Quantitative Methods in Chemistry
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Lecture – 48
Course Revision (Week 01 to 03)

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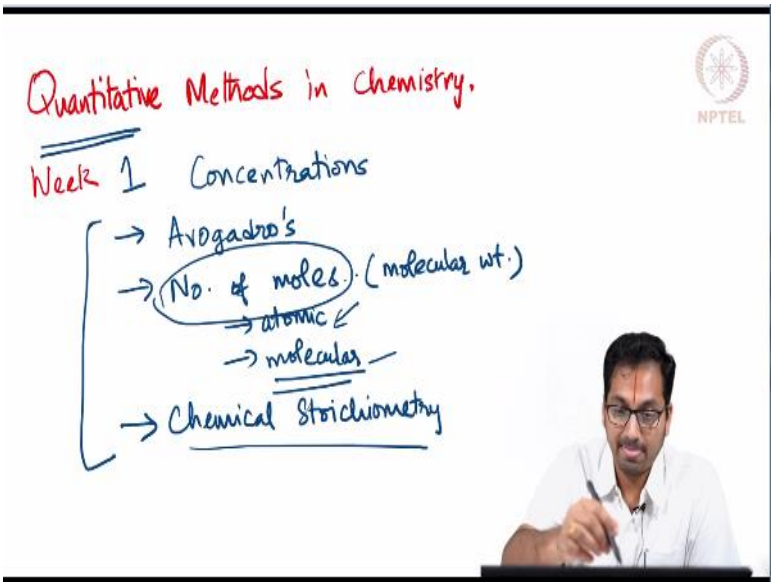

So this lecture started in Week 1, looking at how to quantify concentration so that was the main topic that we wanted to understand in very different units. In order to do this the first topic that was introduced is how did quantitation start in chemistry itself. The first step towards this was by Avogadro's estimation of the number of particles in a given mole of a substance; this is why; this is how the definition of quantitation started.

Then going to; from that going to the number of moles of a given substance and which required the definition of something like molecular weight. So this was then introduced in terms of atomic weight of a given atom and from there on going to something called like a molecular weight where you have a chemical composition using the chemical composition that has different atoms you try to determine their atomic weights and put them together to get the molecular weight.

Once you have determined what is the molecular weight, then for a given amount of substance you determine what is the number of moles, so this is where the whole thing started. Then moving on we try to understand what is chemical stoichiometry, we had many, many examples taken in this regard where we also took an example of a redox reaction, basic reaction that ends up precipitating a certain cation and all that.

So basically what we understood here is that when two reactants are reacting with one another what is a stoichiometry, what is the equivalence of each such that when these to react how much of products would come. So all these concepts started the whole idea of quantitation in chemistry where okay whether the number of moles come, how does one describe how much of what he or she has in hand and then when you make them react with one another what is the total amount of concentration, that would end up coming.

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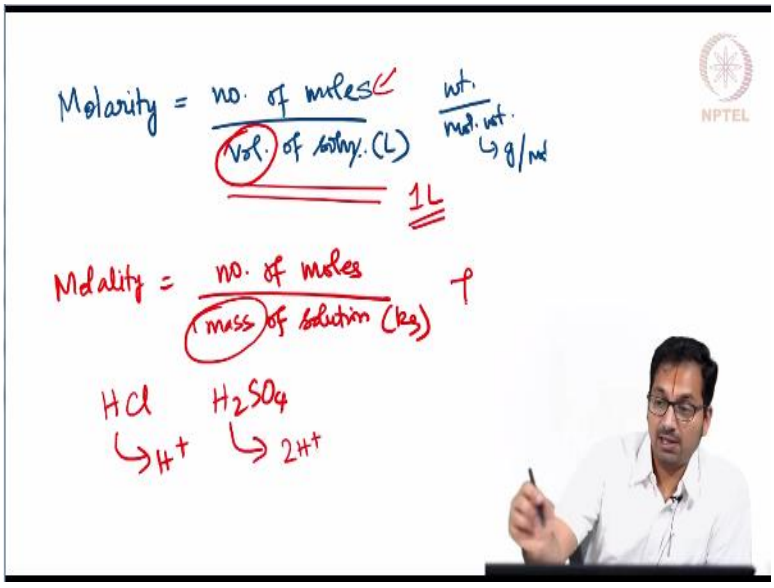

Moving on not just by trying to say the number of moles is enough we try to also define the parameters of molarity where the molarity is defined as the number of moles in a given volume of solution in liters, so this was one of the initial definitions where once again the number of moles are determined from the equation that I have shown earlier that is weight by molecular rate would give you the number of moles.

And of course molecular weight is given generally in grams per mole so therefore, one helps in defining the number of moles this way and from there you have a total volume of solution and liters then you get what is molarity. However, one is able to understand that at times it could be a little complicated where if you want a total amount of volume of solution to be let us say 1 liter but adding a certain amount of weight or the number of moles of a certain compound but change the volume a little bit.

So therefore came the definition of molality and also in addition volume is not to change with temperature so therefore the number of moles define per mass of solution in kg became the definition of molarity where the mass is independent of temperature because the density might change with temperature while the mass is independent of; (()) (03:59) assumption. So therefore molarity got defined. On the other hand, some started to realize that let us say you have monoprotic and diprotic acids where HCl furnishes 1 mole of; or 1 equivalence of H+ H2SO4 2 equivalence of H+.

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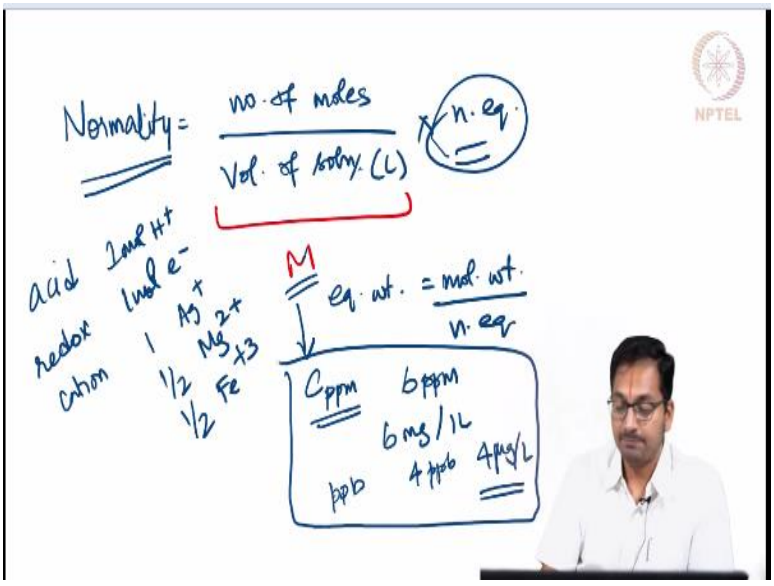

So that introduced us to the next concentration unit called normality where it is given by number of moles, volume of solution in liters times the number of equivalence. So this part as we are able to understand is molarity so only thing that we need to understand here what is the number of equivalence and the number of equivalence was defined for very many different categories of

such as acids where any amount of chemical that furnishes one mole of H+ was defined as the number of equivalence or rather the equivalent weight.

So one keeps switching between number of equivalence and equivalent weight, equivalent weight is defined as the molecular weight divided by the number of equivalence which is essentially why this comes up here when the definition of molarity is given such. And for something like redox reactions it was 1 mole of electrons and for any cation it was the charge on the cation. For instance, it is one for a cation that has a single charge, 1/2 for something that has charge 2 associated 1/3 for something that has 3 charges associated.

So having done this one is able to understand how to convert molarity into normality so therefore if people are using the normality as a definition to; for two interacting chemicals so that makes the calculations much easier but if somebody is using molarity one has to be little careful because then you could have different number of equivalence like I just gave an example of HCl and H2SO4. You could have different amounts of equivalence of H+ coming out which could change the amount of interacting species that ends up coming.

So molarity helps in such an aspect. We also define other parameters such as ppm which is Parts Per Million. This is given as the mass of solute divided by the mass of solution in kg times 10 power 6. So basically, this indicated you have something like 6 ppm is something like 6 milligrams per liter, this is the example that was given in the class, and ppb is something similar where you have something like 4 ppb it ended up being 4 micrograms per liter in the solution.

So this definition also assumes the fact that you are adding so much less of the solute the total mass of the solution comes from the solvent only and therefore this gets back to the definition very similar to that of molarity. Then you; one might always ask when to use molarity, when to use ppm and ppb, when to use normality. So that depends on the purpose that you are having, generally people define things in molarity.

However, when you have different equivalence that ends up coming from the same chemical people end up using normality and when it comes to very small amount of concentration of a solute in a solution then people end up resorting for parts per million and parts per billion.

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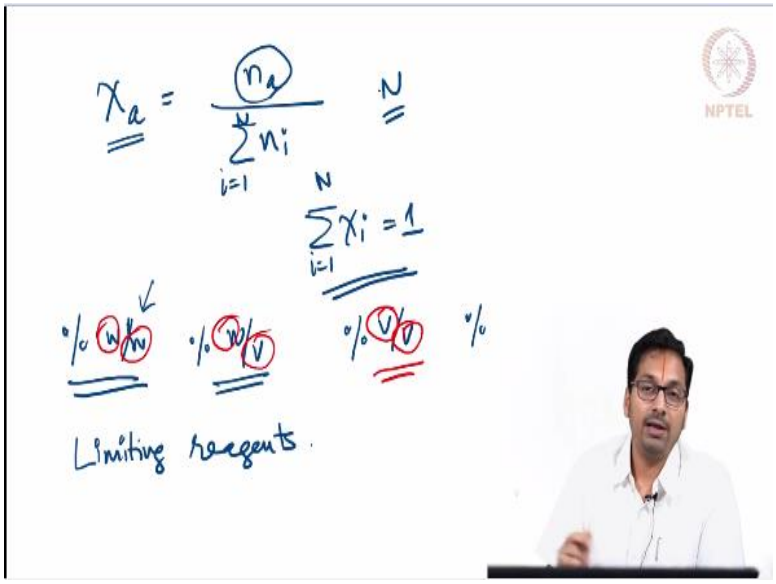

Moving on the other definition that was important was something like mole fraction where mole fraction is given as a number of moles of a given species in this case a divided by the total number of moles that is present in the entire system. Let us say you have n different chemicals in a system then you have the number of moles of each one of them and then Na divided by the sum of all number of moles would give you what is the mole fraction of a.

So one is able to understand sigma chi I, where i goes from 1 to N will be equal to 1 because you are trying to define a fraction. This would help one person understand how many moles are actually present therefore their interaction could also be easily mapped using mole fractions. One important thing that we also understood in these definitions is that people also use other metrics of measuring concentration which is percentage weight-by-weight.

When you are having two solids that are mixed to each other; mixed with each other then you have a weight-by-weight definition when you have a solid mixed in solution or a solvent you have a definition of percentage weight-by-volume and the other hand when you have two liquids that are mixed then you have percentage weight-by-weight. So therefore, when somebody says

okay this is the percentage concentration present one must be very careful on what definition is being used whether it is weight-by-weight or weight-by-volume or volume-by-volume.

If one does not define what type of measurement is being made then it is very difficult to understand from the percentage concentration, what is the actual final concentration of a given chemical that is present. One other topic that was also covered in stoichiometry was the concept of Limiting reagents. This is an important topic because when you have multiple chemicals that are present and one is present in amounts that are less than its stoichiometric amounts that one itself happening is that the chemical reaction goes to completion where one of the reacts; reactants is present in excess.

Whichever reagent is completely utilized would then be called the limiting reagent because it is not allowing the reaction to go forward. In fact, this concept is used quite often in order to push the reaction to give products where you keep on adding the limiting reagent and keep on reviewing the product and therefore (()) (09:38) principle, one will be able to maximize the amount of products that would end up coming.

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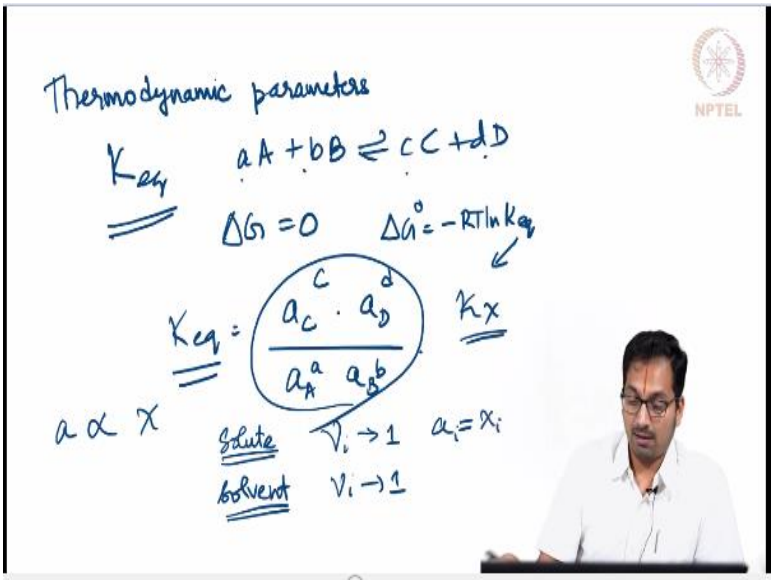

So after having done this the next topic that was introduced was more like thermodynamic parameters where we define what is an equilibrium constant, once equilibrium constant was defined for a simple reaction such as aA + bB in equilibrium its cC +dD where small a, small b,

small c, small d are the stoichiometric amounts while A, B, C, D are the chemical reagents that are involved in the reaction.

Then we were able to define when it reaches a chemical equilibrium that is defined as Delta G is equal to 0, Delta G naught is defined as - RT times lawn of the equilibrium constant. The equivalent weight is defined as the ratio of activities of the products to that of the reactants of each coefficient raised to the power of their stoichiometry. So meaning that for; in this case it is going to be ac power small c times a, capital D times small d divided by aA times small a, aB times small b.

So; and then from here we went on to understand how activity can be related to concentration in terms of mole fraction and therefore we saw for solute versus solvent how this activity is defined. So basically, for a solute and the solute is present at very low concentrations then you put the activity coefficient of that solute tending to 1 so therefore activity becomes equal to the amount of number of moles that is present.

And for the solvent when the solvent becomes more pure meaning that when you are very little of any other thing that is present then the activity coefficient was set to 1, so 1 is able to understand at very low concentration of the solute; the activity coefficient goes to 1 and in terms of the solvent when the solvent becomes more pure basically when it becomes; the entire concentration becomes itself then the activity coefficient becomes equal to the number of moles.

Having defined this then this can be defined in many; very many different ways in terms of concentration as a molarity, molarity normality or in terms of the mole fractions so therefore, the K chi and K; very different types of equilibrium constants were also defined.

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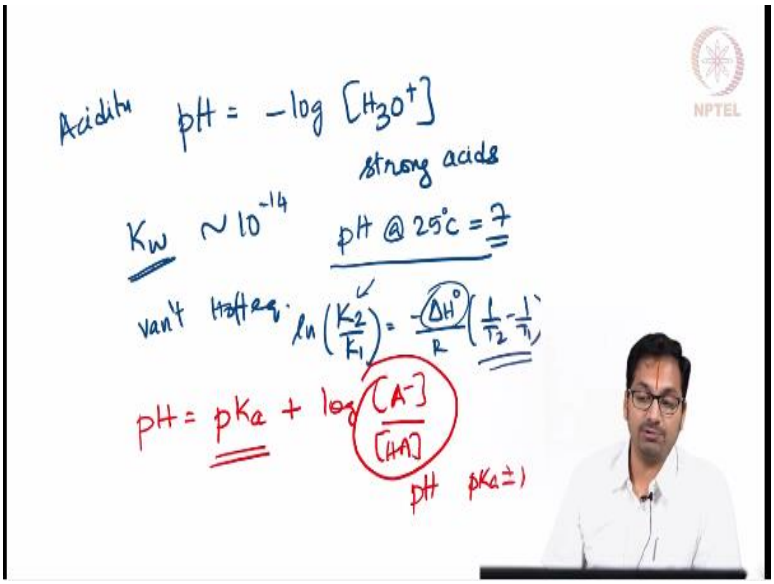

After having done, the next topic that we moved on is to understand how acidity and basicity can be quantified. So this was quantified; this is quantified by this parameter called power of hydrogen that is pH that is given by - log of H3O+ hydronium ion concentrations, where this is defined for strong acids. And then the concept of self ionization of water which is another equilibrium constant was defined which is something like 10 power - 14 for water and the for pH of water at 25 degree Celsius we come to know about is 7.

And similarly, this pH can change as a function of temperature which we saw from the Van't Hoff equation where the equilibrium constant lawn of K2 / K1 is related to -Delta H naught divided by R, 1 over T2 - 1 over T1. So depending upon whether a given reaction is endothermic or exothermic the equilibrium constant changes and in this case since water (()) (13:10) require breaking of energy it is an endothermic reaction, so one is able to understand as a function of temperature the kW changes so therefore the referencing for pH change.

So this was the main reason why the thermodynamic parameters were introduced. So as to understand when you are setting up a chemical reaction or when you are preparing a buffer this would matter. Now that I have already started speaking about the buffer, the next thing that we were able to understand for weak acids and weak bases how did we define; this was different defined using the Henderson–Hasselbalch equation where it is given; this was derived in the class. I am sure you would be able to recollect that we were able to get something like this.

So the buffering capacity of a given weak acid or a weak base is defined right around its pKa where the pH can be equilibrated within pKA + - minus 1 unit, meaning that when you have about ten times difference and concentration of A- to HA or HA to A- you would be able to buffer quite effectively. So these concepts were also defined immediately after exposing you towards different units of measuring concentration largely because when you are trying to quantify anything that you end up doing in chemistry these parameters come in very handy.

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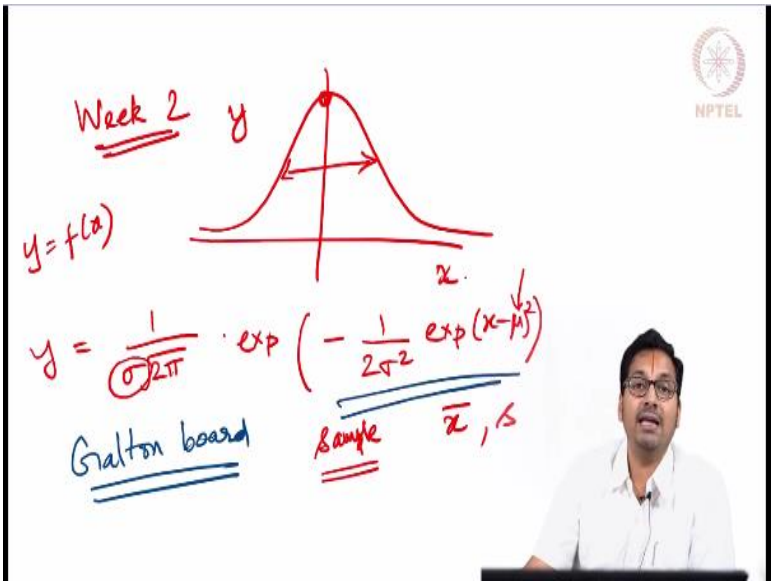

Following this, we moved on to week 2, where we try to understand what is data; so week two started with an idea of trying to say you have a certain measurement that ends up coming and that already has a distribution that goes along with it. Let us say this the x variable that you are trying to measure and the y is the response. So basically y = f(x), when you are measuring something like that you have a peak that ends up coming and you have a spread that has a certain meaning.

Now that as we get to know this is nothing but the Gaussian function which is given by something like; as we are able to realize this is the Gaussian function where the Sigma is called the standard deviation which gives the spread of that given distribution and mu is the mean, and in this case I am using Mu so that its population mean that you are talking about.

Meaning that when you are trying to understand statistics and what is going on in theory what you would like to do is to take the entire population and survey them on the variable that you would like to measure. For instance, if you would like to get the age of the entire population what you would end up doing is to integrate everybody that is present and find their age and you would find probably a similar distribution that would end up coming in a classroom for instance.

However, on the other hand let us say that you have the entire classroom but only 10 of out of the 40 students are present you just pick them up and then try to understand what is the statistics that ends up coming, so that is what is defined as a sample. So when you have a small portion of the entire population being interrogated that ends up being the sample mean and the sample standard deviation which is given by x bar and s.

So one; we also did one simple experiment to understand such a distribution that ends up coming where you end up releasing some beans from top of; from the top where it starts to fall into several bins and we also saw this very nice simulation using the Galton board where we were able to realize that the spread comes up by itself largely because the hurdles that it ends up each of the mean ends up encountering pushes it to the left bin or the right bin in a probabilistic fashion. So this is what ends up finally designing the overall distribution of any data that you end up measuring.

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And from here on what we ended up doing is that okay let us say you are on an entire population and you are using a certain amount of sample to get your data so what we did is to define two major parameters called mean, the standard deviation, where mean is nothing but taking the average of all the measurements that one ended up having. On the other hand, standard deviation where s and x bar standard deviation is given by square root of some of squares of deviations of each of this variable to the; to that of the mean that is measured.

So this is the case where you have small data set that is present. In the moment that you start to have a large data set this will be changed to n, this will become mu while this will be Sigma. So this is one of the important things that we were able to understand and as we went forward we started to see how a spreadsheet program could be used to analyze this data. Let us say that you have 100 such data points. Let us take the population of the entire country.

You are not going to be sitting and calculating average and standard deviation. It is not going to be easy task either. So therefore what we ended up understanding is to use state-of-the-art simple spreadsheet programs in order to estimate all of this. After having understood this, the next thing that we embarked on is to understand let us say we have three different data sets that end up coming. Each of the data set is associated with a certain mean and a certain standard deviation; sample mean and sample standard deviation let us say.

How can these numbers be compared? So basically we were trying to understand with the framework of the normal distribution is the measurement A and B agreeing with each other or not; B and C agreeing with it with each other or not; A and C are they agreeing with each other or not and this was done; how did we do this, by taking the difference between the mean and trying to compare them with the standard deviation. Basically, in this aspect one has to understand how the standard deviation propagate when you have multiple such measurements.

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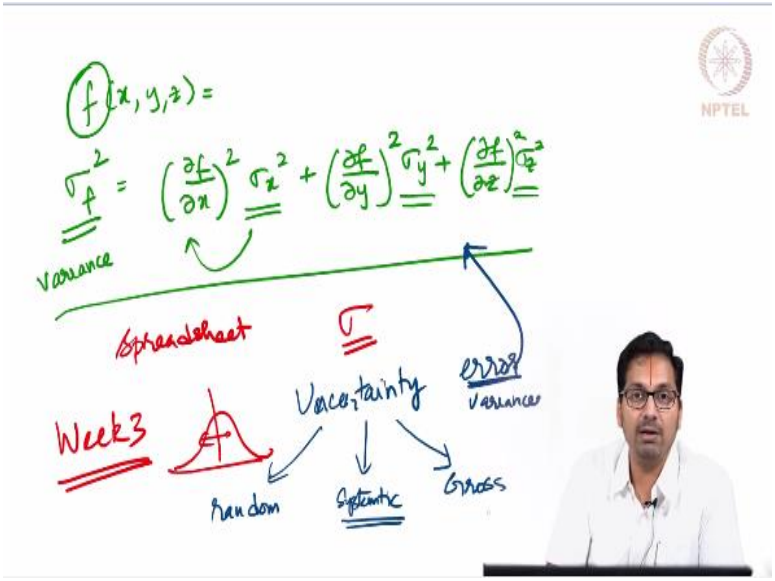

So in order to do this we wrote a very important equation. Let us say you have f as a function of x, y and z. How does Sigma f change? So this was given by dou f by dou x the whole square Sigma x square dou f dou y, the whole square Sigma y square + dou f by dou z the whole squared Sigma z square, so this was a very important equation to understand how variance propagates.

So variance s is based on variance of x, y and z. So this is a general equation that was written, and for any given model that you would like to adopt it to one should be able to understand how the Sigma f can be determined. So in the previous example as we were discussing a moment earlier the way that one would end up determining this; let us say you want to get mod of XA - XB bar, one would try to get then square root of sum of squares of sA square + sB square.

And you would try to see whether the difference between x bar A and x bar B is less than that of this in which case A and B agree with each other. And if they are farther away from that then you would say they are different. One has to be also careful; so in order to do a conservative estimation it is always better to go 3 times such standard deviation for such a measurement. So the next thing that we ended up resorting after understanding how variance for large measurement goes is to apply it to very many different problems.

Here also I introduced you to the fact that a spreadsheet program might help you carefully calculate what is the variance that comes up in an overall calculation, and we also solved a few assignment problems where a certain complicated equation was given and you were able to determine what is the standard deviation that goes for such a measurement and following this the next week that is week 3.

In week 3 we were trying to understand how the uncertainties that came up in the measurement in terms of the mathematical framework we have developed. How will they actually come up in an experiment? Where they are set up? And in order to do this, we were able to talk about the uncertainty in the measurement that is related to the error that we were trying to discuss and the; when we mean error we were talking about the variance that is associated with our measurement.

So when we are able to do this we realize that the uncertainties could come largely due to three different reasons, one is random reason meaning that you could have fluctuations that could end up happening and this would result in actually the Gaussian curve that ends up coming and would end up increasing the width of the Gaussian curve. On the other hand, you could have something called systematic errors which we discussed in detail.

Because this is something that would end up resulting in a biased analysis and in; in order to avoid that we have a certain set of protocols that one could follow in order to minimize systematic errors coming up. And some are gross errors meaning that it is a huge error that you did and you will be able to find it out right away where things went back.

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And from here we discussed a little more on what are systematic errors, and how they could be classified. And the three major ways where this could end up coming where the instrumental error were before a person ends up beginning an experiment he or she should start ending up calibrating the instrument. There are standard operating protocols. There are reference standards that are available which will ensure that if you're using a certain instrument how it should be calibrated.

And if it starts deviating from a certain expected value how to ensure that such errors do not end up coming. So that was what was significantly described in this instrumental error. Then you had something even more important called method errors which ends up coming up because the protocol that you end up having has to be properly written has to be very detailed; it has to be systematic and carefully probing different aspects of the experiment that you are trying to perform.

So this also forms a very major aspect before you set up an experiment the way the method has to be performed which are step has to be done first, which step follows that has to be carefully taken care of and the last one that ended up coming here is our personal errors which come up due to a certain personal bias that you end up having or probably you are not viewing the entire experimental setup the certain in the correct fashion.

So all these errors can actually be easily minimized by following standard protocols, we ended up using an experiment where we determine the critical micellar concentration of surfactant called sodium dodecyl sulfate in order to exemplify what is; what are 3 different parameters of repeatability, replicability and a reproducibility. In repeatability, we were trying to say when the same experimenter repeats the same experiment with the exactly same setup within a very short period of time whether the values that he or she ends up measuring are agreeable with each other.

If yes, then it is called repeatable and we said, in case they do not end up agreeing with each other then it could mean that probably the experimenter has not properly calibrated the instrument or could be that the method that has been returned but not comprehensive or there are mistakes in the experiment that ends up coming or there is a serious personal bias or all three could exist simultaneously, which is a very bad scenario.

So therefore, this helped us understand what is repeatability; on the other hand, replicability is one where another person takes up the exact same experimental setup, repeats it to see whether the values that end up coming in terms of the average and the standard deviation agree with the first experimenter. If it does agree then it indicates that the experiment is replicable then it means that no personal bias existed; on the other hand, let us say the replicability is a problem one has to once again interrogate what is the reason for it.

So most often replicability problems come up because of the fact that method has not been comprehensively written, meaning that each step is not properly written or it could be once again that the instrument that has been handled by these two people are not handled the same way in which case once again calibration and proper protocols must be written or it could be that a person expects a certain answer and has a personal bias which could end up resulting in a problem.

And we ended up looking at this example in case of fluorimetry and due to conductometry and luckily we were at least able to show some demonstration of experiments on how the experiment is setup and how errors could come up and which all places could this finally effect in the final

measurement that one is expected to have. But all this framework setup, this lecture series was taken over by Aasheesh.

So that the data that one ends up measuring he would be showing how this data could be treated to understand; how one could pick up models; how to end up fitting data and all that. So I will pass it on to Aasheesh so that he takes over for his 2 weeks, and I will come back in the 6th and 7th week.