Experiment 4: Chemical Kinematics

CHM1311

Introduction

Chemical Kinematics is the study of chemical reactions within the context of reaction rates. The reaction equation shows that the rate is equal to the concentrations of the reactants (A and B) to the power of their respective orders (x and y), multiplied by an equilibrium constant (k).

$$\text{Rate} = k\,[A]^x\,[B]^y \qquad [1]$$

The order of the reaction is found through the addition of the order of each reactant (x +y). Therefore, to find the order of the reaction, the partials orders must be found first, and this can only be done through experimentation. A first order reaction is defined as a reaction where the rate is directly proportionate to one reactant.

$$\text{Rate} = k\,[A]^1 \qquad [2]$$

A pseudo first order reaction is one where a second order reaction appears to behave like a first order reaction. This may occur when one reactant in the equation is present in great excess, while the other is not. In that case, the reactant in excess may act as though it is static throughout the reaction.

In this experiment, the concentrations of the reactants are observed to determine the order of the reactants and finally the order of the reaction. The concentrations are determined through the usage of spectrophotometry. Spectrophotometry is the usage of electromagnetic radiation and the analysis of its interaction with matter. A spectrophotometer is a machine that is the medium for this analysis. In this experiment, the machine was used to determine transmittance and absorbance, which led to the concentration of the chromium ion.

Image 1. LAMBDA™ Spectrophotometer

Procedure

As described in the lab manual (What in the World ISN'T Chemistry, Dr. Rashmi Venkateswaran, 2000, Exp. 4, p. 43-54)

Observations and Data

In all three trials, the observations made were identical. The solution began as a clear, greyish liquid, and became dark purple when heated.

Table 1. Data for 4.0 pH

Time	Trans @563.2 nm (%)	A(t)	A Cr(III)	log A Cr(III)	Rate	Log R
2	80.27	0.095	1.543	0.188	0.000	
4	80.45	0.094	1.544	0.189	0.000	-3.416
6	80.03	0.097	1.542	0.188	0.001	-3.162
8	79.79	0.098	1.540	0.188	0.001	-3.180
10	79.61	0.099	1.539	0.187	0.001	-3.113
12	79.31	0.101	1.538	0.187	0.001	-2.981
14	78.77	0.104	1.535	0.186	0.001	-2.934
16	78.40	0.106	1.533	0.185	0.001	-2.952
18	78.02	0.108	1.531	0.185	0.001	-2.929
20	77.55	0.110	1.528	0.184	0.001	-2.907
22	77.13	0.113	1.526	0.183	0.001	-2.884
24	76.68	0.115	1.523	0.183	0.001	-2.825
26	76.03	0.119	1.519	0.182	0.002	-2.803
28	75.51	0.122	1.517	0.181	0.001	-2.827
30	75.05	0.125	1.514	0.180	0.002	-2.818
32	74.48	0.128	1.511	0.179	0.002	-2.793
34	73.91	0.131	1.507	0.178	0.002	-2.772
36	73.37	0.134	1.504	0.177	0.002	-2.722
38	72.87	0.137	1.501	0.176	0.003	-2.567
40	71.38	0.146	1.492	0.174	0.004	-2.438

Table 2. Data for 4.5 pH

Time	Trans @563.2 nm (%)	A(t)	A Cr(III)	log A Cr(III)	Rate	Log R
2	88.50	0.053	1.585	0.200	0.000	-3.447
4	88.37	0.054	1.585	0.200	0.000	-3.361
6	88.22	0.054	1.584	0.200	0.001	-3.224
8	87.91	0.056	1.583	0.199	0.001	-3.083
10	87.51	0.058	1.581	0.199	0.001	-3.000
12	87.11	0.060	1.579	0.198	0.001	-2.929
14	86.57	0.063	1.576	0.198	0.001	-2.868
16	86.02	0.065	1.573	0.197	0.002	-2.824

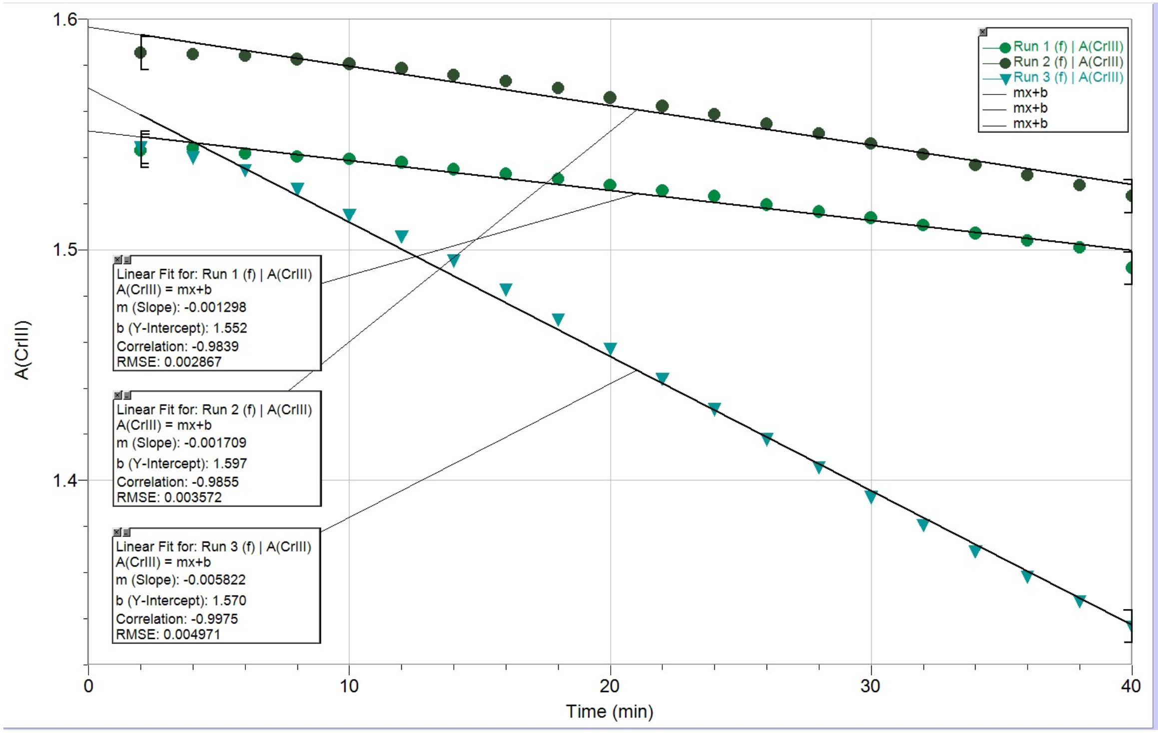
18	85.43	0.068	1.570	0.196	0.002	-2.760
20	84.61	0.073	1.566	0.195	0.002	-2.727
22	83.91	0.076	1.562	0.194	0.002	-2.728
24	83.20	0.080	1.559	0.193	0.002	-2.711
26	82.43	0.084	1.555	0.192	0.002	-2.689
28	81.64	0.088	1.550	0.190	0.002	-2.672
30	80.84	0.092	1.546	0.189	0.002	-2.652
32	79.97	0.097	1.541	0.188	0.002	-2.641
34	79.12	0.102	1.537	0.187	0.002	-2.647
36	78.33	0.106	1.532	0.185	0.002	-2.650
38	77.53	0.111	1.528	0.184	0.002	-2.646
40	76.71	0.115	1.523	0.183	0.002	-2.642

Table 3. Data for 5.0 pH

Time	Trans @563.2 nm (%)	A(t)	A Cr(III)	log A Cr(III)	Rate	Log R
2	80.56	0.094	1.545	0.189	0.002	-2.611
4	79.73	0.098	1.540	0.188	0.003	-2.544
6	78.73	0.104	1.535	0.186	0.004	-2.447
8	77.26	0.112	1.526	0.184	0.005	-2.346
10	75.32	0.123	1.515	0.181	0.005	-2.303
12	73.72	0.132	1.506	0.178	0.005	-2.283
14	71.93	0.143	1.495	0.175	0.006	-2.241
16	69.90	0.156	1.483	0.171	0.006	-2.207
18	67.83	0.169	1.470	0.167	0.006	-2.194
20	65.88	0.181	1.457	0.164	0.006	-2.190
22	63.93	0.194	1.444	0.160	0.007	-2.186
24	62.01	0.208	1.431	0.156	0.006	-2.188
26	60.18	0.221	1.418	0.152	0.006	-2.198
28	58.53	0.233	1.406	0.148	0.006	-2.203
30	56.81	0.246	1.393	0.144	0.006	-2.210
32	55.25	0.258	1.381	0.140	0.006	-2.230
34	53.83	0.269	1.369	0.137	0.006	-2.247
36	52.45	0.280	1.358	0.133	0.005	-2.260
38	51.20	0.291	1.348	0.130	0.005	-2.265
40	49.92	0.302	1.337	0.126	0.005	-2.264

*Data from Section A5: Shravana Ramgoolam (8716990), Andrea Rondeau-Brown (8708017), and Anushka Shah (8675301)

Figure 1. A Cr(III) as a function of time for all pH values

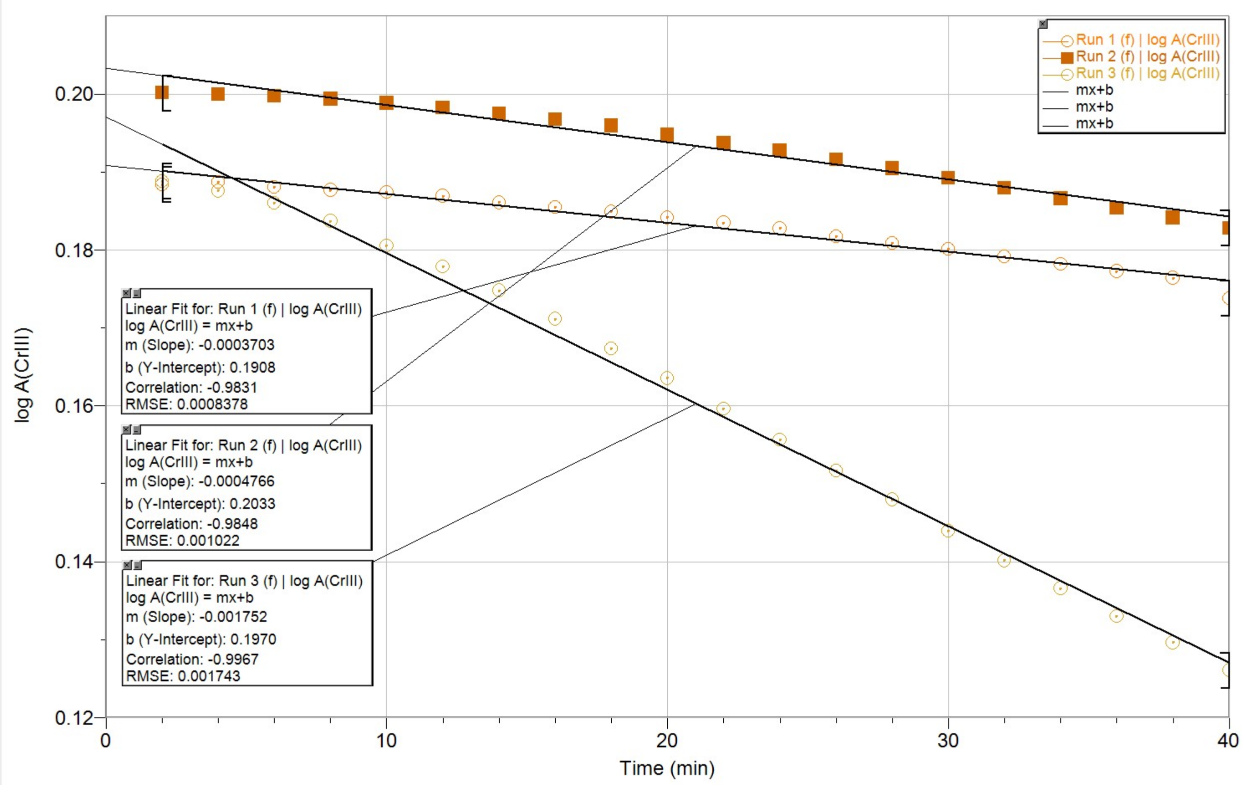


Linear Fit for: Run 1 (f) | A(CrIII)
A(CrIII) = mx+b
m (Slope): -0.001298
b (Y-Intercept): 1.552
Correlation: -0.9839
RMSE: 0.002867

Linear Fit for: Run 2 (f) | A(CrIII)
A(CrIII) = mx+b
m (Slope): -0.001709
b (Y-Intercept): 1.597
Correlation: -0.9855
RMSE: 0.003572

Linear Fit for: Run 3 (f) | A(CrIII)
A(CrIII) = mx+b
m (Slope): -0.005822
b (Y-Intercept): 1.570
Correlation: -0.9975
RMSE: 0.004971

Figure 2. log (A Cr(III)) as a function of time for all pH values



Linear Fit for: Run 1 (f) | log A(CrIII)
log A(CrIII) = mx+b
m (Slope): -0.0003703
b (Y-Intercept): 0.1908
Correlation: -0.9831
RMSE: 0.0008378

Linear Fit for: Run 2 (f) | log A(CrIII)
log A(CrIII) = mx+b
m (Slope): -0.0004766
b (Y-Intercept): 0.2033
Correlation: -0.9848
RMSE: 0.001022

Linear Fit for: Run 3 (f) | log A(CrIII)
log A(CrIII) = mx+b
m (Slope): -0.001752
b (Y-Intercept): 0.1970
Correlation: -0.9967
RMSE: 0.001743

Figure 3. log (rate) as a function of log (A Cr(III)) for 4.0 pH

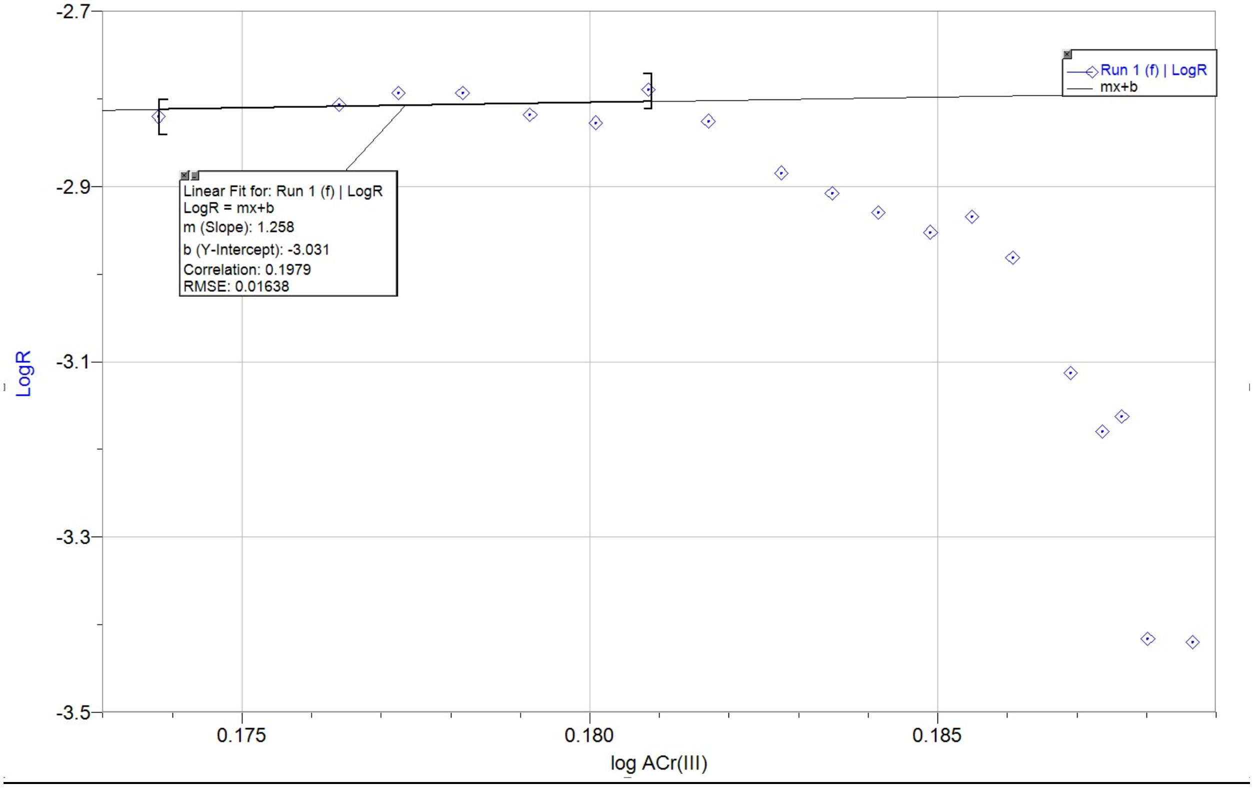


Figure 4. log (rate) as a function of log (A Cr(III)) for 4.5 pH

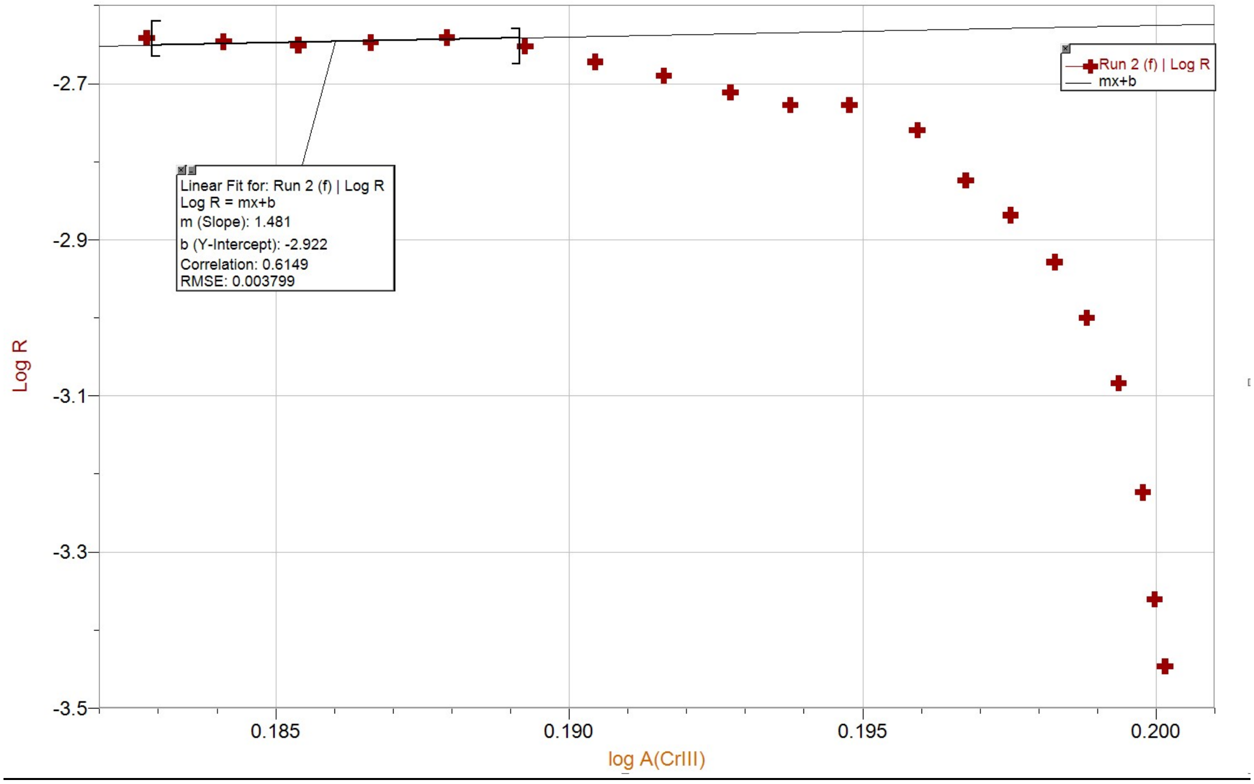
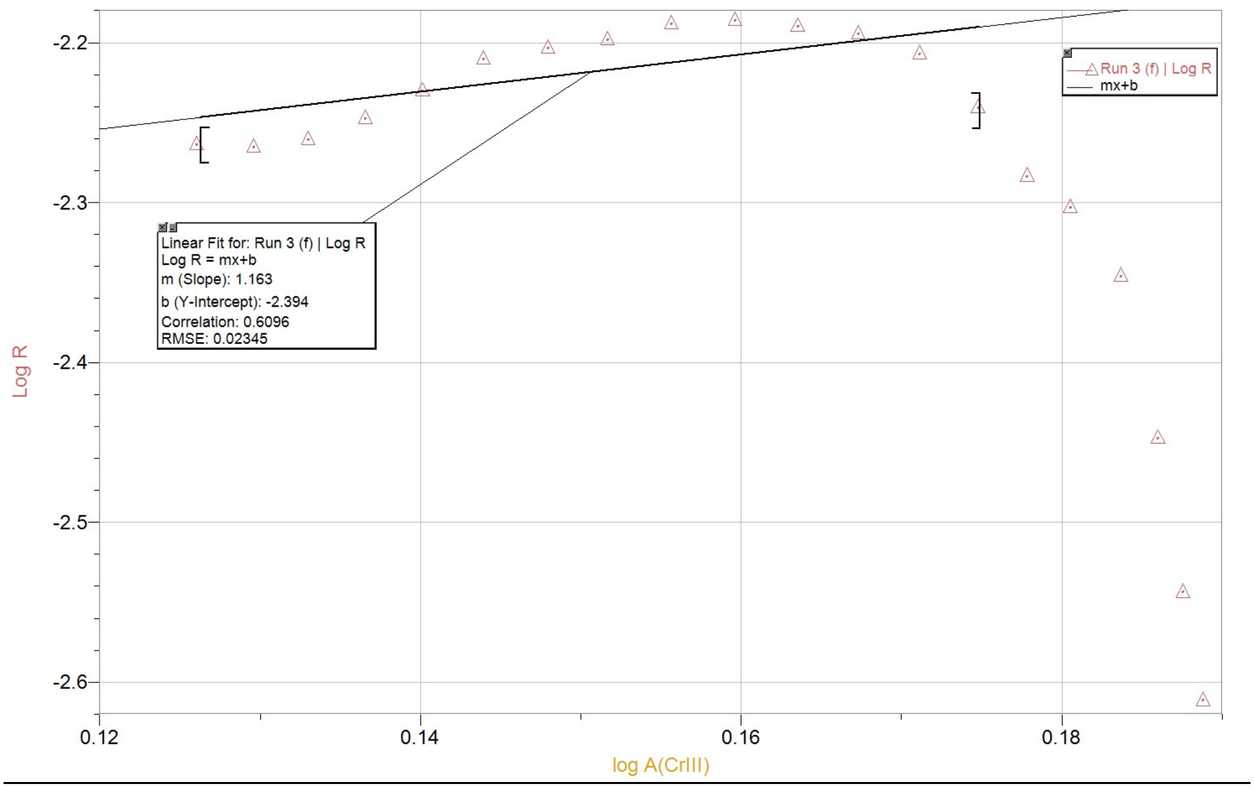


Figure 5. log (rate) as a function of log (A Cr(III)) for 5.0 pH



Sample Calculations

t=10 for pH 4.0

A(t) = log (100/Trans@563.2nm)
A(10) = log (100/79.61)
A(10) = 0.099

A Cr(III) = A∞ – A(10)
A Cr(III) = 1.6385 – 0.099
A Cr(III) = 1.539

Log A Cr(III) = log (A Cr(III))
Log A Cr(III) = log (1.539)
Log A Cr(III) = 0.187

Log R = log (Rate)
Log R = log (0.001)
Log R = -3.113

Discussion

The result of experiment was the determination of the concentration of chromium (III) ion over time, at three different pH levels. To find this, the absorption of the chromium was calculated using the percent transmittance. Then this value was subtracted from the final absorption (A_∞). When plotted against time, the graph of all three pH levels returned linear data sets. The slopes of the line of best fit became increasingly negative (steeper) as the pH increased. This same trend was seen when the log of the concentration of the chromium ion was plotted against time.

It is believed that this is because the both the concentration of hydronium and chromium impact the rate. This can be seen when looking at the rate equation, even though the order of the reaction with respect to each reaction is not known.

When looking at the data on the graph of log (rate) as a function of log (A Cr(III)) (before the points begin to drop off), we can see that the slope of the line of best fit is generally equal to 1. This value represents pseudo first-order kinetics, as the rate is directly proportional to the concentration of Cr(III) ions. The reason this phenomenon occurs is the limiting of the effect of pH. Changes in both pH and [Cr(III)] impact the rate, however if the pH is kept static, then the effect of the concentration of Cr(III) ions can be isolated.

A source of error in this experiment was the impact of the values at $t=0$ and $t=\infty$. At time 0, there was no solution placed in the spectrophotometer, therefore the point that was achieved doesn't reflect the actual reaction. At time infinity (seen as $t=42$), the heated and cooled solution was placed in the machine. This point was the end result of the reaction and in reality, would have taken very long to naturally arrive, due to the slow reaction. As a result, these values were removed from our data.

Conclusion

The partial order of each reaction with respect to the Cr(III) ion is 1.

Data from Section A5: Shravana Ramgoolam (8716990), Andrea Rondeau-Brown (8708017), and Anushka Shah (8675301).

References:
www.britannica.com/science/kinetics, Kinetics: Dynamics
www.britannica.com/science/Beers-law, Rafferty J, Beer's Law: Physics
Image: www.laboratory-equipment.com/laboratory-equipment/Perkin-Spectrophotometer-LAMBDA-Bio.php, Perkin Elmer LAMBDA™ Bio+ Spectrophotometer from Terra Universal