

Advanced Chemical Thermodynamics & Kinetics
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Lecture - 41
Chemical Kinetics: Hydrolysis of an ester

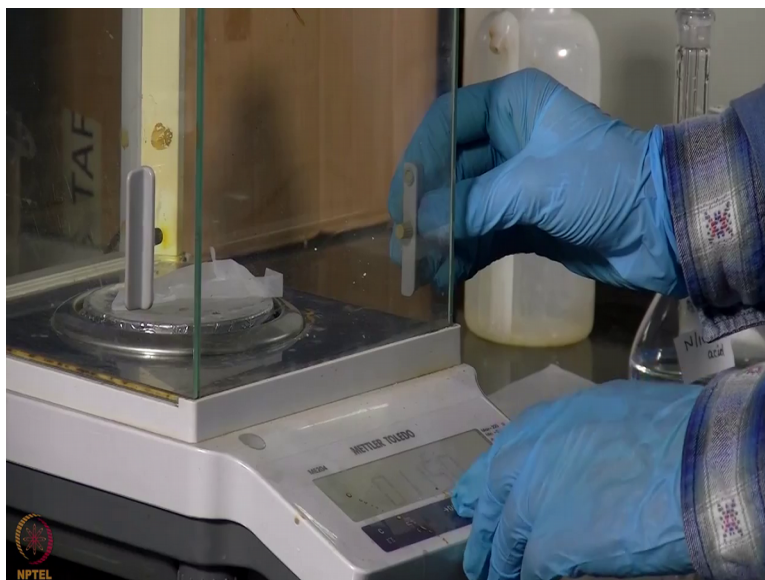
Hello into today's experiment, we will be performing the hydrolysis of an ester, methyl acetate which is catalyzed by the acid HCL. So, as we know that hydrolysis product of any ester are usually an carboxylic acid and then alcohol. So, here the products of hydrolysis of methyl acetate are acetic acid and methanol.

So, when we write the rate of reaction for this, we will see that the rate of reaction seems to be of a higher order. But since acid here is the catalyst so; its concentration remains constant throughout the reaction. And water which is present in excess amount has also an active mass constant throughout the reaction.

So, we see that the rate of reaction only varies with the concentration of methyl acetate. So, the reaction is usually a first order reaction, we call such reaction as pseudo first order reactions. So, the kinetics of the reaction will be performed by titrating the produced acetic acid with a certain concentration of NUL. Here, we are using n by 15 normal NUL solution for titrating the acid produced during the reaction. And the HCL used for catalyzing the reaction is roughly n by 2 normal N O HCL solution. So, we need to first determine the actual concentration of our HCL and NUL used for the reaction.

So, for exactly determining the concentration of NUL, we will standardize it using a 0.1 normal oxalic acid. This standardized NAOH will then be used to standardize the given or the used HCL solution in the reaction. So, to prepare 0.1 normal oxalic acid we will need to weigh 0.63 gram of oxalic acid, dihydrate and then dissolve it in 100 milliliter of water.

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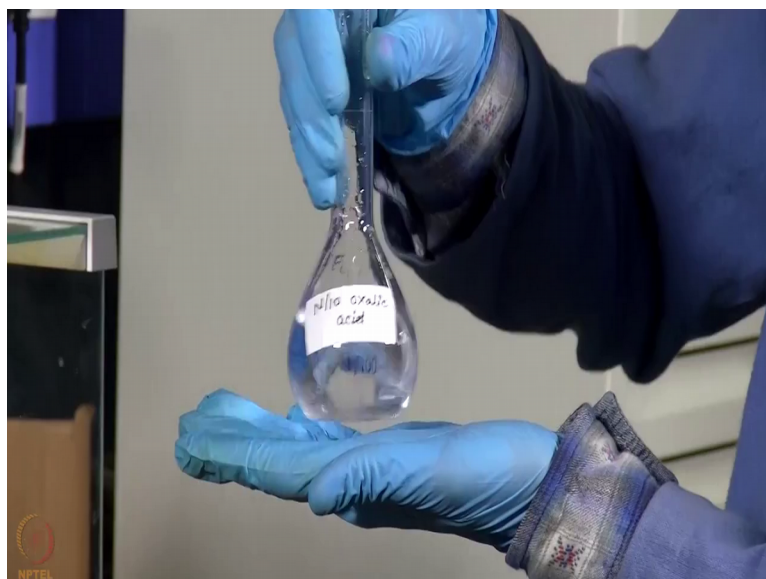
So, we will now weigh 0.63 gram of oxalic acid dihydrate. So, we have now around 0.63 gram of oxalic acid we will take it out and we will then add it to a 100 ml volumetric flask.

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We will first dissolve it using the swirling motion. So, now our oxalic acid is dissolved in this water. We will now make the volume up to the work mark by adding some more water.

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So, now that we have our 0.1 normal oxalic acid prepared which you prepared by adding 0.63 gram of solid oxalic acid dehydrate into 100 ml of water. So, what will we do next? We will take 10 ml of this oxalic acid solution into a 100 ml conical flask.

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And we will then add phenolphthalein to it as an indicator. So, we know that under basic condition phenolphthalein changes its color from colorless to pink color or purple color which shows that indication of the reaction that the reaction is completed.

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So, now we will take 10 ml of oxalic acid into to this pipette. This 10 ml oxalic acid will now add to this 100 ml conical flask. We will then add few drops of phenolphthalein indicator to it. After adding the phenolphthalein indicator, we will now perform the titration using NaOH.

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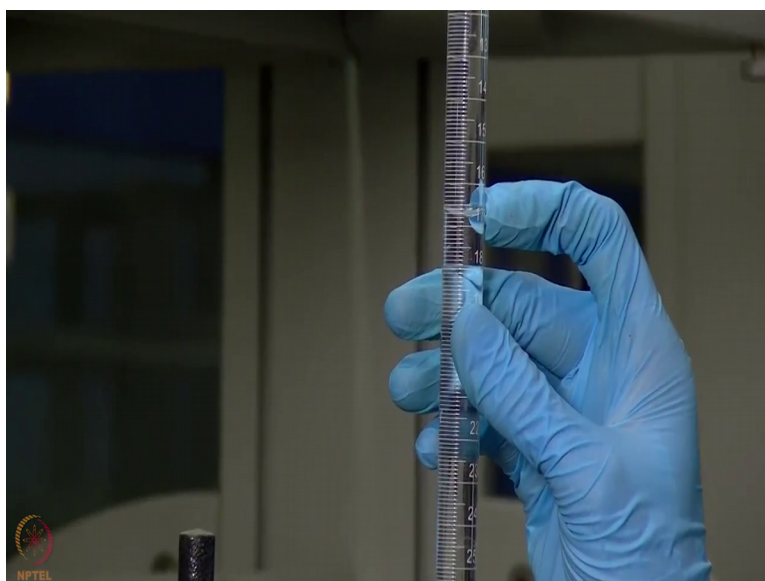


So, now we can see that our solution has changed from colorless to slightly purple color which indicates that the reaction has raised its end point. So, because phenolphthalein is colorless in neutral or acidic condition but it purple in slightly alkaline or alkaline medium. So, because we have added a slight excess of NaOH to determine its end point so, the solution has turned to purple color. And we can see that we started from 0 marker of our burette and we have reached at around 16.8 ml.

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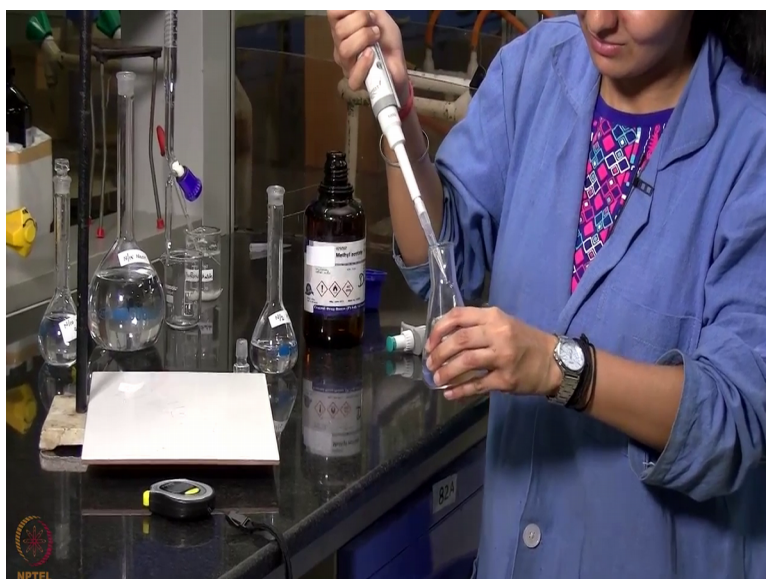
So, 16.8 ml of NaOH is required to neutralize this 0.1, normal 10 ml of 0.1 normal oxalic acid solution. Now, you will repeat this experiment two more times to get concordant readings. We will then average these readings for our further calculations. So, now, that our standard calculation of NaOH is complete. We will now standardize our HCL using this NaOH. We will take 5 ml of HCL into this conical flask and then add phenolphthalein indicator to it.

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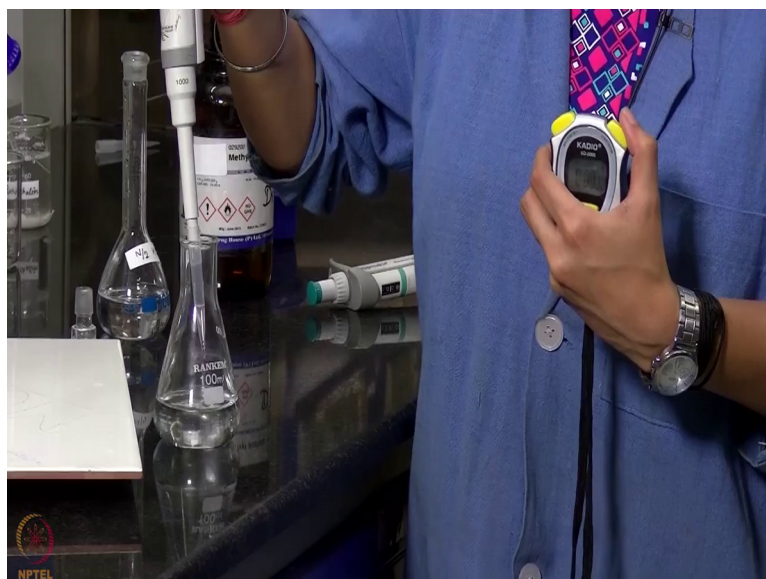


And we will now titrate it using NaOH. So, now, the titration of our HCL is complete. Now, we will perform this experiment two more times and try to get concordant readings and then we will use these readings for our calculation. Now, that we have standardized our NaOH and HCL solutions will be taking 50 ml of the HCL solution that we had prepared in this conical flask. And then we will be adding 2 ml of methyl acetate to it.

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And when we are half way through our addition will start the stop watch.

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Now, will be immediately taking 2 ml of this solution and we will be adding it to 20 ml of ice cold water. Now that we have added the 2 ml solution to ice cold water in order to quench the reaction. Now will be titrating it against NaOH solution using phenolphthalein as indicator.

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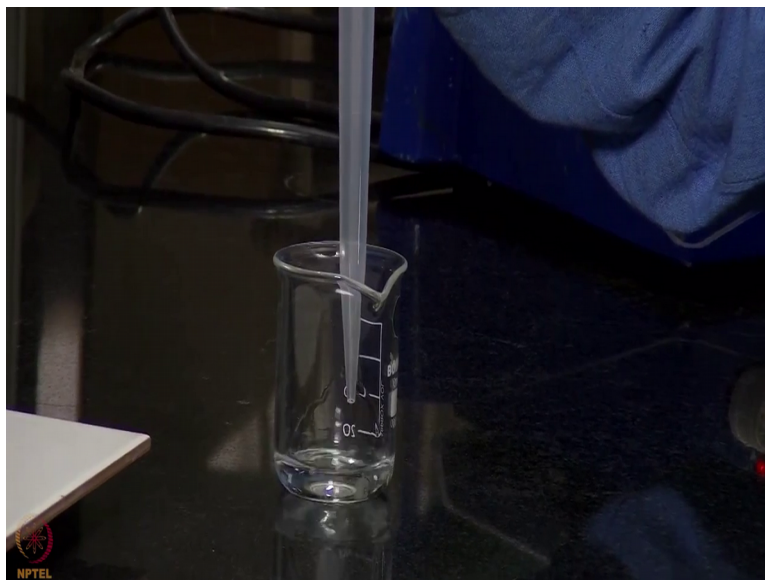
Now that the titration is complete and the color of solution has changed to purple. The value that we are getting here corresponds to the V_{naught} value that will be using for further calculation. Now similarly, we will be titrating the solution which we have kept at different intervals of time will be withdrawing the solutions and titrating in a similar manner and will proceed.

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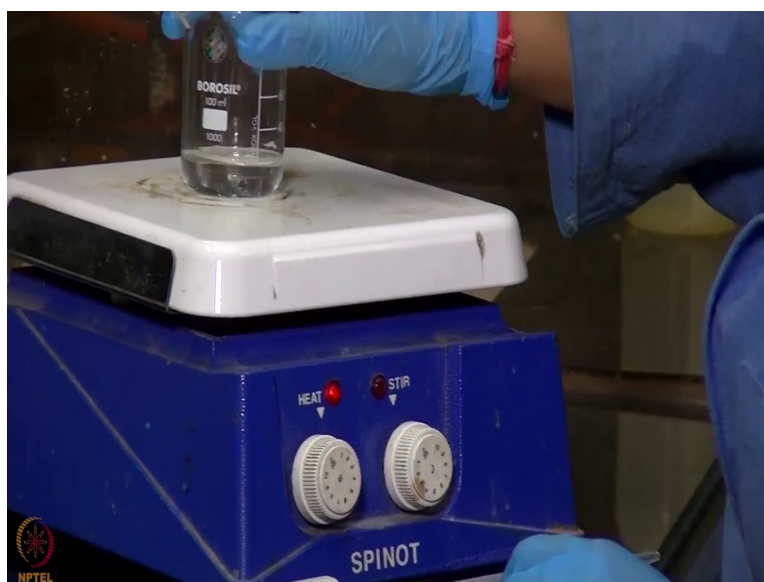


This is the methyl acetate and HCL mixture that we had. So, we will be withdrawing 10 ml from the solution. And will be putting it inside a beaker then will heat on a heating mantle at 70 degree celsius for half an hour.

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We are heating the solution, because we are assuming that within this time period the reaction will be complete. Now, the other solution is being heated up for half and hour will switch off the heating mantle and bring it to room temperature. Now that the solution has come to room temperature, we will be withdrawing 2 ml from this. And

adding it to ice cold water and then titrating it against NaOH solution. As we, as we were doing earlier and the titer value that will get now will correspond to V_{∞} that will be using for calculations.

So, now that we are done with performing the experiment, we have the readings for volume at time t is equal to V_t . Volume at various time which we call as V_t and volume at time t is equal to infinity. We will now get a plot between \log of infinity minus V_t divided by V_{∞} minus V_t versus time in minutes. The slope of this curve will now be used to determine the rate constant for the reaction. So, in this way, we are able to determine the rate constant of hydrolysis of methyl acetate using HCL as a catalyst. We have a similar reaction in which we use base as a catalyst, but that reaction is a second order reaction.

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Observations

Determination of rate constant

(Titration of Reaction mixture with NaOH solution at different times)

S.No.	Time(min)	Volume of NaOH used(ml)	$V_{\infty} - V_t$	$\frac{V_{\infty} - V_0}{V_{\infty} - V_t}$	$\log \frac{V_{\infty} - V_0}{V_{\infty} - V_t}$	$k = \frac{2.303}{t} \log \frac{V_{\infty} - V_0}{V_{\infty} - V_t}$
1.	0	15.2	17.0	1.0	0.0	----
2.	6 ✓	16.1	16.1	1.06	0.025	0.0096
3.	12 ✓	17.0	15.2	1.12	0.049	0.0094
4.	18 ✓	17.5	14.7	1.16	0.064	0.0082
5.	30 ✓	18.8	13.4	1.27	0.104	0.0080
6.	36 ✓	19.2	13.0	1.31	0.117	0.0075
7.	41 ✓	20.0	12.2	1.39	0.143	0.0080
8.	∞ ✓	32.2	0.0	----	----	----

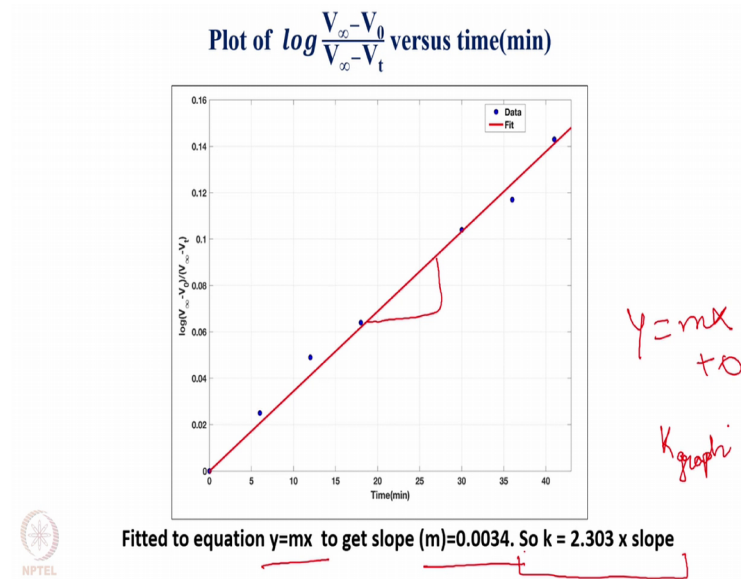
$$k_{\text{avg}} = 8.5 \times 10^{-3} \text{ min}^{-1}$$



These are the observations that we are getting for this experiment. So, this table shows the values of time at which the solution is withdrawn. And the volume of NaOH which, which is used to titrate the solution. So, at different times the solution is withdrawn from the flask that we had kept which contains the acid and the ester. So, we withdrew the solution at 6 minutes, 12 minutes, 18, 30, 36 and 40 minutes. And the initial value is the value of V_{∞} and the value, which corresponds to different times is V_t and after heating the solution that the value that we obtain is known as V_{∞} .

So, using these values we are calculating the value of $V_{\infty} - V_t$. And then we are calculating $V_{\infty} - V_0$ divided by $V_{\infty} - V_t$ and then we are taking the log of these values. And the rate constant is given by this expression, 2.303 by $t \log \frac{V_{\infty} - V_0}{V_{\infty} - V_t}$. And then we are plotting the value of $\log \frac{V_{\infty} - V_0}{V_{\infty} - V_t}$ versus time.

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And this is the plot that we obtain which and then these are the values that we got. And this is then fitted to an equation of the kind y is equal to $m x$ with a 0 intercept value. And the value of slope which is obtained is equal to 0.0034 and the value of k is equal to 2.303 times the slope value that we are getting here. So, this will be the k value which will be obtained from the graph and the previous value which was mentioned here, k average that is the one which is obtained by averaging these values.

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Result

The rate constant as calculated from the table is $k_{\text{avg}} = 8.5 \times 10^{-3} \text{ min}^{-1}$

The rate constant as calculated from the graph is $k_{\text{graph}} = 7.8 \times 10^{-3} \text{ min}^{-1}$



So, this is the result that the value of calculate, the value of rate constant which is calculated from the table is 8.5 into 10 to the power minus 3 minute inverse. And the value which is calculated from the graph is 7.8 into 10 to the power minus 3 minute inverse for an acidic hydrolysis of ester.