Material and Energy Balances
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Module No # 02
Lecture No # 10
Fundamentals of Reactive Processes

Hello everybody welcome to today's introduction on the fundamental of reactive process now that we have performed many material balance problems for processes which are non-reactor we will move on to performing material balance for reactive processes. In most industry you would always find some process which involves reaction that is how you produce the product before we start performing these material balances we need to understand some of the fundamental or the terminologies associated with such reactive process.

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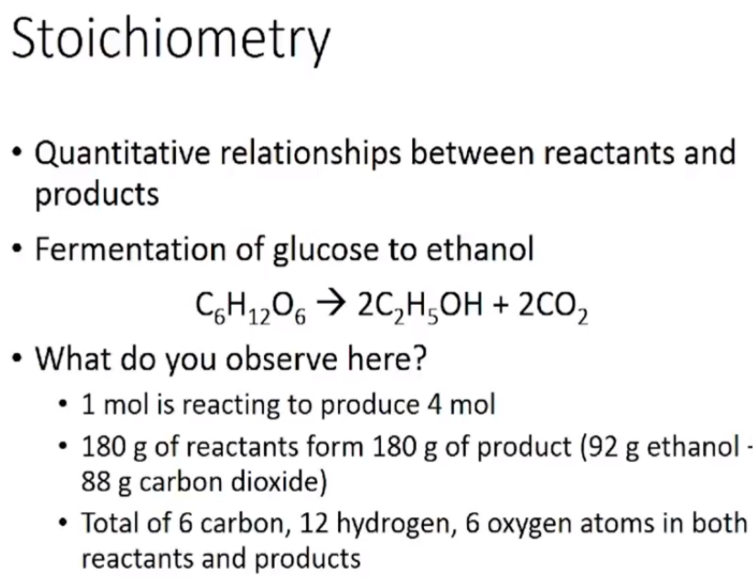

Let us start with this stoichiometry defines the quantitative relationships between reactants and products look at this equation. This is a fermentation of glucose to form ethanol glucose forms two ethanol and two carbon di oxide C6H12 O6 gives 2C2H5OH +2CO2 what do you observe here. If you look at the equation carefully you will see that one mole of glucose is reacting to produce 2 moles of product which are 2 moles of ethanol and 2 carbon dioxide.

However if you were to consider the mass 180 grams of reactors which is 1 mole of glucose which would weight its molecular weight which is 180 grams ends up forming 180 grams of the product which is 92 grams of ethanol and 88 grams of carbon dioxide you also can see that a total of 6 carbon, 12 hydrogen and 6 hydrogen atoms are present in both reactants and the products.

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Stoichiometry

- Quantities that are conserved
  - Total mass
  - Number of atoms of each element
- Moles of reactants ≠ Moles of products
- Stoichiometric quantity – amount based on the stoichiometric coefficients of a balanced reaction
- Stoichiometric ratio – ratio of the stoichiometric coefficients of two reactants in a balanced reaction equation

What is this mean we can identify which quantities or conserved from this we know that the total mass is conserved and the number of atoms of each of elements are conserved however the moles of the reactants is not equal to the moles of products this is an important distinction which we should know until now for non-reactive processes it would not have mattered with whether we wrote the balances either in terms of masses or moles because the reaction were not taking place and they were not being converted from one form to another.

However form now on as we perform balances for reactive processes we need ensure that balances return in terms of masses or as number of atoms of each elements. This way we will ensure that the law of conservation is obeyed. We also need to know some terminologies such as stoichiometric quantity is the amount based on the stoichiometric coefficients of a balanced equation and stoichiometric ratio is given as the ratio of coefficient of two reactants in a balanced reaction.

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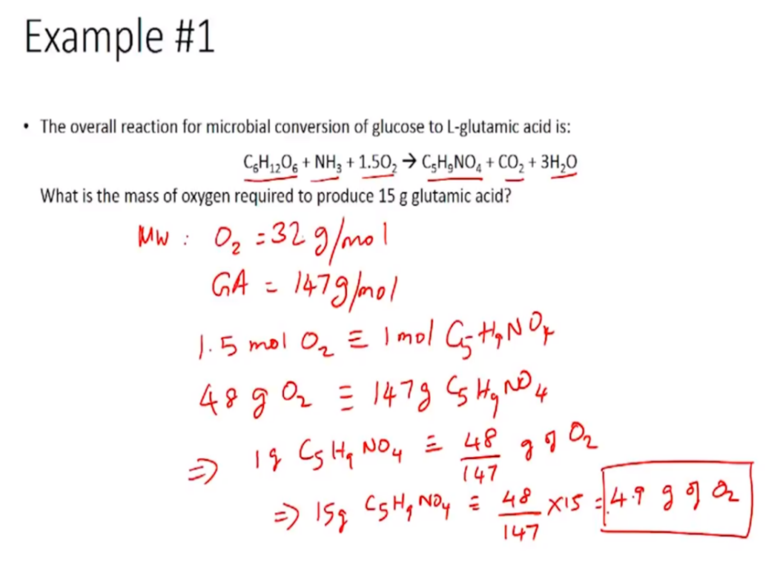

So here is an example problem to help us brush on the fundamental related to stoichiometric the overall reacting for microbial conversion glucose to L-glutamic acid is given here. You are asked to calculated the mass of oxygen required produce 15 grams of glutamic acid. Let us now try and solve this problem for solving the problem we need to know the molecular weight of some of the component involved the molecular weight of oxygen would be 32 grams per mole and molecular weight of glutamic acid is 147 grams per mole.

So now that we know this look at the stoichiometric of equation it says that one mole of glucose react with one mole of ammonia and 1.5 moles of oxygen to form one mole of glutamic acid one mole of carbon dioxide and 3 moles of water. So one mole of glutamic acid is produced by 1.5 moles of oxygen so writing this down we can say that 1.5 moles of oxygen produces one mole of glutamic acid which is $C_5H_9NO_4$.

So substituting molecular weights we can convert these two masses 1.5 mole of oxygen would weight 48 grams of oxygen this would produce 147 grams of glutamic acid we need to calculate the amount of oxygen which is producing 15 grams of glutamic acid this implies so 1 gram of glutamic acid is produced by 48 / 147 grams of oxygen so therefore 15 gam of glutamic is produced by 48 / 147 times 15 which is 4.9 grams of oxygen.

So the mass of oxygen required for producing 15 grams of glutamic acid is 4.9 grams here is another example problem.

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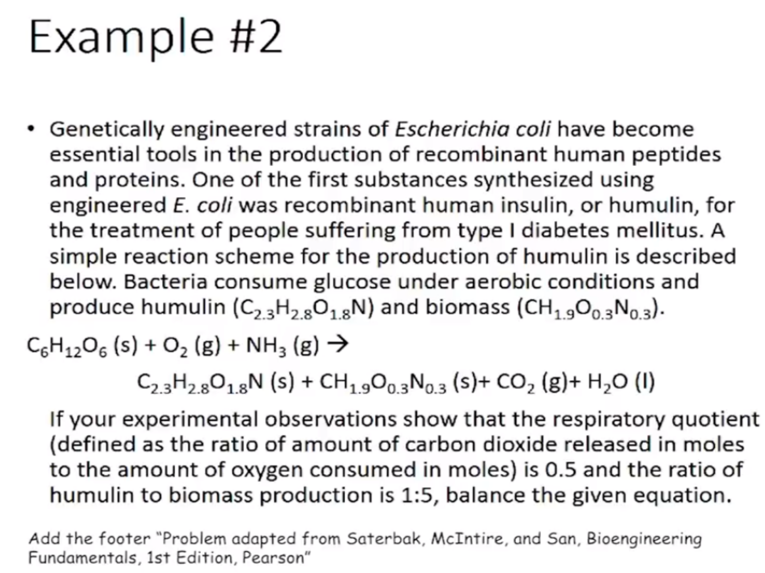

When I was talking stoichiometric one of the terminology I used was a balanced equation. All of the us have used balanced equation we know what balancing equation is usually for chemical reactions balancing equation is reasonably simple however for biochemical reaction it might be not that simple and straight forward. To illustrate this to understand how to perform stoichiometric balancing you will look at this example problem.

Genetically engineered strains of Escherichia coli have become essential tools in production of recombinant human peptides and proteins. One of the first substance synthesized using engineered E. Coli was recombinant human insulin or humulin for the treatment of people suffering from type 1 diabetes. A simple reaction scheme for the production of humulin is shown below the bacteria basically consumes glucose under aerobic conditions and produces humulin and also grows to form biomass.

So the reaction is given as glucose + oxygen + ammonia forms bio mass and humulin carbon dioxide and water. So if you experimental observations shows that the respiratory quotient which is defined as the ratio of amount of carbon dioxide released in moles to the amount of oxygen consumed in mole which is 0.5 and that ratio of humulin to bio mass production is 1 is to 5 balance the given equation.

So all the information you need for balancing the given equation have been provided now we need to look at how about solving this problem.

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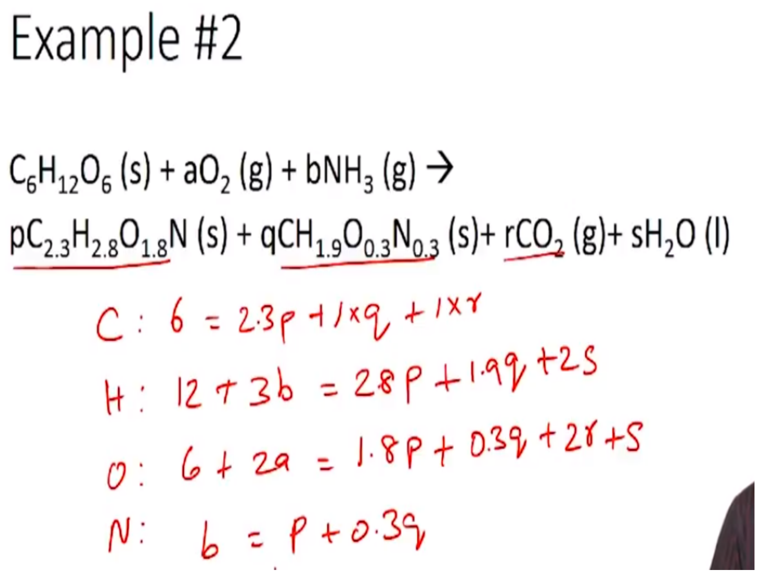

So to identify the stoichiometric coefficient of all these terms we will introduce these variables AB, PQ, R and S. So we assume that 1 mole of glucose is taking part in the reaction and we will try to calculate the stoichiometric coefficient for all the other terms assuming 1 mole of glucose is being consumed during these reactions. So how do we go about this what we need to do is we need to make sure that number of atoms of each of the elements are the same on both the reactant side and the product side.

For this we will start writing balance equations for each of the elemental atoms so let us first start writing the balance equation for carbon. So carbon is entering the reaction through glucose and 6 atoms of carbon is present in the glucose as we can assume the stoichiometric coefficient of glucose to be 1 we have 6 atoms of carbon entering so the product stream of carbon coming in humulin and as bio mass.

So the humulin coefficient has given as P you also have carbon in carbon dioxide so using this you have 2.3 times P + 1 times Q + 1 times R so this becomes your balance equation for carbon you have 2.3 atoms of carbon in humulin 1 atom of carbon in the bio mass and 1 atom of carbon in your carbon dioxide.

Similarly we will have to write the balance equation for hydrogen as 12 atoms of hydrogen in glucose + 3 times B hydrogen atoms in ammonia ends up forming 2.8 times P atoms hydrogen in humulin + 1.9 times Q atoms in bio mass + 2 times S atoms in water. We can also write the balance equations for oxygen and nitrogen oxygen would be 6 + 2A equals 1.8 P + 0.3 A + 2 R + S and we can write the nitrogen balance as B = P + 0.3 Q + 0.

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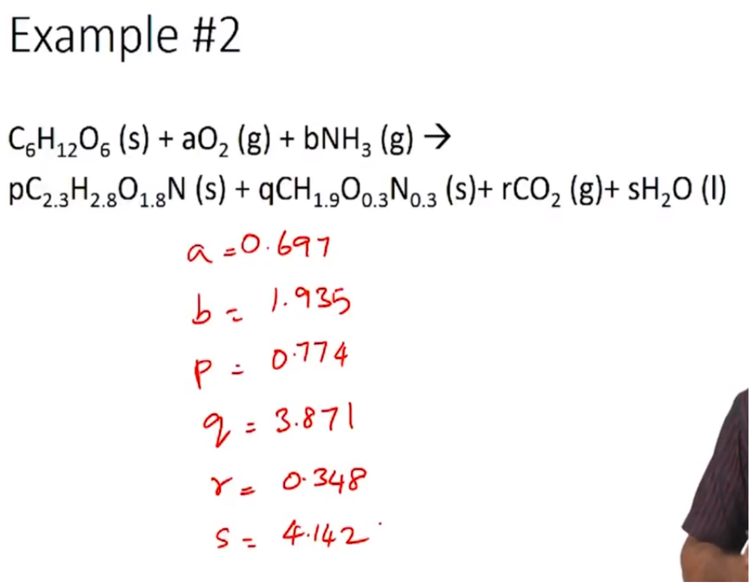

So there is not nitrogen in other thing so we just have B = P + 0.3Q in addition to this stoichiometric quantities which we got from the equation two other information has been provided to you in the problem the problem statement tells you that the respiratory quotient is 0.5 and it also defines what the respiratory coefficient is it is said to be the ratio of amount of carbon dioxide released in moles to the amount of oxygen which is consumed in the moles.

So based on the reaction we have we know that the amount of oxygen which is consumed is A moles and that amount of carbon dioxide which is produced is R moles. So based on the value given for respiratory quotient we know that we can write R = 0.5 A and another information which has been provided to us in the problem is we have the ratio of humulin to bio mass production as 1 is to 5.

So this means we know that humulin to bio mass ratio would be P / Q = 1 /5 which implies P = 0.2 Q we now have 1, 2, 3, 4 ,5 and 6 equations and we have 1 A, B, P, Q, R and S which are 6 unknowns. Solving this equations simultaneously we would be able to get the values for these stoichiometric coefficient when we perform these calculations we will end up with following answers.

So A will be equal to 0.697 B will be equal to 1.935 P will be equal to 0.774 Q would be equal to 3.871 R would be equal to 0.348 and S would be equal to 4.142. You can perform these calculation and confirm whether the values are written here are correct and these would give you an understanding about how would you balance an equation which has more tedious numbers than the one which is used to in the chemical reactions.

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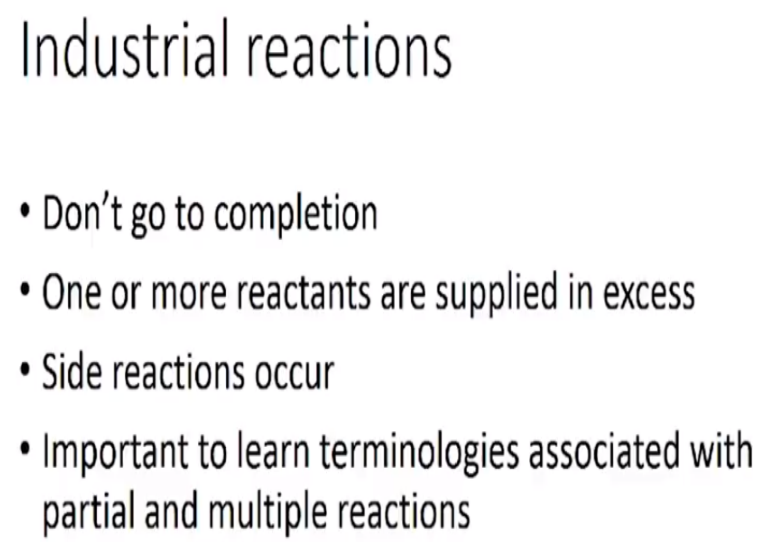

So now that we have looked simple reaction in bio chemical reaction let us move on to what you would see in an industrial setup. In industrial set up the reaction do not go to completion there could always be one or more reactions which are supplied in excess. This would be because not all reactors are going to be of the same cost so you would want to make sure that the reactant which is more expensive which is fully utilized therefore you would supply the cheaper reactants in excess you would ensure that the more expensive reactants are fully consumed.

There can always be side reactions that are occurring resulting in formation of bi-products which are which may not be desirable. It is important to learn terminologies which are associated with such partial and multiple reactions which will help us in performing material balances for reactive processes in an industrial scale.

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Terminologies

- Fractional conversion – fraction of a reactant converted to products

$$f = \frac{moles\ of\ reactant\ consumed}{moles\ of\ reactant\ fed}$$

- Percentage conversion – fractional conversion × 100
- Degree of completion – fraction or percentage of the limiting reactant converted into products

Let us look at some of the terminologies associated with this limiting reactant is the reactant which is supplied in the smallest stoichiometric amount and you have excess reactants which is the one which is supplied at the ratio more than what is required. The stoichiometric requirement is the terminology which is used to define the amount of reactants that is needed to react completely with the limiting reactant.

You also have a term called fractional excess which is defining how much of excess reactant is actually supplied and at what fraction it is in excess. So this is defined as moles present – moles required divided by moles required this fractional excess can also be written as percentage excess which would be fractional excess times 100 you have a term called fractional conversion as I said reaction do not always go to completion which means only the fraction of the reaction sorry fraction of the reactant gets converted to products.

So the fraction of reactants actually get converted to the product is called as the fractional conversion it is defined as it is defined as the moles of the reactants consumed to the moles of reactant fed. Percentage conversion is expressed as fractional conversion times 1000 there is also another terminology called degree of completion which helps us understand to what extent the reaction as gone to completion.

So this is defined usually in terms of the limiting reaction so it is defining as the fraction or percentage of limiting reaction which is converted to products.

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Terminologies

- Extent of reaction
  - Ratio of change in the number of moles of a reactant or product to its stoichiometric coefficient

$$\xi = \frac{(n_i)_{final} - (n_i)_{initial}}{v_i}$$

  - Extent of reaction is always positive
  - Stoichiometric coefficient is +ve for products and –ve for reactants
- Selectivity
  - Ratio of the moles of the desired product formed to the moles of the undesired product formed
  - May be expressed as percentages also
  - Describes the processes ability to select for the desired product relative to the undesired product

Extent of reaction is another terminology which is performed material balances and this will also be used in perform energy balances for reactive process. So extent of reaction is defined as the ratio of change in number of moles in the reaction or product to its stoichiometric coefficient.

So the equation is given here so the number of moles in final condition – the number of moles which was present initially divided by the stoichiometric coefficient will give you the extent of reaction. So the extent of reaction is always positive why would that be required that is because stoichiometric coefficient is positive for products and it should be used as negative for reaction. So in case of reactants the final number of moles will be lesser than the initial number of moles.

However the stoichiometric coefficient will be negative thereby your extent of reaction ends up being positive. For products your final number of moles would be higher than the initial number of moles so your numerator is positive and your denominator which is stoichiometric coefficient will also be positive giving a positive extent of reaction. It does not matter how you calculate the extent of reaction which component you use for calculating the extent of reaction.

Because all the components of the same equation will give you the exact same value for extent of reaction assuming all of them are taking part only in that particular reactant. Selectivity is another terminology which is used to define how favorable the condition are to produce one product over other. So it is defined as the ratio of moles of a desired product formed to the moles of the undesired product form.

This can also expressed as percentages and this tell us the processes ability to select the formation of desired product relative to the undesired product. This is the terminology can be used for optimizing processes in a way that you produce more of the desire product.

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Terminologies

- Yield
  - important term used to describe efficiency of a process
  - Based on feed = $\frac{mass\ or\ moles\ of\ a\ product\ formed}{mass\ or\ moles\ of\ the\ reactant\ fed}$
  - Based on reactant consumed = $\frac{mass\ or\ moles\ of\ a\ product\ formed}{mass\ or\ moles\ of\ the\ reactant\ fed}$
  - Based on theoretical consumption of limiting reactant = $\frac{mass\ or\ moles\ of\ a\ product\ formed}{mass\ or\ moles\ of\ the\ product\ that\ would\ have\ formed\ if\ there\ were\ no\ side\ reactions\ and\ the\ limiting\ reactant\ had\ reacted\ completely}$

Yield is another important terminology yield can be defined in many terms it is used to describe the efficient of the product the process. So yield can be defined based on feed which is given so it is mass or moles of the product which is formed divided by mass or moles of the reactants which is fed. Based on the reactant consumed you can define yield as mass or moles of the product formed to the mass or the moles of the reactants fed.

And based on the theoretical consumption of limiting reactants we can define yield as mass or moles of product formed to the mass or moles of product that would have found if no high reaction happen and all the limiting reactants reacted completely to form the product. So these are three different ways yield can be defined and we will look at using these terminologies appropriately while we perform material balance calculations.

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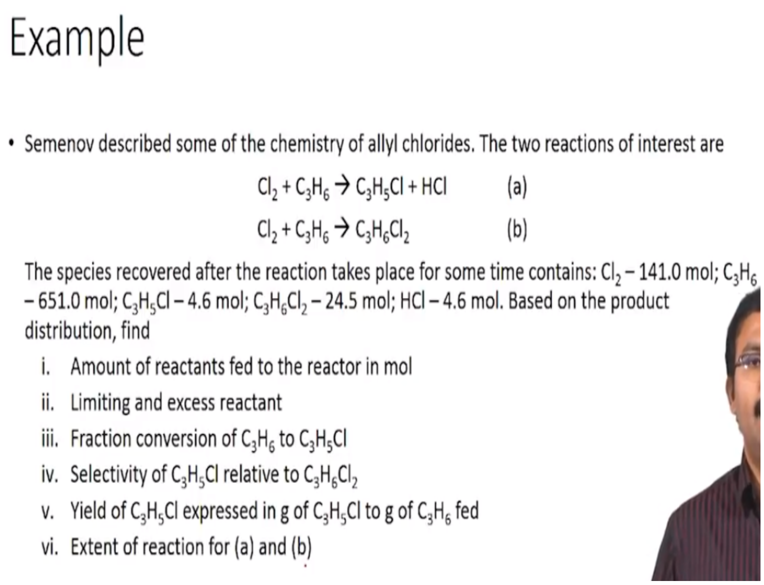

Here is an example problem where you will try to solve for all the terminologies which we just learnt. Seminar described some of the chemistry of allyl chlorides the two reaction that are of interest for this problem are also given here the species recovered after the reaction takes place for some time contains chlorine C386 C385 TL C386TL2 and ACL.

Based on the product distribution you are asked to calculate the amount of reaction which is fed to the reactor the limiting and the extent reactants. Fractional conversion of C356 2C3H5CL selectivity of C3H5L relative to C3H6CL2 yield of C3H5CL expressed in terms of grams of C3 H5CL 2 grams of C386 fed and the extent of reaction for these two reactions for which are A and B.

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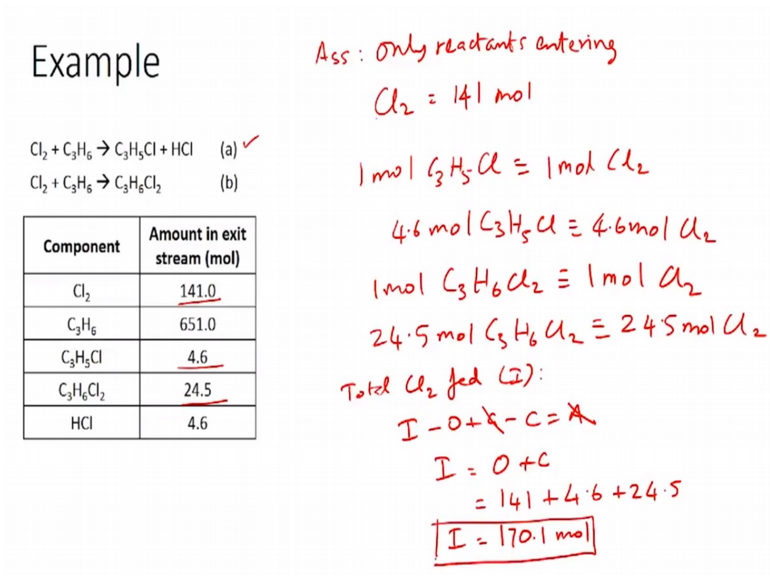

So let us see if we can calculate all these values all the information that has been given to you in the problem has been shown so you have both the reaction that have been listed and you also have all the component all their moles in the exit stream. So now let us try to solve this problem for solving this problem the first step is to identify how much of the reactants are actually entering into the system for this we need to make an assumption what do you think that assumption should be?

The assumption would use here would be only the reactants are entering into the system if we do not have the assumption we would not be able to solve for this problem as you would have this variables with respect to which of the reactor which of the products are coming in at what amount they are coming in. So for that reason we will assume that the initial condition as only the reactants.

So we start up with the assumption only reactants are entering now based on the equations we have we know that the exit stream contains chlorine at 141 moles which is given here and chlorine is at 141 moles and you have C3H5CL which is leaving at 4.6 moles from the reaction A we know that one mole of C3H5CL is produced by 1 mole of chlorine. So this means 4.6 moles of C3H5CL was produced by 4.6 moles of chlorine so in the first reaction we know that 4.6 moles of chlorine as actually with consumed.

So now we have the second reaction through which chlorine could have been consumed so again we know that 1 mole of C386CL2 is produced by 1 mole of chlorine. So this means 24.5 moles of C3H6CL2 that is present in the exit stream would have been produced by 24.5 moles of chlorine. So now that we have calculated these we can calculated the total amount of chlorine which is fed which is the input.

So we can go back to the balance equation which we had which is input – output + generation – consumption = accumulation as the process is at steady state we will have accumulation to be 0 chlorine is not generated so you have only consumption so you end up with input = output + consumption so the consumption terms are 24.5 and 4.6 and your output is 141 + 4.6 + 24.5 would be the input giving you the value for the input as 170.1 moles so this is the number of moles of chlorine which is entering into the system.

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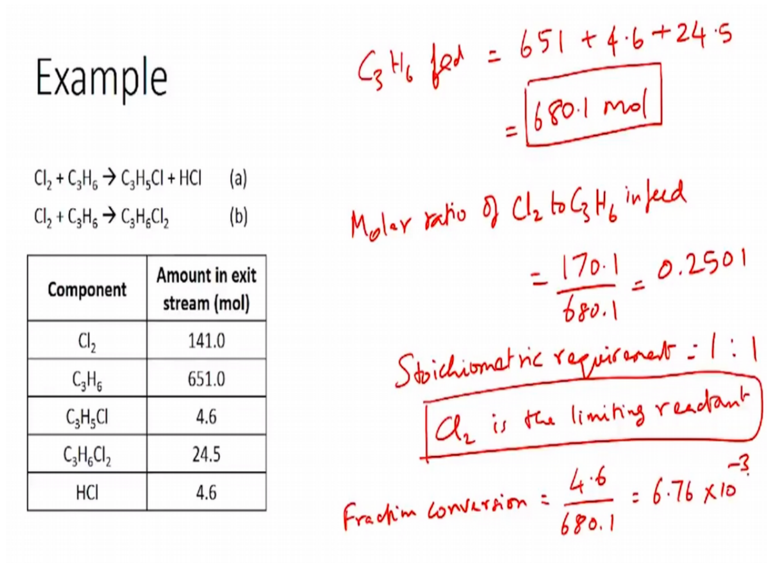

Looking at those equation we know that stoichiometric ratio of chlorine and C2H6 as 1 is to 1 which means if 4.6 moles of chlorine is consumed by reaction 1 and 24.5 moles of chlorine is consumed by chlorine 2 the same number of moles of C3H6 is also consumed by these two reaction there by the amount of reactants C3 H6 fed would basically be the amount of reactant which is leaving the system which is 651 moles + 4.6 which was consumed by the first reaction + 24.5 which is consumed by the second reaction giving you the value of 680.1 moles.

So this would have been the amount of C3H6 fed to the system so this gives us the values for the first part now the second part of the problem ask us to calculate which of these two reactions was in excess and which was the limiting reaction. So the limiting reaction is basically defined as the one which is defined as the lower stoichiometric requirement. So for this we need to identify the molar requirement and the stoichiometric ratio compared to what was being fed.

So the molar ratio in the feed molar ratio of chlorine 2C3H6 in the feed is actually 170.1 / 680.1 giving you a value of 0.2501 whereas the stoichiometric requirement is actually 1 is to 1 as the stoichiometric requirement is higher for chlorine and it is being supplied as ratio lower than the stoichiometric requirement we can identify that chlorine is the limiting reactant and C3H6 is actually being supplied in excess.

So the next part of the problem ask us to calculate the fraction conversion of C3H6 to C3H5CL so we know that C3H6 actually take part in both the reactions it is getting converted to C3H6CL and sorry C3H5CL and C3H6CL2. So we need to identify how much of C3H6 actually went into the first reaction to produce C3H5CL. So based on the stoichiometric we know that 4.6 moles of C3H6 actually got converted to form C3H5CL.

So the fraction conversion which has been asked for basically would be the amount of C3H6 which is reacted would be formed C3H5CL which is 4.6 moles divided by the total amount C3H5 sorry total amount of C3H6 which is fed which is 680.1 giving you a value of 6.76 times 10 power -3.

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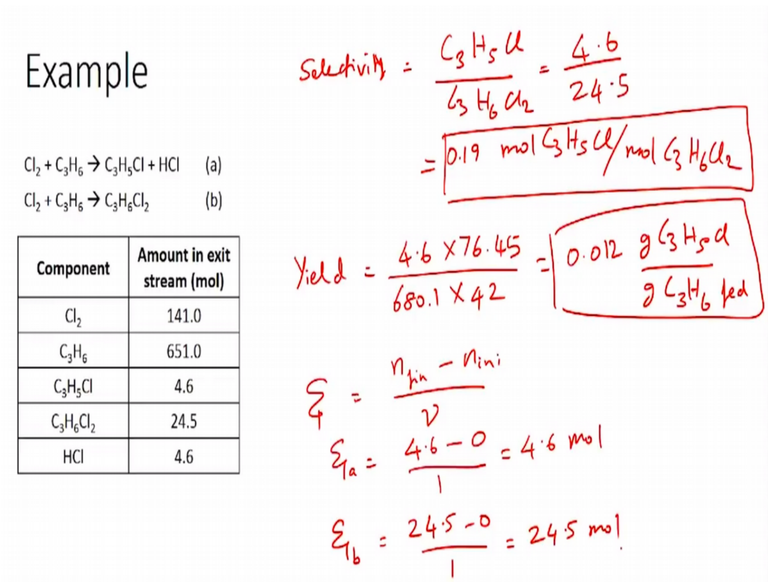

So the next problem is to calculate selectivity we have been asked to calculate the selectivity of C3H5Cl relative to C3H6CL2 indicating C3H5CL is probably desired product so we will calculate this selectivity as C3H5CL as we formed to C3H6CL2 that as been formed so which gives you a value of 4.6 / 24.5 which is 0.19 moles of C3H5CL per mole of C2H6CL2. So this gives you the selectivity for one product over the other.

So the next part of the problem is to calculate yield it has been also stated clearly that have been asked to calculate yield in terms of grams of product formed per gram of reactant fed based on this you will calculate the yield as 4.6 moles of the product C3H5CL which is formed times is molecular weight which is 76.45 divided by 680.1 moles of C3H6 which has been fed times 42 the molecular weight of C3H6 which is fed so this gives you value of 0.012 grams of C3H5CL per gram of C3H6 which is fed so this gives you an yield which has been asked for.

The last value which has been asked to which have been to is to calculate the extent of reaction so the extent of reaction is calculated as N final – N initial / stoichiometric coefficient. So for reaction 1 we would calculated as 4.6 which is the number moles of C3H5CL which has been formed – 0 which would be the number of C3H5 CL 2 moles which has been supplied initially divided by it is stoichiometric coefficient which is 1 giving you a extent of reaction as 4.6.

One thing you should note here is we have used C3H5CL for performing the calculation for extent reaction why? Why not chlorine or C3H6? Because chlorine and C3 H6 do not take part extent the first equation they take part in both the equation so to actually calculate the extent of reaction for first reaction we need to use a component which is unique to the first reaction.

So we could either use C3H5CL or HCL just we have the information for both you could choose anything and we have here we have chosen the amount of C3H5CL and calculated as 4.6 moles. Similarly we can calculate the extent of reaction for the second reaction using a component which is unique to the second reaction which is C3H6CL2. So that would be 24.5 -0 divided by 1 giving you 24.5 moles.

So these values have been calculated and hopefully you have now understood how to use this formula for calculating the terminologies now with understanding of these terminologies we will move to material balances on processes with reactions thank you.