. The rate of degradation of the herbicide, A, is assumed irreversible and to follow first-order homogeneous kinetics.

$$A \xrightarrow{k_1} \text{Products.}$$

This process is represented by the differential equation

$$V\frac{\mathrm{d}A}{\mathrm{d}t} = qA_0 - qA - Vk_1A. \qquad (1)$$

Assume that the marsh is rectangular with width $W = 100\,\mathrm{m}$, length $L = 1000\,\mathrm{m}$ and average depth $D = 0.25\,\mathrm{m}$. The other parameter values are: $A_0 = 10^{-2}\,\mathrm{mol\,m^{-3}}$, $k_1 = 16 \times 10^{-5}\,\mathrm{h^{-1}}$, $q = 2\,\mathrm{m^3hr^{-1}}$.

(a) In equation (1) what do the symbols $A, A_0, V, k_1, q\,\&\,t$ mean?

Solution.

A is the concentration of herbicide in the marsh at time t.

A_0 is the concentration of herbicide flowing into the marsh.

V is the volume of the marsh.

k_1 is the rate of which the herbicide degrades.

q is the flowrate of water through the marsh.

t is time.

(b) Given that initially there is no herbicide present in the marsh: obtain the solution to equation (1).

Solution. Note the initial condition is $A(0) = 0$.

$$\begin{aligned}
\int_0^A \frac{V\mathrm{d}A}{qA_0 - (q + Vk_1)A} &= \int_0^t \mathrm{d}t \\
\frac{-V}{q + Vk_1}\left[\ln\{qA_0 - (q + Vk_1A)\}\right]_0^A &= [t]_0^t \\
\frac{-V}{q + Vk_1}\ln\left[\frac{qA_0 - (q + Vk_1)A}{qA_0}\right] &= t \\
\ln\left[\frac{qA_0 - (q + Vk_1)A}{qA_0}\right] &= \frac{-(q + Vk_1)}{V}t \\
qA_0 - (q + Vk_1)A &= qA_0 \exp\left[\frac{-(q + Vk_1)}{V}t\right] \\
A &= \frac{qA_0}{q + Vk_1} - \frac{qA_0}{q + Vk_1}\exp\left[\frac{-(q + Vk_1)}{V}t\right] \\
&= \frac{qA_0}{q + Vk_1}\left\{1 - \exp\left[\frac{-(q + Vk_1)t}{V}\right]\right\}
\end{aligned}$$

(c) (i) Let $A(\infty)$ be the concentration of herbicide in the marsh at time $t = \infty$. What is $A(\infty)$?

(ii) How many days does it take for the level of herbicide in the marsh to reach half of its final value?

(iii) Suppose that the legal maximum level of herbicide in the marsh is given by $A_{\max} = \frac{1}{30}A(\infty)$. On which day must the company stop pumping herbicide into the marsh?

Solution.

(i) Note that as $z \to \infty$ then $\exp[-z] \to 0$. Thus

$$A(\infty) = \frac{qA_0}{q + Vk_1}.$$

(ii) When the level of herbicide in the marsh has reached half of its final value we have

$$A = \frac{1}{2}\cdot\frac{qA_0}{q + Vk_1}.$$

Thus

$$\begin{aligned}
\frac{1}{2}\cdot\frac{qA_0}{q+Vk_1} &= \frac{qA_0}{q+Vk_1} - \frac{qA_0}{q+Vk_1}\exp\left[\frac{-(q+Vk_1)}{V}t\right] \\
\exp\left[\frac{-(q+Vk_1)}{V}t\right] &= 0.5 \\
\frac{-(q+Vk_1)}{V}t &= \ln(0.5) \\
t &= \frac{V}{q+Vk_1}\ln(2) \\
&= 2888.1\,\text{hr} \quad \text{or } 120.3\,\text{day}
\end{aligned}$$

(iii) We need to find the time at which

$$A = \frac{1}{30}\cdot\frac{qA_0}{q+Vk_1}.$$

Thus

$$\begin{aligned}
\frac{1}{30}\cdot\frac{qA_0}{q+Vk_1} &= \frac{qA_0}{q+Vk_1} - \frac{qA_0}{q+Vk_1}\exp\left[\frac{-(q+Vk_1)}{V}t\right] \\
\exp\left[\frac{-(q+Vk_1)}{V}t\right] &= \frac{29}{30} \\
\frac{-(q+Vk_1)}{V}t &= \ln\left(\frac{29}{30}\right) \\
t &= \frac{V}{q+Vk_1}\ln\left(\frac{30}{29}\right) \\
&= 141.3\,\text{hr} \quad \text{or } 5.8\,\text{day}
\end{aligned}$$

The company must stop pumping herbicide into the march on day 5.