

CL 433 Chemical Engineering Lab-4 [2024]

Experiment Number	MT407
Title	Kinetics of Esterification Reaction

Sub-group Code	A8a
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Date of Experiment	13/8/2024
Date of Report Submission	16/8/2024

Roll Number	Name	Responsibility owned (data, analysis, plots, report)
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(For use by examiners only)

Criterion		Faculty assigned marks
Calculations		
Graphical plots		
Hypothesis testing		
Report quality		
Initials with date		

R&P TA initials with date		
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OBJECTIVE

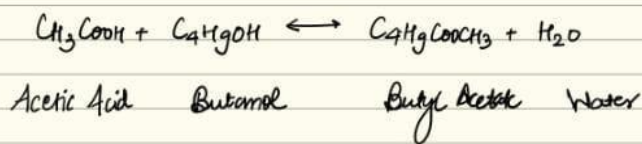
Kinetics of a (Solid-liquid) Esterification Reaction

Aim

To determine the reaction rate constants for the forward and backward reactions for esterification of acetic acid with butanol at different temperatures.

REACTION

Reaction



THEORY

Theory

The synthesis of butyl acetate is done through esterification of acetic acid with n-butanol. The ester has wide application as a versatile solvent in chemical industry. It is a reversible reaction that takes place in the presence of acid catalyst. The catalyst used in the present experiment is a solid heterogeneous catalyst. Hence, reaction takes place on the surface of the catalyst. If the reaction is performed in a batch reactor, the conversion will increase and the reaction rate will drop with respect to time. Eventually it will attain equilibrium.

Kinetic Model

Among all the models the simplest model is the pseudohomogeneous model given by the following rate equation:

$$-r_{\text{CH}_3\text{COOH}} = k_1 \text{CH}_3\text{COOH} \text{C}_4\text{H}_9\text{OH} - k_2 \text{C}_4\text{H}_9\text{COOCH}_3 \text{H}_2\text{O}$$

where k is the reaction equilibrium constant (i.e. k_1/k_2) that can be independently calculated using the following relation:

$$\ln \frac{k}{k^0} = \frac{\Delta H_R^{\circ(l)}}{R} \left[\frac{1}{T_0} - \frac{1}{T} \right]$$

$$\text{where, } k^0 = \exp \left[- \frac{\Delta G_R^{\circ(l)}}{RT_0} \right]$$

$$\Delta H_R^{\circ(l)} = -3.887 \text{ KJ/mol}, \quad \Delta G_R^{\circ(l)} = -8.889 \text{ KJ/mol}$$

SCHEMATIC DIAGRAM

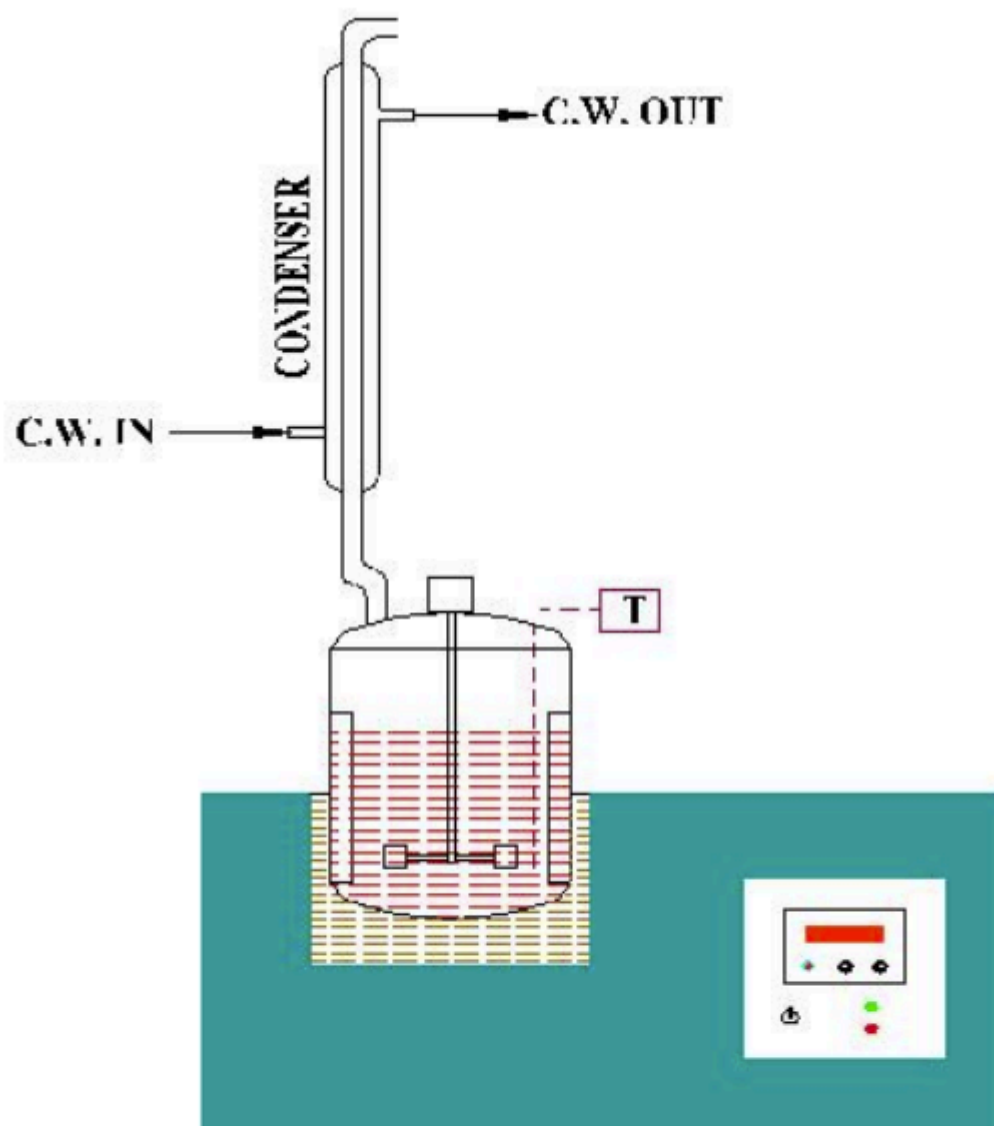


Figure 38.1: Schematic diagram of the Esterification setup

RAW DATA

DATA SHEET

Course: CL 433 A-8 (a8b) Date: 13/8/24

Expt. Number & Name: MT 407 Rⁿ Kinetic & Esterification

Reactor 1			Reactor 2		
Time (min)	Temp (°C)	Vol (ml)	Time (min)	Temp (°C)	Vol (ml)
0	43	8	0	42	7.9
5	46	7.6	5	44	7.5
10	46	7.4	10	44	7.2
20	46	7.1	20	43	6.4
30	45	6.8	30	42	6.2
45	45	6.1	45	41	5.7
60	44	5.9	60	41	5.2

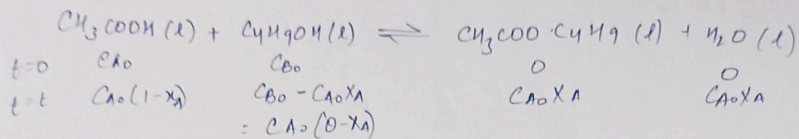
Reactor 3			Reactor 4		
Time (min)	Temp (°C)	Vol (ml)	Time (min)	Temp (°C)	Vol (ml)
0	70	7 ml	0	83	8
5	75	6.4	5	85	5.8
10	76	5.6	10	85	4.9
20	75	4.8	20	85	4.2
30	73	4.2	30	83	4
45	74	4.2	45	83	3.2
60	73	3.5	60	83	2.1

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SAMPLE CALCULATIONS

SAMPLE CALCULATIONS



for C_{A0} and C_{B0} ,

2 moles of each were taken

$$C_{A0} = C_{B0} = \frac{2}{V_{\text{ac}} + V_{\text{EtOH}}} = \frac{2 \text{ mol}}{\frac{120}{1.05} + \frac{148}{0.81}} \times 1000 = 6.734$$

$$\theta = \frac{C_{B0}}{C_{A0}} = 1$$

Titration

$$N_1 V_1 = N_2 V_2$$

$$N_2 = 1 \text{ M NaOH}$$

V_1 = Sample volume = 1 ml, V_2 = Vol of NaOH used.

$$N_1 = \text{conc of acetic acid} = C_{A0}(1-x_A)$$

$$C_{A0}(1-x_A) = 1 \cdot V_2 \Rightarrow x_A = 1 - \frac{0.5 V_2}{C_{A0}}$$

For reactor 1 @ $t = 5 \text{ min}$

$$x_A = 1 - \frac{0.5 \times 7.6}{6.734} = 0.406 \quad 0.436$$

Rate Law

$$-r_A = -\frac{dC_A}{dt} = k_1 C_A C_B - k_2 C_{\text{ester}} C_{\text{H}_2\text{O}}$$

$$-\frac{d[C_{A0}(1-x)]}{dt} = k_1 C_{A0}^2 (1-x)(0-x) - k_2 C_{A0}^2 x^2$$

$$\frac{dx}{dt} = C_{A0} \left[k_1 (1-x)(0-x) - k_2 x^2 \right] = k_1 C_{A0} \left[(1-x)(0-x) - \frac{x^2}{k_1/k_2} \right]$$

$$\frac{dx}{dt} = k_1 C_{A0} \left[(1-x)(0-x) - \frac{x^2}{K} \right] \quad K = K_{\text{eq}} = \frac{k_1}{k_2} = \exp\left(-\frac{\Delta G}{RT}\right)$$

By Arrhenius Equation $\ln\left(\frac{k}{k_0}\right) = -\frac{\Delta H^\circ}{R}\left(\frac{1}{T} - \frac{1}{T_0}\right)$

$$k_0 = \exp\left(\frac{-\Delta H^\circ}{RT_0}\right) \Rightarrow k_0 = \exp\left(\frac{-3.187 \times 10^{-3}}{8.314 \times 298.15}\right)$$

$$= 36.089$$

$$k = k_0 \exp\left(-\frac{\Delta H^\circ}{R}\left(\frac{1}{T} - \frac{1}{T_0}\right)\right)$$

Differential Analysis

$$\frac{dx}{dt} = k_1 C_{A0} \left[(1-x)(0-x) - \frac{x^2}{K} \right] = k_1 f_2(x)$$

Consider reactor 1, $t = 5 \text{ min}$

$$\frac{dx}{dt} = \frac{x(t=5) - x(t=0)}{5 - 0} = 0.406$$

$$\frac{0.436 - 0.406}{5} = \frac{0.03}{5} = 0.006$$

$$f_2(x) = 6.734 \left[(1 - 0.436)^2 - \frac{0.436^2}{36.089 \exp\left(\frac{3887}{8.314(273+45)} - \frac{1}{25+273}\right)} \right]$$

$$= 2.12$$

Similarly we find $\frac{dx}{dt}$ and $f_2(x)$ for all times.

Upon performing linear regression, we obtain slope

$$k_1 = 4.73 \times 10^{-3}$$

$$k_2 = \frac{k_1}{K} = \frac{4.73 \times 10^{-3}}{32.701} = 0.00014$$

By Arrhenius law, $k = A e^{-E/RT} \Rightarrow \ln k = \ln A - \frac{E}{RT}$

Upon linear regression between $\ln k_1$ vs $1/T$

we get slope = $-\frac{E}{R} = -5633$ $E = 8.314 \times 5633$
 $4.68 \times 10^4 \text{ J/mol}$
 Intercept = $\ln A_f = 11.3$
 $A_f = 80,821$

Similarly $-\frac{E_b}{R} = -6100$ $E_b = 5.07 \times 10^4 \text{ J/mol}$
 $\ln A_b = 9.25$ $A_b = 10,404$

Integral Analysis

$$\frac{dx}{dt} = k_1 C_{A0} \left[(1-x)(0-x) - \frac{x^2}{K} \right]$$

$$k_1 \int_{x_0}^x dt = \int_{x_0}^x \left[C_{A0} \left((1-x)(0-x) - \frac{x^2}{K} \right) \right]$$

$$k_1 t = f_1(x)$$

where $f_1(x) = g(x) - g(x_0)$ $x_0 = \text{conversion at } t=0$

$$\text{and } g(x) = \frac{K}{\sqrt{K(0-1)^2 + 40}} \ln \left[\frac{2(K-1)x - \sqrt{K(0-1)^2 + 40} - K(0+1)}{2(K-1)x + \sqrt{K(0-1)^2 + 40} - K(0+1)} \right]$$

$t = 5$, for reactor 1.

$$f_1(x) = \frac{32.701}{\sqrt{4 \times 1}} \ln \left[\frac{2(32.701)(0.436) - \sqrt{4} - 32.701(2)}{2(32.701)(0.436) + \sqrt{4} - 32.701(2)} \right]$$

$$- \frac{32.701}{\sqrt{4}} \ln \left[\frac{2(32.701-1)(0.0347) - \sqrt{4} - 32.701(2)}{2(32.701-1)(0.0347) + \sqrt{4} - 32.701(2)} \right]$$

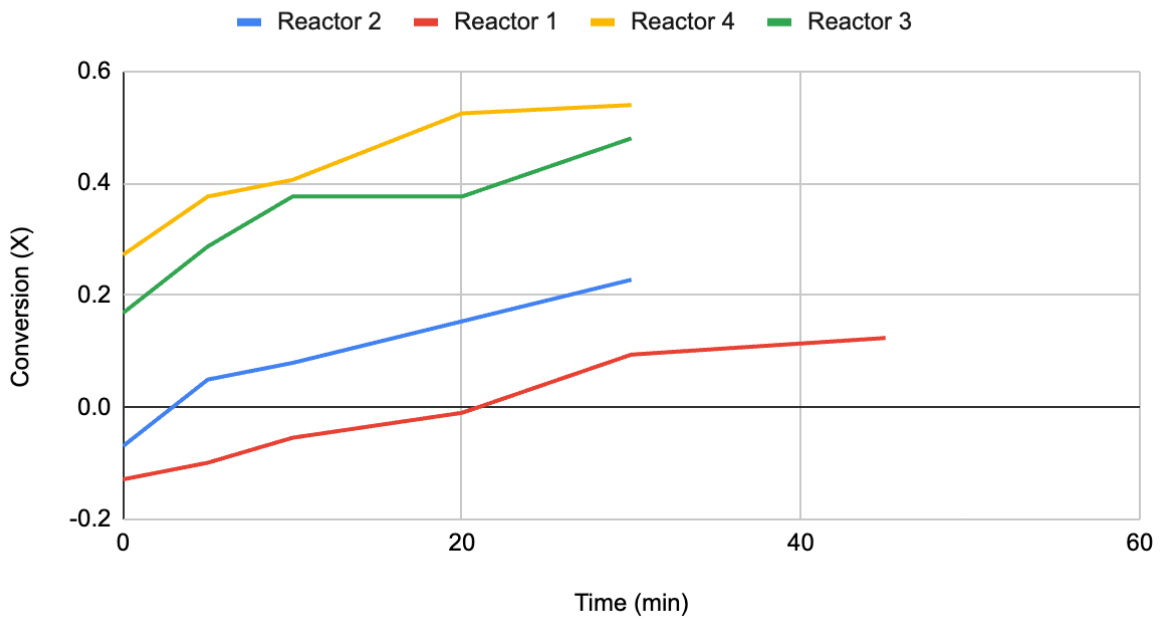
plotting $f_1(x)$ vs t and performing linear regression

we get slope

$$k_1 = 1.5 \times 10^{-3} \quad k_2 = \frac{k_1}{32.701} = 0.000046$$

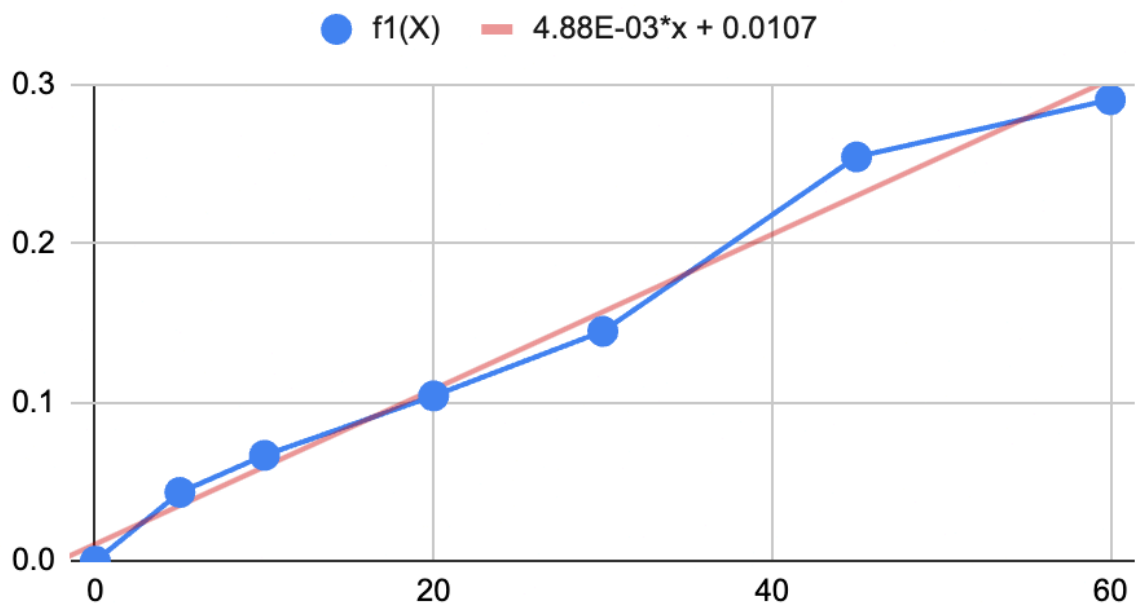
PLOTS

Conversion (X) vs. Time (min)

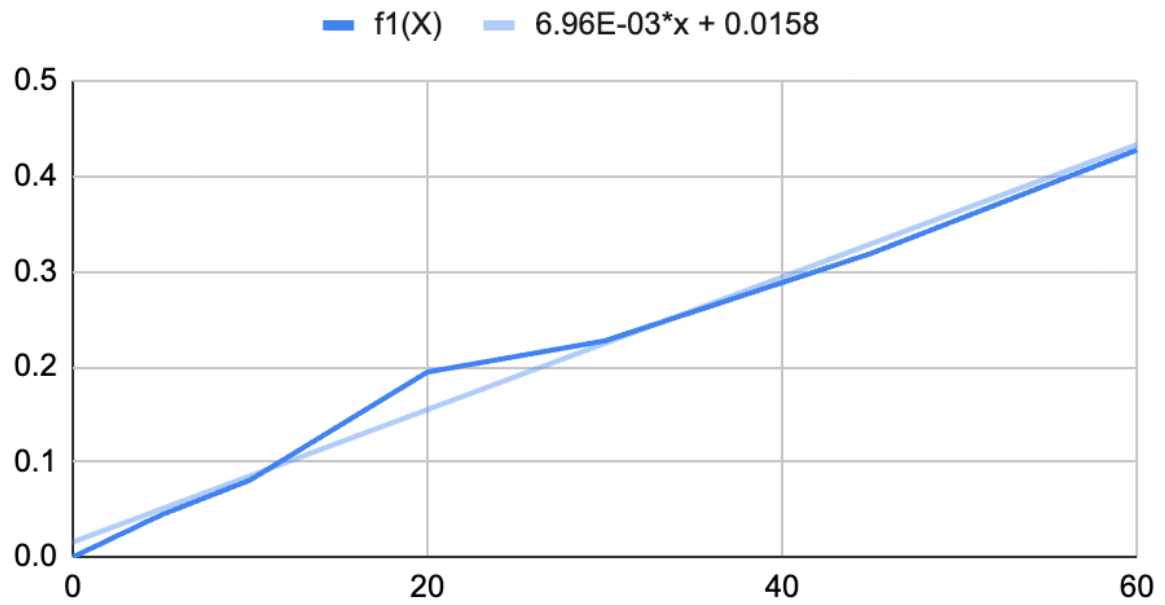


Integral Analysis

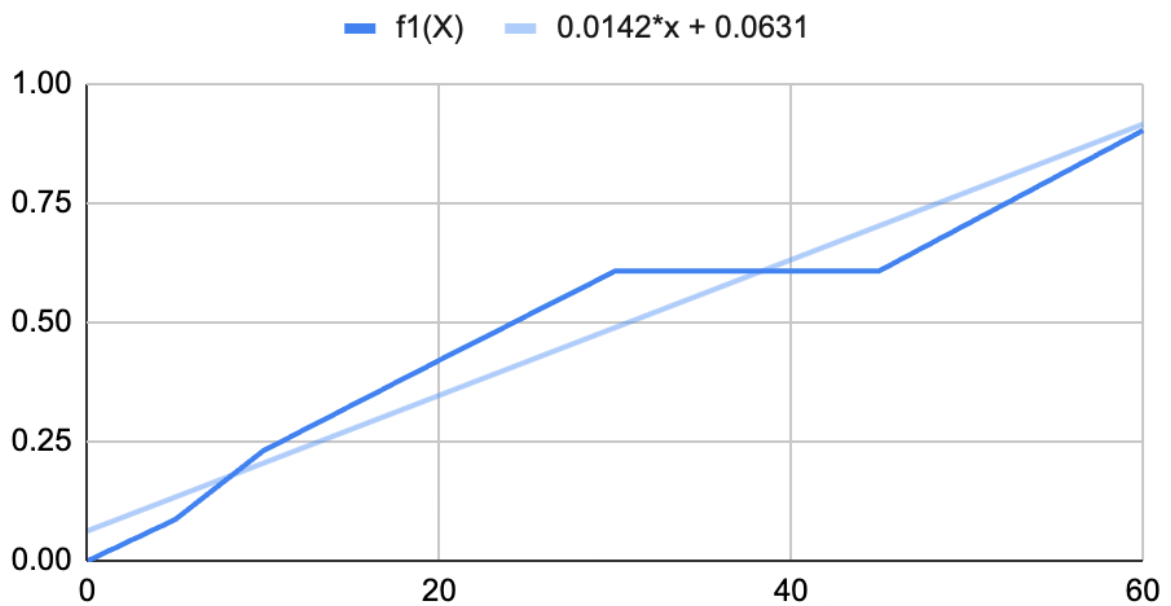
Time (min) and f1(X) -R1



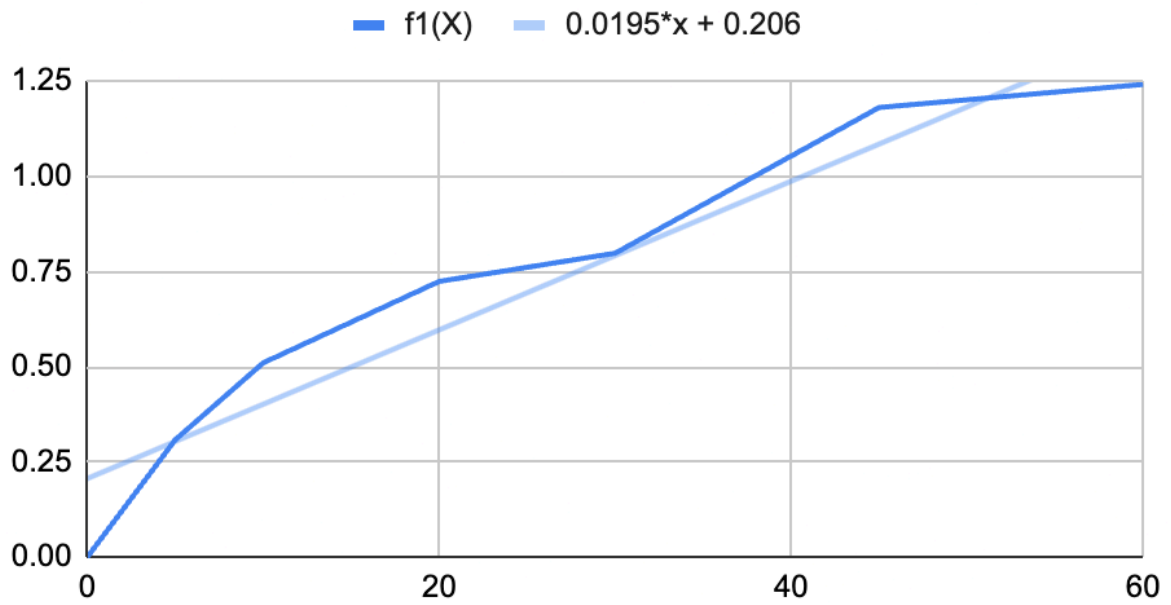
Time (min) and f1(X) -R2



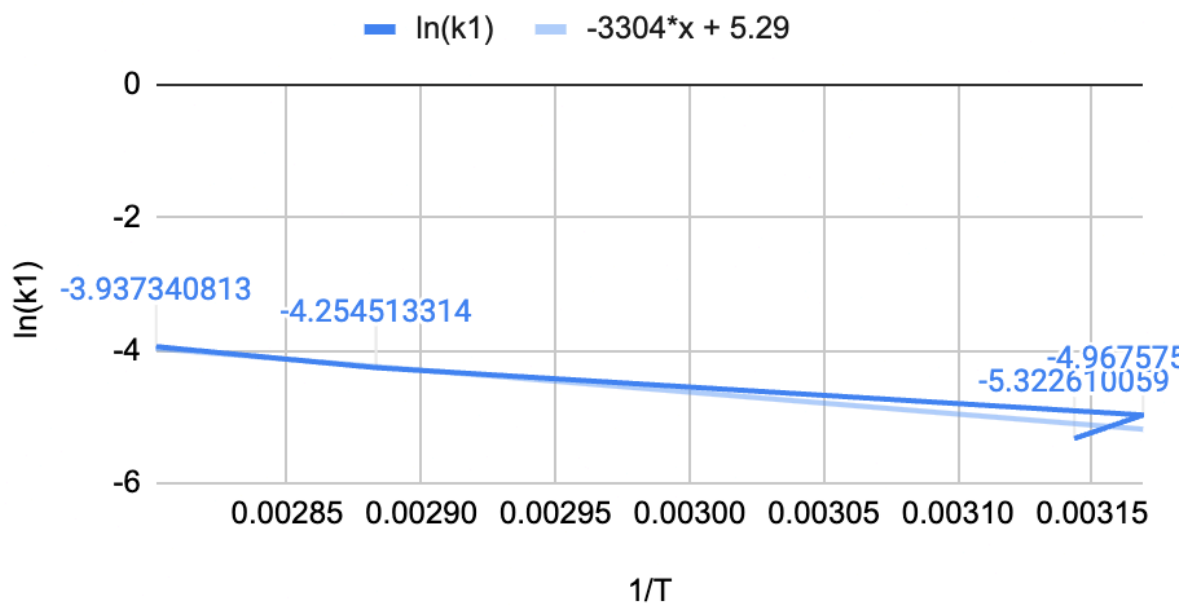
Time (min) and f1(X) - R3



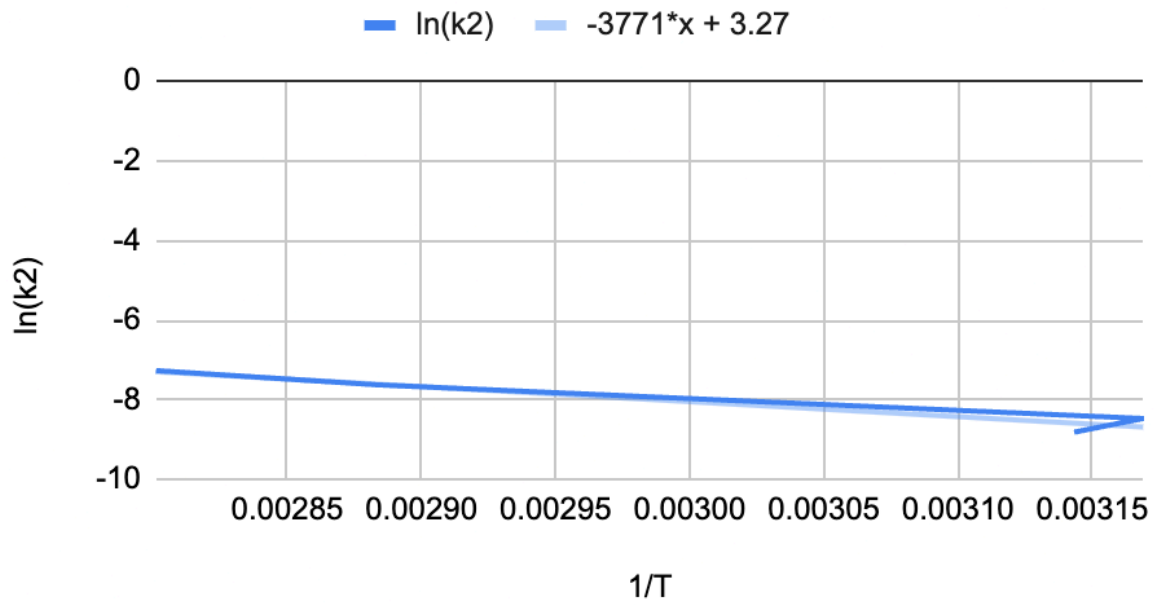
Time (min) and f1(X) -R4



ln(k1) vs. 1/T

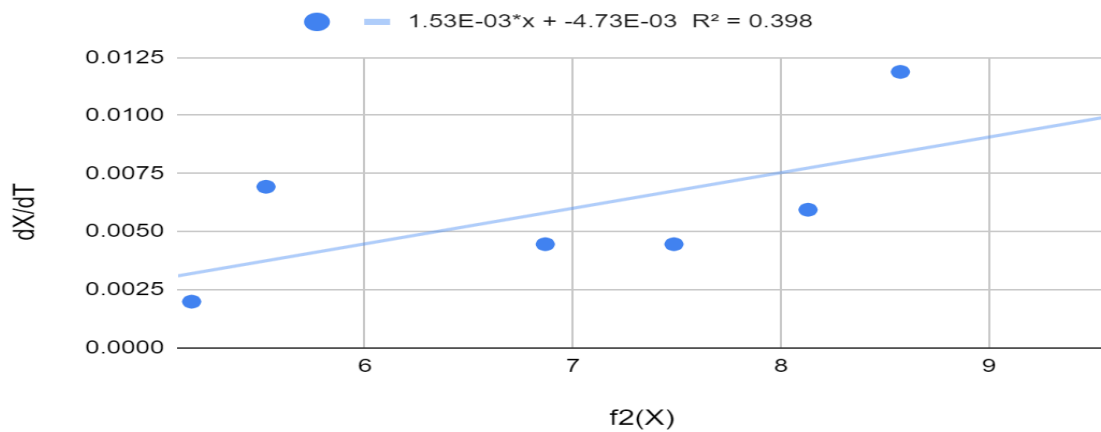


ln(k2) vs. 1/T

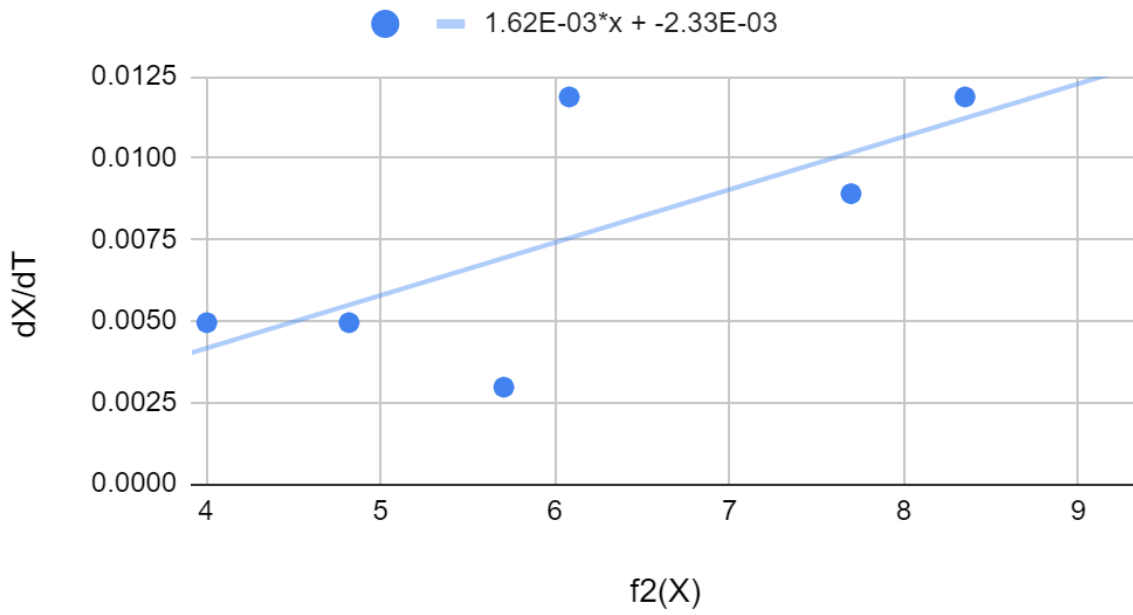


Differential Analysis

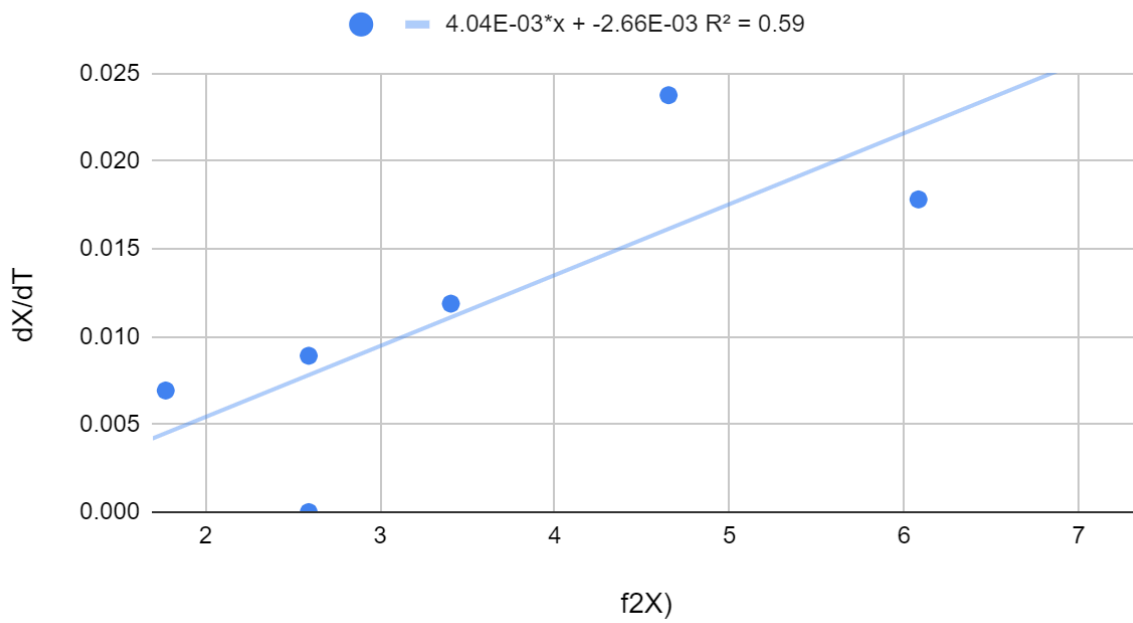
dX/dT Vs f2(X) -- Reactor 1, T= 45 deg C



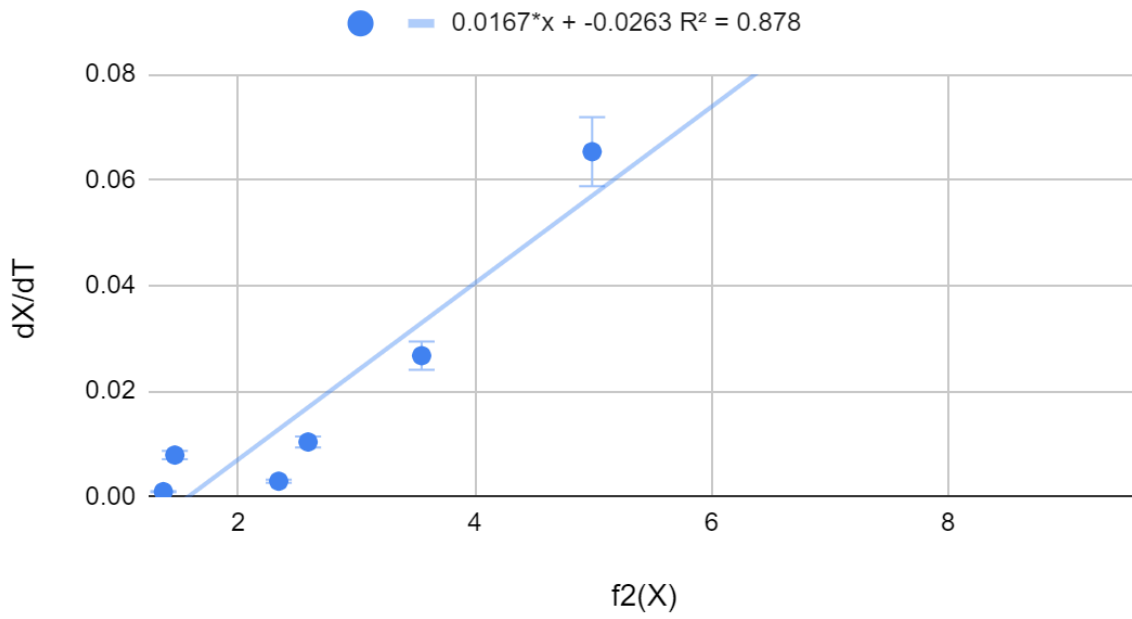
dX/dT Vs f2(X) -- Reactor 2, T= 42.42 deg C



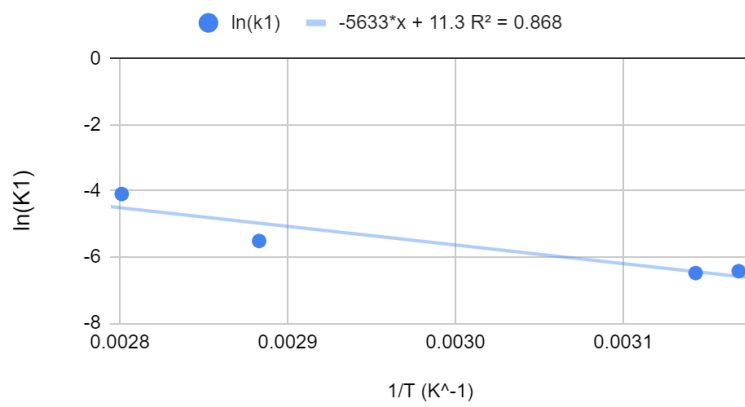
dX/dT Vs f2(X) -- Reactor 3, T= 73.17 deg C



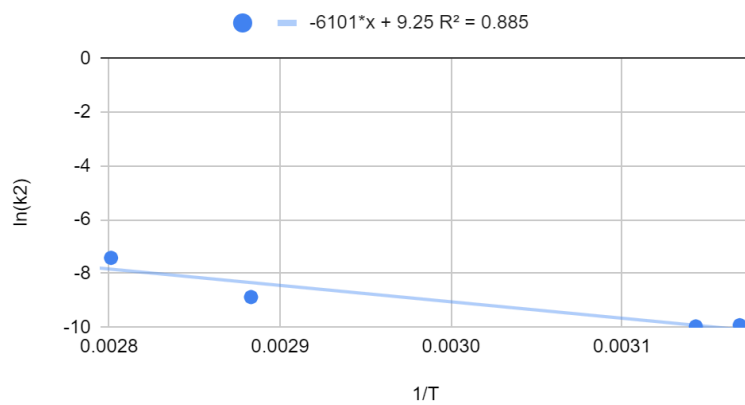
dX/dT Vs f2(X) -- Reactor 4, T=83.58 deg C



$\ln(K1)$ vs $1/T$



$\ln(k2)$ vs. $1/T$



Integral Analysis

CALCULATIONS

Reactor 1									
Time (min)	Vol of sample (ml)	T (degC)	Vol of NaOH (ml)	Conc of AA (M)	Conversion (X)	$a=2*(K-1)*X$	$f1(X)$		
0	1	43	8	8	-0.1880070547	-11.92003367	0		
5	1	46	7.6	7.6	-0.1286067019	-8.153929225	0.04333791017	K	32.70102764
10	1	46	7.4	7.4	-0.09890652557	-6.270877002	0.06671606803	$b = \sqrt{K*(T_{heta}-1)^2 + 4*\theta}$	2
20	1	46	7.1	7.1	-0.05435626102	-3.446298666	0.1041830457	$c = (T_{heta}+1)*K$	65.40205528
30	1	45	6.8	6.8	-0.009805996473	-0.6217203304	0.1448586168		
45	1	45	6.1	6.1	0.09414462081	5.968962453	0.2548193653		
60	1	44	5.9	5.9	0.1238447972	7.852014676	0.2908679451		

Reactor 2									
Time (min)	Vol of sample (ml)	T (degC)	Vol of NaOH (ml)	Conc of AA (M)	Conversion (X)	$a=2*(K-1)*X$	$f1(X)$		
0	1	42	7.9	7.9	-0.1731569665	-11.11492618	0		
5	1	44	7.5	7.5	-0.1137566138	-7.302024224	0.04445364121	K	33.09494368
10	1	44	7.2	7.2	-0.06920634921	-4.44234776	0.08094592244	$b = \sqrt{K*(T_{heta}-1)^2 + 4*\theta}$	2

								2 + 4*theta)	
20	1	43	6.4	6.4	0.04959 435626	3.18345 6142	0.19446 83516	c= (Theta+1) *K	66.1898 8736
30	1	42	6.2	6.2	0.07929 453263	5.08990 7118	0.22728 11266		
45	1	41	5.7	5.7	0.15354 49735	9.85603 4557	0.31904 10146		
60	1	41	5.2	5.2	0.22779 54145	14.6221 62	0.42778 61484		
		42.4285 7143							

Reactor 3									
Time (min)	Vol of sample (ml)	T (degC)	Vol of NaOH (ml)	Conc of AA (M)	Conversi on (X)	a=2*(K-1) *X	f1(X)		
0	1	70	7	7	-0.03950 617284	-2.20882 1942	0		
5	1	75	6.4	6.4	0.04959 435626	2.77286 0403	0.08713 536679	K	28.9554 0271
10	1	76	5.6	5.6	0.16839 50617	9.41510 3529	0.23120 56085	b = sqrt(K*(T heta-1)^ 2 + 4*theta)	2
20	1	75	4.8	4.8	0.28719 57672	16.0573 4666	0.42109 58794	c= (Theta+1) *K	57.9108 0541
30	1	73	4.2	4.2	0.37629 62963	21.0390 29	0.60852 77496		
45	1	74	4.2	4.2	0.37629 62963	21.0390 29	0.60852 77496		
60	1	73	3.5	3.5	0.48024 69136	26.8509 9174	0.90346 12282		
		73.7142 8571							

Reactor 4									
Time (min)	Vol of sample (ml)	T (degC)	Vol of NaOH (ml)	Conc of AA (M)	Conversi on (X)	$a=2*(K-1)*X$	$f1(X)$		
0	1	83	8	8	-0.18800 70547	-10.1025 7883	0	K	27.8675 5252
5	1	85	5.8	5.8	0.13869 48854	7.45278 4232	0.30820 55804	$b = \sqrt{K*(T_{heta}-1)^2 + 4*\theta}$	2
10	1	85	4.9	4.9	0.27234 5679	14.6345 2367	0.51032 4174	$c = (T_{heta}+1)*K$	55.7351 0503
20	1	85	4.2	4.2	0.37629 62963	20.2203 21	0.72419 77475		
30	1	83	4	4	0.40599 64727	21.8162 631	0.79828 46229		
45	1	83	3.2	3.2	0.52479 71781	28.2000 3149	1.18090 6669		
60	1	83	3.1	3.1	0.53964 72663	28.9980 0254	1.24164 7696		
		83.8571 4286							

For kf			For kb		
slope	-6115		slope	-6582	
intercept	14.1		intercept	12.1	
Ef	50840.11	J/mol	Eb	54722.748	J/mol
Af	1329083.281		Ab	179871.8623	

Differential Analysis

Reactor 1		K	32.701027 64				
Time (min)	Vol of sample (ml)	T (degC)	Vol of NaOH (ml)	Conc of AA (M)	Conversion (X)	dX/dt	f2(X)
0	1	43	8	8	-0.1880070 547		9.49677767
5	1	46	7.6	7.6	-0.1286067 019	0.0118800705 5	8.574004997
10	1	46	7.4	7.4	-0.0989065 2557	0.0059400352 73	8.129893825
20	1	46	7.1	7.1	-0.0543562 6102	0.0044550264 55	7.485321026
30	1	45	6.8	6.8	-0.0098059 96473	0.0044550264 55	6.866660975
45	1	45	6.1	6.1	0.0941446 2081	0.0069300411 52	5.523892655
60	1	44	5.9	5.9	0.1238447 972	0.0019800117 58	5.166157311

Reactor 2		K	33.094943 68				
Time (min)	Vol of sample (ml)	T (degC)	Vol of NaOH (ml)	Conc of AA (M)	Conversion (X)	dX/dt	f2(X)
0	1	42	7.9	7.9	-0.1731569 665		9.2617657 1
5	1	44	7.5	7.5	-0.1137566 138	0.0118800 7055	8.3505098 14
10	1	44	7.2	7.2	-0.0692063 4921	0.0089100 5291	7.6972994 32
20	1	43	6.4	6.4	0.0495943 5626	0.0118800 7055	6.0820896 26
30	1	42	6.2	6.2	0.0792945 3263	0.0029700 17637	5.7070791 17
45	1	41	5.7	5.7	0.1535449 735	0.0049500 29394	4.8199387 45
60	1	41	5.2	5.2	0.2277954 145	0.0049500 29394	4.0047782 3
		42.428571 43					

Reactor 3		K	28.955402 71				
Time (min)	Vol of	T (degC)	Vol of	Conc of AA	Conversion	dX/dt	f2(X)

	sample (ml)		NaOH (ml)	(M)	(X)		
0	1	70	7	7	-0.0395061 7284		7.2762218 15
5	1	75	6.4	6.4	0.0495943 5626	0.0178201 0582	6.0820896 26
10	1	76	5.6	5.6	0.1683950 617	0.0237601 4109	4.6511482 54
20	1	75	4.8	4.8	0.2871957 672	0.0118800 7055	3.4044753 14
30	1	73	4.2	4.2	0.3762962 963	0.0089100 5291	2.5903967 68
45	1	74	4.2	4.2	0.3762962 963	0	2.5903967 68
60	1	73	3.5	3.5	0.4802469 136	0.0069300 41152	1.7716418 04

Reactor 4		K	27.867552 52				
Time (min)	Vol of sample (ml)	T (degC)	Vol of NaOH (ml)	Conc of AA (M)	Conversion (X)	dX/dt	f2(X)
0	1	83	8	8	-0.1880070 547		9.4967776 7
5	1	85	5.8	5.8	0.1386948 854	0.0653403 8801	4.9916084 31
10	1	85	4.9	4.9	0.2723456 79	0.0267301 5873	3.5502322 52
20	1	85	4.2	4.2	0.3762962 963	0.0103950 6173	2.5903967 68
30	1	83	4	4	0.4059964 727	0.0029700 17637	2.3420708 07
45	1	83	3.2	3.2	0.5247971 781	0.0079200 47031	1.4639347 34
60	1	83	3.1	3.1	0.5396472 663	0.0009900 058789	1.3671240 98
		83.857142 86					

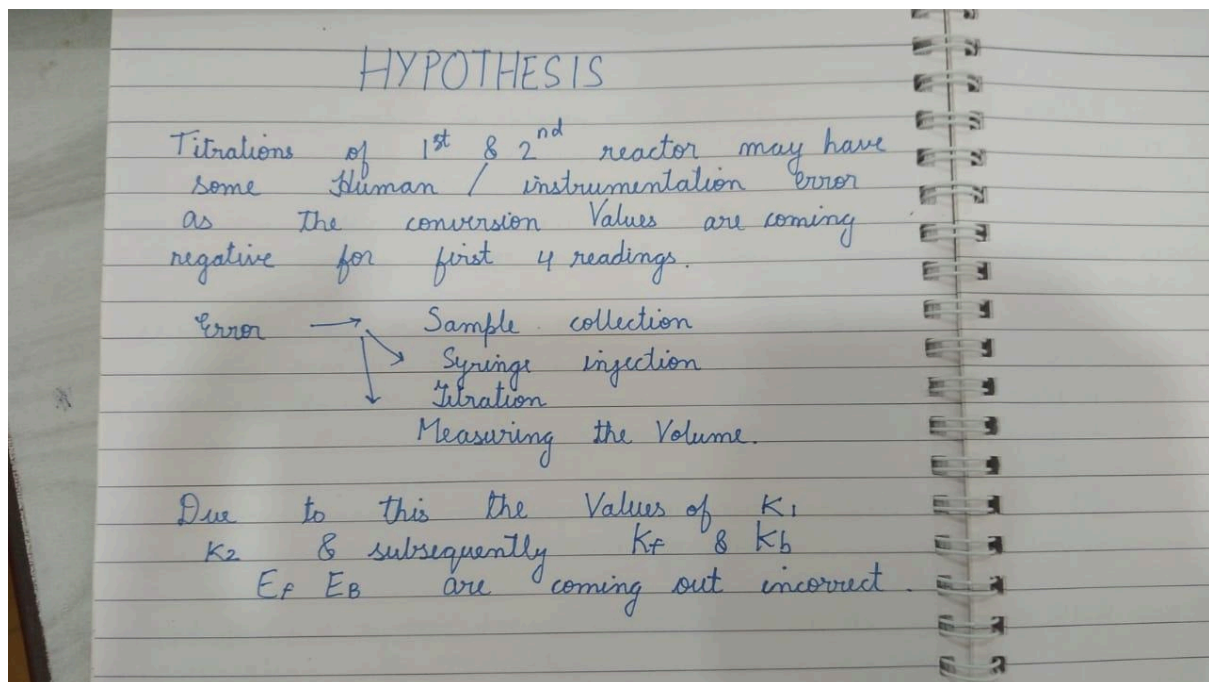
Arrhenius Calculations

T (degC)	T (K)	1/T	K	k1	k2	ln(k1)	ln(k2)
45	318.15	0.0031431 7146	32.701027 64	1.53E-03	4.68E-05	-6.4824875 44	-9.9698940 47
42.42	315.57	0.0031688 69031	33.094943 68	1.62E-03	4.90E-05	-6.4253291 3	-9.9247096 42
73.71	346.86	0.0028830 07553	28.955402 71	4.04E-03	1.40E-04	-5.5115105 87	-8.8772673 96

83.85	357	0.0028011 20448	27.867552 52	1.67E-02	5.99E-04	-4.0923465 6	-7.4198095 79
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DISCUSSIONS

1 HYPOTHESIS



2 QUESTIONS

DISCUSSIONS

1. If K is not known, how will you evaluate k , and K from the kinetic data you have generated?

Ans. We see that the conversion begins to saturate with time. Eventually, we will reach a point when $\frac{dX}{dt} = 0$ (ie, NaOH titrant values are consecutively same).

$$\text{At this point, } k_1 a_0 \left[(1-x)(\theta-x) - \frac{x^2}{K} \right] = 0$$

$$\therefore \frac{x^2}{K} = (x-\theta)(x-1)$$

$$\frac{x^2}{K} = (x-1)^2$$

$$\underline{\underline{K = \left(\frac{x}{x-1} \right)^2}}$$

Now, the above procedure can be followed again to get k_1 - either integral or differential analysis.

CONCLUSIONS

1. We see that the rate constants increase with temperature, as predicted by the Arrhenius equation.
2. By comparing the activation energies for the forward and backward reactions, we see that the reaction is exothermic.

