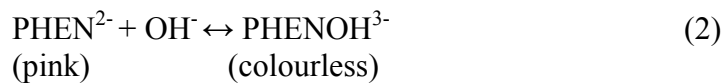
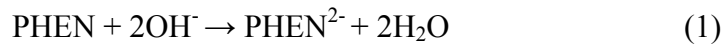


Department of Chemical Engineering  
University of Cambridge – Weblab Exercise (due April 6, 2007 at 1 pm)

*Note: Parts A – D should be completed before the Weblab on Monday, March 19, 2007, but don't have to be turned in until April 6, 2007.*

### Introduction

This exercise concerns the reaction of phenolphthalein (PHEN) in an aqueous solution of sodium hydroxide:



Reaction (1) can be assumed to occur rapidly, so the rate determining step is reaction (2). The rate laws for reaction (2) are:

$$r_1 = k_1[\text{PHEN}^{2-}][\text{OH}^-] \quad (3)$$

$$r_2 = k_2[\text{PHENOH}^{3-}] \quad (4)$$

The purpose of this exercise is to determine the reaction constants for this reaction, and to predict the operating conditions required to achieve a given conversion of  $\text{PHEN}^{2-}$  to  $\text{PHENOH}^{3-}$  in a non-ideal reactor. You will test your predictions by running experiments on the reactor in question.

### PART A

[http://weblabs.cheng.cam.ac.uk/reactors\\_batchdata.html](http://weblabs.cheng.cam.ac.uk/reactors_batchdata.html) contains experimental data from reactions (1) and (2) carried out in a batch reactor. To track the progress of the reaction, a spectrophotometer has been used to measure the intensity of light (550 nm) transmitted through the reaction solution. This intensity,  $I$ , is related to the concentration,  $c$ , by the Beer-Lambert law:

$$c = -b * \ln (I/I_0) \quad (5)$$

Note: As concentration increases (more pink stuff), the intensity of light passing through the sample decreases ( $c$  up,  $I$  down).  $b$  is positive, but knowing the value is unnecessary because it will cancel out.

Show that the time variation of the intensity,  $I$ , through the experiment can be expressed as: (give an expression for the pseudo first order rate constant  $k_1$ )

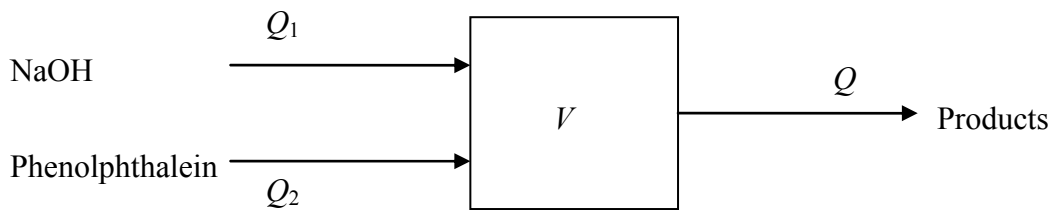
$$\frac{\ln(I) - \ln(I_{t=\infty})}{\ln(I_{t=0}) - \ln(I_{t=\infty})} = \exp[-(k_1' + k_2)t] \quad (6)$$

Use the experimental data to determine the rate constants  $k_1$  and  $k_2$  for the first set of data (collected at 20.0 °C). The above data was taken in an IDEAL BATCH REACTOR, unlike Part B and beyond.

### Part B

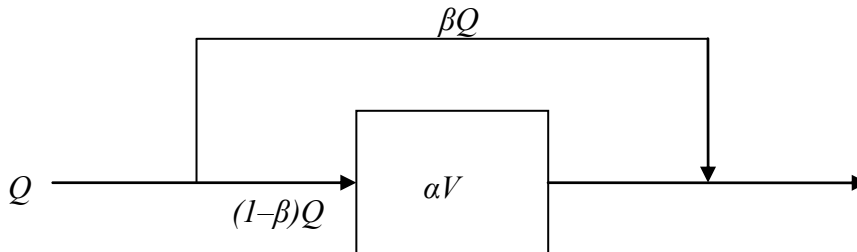
The reaction is to be carried out in a continuous reactor (CSTR - Figure 1). More information on the reactor setup can be found at <http://weblabs.cheng.cam.ac.uk/reactors.html>. The available reactant concentrations are:

NaOH:  $[\text{OH}^-]_{in} = 0.20 \text{ mol/l}$   
 Phenolphthalein:  $[\text{PHEN}]_{in} = 7.2 \times 10^{-5} \text{ mol/l}$



**Figure 1:** A schematic of the reactor

In most cases, modeling a reactor as a stirred tank is not sufficiently accurate. One model for a non-ideal reactor is the bypass/dead volume model, in which a fraction  $\beta$  of the flow bypasses the reaction zone, and only a fraction  $\alpha$  of the reactor volume is utilized. This is shown schematically in figure 2.



**Figure 2:** A schematic of the bypass/dead volume reactor model

Reactor characteristics can be determined by examining the residence time distributions under continuous operation. Using Laplace Transforms show that for a pulse input of  $N_t$  moles of tracer at  $t = 0$ , the outlet concentrations for the two reactor models are:

$$\text{CSTR:} \quad \frac{c(t)}{N_t/V} = e^{-t/\tau}, \quad (7)$$

$$\text{Bypass/Dead volume:} \quad \frac{c(t)}{N_t/V} = \beta\delta(t)\tau + \frac{(1-\beta)^2}{\alpha} \exp\left(-\frac{1-\beta}{\alpha\tau}t\right), \quad (8)$$

where  $\tau = V/Q$ .

### Part C

Use the experimental data at [http://weblabs.cheng.cam.ac.uk/reactors\\_tracerdata.html](http://weblabs.cheng.cam.ac.uk/reactors_tracerdata.html) to determine  $\alpha$  and  $\beta$  for the bypass/dead volume model when applied to the reactor in non-ideal setup. Note: Data is given for the reactor when run as close to being a perfect CSTR as possible, as well as when it is run as a non-ideal CSTR. The perfect CSTR data will allow you to relate  $I(t=0)$  to  $I_0$ , which is just a reference value.  $I(t=0)$  is the intensity directly AFTER the pulse is given, when the concentration is  $N_t/V$ .

### Part D

It is desired to run the reactor at a product flowrate,  $Q$ , of 25 ml/min and a conversion,  $X$ , of 30%. In this case, conversion is defined as:

$$X = \frac{[\text{PHENOH}^{3-}]}{[\text{PHEN}^{2-}] + [\text{PHENOH}^{3-}]}, \quad (9)$$

to avoid any ambiguities due to dilution of the feed streams.

Assume that this reactor can be modeled as an ideal continuous stirred-tank reactor (CSTR) of volume  $V = 250$  ml. Use steady state material balances to show that to achieve a product flowrate,  $Q$ , at conversion,  $X$ , the NaOH flowrate must be:

$$Q_1 = \frac{X}{1-X} \frac{Q(k_2V + Q)}{k_1V[\text{OH}^-]_{in}} \quad (10)$$

Now assume that the reactor behaves according to the bypass/dead volume model. What value of  $Q_1$  is required to give a product flowrate of 25 ml/min at a conversion of 30%?

In order to avoid too much unnecessary algebra, it may be useful to set up an Excel spreadsheet (or similar) so that you can determine the conversions at different flowrates with your calculated values of the parameters  $\alpha$  and  $\beta$ .

## **Part E**

### **Experimental Procedure – this will be done as a group in recitation on Monday, March 19, 2007**

The aims of the experiment are:

1. To test the assumption that the reactor behaves as a CSTR.
2. To test the non-ideal model and parameters you have derived in your preliminary analysis.

To determine a baseline reading for the intensity, set the flowrate of NaOH to the value calculated from equation (10). Once a steady value for  $I_0$  is achieved, set the flowrate of phenolphthalein to give a total flowrate of 25 ml/min.

Let the reactor equilibrate and record the steady state intensity.

Adjust the flowrates of the two reactants to the values calculated for the non-ideal reactor setup. Again, let the reactor equilibrate and record the steady state intensity.

The plan is that each recitation will perform two runs, and you will analyze the data from both recitations (up to four sets of data).

## **Part F**

### **Experimental Data Analysis**

Data analysis requirements will be posted on the 10.37 Stellar website after the Weblab is completed, and will be due with the rest of the write-up on April 6, 2007.