

hello welcome back to the lecture on basic principles of organic chemistry and some methodologies that are used in organic chemistry in the previous lecture we were discussing the method of estimation of carbon and hydrogen in order to determine the percentage of carbon and hydrogen in an organic molecule now organic molecules can also contain nitrogen halogen phosphorus sulfur and

So on

So let us have look at the methodology used for the estimation of nitrogen first in a quantitative manner there are two methodologies that are used for the estimation of nitrogen the first methodology is known as dumos method in this particular methodology the organic compound containing nitrogen is treated with copper oxide and copper in the process of heating the organic compound let us say the organic compound has this kind of a molecular formula when it is heated over a surface of copper oxide and copper metal under a stream of carbon dioxide the carbon present in the organic compound is converted into carbon dioxide completely and the hydrogen that is present in the organic compound is converted into water and the nitrogen is converted into N_2 gas

So the amount of nitrogen that is liberated during the process of this heating is measured using a nitrometer a nitrometer it is a device which is used for measuring the volume of the nitrogen that is evolved during the course of this particular reaction and from the estimation we will essentially get for example volume of nitrogen liberated from the organic compound from the volume of nitrogen liberated from the organic compound one can directly find out the percentage of nitrogen that is present in the organic compound let us take an example let us say m grams of an organic compound is subjected to dumas method of estimation and if the volume of nitrogen collected is v_1 v_1 milliliters at a temperature of t_1 and a vapor pressure of p_1 for example now this is the laboratory temperature at which the gas is collected and this is the pressure at which the gas is collected this pressure need not be atmospheric pressure because there will be some water vapor pressure because of the fact that the nitrogen is collected over water So one need to correct the vapor pressure for the actual vapor pressure of nitrogen by subtracting the vapor pressure of water vapor at that particular temperature then one uses the equation v_1 by t_1 is equal to $p_2 v_2$ by t_2 in order to find out the volume of nitrogen gas that is collected under standard temperature and pressure in other words at 273 kelvin temperature and 760 millimeter of mercury atmosphere that is one atmosphere of the pressure of nitrogen

So let us say for example this is the p_1 which is the pressure at which the nitrogen is collected v_1 is the volume of the nitrogen that is collected and t_1 is the temperature at which this is collected we want to find out v_2 now

So v_2 will be equal to $p_1 v_1$ multiplied by 273 kelvin which is the standard temperature condition divided by t_1 that is the temperature at which the experiment is carried out or the nitrogen is collected multiplied by p_2

So if you solve this then you can get the volume of nitrogen at standard temperature and pressure or normal temperature and pressure now once you have the volume of nitrogen that is collected at a standard temperature and pressure that is 273 kelvin and 1 atmosphere this is 760 millimeter of mercury the standard condition then one can use the expression if we have twenty two thousand four hundred milliliters of nitrogen at stp this would correspond to twenty eight grams of nitrogen this is the one mole of nitrogen essentially contains 22.4 liters or 22400 milliliters of nitrogen

So what would be the amount of nitrogen for v_2 sorry the v_1 which is collected the v_2 which is such standard temperature and pressure which we calculated from this expression what would be the weight of nitrogen that is present

So if it is 22400 ml it corresponds to 28 grams

So for v_2 how much will be the weight of nitrogen corresponding to v_2 ml of nitrogen if twenty two point four liter or twenty two thousand four hundred milliliters of nitrogen weighs twenty eight grams of nitrogen that is one mole of nitrogen then how much will be the v_2 ml of nitrogen corresponding weight of nitrogen that is calculated by this expression here now this is coming from m grams of the compound

So for 100 grams how much will be this would be the percentage of nitrogen that is present in the organic compound

So the basic principle is the organic compound is converted the nitrogen present in the organic compound is converted into gaseous N_2 and the N_2 is collected in a nitrometer and the volume of N_2 collected is at the laboratory temperature and pressure and that is converted using this expression $p_1 v_1$ by t_1 equal to $p_2 v_2$

two by two into standard conditions namely one atmospheric pressure that is seven hundred and sixty millimeters of mercury and two hundred and seventy three kelvin of temperature once you convert that then we have this expression that twenty two thousand four hundred milliliters of nitrogen at standard temperature and pressure condition corresponds to one mole of nitrogen or one molecular weight of nitrogen that is twenty eight grams of nitrogen

So if the weight of nitrogen has to be found out for the V_2 which is a volume that is being collected at s, t, p this would be the expression that is for twenty two thousand four hundred milliliters it is twenty eight grams therefore for V_2 volume of the nitrogen collected at t, p how many grams of it

So this will give the weight of nitrogen that is being collected in the nitrometer that is coming from m grams of the substance

So for hundred grams of substance what will be the weight of nitrogen that will correspond to essentially this particular expression will give you the percentage volume of percentage weight of the nitrogen present in the organic substance let us illustrate this with an example let us say for example 0.3 grams of an organic substance on dumas method gives 50 ml of nitrogen is evolved during the estimation of nitrogen

So from 0.3 grams of organic substance 50 milliliters of nitrogen is evolved at 300 kelvin and 715 millimeter of mercury that is the pressure at which the nitrogen is collected for example now water vapor pressure at three hundred kelvin is equal to fifteen millimeters of mercury

So you need to subtract the actual pressure p_1 will be equal to then seven hundred and fifteen minus fifteen which is due to the water vapor pressure

So actually it is seven hundred millimeters of mercury is the actual pressure due to the nitrogen

So if it is p_1 if V_2 is equal to p_1 V_1 by T_1 this expression that we are having here multiplied by T_2 by p_2 if you substitute the values here p_1 will be equal to seven hundred and volume of nitrogen that is collected is fifty milliliters and temperature T_2 will be two hundred and seventy three kelvin which is the standard temperature T_1 is given as three hundred kelvin and p_2 corresponds to seven hundred and sixty millimeters of mercury which would be one atmospheric pressure if you solve this it amounts to forty one point nine ml of nitrogen is collected at stp therefore weight of nitrogen is equal to for twenty two thousand four hundred milliliters it corresponds to twenty eight grams

So at four for forty one point nine milliliters how much it corresponds to

So one can solve this particular arithmetic problem the percentage weight of nitrogen present in the molecule nitrogen present in the entire mass that is taken the mass taken is 0.3 grams

So 28 multiplied by 41.9 divided by 22400 this is from point three grams of the substance therefore for hundred grams of the substance how much will be the weight of nitrogen that would correspond to the percentage of nitrogen in the organic compound if we solve this particular simple arithmetic it turns out 17.46 percentage of nitrogen is present in the organic molecule

So this illustrative example i hope helps you to understand the basic principle behind the methodology that is used for the estimation using the dumas method of analysis of So i hope the basic principle is clear the nitrogen present in the organic compound is completely converted into N_2 nitrogen gas and the volume of gas measured at a particular temperature and pressure is converted into standard temperature and pressure and from the avogadro volume for example 22400 milliliters of nitrogen which corresponds to one mole of mole weight of nitrogen nitrogen has an atomic weight of twenty four fourteen

So N_2 would correspond to 14 plus 14 which is 28 grams of

So this volume of nitrogen we know is 28 grams

So the volume that is collected how many grams is what is calculated using this expression here and that comes from the mass that is taken of the organic substance

So for hundred grams of the organic substance what would be the

So this would be corresponding to the percentage of nitrogen that is present in the organic compound

So this is the methodology that is used conventionally for estimating nitrogen there is one other methodology which is known as gel dal's method of estimation we will discuss the generals method of estimation next the second methodology is geldale's method of

estimation of nitrogen in an organic compound in this method the organic compound is strongly heated with sulfuric acid in the presence of copper sulphate as a catalyst and in the process the nitrogen present in the organic compound gets converted into ammonia and in the presence of sulfuric acid of course the ammonia will react with sulphuric acid and it will form ammonium sulphate as the inorganic form of the nitrogen that is present in the organic compound

So all of the nitrogen that is present in the organic compound is converted into ammonium sulphate now the ammonium sulphate once it is formed it will be present along with the excess sulfuric acid because you take excess of sulfuric acid and essentially boil it in excess sulfuric acid strongly heat it in excess sulfuric acid wherein the nitrogen of the organic compound is gets converted into ammonium sulphate now this is neutralized with sodium hydroxide it is boiled with sodium hydroxide

So in what happens when you take an ammonium salt and boil it with sodium hydroxide initially the sodium hydroxide will neutralize the excess of sulfuric acid into sodium sulphate and water and then the excess sodium hydroxide will react with ammonium sulphate to produce ammonia gas this ammonia gas that is formed in the reaction is adsorbed on excess of acid 0.1 molar solution of hydrochloric acid is used in order to absorb the ammonia upon which the ammonia forms ammonium chloride since a known volume of more than what is necessary for neutralizing the required amount of ammonia is taken there will be excess of hydrochloric acid this is essentially a titrimetric method ammonium chloride is formed plus excess hcl will be present here this is once again neutralized with known concentration of sodium hydroxide

So essentially what you are doing is a back titration methodology in order to estimate the amount of substance that is being converted into ammonia in an organic molecule this can be explained as follows using illustrative example one can 0.257 grams of an organic substance was treated with sulfuric acid copper sulphate in other words the general reaction was carried out and liberated ammonia on treatment with sodium hydroxide is neutralized adsorb absorbed on fifty ml of molar by ten concentration of hcl now the excess acid required 23.2 ml of molar by ten concentration sodium hydroxide

So this is the given data what is done is the compound is treated with sulfuric acid and copper sulfate thereby ammonia ammonium sulphate is formed ammonium sulphate is liberating the ammonia on treatment with sodium hydroxide the liberated ammonia is absorbed with 50 ml of molar by 10 of concentrated hydrochloric acid

So this is the concentration this would correspond to 0.1 molar of hcl similarly this would correspond to 0.1 molar of sodium hydroxide

So this is a large excess of hcl is what is taken

So the excess acid required 40 ml sorry 23.2 ml of sodium hydroxide for neutralization

So from this calculate percentage of nitrogen in the organic compound this is the question that one needs to be addressed now volume of m by ten sodium hydroxide needed for the neutralization is twenty three point two milliliter this would essentially correspond to 23.2 milliliters of molar by 10 concentration of hcl that was neutralized therefore unused hcl is equal to or the excess unused hcl is equal to 23.2 ml of hcl of m by ten molarity

So the hcl used for absorbing the ammonia ammonia absorption will be equal to originally 50 milliliters was taken twenty three point two remained unreacted or excess

So that would correspond to essentially twenty six point eight ml of m by ten hcl

So all we need to do is convert that into mass that is easily done

So the twenty six point eight ml of m by 10 hcl will be equal to in terms of the neutralization reaction 26.8 ml of m by 10 ammonia solution which was originally liberated by the general method of liberating the ammonia we know that one thousand ml of one molar ammonia corresponds to fourteen grams of ammonia fourteen grams of nitrogen in other words if you take one mole of ammonia 100 ml one molar solution there will be one mole of ammonia in one mole of ammonia essentially you will have 14 grams of ammonia from the molecular formula NH_3 amount of nitrogen present is fourteen grams

So what we are having here is n by 10 of ammonia solution

So 1000 ml of m by 10 ammonia would correspond to 1.4 grams of nitrogen

So the weight of nitrogen will be from the ammonia that is liberated would correspond to for 1000 milliliters it is one point four grams from twenty six point eight milliliters how many grams of nitrogen is present here

So if you want the percentage of nitrogen in the organic compound you have to take the weight of the organic compound that is taken weight of the organic compound that is taken

is point two five seven grams of the organic compound

So point two seven five grams of organic compound will contain this much of nitrogen
So hundred grams will contain how much of nitrogen if you solve this numbers it will correspond to fourteen point six percent of nitrogen present in the organic compound
So let me go through this once again 0.257 grams of organic compound is treated with sulfuric acid and copper sulphate in a gelatine reaction that is this methodology of estimation it liberates ammonia by first it forms ammonium sulphate ammonium sulphate liberates ammonia on treatment with sodium hydroxide the liberated ammonia is absorbed on excess of sulfuric acid how much of excess of sulfuric acid 50 milliliters of molar by 10 concentration of hydrochloric acid

So the excess acid required this much of the sodium hydroxide for neutralization
So you take 50 milliliters of m by 10 hcl some of it is consumed by the ammonia that is liberated the remaining portion is neutralized with sodium hydroxide essentially to estimate the amount of excess acid that is being present

So the unused acid would essentially correspond to the 23.2 ml of hydrochloric acid because the molarities are same for sodium hydroxide it is a monobasic acid and the mono acidic base they will neutralize equal volumes will neutralize completely of each other
So the volume of sodium hydroxide essentially corresponds to the volume of hydrochloric acid because both of them are equimolar solution 0.1 molar solution the unused hydrochloric acid essentially would correspond to 23.2

So therefore the used hydrochloric acid the hydrochloric acid that is used for absorption of ammonia will be total hydrochloric acid taken minus the excess hydrochloric acid that was present after ammonia absorption which would be 26.8 milliliters this 26.8 milliliters of hydrochloric acid essentially corresponds to twenty six point eight milliliters of ammonia of equal molarity that is point one molar solution therefore for thousand milliliters of one molar ammonia contains fourteen grams this is essentially corresponding to one mole of ammonia dissolved in one thousand milliliters of water
So that has fourteen grams from the molecular formula you can tell it is fourteen grams for one mole of the ammonia that is dissolved

So for the m by ten concentration it will be about one point four grams one tenth of the weight will be there

So the weight of nitrogen essentially corresponds to for thousand milliliters it is about one point four therefore for twenty six point eight milliliters of ammonia how much is the weight percentage weight for two point four point two five seven grams of the substance that is taken this will be the nitrogen that is present for 100 grams how much will be the present nitrogen that is 14.6 percentage of nitrogen that is present in the organic compound let us illustrate this one more with one more example also just to familiarize yourself with the problem of estimation of nitrogen using the geldal method essentially it is a titraometric method you do back titration of an excess acid that is originally taken for absorbing the ammonia and the unused amount of acid is subtracted from the original amount of acid that is taken and that gives you the amount of acid that is used for ammonia absorption

So on let me clean up this board completely

So that we can use up the point three five grams of an organic substance was generalized generalized means essentially treated with sulfuric acid and copper sulphate and the ammonia obtained was passed into 100 ml of m by 10 sulfuric acid the excess acid required 154 ml of m by ten sodium hydroxide calculate the percentage of nitrogen in the system in the organic compound this is the problem now you start from here 154 ml of sodium hydroxide which is needed for removing the excess acid this would essentially correspond to if you take the sodium hydroxide plus H_2SO_4 you need two equivalents of sodium hydroxide because this is a dibasic acid $\text{N}_2\text{S}_4\text{H}_2\text{O}$ is the formula

So if you are taking 154 milliliters of sodium hydroxide of m by 10 concentration this would correspond to half the amount of the sulfuric acid that is needed

So this will correspond to 154 divided by 2 milliliters of m by 10 sulfuric acid which is 77 milliliters of sulphuric acid originally the amount of sulfuric acid taken is 100 ml therefore sulfuric acid used for ammonia absorption will be is equal to 100 minus 77 which is equal to 23 milliliters of m by 10 sulfuric acid

So 23 milliliters of sulfuric acid is actually used for the absorption of ammonia in this particular case now ammonia is also the form of ammonium hydroxide you need two equivalents of ammonium hydroxide to neutralize this

So the 23 ml of m by 10 sulfuric acid is actually equal to 46 milliliters of ammonia of m by ten concentration the same concentration has to be maintained here

So if one thousand milliliters of ammonia corresponds to 14 grams of 1000 milliliters of 1 molar ammonia corresponds to 14 grams of nitrogen one thousand milliliters of m by ten ammonia would contain one point four grams of nitrogen therefore weight of nitrogen is equal to one point four grams in one thousand milliliters of m by ten

So how much will be present in the 46 milliliters of the solution that is used for the neutralization purposes the percentage nitrogen will be equal to one point four times forty six divided by one thousand this is present in point three five grams of the organic compound therefore for hundred grams of organic compound how much will it be if we solve all these things this would essentially correspond to eighteen point four percent of nitrogen being present in the organic compound

So this is a second example of the gel dal's method of estimation of organic compound using the sulfuric acid and copper sulfate method

So essentially if you are familiar with titrametric method you will not have any problem solving this kind of problems you will not have any difficulty in solving this kind of problems during the examination basic principle is simple ammonia is liberated it is absorbed onto excess sulfuric acid or excess hydrochloric acid depending upon the acid that is taken the excess sulfuric acid is neutralized with sodium hydroxide from the volume of sodium hydroxide we know how much of sulfuric acid is present in the system after the ammonia absorption

So the difference will give you the actual amount of sulfuric acid that is used for the ammonia absorption or ammonia neutralization that will be twice the volume of the ammonia because it is a dibasic acid you need two equivalence of ammonium hydroxide once you have the exact volume of ammonia in terms of the concentration you convert it into weight because we know one molar solution of 1000 ml contains one mole of ammonia which is 14 grams of nitrogen in one mole of ammonia essentially you have fourteen grams of nitrogen in other words seventeen grams of ammonia which is corresponding to one molar solution of one thousand ml contains fourteen grams of nitrogen

So for one tenth of the molar solution it will be one tenth of the weight and that is present in the given organic compound

So percentage weight you need to calculate by multiplying by hundred which gives you the percentage of nitrogen present in the organic compound

So i hope these two examples arithmetic examples illustrate the use of the gelals method for the nitrogen estimation the next estimation is halide estimation estimation of halogen is done by carious method caries spelling is c a r i u s carriers method of estimation of halogen when you say estimation of halogen we are primarily talking about the estimation of chlorine bromine and iodine only not necessarily fluorine this is easily done by taking a sealed tube or a thick walled tube in which the organic substance is taken concentrated nitric acid is added along with silver nitrate

So silver nitrate concentrated nitric acid plus the substance is taken and this is fused at one end in other words it is completely closed and this is tube is what is known as the carious tube the methodology is known as the carious methodology of estimation of halogen the organic compound let us say contains some x halogen is at times the x is equal to chlorine or bromine the number of chlorine and bromine present are corresponding to z in this particular case on treatment with nitric acid and silver nitrate h x is formed during the course of the decomposition of the organic compound the hs reacts with the silver nitrate producing silver x which is precipitated

So at the end of the reaction you will see a precipitate in the carious tube that precipitate is filtered washed thoroughly and dried

So the dry weight of silver x formed is estimated or measured now we know in the case of silver salts what is the amount of halogen that is being present we take silver chloride silver chloride molecular weight corresponds to 143.5 and this contains 35.5 grams of chlorine in other words one mole of silver chloride contains 35.5 grams of chlorine So if x is the weight of x grams of silver chloride obtained in the carious method how much will it be

So 35.5 grams are from 143.5 grams therefore for x grams how much of this this will be from a known amount of the mass of the organic compound and for 100 grams how much will it be this will be giving the percentage of chlorine in the organic compound you will illustrate this with a simple arithmetical problem let us say for example 0.15 gram of an organic substance gave point one two grams of silver bromide when it is treated with

sulphur it is a nitric acid and silver nitrate using carious method what is the percentage of bromine in the organic compound is the question that one needs to be addressed silver bromide molecular weight corresponds to silver is one hundred and eight plus bromine is eighty one

So one hundred and eighty sorry bromine is

So it corresponds to 188 grams is the per mole of the silver bromide 188 grams per mole of silver bromide is equal to 80 grams of bromine therefore for point one five grams of the silver bromide how much is the sorry point one two grams of the this would be equal to eighty divided by one hundred and eighty eight multiplied by 0.12

So this is the amount of bromine that is present in the compound if you want the percentage of bromine in the organic compound this would be equal to 80 multiplied by 0.12 divided by one eighty eight this is present coming from point one five grams of the organic compound for hundred grams of the organic compound how much will it be it turns out it is about thirty four point zero four percent if you work out this example here So that much amount of the bromine is present in the organic compound

So one can do either bromine estimation or chlorine estimation the point is 143.5 grams of silver chloride which is one mole of silver chloride contains 35.5 grams of chlorine which is atomic weight of chlorine

So if you get a precipitate of x grams of silver chloride how much will be the compound how much amount of the chloride will be present is given by this expression that is coming from certain weight of the organic compound

So for hundred grams of organic compound how much will be the chlorine that is present in terms of the percentage weight of the chlorine in the organic compound now let us move on to sulphur estimation sulphur is estimated in the form of sulphate

So the organic compound has to be containing the sulphur has to be oxidized

So a sulfur compound is treated with concentrated nitric acid and sodium peroxide

So concentrated nitric acid and sodium peroxide essentially converts the compound into sodium sulphate to which barium chloride is added a solution of barium chloride is added which forms barium sulphate which is an insoluble precipitate

So the basic principle chemistry is that the compound let us say for example ethyl is taken it is completely oxidized to the sulfate to convert the sulphur is converted into an inorganic sulphate and the inorganic sulfate essentially is converted into barium sulphate which is an insoluble compound in case of barium sulfate the molecular weight is 137 for barium 32 for sulfur and 64 for oxygen totally it is 233 grams 233 grams of barium sulphate contains 32 grams of sulfur

So the weight of barium sulphate you get from here let us say it is x grams of barium sulphate would contain 32 divided by 230 multiplied by x grams this is coming from a known weight of the organic compound m

So the percentage of sulfur would be equal to 32 multiplied by x divided by 233 from known mass m

So for 100 grams how much will it be

So that will be the percentage of sulphur present in the organic compound one example we will solve and then we will conclude this lecture with a summary point one five seven grams of an organic compound gave point four eight three grams of barium sulphate using the barium sulphate estimation method or sulfur estimation method what is the percentage of sulfur in the organic compound

So you use the expression 233 grams of barium sulphate is equal to 32 grams of sulfur this much amount of barium sulphate how much will it be 32 divided by 233 multiplied by 0.4813 grams 0.157 grams of organic substance gave this many grams of sulphur 100 grams of organic substance will give 32 four multiplied by three divided by two hundred and thirty three multiplied by point one five seven multiplied by hundred if you work this out it corresponds to about 42.10 percent of sulfur being present in the organic compound

So overall what we have seen in this particular lecture is the methodology for the estimation of nitrogen in the organic compound using lumos methodology where nitrogen is evolved from the organic compound and the measured nitrogen is essentially converted into the weight and percentage weight in the gel doll method the nitrogen present in the organic compound is converted into ammonia it is absorbed in excess acid and using a titraometric estimation we estimate the ammonia that is liberated from the ammonia that is liberated we calculate the weight of the nitrogen present in the organic compound and hence the percentage weight of the nitrogen present in the organic compound for the halogen estimation we have carious methodology where the halogen is converted into an

inorganic halide and precipitated using silver nitrate using silver nitrate you get the silver halide precipitate from the silver highlight precipitate weight of the silver halide precipitate one can estimate the amount of halogen that is present couple of representative examples were given similarly for sulfur it is estimation of sulphur using the conversion of the sulfur compound into sodium sulphate and finally to barium sulphate which is a precipitate from the amount of barium sulphate precipitate that is obtained one can estimate the amount of sulfur that is present in the organic compound with this we conclude this lecture thank you very much for your kind attention
So you

Prutor@elitk