

Quality Control of a Paint Production Process

The challenge: To validate production concentration by assessing the quality of paint produced in a chemical process

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** This application was developed using [Maple](#)

▼ Executive Summary

Quality control is essential in engineering and manufacturing operations. It ensures that the plant is being utilized efficiently and that the products delivered are of the highest quality. Quality control, in terms of paint production, generally involves sampling, where the paint produced in the reactor is sampled regularly to ensure that it meets a set of target criteria, which include desired yield and concentration levels, as determined by a reaction kinetics model. Occasionally, errors between the expected and actual product requirements arise. These errors are frequently detected by a quality control engineer.

In this particular case, a discrepancy was detected in the expected and actual concentration of paint produced in the reactor. The concentration of paint produced was found to be 0.022 mol/L, which is 1.5 times greater than the expected concentration of 0.012 ± 0.002 mol/L. Investigation into the potential sources of error during production did not provide any more insight, which raised doubt in the validity of the original model.

Comparison between the experimental data and the data used to predict the model led to the source of the discrepancy. The error stemmed from an inaccurate prediction of one of the rate constant controlling the formation and consumption of compound A. Using the least-squares approximation method, the actual rate constant for this reaction was determined to be approximately 2.6 times smaller than the rate used to develop the initial model (10.925 versus 28.7). Redevelopment of the model using the new rate constant showed that the concentration measured by the quality control engineer was indeed the correct concentration.

▼ Introduction

Quality control in terms of paint production consists of sampling at regular intervals to ensure that the end product meets a set of target criteria, which include desired yield and concentration levels. These criteria are determined by developing a model to accurately represent the reaction kinetics of the system. With a highly accurate model of the chemical process one can quickly identify and correct sources of error during the production process.

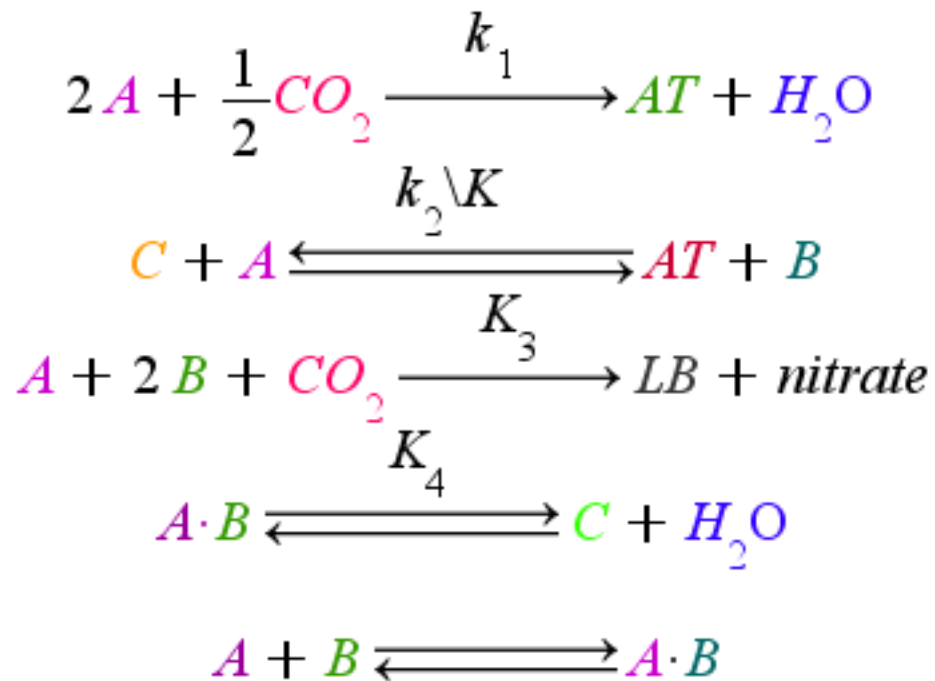
▼ Problem Description

During a routine sample control inspection, a quality control engineer identified a significant discrepancy between the expected and actual concentration of paint produced in the reactor; the concentration of paint produced was double the expected value.

This [Maple](#) document offers details into the investigation and subsequent correction of the source of error between the model-predicted and actual concentrations of paint produced.

▼ 1. Formulation of the Reaction Kinetics Equation

The equations that define the chemical process are shown below. The reactants, A and B, are mixed together while carbon dioxide is continuously added to produce a desired third compound C. In the interest of commercial competition, the names of the chemical species have been changed.



We can define the above reaction scheme as a mathematical system, using the equation below:

$$M \cdot \frac{dy}{dt} = f(y), y(0) = y_0$$

with $y \in \mathbb{R}^6$ and $0 \leq t \leq 180$.

The matrix, M, is of rank 5 and given by:

$$M := \begin{bmatrix} 1 & 0 & 0 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 \end{bmatrix} :$$

and the function f by:

$$f := y \rightarrow \begin{bmatrix} -2r1 + r2 - r3 - r4 \\ -\frac{1}{2}r1 - r4 - \frac{1}{2}r5 + Fin \\ r1 - r2 + r3 \\ -r2 + r3 - 2r4 \\ r2 - r3 + r5 \\ Ksy1(t)y4(t) - y6(t) \end{bmatrix} :$$

where the r_i and Fin are auxiliary variables given by:

$$r1 := k1 y1(t)^4 \sqrt{y2(t)} : \quad r2 := k2 y3(t) y4(t) :$$

$$r3 := \frac{k2 y1(t) y5(t)}{K} : \quad r4 := k3 y1(t) y4(t)^2 :$$

$$r5 := k4 y6(t)^2 \sqrt{y2(t)} : \quad Fin := klA \left(\frac{p}{H} - y2(t) \right) :$$

The variables $y1(t)$, $y2(t)$, $y3(t)$, $y4(t)$, $y5(t)$, and $y6(t)$, are the concentrations of the following compounds [A], [CO₂], [AT], [B], [C] and [A.B], respectively. The partial pressure of CO₂ is given by p and H is Henry's law constant.

Using the information above, we can derive the system of nonlinear differential-algebraic equations (DAEs) that models the chemical process described above.

$$dy := \begin{bmatrix} \frac{d}{dt} y1(t) \\ \frac{d}{dt} y2(t) \\ \frac{d}{dt} y3(t) \\ \frac{d}{dt} y4(t) \\ \frac{d}{dt} y5(t) \\ \frac{d}{dt} y6(t) \end{bmatrix} :$$

$syst_of_DAEs := M.dy = f(y)$

$$\begin{aligned}
 & \begin{bmatrix} \frac{d}{dt} y1(t) \\ \frac{d}{dt} y2(t) \\ \frac{d}{dt} y3(t) \\ \frac{d}{dt} y4(t) \\ \frac{d}{dt} y5(t) \\ 0 \end{bmatrix} \\
 & = \left[\left[-2 k1 y1(t)^4 \sqrt{y2(t)} + k2 y3(t) y4(t) - \frac{k2 y1(t) y5(t)}{K} - k3 y1(t) y4(t)^2 \right. \right. \\
 & \left. \left. \left[-\frac{1}{2} k1 y1(t)^4 \sqrt{y2(t)} - k3 y1(t) y4(t)^2 - \frac{1}{2} k4 y6(t)^2 \sqrt{y2(t)} + k4A \left(\frac{\rho}{H} - y2(t) \right) \right] \right. \right. \\
 & \left. \left[k1 y1(t)^4 \sqrt{y2(t)} - k2 y3(t) y4(t) + \frac{k2 y1(t) y5(t)}{K} \right], \right. \\
 & \left. \left[-k2 y3(t) y4(t) + \frac{k2 y1(t) y5(t)}{K} - 2 k3 y1(t) y4(t)^2 \right], \right. \\
 & \left. \left[k2 y3(t) y4(t) - \frac{k2 y1(t) y5(t)}{K} + k4 y6(t)^2 \sqrt{y2(t)} \right], \right. \\
 & \left. \left[Ks y1(t) y4(t) - y6(t) \right] \right] \tag{1}
 \end{aligned}$$

Rearranging the equations derived above, we end up with a stiff system of 6 non-linear DAEs of index 1. Although there is no single formulation, stiffness is usually defined as an equation (or system of equations) with terms that can lead to rapid variations in the solution.

for i from 1 to 6 do

$$eq[i] := lhs(syst_of_DAEs)[i] = rhs(syst_of_DAEs)[i]$$

end do:

$$eq[1] = \frac{d}{dt} y1(t) = -2 k1 y1(t)^4 \sqrt{y2(t)} + k2 y3(t) y4(t) - \frac{k2 y1(t) y5(t)}{K} - k3 y1(t) y4(t)^2$$

$$eq[2] =$$

$$\frac{d}{dt} y_2(t) = -\frac{1}{2} k_1 y_1(t)^4 \sqrt{y_2(t)} - k_3 y_1(t) y_4(t)^2 - \frac{1}{2} k_4 y_6(t)^2 \sqrt{y_2(t)} + k_1 A \left(\frac{p}{H} - y_2(t) \right)$$

$$eq[3] = \frac{d}{dt} y_3(t) = k_1 y_1(t)^4 \sqrt{y_2(t)} - k_2 y_3(t) y_4(t) + \frac{k_2 y_1(t) y_5(t)}{K}$$

$$eq[4] = \frac{d}{dt} y_4(t) = -k_2 y_3(t) y_4(t) + \frac{k_2 y_1(t) y_5(t)}{K} - 2 k_3 y_1(t) y_4(t)^2$$

$$eq[5] = \frac{d}{dt} y_5(t) = k_2 y_3(t) y_4(t) - \frac{k_2 y_1(t) y_5(t)}{K} + k_4 y_6(t)^2 \sqrt{y_2(t)}$$

$$eq[6] = 0 = K s y_1(t) y_4(t) - y_6(t)$$

We now create a system model containing the equations derived above and the initial conditions.

System := {seq(eq[i], i = 1 ..6)} **union** {ics}

$$\left\{ ics, 0 = K s y_1(t) y_4(t) - y_6(t), \frac{d}{dt} y_1(t) = -2 k_1 y_1(t)^4 \sqrt{y_2(t)} + k_2 y_3(t) y_4(t) \right. \quad (2)$$

$$- \frac{k_2 y_1(t) y_5(t)}{K} - k_3 y_1(t) y_4(t)^2, \frac{d}{dt} y_2(t) = -\frac{1}{2} k_1 y_1(t)^4 \sqrt{y_2(t)}$$

$$- k_3 y_1(t) y_4(t)^2 - \frac{1}{2} k_4 y_6(t)^2 \sqrt{y_2(t)} + k_1 A \left(\frac{p}{H} - y_2(t) \right), \frac{d}{dt} y_3(t)$$

$$= k_1 y_1(t)^4 \sqrt{y_2(t)} - k_2 y_3(t) y_4(t) + \frac{k_2 y_1(t) y_5(t)}{K}, \frac{d}{dt} y_4(t) = -k_2 y_3(t) y_4(t)$$

$$+ \frac{k_2 y_1(t) y_5(t)}{K} - 2 k_3 y_1(t) y_4(t)^2, \frac{d}{dt} y_5(t) = k_2 y_3(t) y_4(t) - \frac{k_2 y_1(t) y_5(t)}{K}$$

$$\left. + k_4 y_6(t)^2 \sqrt{y_2(t)} \right\}$$

▼ 2. Derivation of the Reaction Kinetics Model

The values of the physical parameters and initial conditions of the system are given by:

Parameters		Initial Conditions	
k_1	<input type="text" value="28.7"/>	$y_1(0)$	<input type="text" value="0.444"/>
k_2	<input type="text" value="0.58"/>	$y_2(0)$	<input type="text" value="3"/>
k_3	<input type="text" value="0.09"/>	$y_3(0)$	<input type="text" value="0"/>
k_4	<input type="text" value="0.42"/>	$y_4(0)$	<input type="text" value="0.007"/>
K	<input type="text" value="34.4"/>	$y_5(0)$	<input type="text" value="0"/>
klA	<input type="text" value="3.3"/>	$y_6(0)$	<input type="text" value="0.36"/>
K_s	<input type="text" value="115.83"/>		
ρ	<input type="text" value="0.9"/>		
H	<input type="text" value="737"/>		

Get Values

params

$$[k1 = 28.7, k2 = 0.58, k3 = 0.09, k4 = 0.42, K = 34.4, k1A = 3.3, Ks = 115.83, \rho = 0.9, H = 737] \quad (3)$$

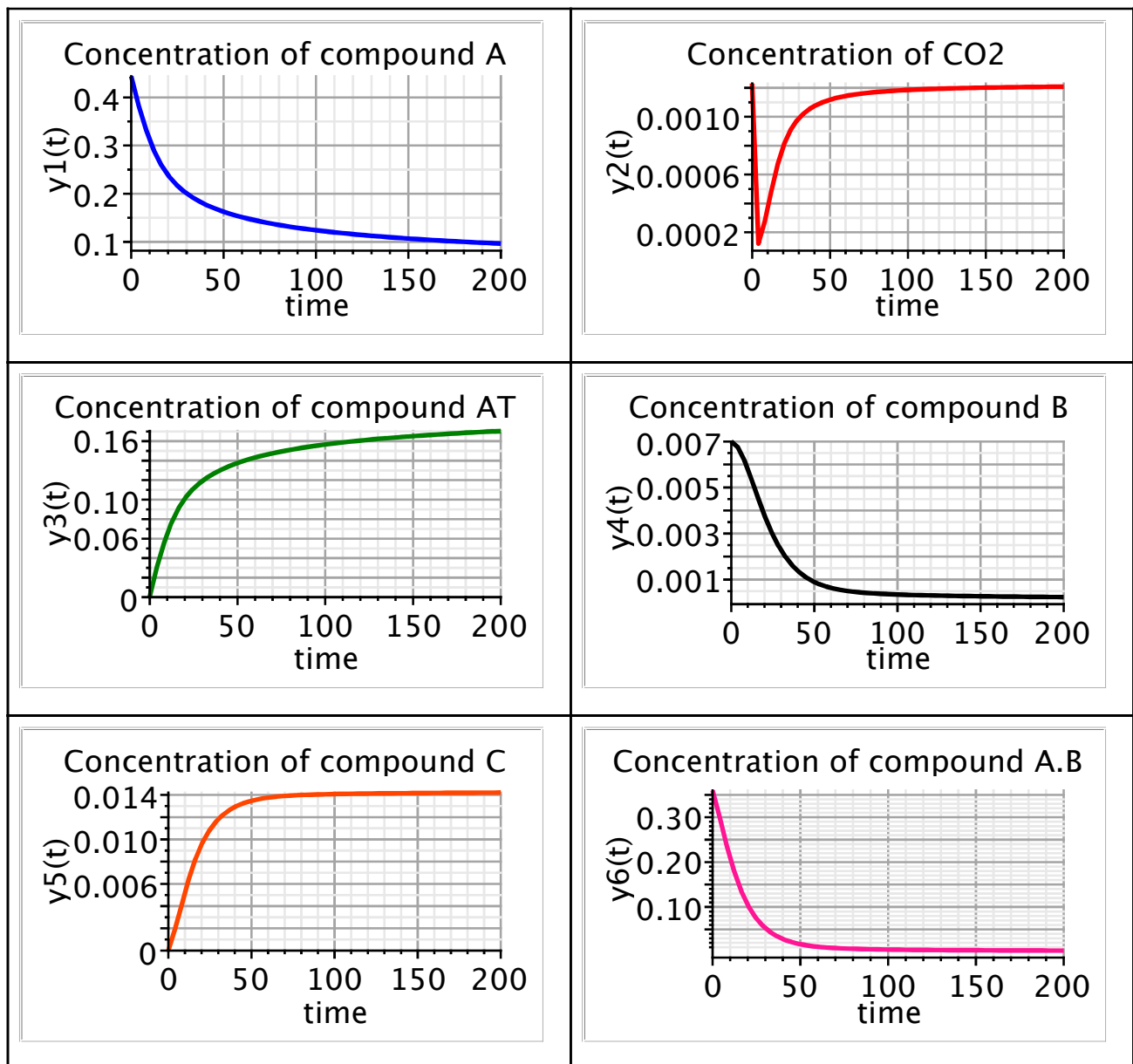
ic

$$y1(0) = 0.444, y2(0) = 0.00123, y3(0) = 0, y4(0) = 0.007, y5(0) = 0, y6(0) = 0.36 \quad (4)$$

We can now solve the DAE system and plot how the concentrations of the various compounds change with time using the *odeplot* command

```
sol := dsolve(subs(ics = ic, params, System), {y1(t), y2(t), y3(t), y4(t), y5(t), y6(t)}, numeric,  
output = procedurelist)
```

proc(x_rkf45_dae) ... end proc (5)



Generate Plots

The concentration of compound C at steady state is:

```
SteadyStateConcentrationC := evalf[6](rhs(select(has, sol(200), y5(t)) [ ]) · [[mol]]) =  
0.0142085 [[mol]]
```

This is 1.5 times lower than the steady state concentration observed by the quality control engineer.

▼ 3. Validation of Reaction Kinetics Model

The discrepancy between the actual and expected concentration of compound C was revealed by comparing the experimental reaction kinetics for each compound to the predicted values.

The experimental data, stored in an Excel file, was extracted using the following commands:

```
ExperimentalData := Import("ExperimentalData.xls", "Experimental", "A2:G12")
```

```
1..11 x 1..7 Array  
Data Type: anything  
Storage: rectangular  
Order: Fortran_order
```

 (6)

The following commands extract the values from Excel:

```
ExperimentalConcA := Matrix(ExperimentalData[1 .. -1, 1 .. 2]) :
```

```
ExperimentalConcCO2 := ArrayTools:-Concatenate(2, Vector[column](ExperimentalData[1 .. -1,  
1]), Vector[column](ExperimentalData[1 .. -1, 3])) :
```

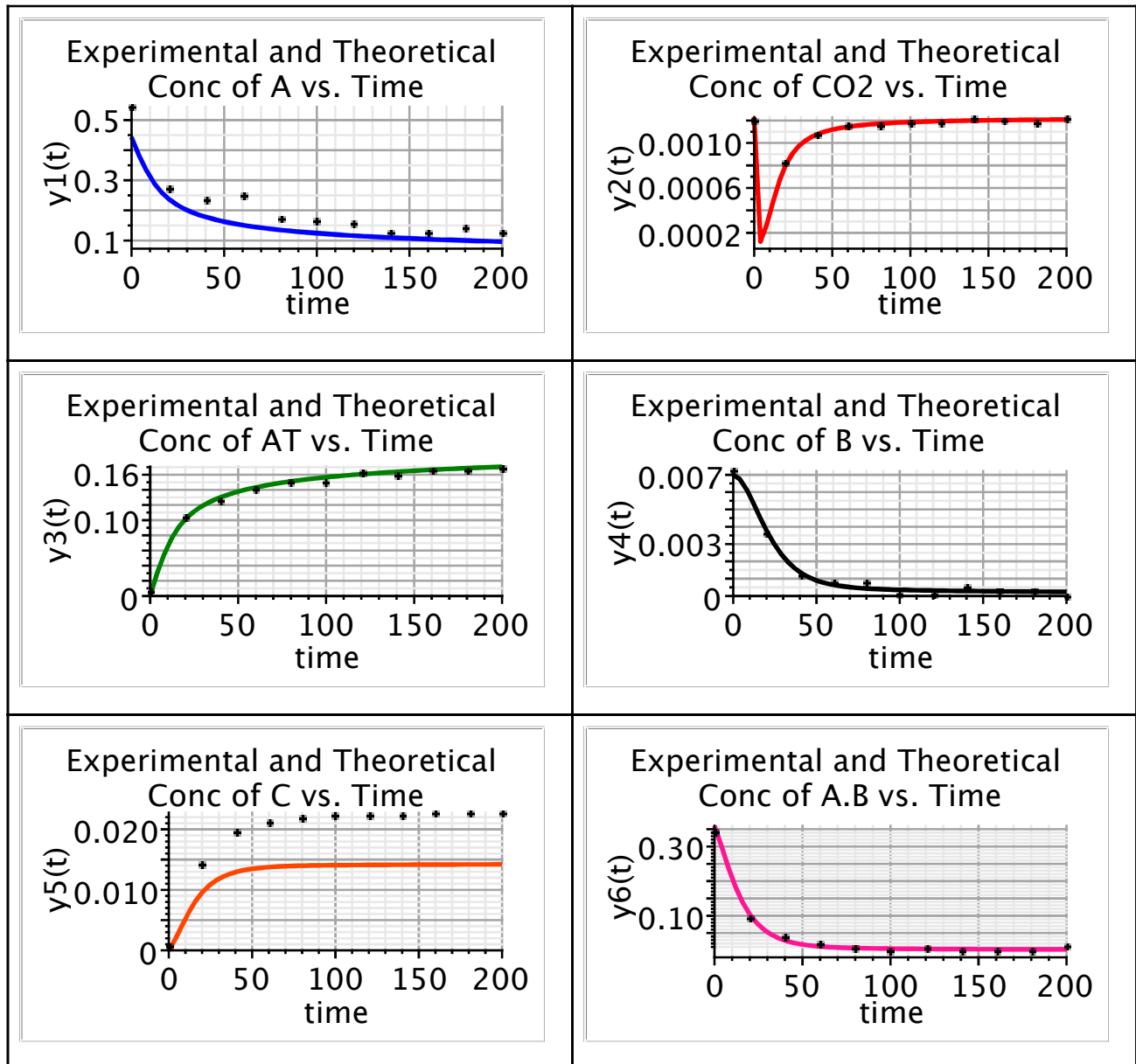
```
ExperimentalConcAT := ArrayTools:-Concatenate(2, Vector[column](ExperimentalData[1 .. -1,  
1]), Vector[column](ExperimentalData[1 .. -1, 4])) :
```

```
ExperimentalConcB := ArrayTools:-Concatenate(2, Vector[column](ExperimentalData[1 .. -1,  
1]), Vector[column](ExperimentalData[1 .. -1, 5])) :
```

```
ExperimentalConcC := ArrayTools:-Concatenate(2, Vector[column](ExperimentalData[1 .. -1,  
1]), Vector[column](ExperimentalData[1 .. -1, 6])) :
```

```
ExperimentalConcAB := ArrayTools:-Concatenate(2, Vector[column](ExperimentalData[1 .. -1,  
1]), Vector[column](ExperimentalData[1 .. -1, 7])) :
```

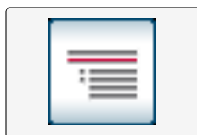
The following plots show the experimental versus predicted reaction kinetics for each compound. From these results, it is apparent that the model derived in the previous section does not adequately predict the experimental results for compound A and compound C.



Generate Plots

(7)

The statistical calculations (mean, standard deviation, and root-mean square error), confirm the presence of an error in one of the rate constants controlling the concentration of compound A. The data, summarized below, show the root mean square error of compound A to be 0.00301799 which is several orders larger than the root mean square error values of the other compounds.



Extract statistical data

$$\text{StatsA} := \text{Stats}(\text{TheoreticalConcA}, \text{ExperimentalConcA})$$

[Predicted Mean=0.152500, Experimental Mean=0.211500, Mean Difference=-0.058990, Predicted Std.=0.074670, Experimental Std.=0.122800, Std. Difference=-0.048100, Root Mean Square Error=0.00301799] (8)

$$\text{StatsCO2} := \text{Stats}(\text{TheoreticalConcCO2}, \text{ExperimentalConcCO2})$$

[Predicted Mean=0.001096, Experimental Mean=0.001145, Mean Difference=-0.000050, Predicted Std.=0.000234, Experimental Std.=0.000116, Std. Difference=0.000118, Root Mean Square Error=4.14958e-10] (9)

$$\text{StatsAT} := \text{Stats}(\text{TheoreticalConcAT}, \text{ExperimentalConcAT})$$

[Predicted Mean=0.142800, Experimental Mean=0.136600, Mean Difference=0.006277, Predicted Std.=0.036460, Experimental Std.=0.048210, Std. Difference=-0.011740, Root Mean Square Error=1.03883e-05] (10)

$$\text{StatsB} := \text{Stats}(\text{TheoreticalConcB}, \text{ExperimentalConcB})$$

[Predicted Mean=0.001180, Experimental Mean=0.001394, Mean Difference=-0.000214, Predicted Std.=0.001785, Experimental Std.=0.002190, Std. Difference=-0.000404, Root Mean Square Error=4.33327e-08] (11)

$$\text{StatsC} := \text{Stats}(\text{TheoreticalConcC}, \text{ExperimentalConcC})$$

[Predicted Mean=0.012760, Experimental Mean=0.019370, Mean Difference=-0.006607, Predicted Std.=0.003177, Experimental Std.=0.006637, Std. Difference=-0.003459, Root Mean Square Error=5.53026e-05] (12)

$$\text{StatsAB} := \text{Stats}(\text{TheoreticalConcAB}, \text{ExperimentalConcAB})$$

[Predicted Mean=0.035610, Experimental Mean=0.047870, Mean Difference=-0.012260, Predicted Std.=0.076580, Experimental Std.=0.101900, Std. Difference=-0.025310, Root Mean Square Error=6.80798e-05] (13)

Predicted and Experimental Mean of the Reaction Kinetics for each Compound

	Predicted Mean	Experimental Mean	Difference
[A]	0.152500	0.211500	-0.058990
[CO ₂]	0.001096	0.001145	-0.000050
[AT]	0.142800	0.136600	0.006277

[B]	0.001180	0.001394	-0.000214
[C]	0.012760	0.019370	-0.006607
[A.B]	0.035610	0.047870	-0.012260

Predicted and Experimental Standard Deviation of the Reaction Kinetics for each Compound

	Predicted Std	Experimental Std	Difference
[A]	0.074670	0.122800	-0.048100
[CO ₂]	0.000234	0.000116	0.000118
[AT]	0.036460	0.048210	-0.011740
[B]	0.001785	0.002190	-0.000404
[C]	0.003177	0.006637	-0.003459
[A.B]	0.076580	0.101900	-0.025310

Root-Mean Square Error	
[A]	1799
[CO ₂]	8e-10
[AT]	3e-05
[B]	7e-08
[C]	6e-05
[A.B]	

Update Table

▼ 4. Updated Reaction Kinetics Model

We can obtain a better prediction of the reaction kinetics of compound A by parameterizing the numerical solution for the differential equation obtained earlier, and fitting the theoretical model to the experimental data using the least-squares approach.

The following procedure calculates the sum of the squares of the error between the experimental data and the model prediction for the rate constant kI . It assumes that the only uncertainty in the experimental data exists in the concentration, $yI(t)$. In reality, the time the reading was taken will also be subject to a degree of error. If this was to be taken into account, then the following procedure can be easily modified to calculate the sum of the short orthogonal distance between the data points and model predictions; this is also known as orthogonal regression.

(14)

```

SumOfSquaresError := proc(kI_val)
local temp, yI_temp;
temp := dsolve(subs((kI = kI_val, ics = ic, params), System), {y1(t), y2(t), y3(t), y4(t), y5(t),
y6(t)}, numeric, output = listprocedure, range = 0 .. 200) :
yI_temp := rhs(select(has, temp, yI(t)) [ ] ) :
return add( (ExperimentalConcA[i, 2] - yI_temp(ExperimentalConcA[i, 1]))2, i = 1 .. 11) :
end proc:

```

The value of kI that best describes the experimental data is

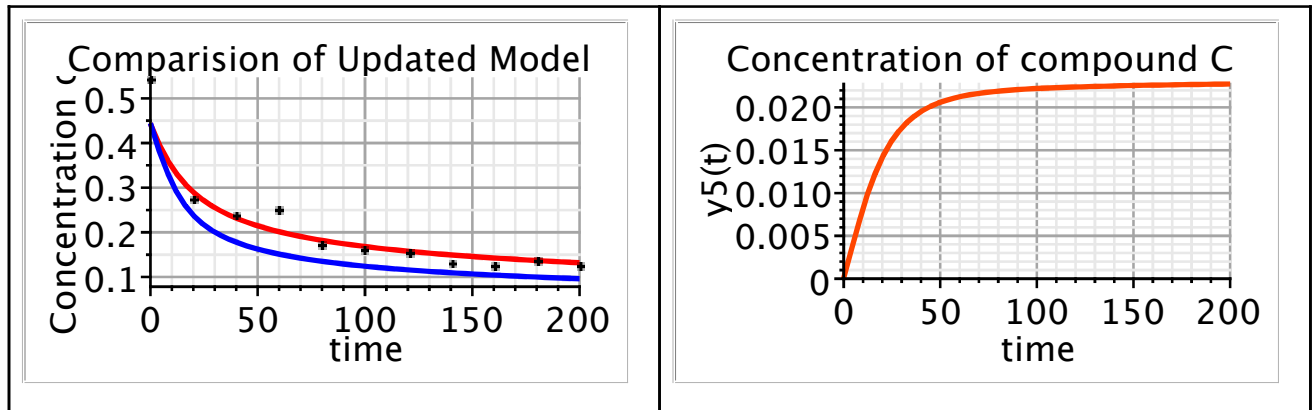
$kI_{\text{experimental}} := \text{evalf}[6](\text{rhs}(\text{Minimize}('SumOfSquaresError'(var), var = 1 .. 50) [2] [])) = 10.9259$

This value for kI is much smaller than the value of kI that was used to develop the original model (that is, 10.925 vs. 28.7).

Taking into account the new value of kI as shown below, the theoretical model accurately predicts the experimental results.

(15)

$UpdatedSystem := dsolve(subs((kI = kI_{experimental}), ics = ic, params), System), \{y1(t), y2(t), y3(t), y4(t), y5(t), y6(t)\}, numeric, output = listprocedure) :$



Generate Plots

With this new rate constant the concentration of compound C now more accurately matches the concentration being produced at the plant.

$UpdatedSteadyStateConcentrationC := evalf[6](rhs(select(has, UpdatedSystem(200), y5(t)) [] \cdot [mol]))$
 $= 0.0227357 [mol]$

▼ Results

In this document, the chemical kinetics model of a paint production process was reformulated to more accurately predict the reaction kinetics of the system.

The model was reformulated as a result of quality control tests that yielded a significant difference between the expected and actual concentration of paint produced in the reactor. Comparison between the experimental data and the data used to predict the original model led to the source of the error - the rate constant used for one of the reactions was incorrect. Using the least-squares method approach, the actual rate constant was recalculated and found to be 10.925, a value 2.5 times smaller than the value used in the initial model formulation. Incorporating this new rate constant into the model gave rise to a final concentration that is more accurately predicted by the quality control engineer. This in turn resulted in added value as the plant was able to supply a higher quality of paint at a the same cost point.



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