

Chemical Kinetics

By Hannah St. John

8608447

Partner: Julia Dobrowolski 8622234

CHM1311 Section B9

Friday, Lab Week 1

Demonstrator:

Brandon Fitchett

November 11, 2016

Department of Chemistry

University of Ottawa

The rate of reaction is the speed it takes for a chemical reaction to proceed, and can also be viewed as the amount of reactants consumed or products formed in an amount of time (K. J. Laidler, 2016). It can be expressed as:

$$\text{Rate} = k [A]^n [B]^m$$

[A] and [B] being the concentrations of the reactants. K is the rate constant and a proportionality constant. It expresses the relationship between the rate of the chemical reaction and the concentrations of the reactants (K. J. Laidler, 2016). The exponents in the equation refer to the order of the reaction. The total order of the reaction can be determined through the sum of the exponents. Order of a reaction can only be determined experimentally.

The instantaneous rate is the rate at any point in time during the reaction. It can be found graphically by taking the slope of the tangent at a specific time, as long as the graph represents concentration (or a value that reflects concentration) as a function of time (Venkateswaran, 2016).

Complexation is the combination of individual molecules to create one large molecule ("Complexation," 2016). A complex mechanism is an elementary reaction, and multiple complex mechanisms create a composite reaction (K. J. Laidler, 1996). The final product of a composite reaction is referred to as a complex.

A spectrophotometer is a tool that can further the knowledge on any given chemical substance by separating electromagnetic radiation into its component wavelengths and by measuring the intensity of radiation after passing through a substance (*Spectrophotometry*, n.d.). Every substance absorbs and transmits specific wavelengths of radiant energy; spectrophotometry is the study of this information. Transmittance is the ratio of the intensity of the light that passed through the substance to the intensity of light before it passed through the substance (*Spectrophotometry*, n.d.). An equation for transmittance is:

$$T = I/I_0$$

Spectrophotometers record transmittance as percent transmittance, which can be found by multiplying the transmittance by 100%:

$$\%T = T \times 100\%$$

Absorbance is the negative log of transmittance. It can be expressed by the following equation:

$$A = -\log(I/I_0)$$

Any substance that absorbs light has a constant molar absorptivity, and if all measurements are taken using the same equipment, the concentration of that substance will be directly proportional to the absorbance (Venkateswaran, 2016). This expressed by the following equation:

$$A = \epsilon b c$$

In this equation, ϵ represents the molar absorptivity, b represents the path length, and c represents the concentration of the absorbing species. When molar absorptivity and path length are consistent, absorbance and concentration are equal.

Procedure

As described in the lab manual (Venkateswaran, 2016), except for step 34 and 36. The recorded values of percent transmittance were taken at 30 minutes instead of 40 minutes (step 34), and 32 minutes instead of 42 minutes (step 36).

Observations

All of the EDTA's (pH 4.0, 4.5, and 5.0) were colourless and odourless. All of them turned a faint purple grey colour once the Cr(III) solution was added, and turned a dark violet colour when heated in boiling water.

Results

Table 1. Independent Measurements for Trials 1-3

	Trial 1	Trial 2	Trial 3
Volume of EDTA solution (mL)	10.1	9.9	10.0
pH of EDTA solution	4.0	4.5	5.0
Length of trial (min)	30	30	30
Wavelength used (nm)	586.10	586.10	586.10
A_{∞} (Absorbance when no Cr(III) ion is left)	1.744	1.490	1.256

Table 1. Time-Dependent Spectrometer Measurements for Trial 1

Time (minutes)	% Transmittance @ 586.1 nm	Absorbance	Absorbance of Cr(III)	Log of Absorbance of Cr(III)	Rate	Log of the Rate
2	83.04753	0.080673	1.663727	0.221082	0.00014	-3.85403
4	82.90414	0.081424	1.662976	0.220886	0.000496	-3.30414
6	82.62438	0.082892	1.661508	0.220502	0.000725	-3.13958
8	82.38767	0.084138	1.660262	0.220177	0.001018	-2.99229
10	81.70447	0.087754	1.656646	0.21923	0.000957	-3.019
12	81.66647	0.087956	1.656444	0.219177	0.000906	-3.043
14	81.17002	0.090604	1.653796	0.218482	0.00118	-2.92818

16	80.75348	0.092839	1.651561	0.217895	0.001408	-2.85139
18	80.10318	0.09635	1.64805	0.21697	0.001594	-2.79758
20	79.55088	0.099355	1.645045	0.216178	0.001681	-2.7744
22	78.84558	0.103223	1.641177	0.215156	0.001701	-2.76925
24	78.30603	0.106205	1.638195	0.214366	0.001703	-2.76875
26	77.67934	0.109694	1.634706	0.21344	0.024387	-1.61284
28	76.97646	0.113642	1.630758	0.21239	0.096631	-1.01488
30	76.23097	0.117869	1.626531	0.211262	0.328785	-0.48309

Table 2. Time-Dependent Spectrometer Measurements for Trial 2

Time (minutes)	% Transmittance @ 586.1 nm	Absorbance	Absorbance of Cr(III)	Log of Absorbance of Cr(III)	Rate	Log of the Rate
2	81.25181	0.090167	1.399533	0.145983	0.002941	-2.53147
4	80.24202	0.095598	1.394102	0.144294	0.001852	-2.73237
6	80.2189	0.095723	1.393977	0.144256	0.001552	-2.80924
8	79.42675	0.100033	1.389667	0.142911	0.002066	-2.68481
10	78.60204	0.104566	1.385134	0.141492	0.002474	-2.60653
12	77.60958	0.110085	1.379615	0.139758	0.002822	-2.54937
14	76.57825	0.115895	1.373805	0.137925	0.003099	-2.50881
16	75.37407	0.122778	1.366922	0.135744	0.003254	-2.48752
18	74.34482	0.128749	1.360951	0.133842	0.003487	-2.45753
20	73.05419	0.136355	1.353345	0.131409	0.003881	-2.41101
22	71.71581	0.144385	1.345315	0.128824	0.004222	-2.37452
24	70.22727	0.153494	1.336206	0.125873	0.004439	-2.3527
26	68.78834	0.162485	1.327215	0.122941	0.022532	-1.64719
28	67.4107	0.171271	1.318429	0.120057	0.080376	-1.09487
30	65.95967	0.180722	1.308978	0.116932	0.266374	-0.57451

Table 2. Time-Dependent Spectrometer Measurements for Trial 3

Time (minutes)	% Transmittance @ 586.1 nm	Absorbance	Absorbance of Cr(III)	Log of Absorbance of Cr(III)	Rate	Log of the Rate
2	85.87757	0.06612	1.18978	0.075467	-0.00137	0
4	84.8098	0.071554	1.184346	0.073479	0.002036	-2.69127
6	83.35352	0.079076	1.176824	0.070711	0.003455	-2.46151
8	81.96371	0.086378	1.169522	0.068008	0.004364	-2.36012
10	80.16919	0.095992	1.159908	0.064423	0.005188	-2.28504
12	78.03083	0.107734	1.148166	0.060005	0.005716	-2.24292
14	75.93905	0.119535	1.136365	0.055518	0.005918	-2.22781

16	73.87828	0.131483	1.124417	0.050927	0.006002	-2.22174
18	71.8745	0.143425	1.112475	0.04629	0.006089	-2.21542
20	69.75174	0.156445	1.099455	0.041177	0.005896	-2.22946
22	68.08411	0.166954	1.088946	0.037006	0.005688	-2.24504
24	66.1818	0.179261	1.076639	0.03207	0.005445	-2.26402
26	64.72404	0.188934	1.066966	0.02815	0.019529	-1.70932
28	63.22066	0.199141	1.056759	0.023976	0.065583	-1.18321
30	61.72451	0.209542	1.046358	0.01968	0.213792	-0.67001

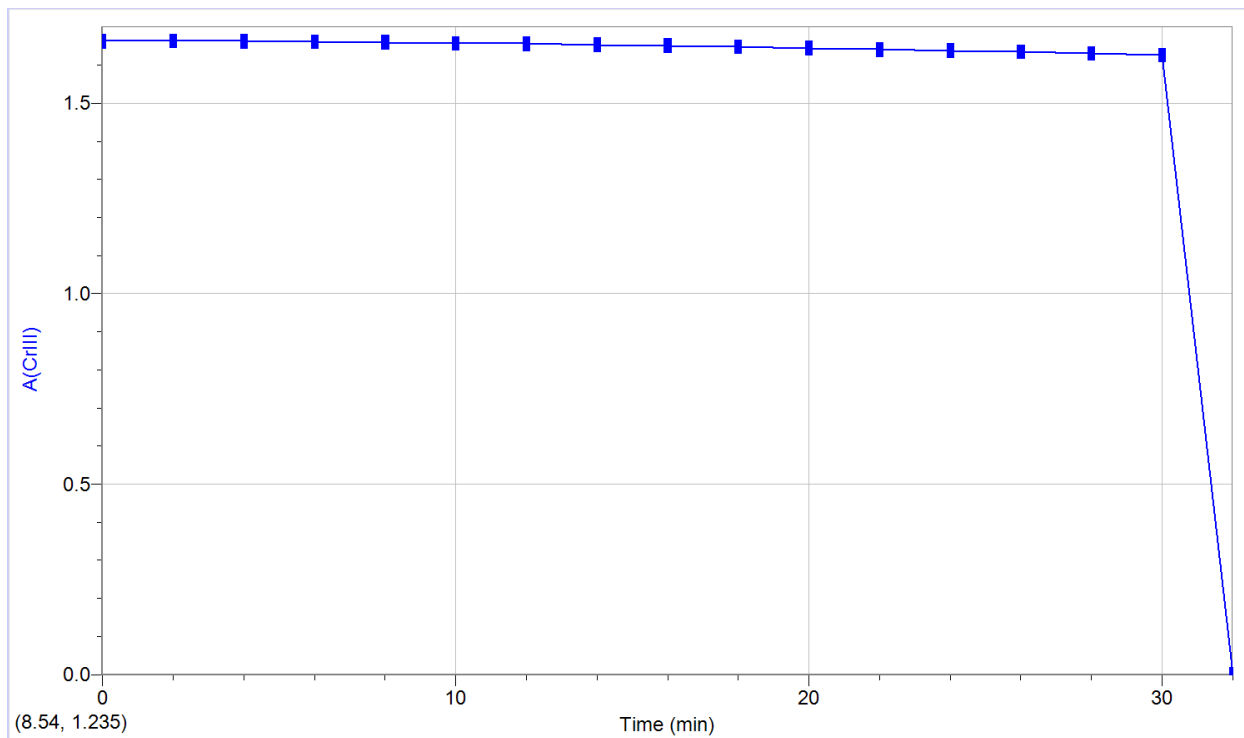


Figure 1. The absorbance of Cr(III) for trial 1.

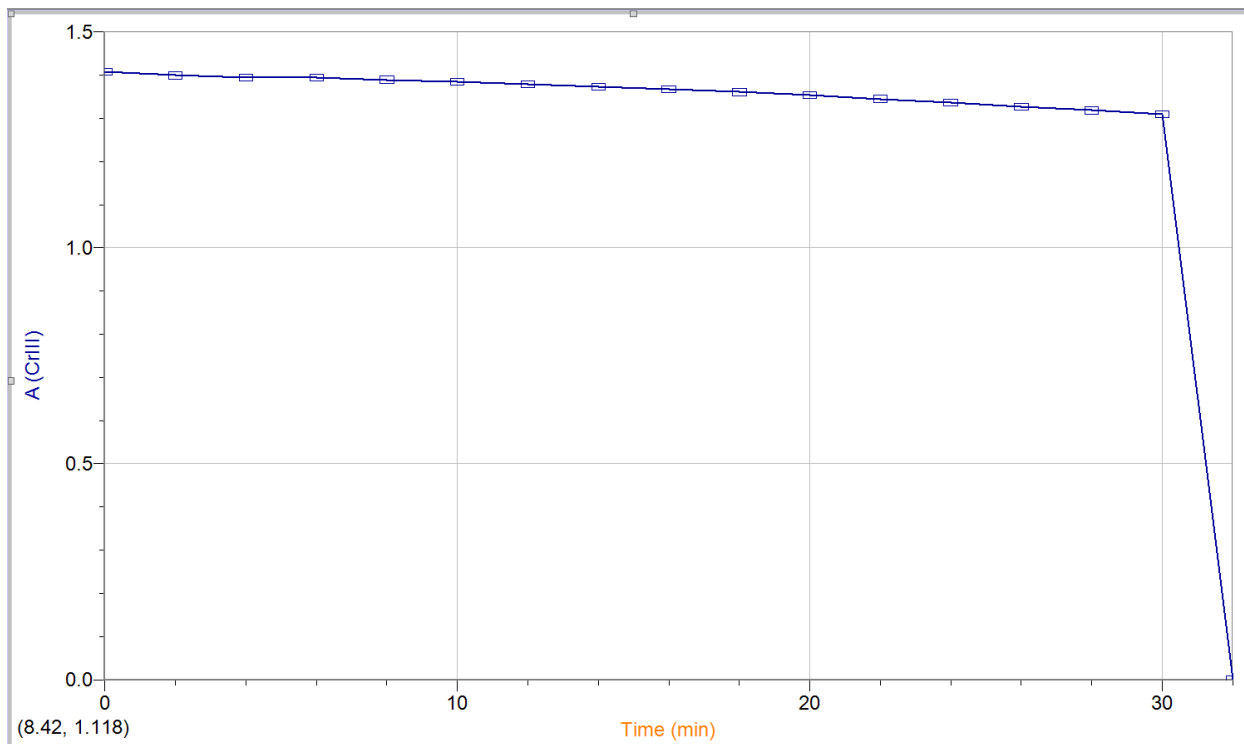


Figure 2. The absorbance of Cr(III) for trial 2.

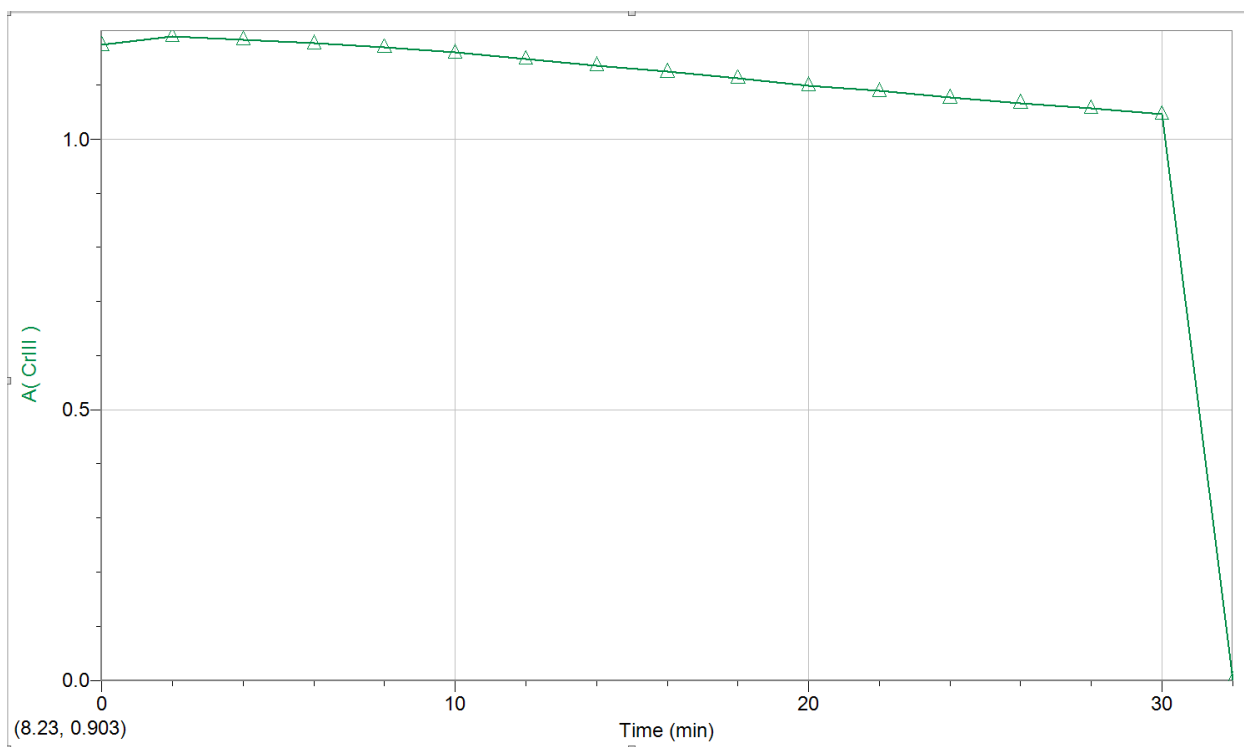


Figure 3. The absorbance of Cr(III) for trial 3.

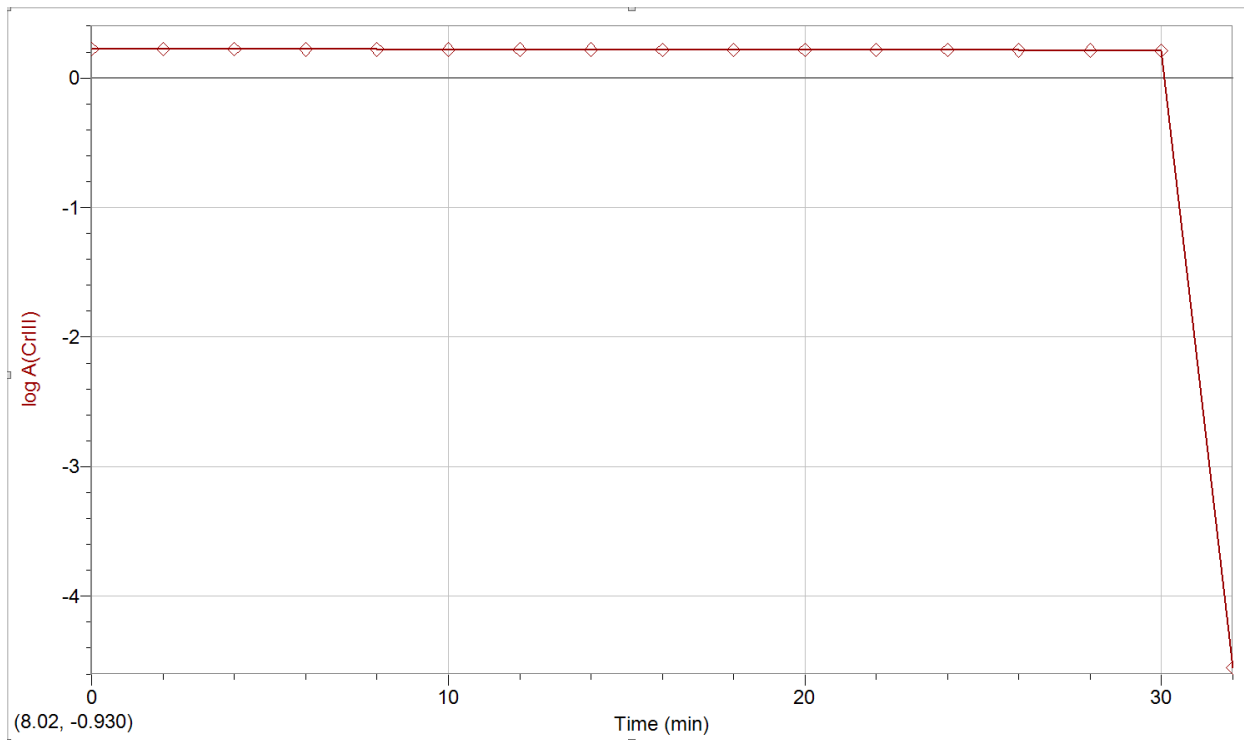


Figure 4. The log of the absorbance of Cr(III) for trial 1.

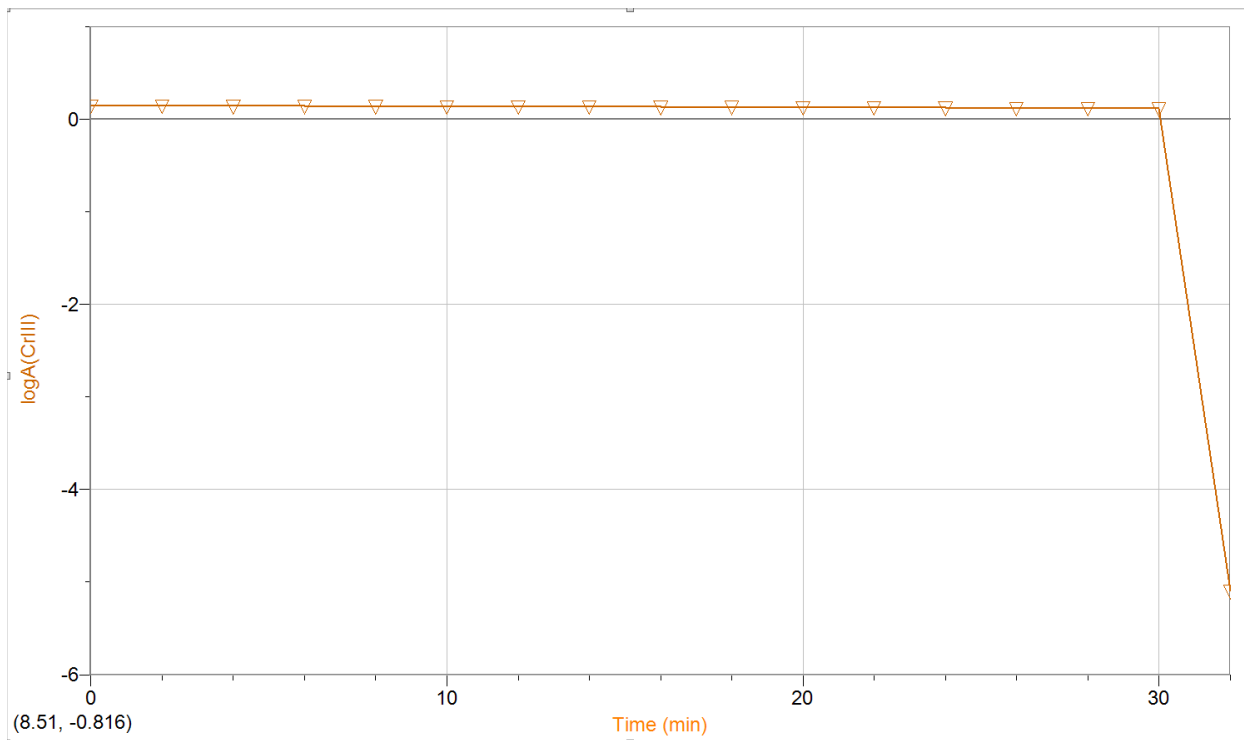


Figure 5. The log of the absorbance of Cr(III) for trial 2.

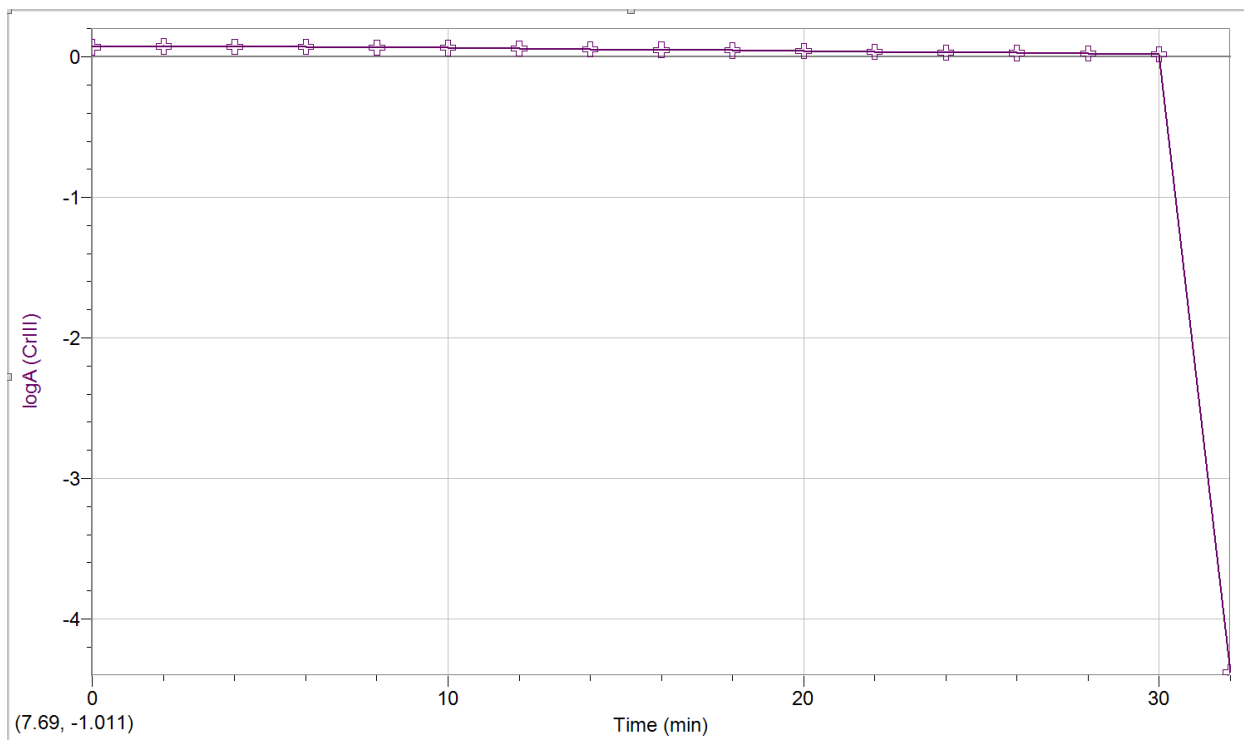


Figure 6. The log of the absorbance of Cr(III) for trial 3.

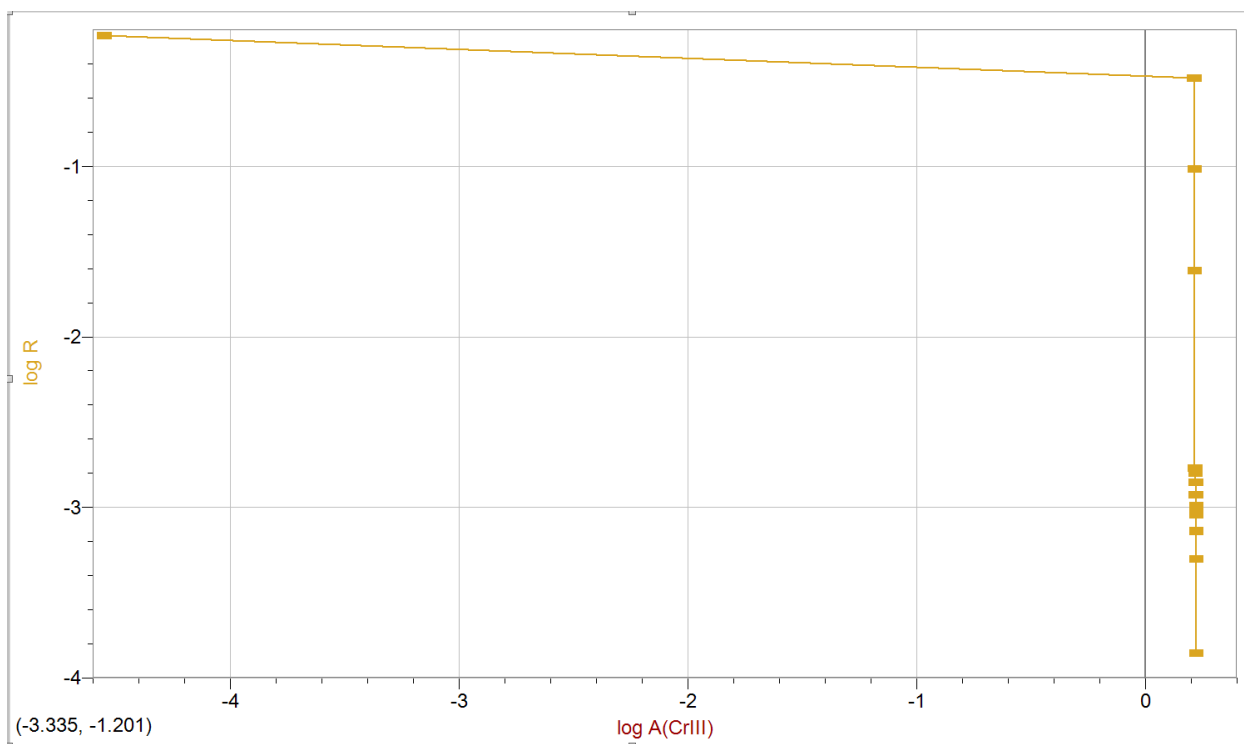


Figure 7. The log of the rate as a function of the log of the absorbance of Cr(III) for trial 1.

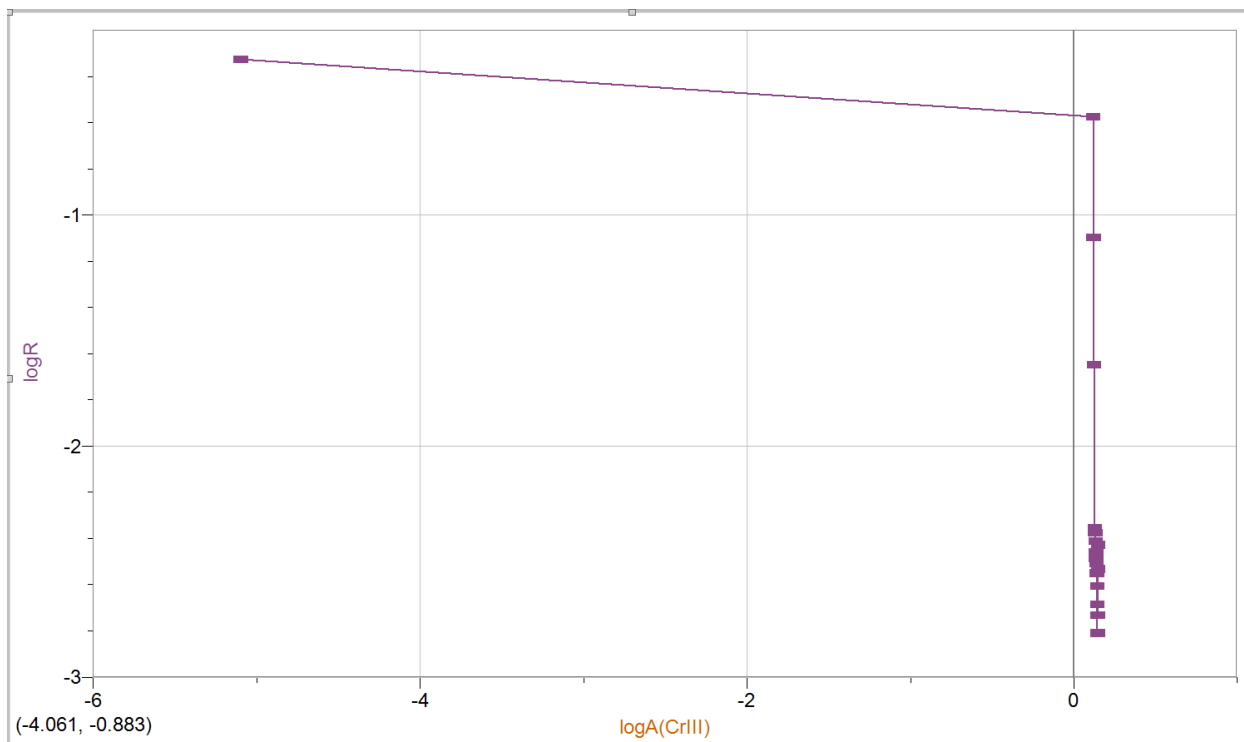


Figure 8. The log of the rate as a function of the log of the absorbance of Cr(III) for trial 2.

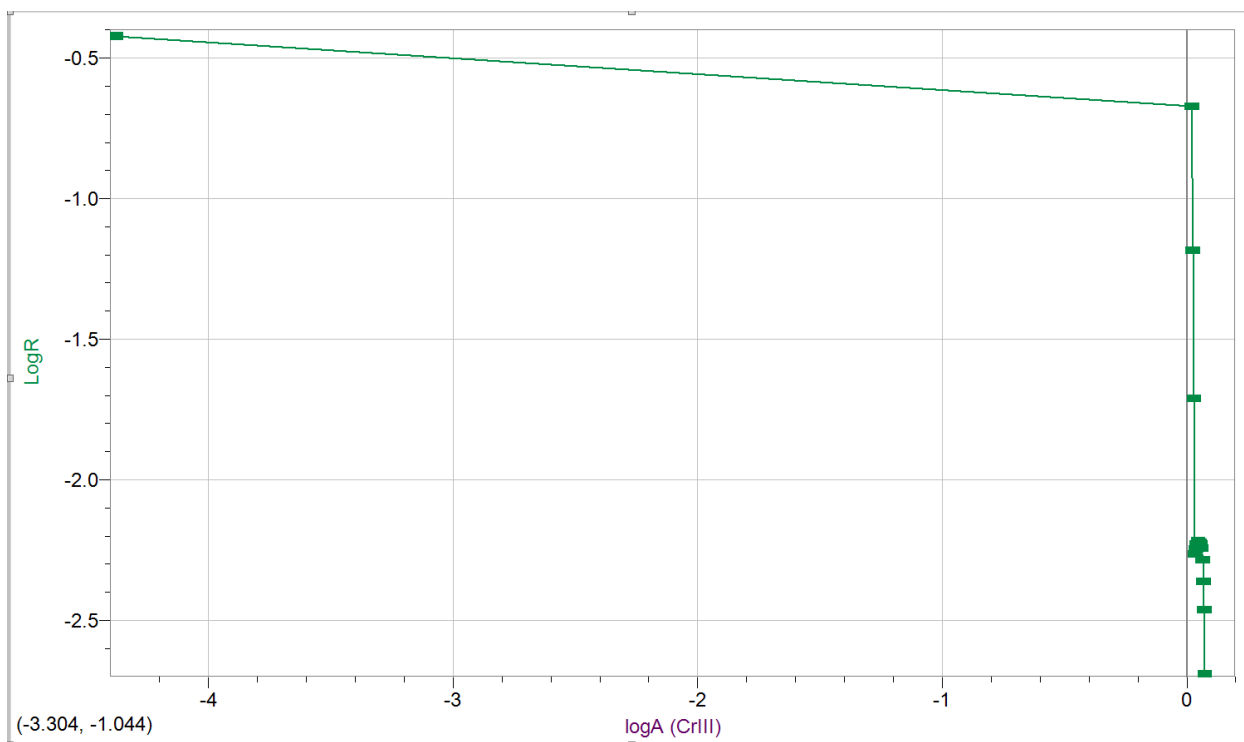


Figure 9. The log of the rate as a function of the log of the absorbance of Cr(III) for trial 3.

Calculations

All sample calculations are done using trial 1 at t=2.

Sample calculation for absorbance:

$$\begin{aligned} A &= -\log T \\ &= -\log (0.83) \\ &= 0.08 \end{aligned}$$

Sample calculation for $A_{\text{Cr(III)}}$:

$$\begin{aligned} A_{\text{Cr(III)}} &= A_{\infty} - A_t \\ &= 1.7 - A_2 \\ &= 1.7 - 0.08 \\ &= 1.6 \end{aligned}$$

Sample calculation for the log of the absorbance:

$$\begin{aligned} \text{Log of absorbance} &= \log A \\ &= \log (1.6) \\ &= 0.22 \end{aligned}$$

Sample calculation for the log of the rate:

$$\begin{aligned} \text{Log of rate} &= \log R \\ &= \log (0.00014) \\ &= -3.9 \end{aligned}$$

Discussion

The first and last data points were left out of the tables because they do not represent the progress of the reaction. There is no solution in the spectrometer at $t = 0$, and the solution at $t = 32$ has no Cr(III) ions left in it (since the reaction has been driven to completion), making both values useless in measuring absorbance.

Over the course of the 32 minutes in the spectrometer, the %T decreased for all trials (Tables 2, 3 and 4). This is because as the absorbance of the Cr(III) ion increased (and therefore concentration), the amount of light that could pass through the cuvette decreased. Tables 2, 3,

and 4 show that the trials using a higher pH had higher absorbance values, meaning that the higher the pH value the higher the absorbance.

The linearity of the graphs that show the log of absorbance of Cr(III) over time (Figures 4, 5, and 6) show that the overall reaction represents first order chemical kinetics.

The partial order of each reaction is not accurate as shown in figures 7-9. The slope of each graph (which is what represents the partial order) is very steep and also negative. Because of this, the actual slope was not calculated as it would not have been a good representation of the partial order. The reason for this could have been because of the short time frame of the experiment. If all of the reaction was observed and documented, as opposed to only 30 minutes, the graph should have had a slope that would have represented the true partial order.

The reaction between Cr(III) and EDTA is very slow. Due to the short time trial of only 30 minutes, only a small section of the reaction could be observed. This resulted in the graphs showing absorbance of Cr(III) over time (Figures 1, 2, and 3) appearing linear when in reality it should be exponential.

Since the volumes of each sample of EDTA were fairly consistent, the volume had no effect on the results. Temperature did affect the results, as shown when the sample was heated. An increase in temperature causes the reaction to proceed at a faster rate, and a decrease in temperature causes the reaction to proceed at a slower rate.

The cuvette may not have been properly cleaned before being placed in the spectrometer. This would have changed the way the light went through. A similar issue could have occurred if the cuvette was scratched or damaged. Another error that could have occurred could have been during the calibration. Poor calibration would have led to the wavelength being improperly recorded, resulting in the absorbance for all trials appearing lower than it truly was. Because of the amount of human error possible, the results are not easily reproducible.

Conclusion

The order of the reaction is first order. The partial order of Cr(III) for the reaction should be one, as the rate is directly proportional to the concentration, and therefore absorbance, of Cr(III). None of the trials exhibit this due to the observed reaction time being too short.

References

Dr. R. Venkateswaran, "If It Were Done... Then 'Twere Well It Were Done Quickly",
General Chemistry Laboratory Manual, 2016, Experiment 4, p (43-54)

Complexation. (2016). Retrieved November 10, 2016, from

<https://www.corrosionpedia.com/definition/305/complexation>

Laidler, K. J. (1996). International Union Of Pure and Applied Chemistry a Glossary of
Terms Used in Chemical Kinetics, Including Reaction Dynamics. *Pure & Appl.
Chem*, 68(1), 149–192.

Laidler, K. J. (2016). Reaction Rate. Retrieved November 7, 1998, from

<https://www.britannica.com/science/reaction-rate>

Spectrophotometry. (n.d.).

Raw Data

Run 1			Run 2			Run 3		
Time (min)	s @ 586.1 (%)	A	Time (min)	s @ 586.1 (%)	A	Time (min)	s @ 586.1 (%)	A
0	82.906	0.081415	0	82.892	0.081487	0	82.796	0.081989
2	83.048	0.080673	2	81.252	0.090167	2	85.878	0.066120
4	82.904	0.081424	4	80.242	0.095598	4	84.810	0.071554
6	82.624	0.082892	6	80.219	0.095723	6	83.354	0.079076
8	82.388	0.084138	8	79.427	0.10003	8	81.964	0.086378
10	81.704	0.087754	10	78.602	0.10457	10	80.169	0.095992
12	81.666	0.087956	12	77.610	0.11008	12	78.031	0.10773
14	81.170	0.090604	14	76.578	0.11589	14	75.939	0.11953
16	80.753	0.092839	16	75.374	0.12278	16	73.878	0.13148
18	80.103	0.096350	18	74.345	0.12875	18	71.874	0.14343
20	79.551	0.099355	20	73.054	0.13635	20	69.752	0.15644
22	78.846	0.10322	22	71.716	0.14439	22	68.084	0.16695
24	78.306	0.10620	24	70.227	0.15349	24	66.182	0.17926
26	77.679	0.10969	26	68.788	0.16249	26	64.724	0.18893
28	76.976	0.11364	28	67.411	0.17127	28	63.221	0.19914
30	76.231	0.11787	30	65.960	0.18072	30	61.725	0.20954
32	1.801	1.7444	32	3.238	1.4897	32	5.548	1.2559

Hannah St. John
860 8447

* did ^{all} last 2 pH's
with 35 min
instead of 45

Experiment 4

[% transmittance is measured from 0-100]

pH 4.5 EDTA - clear, no odour

↳ 4.0 mL in beaker test tube

↳ add 2 drops chromium nitrate to cuvette & it
turned light purple

Calibration

• min = 44.706 @ $\overset{586.10 \text{ nm}}{405.40}$ wavelength 49.489%

• max = 49.489 @ 425.50 51.783%

• mean = 45.905

• std devi = 1.3609

$\Delta y = 4.783$

• samples = 34

Starting the Experiment

pH 4.0 EDTA - 10.1 mL

↳ heated → turned dark purple

↳ % 30 min - 76.231%

↳ % 32 min - 1.801%

pH 4.5 EDTA - 9.9 mL

↳ heated → turned dark purple

↳ % 30 min - 65.960%

↳ % 32 min - 3.238%

pH 5.0 EDTA - 10 mL

↳ heated - turned dark purple

↳ % 30 min - 61.725%

↳ % 32 min - 5.548%

* all pHs of EDTA were colourless & odourless

* all pHs of EDTA turned a very very faint purple / grey
colour when the $\text{Cr}(\text{III})$ ion solution was added