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Kinetic Modeling of the Hydrolysis of Acetic Anhydride at Higher Temperatures using Adiabatic Batch Reactor (Thermos-Flask)

Asiedu N*, **Hildebrandt D and Glasser D**

Centre of Material and Process Synthesis, School of Chemical and Metallurgical Engineering, University of Witwatersrand, Johannesburg, South Africa

Abstract

The kinetics of the reactions of acetic anhydride-excess water has been studied at higher temperatures up to 366K under adiabatic conditions in a thermos-flask fitted with a negative coefficient thermistor and kinetic data reported in this work. The same techniques were applied for the kinetic studies of excess acetic anhydride-water reactions at higher temperature up to 368 K. The reaction kinetics of excess acetic anhydride-water reactions which has not been determined previously was modeled using the same adiabatic analysis and the average activation energy, heat of reaction, pre-exponential factor and the order of reaction with respect to water has been determined. The studies have shown that the two processes appear to be completely different and might proceed through different reaction mechanisms pathways for the production of acetic acid.

Keywords: Kinetic modeling; Thermos flask; Hydrolysis; Esterification; Exothermic reactions; Temperature

Introduction

Classical techniques for modeling reaction kinetics have been depended on measuring or monitoring concentration-time profiles of liquid phase reactions. This method requires that at some time the researcher must have means of arresting the reaction and take measurement rapidly and continuo the process. With this approach some continuous measuring techniques are possible, pH, conductivity, Kralj [1], Fourier transfer infrared Haji et al. [2]. These methods actually require different approach when it comes to the analysis of the experimental results, and one is always at the disadvantage when reaction rates are extremely fast. Temperature-time profiles of exothermic reaction are used instead of concentration-time profiles for the determination of the kinetic parameters. This method is now used in modern laboratories and can be done with a high degree of accuracy. Most reactions have reasonable amount of heat of reaction and measuring dices such as thermistor can be used to measure temperature changes up to accuracy on 0.0001°C. It follows that in principle an adiabatic reaction covering only 10°C should be measureable to one part in 10^5, which compares very well with the accuracy of chemical titration used in isothermal experiments. Thus reactions with very small heat of reactions could be handled easily. If one is to model an exothermic reaction by estimating the kinetic parameters of a process when concentration and temperature vary simultaneously, one need to perform regression analysis directly on the differential equations describing the process [3]. Recently this regression analysis is easily performed by high speed digital computers. Previous researchers have been confined to the case where reactions occur under adiabatic conditions [4]. Bell and Clunie [5] used flow reactors and it has generally been used for fast reactions. The temperature-time profiles have been converted directly concentration-time profiles and then been analyzed by the classical methods. The method of Schmidt et al. [6] requires numerical evaluations of the first and second derivatives functions of concentration.

The current technique applied for the analysis of the results in this paper is not subject to any limitations and does not require prior knowledge of the heat of reaction. Some studies have been reported in elsewhere in the literature on the kinetic parameters of acetic anhydride hydrolysis. Eldridge and Pirect [7] obtained the pseudo-first order reaction rate constant using a batch reactor. It is well-known that the reaction rate increases with temperature increase. The rate of temperature rise can be represented as a slope of the temperature-time curve. Some studies has been reported in the past using temperature-time profiles to predict the kinetics of the hydrolysis of acetic anhydride in excess distilled water. Williams [8] reported the kinetics and stoichiometry of the reaction between hydrogen peroxide and sodium thiosulphate. An adiabatic reactor was used with a thermocouple and a strip-chart recorder to determine the kinetic parameters of the hydrolysis of acetic anhydride in dilute aqueous solutions Glasser and Williams [9]. A vessel was placed in a constant temperature bath and the heat lost from the reactor was described mathematically. A thermistor was used for the temperature readings. King and Glasser [10] studied the kinetic parameters of the hydrolysis of acetic anhydride in dilute solutions. An adiabatic reactor was used in the experiments. The walls of the reactor were kept at the same temperature as the fluid by passing a high current through the reactor walls. Temperature readings were taken by the use of thermocouples. In this work hydrolysis of acetic anhydride in excess distilled water (dilute solution) was studied and compared with hydrolysis in excess anhydride solution in adiabatic conditions. It is known that not much work has been done on the case where hydrolysis is carried out in excess acetic anhydride solution using adiabatic batch reactor. Moreover this work is also to test the current model of the hydrolysis of excess acetic anhydride under adiabatic conditions. It is claimed that the hydrolysis follows a first order kinetic model. The same method is also used to elucidate the kinetic parameters of the reaction between acetic anhydride and methanol. This process has not been studied in this manner as known to the authors.

***Corresponding author:** Nana Yaw Asiedu, Centre of Material and Process Synthesis, School of Chemical and Metallurgical Engineering, University of Witwatersrand, Private mail Bag X3, Wits 2050, Johannesburg, South Africa, E-mail: nasiedusoe@yahoo.co.uk

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The Mathematical Model of the Reacting System-Thermos-Flask

Given an adiabatic batch reactor (thermos-flask) the mathematical model is made up of a set of differential equations resulting from the mass and energy balances referred only to the reaction mixture because there is no heat transfer.

The stoichiometry of the reactions studied is given below:

$$(CH_3CO)_2O + H_2O \rightarrow 2CH_3COOH \ \Delta H\ (298K) = -56kJ/mol \qquad (1)$$

For a constant –volume batch reactor one can write:

$$-r_A = \frac{1}{V}\frac{dN_A}{dt} = -\frac{dC_A}{dt} \qquad (2)$$

The energy balance equation can be established as:

Heat generated = Heat absorbed by reactor contents + Heat transferred through reactor walls (3)

$$(-\Delta H)(-rA)Vdt + Qstirrer\ dt = mC_p\ dT + UA\ (\Delta T)dt \qquad (4)$$

Given $(-r_A) = \frac{d\varepsilon}{dt}$ (5)

where (ε) is the extent of reaction, we can rearrange eq 4 to give eq 6 below:

$$UA(\Delta T)dt + mC_p = (-\Delta H)\frac{d\varepsilon}{dt} \qquad (6)$$

Assume that heat given by stirrer speed ($Q_{strirrer}$) is negligible. Integrating eq 6 gives

$$(T - T_o) + \frac{UA}{mC_p}\int_0^{\infty}(T - T_O)dt = \frac{(-\Delta H)}{mC_p}\Delta\varepsilon \qquad (7)$$

The left hand side of eq 7 can be used to correct experimental data to adiabatic conditions. It is assumed that the reaction is independent of temperature, hence correcting the experimental data the adiabatic temperature rise parameter (ΔT_{ad}) can be obtained from the experimental result for the process. This adiabatic temperature rise is equal to the right hand side of eq 7 or we can write;

$$\Delta T_{ad} = \frac{(-\Delta H)\varepsilon}{mC_p} \qquad (8)$$

From eq 8 one can easily show that the energy balance equation of an adiabatic batch reactor reduces to a linear form given by eq 9 as:

$$T = T_0 + \Delta T_{ad\varepsilon} \qquad (9)$$

where (ε) is the extent of reaction with respect to the reactant of interest and its value can be computed in advance from the initial conditions (temperature and heat capacities) of the reacting species. Equation 9, also allows one to find conversion at any instant under adiabatic conditions by using only one measure of temperature. Then from the initial concentrations of the reactants the concentrations products can be monitored at any instant in the reactor.

The Experimental Set Up

The experimental set- up as shown in Figure 1 was used in all the reactions studied. The adiabatic batch reactor used in the experiments is 18/8 stainless steel thermos-flask of total volume of 500 mL equipped with a removable magnetic stirrer. The flask is provided with a negative temperature coefficient thermistor connected on-line with a data-logging system. The signal from the sensor (thermistor) is fed to a measuring and a control unit amplifier and a power interface. The acquisition units are connected to a data processor. A process control engineering support data management.

The data acquisition system called Clarity has the following part numbers: C50 Clarity Chromatography SW, single instrument, 3 x 55 Clarity Add-on instrument SW, 194 (INT9 quad channel A/D converter card). The hardware is INT9 PCI A/D 24 bit converter. The properties: Input signal range 100mV -10V, Acquisition frequency 10-100Hz, Internal A/D converter (INT9-1 to 4 channel PCI A/D converter). All physically available analog inputs and outputs as well as virtual channel are all automatically monitored and the process values are stored. The process values are transmitted in such a way that the computer screen displays profiles of voltage-time curves. Data acquisition software was used to convert the compressed data form of the history file on the hard disk into text file format. The text files are converted to excel spreadsheet and the data are then transported into MatLab 2010a for analysis.

The Thermistor Calibration

The thermistor used in the experiments was negative temperature coefficient with unknown thermistor constants. The calibrations involve the determination of the thermistor constants and establish the relationship between the thermistor's resistance and temperature. This was done by fitting both the thermistor and an electronic digital temperature measuring device in a sealed vessel and the system was slowly warmed until the voltage reaches it asymptotic state. The thermistor was connected to a computer with data acquisition software to provide data of voltage-time real-time plot. The voltage-time data was used to match the temperature-time data obtained from the electronic digital temperature device. Thermistor resistance (R_{TH}) and Temperature (T) in Kelvin was modeled using the empirical equation given developed by Considine [11].

$$R_{TH} = exp\left(\frac{B}{T} + C\right) \qquad (10)$$

or

$$\ln(R_{TH}) = \frac{B}{T} + C \qquad (11)$$

Where the parameters (B) and (C) are the thermistor constants. The constants were determined by fitting the "best" least square straight line plot of $\ln(R_{TH})$ against 1/T, giving the thermistor equation as:

$$\ln(R_{TH}) = \frac{1773.8}{T} + 18.178 \qquad (12)$$

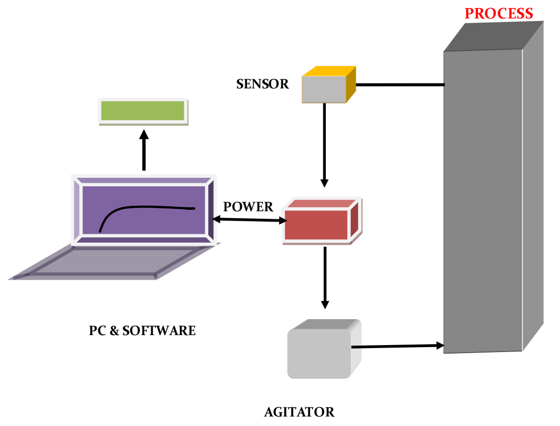

Figure 1: Block diagram of experimental set-up.

Experimental Procedures and Results

Excess water-acetic anhydride reactions-hydrolysis-A

Analytical reagent grade acetic anhydride and distilled water was used in all experiments. In all experiments 1 mol of acetic anhydride was injected into the reaction vessel followed by 10 mols of distilled water. These quantities (volumes) were used so that at least 60% of the length of the sensor (thermistor) would be submerged in the resulting initial reacting mixture. Reactants were brought to a steady-state temperature before starting the stirrer to initiate the reaction. In course of the reaction, the stirrer speed was set at 1000 rev/min, the resulting voltage-time profiles were captured and the corresponding temperature-time curve was determined using the thermistor equation derived above. Runs were carried out adiabatically at the following initial temperatures: 305K, 310K and 328K.

Experimental determination of heat transfer coefficient of the process

For a given system (reaction vessel and content) one can write:

$$\left(\frac{mC_p}{UA}\right)_{system} = \left(\frac{mC_p}{UA}\right)_{water} + \left(\frac{mC_p}{UA}\right)_{vessel} \tag{13}$$

In this experiment different amount of water (m_w) (200 g, 300 g and 400 g) was injected into the reaction flask at 343.08K, 347.77K and 347.85K and allowed to cool until the temperature reaches a steady-state temperature (T_s). The cooling process thus follows equation 14. A nonlinear least-square regression analysis was performed on all the three experimental curves and the value of UA/mCP for each cooling curve was determined.

$$T = T_s + (T_0 - T_s)\exp\left(-\frac{UA}{mC_p}t\right) \tag{14}$$

From Table 1, a plot of mass of water (m) against (mC_p/UA) is shown.

Determination of UA/mC_p for the reaction mixture

Table 2 consists of some of the physical constants of the reacting species which was used in the determination of the quantity UA/mCP.

Equation 23 was used to determine specific heat of the reacting mixture ($C_{P.mix}$) and the quantity $M_{TCP.mix.}$

$$C_{P.mix} = \frac{m_{AA}}{MT}C_{P.AA} + \frac{m_W}{MT}C_{P.W} \tag{15}$$

M_T, is the total mass of the reacting mixture and $M_{TCP.mix}$ was calculated to be 943.64 J/K. Since the reaction is not pure water we therefore determined its equivalent mass of water by dividing 943.64 J/K by the specific heat of water:

$$m_{eqv}water = \frac{(M_T C_P)_{mix}}{C_{P.water}} = 225.5g\ water \tag{16}$$

Mass of water(g)	Initial Temperature(K)(T_O)	Final Temperature(K)(T_S)	UA/mCp (min^{-1})
200	343.08	292.13	0.00215
300	347.77	293.00	0.00189
400	347.84	293.38	0.00178

Table 1: Summary of characteristics of the cooling curves.

Species	Moles	Molar mass(g/mol)	C_P (J/mol.K)
Acetic anhydride	1.0	102.9	189.7
Water	10.0	18.01	75.4

Table 2: Some constants of reacting species.

From Figure 2 the value of the quantity $(UA/mC_p)_{mix}$ was determined to be 0.00209/min. This value was plugged in eq 7 above and the correction of the experimental results to adiabatic conditions was performed. The Figures 3-5 shows the experimental and the corrected temperature profiles for all the three runs.

From eq 9 the variation of acetic anhydride concentration with temperature/time was deduces as:

$$C_{AA} = 3.64 - a\,(T\text{-}T_o) \tag{17}$$

The constant (α) in eq 17 was calculated using the initial concentration of the acetic anhydride, 3.64 mol/L and the adiabatic temperature change $(\Delta T)_{adiabatic}$ values provided in Table 3.

Variation of rate of reaction with concentration change

The average rate of a reaction ($-r_A$) which is a function of

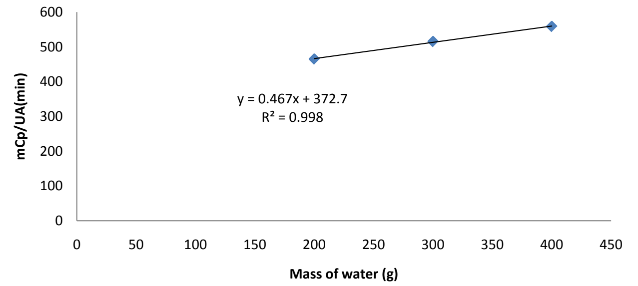

Figure 2: A plot of mass of water (m) against (mC_p/UA).

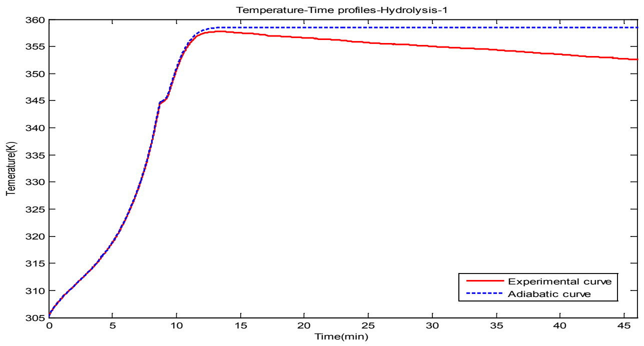

Figure 3: Temperature-time plots of acetic anhydride-excess water reaction at 305K.

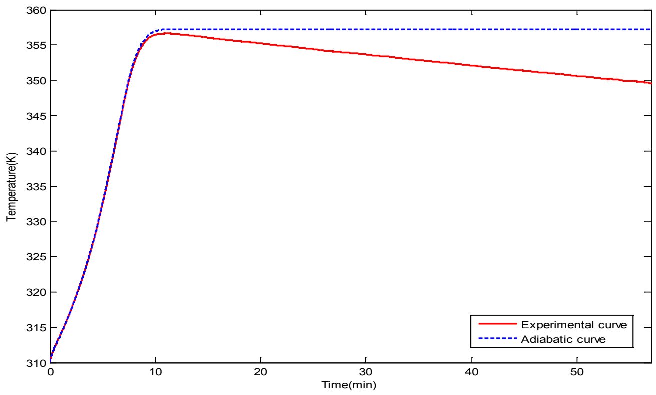

Figure 4: Temperature-time plots of acetic anhydride-excess water reaction at 310K.

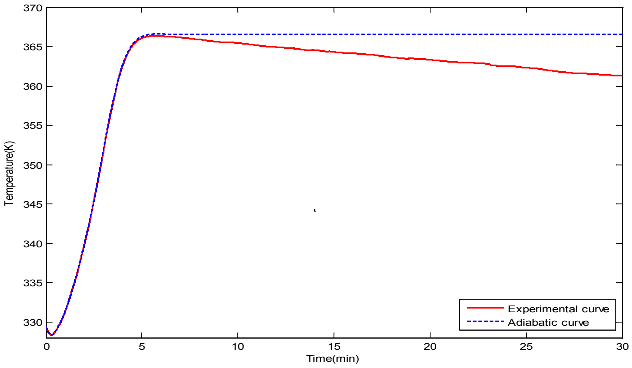

Figure 5: Temperature-time plots of acetic anhydride-excess water reaction at 328K.

Experiment	T(o)(K)	$T_{(max\ adiabatic)}$(K)	$(\Delta T)_{adiabatic}$(K)
1	305.10	358.50	52.67
2	310.10	358.70	56.40
3	328.40	366.40	38.00

Table 3: Summary of the characteristics of the above temperature-time plots of figures (3-5).

temperature and concentration and for a pseudo-first process such acetic anhydride reacting in excess water, at a particular temperature the specific rate constant value should be the same in all three cases of the processes considered (Figures 6-8).

Recall that $k(T) = \dfrac{-r_A(T)}{C_A}$ (18)

The average rate of reaction at a particular time was determined from the concentration time-time plots by determining the first derivatives at different time intervals numerically using the concentration-time data of the runs (Tables 4-6).

Kinetics and thermodynamic analysis of the experiments

The rate information obtained from the concentration-time plot enabled one to calculated specific rate constant k(T) of the processes at any time (t) and temperature (T). Arrhenius plots was thus generated from which kinetic parameters of runs was extracted (Figures 9-11).

The values obtained for the specific rate constants as a function of temperature are given in equations 27, 28 and 29 below:

$$k_1(T)=1.68*10^7\, exp\left(-\frac{6078.7}{T}\right) \quad (19)$$

$$k_2\left(T\right)=1.78*10^7\, exp\left(-\frac{6108.3}{T}\right) \quad (20)$$

$$k_3(T)=1.22*10^7\, exp\left(-\frac{6062.2}{T}\right) \quad (21)$$

The thermodynamic information extracted from the experiments was the heat of the reaction (ΔH_{rxn}). This was assumed to be independent of temperature and was determined by using equation 10. Table 7 shows ΔH_r values of the various experiments.

Experimental Procedures and Results

Excess acetic anhydride-water reactions-hydrolysis-B

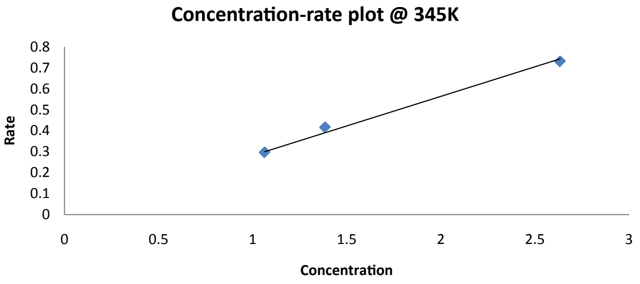

Figure 6: Concentration-rate plot at 345K.

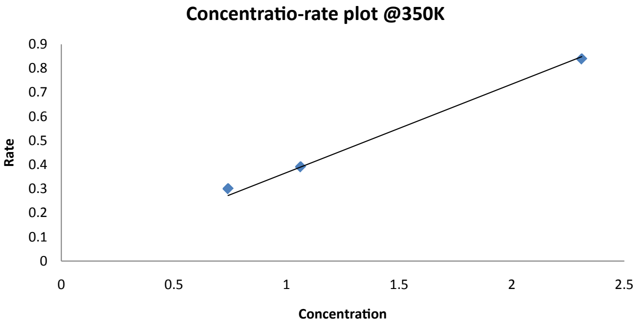

Figure 7: Concentration-rate plot @ 350K.

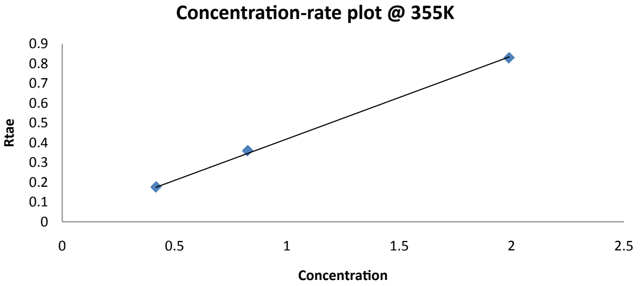

Figure 8: Concentration-rate plot @ 355K.

T=345K			
Experiment	Concentration	Rate	Rate constant (k)
1	1.0637	0.2965	0.2787
2	1.3848	0.4160	0.3004
3	2.633	0.7300	0.2772
Average (k)		**0.2854**	
Standard deviation (k)		**0.0013**	

Table 4: Variations of temperature, rate and concentration at T =345K.

T=350K			
Experiment	Concentration	Rate	Rate constant (k)
1	0.7403	0.3005	0.4059
2	1.0623	0.3913	0.3684
3	2.3109	0.8391	0.3613
Average (k)		**0.3785**	
Standard deviation (k)		**0.024**	

Table 5: Variations of temperature, rate and concentration at T=350K.

Analytical reagent grade acetic anhydride and distilled water was used in all experiments. In these experiments 2.645 mols of acetic anhydride was injected into the reaction vessel followed by 0.556 mols of distilled water. These quantities (volumes) were used so that at least 60% of the length of the sensor (thermistor) would be submerged in the

T=355K			
Experiment	Concentration	Rate	Rate constant (k)
1	0.4177	0.1746	0.4199
2	0.8256	0.3590	0.4348
3	1.9893	0.8283	0.4164
Average (k)		**0.4237**	
Standard deviation (k)		**0.0098**	

Table 6: Variations of temperature, rate and concentration at T=355K.

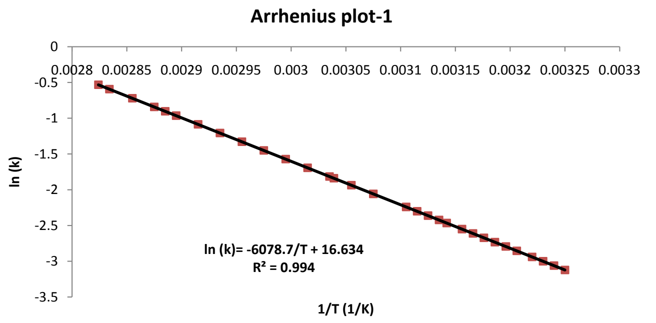

Figure 9: Arrhenius plot of experiment-1.

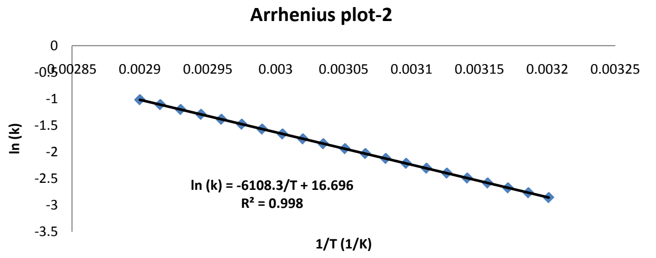

Figure 10: Arrhenius plot of experiment-2.

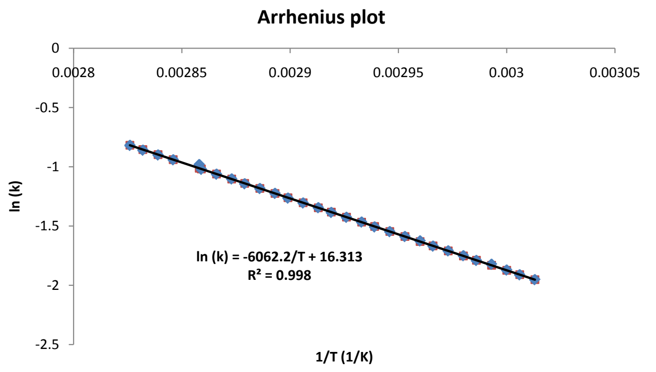

Figure 11: Arrhenius plot of experiment-3.

resulting initial reacting mixture. Reactants were brought to a steady-state temperature before starting the stirrer to initiate the reaction.

The stirrer speed was set at 1000 rev/min, the resulting voltage -time profiles were captured and the corresponding temperature-time curve was determined using the thermistor equation derived above. Runs were carried out adiabatically at the following initial temperatures: 286.8K, 293.6K and 304.5K.

Determination of UA/mC_p for the reaction mixture

The quantity UA/mC_p was determined for each of the runs using the cooling parts of the experimental curves. It is noticed from the cooling parts of the runs were similar to the curve cooling water experiments described in section above. It was an indication the cooling part of the experimental runs was real cooling process and no reaction took place during that process. The cooling parts thus follow eq 14 above. A nonlinear regression analysis was performed on all the cooling parts and the value of UA/mC_p was determined for all the experimental runs. The steady-state temperature (T_s) for the experiments was 293K. The regressed lines of the experiments cooling sections and their UA/mC_p was obtained and used for the corrections of the experimental curves, corresponding experimental and adiabatic curves are shown in Figures 12-14. The adiabatic curve was determined using equation 7 above.

Table 8 shows initial temperatures and the corresponding values of the UA/mC_p of the runs.

From eq 11 the variation of water concentration with temperature/time was deduces as:

$$C_{H20}=2.13 - a\,(T-T_o) \qquad (22)$$

The constant (α) in eq 22 was calculated using the initial

Experiment	1	2	3
ΔH_{rxn}(kJ/mol)	-53.36	-53.44	-53.51

Table 7: Thermodynamic information of the experiments.

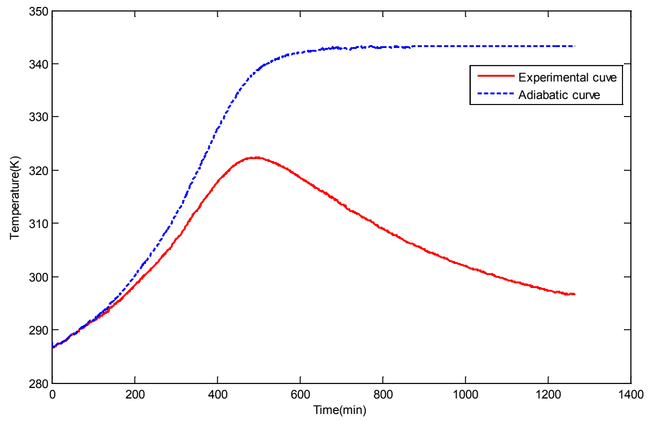

Figure 12: Experimental and Adiabatic curves of experiment-4.

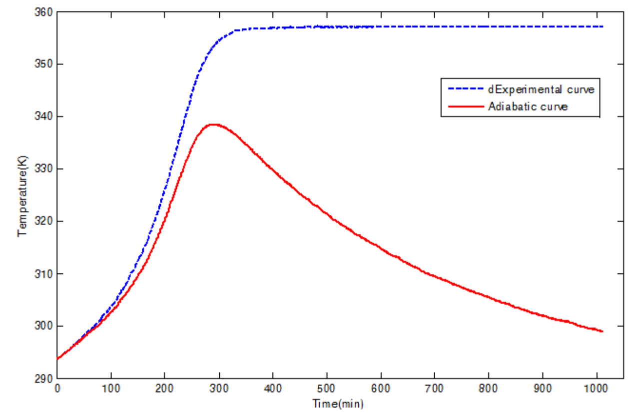

Figure 13: Experimental and Adiabatic curves of experiment-5.

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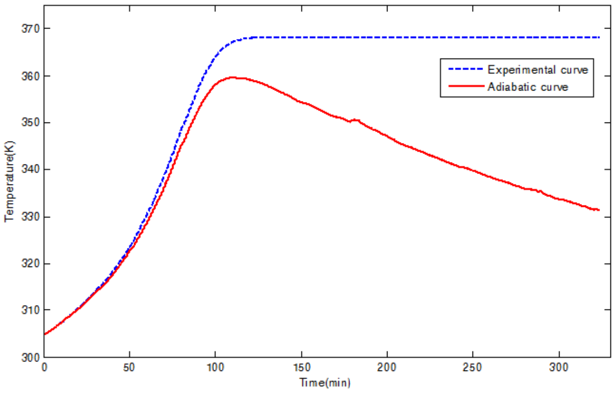

Figure 14: Experimental and Adiabatic curves of experiment-6.

Experiment	Initial Temperature(K)	UA/mC_p (min^{-1})
4	286.8	0.002030
5	293.6	0.002698
6	304.5	0.002795

Table 8: UA/mC_p of hydrolysis-B experiments.

Experiment	T(0)(K)	$T_{max(adiabatic)}$(K)	$\Delta T_{exp(adiabatic)}$(K)
4	286.8	343.2	56.4
5	293.6	357.1	63.5
6	304.5	368.3	63.8

Table 9: Summary of the characteristics of the above temperature-time plots.

T=320K			
Experiment	Concentration	Rate	Rate constant (k)
4	1.42458	0.0050506	0.0003545
5	1.55912	0.0.008286	0.0053150
6	1.79670	0.0.014893	0.0082890
Average (k)		**0.0057163**	
Standard deviation (k)		**0.0023973**	

Table 10: Variations of temperature, rate and concentration at T =320K.

concentration of the water 2.13 mol/L and the adiabatic theoretical temperature change $(\Delta T)_{adiabatic}$ (Table 9).

Variation of rate of reaction with concentration change

The tables and the profiles below show the variation of concentration, rate of reaction at specific temperatures of hydrolysis B experiments (Table 10 and Figures 15-17).

Kinetics and thermodynamic analysis of the experiments

The rate information obtained from the concentration-time was to calculated specific rate constant k(T) of the processes at any time (t) and temperature (T). Arrhenius plots was thus generated from which kinetic parameters of runs was determined. The Figures 18-20 shows the Arrhenius plots for all the three experiments.

The values obtained for the specific rate constants as a function of temperature are given in equations 23, 24 and 25 below:

$$k_1(T)=5.99*10^3\,exp\left(-\frac{4598.1}{T}\right) \tag{23}$$

$$k_2(T)=1.25*10^3\,exp\left(-\frac{4015.6}{T}\right) \tag{24}$$

$$k_3(T)=7.69*10^7\,exp\left(-\frac{4711.5}{T}\right) \tag{25}$$

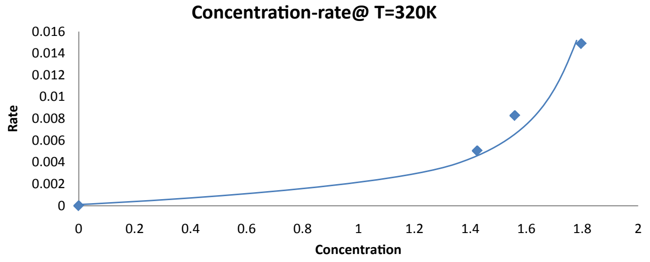

Figure 15: Concentration-rate plot at 320K.

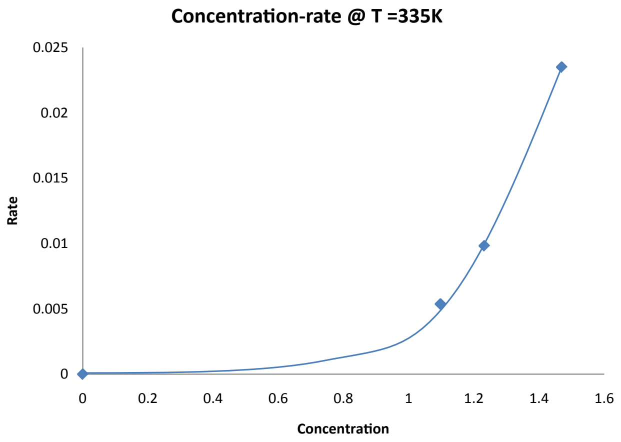

Figure 16: Concentration-rate plot @ 335K.

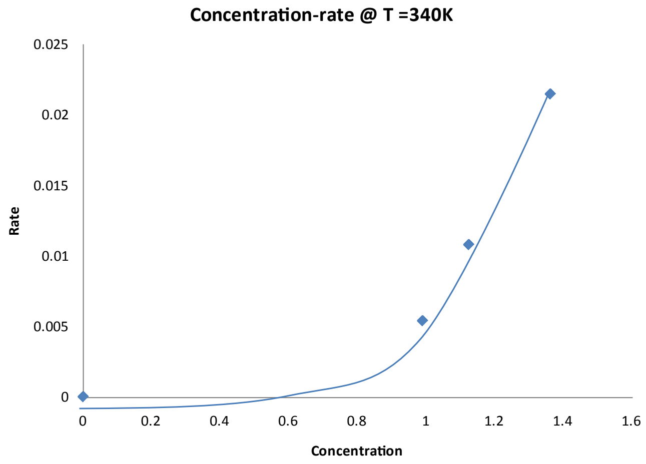

Figure 17: Concentration-rate plot at 340K.

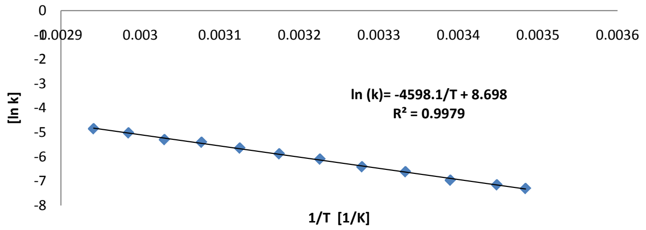

Figure 18: Arrhenius plot of experiment-4.

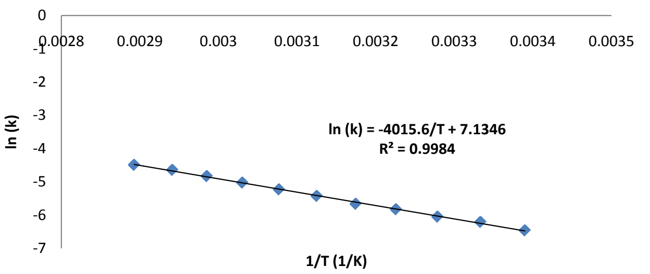

Figure 19: Arrhenius plot of experiment-5.

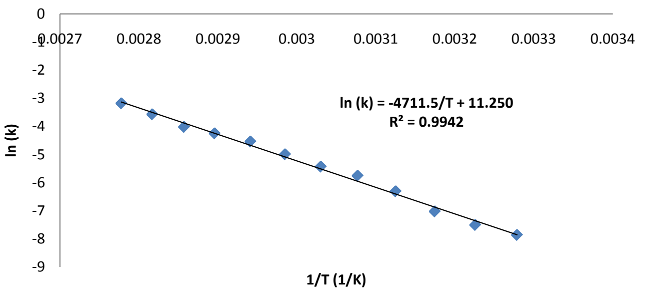

Figure 20: Arrhenius plot of experiment-6.

The thermodynamic information extracted from the experiments was the heat of the reaction (ΔH_{rxn}). This was assumed to be independent of temperature and was determined by using eq 8. Tables 11-13 shows ΔH_r values of the various experiments.

T=335K			
Experiment	Concentration	Rate	Rate constant (k)
4	1.0972539	0.0053749	0.0048985
5	1.2317951	0.0098262	0.0079771
6	1.4693163	0.0235028	0.0159953
Average (k)		**0.0096236**	
Standard deviation (k)		**0.0057287**	

Table 11: Variations of temperature, rate and concentration at T =335K.

T=340K			
Experiment	Concentration	Rate	Rate constant (k)
4	0.9881278	0.0053892	0.0054539
5	1.1226940	0.01079109	0.0096116
6	1.3602177	0.0214770	0.0157889
Average (k)		**0.0125524**	
Standard deviation (k)		**0.0081873**	

Table 12: Variations of temperature, rate and concentration at T =340K.

Experiment	4	5	6
ΔH_{rxn}(kJ/mol)	-53.92	-60.71	-60.99

Table 13: Thermodynamic information of the experiments..

Discussion of Results

The experimental results in all the processes studied showed that a strong relationship exists between reaction rates and changes in temperature for exothermic reactions as stated in the literature [9,10]. The reactions between excess water (10 mols) and acetic anhydride (1 mol) thus hydrolysis reactions-(A) were carried out at 305K-366K. The extent of the reactions was followed by monitoring the changes in temperature in the reaction vessel (thermos-flask). The experimental and the adiabatic curves are shown in Figures 3-5. The reactions between excess acetic anhydride (2.65 mols) and water (0.55 mol) thus hydrolysis reactions-(B) were carried out at 286 K-368 K. The profiles of experimental and adiabatic curves are shown in Figures 12-14 respectively. The experimental reaction profiles (Hydrolysis process-A and Hydrolysis process-B) of this study shows that hydrolysis process-A and hydrolysis process-B are completely two different processes. One unanticipated finding was the nature of the hydrolysis-B profiles compared with the hydrolysis-A profiles. On the other hand, another interesting finding was the cooling parts of the processes. Hydrolysis-A, showed very gradual cooling process as compared with Hydrolysis-B which showed a cooling process similar to the cooling process of the experimental determination of heat transfer coefficient of the of the reaction vessel (thermos-flask). There may be several possible explanations to these observations. A possible explanation for this might be that the rate of heat loss during the cooling processes is higher for hydrolysis-B than that of hydrolysis-A under the same experimental conditions these parts thus suggests real cooling process. On the other hand, the rate of cooling of the hydrolysis-A processes, although very slow there might be some amount of hydrolysis reactions taking place. It is also interesting to note that, the processes (hydrolysis A and B) showed different reaction times for the processes to reach their maximum temperatures during their reactions. This finding was somewhat not surprising. The observed differences discussed is however very significant. The reaction order for all the hydrolysis-A experiments were first order with respect to the acetic anhydride. This is shown in the rate-concentration plots in the Figures 6-8. This result is consistent with other researchers Kralj [2] and Haji et al. [1].

However, contrary to our expectations the rate -concentration plots of the hydrolysis-B was very surprising as the profiles appeared to be part of a parabola suggesting a second other process. This finding is unexpected and has not previously been reported. The rate law temperature dependence were satisfactorily correlated by means of the Arrhenius function for the hydrolysis-A. Figures 9 -11 shows the Arrhenius plots of the hydrolysis-A. From the plots the values of the activation energies and pre-exponential factors were determined as shown in the equations 19-21. Similarities of the activation energies (50.54 kJ/mol, 50.78 kJ/mol, 50.40 kJ/mol) which agrees very well with what is reported by Haji [1] and Kralj [2]. The average activation energy reported in the literature is 50.24 kJ/mol, Haji [1] which differs by +0.65% from the average value reported in this work. For the hydrolysis-B processes, Arrhenius functions for the hydrolysis-B are shown in Figures 18-20. From the plots, the values of the activation energies and pre-exponential factors were determined as shown in the equations 23-25. The activation energies (38.23 kJ/mol, 33.89 kJ/mol, 39.19 kJ/mol) are however smaller than that of the hydrolysis-A, this is not surprising since the studies has shown that the kinetics of the hydrolysis-A and hydrolysis-B appears very different processes. These activation energies of the hydrolysis-B reactions have not been reported in the literature. The heat of the reactions determined from the experiments was assumed to be independent of temperature. The values obtained for hydrolysis-A is shown in Table 7. The average value compared well with what was obtained by Glasser and Williams [9]. The values determined for the hydrolysis-B are shown in the Table 13.

Conclusions

The kinetics of the reactions acetic anhydride-excess water, excess acetic anhydride-water has been modeled as a function of temperature in an adiabatic batch reactor (thermos-flask) using a negative coefficient thermistor as a measuring device. The results has shown that the acetic anhydride-excess water process at 1: 10 mole ratio the process remains first order at higher temperatures up about 366K with the activation energy similar to that reported at 298K.

Excess acetic anhydride-water reactions which have no literature information on its kinetics were shown to follow a second order kinetics with respect to the water. The activation energy is approximately 37.1 ± 2.8 kJ/mol. The heat of reaction which was assumed to be independent of temperature for the excess acetic anhydride/water is approximately 58.5 ± 4.0 kJ/mol. The heat of mixing was assumed negligible and was not considered in the heat of reaction calculations. This studied has shown that the two processes studied appears to be completely different processes and may have completely different reaction mechanisms pathways for the acetic acid production.

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Nomenclature

ΔH_{rxn}- heat of reaction (KJ/mol)

ΔT (ad) – adiabatic temperature change (K)

$\Delta\varepsilon$ – extent of reaction

A – preexponential factor

B,C – thermistor constants

C_A - concentration of A (mol/L)

C_P – specific heat capacity

$C_{P,AA}$ – specific heat capacity of acetic anhydride

$C_{P,mix}$ - constant heat capacity of reaction mixture (kJ/mol.K)

$C_{P,W}$ – specific heat capacity of water

E_a – activation energy

I_{total} – total current of the circuit

k_1, k_2, k_3 - specific rate constant

m – mass

M_{AA} – Mass of acetic anhydride

M_{AA} – Mass of water

M_{eqv} – Equivalent amount of water

M_T - mass of reaction mixture(Kg)

N_A – mole of A (mol)

p - probability factor

Q - heat produced by stirrer

R – molar gas constant

R_2 – known resistance in the circuit

r_A – rate of reaction of (A)

R_{TH} – Thermistor resistance

t – time

T – absolute temperature

T_{max} – maximum temperature (K)

T_o – initial temperature

T - reactor temperature (K)

T_S – steady state temperature (K)

T_s – steady-state temperature

U – heat transfer coefficient (J/m^2 s.K)

v – total voltage of the circuit

V -volume

V_{out} – voltage measured by thermistor

V_{TH} – voltage across thermistor resistance

Z - collission frequency

α, β - constants

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