Quantitative Methods in Chemistry
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Lecture-10
Classification of errors

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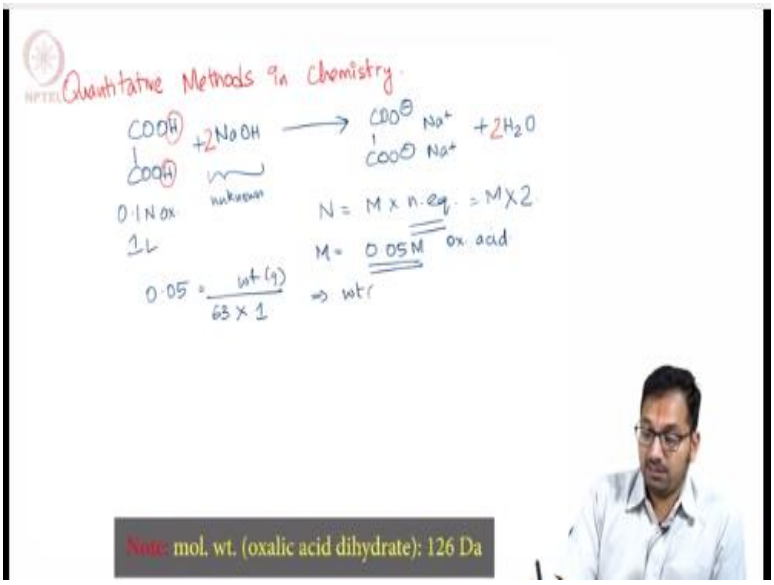

Welcome back to the lecture series in quantitative methods in chemistry. We are entering in to the third week. The week we saw how to quantitate concentration of different chemicals and different units that we would end up using. And in the next week we started to understand where do measurement uncertainty is how do they look in a data and how to understand them in terms of means, standard deviation.

And also how the uncertainty each of the measurement that you made end up doing would result an overall uncertainty and a final measurement. We also define terms like accuracy and precision that helps us understand what is the truth that we steak that is from the series of experiments that we end up doing. This week of lecture would be trying to understand where do these uncertainty is arise from.

It could be an experimental reason why it comes up or it could be a random reason why it comes up here will be trying to understand. What are the characteristics of such errors and how they can

be distinguish how they can be minimized if possible. So in order to do this why do not we start with an example. So let us take the example of something that we have done quite regularly in the initial part of this lecture.

Let us about oxalic acid neutralization with a sodium hydroxide say you are goanna form oxalates. And then water needless to say you will have to balance the equation that will end up becoming like this. So once we have balanced equation let us assume that we will be having this as the unknown you will see as we go forward in the lectures. That whenever you are doing standardization you always have a primary standard versus secondary standard NaOH is secondary standard.

So that for you generally standardize it against something that you know and in this case you will be standardizing it against oxalic acid. And let us say that we need to prepare 0.1 normal oxalic acid in order to do this purpose. Let us say we will prepare 1 litre of it, so the first step of this endeavor will be trying to understand how much grams you would end up using.

So let us quickly calculate that before going ahead we would also like to remind ourselves of the relation between normality and molarity. Remember the number of equivalence in this case would come up because of the 2 protons that get abstracted. So therefore this is going to be nothing but molarity times 2. So when you have something like this, makes life a little easy, so basically you want a calculate 0.05 molar of oxalic acid.

So with this being set, the next thing that you like to do is how much should you weigh of oxalic acid in order to prepare a 0.05 molar solution in 1 litre. So in order to do this all that you got it do is the do a simple math. So weight by molecular weight which I am sure we remember is 63 grams per mole times 1 litre of solution.

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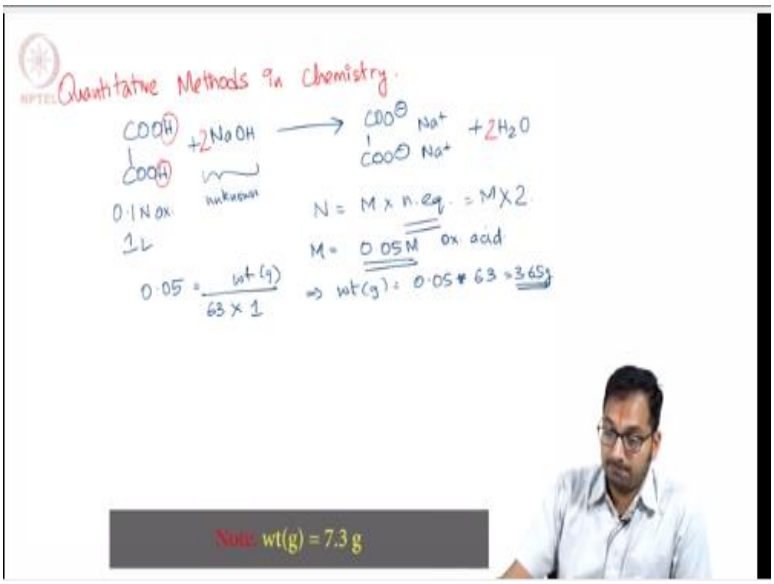

So this indicates that weight in grams is goanna be 0.5 times 6 that happens to be 3.65 grams. So if you dissolve 3.65 grams of oxalic acid in 1 litre of solution you end up getting 0.05 molar oxalic acid which in this context is 0.1 normal oxalic acid ok. Now that we have seen this you are able to recognize that there are 2 things that we are doing.

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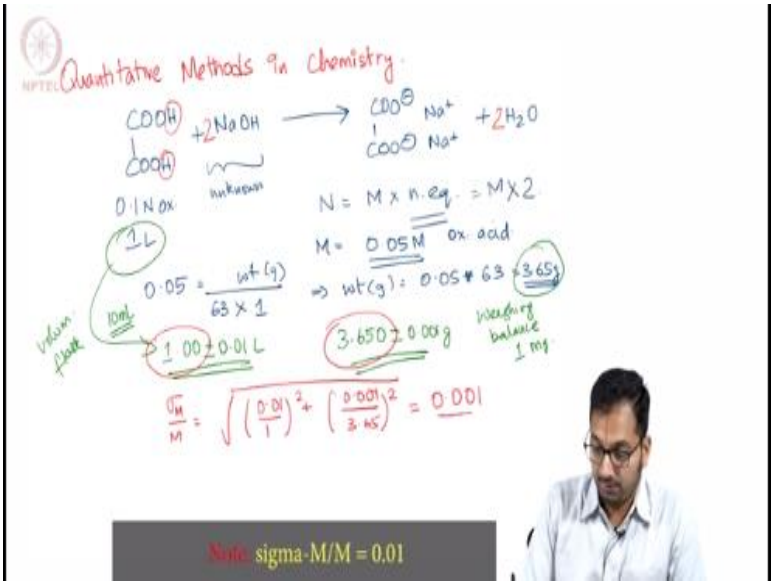

One is that we have to measure out a certain weight of oxalic acid and we have to dissolve it in 1 litre of a total solution. So little bit of thinking makes you understand you have to use the weighing balance. Most often it is an analytical balance we have use which gives us very good precision of about 0.1 milligrams. But for the sake of understanding here let assume that the weighing balance that we are using as the 1 milligram precision.

So therefore this is going to be nothing but 3.650 + - 0.001 grams and let us assume once again for the sake of argument the volumetric flask that you will be using has something like a 10 ml error, that could come up ok. So now when you have something like that you are goanna have 1.00 + - 0.01 litres. So now what you are able to realize is that you need to combine the 3.65 grams in 1 litre of solution to get the desired 0.1 normal oxalic acid for you to perform this titration.

So what you are able to realize you are going to be dividing 3.65 divided by 1 and if you recollect the error propagation that we did last time. So this is going to be governed by square root of 0.1 divided by 1 the whole square + 0.001 divided by 3.65 the whole square. So let us quickly see what it amounts to, so this amounts to something like 0.001.

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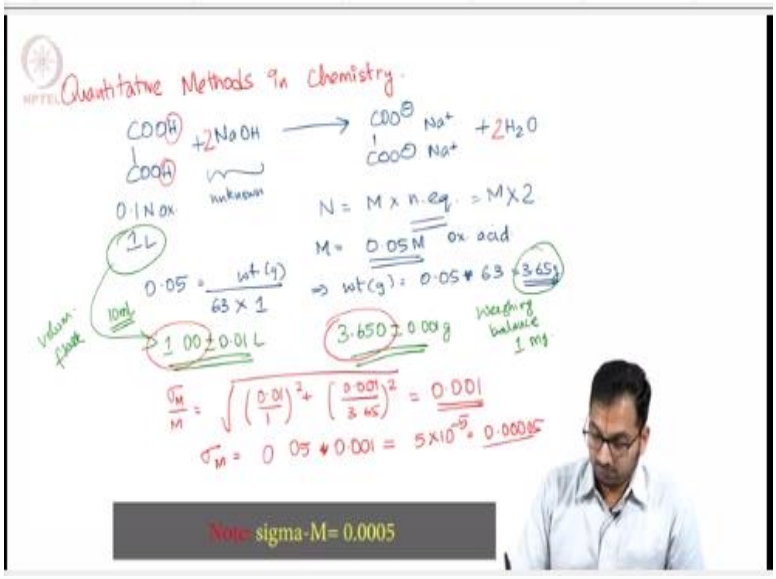

Of course this does not fully translate so this is going to be equal to 0.05 times 001, this will be nothing but 5 into 10 to the power of - 5. So which is goanna be ok.

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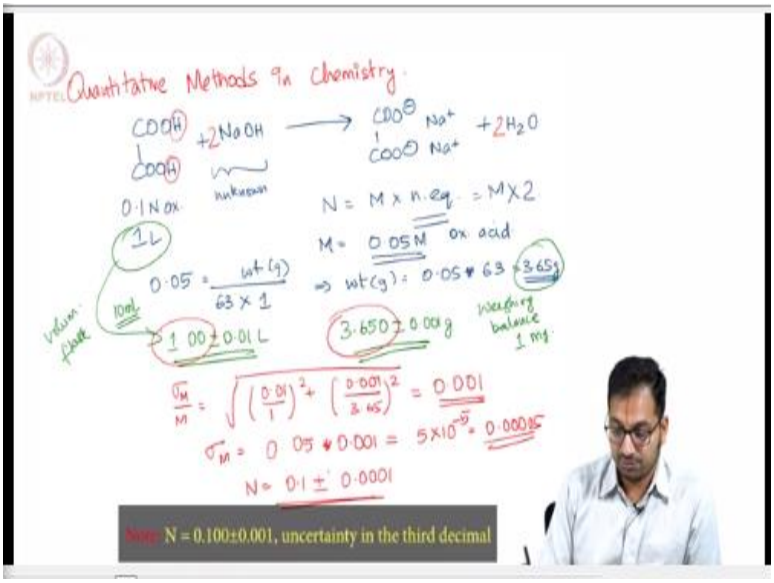

So this indicates the normality for this is going to be nothing but 0.1 + - 2 times of this that will be 0.0001.

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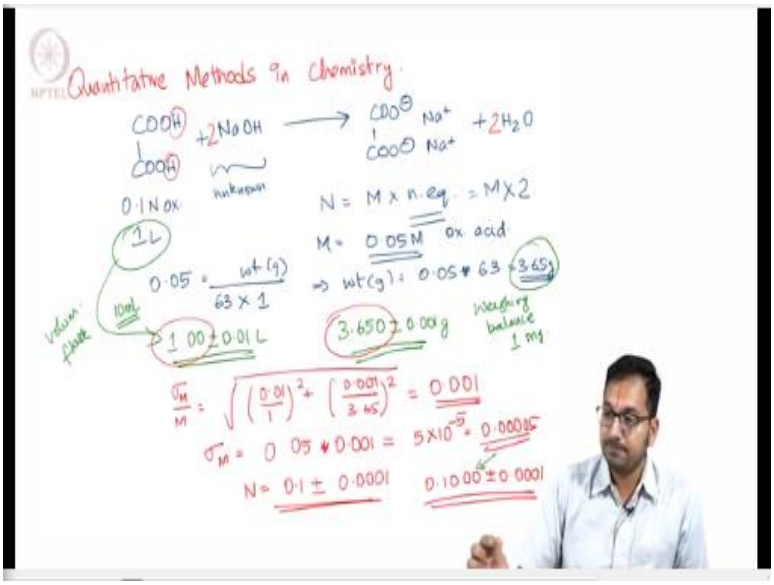

Of course this should not be written this way you gotta write something like this. This indicates once again that the lack of certainty comes from this value ok. So now that we have found this let us go to the next part.

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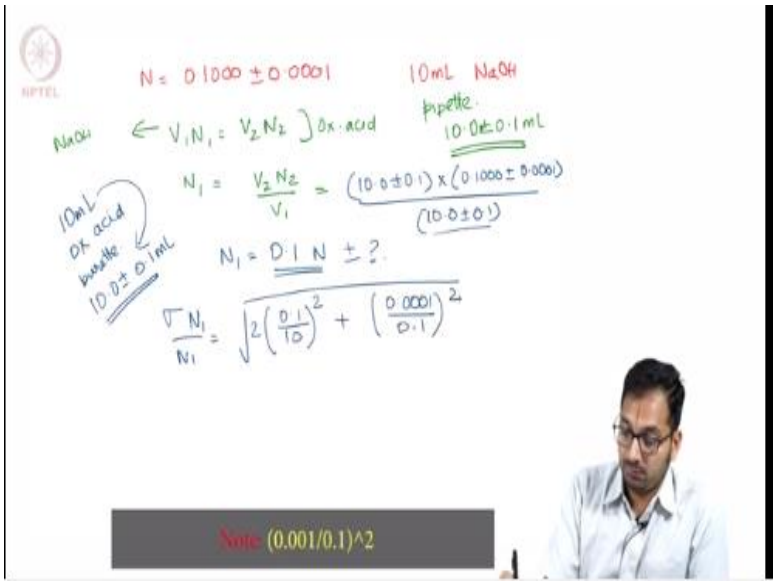

With the normality define at a certain level of precision to force significant figures, now the next question is let us say you are titrating 10 ml of NaOH, how do you get this NaOH. You generally use a pipette and this pipette would also have an error associated with it. So let us assume this is the 10.1 + - 0.1 ml that is the precision sorry 10.0 + - 0.1 ml precision that comes up. So now that you have this the equation that governs the relation between this 2 would be V 1 N 1 = V 2 N2.

Let us say this is for oxalic acid and this is for NaOH, so what is this going to end up happening is that the normality of NaOH is goanna be given by V 2 N 2 by V 1. And let us say now that you have pipette it 10 ml out and what volume of oxalic acid was required, just for the sake of math let us keep 10 ml of oxalic acid was required. So of course and this will be measured from a burette.

So **so** far what all you have seen you have seen the use of 4 different pieces of instruments or equipment where apparatus let us say where you have use the weighing balance which has a certain precision that it goes with . A volumetric flask pipette and burette let us also assume here also it is a 0.1 ml precision that you have. So what ends up happening is that you have 10.0 + - 0.1 multiplied by normality which is 0.1 followed by 000 + - it is precision divided by 10 + - 0.1.

Of course we are able to see the normality it cancels out, it comes up to be 0.1 normal of course this not the piece of the exercise, what we would like to understand is what is the error of the

precision that goes with it. So the N 1 the sigma N 1 is going to be given by N 1 with a square root of 0.1 by 10 0.1 the whole square since we are goanna write a 2 times because of the numerator and denominator, you can also put a 2 there times point the whole square.

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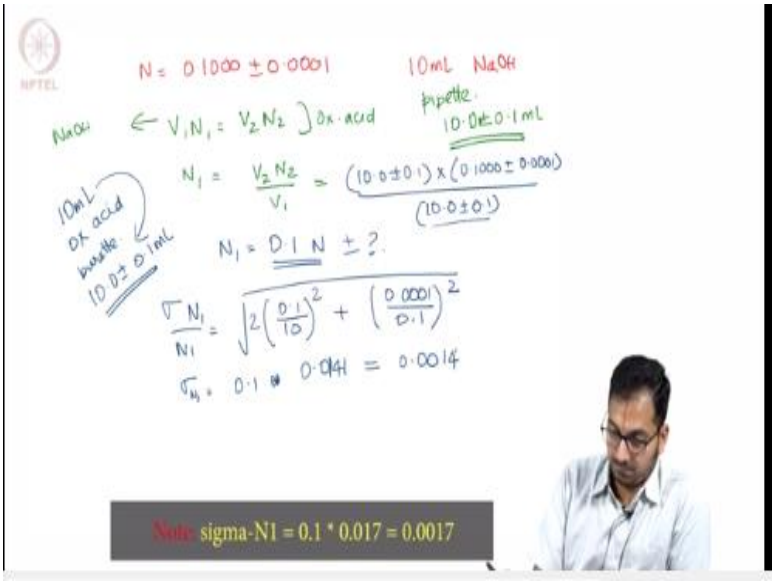

So now sigma N 1 comes out to be 0.1 times 0.041, so finally you are goanna get something like sorry.

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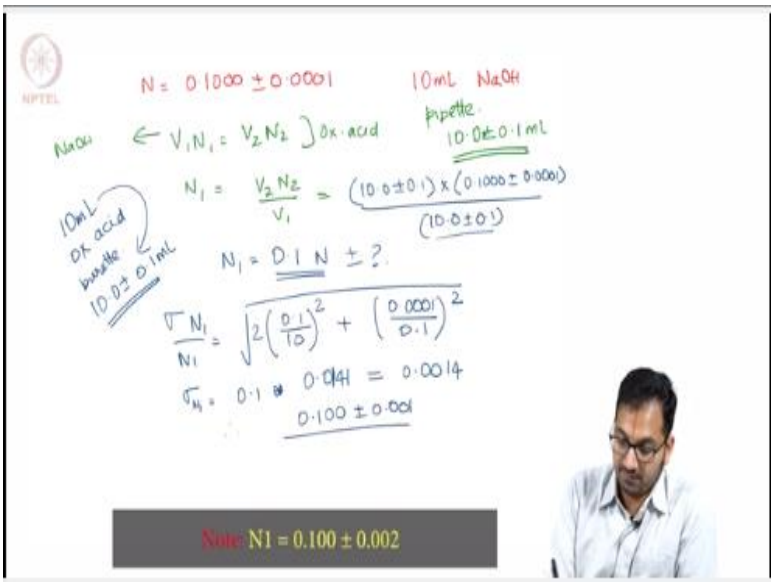

So therefore the normality is goanna be given as 0.100 + - 0.001, what you are able to realize is that depending upon the precision that each of the apparatus that we end up happening the final precision is changing.

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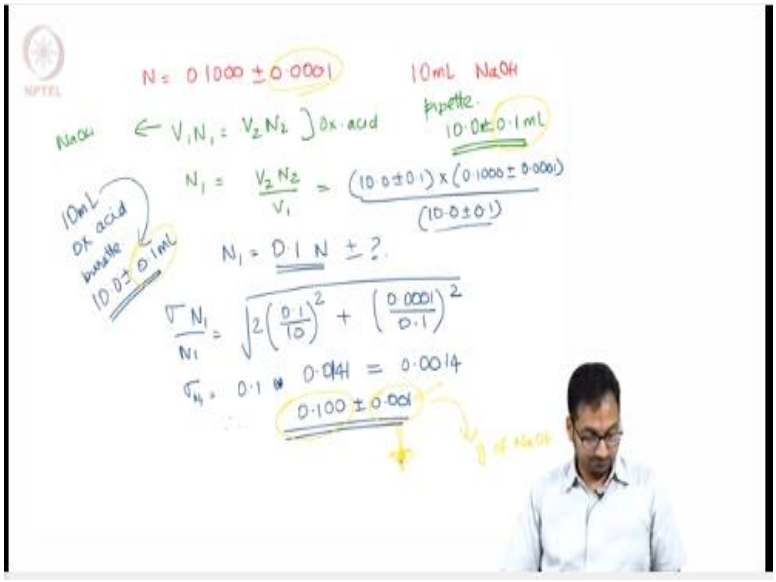

Although you had a very high precision to start with you are able to realize that an order of precision is being last in the way that you are measuring the final concentration of N 1. Of course do not forget that this has to be back calculated in to the number of grams of NaOH and what is that going to involve is the this is going to come up as an error in the weight that you are goanna end up measuring that you might have ended up measuring to start with.

So now the point is why what is the reason behind NaOH is not being used as a primary standard is because it is extremely hygroscopic. So when you try to measure it is weight during the process of weighing it ends up absorbing a lot of water which results in the concentration not being exactly what you wanted it to be. So therefore this way of standardizing using something like oxalic acid which does not suffer from such problems helps you determine the concentration of NaOH which you might end up using for titrating against other acids.

For instance let us say you want to understand how much amount of phenol is being dissolved in water as a function of temperature. In which case as you change the temperature you will dissolve different amounts of phenol then you will titrate it against the standardized NaOH in order to back calculate. So of course you must remember that this error that you have calculated here will propagate to the concentration estimation of phenol in this case ok.

Now that we have set the premise meaning that every measurement that we might end up doing every simple measurement even in terms of weighing balance taking it titration gives us this much amount of error, let us go into the aspect of understanding where these arise from.

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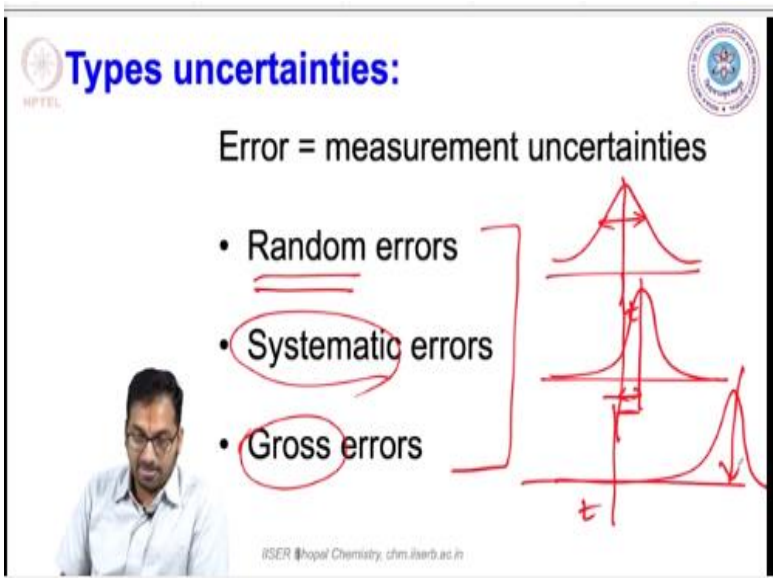

So basically the term error is generally used by an analytical chemist in the context of measurement uncertainties. One has to remember error does not mean the mistake that you end up doing. But the level at which we cannot be sure of a certain measurement that comes up intrinsically or maybe due to our own reasons. Most often these type of errors can be classified into these 3 major types one as random error quite a bit of which we solve the previous week.

We will be seeing more about it as we go forward, this is one error where let us say this is a true value you are goanna have a distribution that comes across. This results in the spread across mean value which you ended up measuring. On the other hand you could have systematic errors, what we mean by a systematic error is let us say this is a true value that you are looking at you did some mistake where you reproducibly did that mistake where the true value and a measured value end up being subtly different between each other.

On the other hand you could also have gross errors which completely take the truth away from the actual value which clearly indicating an out layer and these are errors that can be easily figured out and minimize as you do an experiment.

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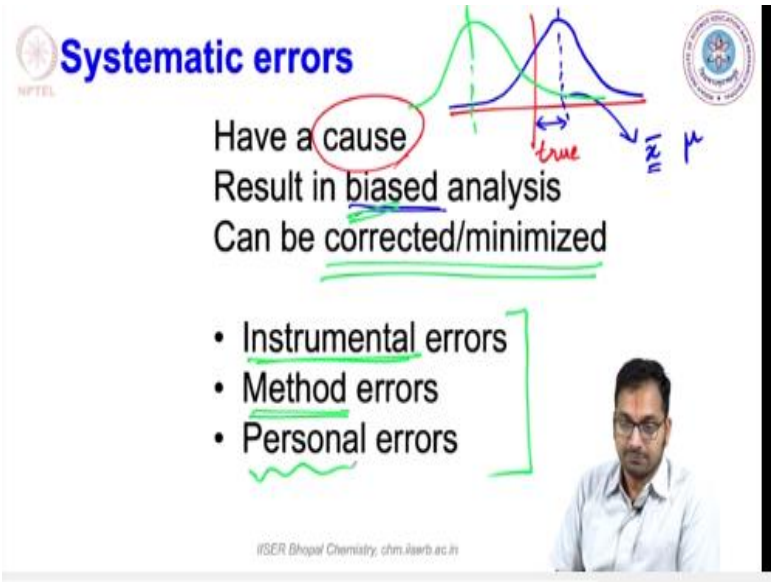

So let us start taking a look into most specifically how these errors are and what comes up I mean how do they come up. So if you take a look at systematic errors that is always a cause associated with the systematic difference that comes in the way you are evaluating. And remember this kind of a shift so let me draw the distribution again let us say this is the true value where you expect the true value to be in the line that has been drawn.

And let us say the actual distribution comes up cross like this whereas this is the measured value. Of course we always refer to the mean as the measured value, so the difference that comes up here could result in a biased way of analysis, you might start interpreting that this is indeed my true value which is not the case. This is actually the observed mean of the sample that you have got this is not even the population mean maybe.

So in such cases what ends up happening you end up doing a biased analysis you might start to over interpreting. In this case let us say this is the true value you are over estimating x bar on the other hand if your distribution that goes like this, you might end up underestimating it. So basically all this results in a bias in your measurement and probably the analysis that would end up doing as you go forward.

But the good thing here is that these errors can be corrected in some cases to as minimum as possible. So when you take close attention to where this errors could come from these 3 are the major sources of such thing happening. So one is the instrumental imperfections or instrumental errors that come up the other could be methodical errors which could be some of the protocols that are followed by scientist or it could be just personal errors that comes up from biase of the **experiment is** experimental himself or herself.

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So as we just saw in a simple example where when you titrating oxalic acid versus sodium hydroxide you are able realize jus the glassware results in some error that could come up. Here in this slide I am showing some example of that, in this case what you are able to realize is that this glassware is optimize to work at 20 degree Celsius. And the standard deviation that is associated with that would be 0.1 ml of this for this given glassware.

On the other hand if you take a look at this burette which measures 50 ml you are able to realize the precision is about 0.08 ml at 20 degree Celsius. Of course not everything has to be prescribe it 20 degree Celsius but most often glassware do end up being prescribe to be used at that given temperature. So now what would happen if you do use it at a slightly different temperature you are going to expect some volume expansion to happen that results in increasing the standard deviation for such measurements.

So this is the case of a volumetric flask which also has a 0.8ml on the 1 litre measurement. Of course we assume that 10 ml error that would come up if you redo the math you are goanna have lesser error in the sodium hydroxide normality measurement. But I just did that so that you understand how errors propagate and what could end up happening. On the other hand the burette once again as I said also contributes to an error.

This is an example of a measuring cylinder where you are also able to realize this has about 0.5 ml error rather 1 ml error for a 100 ml measurement that could come up. And this is also prescribe to be used at 28 degree Celsius. So almost all equipment that you might end up using in the laboratory has a certain least count which comes up as an error on top of it you could also have differences that come up due to the apparatus itself.

So it is just not the least count but let us say you repeat the measurement enough there will be a certain region of deviation that could come up and that would result in an overall error ok.

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The weighing balance is say I could also result in an error, so what generally gets done is that these weighing balances one would end up using standard weights that have a specific grams associated with them which when calibrate it against the weighing balance you end up using would help you ensure a less amount of error would come up in the weighing balance. And most often as you are able to see a digital weighing balance here.

The number of digits that they end up displaying indicates the uncertainty comes up in the last digit. If you pay close attention here it also says the error is in 0.0001 grams which is why 4 decimals are displayed in this analytical balance. So be careful when you are using analytical balance where the number of displayed digits could indicate the error that is associated with them.

And that are some instruments where in the last digit they will end up underlining to indicate that is where the uncertainty lies. So generally people tend to show the first digit that indicates the uncertainty and this quite commonly is used across equipment and on the other hand you are looking at a pH meter here where 2 digits are indeed displayed. And how would you calibrate a pH meter is that quite commonly people use pH solutions standard solutions across at least 3 different pH's, that is pH 4, 7 and 10.

And you would be using the probe in the reference solution and using the same pH meter at let us say a given temperature and then calibrate the pH. So this would ensure that as a function of pH even if you are changing the temperature you are carefully calibrating things across in order to ensure that whatever you are measuring is the right pH. In general for pH people generally give only one decimal indicating that the precision exist within that decimal only ok.

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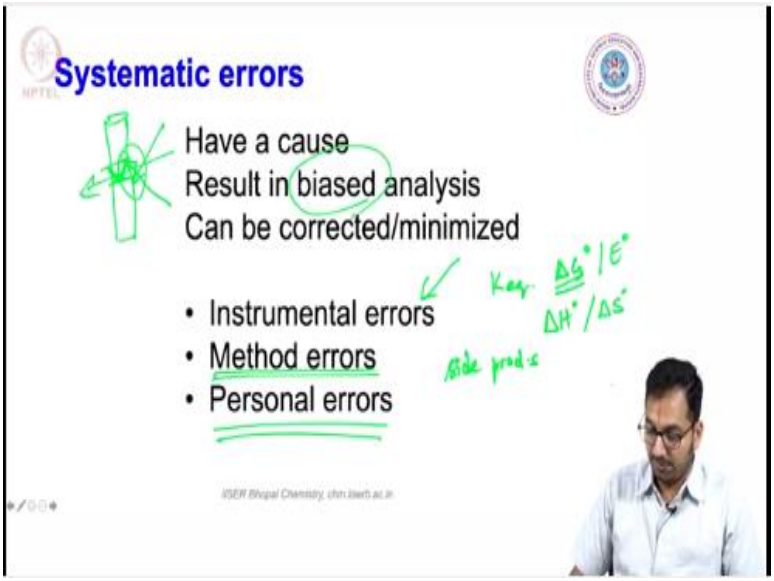

So now that we have seen instrumental errors that would come up what other things could happen is that you could also have method errors that could arise. What do we mean by method errors, let us say in the experiment that you are doing subtle mistakes that could end up happening. What do you mean by subtle mistakes is let us say that you have to do an equilibrium experiment meaning that once you make up a solution you go to wait for a certain amount of time before you can start doing the experiment.

Let us say the rate kinetics are slope for the solution that you are preparing, what might end up happening the equilibrium might not be reached and you might start doing your analysis by then itself. So what could this resultant you could misestimate the equilibrium constant which would in turn cause an error in delta G 0. And as you might fit this to other values it would propagate to the other thermodynamic parameters, you might end up estimating using this parameter ok.

That is one thing that could happen, on the other hand what could also happen is that as you dissolve this chemical reagents they might not be stable enough to reach equilibrium. So what ends up happening as you prepare the solution these species might end up becoming something else or actually disintegrating where even before they reach equilibrium you might end up losing them.

Such experiments have to be very carefully set and a protocol has to be strictly followed in order to ensure that reliable and repeatable and replicable measurements can be performed. On top of it what could happen is that if you let us say wait long enough it could be that you start forming side products for the chemical that you are using. So when this has to happen it might interfere with a kind of analysis that you are trying to do.

Let us say that you are doing a fluorescence acids and let us say the byproduct that ends up coming has a different fluorescence absorption and emission maxima. It could start interfering let us say that is close enough to the analyte that you are trying to look at, it will start giving you any biased results. Of course in instrumental error I already pointed out to the fact that the weighing balance can be calibrated a pH can be calibrated**.**

What one could do is to come up with comprehensive methodology incorporating all this that could happen for an experiment prioritize to setting this experiment. That will help you minimize errors that could happen. For instance let us say that you know for a fact, let us you are adsorption experiment that takes an overnight to equilibrate it is always a good idea to start your experiment a day earlier and get this going.

On the other hand let us say that you are trying to do a kinetic experiment where the starting material will change very quickly you need to learn how to minimize the dead time meaning that when you start the reaction kinetics in the vessel and the time from which you actually start making the measurement. That could be a difference between these 2 types which is called as the dead time and this would influence the final results that you might end up getting.

So therefore minimizing dead time in a kinetic experiment is important while making sure equilibration happens in the thermodynamic experiment is extremely important. Now coming to the final point that might that will help us conclude the systematic errors you would also personal errors that would come in, what do we mean by personal errors. It could be that a person is trying to do a titration where the indicator that you end up using actually gives the color that this person is not perceiving it due to whatever problems.

It could be that it is color change that happens between green to red in a fluorescence experiment where this person is not able to see probably because this person is color blind. Or what could end up happening is that when you have a burette when you are trying to read make a reading you might make a mistake where instead of reading the lower meniscus you end up seeing the upper meniscus.

Of course whichever has a different meniscus opposite meniscus you will start seeing the supper meniscus. But in general cases you will have to see the lower meniscus that comes up or on the other hand you could also perform a personal error where if you are using burette the last portion of the burette which does involve a certain amount of volume is not properly used in the first step.

Meaning that when you are burette you might not have fill the bottom but and when you are titrating the volume change would be higher indicating more concentration of the analyte that you are trying to look at. That could also be personal error, on top of it let us say you are looking at the burette and instead of looking at it at the eye level you might be looking at it a little lower or a little higher instead of looking at the straight eye level reading.

So what might end up happening you might have an error that comes up basically in the way you read out a given value. All these contribute towards personal error, and one thing that is very important to understand here not just this there are some biases that comes up with an experimental is. Because most often when you are doing science when you are setting up a hypothesis you already have a preconceive notion towards what to expect.

But remember one thing the moment you start expecting something you become a biased researcher and many this ends up happening when you are setting up an experiment where you expect a value to come off. And when you are doing a titration close to that value you are careful but any value ahead or later than that you might be a little careless.

And this could happen in a way where you are expecting higher value and you titrate it all the way just to see that the color changes already happen. So these kind of personal errors can be avoided by carefully following a protocol and doing things in a systematic and an unbiased fashion ok. So now that we have done with this let us take a small look at what type of errors could come up when you are using different equipment.

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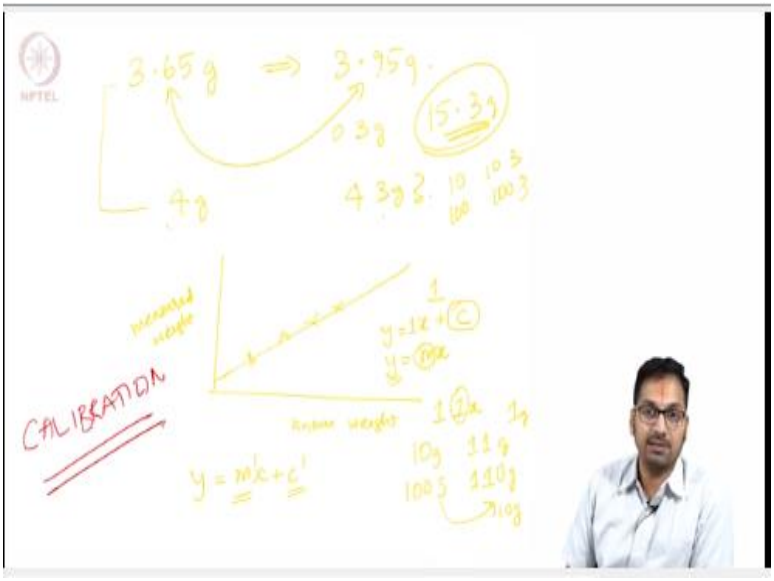

So let us say in this case where you are trying to make a weighing balance help you measure some amount of oxalic acid. Let us say you wanna measure 3.65 grams of oxalic acid and let us say the actual reading that comes up is 3.95 grams. So now the question that comes up is **is** that oh that is the 0.3 gram difference. So does it mean if I weigh 4 grams will it weigh 4.3 grams or maybe there is a slope that is associated with it, meaning that as a keep increasing when I go from here to here it need not be 4.3 grams, it could be little more than 4.3 grams or little less than 4.3 grams.

So this is basically something like a calibration graph where if you add a known amount of grams and if you are able to measure it. And then you would try to get a correlation between these through this is like known weight, this is the measured weight from your analytical balance for instance. Then you get points which you can fit and then let us say there is an interested that comes where the slope is equal to 1.

But the intercept comes as something let us say the y in this case is x + c where the slope is 1. In the c indicates there is a constant offset that comes in measurement, if there is a constant offset what is going to end up happening b 3.65 grams when you measure it is goanna be 0.3 grams higher or if you measure 4 grams it is goanna be 0.3 grams higher. Even if you measure something like 15 grams it is goanna be 15.3 grams.

On the other hand it could be the case where you are having a slope that comes up, so what happens with this slope is that as you keep increasing the weight that you are going to measure you could have a more estimation or less estimation depending upon the slope that you are having. Let us say you have a 1.1 times x what is goanna happen you are goanna have a 10% error that is going to be associated as a keep on weighing more.

For instance when you weigh something like 10 grams you are goanna get 11 grams, you are goanna weigh 100 grams you are goanna get something like 110 grams. So ends up happening here it is a 1 gram error while here it is a 10 grams error. So you are able to realize that it proportionally keeps increasing while on the previous example weigh it 10 grams you measure you are goanna get 10.3 weigh it 100 grams you measure you are goanna get 100.3.

This indicates there is a difference between constant error versus proportional error. On the other hand you could have cases where you are having the case such as m prime x + c prime where there could be a slope and an intercept associated where one has to be extremely careful. And these are the reasons why one should always calibrate an instrument before ending up using it for any experiments.

So calibration for different experiments is an extremely important step in order to get as reliable values as possible and minimize systematic errors that could come up alright. So now we would stop this lecture here and we will continue with understanding other ways to determine what kind of errors exist and what are random errors as we go forward. And we will also take an example of how this works out in an experimental scenario, thank you.