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PLEASE NOTE: **If ANY of the above information is UNCLEAR or not provided, your grade will NOT be recorded!!**

Lab Day (circle): ***Fri***

Lab Week (circle): ***2***

Laboratory Report Form

Experiment 4.

Chemical Kinetics

Student's Initials: I.A.

18 November, 2016.

Experiment 4. Chemical Kinetics

Introduction:

Chemical reactions have a wide range of time that it takes to come to completion and among this variety are variables that can affect the speed of a reaction. One very common variable that has a great effect on a given reaction's rate is the concentration of reactants present. Much like chemical reactions themselves, each reactant in a given reaction is very unique and has it's own independent influence on the overall rate. A general equation can be used to describe the proportional relationship between rate and reactants:

$$Rate=k[A]^m[B]^n \text{ , where } A + B \rightarrow C + D$$

This represents the rate for the total reaction, however the rate can also be viewed in respect to each independent reactant, which is referred to as pseudo-order kinetics. The m and n exponents represent the order of the reaction, where m is the order with respect to A, n is the order with respect to B and m+n is the overall order.

While it is useful to determine the orders of a reaction rate, it can only be done through experiments and is not stoichiometricly related to its related chemical equation. In order to do so, the change in the rate of a reaction must be observed with respect to time, which can be done using a variety of methods. One approach is through tracking change using spectrophotometry.

Spectrophotometry explores the transmittance and absorbance of light through a substance and can be used to track the presence of that given substance. Transmittance is the ratio of intensity of light before and after it passes through a substance, while absorbance is the negative log of transmittance (Clarke, 1998):

$$T= I/I_o \text{ , } A=-\log T$$

In order to be used in the analysis of reaction rates, spectrophotometry, or more precisely absorbance, can be related to the concentration of a solution through Beer-Lambert's Law. It states that absorbance can be described as molar absorptivity coefficient times the path length times the concentration of the substance absorbing the light (Clarke, 1998):

$$A= \varepsilon bc \quad , \quad A \alpha c$$

If the molar absorptivity coefficient is a constant and the path length is held constant, the relationship can be found that A is proportional to concentration of the substance absorping the light. This would then reveal the concentration of the absorbing species in any given solution (Venkateswaran, 2016).

In this experiment, pseudo-first order kinetics will be demonstrated through the reaction of chromium (III) salt with EDTA of various pHs. Through the use of spectrophotometry and discussed theories, the final relationship of the partial-order with respect to Cr(III) ion can be found (Venkateswaran, 2016).

The reaction itself is that of a chromium (III) salt with EDTAs of varying pHs where the Cr(III) ions react with the hydrogen ions to form a Cr(III)-EDTA complex that is very absorptive, as it turns to a dark, aubergine colour. The overall reaction rate can therefore be written as:

$$\text{Rate}=k[\text{Cr(III)}]^{a}[\text{H}^{+}]^{b}$$

The 'a' value represents the partial-order with respect to Cr(III), making it the pertinent one in this lab. In order to find it, the reaction law can be rearranged to terms of Cr(III)

$$\text{Rate}=k_{\text{Cr}}[\text{Cr(III)}]^{a}\text{, where } k_{\text{cr}}= k[\text{H}^{+}]^{m}\,[\text{EDTA}]^{p} \text{ and is relative to Cr(III) only}$$

Using simple manipulations, a can be isolated as:

$$\log(\text{Rate}) = \log(k_{\text{Cr}}) + a\log[\text{Cr(III)}]$$

log(Rate) = ~~$\log(k_{Cr})$~~ + a log[Cr(III)], k_{Cr} and consequently it's log will be constant

$$\log(\text{Rate}) = a\log[\text{Cr(III)}]$$

$$a = \log(\text{Rate})/\log[\text{Cr(III)}]$$

In order to find the concentration of Cr(III), spectrophotometry can be used. The reaction will take place in a spectrometer, which will measure percent transmittance that can be changed into absorbance. This absorbance can be used to calculate the concentration of absorbing species, which is the the Cr(III)-EDTA complex. As the complex is formed, the Cr(III) decreases in concentration. In order to find the difference in absorbance to determine the absorbance of only Cr(III), the reaction will be forced to completion using a hot water bath and the absorbance of the final solution will be measured and used as the absolute value (Venkateswaran, 2016):

$$A_{\text{Cr(III)}}=A_{\text{final}}-A(t)$$

The absorbance of the Cr(III) ions is proportional to the Cr(III) concentration, therefore all that is left is to find rate. The rate at which the Cr(III) disappears is the equal to the change in [Cr(III)] over time, or the derivative of [Cr(III)] with respect to time. As log([Cr(III)]) represents the concentration of Cr(III) at a given time, the first derivative of this relationship is equal to the rate of the Cr(III) disappearance. This is the negative of the Cr(III)-EDTA complex appearance.

Using these two variables, their relationship can be graphed where log(Rate) is a function of log([Cr(III)]) and the slope of their linear relationship will be equal to the partial-order with respect to Cr(III).

Procedure: As described in the lab manual, with the modification in step 34 from 40 min to 30 min, and in step 36 from 42 min to 32 min. ("If It Were Done…Then 'Twere Well It Were Done Quickly" Chemical Kinetics, Dr. Rashmi Venkateswaran, 2016, Exp. 4, p. 44).

Observations/Data/Results:

Table 1: Observations of three experiment trials

Trial	State of reaction		
	Initial	Heated in hot water bath	Final
Calibration	The chromium nitrate in the cuvette was transparent and grey in colour, giving a minimum wavelength of 573.50nm avec un absorbance de 32.22%		
1 (pH of 4.0)	10.0 mL of pH 4.0 EDTA was observed as clear, transparent and odorless. With the addition of 2 drops of Cr(III) ion solution, the solution turned grey and slightly purple while remaining transparent.	The solution quickly turned a translucent, dark, aubergine purple within seconds of being submerged. The solution was only partially submerged in the hot water bath as the water had evaporated.	As the heated solution was cooled, there was no change in colour, transparency or odor. When the cuvette of original non-heated solution was removed, it was lavender in colour and slightly less transparent.
2 (pH of 4.5)	9.9 mL of pH 4.5 EDTA was observed as clear, transparent and odorless. With the addition of 2 drops of Cr(III) ion solution, the solution turned grey and slightly purple while remaining transparent.	The solution quickly turned a translucent, dark, aubergine purple within seconds of being submerged. The colour change begins at the top and of the test tube and moves down. The solution completely submerged in the hot water bath in this trial.	As the heated solution was cooled, there was no change in colour, transparency or odor. When the cuvette of original non-heated solution was removed, it was lavender in colour and slightly less transparent.
3 (pH of 5.0)	10.0 mL of pH 5.0 EDTA was observed as clear, transparent and odorless.	The solution quickly turned a translucent, dark, aubergine purple within seconds of being submerged.	As the heated solution was cooled, there was no change in colour, transparency or odor. When the cuvette of

	With the addition of 2 drops of Cr(III) ion solution, the solution turned grey and slightly purple while remaining transparent.	Colour change occurred faster than in previous 2 trials The solution completely submerged in the hot water bath in this trial.	original non-heated solution was removed, it was lavender in colour and slightly less transparent.

Table 2: Results of Trial 1, EDTA of pH 4.0

Time (min)	Transmittance %	Absorbance	Absorbance of Cr(III)	Log(Absorbance of Cr(III))	Rate of Cr(III)	Log(Rate)
0	81.3734848	0.089517085	1.550582915	0.190494994	0.028833192	-1.540107281
2	67.80036084	0.168767995	1.471332005	0.167710682	0.016495566	-1.782632765
4	67.62977661	0.169862047	1.470237953	0.167387629	0.00567515	-2.246022676
6	67.10904979	0.17321891	1.46688109	0.16639491	0.002566232	-2.590704052
8	66.67612672	0.176029637	1.464070363	0.165561949	0.001745399	-2.758105163
10	66.01417157	0.180362822	1.459737178	0.164274669	0.001925189	-2.71552665
12	65.46467055	0.183993013	1.456106987	0.163193286	0.001999327	-2.699116246
14	64.90099446	0.187748649	1.452351351	0.162071693	0.002346347	-2.629607753
16	64.08906805	0.193216044	1.446883956	0.160433701	0.002757311	-2.559514284
18	63.22098051	0.199138773	1.440961227	0.158652295	0.00300936	-2.521525875
20	62.28285339	0.205631499	1.434468501	0.156691016	0.003072703	-2.512479396
22	61.45219199	0.211462621	1.428637379	0.154922009	0.003118175	-2.506099515
24	60.56393618	0.217785907	1.422314093	0.152995513	0.00329195	-2.482546718
26	59.65418967	0.224359049	1.415740951	0.150983794	0.022929932	-1.639597234
28	58.52290224	0.232674145	1.407425855	0.148425525	0.084898677	-1.071099076
30	57.68150561	0.238963412	1.401136588	0.146480474	0.284210054	-0.546360562
32	2.290392494	1.640090088	9.91E-06	-5.00385329	0.506892193	-0.295084397

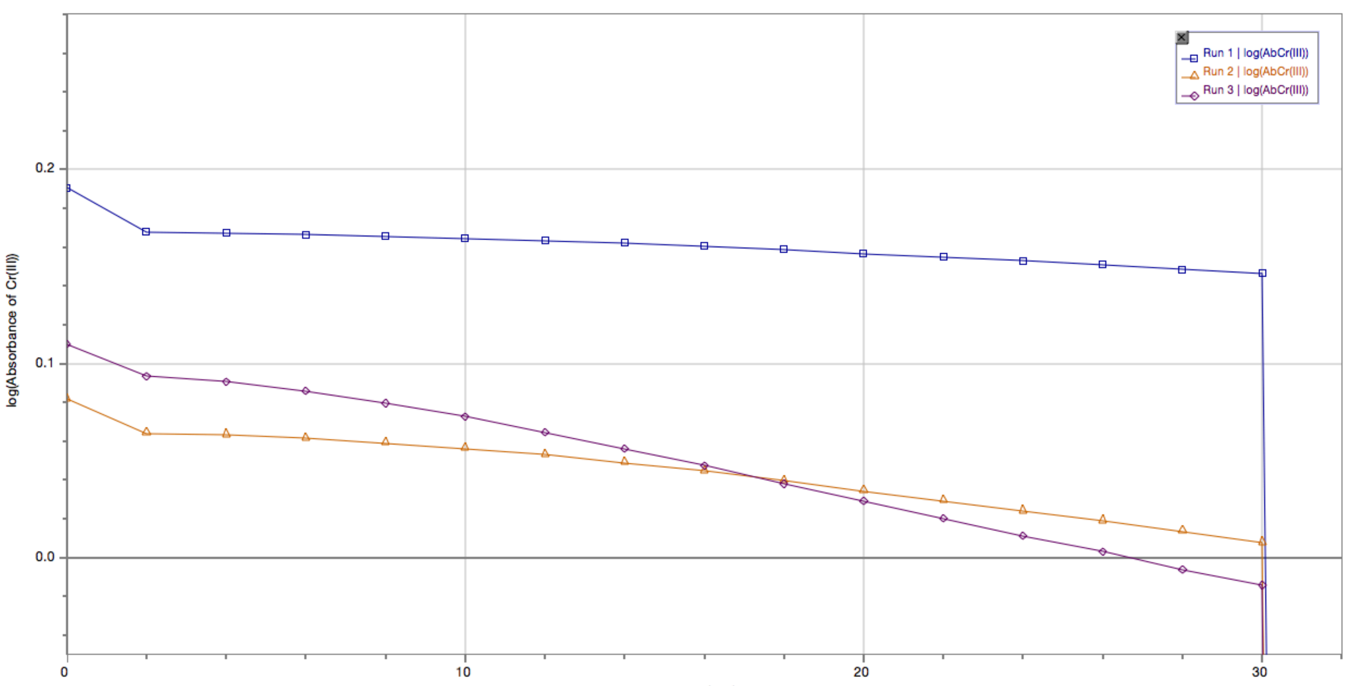
Table 3: Results from Trial 2, EDTA with pH of 4.5

Time (min)	Transmittance %	Absorbance	Absorbance of Cr(III)	Log(Absorbance of Cr(III))	Rate of Cr(III)	Log(Rate)
0	80.94078779	0.091832573	1.206867427	0.081659566	0.017752661	-1.750736545
2	72.44359561	0.140000002	1.158699998	0.063971006	0.01060991	-1.974288287
4	72.10950688	0.142007474	1.156692526	0.063217929	0.004564501	-2.340606687
6	71.3022455	0.146896793	1.151803207	0.061378283	0.003330906	-2.47743757
8	70.27147332	0.153220941	1.145479059	0.058987154	0.00338867	-2.469970757
10	69.1025718	0.160505789	1.138194211	0.056216372	0.004051621	-2.392371149
12	67.72994532	0.169219275	1.129480725	0.052878824	0.004771437	-2.321350787
14	66.08945132	0.179867854	1.118832146	0.048764936	0.00536616	-2.270336353
16	64.44273715	0.190826022	1.107873978	0.044490362	0.005867193	-2.231569623
18	62.60853638	0.203366449	1.095333551	0.039546391	0.006294775	-2.201019796
20	60.73768166	0.216541789	1.082158211	0.034290759	0.006435593	-2.191411435
22	58.95371934	0.22948879	1.06921121	0.029063503	0.006381918	-2.195048785
24	57.26135871	0.242138351	1.056561649	0.023894843	0.00628774	-2.201505404
26	55.69388582	0.25419248	1.04450752	0.018911571	0.020340738	-1.691633285
28	54.0160771	0.26747696	1.03122304	0.013352608	0.065185252	-1.185850652
30	52.36667099	0.280945034	1.017754966	0.00764323	0.20893447	-0.679989905
32	5.027374627	1.298658751	4.12E-05	-4.384587223	0.369373197	-0.432534621

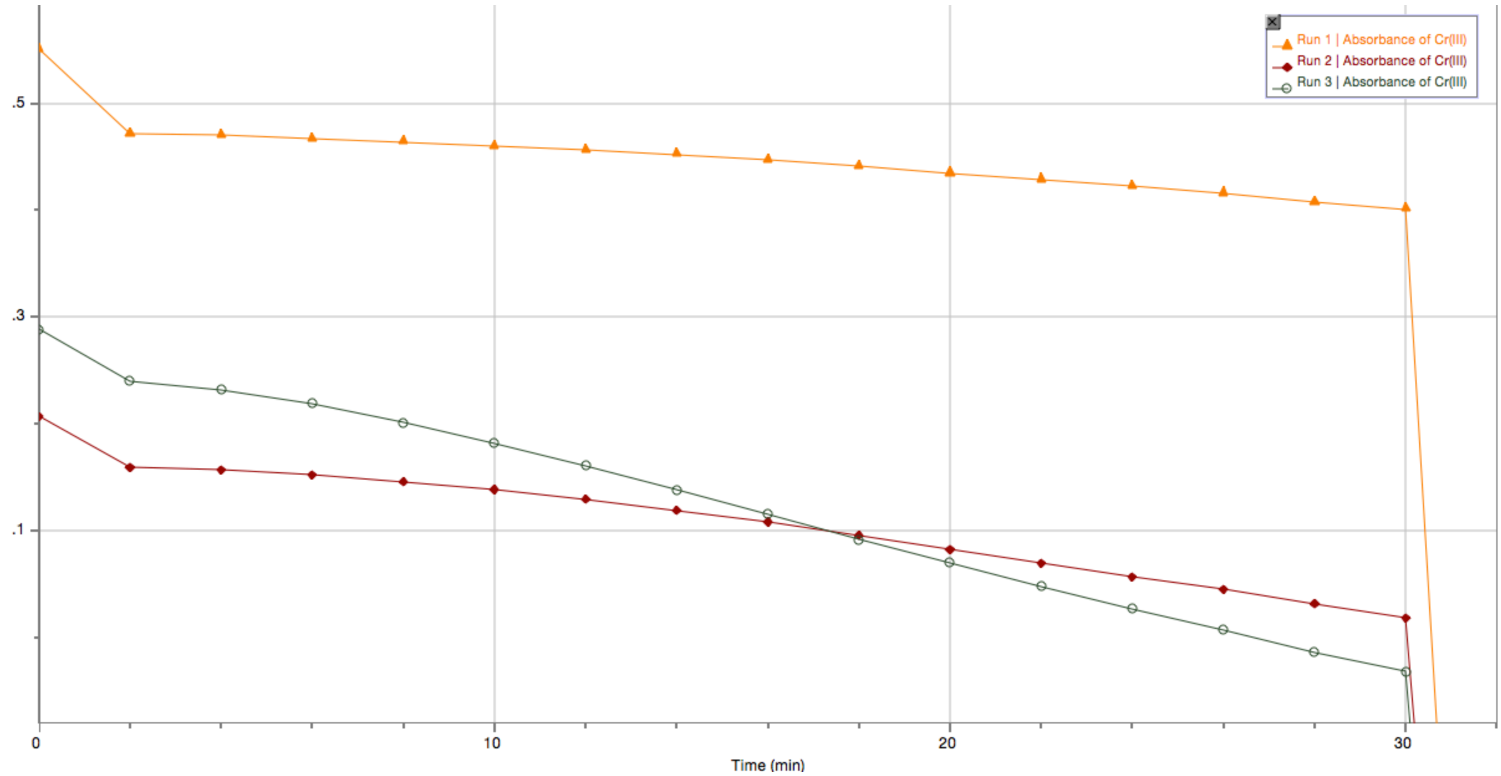
Table 4: Results from Trial 3, EDTA with pH of 5.0

Time (min)	Transmittance %	Absorbance	Absorbance of Cr(III)	Log(Absorbance of Cr(III))	Rate of Cr(III)	Log(Rate)
0	80.70031788	0.093124755	1.288275245	0.110008662	0.018723466	-1.72761376
2	72.20133749	0.141454757	1.239945243	0.093402507	0.012746064	-1.894623898
4	70.85554436	0.149626161	1.231773839	0.090530976	0.008067327	-2.093270354
6	68.75506922	0.162695276	1.218704724	0.085898494	0.00804868	-2.09427519

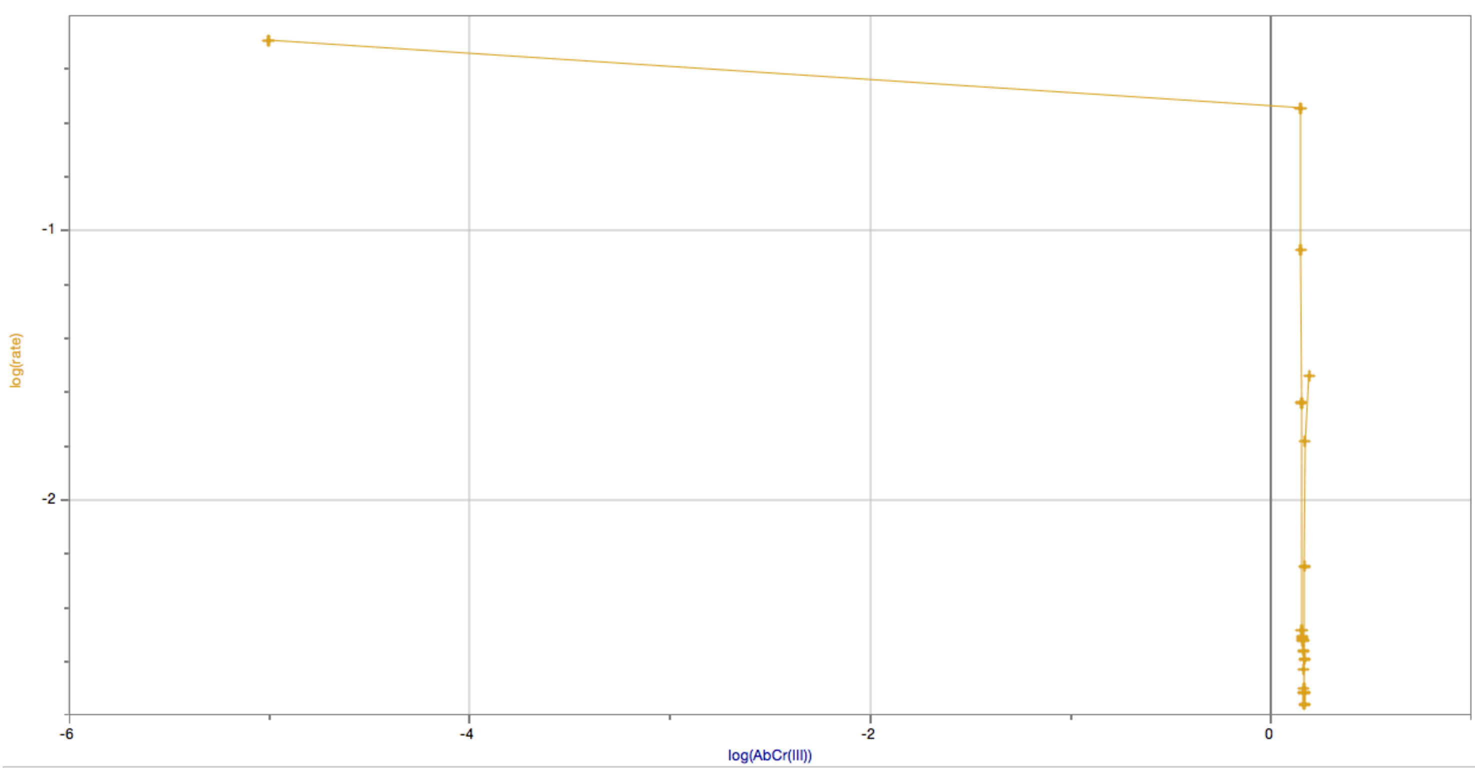
					3	
8	66.00760776	0.180406007	1.200993993	0.079540835	0.009009196	-2.045313975
10	63.14553764	0.199657335	1.181742665	0.072522915	0.010051316	-1.997777053
12	60.11687934	0.221003572	1.160396428	0.064606383	0.010794018	-1.96681688
14	57.10496943	0.243326097	1.138073903	0.056170465	0.011219014	-1.95004532
16	54.19379939	0.266050401	1.115349599	0.047411016	0.011475969	-1.940210631
18	51.29647233	0.2899125	1.0914875	0.038018766	0.011369599	-1.944254856
20	48.7541919	0.311988038	1.069411962	0.029145038	0.011005748	-1.958380447
22	46.37713594	0.333696075	1.047703925	0.020238571	0.010715786	-1.969975952
24	44.15033208	0.355066025	1.026333975	0.011288706	0.010325176	-1.986102525
26	42.20453462	0.374640884	1.006759116	0.002925571	0.023265036	-1.633296274
28	40.20684743	0.395699978	0.985700022	-0.006255234	0.065106007	-1.18637894
30	38.57570857	0.413686088	0.967713912	-0.014253015	0.200524517	-0.697832521
32	4.155324954	1.381395008	4.99E-06	-5.301721262	0.352033875	-0.453415544



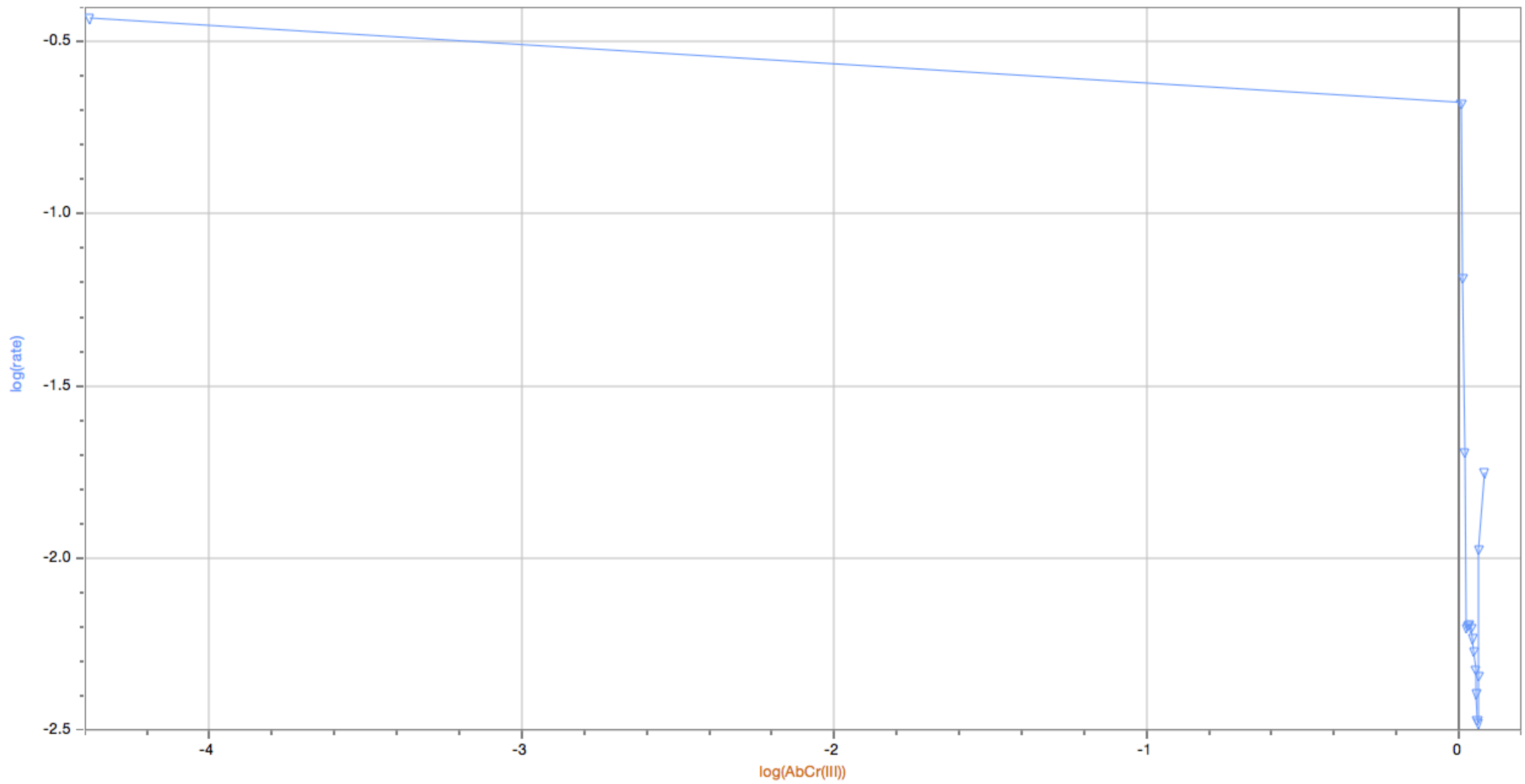
Graph 1: The absorbance of Cr(III) ion as a function of time, in min, for all 3 trials (see legend). There is a negati linear relationship between the two variables that is seen in all 3 trials.



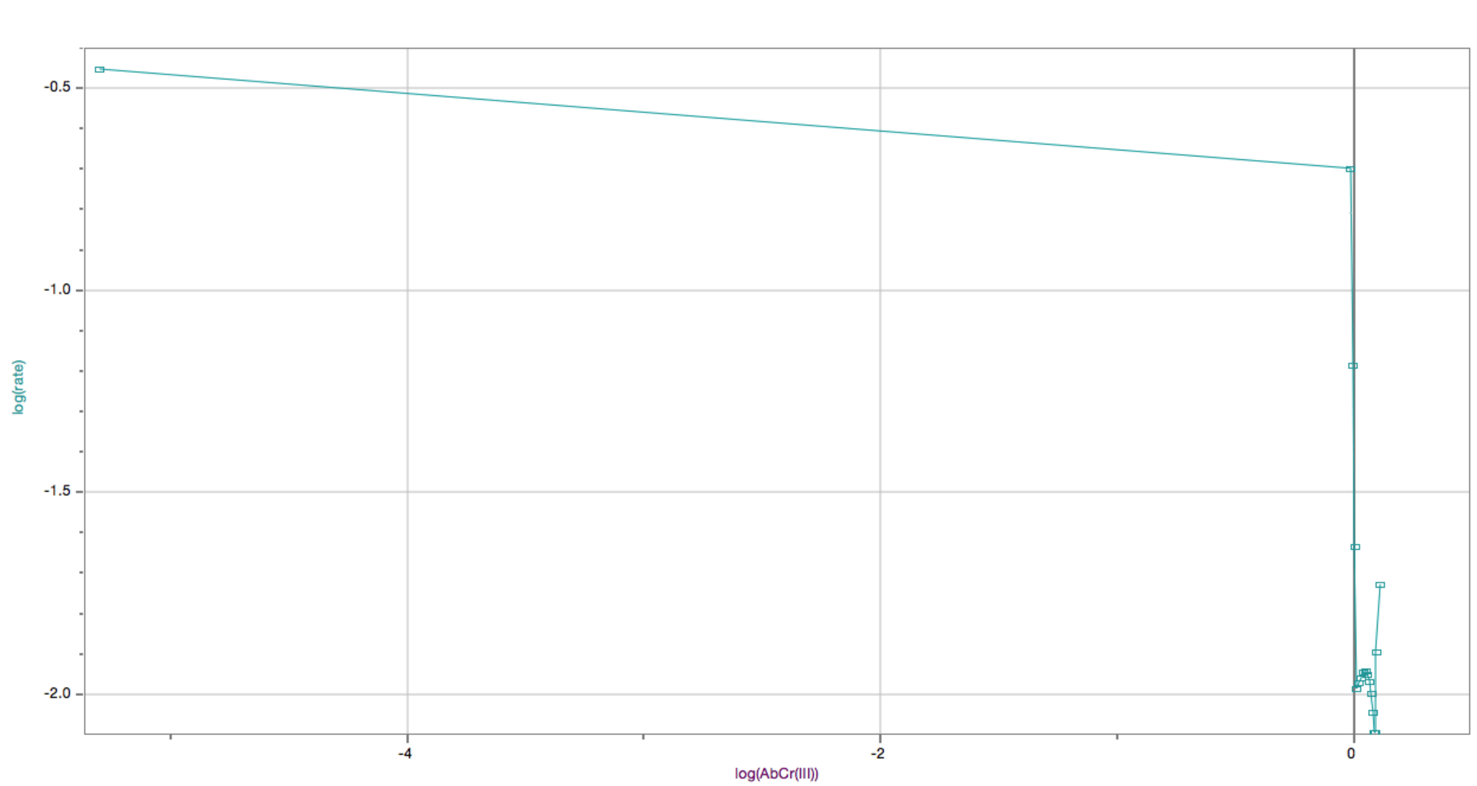
Graph 2: Log of the absorbance of the the Cr(III) ion as a function of time, in minutes, for all 3 trials. There is a negative, linear relationship seen between the two variables for all 3 trials.



Graph 3: Log of the rate as a function of the log of the Cr(III) ion's absorbance for trial 1 with an EDTA of pH 4.0. The relationship is irregular and no distinct pattern can be observed.



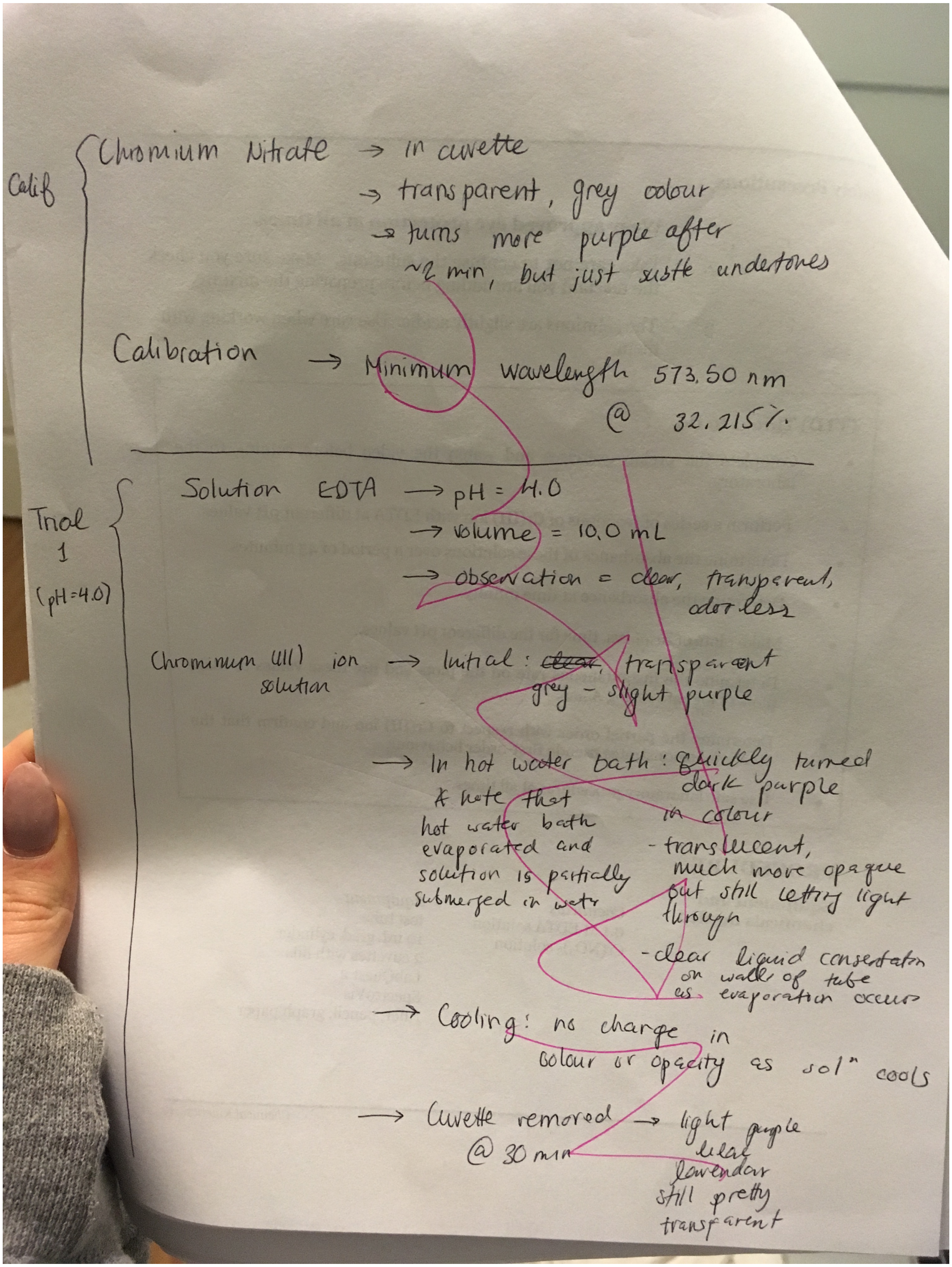
Graph 4: Log of the rate as a function of the log of the Cr(III) ion's absorbance for trial 2 with an EDTA of pH 4.5. The relationship is irregular and no distinct pattern can be observed.



Graph 5: Log of the rate as a function of the log of the Cr(III) ion's absorbance for trial 3 with an EDTA of pH 5.0. The relationship is irregular and no distinct pattern can be observed.

Table 4: Raw Data Results from Logger Pro for 3 trials

Run 1			Run 2			Run 3		
Time (min)	Trans @ (%)	A	Time (min)	Trans @ (%)	A	Time (min)	Trans @ (%)	A
0	81.373	0.089517	0	80.941	0.091833	0	80.700	0.093125
2	67.800	0.16877	2	72.444	0.14000	2	72.201	0.14145
4	67.630	0.16986	4	72.110	0.14201	4	70.856	0.14963
6	67.109	0.17322	6	71.302	0.14690	6	68.755	0.16270
8	66.676	0.17603	8	70.271	0.15322	8	66.008	0.18041
10	66.014	0.18036	10	69.103	0.16051	10	63.146	0.19966
12	65.465	0.18399	12	67.730	0.16922	12	60.117	0.22100
14	64.901	0.18775	14	66.089	0.17987	14	57.105	0.24333
16	64.089	0.19322	16	64.443	0.19083	16	54.194	0.26605
18	63.221	0.19914	18	62.609	0.20337	18	51.296	0.28991
20	62.283	0.20563	20	60.738	0.21654	20	48.754	0.31199
22	61.452	0.21146	22	58.954	0.22949	22	46.377	0.33370
24	60.564	0.21779	24	57.261	0.24214	24	44.150	0.35507
26	59.654	0.22436	26	55.694	0.25419	26	42.205	0.37464
28	58.523	0.23267	28	54.016	0.26748	28	40.207	0.39570
30	57.682	0.23896	30	52.367	0.28095	30	38.576	0.41369
32	2.290	1.6401	32	5.027	1.2987	32	4.155	1.3814



Calib

Chromium Nitrate → in cuvette
→ transparent, grey colour
→ turns more purple after ~2 min, but just subtle undertones

Calibration → Minimum wavelength 573.50 nm @ 32.215%

Trial 1 (pH=4.0)

Solution EDTA → pH = 4.0
→ volume = 10.0 mL
→ observation = clear, transparent, odorless

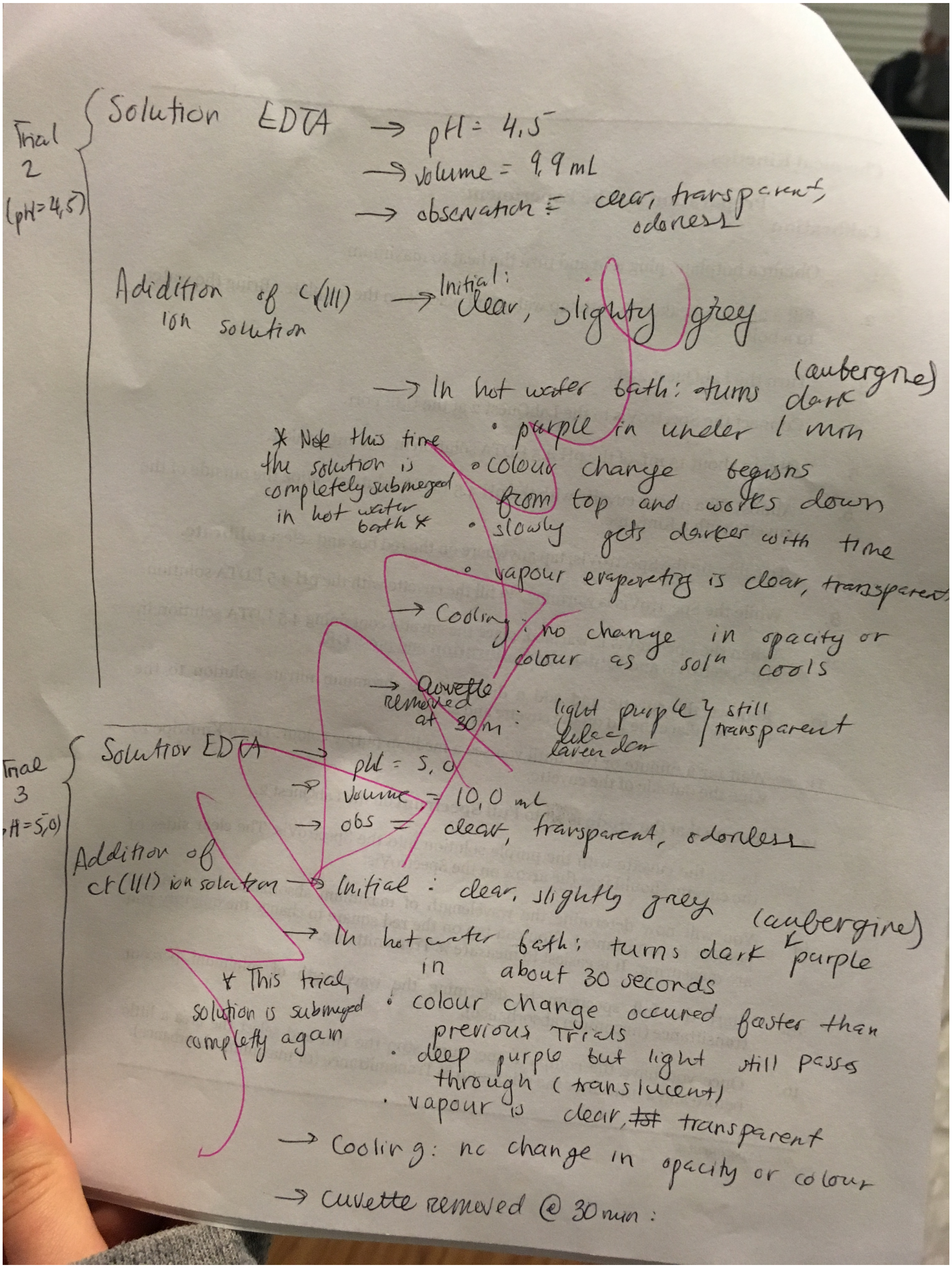
Chromium (III) ion solution → Initial: ~~clear~~, transparent grey - slight purple
→ In hot water bath: Quickly turned dark purple in colour
- translucent, much more opaque but still letting light through
- clear liquid condensation on walls of tube as evaporation occurs

* note that hot water bath evaporated and solution is partially submerged in water

→ Cooling: no change in colour or opacity as sol^n cools

→ Cuvette removed @ 30 min → light purple, lilac, lavender, still pretty transparent

Figure 1: Raw Data for Calibration and Trial 1



Trial 2 (pH = 4,5)

Solution EDTA → pH = 4,5
→ volume = 9,9 mL
→ observation: clear, transparent, odorless

Addition of Cr(III) ion solution → Initial: clear, slightly grey

→ In hot water bath: turns dark (aubergine) purple in under 1 min

- colour change begins from top and works down
- slowly gets darker with time
- vapour evaporating is clear, transparent

* Note this time the solution is completely submerged in hot water bath *

→ Cooling: no change in opacity or colour as soln cools

→ Cuvette removed at 30 m: light purple / lilac / lavender, still transparent

Trial 3 (pH = 5,0)

Solution EDTA → pH = 5,0
→ Volume = 10,0 mL
→ obs = clear, transparent, odorless

Addition of Cr(III) ion solution → Initial: clear, slightly grey

→ In hot water bath: turns dark (aubergine) purple in about 30 seconds

- colour change occured faster than previous Trials
- deep purple but light still passes through (translucent)
- vapour is clear, ~~##~~ transparent

* This trial, solution is submerged completly again

→ Cooling: no change in opacity or colour

→ Cuvette removed @ 30 min:

Figure 2: Raw Data for Trial 2 and Trial 3

Calculations:

Sample Calculation for each calculated column in Logger Pro.
1. Absorbance – absorbance at 2 minutes for Trial 1

$A = -\log(T)$

$A = -\log\left(\frac{\%T}{100\%}\right)$

$A = -\log\left(\frac{1}{67.800}\right)$

$A = 0.16877$

2. Absorbance of Cr(III) – absorbance at 2 minutes for Trial 1

$A_{Cr(III)} = A_{\infty} - A_t$

$A_{Cr(III)} = 1.64010 - 0.16877$

$A_{Cr(III)} = 1.471$

3. Log of Cr(III) absorbance – absorbance at 2 minutes for Trial 1

$\log(A_{Cr(III)}) = \log(1.471)$

$\log(A_{Cr(III)}) = 0.168$

4. Rate
Calculated by Logger Pro value by the tangent of the log(Absorbance of Cr(III)) at a given time.

5. Log of rate – absorbance at 2 minutes for Trial 1

$\log(Rate) = \log(0.0165)$

$\log(Rate) = -1.783$

6. Determination of partial order with respect to Cr(III)
The order would be found by taking the derivative of the final graph (log(rate) as a function of log(absorbance of Cr(III)), however due to the shape of the graph, a linear regression could not be done and therefore the order was not found. (See Discussion for further explanation)

Discussion:

This experiment made use of spectrophotometry to study the kinetics of a reaction by recording the percent transmittance of a solution throughout the course of a reaction. As EDTA with different pH values reacted with Cr(III) ions, a complex formed that absorbed more light and consequently the presence of the new complex could be determined based on the percent transmittance of light. Through manipulations of the rate law, as outlined in the introduction, the partial order of the reaction with respect to Cr(III) could be determined:

$$\text{Rate} = k_{Cr}[Cr(III)]^{a}$$

(note that k_{Cr} is the constant relative to Cr(III); $k_{Cr} = k[H^{+}]^{m}[EDTA]^{p}$)

$$\log(\text{Rate}) = \log(k_{Cr}) + a\log[Cr(III)]$$

Given that the k_{Cr} is a constant, the $\log(k_{Cr})$ would also be constant and therefore not affect the relationship between the rate and concentration of Cr(III). Their relationship, therefore, should be directly proportional and when plotted as log(rate) as a function of log([Cr(III)]), the slope of their linear relationship would give the 'a' value. This 'a' value is the exponent that Cr(III) has in the rate law, therefore describes the partial order of the rate with respect to Cr(III).

With this unique approach to kinetics, the temperature and volume did not have any effect on the calculations. While the solution was heated up to ensure completion of reaction, this value was only used a reference to what the final absorbance is. It was not used to compare any relationships or directly observe trends, and therefore the temperature of the actual reaction was constant throughout.

This is the theoretical approach to finding the partial order, however in the experiment there were errors that prevented a final answer from being found. When the relationship was plotted on a graph, all three trials showed an irregular pattern for which a linear regression could not effectively be done. A piece of the graph could be selected to force a slope of 1, which was the expected partial order (see discussion below), however this would not be representative of the collected data.

Although the patterns of the graphs seemed irregular, they were consistent with one other. As the trials were repeated, they reproduced consistent trends. This is important as it suggests that rather than there being an error with each individual trial, the issue was common for all of them. One plausible explanation is the fact that the trial time was very short and a steady pattern was not able to establish for the trials, resulting in data that was very scattered and incomplete. The original reaction of EDTA with chromium ion takes hours but, due to limited time in the laboratory, the reaction was only able to proceed for 30 minutes until it was forced to completion. This could result in a sampling error where the sample size was too small and therefore did not accurately represent what was taking place. Had the reaction had more time to proceed, results may have established a clearer pattern and gave more accurate results.

Nonetheless, the results did show other consistent relationships throughout the experiment. As time went on, the reaction proceeded and there were more Cr(III)-EDTA complex products forming to absorb the light, which resulted in a linear decrease of transmittance over time/linear increase of absorbance over time. Furthermore, the log(Cr(III)) as a function of time showed a negative, linear relationship for all 3 trials. The derivative of this relationship represented the rate of disappearance of Cr(III) ion solution and consequently the negative rate of the Cr(III) ion production. Having a linear relationship as such suggests that the rate of production is therefore linear and in the first order with respect to Cr(III) ion.

The different values of pH for the EDTA solutions used gave different results but still supported consistent relationships, as previously discussed. In addition, the changes in pH and the range of the values they generated suggest some information about the partial order with respect to the [H^+] ion. As the pH increased linearly by intervals of 0.5, the absorbance and and log([Cr(III)]) did not change correspondingly. In this perspective, the [H+] ions were the independent, changing variable and as pH increased, the [H^+] decreased. The trend in absorbance, however, did not change consistently between trials, as Trial 2 started with a high absorbance and decreased, however Trial 3 began with an even higher absorbance yet decreased to a final lower one. The same can be said for the relationship of log([Cr(III)]) as a function of time. This suggests that the partial order of with respect to the hydrogen ion is neither first or second order, but rather a more complex number for which a separate experiment would need to be done.

Regardless of an accurate slope not being possible to read on the final graphs, these observations support that the reaction has a partial first order of 1 with respect to the Cr(III) ions.

Conclusion:

Although the partial-order could not be calculated through an algebraic comparison of 'log(rate)' as a function of 'log([Cr(III)])', the linear relationships of 'log([Cr(III)])' and 'Absorbance of Cr(III)' as functions of time strongly suggest that the partial order of the reaction with respect to Cr(III) is 1.

References:

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