Modelling and Kinetics 2

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1 Definitions

Numerical Analysis

Numeric analysis is a branch of mathematics[1] and computer science[2] that uses a series of equations, or algorithms, to find the approximate solution to a problem, e.g. the Newton-Raphson approximation for finding the root of a polynomial.[3]
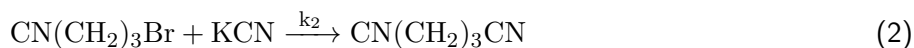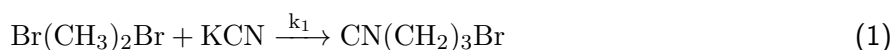
Analytic Analysis

Analytic analysis is the decomposition of a problem into its substituent parts[4] for determination of a quantitative solution using mathematical or chemical methods.

Explicit Solution

The explicit solution is the true and exact solution to a problem/equation.[5]

2 Analytical Model

In this practical, the following pair of chemical reactions were studied:

$$\mathrm{Br(CH_3)_2Br + KCN \xrightarrow{k_1} CN(CH_2)_3Br} \tag{1}$$

$$\mathrm{CN(CH_2)_3Br + KCN \xrightarrow{k_2} CN(CH_2)_3CN} \tag{2}$$

For the sake of readability, the species will henceforth be referred to as follows:

Species	Abbreviation
$\mathrm{Br(CH_2)_3Br}$	A
KCN	B
$\mathrm{Br(CH_2)_3CN}$	C
$\mathrm{CN(CH_2)_3CN}$	D

Table 1: A table of abbreviations used for the species in this report.

Thus the system of chemical equations can be rewritten as:

$$\mathrm{A + B \xrightarrow{k_1} C} \tag{3}$$

$$\mathrm{C + B \xrightarrow{k_2} D} \tag{4}$$
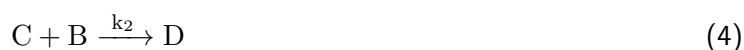
2.1 Generating the Analytic Model

3i. $[A]_0 = [A] + [C] + [D]$

3ii. $[B]_{cons} = 2[D] + [C]$

4. $[C] = 2[A]_0 - 2[A] - [B]_{cons}$

5. $\frac{d[A]}{d[B]} = \frac{-k_1[A]}{k_1[A] + k_2[C]}$

6.

$$k_1 = 2k_2$$

$$\frac{d[A]}{d[B]_{\text{cons}}} = \frac{-k_1[A]}{k_1[A] + k_2[C]}$$

$$= \frac{-2k_2[A]}{2k_2[A] + k_2[C]}$$

$$= \frac{-2k_2[A]}{k_2(2[A] + [C])}$$

$$= \frac{-2[A]}{2[A] + [C]}$$

7.

$$[C] = 2[A]_0 - 2[A] - [B]_{\text{cons}}$$

$$\frac{d[A]}{d[B]_{\text{cons}}} = \frac{-2[A]}{2[A] + [C]}$$

$$= \frac{-2[A]}{2[A] + 2[A]_0 - 2[A] - [B]_{\text{cons}}}$$

$$= \frac{-2[A]}{2[A]_0 - [B]_{\text{cons}}}$$

8 & 9.

$$\frac{d[A]}{d[B]_{\text{cons}}} = \frac{-2[A]}{2[A]_0 - [B]_{\text{cons}}}$$

$$-\int_{[A]_0}^{[A]} \frac{1}{2[A]} d[A] = -\int_0^{[B]_{\text{cons}}} \frac{1}{2[A]_0 - [B]_{\text{cons}}} d[B]_{\text{cons}}$$

$$-\left(\frac{1}{2} \ln 2[A]\right)_{[A]_0}^{[A]} = -(\ln(2[A]_0 - [B]_{\text{cons}}))_0^{[B]_{\text{cons}}}$$

$$-\frac{1}{2}\ln(2[A]) + \frac{1}{2}\ln(2[A]_0) = -\ln(2[A]_0 - [B]_{\text{cons}}) + \ln(2[A]_0)$$

$$-\frac{1}{2}\ln(2[A]) = \ln(2[A]_0) - \ln\sqrt{2[A]_0} - \ln(2[A]_0 - [B]_{\text{cons}})$$

$$\ln(2[A])^{-\frac{1}{2}} = \ln\frac{2[A]_0}{(2[A]_0)^{\frac{1}{2}}} - \ln(2[A]_0 - [B]_{\text{cons}})$$

$$\ln(2[A])^{-\frac{1}{2}} = \ln\frac{2[A]_0}{(2[A]_0)^{\frac{1}{2}}(2[A]_0 - [B]_{\text{cons}})}$$

$$\frac{1}{\sqrt{2[A]}} = \frac{2[A]_0}{\sqrt{2[A]_0}(2[A]_0 - [B]_{\text{cons}})}$$

$$\sqrt{2[A]} = \frac{\sqrt{2[A]_0}(2[A]_0 - [B]_{\text{cons}})}{2[A]_0}$$

$$2[A] = \frac{2[A]_0(2[A]_0 - [B]_{\text{cons}})^2}{4[A]_0^2}$$

$$[A] = \frac{(2[A]_0 = [B]_{\text{cons}})^2}{4[A]_0}$$

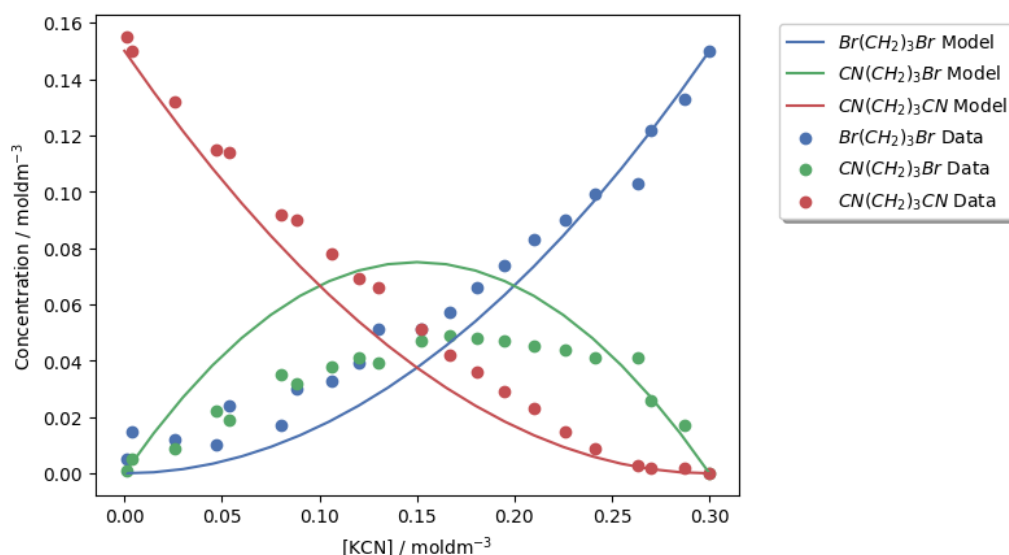## 2.2 Comparing the Analytical Model to Experimental Data

Fig. 1: A plot comparing the analytically modelled concentrations of species in solution compared to experimentally determined data.

Overall, the plotted experimental data and model data match moderately well - the overall mean squared error was 0.017. Visually, the $\text{CN}(\text{CH}_2)_3\text{Br}$ model and data appear to have the worst discrepancy. This could be due to the simplifying assumption of $k_1 = 2k_2$, which does not account for the effect of the presence of the CN^- group on the molecule compared to the Br^- group - they have different electronegativities and group sizes for example, which will have steric and electronic effects on the molecule and its reactivity. An

additional factor is possible error in calculations or code.

3   Numerical Analysis

3.1   Generating the Numerical Model

1. $\Delta[A] = -\frac{k_1[A]}{k_1[A] + k_2[C]}\Delta[B]_{\text{cons}}$

2. $\Delta[A] = -\frac{[A]}{[A] + K[C]}\Delta[B]_{\text{cons}}$

3.

$$\frac{\Delta[D]}{\Delta t} \times \frac{\Delta t}{\Delta[B]_{\text{cons}}} = -\frac{k_2[B][C]}{k_1[A][B] - k_2[B][C]}$$

$$\Delta D = -\frac{k_2[C]}{k_1[A] - k_2[C]}\Delta[B]_{\text{cons}}$$

4.

$$[A]_0 = [A] + [C] + [D]$$
$$\Delta[A] = [A] - [A]_0$$
$$\Delta[C] = [C]$$
$$\Delta[D] = [D]$$
$$0 = [A] - [A]_0 + [C] + [D]$$
$$0 = \Delta[A] + \Delta[C] + \Delta[D]$$
$$\Delta[C] = -\Delta[A] - \Delta[D]$$

3.2   Analysis of the Numerical Model with Python

When the same assumption is used as section 3, with $K = 0.5$, a slightly different plot is generated due to the way in which the relationships between species are modelled. In the analytical model, major simplifications were made about the relationship between the two rate constants, whereas in the numerical model, no such assumptions were made. This means that the numerical model should theoretically be much more accurate.
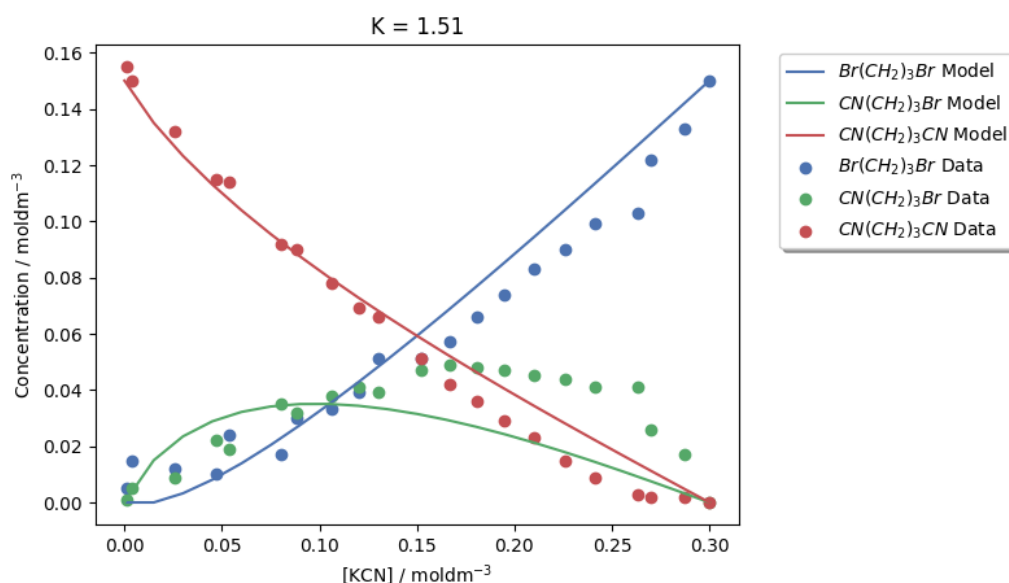

Fig. 2: A plot comparing the numerically modelled concentrations of species in solution compared to experimentally determined data.

In comparison to Fig. 1, the fit of the model appears much closer to the experimental data. Additionally, the mean squared error was slightly lower. Compared to the analytical model, the K value is much higher (≈ 3 times). However, the model is still not a perfect fit to the experimental data. This is to be expected, as there are visually outliers in the experimental data, e.g. the $CN(CH_2)_3Br$ point at ~ 0.26 [KCN] mol dm^{-3}. Additionally, no model is perfect - they cannot account for every possible factor that can affect the rate of equation, e.g. stirring, temperature, etc.

4 Appendix

Full code and LATEXavailable on GitHub.

```python
...
import numpy as np
import matplotlib.pyplot as plt
from sklearn.metrics import mean_squared_error, r2_score
plt.style.use("seaborn-v0_8-deep")

Br2_data=[0.15, 0.133, 0.122, 0.103, 0.099, 0.09, 0.083, 0.074, 0.066, 0.057,
          0.051, 0.051, 0.039, 0.033, 0.03, 0.017, 0.024, 0.01, 0.012, 0.015, 0.005]
BrCN_data=[0, 0.017, 0.026, 0.041, 0.041, 0.044, 0.045, 0.047, 0.048, 0.049,
          0.047, 0.039, 0.041, 0.038, 0.032, 0.035, 0.019, 0.022, 0.009, 0.005, 0.001]
CN2_data=[0, 0.002, 0.002, 0.003, 0.009, 0.015, 0.023, 0.029, 0.036, 0.042,
          0.051, 0.066, 0.069, 0.078, 0.09, 0.092, 0.114, 0.115, 0.132, 0.15, 0.155]
KCN_data=[0.3, 0.287, 0.27, 0.263, 0.241, 0.226, 0.21, 0.195, 0.181, 0.167,
          0.152, 0.13, 0.12, 0.106, 0.088, 0.08, 0.054, 0.047, 0.026, 0.004, 0.001]

def plot_data():
    plt.tight_layout()
    plt.plot(KCNcons_model, Br2_model, label='$Br(CH_2)_3Br$ Model')
    plt.plot(KCNcons_model, BrCN_model, label='$CN(CH_2)_3Br$ Model')
    plt.plot(KCNcons_model, CN2_model, label='$CN(CH_2)_3CN$ Model')
    plt.scatter(KCN_data, Br2_data, label='$Br(CH_2)_3Br$ Data')
    plt.scatter(KCN_data, BrCN_data, label='$CN(CH_2)_3Br$ Data')
    plt.scatter(KCN_data, CN2_data, label='$CN(CH_2)_3CN$ Data')
    plt.legend(bbox_to_anchor=(1.05, 1), loc='upper left', fancybox=True, shadow=True)
    plt.xlabel('[KCN] / moldm$^{-3}$')
    plt.ylabel('Concentration / moldm$^{-3}$')
    plt.savefig("PartA_Plot.png")
    plt.show()

BrCN_model = []
Br2_model = []
KCNcons_model = np.linspace(0, 0.3, len(KCN_data))
KCN_model = [0.3-x for x in KCNcons_model]
CN2_model = [((0.3-x)**2)/0.6 for x in KCNcons_model]

for i in range(len(KCNcons_model)):
    BrCN_model.append(0.3-2*CN2_model[i]-KCNcons_model[i])
    Br2_model.append(0.15-CN2_model[i]-BrCN_model[i])

r2 = r2_score(Br2_data, Br2_model) + r2_score(BrCN_data, BrCN_model) + r2_score(CN2_data, CN2_model)
mse = mean_squared_error(Br2_data, Br2_model) + mean_squared_error(BrCN_data, BrCN_model) + mean_squared_error(CN2_data, CN2_model)

print(r2)
print(mse)
plot_data()
```

Fig. 3: The python code used for part A.

References

[1] MathWorks, *What Is Numerical Analysis*, https://uk.mathworks.com/discovery/numerical-analysis.html.

[2] K. Atkinson, *numerical analysis*, https://www.britannica.com/science/numerical-analysis.

[3] R. Anstee, *The Newton-Raphson Method*, https://personal.math.ubc.ca/~/newtonmethod.pdf.

[4] Cambridge Dictionary, *analysis*, https://dictionary.cambridge.org/dictionary/english/analysis.

[5] Cambridge Dictionary, *explicit*, https://dictionary.cambridge.org/dictionary/english/explicit.