Reactor Mixing

CSTR - 1

CHEC 3128
What do your instincts tell you about mixing?

Steady State Operation

Instantaneous, homogeneous distribution of feed, reagent and product streams

in CSTRS

Conventional Thinking for Mixing
Anything else...?

Impeller Speed
Impeller Size
Number of Impellers
Reactor Shape
Reactor Aspect Ratio
Reactor Volume

Influential Factors in CSTR Mixing
equations you derive in 2103 and 3151?
How do these impact mixing and the
residence time (distribution or residence time)
Now, every molecule has a different

What artifacts to These Create in
Some Additional Resources

- "Residence Times for Chemical Reactors"
- "Laminar & Turbulent Disturbances of Mixing in Chemical Reactors"
- "Mixing in Chemical Reactors"

- http://www.cheme.wisc.edu/home/ibraw/chemr}

Chemical Engineering Junior Lab (CHEG 3128) Spring 2017
Material Balance Equation

\[ \text{In} - \text{out} + \text{gen} - \text{consumption} = \text{Accumulation} \]

In an ideal CSTR with a pulse feed,

"In" = 0

since there is no reaction

"gen" = "consumption" = 0

Therefore,

\[-\text{out} = \text{accumulation}\]

In our experiment, we will measure the pH, but we are interested in the acetic acid concentration (Note: these are NOT the same, we will discuss later)

At constant volume (V) + volumetric flow rate (V)

\[-\frac{V}{V} C_{HA} = V \frac{dC_{HA}}{dt}\]

\[-\frac{V}{V} dt = \frac{dC_{HA}}{C_{HA}}\]

\[-\int_{t_0}^{t} dt = \ln C_{HA} \bigg|_{C_{HA0}}^{C_{HA}}\]

\[\frac{1}{V} \int_{t_0}^{t} dt = \ln C_{HA} \bigg|_{C_{HA0}}^{C_{HA}}\]

\[C_{HA} = C_{HA0} \exp \left[-t/t_0\right]\] → this is a dilution experiment
Why can't we just measure the pH and assume that [H⁺] = [Acetic Acid]?

Weak acids do not fully dissociate.

So:

\[
HA \rightarrow H^+ + A^-
\]

Acidity is also controlled by water:

\[
H_2O \rightarrow H^+ + OH^-
\]

.: At relatively high pH values (low acidity) the acid is mostly dissociated. However, as the acid concentration is increased most molecules remain in their conjugated form.

So, now we need to understand how pH + CHA are related for weak acids.
2 reactions:

\[
\begin{align*}
\text{HA} & \overset{\varepsilon_1}{\Longleftrightarrow} H^+ + A^- \\
\text{H}_2\text{O} & \overset{\varepsilon_2}{\Longleftrightarrow} H^+ + \text{OH}^-
\end{align*}
\]

\[
\text{RXN 1: } K_a = \frac{[H^+][A^-]}{[\text{HA}]} \Rightarrow \varepsilon_0, 7
\]

\[
\text{RXN 2: } K_w = \frac{[H^+][\text{OH}^-]}{[\text{H}_2\text{O}]} \Rightarrow \varepsilon_0, 8
\]

Reaction Table:

<table>
<thead>
<tr>
<th>Species</th>
<th>initial</th>
<th>(\Delta)</th>
<th>final</th>
</tr>
</thead>
</table>
| HA      | \(c_{HA}\) | \(-\varepsilon_1\) | \(c_{HA} - \varepsilon_1\) | \(\rightarrow\) \(\varepsilon_0, 9\) | \([HA] = c_{HA} - [A^-] \)
| \(H^+\) | 0       | \(\varepsilon_1 + \varepsilon_2\) | \(\varepsilon_1 + \varepsilon_2\) | \(\rightarrow\) \(\varepsilon_0, 11\) | \([A^-] = [H^+] - [OH^-] \)
| \(A^-\) | 0       | \(\varepsilon_1\) | \(\varepsilon_1\) |
| \(\text{OH}^-\) | 0     | \(\varepsilon_2\) | \(\varepsilon_2\) |
| \(\text{H}_2\text{O}\) | \(\infty\) | \(-\infty\) | \(\infty\) |

Two ways to solve: 1) Solve for \(\varepsilon_1\)'s, then calculate \([H^+]\)

\[\text{Eqn 1: } (K_a)(c_{HA} - \varepsilon_1) - (\varepsilon_1 + \varepsilon_2)(\varepsilon_1) = 0\]

\[\text{Eqn 2: } K_w = (\varepsilon_1 + \varepsilon_2)(\varepsilon_2)\]

Method 2) Rearrange to be explicit \(w/[H^+]\)
Eql 1 above is really:

\[(K_a)(C_{HA}-[A])-[H^+][A]=0\]

\[K_a\left(C_{HA}-(\frac{[H^+][OH^-]}{[H^+]})\right)-[H^+][CH^+]\left(\frac{[H^+]\cdot [OH^-]}{[H^+]}\right)\]

\[K_a\left(C_{HA}-(\frac{[H^+]\cdot KW}{[H^+]})\right)-[H^+][CH^+]\left(\frac{[H^+]\cdot KW}{[H^+]}\right)=0\]

\[K_a[H^+]\left(C_{HA}-(\frac{[H^+]\cdot KW}{[H^+]})\right)-[H^+]^2\left(\frac{[H^+]\cdot KW}{[H^+]}\right)=0\]

\[K_aC_{HA}[H^+]-K_a[H^+]^2+K_aKW-[H^+]^3+KW[H^+]=0\]

\[\left([H^+]^3+[H^+]^2K_a-[H^+](K_aC_{HA}+KW)-KaKW\right)=0\]

Now we need to find a numerical method to solve cubic equations

One such method follows
A.7 Solutions to cubic equations

In order to predict phase changes in fluids, equations of state must predict a dependence on volume that is cubic, or higher. Hence, many equations of state are cubic, and methods for inverting cubic equations are helpful for studying stability. We first write our cubic equation for \( x \) in the form

\[
x^3 + a_2x^2 + a_1x + a_0 = 0. \tag{A.30}
\]

The equation may have 1, 2 or 3 roots; we are interested only when there exist either 1 or 3 roots.\(^1\) We can determine the number of roots from the sign of the discriminant \( q^3 + r^2 \) where

\[
q := \frac{3a_1 - a_2^2}{9}, \tag{A.31}
\]
\[
r := \frac{a_2(9a_1 - 2a_2^2) - 27a_0}{54}. \tag{A.32}
\]

When \( q^3 + r^2 > 0 \) there is a single real root to Eqn.(A.30)

\[
x_1 = \left( r + \sqrt[3]{q^3 + r^2} \right)^{1/3} + \left( r - \sqrt[3]{q^3 + r^2} \right)^{1/3} - \frac{a_2}{3}. \tag{A.34}
\]

When \( q^3 + r^2 < 0 \), then Eqn.(A.30) has three real roots

\[
\begin{align*}
x_1 &= 2\sqrt{-q} \cos \left( \frac{\theta}{3} \right) - \frac{a_2}{3} \\
x_2 &= -2\sqrt{-q} \cos \left( \frac{\theta - \pi}{3} \right) - \frac{a_2}{3} \\
x_3 &= -2\sqrt{-q} \cos \left( \frac{\theta + \pi}{3} \right) - \frac{a_2}{3},
\end{align*} \tag{A.35}
\]

where

\[
\theta := \cos^{-1} \left( \frac{r}{\sqrt{-q^3}} \right). \tag{A.36}
\]

These equations are particularly useful for programming spreadsheets, for example.

From "Molecular Engineering Thermodynamics"

- J. de Pablo and J. Schieber

- Attached is a solution plot for a chemical with a pKₐ = 3.75 (i.e., formic acid) for you to compare to !
Mixing Discussion

→ Laminar flow demo
   → low rotation rates or
   → high viscosity

→ Analogy to 1-D shear
   → rotating cylinder → From GE36 3123
   → poor mixing

→ what should you do?
   → most just stir faster
   → what does that do?

↓
Let's turn on the CSTRs and find out

↓
Is this "ideal" or "perfect" instantaneous, homogeneous mixing?

→ That's what this lab is all about!