Thoughts for Friday Recitation

- Calculation of pH, measurement of pH are not the Big Things

Big Things → • Use of mass balance eq's.
  • Translating for your problem
  • Solving
  • Ideas of feedback control
  • Putting these together in a model of the process

Progression of Problems in a Stirred Tank Reactor

- Constant Volume Situation

\[ \begin{align*}
\text{①} & \rightarrow \text{Salt Stream,} & c_{1\text{salt}} &= 1 \\
& & q_1 &= 1 \\
\text{②} & \rightarrow \text{Pure Water} & c_{2\text{salt}} &= 0 \\
& & q_2 &= 1
\end{align*} \]

The question we wish to ask is: What is concentration after a long time? (Presumably it will not depend on the initial conditions.)
Start of answer:

How to think of this problem if you had never taken this class:

Not a perfect analogy but could think of fluid "parcels" marching along. Since we have equal flowrates, we have equal volumes.

<table>
<thead>
<tr>
<th>Water</th>
<th>=</th>
<th>All Mixed Up</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Salt Water</td>
<td>=</td>
<td>C_{3\text{salt}} = 0.5</td>
</tr>
</tbody>
</table>

Obviously \( \Theta \rightarrow \) Water

\( \Theta \rightarrow \) Salt Water

\( \Theta \rightarrow \) All Mixed Up

We find the answer by asking: \( \frac{\text{How Much Salt}}{\text{How Much Total Water}} \)

At long times this is "True" at any time.

You have the correct answer by figuring out what makes sense. You did not consider a flowing system, but one \( \Delta t \) of a flowing system. For a steady state situation, this worked OK.

Look at balance eq.

\[
\frac{dc_i V}{dt} = \Sigma q_j c_{ji} + r_i V
\]

\( \rightarrow \) No Change in Volume \( \quad \) No rxn \( \quad r_i = 0 \)

\( V = \text{Const} \)

\( V \frac{dc_i}{dt} = \Sigma q_j c_{ji} \)

\( \rightarrow \) Long Time, the initial transients have died out.

\( 0 = \Sigma q_j c_{ji} = 0 \)

There is no salt in the \( \Theta \) stream so that we have

\( q_1 c_{1\text{salt}} - q_3 c_{3\text{salt}} = 0 \)
\[ c_{3\text{salt}} = \frac{q_1 c_{1\text{salt}}}{q_3} \]

\[ c_{3\text{salt}} = \frac{1}{1 + 1} = .5 \]

Now change the relative flow rates \( \rightarrow \) first look at Eq.

\[ c_{3\text{salt}} = \frac{q_1 c_{1\text{salt}}}{q_1 + q_2} = \frac{c_{1\text{salt}}}{1 + \frac{q_2}{q_1}} \]

As \( q_2 \uparrow \) what happens to \( c_{3\text{salt}} \downarrow \) and eventually \( \rightarrow 0 \).

As \( q_1 \uparrow \) \( c_{3\text{salt}} \uparrow \rightarrow c_{1\text{salt}} \) in either case you get the dominant inlet stream composition -- just as you would expect.
Now let us consider a Simple Reacting System

\[
\text{HCl} \quad + \quad \text{NaOH}
\]

Strong Base        Strong Acid

These will be completely dissociated. The reaction is instantaneous and irreversible except to the extent that that water dissociates:

\[
K_w = [\text{H}_3\text{O}^+] [\text{OH}^-] = 1 \times 10^{-14}
\]

We again wish to figure out the exit composition.

The Volume will be kept constant.

\[
\Theta \rightarrow 1 \text{ mol/l} \quad \text{HCl} \quad 1 \text{ l/s}
\]

\[
\Theta \rightarrow 0.5 \text{ mol/l} \quad \text{NaOH} \quad 1 \text{ l/s}
\]

Again we choose parcels of fluid
We again ask the sensible question:

**How much HCl is left in a volume of water**

**Total volume of water**

The answer to this is

\[
\frac{1 \text{ mol/l}}{1 \text{ l/s}} - \frac{.5 \text{ mol/l}}{1 \text{ l/s}} = \frac{.25 \text{ mol/l}}{2 \text{ l/s}}
\]

We have gotten the correct answer without using the formal mass balance equations. For more complex problems this would not be possible. However, this should give us some insight into how the equations work and (hopefully) build your trust in the equations.

Now solve the problem by looking at the balance eq's

**Long time, s.s. const V**

\[
\begin{align*}
\text{HCl Balance} \quad (H_3O^+) & \quad 0 = q_1 c_{1\text{HCl}} - q_3 c_{3\text{HCl}} - r_{\text{HCl}} V \\
\text{NaOH Balance} \quad (OH^-) & \quad 0 = q_2 c_{2\text{NaOH}} - q_3 c_{3\text{NaOH}} - r_{\text{NaOH}} V
\end{align*}
\]

From Chemistry:

Reaction of $H_3O^+ + OH^-$ is instantaneous, and reversible only to the equilibrium:

\[
K_w = [H_3O^+] [OH^-] = 1 \times 10^{-14} \text{ mol}^2/l^2
\]

So it is mostly to completion.

HCl is obviously in excess so

\[
c_{3\text{NaOH}} = 0
\]

\[:. \text{ from the second equation}\]

\[
q_2 c_{2\text{NaOH}} = r_{\text{NaOH}} V
\]
Further from the reaction stoichiometry, the rate of reaction of the acid is the same as the rate of reaction of the base since there is only 1 reaction and one mol of each is used up:

\[ r_{\text{HCl}} V = r_{\text{HCl}} V \]

Thus we can write:

\[ 0 = q_1 c_{\text{HCl}} - q_2 c_{\text{NaOH}} - q_3 c_{\text{HCl}} \]

We solve to get:

\[ c_{\text{HCl}} = \frac{q_1 c_{\text{HCl}} - q_2 c_{\text{NaOH}}}{q_3} \]

\[ = \frac{(1)(1) - (1)(.5)}{2} = 0.25 \text{ m/l.} \]

So it matches our sensibility.

What if we increase the concentration of the second stream:

If \( q_1 = 1 \) \( c_{\text{HCl}} = 1 \)

\( q_2 = 1 \) \( c_{\text{NaOH}} = 1 \)

\( c_{\text{HCl}} = 0 \) \( \) Does this meet our expectations?

It does! We have exactly neutralized the acid.
Now what if we go to the other side of pH 7? If the NaOH is in excess, $c_{3\text{HCl}} < 0$?? What, this must be wrong!!!

The resolution is that all of the NaOH would not be consumed. So the assumption that

$$c_{3\text{NaOH}} = 0 \quad \text{and} \quad r_{\text{NaOH}} V = q_2 \ c_{2\text{NaOH}}$$

is incorrect.

It says all NaOH that enters reacts immediately which is not correct.

To fix this we would realize that all of the HCl is used up so that the exit HCl concentration is 0.

For excess NaOH we would have

$$c_{3\text{NaOH}} = \frac{\Phi_2 c_2 \text{NaOH} - \Phi_1 q \text{HCl}}{q_3}$$