Environment Engineering: Chemical Processes
Prof. Dr. Bhanu Prakash Vellanki
Indian Institute of Technology – Roorkee

Module No # 01
Lecture No # 01
Introduction, fundamentals of Equilibrium & Kinetics

Hello everyone I welcome to this NPTEL online course so during the course am going to discuss the chemical process involved which are at the corner stone of environment engineering now. Anyway before I go further I would like to express my thanks and gratitude to Doctor Bill Bachelor my advisor from whom I learnt most of my technical knowledge I guess right. So let us move on and I guess you are concern about is this relevant to you.

So anyway this course is designed for master students and environmental engineering professionals or consultants. So this course will give you a basic idea I guess the fundamentals of chemical process involved in environmental engineering. So expectation from this course once you have done with this course you should be able to critically analyze and if required quantify the chemical changes within either an engineering system as an STP's or CTP's or look at and analyze critically again any of the national systems that you would come across okay.

So again relevance how is this relevant to you now I will give two examples let us see the first aspect is to give you about the background of environment engineering now. Any aspect of environment engineering when you look at it there going to be three aspect now.

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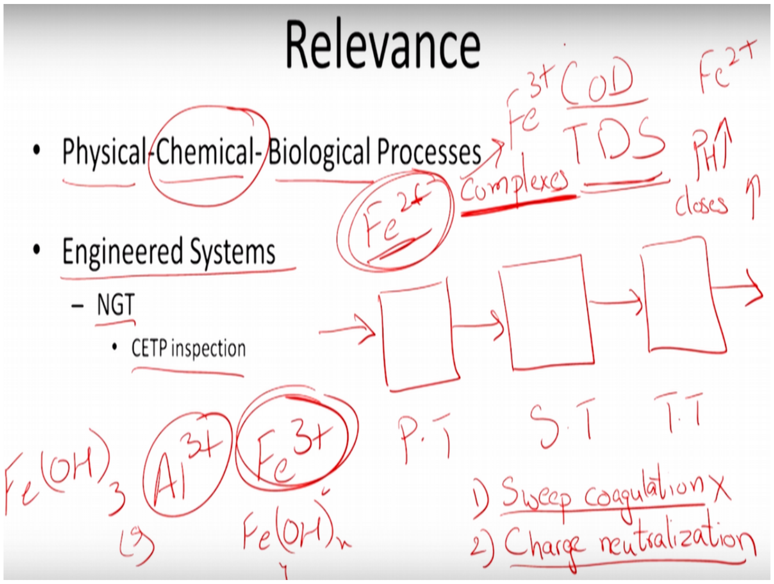

Relevance

- Physical-Chemical-Biological Processes
- Engineered Systems
  - NGT
    - CETP inspection

So here we have the physical, chemical and biological process involved so these three are (()) (01:55) stones of environment engineering the fundamental (()) (01:58). So in this particular course we are going to talk about the chemical process involved with environmental engineering again it is not chemistry now. So those people empathy towards chemistry you know do not be thrown off write it right because these are the chemical process.

So we would not going to in detail with respect to chemistry may be little of it but mostly we are going to discuss the chemical process now. So regarding the example to see I guess or to let u know how it is relevant to you? You know I am going to look at it one example came across recently that it I think it is pertinent here right. So we are going to talk about engineering systems an example here so people might have heard about the national green tribunal the NGT right.

So it has IIT Roorkee right let us it represented to inspect some CETP's recently CETP is a common effluent treatment plant by pardon me. So CETP is the common effluent treatment plant that (()) (02:56) to the industrial waste so let us say there are 100 or 200 industrial houses there and they discharge their waste to the CETP's which than try to degrade the waste to the relevant standards obviously just look at the summary of the process.

So the influent here and then the primary treatment right coagulation, flagellation and so on which you are well verse with and I believe than a secondary treatment I think it is SB or ASB based and then treasury treatment and then the (()) (03:32) right. So when we analyze this particular CETP I took the samples from each unit stage and looked at it I found that the COD was increasing right and the TDS 2 was increasing and thus I guess the obviously (()) (03:50) who want to designed your CETP to able to reduce the BOD, COD and TDS and so on.

So let us look at a pertinent of relevant example here to show you why let us say why you need a background in the chemical process to be able to what we say have a carrier in environment engineering now. So what they were up to is they were dumping ferrous sulphate right a source of FE2 + as their (()) (04:17) now right. Again coagulation, flagellation you are aware of there are two major aspect involved.

One what is that sweep coagulation and the other aspect would be right charge neutralization so again coagulation two major aspects sweep coagulation and charge neutralization. So let us say people traditionally use alum a source of AL3 + or you use the pheri chloride a source of FE3+ so how they traditionally work is you know they form complexes.

Let say if you are taking the case of FE3 + they can form what we say ferric hydroxide complexes now right and charge to obvious let us say you know FE OH let us I say thrice this is one ferric hydroxide complex this obviously would not help with charge neutralization and help or assist with sweep coagulation.

So charge neutralization what we have here we have the collides which are relatively neutrally charged and you have your coagulant which are relatively positively charged or this coagulant charge FE3+ form (()) (05:43) complexes which are again have depending upon the hydroxide concentration there and you are going to again have a positive charge so they are going to able to neutralize the charge of the collides letting the m aggregate right.

And then the other aspect is sweep coagulation where in the ferric hydroxide the solid can precipitate out especially if you done considerable amount of not dump pardon me add ferric in relatively higher concentration now is but what is happening with the FE2 + and why is it a poor substitute for FE3+ now.

So FE2+ right it forms little to know acquiesce complexes so here for charge neutralization you need to look at complexes so at most PH right ferric pardon me does not form complexes so you are charge neutralization can be effected their and most specially you will not sweep coagulation because FE2+ does not form a precipitate let us say does not precipitate out at most PH and most doses so you need relatively high PH and you need have wealthy high PH right and very high doses of FE2+ to be able to get you to able to have an efficient coagulation, flagellation mechanism.

But is the industry using that because source of FE2+ is cheaper than FE3+ and AL3+ but what is happening now so you are unable to have an efficient coagulation and flagellation process and that leading to increase in TDS’s and also what is happening is you know FE2+ right can be oxidized by oxygen to FE3+ now.

So what does it mean FE2+ has an oxygen demand right so again I believe this is the reason I see that the chemical oxygen demand is increasing so to be able to quantify that or at least be able to calculate the PH at which you are system is going to be relatively more effective let us say you are going to look at the equilibrium related aspects. So let us say at the end of this courses at the fag end of this course you will be able to critically analyze and then understand and then obviously again quantify.

Quantify as an put a number down most people will have a generic idea but you as a professional should be able to quantify the relevant aspects. So that is what should be able to do at the end of this course now okay. So we will move on so I guess we will look at a brief course outline a detailed course outline which will give an idea about what an expect from this course will be available on the website.

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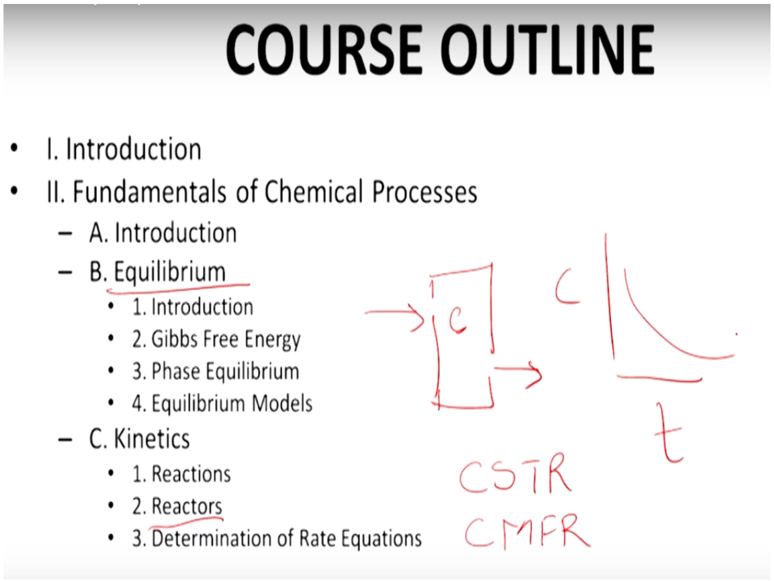

COURSE OUTLINE

- I. Introduction
- II. Fundamentals of Chemical Processes
  - A. Introduction
  - B. Equilibrium
    - 1. Introduction
    - 2. Gibbs Free Energy
    - 3. Phase Equilibrium
    - 4. Equilibrium Models
  - C. Kinetics
    - 1. Reactions
    - 2. Reactors
    - 3. Determination of Rate Equations

So course outline so first we are going to have a introductory class which going to be this session and then next we are going to talk about fundamental chemical process which are equilibrium right and then we are going to talk about the relevant aspect with respect to equilibrium as in those aspects which define not define I guess would drive equilibrium.

Let us say right that is usually going to be the gives free energy now and we are going to look at the various models and then second major aspect would be other than equilibrium it is going to kinetics now. Yes again reactions relevant reactors as a plug flow reactor as CSTR and so on. SO why I have let us say have one more look at this reactors let us say for example I want to model this room let us say assume for my sake and please excuse my poor drawing skills I guess right i have a contaminant flowing through the door of this room and again there is an exit to this room let us say there is window let us say.

Now I want to and there are reactions occurring right and I want to model the concentration of this compound in this room with time. So I need to be able to come up with the case of ideal reactor here and here let us say the fan are turned on I can say that this is a CSTR a continuously stir tank reactor I think people use completely mix flow reactor two and once I define this system I will be able to develop a model and then able to spread it or model the concentration of the compound in the room with respect the time right.

Okay again I am moving on so again we are going to have equilibrium kinetics and then we are going to discuss four major aspects in environmental engineering four major sets of chemical reactions.

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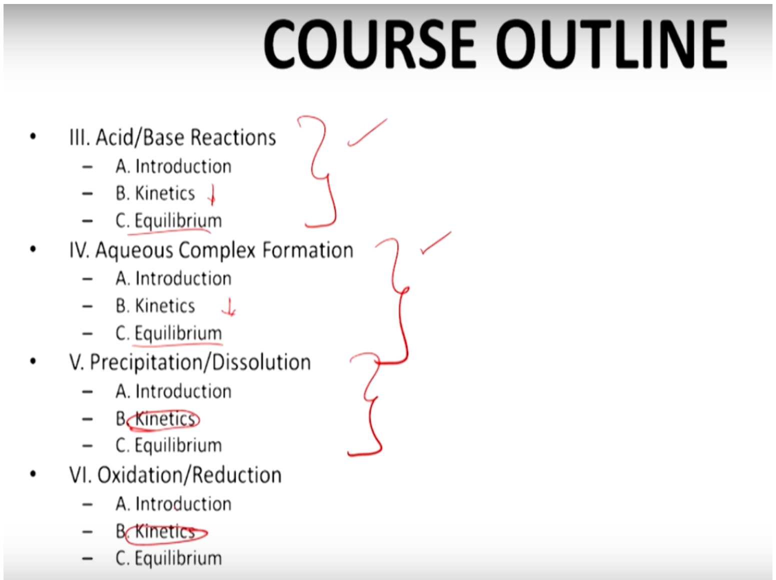

COURSE OUTLINE

- III. Acid/Base Reactions
  - A. Introduction
  - B. Kinetics
  - C. Equilibrium
- IV. Aqueous Complex Formation
  - A. Introduction
  - B. Kinetics
  - C. Equilibrium
- V. Precipitation/Dissolution
  - A. Introduction
  - B. Kinetics
  - C. Equilibrium
- VI. Oxidation/Reduction
  - A. Introduction
  - B. Kinetics
  - C. Equilibrium

So the first one would be acid and base reactions and then we are going to discuss equilibrium and kinetics again in context of acid and base and then moving on aqueous complexes again we are going to discuss equilibrium and (()) (10:25) aspects in complexes again precipitation and dissolution again equilibrium and kinetics and relevant aspects their and most importantly oxidation and reduction of reactions and equilibrium and kinetics here.

So obviously kinetics would have a lesser role to play the acid base reaction and aqueous complex kinetics as a lesser role to play mostly they are defined by a equilibrium but precipitation and equilibrium usually look at kinetics and also for (()) (10:54) you look at kinetics again. So we are going to be able to go through the major aspects here for first we will look at equilibrium and kinetics and then the four majors sets of reactions so types of reactions which we usually encounter in environment engineering and then look at the relevant aspects again.

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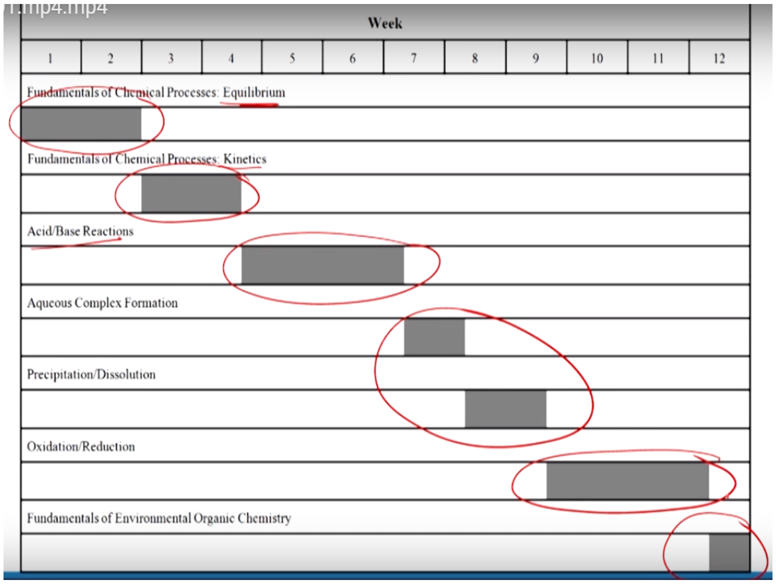

So if we are going to look at the schedule right so we see that we have the couple of weeks for equilibrium and then again the couple weeks for kinetics where we are discuss the fundamentals now right and then we are going to look at the applications of the equilibrium at kinetics in acid base spend relatively less time on aqueous complex complexes and precipitation and dissolution and the considerable time on (()) (11:36) reaction because their our present and are great relevant to environmental engineering per say and then some time on your environment organic chemistry now.

Again obviously if we are dealing with microbes and because you know most of the nature also we have organic compounds we are going to have a brief look at the right. So moving on I guess you want to know let us say you know some of the aspects or text books that you need to refer to.

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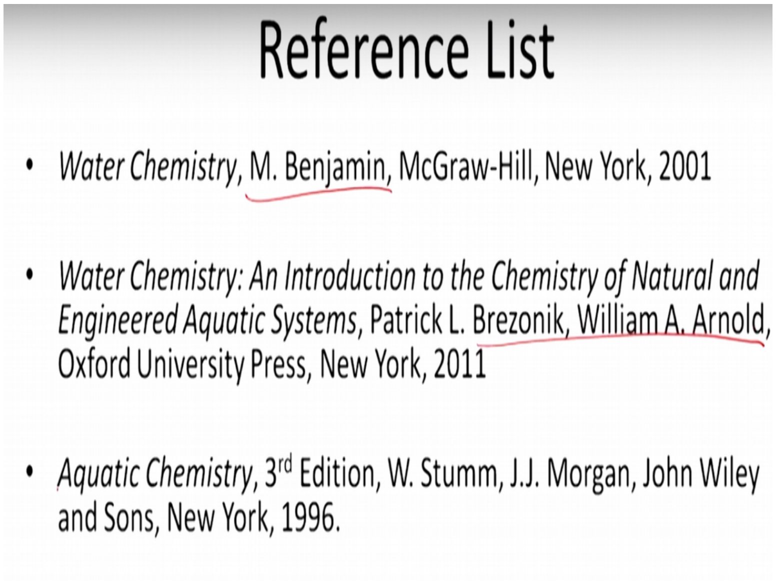

Reference List

- *Water Chemistry*, M. Benjamin, McGraw-Hill, New York, 2001
- *Water Chemistry: An Introduction to the Chemistry of Natural and Engineered Aquatic Systems*, Patrick L. Brezonik, William A. Arnold, Oxford University Press, New York, 2011
- *Aquatic Chemistry*, 3rd Edition, W. Stumm, J.J. Morgan, John Wiley and Sons, New York, 1996.

So in general a very good book pardon me to refer to is water chemistry by Mark M Benjamin and I am not sure of it is available online so I am going to suggest you another book that is available online through most of our libraries and that water chemistry by Brezonik and Arnold right. So preferable look at water chemistry by Mark M Benjamin and that is if not available you can look at water chemistry by Brezonik and Arnold.

And in general there are some concepts that you want to dig into right you want to develop a much more fundamental understanding of the concepts. So then you can refer to the holy bible or holy (()) (12:41) let us say aquatic chemistry by Stumm and Morgan and this is the holy bible with respect to the chemical process involved in the engineering in environment engineering now okay.

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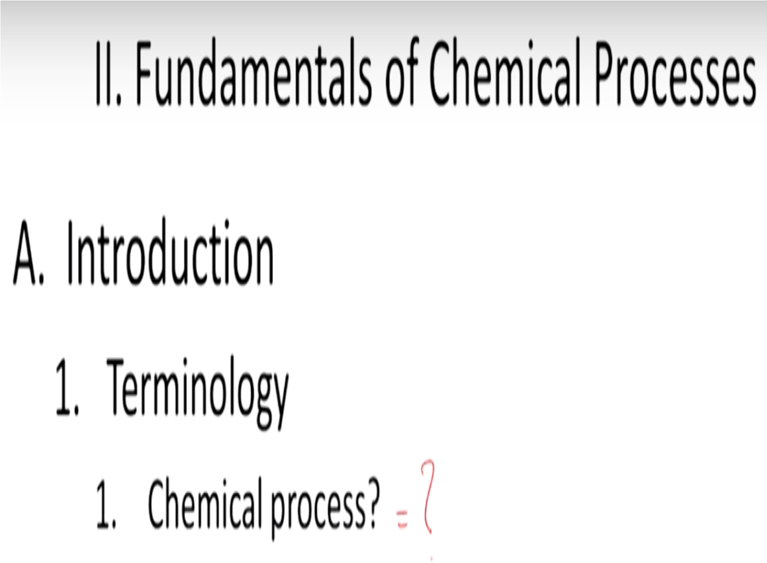

II. Fundamentals of Chemical Processes

A. Introduction

1. Terminology
   1. Chemical process? = ?

Moving on so let us say we are going to discuss the fundamentals of chemical process here right and I guess I believe I have example here that will illustrate to you why we need to look at equilibrium and kinetics but I believe here we are going to first have some terminology. So we have talked about chemical process now right and what is that now what is a chemical process what do you understand by that.

Anyway am not one for mugging up what we say definitions and such as long as you are able to develop and understanding of what it is that we are looking at that is good enough for me any how the chemical process I guess occurs when a materials undergoes change in the chemical bonds right it occurs again I repeat it occurs a chemical process occurs when a material goes or under goes a change in the chemical bonds now or you can call that a chemical reactions too.

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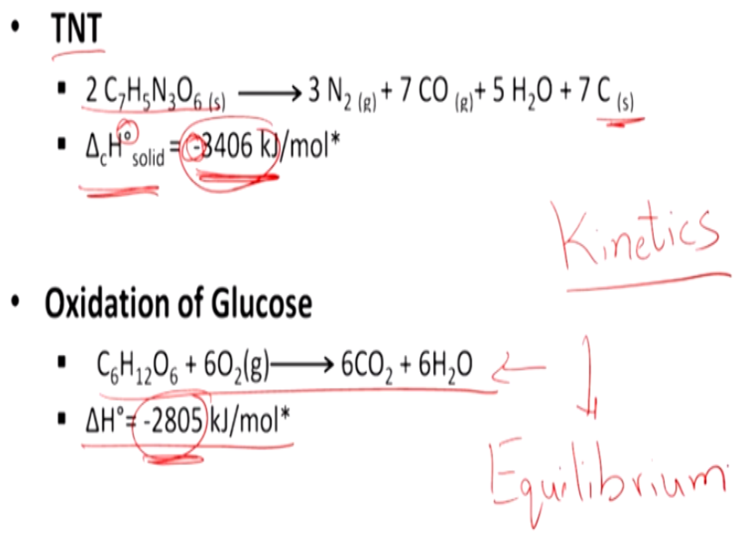

- **TNT**
  - $2\,C_7H_5N_3O_{6\,(s)} \longrightarrow 3\,N_{2\,(g)} + 7\,CO_{(g)} + 5\,H_2O + 7\,C_{(s)}$
  - $\Delta_c H^\circ_{solid} = -3406$ kJ/mol*
- **Oxidation of Glucose**
  - $C_6H_{12}O_6 + 6O_2(g) \longrightarrow 6CO_2 + 6H_2O$
  - $\Delta H^\circ = -2805$ kJ/mol*

Kinetics

Equilibrium

Let us have that in out background now and then moving on I want to illustrate and example so here we have a TNT Trinitrotoluene I guess that is an explosive here you are aware of that. So here we have the relevant reaction for combustion yes combustion of the TNT the solid form going into I guess gas and solid and suite I guess and here we have the change in enthalpy during combustion of the solid and obviously you see there is considerable energy released and negative more or less there is a exothermic reaction and you are having considerable energy keep in mind this are at the standard condition S.

And the next example we are going to look at is oxidation glucose right and this glucose think of have a chocolate now I guess may be sucrose anyway glucose I guess it can oxidized by oxygen as you are aware of for example if I let glucose stay open to the atmosphere this is an reaction that I can except right and again look at the change in enthalpy now right it is -2800 it is almost or near the change in enthalpy that which would observe where during the combustion of TNT now.

Okay think of this if I smuggle TNT in here and through that out in this room the people who are sitting here you know they are scatter out but let us say if I bring glucose here and spread that out in the atmosphere no one going to run there only going to look out if I was a mad man. So please take a couple of seconds and think of what the aspects here we are missing now both more or less released considerable amount of heat energy right.

So what are we missing here so obviously the aspect is that you want to look at how fast these reactions are going through right and in that case we come across kinetics how fast or the relevant reactions now right for example TNT there are combustion of TNT it is remarkably fast process or the kinetics is very fast.

So that is why you would see considerable energy release within a short span of time but oxidation glucose though the kinetics is relatively slow or remarkably slow pardon me is and that is why even though the energy released is comparable to energy released in TNT compression right you have the energy release over a considerable period of time is. So here we are concerned about equilibrium as in what happens after the system has reached the maximum extent possible.

So I guess I use this example to illustrate that we always whenever we consider that system we need to look at or we dealing with kinetics or we dealing with equilibrium let us move on I guess. So again the fundamental aspect chemical process we are going to talk about equilibrium kinetics.

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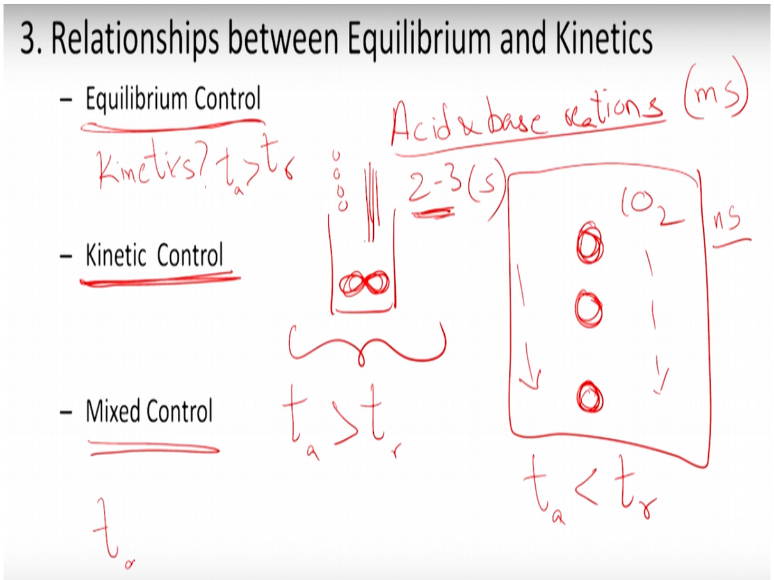

3. Relationships between Equilibrium and Kinetics

- Equilibrium Control
- Kinetic Control
- Mixed Control

So equilibrium will give us an idea about how far can the system go to how far can this chemical process go to right and keep mind it is a state equilibrium is the state of the system and please pardon me for the poor hand writing skills I guess so equilibrium defines a state now and people take about equilibrium saying you know forward reaction rate of the forward reaction is equal to the rate of backward reaction and such.

But I would like to think of that as their the symptoms let us say but what is equilibrium now it is the state let us say which we could describe when a chemical process has gone to the maximum extent possible under the given condition of temperature and pressure. Again I repeat so equilibrium is state when a chemical process as gone to the maximum extent possible under the given condition of temperature and pressure.

Please keep that in mind temperature and pressure I have an important aspect here again enhance a knowledge so equilibrium tells us about how far does the system or can the system go to and the next aspect obviously is kinetics and what that tell us that gives us information about how fast is the system now again (()) (17:59) terms that I think I am trying to help in your understanding rather than mugging up definitions now.

And kinetics what is that it is not a state obvious it is characteristic it is a characteristic of the system that tells you how fast or the rate of change of your chemical process right. So again equilibrium tells us how far can the system go to and kinetics will tell you about how fast the system go. And let us see what I have next so I guess in general when we look at any system we will need to be able to analyze okay what aspect do I need to consider.

Do I need to consider equilibrium related aspects or the kinetic related aspects so in general we break them down into equilibrium control kinetic control and mix control. So let us see what they are about so let us say for example let us say you know I am looking at let us say acid and base reactions okay acid and base reactions and let us take two examples here one is I am adding a drops of acid in an beaker that is continuous listed and this is the symbol for mixing I guess and then I measure the PH after a few seconds let us say two three seconds let us say right.

And the other case is let us say you have the let us say water drop it during a rainfall I guess that is coming down right and you have carbon di oxide in the atmosphere let us say and then you are going to have the relevant acid base reaction I guess and the PH of this particular water drop let will obviously decrease now right. So if you look at that these systems now you know we need to be able to let us say identify which one will be under equilibrium control and which one will be under kinetic control.

So the first and the formal example you know let us say our time of time available let us say you know I am just going to use a generic terms here the time available is much greater than the time or the characteristic time of the reaction for example acid base reaction are remarkably fast I believe in the order of around milli seconds. So by the time if you take your PH reading let us say right which is after two three seconds the system has had enough time to be able to read reach equilibrium now yes.

So that is system you call as equilibrium control but if I look at the second example now where in I have water drop lets you now falling down through the atmosphere under the gravity let us see and you have carbon di oxide what we say interacting with the outer layer of your water drop let and here let us say I only have around nano seconds of time let us say right. So here the time available further reaction or the time I am looking at is less than the characteristic time of the reaction again which is in the order of milli seconds.

So what do we say this milli seconds is the order of your acid base reactions they are relatively fast. So the second one where you to have the less time available for the system to reach it is equilibrium so you are going to say that it is kinetic control now. So why do we look at that well because let us say you have come across the system and you need to be able to quantify that. You need to be able to know have the system reached equilibrium or it is yet to reach equilibrium and I need to look at the kinetics now right.

So when it is equilibrium control kinetics play any role do you care of it is relatively fast or slow not really because when you can identify a particular process as being under equilibrium control you know that you have always have enough time available compare the characteristic time of the reaction.

So you do now really care whether kinetics is slow or fast but when you talking about kinetic control you know that system does not have enough time to reach equilibrium right and in general you need to look at the kinetics of the systems and then obviously you will always have mixed control when more or less the time available is in a same order of the time of the characteristic time of the reaction anyway let us see let us look at what we have next please.

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And I guess example so we have already covered that we are not going to go through that again okay I guess here I wanted to post a question here. So let us say we are going to look at three not three graphs three cases here take a few moments and try to identify which of these would be would you rather classify as equilibrium control kinetic control and mixed control.

So here we have a graph with concentration on the Y axis and time on the X axis on the particular compound let us say and here you have three scenarios right may be not such good representation here so if I can cancel this out and say something like here. So let us say there are three scenarios here right that just represented on the graph so please take a few moments and think of which one would you classify as equilibrium control, kinetic control and so on.

Right so again we are talking about looking at the changes in the reaction or the chemical process pardon me relevant to the time available. So right if you look at this system you have obviously see that there is now further changes in the system and you can thus confidently say it is under equilibrium control. And this one is still see that it is far from reaching equilibrium and the chemical processes is still under is I guess it is undergoing and so this will be kinetic control now.

Again in the formal case which we identified as a equilibrium control we see there as a system had enough time to be able to reach equilibrium is which is not the case with the kinetic control the system as not had enough time to be able to reach equilibrium and you still see the concentration change in considerably with time. And obviously the last case is the mixed control right when you do see changes initially but you also see that the system is approaching equilibrium.

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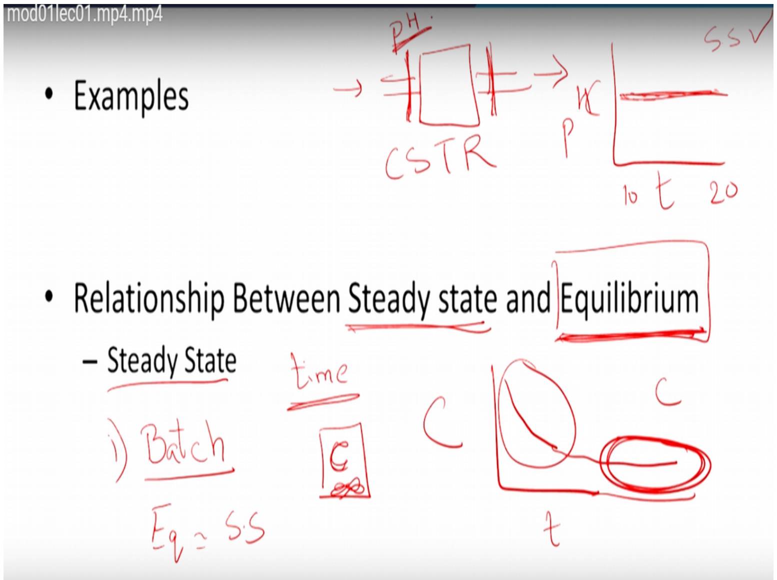

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- Examples
- Relationship Between Steady state and Equilibrium
  - Steady State

So in this case both kinetics and equilibrium play a role here right okay the next aspect we are going to look at is the relationship between steady state and equilibrium right. So first before we go further while we have already discussed what equilibrium gives us the idea about we need to discuss what steady state.

So people might have heard of it but you know there is not harm in looking at it again and the first question that you need to understand obviously that steady state is not relevant to only the chemical process now right or only to environment engineering so steady state is when there is no change in any variable of you system with respect to time.

So you look at any variable in the system that you consider and there should be no change in that variable with respect to time and that is one you would let us say i would call the system to be at steady state right. So let us look at the reply between some of the steady state and equilibrium let us say. Some of the examples where we can look at the interplay between steady state and equilibrium right for example now we will consider I believe a batch reactor.

A batch reactor is the one which is the close reactor let us say and let us say so there are no inputs and outputs and you have a compound here at concentration C and that is well mixed right and let us say it is decaying right. So at this particular point in time is the system at the steady state and equilibrium node because as we are just mentioned concentration is still changing with time right.

So neither as it reached equilibrium because the system as not gone to the far and extent possible and also neither is at the steady state because the concentration is a variable here is changing with time so in this zone neither is it at steady state neither is at equilibrium. And if I take the system further and look at it here though and this particular aspect which are this particular time frame highlighting here.

So in this particular aspect this point in time the system is at equilibrium because it has gone to the far extent possible under the given temperature and the pressure conditions right. And also if you look at it now there is no change in any other variable two a concentration is not changing any more so you can say that the system has reached both steady state in equilibrium.

So what is that mean in batch systems which are close systems equilibrium would be equivalent to let us say a steady state. Again this is a generic example so you need to be careful before you apply such generic skill right. But if it is continuous flow though let us say you know I have a let us say any STP let us say a continuous flow coming in and continuous flow going out and let us say here that trying to maintain a particular PH now right.

So this is let us say call that CSTR let us say continuously stir tank reactor this is are just terms so continuous flow loop. So here let us say while look at it right and with time let us say I have bought it and concentration versus time and let us say this what somebody observes as an after 10 days let us say starting from 10 days to 20 days taking the sample and have seen that the concentration or PH let us say on the Y axis is constant.

So what conclusion can you drawn out can you sure that it that equilibrium can you be sure that it is steady state. So let us look at this system now so with respect to steady state we need to look at is ay variable changing time. So if my only variable is PH right and the flow and I see they are not changing with time so I can say yes system is that steady state. But in this case where we have open flow you know how do I know system is that equilibrium or not.

You know and this is the case where you need to relatively vigilant now so equilibrium is defined only for in general for close system. So in order for open systems so what can you do let us say you can instantaneously turn off the related outlet right and then look at any changes occurring this particular system. If I am able to instantaneously turn off the inlet and outlet and see any change in PH right than if there is no change I will say that is that equilibrium.

If there is any change I will see that say that it is not at equilibrium right so again equilibrium generally defined for closed system now right. So there ways examples where in you can come across what we say a system being at equilibrium and steady state which we have already looked at system being at equilibrium but not at steady state system being at steady state not at equilibrium.

You know there are various examples but we will go through that during the course I guess. So let us move on and see what we have here so I guess we are going to start talking about equilibrium. So for this is the last aspect we are going to talk about and will end with that.

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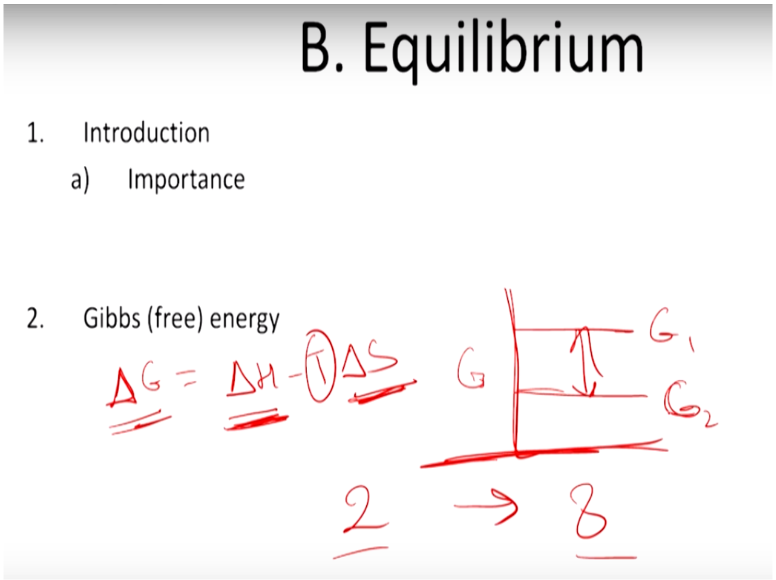

B. Equilibrium

1. Introduction
   a) Importance

2. Gibbs (free) energy

$\underline{\Delta G} = \underline{\Delta H} - T \underline{\Delta S}$

So we are going to just discuss introduction so why is equilibrium important to me let us see. So for example when a common effluent treatment plant and concern with removing the heavy metals right. So I want to know let us say which coagulant to use and to what PH should I maintain so there are different ways to go about it you can run the lab test you can run a full scale or pilot scale test and then calculate or try not to calculate pardon me measure the changes in the system.

But that time and resource intensive right so what can you do though? But if you able to have the relevant background and this particular course or the chemical processes without doing most of the lab test you know we can more or less relatively accurately relatively again because of depends on the other factors which we are always again going to look at I guess be able to you know see or you know identify at which PH would be we have maximum precipitation of the heavy metals and then go for the relevant pilot scale or your full scale test rather than spending time at money now.

So I want to know what happens to the system it has gone to the far that the possible extent right equilibrium and that is what I can see here when I am looking at heavy metal removal that different PH now guess. So next aspect and last aspect which are going to look at is you know equilibrium is going to be dependent upon or is known defined by or driven by define by pardon me driven by thermodynamics right and so we are going look at what this is about.

So equilibrium I guess depends upon the delta G or GIBBS free energy or GIBBS energy gives free energy of the system that is equal to delta G = delta H change in enthalpy and T delta S. So change in GIBBS energy or GIBBS free energy of the system change in enthalpy change in enter P and then temperature right. So as you see we are defining this GIBBS energy or free energy as a change here right.

So it is a change in one state to other so for example if I say G right one state G1 and G2 right and we are looking at the change in this GIBBS energy here of the mixtures let us say and obviously let us see here the GIBBS energy is depends upon enthalpy change in enthalpy. So it changes in the same direction as change in enthalpy and in the opposite direction as a change in entropy.

And entropy will give an idea about degree of disorder for example let us say you have two modes we look at the particular example with respect to TNT I think initially we have two modes of TNT and that I believe what after combustion there are 8 or 10 volts of gases solids. So you see that the degree of disorder ranged right any how we will come back to that again so again GIBBS energy defined as the change in what is equal to delta H – T delta S and H is the delta S is the change in enthalpy and the delta is the change in entropy right.

And say again it was here we are talking about change so similar to C level let us say we can set any point arbitrary but it is not going to be arbitrary going to define it later we are going to we have set any point as your standard or the reference now right. So that can be always be done for example how do you define with G1 or G2. So you define that with respect to your reference here is the one particular case so I guess I am out of time and with that I will stop the class for today and thank you.