

# [Saponifacation of ethyl acetate and soldium hydroxide](https://assignbuster.com/saponifacation-of-ethyl-acetate-and-soldium-hydroxide/)

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Ethyl Acetate – NaOH Reaction Kinetics Experiment Martin Novick Group 14, Chemical Engineering Laboratory Submitted to Prof. David B. Henthorn September 25, 2012 Summary The goal of this project was to determine the pre-exponential factor, k o , the activation energy, E, and the reaction rate constants, k, of the saponification process of ethyl acetate using sodium hydroxide (NaOH) at 5 temperature between 15 and 25 degrees Celsius. Two trails were performed at temperatures 16, 18, 20, 22, and 24 degrees Celsius. The main equipment of the project were the jacketed beaker batch reactor and the LabPro conductivity probe.

The solution’s conductivity throughout the reaction was collected and plotted in a linearized plot against time to retrieve ?????? value for each trial. The rate law was assumed to be ???????????????????????? = ????????????? ???????????? ?????????????????? , where ?????????????????? and ?????????????????? are the concentrations of sodium hydroxide and ethyl acetate respectively. The ln? k) values were plotted against the inverse temperatures to ( linearize the Arrhenius equation. The k o value and E value from the linearized Arrhenius plot were found to be 15 ± 3M ? 1 s ? 1 and ? 6402 ± 8191? j ? mol? 1 respectively. The E value being negative suggests the reaction is exothermic. The large standard errors of the ???????????? and ?????? values were probably caused by the low number of data points collected or the assumed rate law was wrong. Introduction The objective of this project was to determine the pre-exponential factor, k o , the activation energy, E, and the reaction rate constants, k, of the saponification process of ethyl acetate using sodium hydroxide (NaOH). Saponification is a chemical process heavily used in industry, especially in soap production.

Knowing the effects of temperature on the reaction rate allows better control over the reaction process and find the optimizing point of production. The right temperature maximizes production and minimizes reactants and heating or cooling energy, finding the maximum possible profit. 2 The saponification of ethyl acetate with sodium hydroxide (NaOH) is an equi-molar reaction given as NaOH + CH3 COOCH2 CH3 > CH3 COONa + CH3 CH2 OH. [2] The rate was assumed to be second order overall, but first order relative to either reactant,[2] with the disappearance rate of sodium hydroxide given as:[4] dCOH = ? COH Cac , dt (1) where COH is the NaOH concentration, Cac is the concentration of ethyl acetate, and k is the rate constant. COH is represented with x, and Cac is assumed to be in excess with a starting concentration of a. The concentration of ethyl acetate throughout the reaction was given as Cac = a ? xo + x, where xo is the initial starting concentration of NaOH. Substituting the expressions for COH and Cac into Equation 1 results in: dx = ? kx(a ? xo + x). dt Equation 2 is then separated and integrated shown as the following: ? t dx = ? k ? dt. xo x(a ? xo + x) 0 x (2) (3)

The result of equation 3 would become: ln ( xo (a ? xo + x) ) ax = kt. a ? xo (4) Since a 20% excess ethyl acetate solution was used, the initial ethyl acetate concentration was 1. 25 times of the initial starting concentration of NaOH, so a = 1. 25xo . After the substitution of a = 1. 25xo , Equation 4 was simplified to: 3 0. 2x ln ( x o + 0. 8) = kt. 0. 25xo The relationship between xo x (5) and conductivity of the solution was given as:[2] ???????????? ???????????? ? ??????? = , ?????? ?????? ? ??????? (6) where ???????????? is the initial conductivity of NaOH before adding ethyl acetate, ??????? s the conductivity after the reaction has reached completion, and ?????? is the conductivity at any point of time during the reaction process. Substituting Equation 6 into Equation 5 gives the following: ???????????? ? ?????? ln (0. 2 ?????? ? ?????? ? + 0. 8) ? = kt. 0. 25xo (7) Since ???????????? , ???????????? and ??????? are constants, the only variable in the left hand side of Equation 7 being ??????. Each ?????? point can be substituted into the left hand side of Equation 7 and plotted against time to retrieve a linear plot with the slope being the k value. To find the value of the pre-exponential factor, ???????????? and activation energy, ?????? , would require linearizing the Arrhenius equation given as: k = k o ?????? ????????????? , where R is the gas constant and T is the temperature the given k is at in degrees Kelvin. Equation 8 is linearized by taking the natural log of both sides: ln(k) = ln(k o ) ? E . RT 1 ?????? ?????? (8) (9) to retrieve a linear plot with Equation 9 shows a linear relationship between ln(k) and 4 the y-intercept being ln(???????????? ) and the slope being ??????. Hence: k o = ey? intercept . ?????? = ?????????????????????????????? ? ?????? (10) (11) ??????

Equipment, Materials, and Method The equipment used were a jacketed batch reactor beaker, cooling water circulation system, computer, LabPro temperature probe and conductivity probe, mixing stand and magnetic stir bar. The materials used for this reaction were a 0. 08M NaOH solution and a 0. 1M ethyl acetate solution. A 20% excess Ethyl acetate was used to ensure NaOH was the limiting reactant. [1] NaOH was chosen for the limiting reactant because of its high conductivity relative to Ethyl acetate. The extent of the reaction was monitored by measuring the conductivity throughout the reaction.

With NaOH being the limiting reactant, the change in conductivity is more visible, and the termination of the reaction can be more easily observed. The each experimental trail was setup as shown in Figures A1 and A2 of Appendix A. The temperature and conductivity probes were completely submerged under the surface of the reacting solution. One data reading was retrieved per second. Before the reaction process begun, the cooling water circulation system was set at desired temperature and the reactants were cooled to the target temperature to keep an 5 isothermal reactionenvironment.

In Equation 8, the k value was only a function of temperature; if temperature varied throughout the reaction, the k value would also vary throughout the reaction. The reaction was started once thermal equilibrium between the batch reactor beaker and cooling water was established. For about the first half a minute, only the conductivity of NaOH in the reactor was collected, to ensure the initial conductivity in conductivity was more easily observed. The initial conductivity was the first conductivity point after the major drop of conductivity due to the addition of ethyl acetate.

The reaction was started after about half a minute after the start of the data collection by adding the ethyl acetate. The solution was well mixed throughout the reaction to ensure a uniform temperature of the solution, to prevent any local k values being different from the overall k value. If there any temperature gradients throughout the system existed during the reaction process, there would be different local k values throughout the reactor. Data collection was terminated at least half a minute after the reaction had gone to completion, when no conductivity change was observed.

The final reaction completion conductivity, ???????????? , was the conductivity of the solution after the reaction has completed, and was used to find k value. Hysteresis effects were removed by using a random number generator to determine the order of trials. 6 Results and Discussion 1. 2 1. 1 1 0. 9 ln(k) 0. 8 0. 7 0. 6 0. 5 0. 4 0. 3 0. 00335 0. 00337 0. 00339 0. 00341 1/T (T-1) y = -4378. 4x + 15. 713 R? = 0. 7383 0. 00343 1 0. 00345 0. 00347 Figure 1 the plot of the linearized Arrhenius equation where ln(?????? ) ???????????? . ?????? The linearized Arrhenius equation plot shown in Figure 1 has a R2 value of 0. 383 suggesting the data does not have a good linear fit. The lack of data points may have been the cause of the low R2 value. The ln(k) values of the same temperature mostly seem to have small variations, but overall has the predicted trend of decreasing in ln(k) value as ?????? ? 1 increases. The plot has a negative overall trend with and hence retrieving a negative E value. The negative E value suggests the release of energy as the reaction proceeds. Table B1 in appendix B shows the retrieved values of k, ko and E. The positive ko value was expected according to Equation 8.

Since k values are linearly proportional to ko, for k values to be positive, ko must also be positive. The resulting negative E value was an expected result, since the reaction was said to be very spontaneous. The standard errors of ko and E being about 20% to 25% of the original value, suggests the data as imprecise. The imprecision of the data can also be observed from the low R2 value. 7 Looking at the imprecision of the plot in Figure 1, there is a notable difference between the k values at the same temperature for = 0. 003364 (24oC) and ?????? 1 1 ?????? = 0. 03455(16oC). This may be due to the variance in concentration of solutions since solutions were remade each laboratory day. Another possible cause maybe that the contents of solutions may have reacted with the atmosphere introducing extra contents to the reaction. The k values all have standard errors less than 1%. Figures B1 to B5 of Appendix B shows the plots of ???????????????????? ln( 1 ???????????? ???????? ( +1)) 1. 25 ?????????????? 0. 25xo used to find the k values at each temperature. The plots all have a positive trend which is reasonable according to Equation 7.

The resulting slope is the k value of that trial, and the k values cannot be negative. Also the R2 values of the plots were all above 0. 95, suggesting a good fit with the linear best fit line model. Despite the high R2 values, the a clear parabolic trend was observed in all the residual plots shown in Figures B6 to B14 of Appendix B, the linear property of the plots are questioned. Figure B15 of Appendix B shows an example plot of the full data from 16oC trail 1. A clear linear trend was observed from the beginning of the plot, but an obvious curve was observed from the end of the plot.

Thisobservationwas probably due to the fact that as the reaction proceeded, the reaction started behaving like a first order reaction. The first order reaction behavior is because near the end of the reaction of the excess ethyl acetate concentration was much greater than the NaOH concentration and can be treated as a constant. With the concentration of ethyl acetate being constant the only resulting variable would be 8 the NaOH concentration. Conclusion and Recommendations The retrieved ko value and E value were 15 ± 0. 3 and ? 36402 ± 8191.

Since the standard errors of ko and E values were about 20% and 25% of the original value respectively, and the R2 value was only 0. 7383 for the plot in Figure 1, the data is concluded to be imprecise and that more data points should be collected to improve the precision. The assumption of the rate being second order overall, but first order relative to either reactant was concluded to be inappropriate. Though the R2 value for all the trials were above 0. 95, because a clear parabolic trend was observed in all the residual plots, Figures B6 to B14 of Appendix B, it was concluded that all the trial data do not have a linear relationship.

Since it has been concluded that the assumed rate equation, Equation 1, does not describe the reaction, a new rate equation is needed to describe the reaction. The low R2 value in Figure 1 can be improved by increasing the amount of data collected. More trails can be done at each temperature and more temperatures can be tested within the given interval. One large bulk solution can be made and used for all the trails, but stored and isolated from the atmosphere. The error caused by the variation in concentrations of the reactants at different trails can be solved by using the one large bulk of reactants.

The problem of the reactants reacting with the atmosphere can be solved by isolating the reactants from the atmosphere during storage. 9 References [1] Crismyre, Bobby, Do, Bryan, and Kronmiller, Mandy. “ Ethyl Acetate – NaOH Reaction Kinetics Experiment Standard Operating Procedures,” (2010) [2] Julio F. Mata-Segreda, Hydroxide as a General Base in the Saponification of Ethyl Acetate. Journal of the American Chemical Society, (2010), 124 (10), 2259-2262. [3] Keusch Fachdidaktik Chemie. “ Reaction Second Order,” Institute of Organic Chemistry, Universitat Regensburg. [4] Schmidt, Larry D. “ The Engineering of Chemical Reactions,” 2 Ed.

Press, New York (2005) Oxford University 10 APPENDIX A: Experimental Set Up Figure A 1: Shows the theoretical setup and flow of each experiment. Figure A 2: Shows the actual set up used for each experiment. 11 APPENDIX B: Experimental Results and Data Table B 1 shows the result of the desired information Set Temperature (oC) 16 (Trial 1) 16 (Trial 2) 18 (Trial 1) 20 (Trial 1) 20 (Trial 2) 22 (Trial 1) 22 (Trial 2) 24 (Trial 1) 24 (Trial 2) ???????????? (??????? 1 ?????? ? 1 ) ?????? ( ?????? ) ?????????????????? Actual Temperature (oC) 16. 45 ± 0. 05 16. 44 ± 0. 04 18. 33 ± 0. 03 20. 30 ± 0. 05 20. 30 ± 0. 5 22. 24 ± 0. 04 22. 25 ± 0. 05 16. 45 ± 0. 05 16. 45 ± 0. 05 15 ± 3 ? 36402 ± 8191 k-values (??????? 1 min? 1 ) 1. 674±0. 001 2. 023±0. 001 1. 921±0. 002 2. 241±0. 002 2. 247±0. 003 2. 244±0. 006 2. 169±0. 002 2. 572±0. 003 3. 140±0. 002 12 25 20 y = 2. 0232x R? = 0. 9994 15 Y (L/mol) y = 1. 6744x R? = 0. 9972 10 5 0 0 2 ln( 1 ???????????? ???????? ( +1)) 1. 25 ?????????????? 4 6 Time (min) 8 ln( 10 1 ???????????? ???????? ( +1)) 1. 25 ?????????????? 12 Figuer B 1 Plot of ???????????????????? 0. 25xo at 16 degrees Celsius, where ?????? = 0. 25xo . 16 14 12 10 8 6 4 2 0 0 -2 ln( 1 ???????????? ???????? +1)) 1. 25 ?????????????? y = 1. 9206x R? = 0. 9974 Series1 Linear (Series1) 1 2 3 4 5 6 7 8 Figuer B 2 Plot of ???????????????????? 0. 25xo at 18 degrees Celsius, where ?????? = ln( 1 ???????????? ???????? ( +1)) 1. 25 ?????????????? 0. 25xo . 13 25 y = 2. 247x R? = 0. 9964 y = 2. 2407x R? = 0. 9982 Y (L/mol) 15 Trial 1 Trial 2 10 Linear (Trial 1) Linear (Trial 2) 5 20 0 0 2 4 6 Time (min) 1 ???????????? ???????? ( +1)) 1. 25 ?????????????? 1 ???????????? ???????? ( +1)) 1. 25 ?????????????? 8 10 12 Figuer B 3 Plot of ???????????????????? ln( 0. 25xo at 20 degrees Celsius, where ?????? = ln( 0. 25xo . 0 18 16 14 Y (L/mol) 12 10 8 6 4 2 0 0 2 4 Time (min) 1 ???????????? ???????? ( +1)) 1. 25 ?????????????? 1 ???????????? ???????? ( +1)) 1. 25 ?????????????? y = 2. 244x R? = 0. 9909 y = 2. 1687x R? = 0. 9985 Trial 1 Trial 2 Linear (Trial 1) Linear (Trial 2) 6 8 10 Figuer B 4 Plot of ???????????????????? ln( 0. 25xo at 22 degrees Celsius, where ?????? = ln( 0. 25xo . 14 25 20 y = 2. 5723x R? = 0. 9982 15 Y (L/mol) y = 3. 1405x R? = 0. 9992 Trial 1 Trial 2 Linear (Trial 1) Linear (Trial 2) 10 5 0 0 1 2 3 4 Time (min) 5 6 7 8 Figuer B 5 Plot of ???????????????????? ln( 1 ???????????? ???????? ( +1)) 1. 25 ?????????????? . 25xo at 24 degrees Celsius, where ?????? = ln( 1 ???????????? ???????? ( +1)) 1. 25 ?????????????? 0. 25xo . X Variable 1 Residual Plot 0. 8 0. 6 Residuals 0. 4 0. 2 0 -0. 2 -0. 4 0 2 4 6 X Variable 1 8 10 12 Figure B 6 The residual plot for 16 degrees Celsius Trial 1. 15 X Variable 1 Residual Plot 0. 6 0. 4 Residuals 0. 2 0 -0. 2 -0. 4 0 2 4 6 8 10 12 X Variable 1 Figure B 7 The residual plot for 16 degrees Celsius Trial 2. X Variable 1 Residual Plot 0. 8 0. 6 Residuals 0. 4 0. 2 0 -0. 2 -0. 4 0 1 2 3 4 X Variable 1 5 6 7 8 Figure B 8 The residual plot for 18 degrees Celsius Trial 1. X Variable 1 Residual Plot 0. 8 0. 6 Residuals 0. 4 0. 2 0 -0. 2 0 -0. 4 -0. 6 X Variable 1 2 4 6 8 10 12 Figure B 9 The residual plot for 20 degrees Celsius Trial 1. 16 X Variable 1 Residual Plot 1. 5 1 Residuals 0. 5 0 0 -0. 5 -1 X Variable 1 2 4 6 8 10 12 Figure B 10 The residual plot for 20 degrees Celsius Trial 2. X Variable 1 Residual Plot 1. 5 1 Residuals 0. 5 0 -0. 5 -1 0 1 2 3 4 5 6 7 8 X Variable 1 Figure B 11 The residual plot for 22 degrees Celsius Trial 1. X Variable 1 Residual Plot 0. 8 0. 6 Residuals 0. 4 0. 2 0 -0. 2 -0. 4 0 1 2 3 4 5 6 7 8 9 X Variable 1 Figure B 12 The residual plot for 22 degrees Celsius Trial 12 7 X Variable 1 Residual Plot 1 Residuals 0. 5 0 0 -0. 5 1 2 3 4 X Variable 1 5 6 7 8 Figure B 13 The residual plot for 24 degrees Celsius Trial 1. X Variable 1 Residual Plot 0. 6 0. 4 Residuals 0. 2 0 -0. 2 -0. 4 0 1 2 3 4 X Variable 1 5 6 7 8 Figure B 14 The residual plot for 24 degrees Celsius Trial 2. 140 120 100 Y (L/mol) 80 60 40 20 0 0 5 10 15 20 25 30 35 40 45 Time (min) Figure B 15 The plot of all the data from 16oC trail 2 18 APPENDIX C: Sample Calculations Volume of 1M NaOH solution needed to prepare 300mL 0. 08M NaOH solution: 0. 3?????? ? 0. 08?????? = 0. 024?????? = 24????????????? ?????? Volume of ethyl acetate needed to prepare a 300mL 0. 1M ethyl acetate solution: 1000???????????? 88. 105?????? ???????????? 3 0. 001?????? 0. 10?????? ? ? ? ? ? 0. 3 = 2. 96???????????? ?????? ?????????????????? 0. 897?????? ???????????? 3 Finding E value: ?????? ?????????????????? Calculating the k value for time being 1 minute in trial 2 of 16 degrees: ?????? = ?????????????????????????????? ? ?????? = ? 2904. 9 ? 8. 3145 = ? 24153 1 ???????????? ? ??????? ln ( ( + 1)) 1. 25 ?????? ? ??????? 0. 25xo 1 16324. 71 ? 4698. 16 ln ( ( + 1)) 1. 25 8259. 03 ? 4698. 16 0. 25(0. 8) = kt = = 14. 89 19

APPENDIX D: Error Analysis If the result (R) is calculated by the following equation: ?????? = ? ???????????? ?????? where ???????????? is the exponent of the independent variable, ???????????? . The standard error would be calculated by the following equation: 2 2 ???????????? ???????????? = ?????? (? ( ?????????????????? ) ) ???????????? 1 ?????? (1) (2) where????????????? is taken from equation 5, ?????????????????? is the standard error of each individual independent variable. Since the equation used is the following: ???????????? ? ?????? ln (0. 8 ( ?????? ? ?????? ? + 1)) ? 0. 25???????????? = ???????????? , 3) where ?????? is the rate constant, ???????????? is the initial conductivity, ??????? is the conductivity at the end of the reaction, ?????? is the conductivity at any time, and ???????????? is the initial concentration of the NaOH solution. The error of the right hand side of equation 3 with ???????????? = 36. 662 is show as the follow: 36. 662 (( 0. 0339 ) ) = 15. 536. 0. 08 1 2 2 ???????????? was given the value of 0. 08?????? with an uncertainty of ±0. 0339??????. The reaction rate constant, k, were found by the best fit line of the plot, so the uncertainty of the k were found by taking the linear regression.

The rate constant was the slope of the best fit line making the calculation of the error with a 95% confidence level as: ?????????????????????????????? = 1. 96 ? ???????????? ,?????? v? ???????????? 2 ? ????????????? 2 Where ???????????? ,?????? is the standard error of estimate, ???????????? is the x values of the plot, n being the number of points, and ???????????? = ? ??????? ???????????? ?????? = 1 ?????? , (4) . As for the y intercept, or the activation energy, the error with a 95% confidence level would be: 20 ?????????????????????????????? = 1. 96 ? ???????????? ,?????? v??????? 1 (? ??????????? )2 + 2 , ?????? (? ???????????? 2 ? ????????????? 2 ) (5) Where ???????????? ,?????? is the standard error of estimate, ???????????? is the x values of the plot, n being the number of points, and ???????????? = ? ??????? ???????????? ?????? = 1 ?????? . The standard error of estimate, ???????????? ,?????? , seen in both equation 4 and equation 5 is given as: ???????????? ,?????? = v ? (???????????? ? ???????????? )2 , ?????? ? 2 (6) where ???????????? is the y value of the points, ???????????? is the corresponding y value on the best fit line, and n is the number of data points.