

# Experiment-5

## Kinetics Study in a Batch Reactor

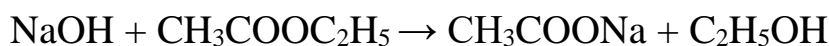
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### Objectives

1. To determine order of reaction between NaOH and CH<sub>3</sub>COOC<sub>2</sub>H<sub>5</sub>
2. To find the rate constant at three temperatures
3. To determine the activation energy and the frequency factor

### Theory

Stoichiometric equation:



(A)

(B)

(C)

(D)

Rate equation:

$$r_A = -\frac{dC_A}{dt} = k_2 C_2 A_0 (1 - X_A)(M - X_A) \text{ (assuming 2nd order reaction)}$$

Where  $M = \frac{C_{B0}}{C_{A0}}$ ; t = time in min;  $X_A$  = conversion of A;  $k_2$  = rate constant in  $\text{l gmol}^{-1} \text{ min}^{-1}$

Integrated form:  $\ln \frac{M - X_A}{M(1 - X_A)} = C_{A0}(M - 1)k_2 t$ , where  $M \neq 1$

### Apparatus

1. Stainless steel batch reactor fitted with stirrer
2. Constant temperature bath
3. Stop Watch
4. Titration Flask

## Chemicals Used

1. N/20 NaOH solution
2. N/50 Succinic acid solution
3. Pure ethyl acetate
4. Phenolphthalein

## Procedure

1. 1 litre of given NaOH solution and 9 ml of ethyl acetate are added at the same time to a batch reactor and stop watch is started.
2. 5 ml solution is pipettes out of the reactor at each one-minute interval and titrated against given succinic acid solution with phenolphthalein as indicator. At least 5 samples are taken at definite time intervals.
3. Repeat the experiment for 3 temperatures: room temperature, 45 °C, and 10 °C. For low temperature, samples are taken at 2-minute intervals.
4. Titrate 5 ml of the given NaOH with succinic acid using phenolphthalein indicator to get  $C'_{A_0}$  gmol/l.
5. Find rate constant  $k_2$  from the plot of  $\ln \frac{M-X_A}{M(1-X_A)}$  vs t.
6. Determine at  $k_2$  at 3 different temperatures and plot  $\ln k_2$  vs  $1/T$ .

## Observations and Calculations

$$C_{A0} = 0.048 \text{ M}$$

$$C_{B0} = 0.091 \text{ M}$$

$$\text{Volume of sample} = 5 \text{ ml}$$

$$M = \frac{C_{B0}}{C_{A0}} = 1.89583333$$

$$X_A = \frac{C_{A0} - C_A}{C_{A0}}$$

Temp.(K)	Time (min)	Volume of succinic acid	Conc. (C <sub>A</sub> )	Conversion (X <sub>A</sub> )	ln ((M-X <sub>A</sub> )/(M(1-X <sub>A</sub> )))	Rate Constant (k <sub>2</sub> )
303.15	3	2	0.008	0.83333333	1.212725595	1.34186047
	6	1.8	0.0072	0.85	1.302275505	
	9	1.5	0.006	0.875	1.460402333	
	12	1.1	0.0044	0.90833333	1.737359192	
285.15	3	5.2	0.0208	0.56666667	0.481141708	0.98837209
	6	4.4	0.0176	0.63333333	0.596737495	
	9	3.6	0.0144	0.7	0.743157601	
	12	3.1	0.0124	0.74166667	0.857224626	
313.15	3	1.3	0.0052	0.89166667	1.5870419	1.91627907
	6	1	0.004	0.91666667	1.824194745	
	9	0.7	0.0028	0.94166667	2.155006178	
	12	0.6	0.0024	0.95	2.300384872	

Temp. T (K)	1/T (K <sup>-1</sup> )	Rate Constant (k <sub>2</sub> )	ln (k <sub>2</sub> )
303.15	0.0032987	1.34186	0.29405706
285.15	0.0035069	0.988372	-0.01169604
313.15	0.0031934	1.916279	0.65038532

Sample calculation :-

$T = 303.15 \text{ K}$ ,  $t = 3 \text{ min}$   
 volume of succinic acid = 2 ml.

Strength of succinic acid = 0.02 N.

eq. balance :-

$$N_1 V_1 = N_2 V_2 \Rightarrow 2 \times 0.02 = N_2 \times 5$$

$$\Rightarrow N_2 = 0.008 \text{ N}$$

$C_A = N_2 = 0.008 \text{ M}$  ( $\because \text{NaOH}$  is monosaccharide base)

$$x_A = \frac{C_{A_0} - C_A}{C_{A_0}} = \frac{0.048 - 0.008}{0.048} = 0.83333$$

$$\ln \left( \frac{M - x_A}{M(1 - x_A)} \right) = \ln \left( \frac{M - 0.8333}{M(1 - 0.8333)} \right)$$

$$M = \frac{C_{B_0}}{C_{A_0}} = \frac{0.091}{0.048} = 1.89583333$$

$$\ln \left( \frac{1.89583333 - 0.8333}{1.89583333(1 - 0.8333)} \right) = 1.212725595$$

similarly, calculating for other  $t$  and plotting points.  
 $k_2$  obtained from slope =  $\frac{\text{slope}}{C_{A_0}(M-1)}$

$$k_2 = \frac{0.0577}{0.048(1.895833 - 1)} = 1.84186047 \text{ l/gmol min}$$

similarly, plotting other curves for 2 other temperatures and obtaining  $k_2$ .

plotting  $\ln(k_2)$  vs  $\frac{1}{T}$ ,

$$\text{slope} = -2021.3$$

$$\text{intercept} = 7.0478$$

$$k_2 = A \exp(-E_A/RT)$$

$$\ln k_2 = \ln A - \frac{E_A}{RT}$$

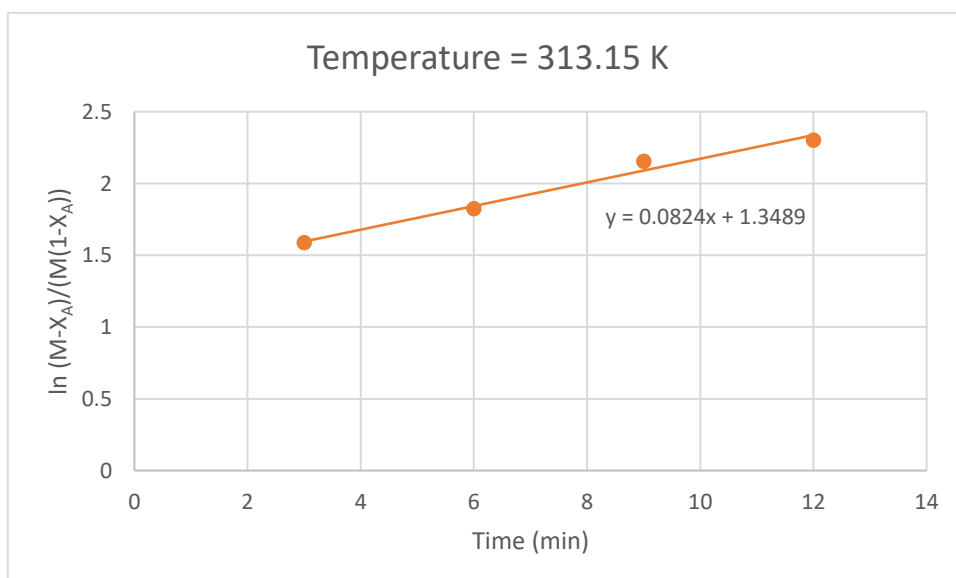
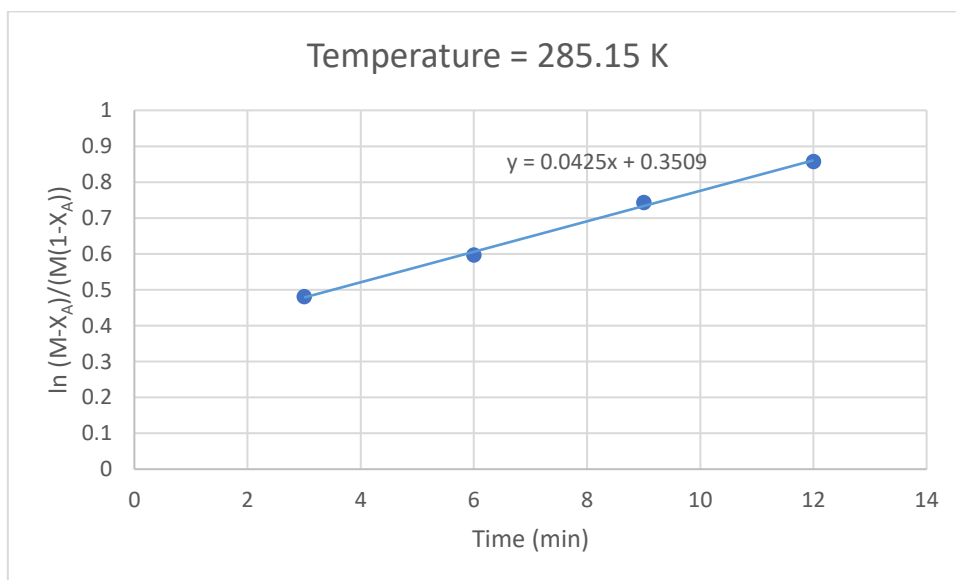
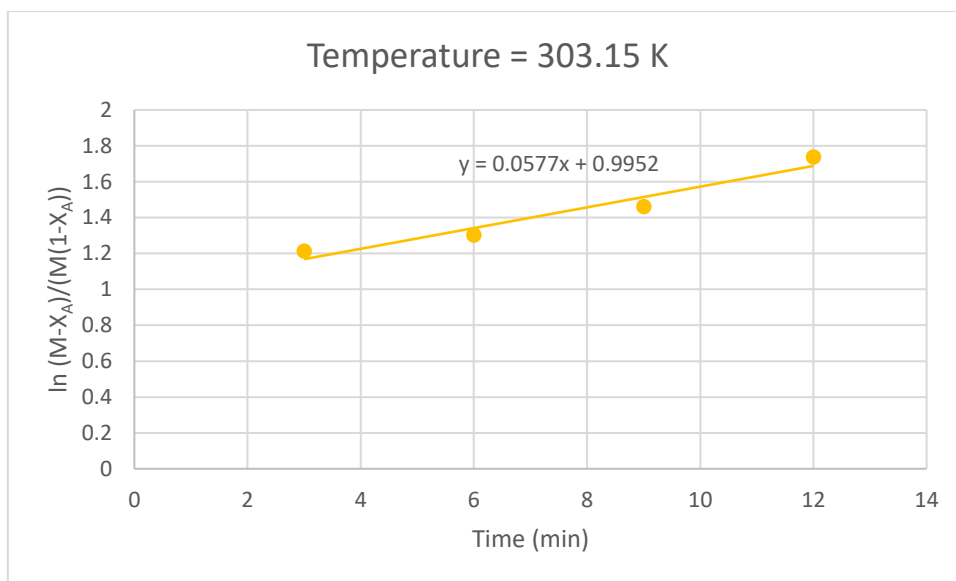
$$\frac{E_A}{R} = 2021.3 \Rightarrow E_A = 2021.3 \times 8.314$$

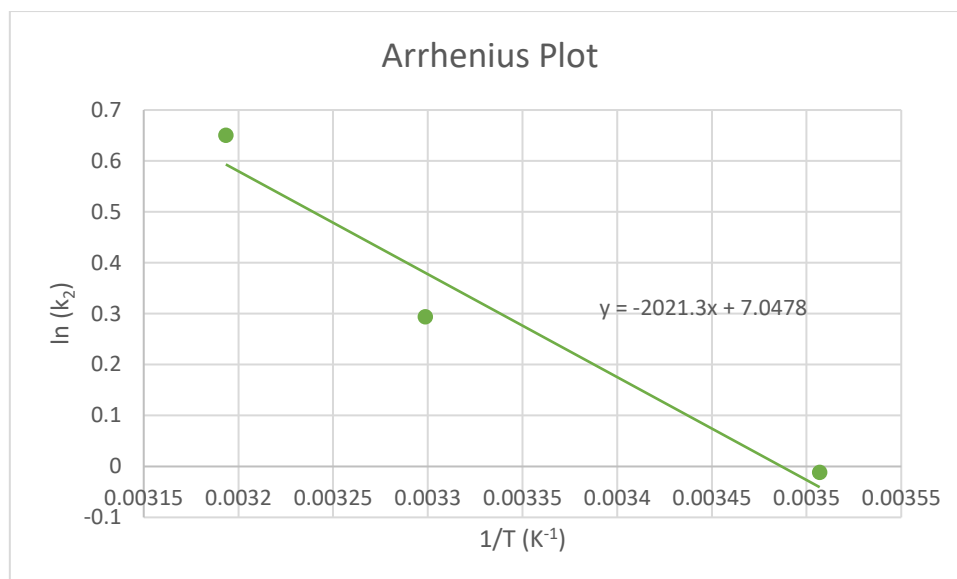
$$= 16805.088 \text{ J/mol}$$

$$\Rightarrow E_A = 16.8 \text{ kJ/mol}$$

$$\ln A = 7.0478 \Rightarrow A = 1150.32 \text{ l/gmol min}$$

# Plots





## Results

Temp. T (K)	Rate Constant $k_2$ ( $\text{l gmol}^{-1} \text{ min}^{-1}$ )	Activation Energy (kJ/ mol)	Frequency Factor ( $\text{l gmol}^{-1}$ $\text{min}^{-1}$ )
303.15	1.34186	16.8	1150.32
285.15	0.988372		
313.15	1.916279		

## Discussion

1. On comparing the values of rate constant obtained with that of plug flow reactor and continuously stirred tank reactor, it is to be noted that the plug flow reactor gave more accurate results when compared with the value given in literature.
2. Care needs to be taken that phenolphthalein is not to be added in excess to the solution being titrated.
3. The titration should be performed carefully so as to obtain the titre value with the last drop, otherwise significant error can be observed in the calculations.
4. The lower meniscus of succinic acid in burette is to be noted correctly to avoid parallax error.
5. The rate constant at lower temperature rightly decreased as compared to other temperatures and it is evident from the Arrhenius equation.

6. Some error can also come up while handling the stopwatch, because it's not necessary that it can be stopped at the right instant to take samples in equal intervals.
7. It's justified to take samples at larger intervals for cold temperature because the activity is reduced and thus, a noticeable change in concentration might not be visible.