Advanced Thermodynamics and Combustion

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Module - VII
Thermodynamics of Reactive Systems
Lecture - 27
Simplified Conservation Equations for Reacting Flows

Dear learner’s greetings from IIT Guwahati we are in the MOOCs course Advanced Thermodynamics and Combustion module 7 Thermodynamics of Reactive Systems.

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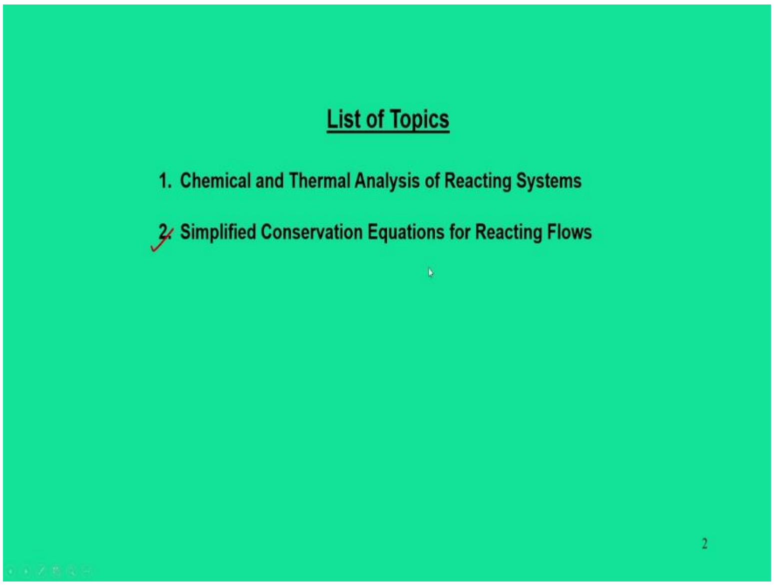

List of Topics

1. Chemical and Thermal Analysis of Reacting Systems
2. Simplified Conservation Equations for Reacting Flows

So, in this module we had two lectures now we will be discussing in the about the second lecture. In the first lecture we discussed about chemical and thermal analysis of reacting systems and in today’s lecture we will be talking about the conservation equations for reacting flows.

So, more or less in our last lecture we have given many reactor models in which the chemical reactions can be quantified theoretically. But when you do these theoretical computations, we also expect that fundamental laws needs to be satisfied. So, in our today’s discussions we will be looking at the simplified conservation of equations for reacting flows.

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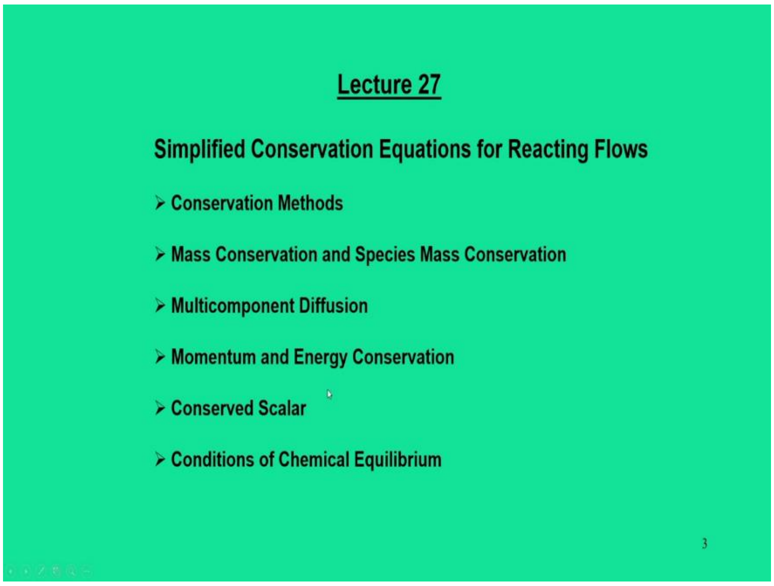

Lecture 27

Simplified Conservation Equations for Reacting Flows

- Conservation Methods
- Mass Conservation and Species Mass Conservation
- Multicomponent Diffusion
- Momentum and Energy Conservation
- Conserved Scalar
- Conditions of Chemical Equilibrium

And in this lecture, we will talk about the conservation methods like we have mass, energy and momentum conservations then we have mass conservation as well as species mass conservations. Because here the conventional mass conservation differs for combustion system is that because the reactant breaks and they form products. So, there is a loss of reactants and gain in the products.

So, in addition to that there are many individual species that are formed in the process of reactions. So, those species also have the principle of satisfying the conservation equations. So, those equations we call as a species mass conservation, then we will discuss about multi component diffusions in a situation that when there are more number of species and during the reaction process one can diffuse others and diffusion also depends on their relative merits.

At the same time diffusion also affects the global chemical kinetics. So, the multi component systems gives certain glimpses of those aspects, then we have momentum and energy conservation equations. Here we will see that how the fundamental forces they balance and in fact, while talking about momentum conservation we are mainly focus on the pressure difference that happens during the reaction process.

Then we have the energy conservation equations which essentially talks about the heat balance equations. And towards the end we will give some important concept one is conserved scalar other is conditions of chemical equilibriums. So, we will cover as and when it appears.

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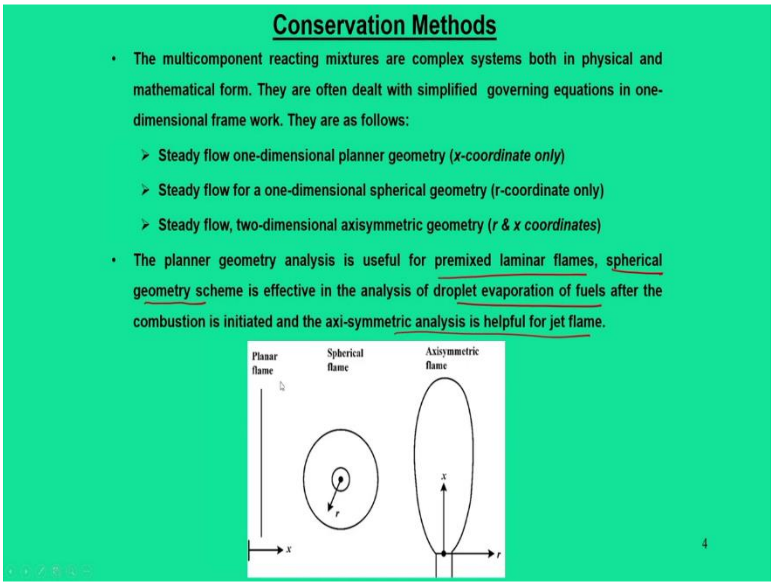

Conservation Methods

- The multicomponent reacting mixtures are complex systems both in physical and mathematical form. They are often dealt with simplified governing equations in one-dimensional frame work. They are as follows:
  - Steady flow one-dimensional planner geometry (*x-coordinate only*)
  - Steady flow for a one-dimensional spherical geometry (r-coordinate only)
  - Steady flow, two-dimensional axisymmetric geometry (*r & x coordinates*)
- The planner geometry analysis is useful for premixed laminar flames, spherical geometry scheme is effective in the analysis of droplet evaporation of fuels after the combustion is initiated and the axi-symmetric analysis is helpful for jet flame.

But before we proceed for that let me give some emphasize that the chemical process or the chemical reaction when it takes place. There are lot of species formations there are many reactions which we have seen that in an H_2O_2 model, in a methane combustions or nitrogen NOx formation, there are many equations are possible. And more or less unless and until we deal specifically as a research topic it is very difficult to give a very overview or fundamental pictures.

So, in our discussion today, we will not discuss every topic elaborately mainly conservation equations because we are not covering the derivations and all. But rather while dealing with the combustion systems how those conservation equations differs than the conventional systems this is the entire philosophy or importance of this lecture.

Now, when you deal with the multi component reaction systems and they are very complex both in physical as well as mathematical form, that is true also. So they are often dealt with simple governing equations mainly in one dimensional frame work. So, one dimensional framework is the simplest methods, it can be two dimensional or three-dimensional framework reactions may be infinite number of reactions, may be hundreds of reactions and for which you require some kind of hands-on packages to deal with all kinds of reaction processes, endothermic, exothermic species, individual species, their enthalpy, balance and so on. But anyway, for our discussion in the one-dimensional framework we will talk about a simple steady flow one dimensional planner geometry, we have also a model for steady flow one dimensional spherical geometry and steady flow two dimensional axisymmetric geometry; these three concepts are very fundamentals.

When you say look at a planar frame because when you deal with the combustion systems we normally see a planar flame, where this planar flame comes? This is basically in during premixed combustions. Premixed combustion means in an SI engines and another situation or geometry that is important that is spherical geometric scheme.

So, spherical geometry scheme means like this is a situation where we have a droplet evaporation or droplet burning of fuels. So, to analyze such kind of energy or mass conservation equations we use spherical flame. The last one is something like axisymmetric analysis which is helpful jet flame or diffusion flame. So, this is axisymmetric, spherical and planar schemes.

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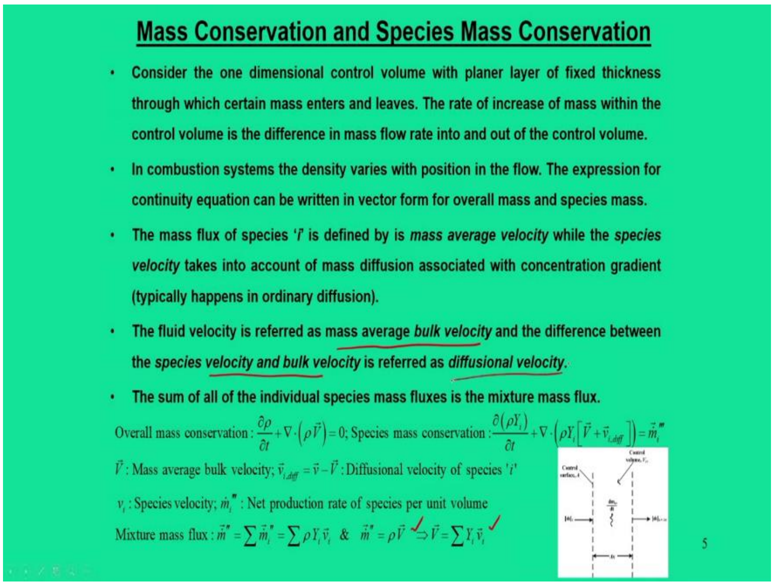

Mass Conservation and Species Mass Conservation

- **Consider the one dimensional control volume with planer layer of fixed thickness through which certain mass enters and leaves. The rate of increase of mass within the control volume is the difference in mass flow rate into and out of the control volume.**
- **In combustion systems the density varies with position in the flow. The expression for continuity equation can be written in vector form for overall mass and species mass.**
- **The mass flux of species '*i*' is defined by is *mass average velocity* while the *species velocity* takes into account of mass diffusion associated with concentration gradient (typically happens in ordinary diffusion).**
- **The fluid velocity is referred as mass average *bulk velocity* and the difference between the *species velocity and bulk velocity* is referred as *diffusional velocity*.**
- **The sum of all of the individual species mass fluxes is the mixture mass flux.**

Overall mass conservation : $\frac{\partial \rho}{\partial t} + \nabla \cdot \left(\rho \vec{V}\right) = 0$; Species mass conservation : $\frac{\partial \left(\rho Y_i\right)}{\partial t} + \nabla \cdot \left(\rho Y_i \left[\vec{V} + \vec{v}_{i,diff}\right]\right) = \vec{\dot{m}}_i'''$

$\vec{V}$: Mass average bulk velocity; $\vec{v}_{i,diff} = \vec{v} - \vec{V}$: Diffusional velocity of species 'i'

v_i : Species velocity; $\dot{m}_i'''$: Net production rate of species per unit volume

Mixture mass flux : $\vec{\dot{m}}'' = \sum \vec{\dot{m}}_i'' = \sum \rho Y_i \vec{v}_i$ & $\vec{\dot{m}}'' = \rho \vec{V} \Rightarrow \vec{V} = \sum Y_i \vec{v}_i$

Now, we will move on to a planar system which is mainly for a pre mixed combustion systems. What you see is that we are looking at a planar medium and that medium which is separated by a distance Δx in which there is some reactants that enters in a single axis that is one dimensional axis, x axis and some products that goes out after forming a certain reactions.

So, during this reaction process, there are some species that gets generated, within this control volume there is also change in the mass. So, this is all about the mass conservations. So, we expect that we have a one-dimensional control volume with planar layer of fixed thickness through which the mass enters and leaves and the rate at which the mass increases within the control volume is nothing but the difference in the mass that flows into and out of the control volume.

This is the very basics of mass conservations and we all know. Another important fact is that many conservation principle when you deal with earlier many a times density is normally a fixed quantity. But here in the combustion system density varies within the position. So, density has to be taken as a variable quantity. So, accordingly we can write the overall mass conservation equations in a vector form like $\frac{\partial \rho}{\partial t} + \nabla \cdot (\rho \vec{V}) = 0$.

This is for mass conservation same mass if we write for individual species instead of ρ we are writing ρY_i; Y_i may be its mole fractions. And in the velocity term we can say that velocity vector in addition to this we have diffusion component of species i. But here when you talk about the species conservations there is a net production of species.

$$\frac{\partial(\rho Y_i)}{\partial t} + \nabla \cdot \left(\rho Y_i\left[\vec{V} + \vec{v}_{i,diff}\right]\right) = \vec{m}_i{}'''$$

So, that is, in the right-hand side it is not 0 it is $\vec{m}_i{}'''$ and this is nothing but the net production rate of species per unit volume. We expect that mixture mass flux is nothing but summation of all these species mass flux and this also can be represented in terms of the mole fraction and velocity vector of the individual species.

In addition to that mixture mass flux is also can be expressed in the form of global velocity and here we introduce two terms; one is mass average bulk velocity which is $\vec{V}$ and species velocity that is $\vec{v}_i$. So, the difference between these two is the diffusional velocity.

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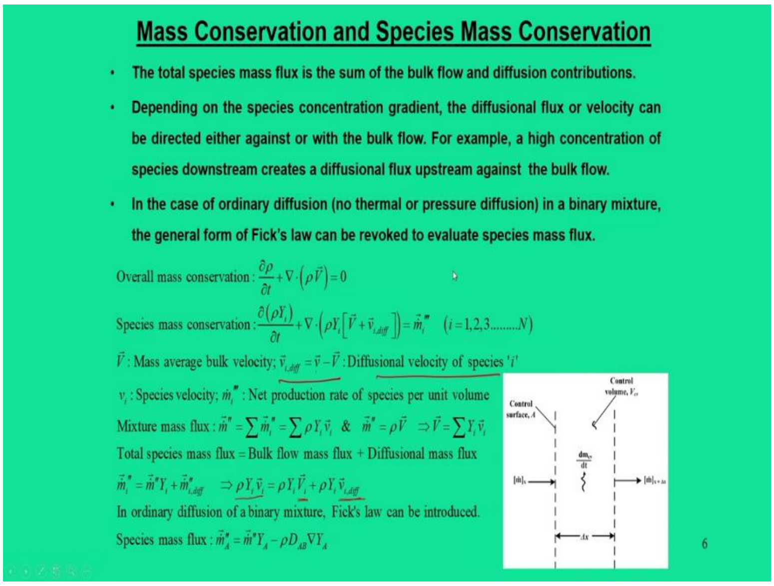

Mass Conservation and Species Mass Conservation

- The total species mass flux is the sum of the bulk flow and diffusion contributions.
- Depending on the species concentration gradient, the diffusional flux or velocity can be directed either against or with the bulk flow. For example, a high concentration of species downstream creates a diffusional flux upstream against the bulk flow.
- In the case of ordinary diffusion (no thermal or pressure diffusion) in a binary mixture, the general form of Fick's law can be revoked to evaluate species mass flux.

Overall mass conservation : $\frac{\partial \rho}{\partial t}+\nabla\cdot\left(\rho\vec{V}\right)=0$

Species mass conservation : $\frac{\partial(\rho Y_i)}{\partial t}+\nabla\cdot\left(\rho Y_i\left[\vec{V}+\vec{v}_{i,diff}\right]\right)=\vec{\dot{m}}_i''' \quad (i=1,2,3.........N)$

$\vec{V}$: Mass average bulk velocity; $\underbrace{\vec{v}_{i,diff}=\vec{v}-\vec{V}}$: $\underbrace{\text{Diffusional velocity of species}}$ 'i'

v_i : Species velocity; $\dot{m}_i'''$: Net production rate of species per unit volume

Mixture mass flux : $\vec{\dot{m}}''=\sum\vec{\dot{m}}_i''=\sum\rho Y_i\vec{v}_i$ & $\vec{\dot{m}}''=\rho\vec{V} \Rightarrow \vec{V}=\sum Y_i\vec{v}_i$

Total species mass flux = Bulk flow mass flux + Diffusional mass flux

$\vec{\dot{m}}_i''=\vec{\dot{m}}''Y_i+\vec{\dot{m}}_{i,diff}'' \quad \Rightarrow \underline{\rho Y_i\vec{v}_i}=\rho Y_i\underline{\vec{V}_i}+\rho Y_i\underline{\vec{v}_{i,diff}}$

In ordinary diffusion of a binary mixture, Fick's law can be introduced.

Species mass flux : $\vec{\dot{m}}_A''=\vec{\dot{m}}''Y_A-\rho D_{AB}\nabla Y_A$

So, how it looks like? We can see here that diffusion velocities for species i is nothing but $\vec{v}-\vec{V}$ which is nothing but the difference between the species velocity and the bulk velocity. Other important aspect is that in addition to the mass conservation, we also expect that there should be species conservations. And the total species mass flux can be equated as bulk mass flow flux plus diffusion mass flux.

So, from these equations we can arrive at another equations involving mole fraction of species I, velocity vector and the diffusional component of the velocity vector for the species i. So, here a simplified assumption is that if there are only two species one can invoke this Fick's law where the diffusion component of velocities can be expressed in the terms of binary diffusion coefficients.

So, you have two species A and B. So, their species mass flux can be quantified in terms of two terms one is the bulk mass flux, other is nothing but the diffusional components of species mass flux. So, this is how the mass and species conservation equation looks like. Then we will move on to multi component systems.

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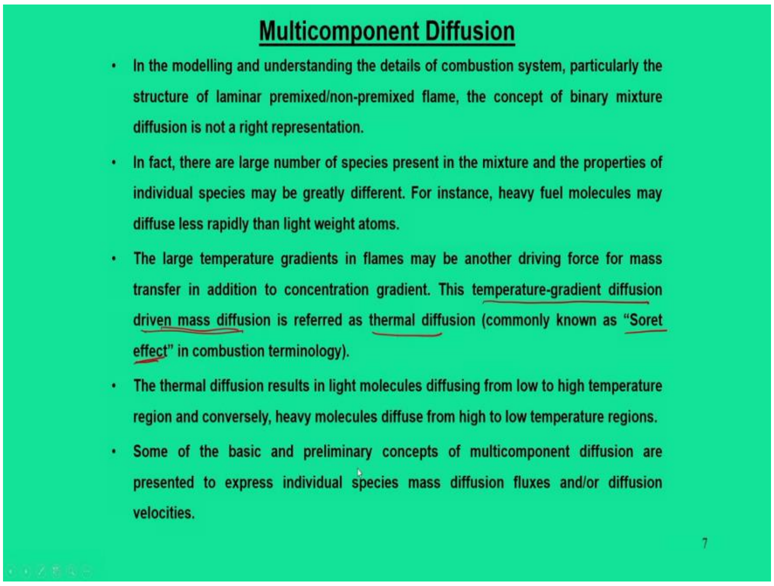

Multicomponent Diffusion

- In the modelling and understanding the details of combustion system, particularly the structure of laminar premixed/non-premixed flame, the concept of binary mixture diffusion is not a right representation.
- In fact, there are large number of species present in the mixture and the properties of individual species may be greatly different. For instance, heavy fuel molecules may diffuse less rapidly than light weight atoms.
- The large temperature gradients in flames may be another driving force for mass transfer in addition to concentration gradient. This temperature-gradient diffusion driven mass diffusion is referred as thermal diffusion (commonly known as "Soret effect" in combustion terminology).
- The thermal diffusion results in light molecules diffusing from low to high temperature region and conversely, heavy molecules diffuse from high to low temperature regions.
- Some of the basic and preliminary concepts of multicomponent diffusion are presented to express individual species mass diffusion fluxes and/or diffusion velocities.

So, let us try to see that what a multi component system is all about and why we need to have a multi component analysis. In the modelling and understanding of detailed combustion systems, particularly laminar premixed and non premixed flame, the concept of binary diffusion is not a right representation.

Because binary diffusion is among two species, but in a combustion system there are may be many numbers of species and there may be interrelated coefficients and also the species can behave in a different manner in a mixture. So, instead of binary diffusion coefficients we can write it as a effective diffusion coefficients. So, a more appropriate when there are multiple number of species.

In fact, there are large number of species present in the mixtures and the properties of individual species may be greatly different. For example, heavy molecules may diffuse less rapidly in a lightweight atom, that is true and many a times there may be large pressure gradient in the flames which may be the driving force for the mass transfer in addition to concentration gradient.

Because, Fick's law only talks about concentration gradient, but it does not talk about any information about thermal gradients or temperature gradients, so this may be another driving force in a multi component diffusion system. This temperature gradient diffusion term during the mass diffusion is commonly referred as thermal diffusions and many a times we call this as a Soret effect in combustion terminology.

So, diffusion process that arises due to the temperature gradient is known as the Soret effect. Other aspect is that the thermal diffusions also result the light molecules diffusing from low to high temperature regions and conversely heavy molecule diffuse from high to low temperature regions.

So, light molecules go up and heavy molecules come down so; that means, this is how the diffusion process looks like. But in these discussions, we will talk about some of the basic preliminary concepts of multi component systems and how they need to be attempted.

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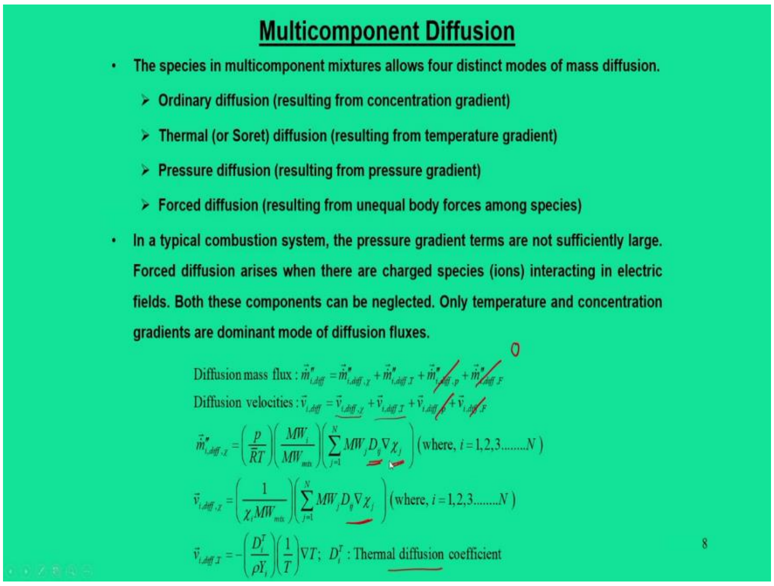

Multicomponent Diffusion

- The species in multicomponent mixtures allows four distinct modes of mass diffusion.
  - Ordinary diffusion (resulting from concentration gradient)
  - Thermal (or Soret) diffusion (resulting from temperature gradient)
  - Pressure diffusion (resulting from pressure gradient)
  - Forced diffusion (resulting from unequal body forces among species)
- In a typical combustion system, the pressure gradient terms are not sufficiently large. Forced diffusion arises when there are charged species (ions) interacting in electric fields. Both these components can be neglected. Only temperature and concentration gradients are dominant mode of diffusion fluxes.

$$\text{Diffusion mass flux}: \vec{\dot{m}}''_{i,diff} = \vec{\dot{m}}''_{i,diff,\chi} + \vec{\dot{m}}''_{i,diff,T} + \cancel{\vec{\dot{m}}''_{i,diff,p}} + \overset{0}{\cancel{\vec{\dot{m}}''_{i,diff,F}}}$$

$$\text{Diffusion velocities}: \vec{v}_{i,diff} = \underline{\vec{v}_{i,diff,\chi}} + \underline{\vec{v}_{i,diff,T}} + \cancel{\vec{v}_{i,diff,p}} + \cancel{\vec{v}_{i,diff,F}}$$

$$\vec{\dot{m}}''_{i,diff,\chi} = \left(\frac{p}{\bar{R}T}\right)\left(\frac{MW_i}{MW_{mix}}\right)\left(\sum_{j=1}^{N} MW_j \underline{D_{ij}} \nabla \underline{\chi_j}\right) (\text{where, } i = 1,2,3........N)$$

$$\vec{v}_{i,diff,\chi} = \left(\frac{1}{\chi_i MW_{mix}}\right)\left(\sum_{j=1}^{N} MW_j \underline{D_{ij} \nabla \chi_j}\right) (\text{where, } i = 1,2,3........N)$$

$$\vec{v}_{i,diff,T} = -\left(\frac{D_i^T}{\rho Y_i}\right)\left(\frac{1}{T}\right)\nabla T; \; D_i^T : \text{Thermal } \underline{\text{diffusion}} \text{ coefficient}$$

So, basically when you talk about the species in a multi component mixtures. There are four distinct modes of mass diffusions one is ordinary diffusions and that results from the concentration gradients and if there is only ordinary diffusion then we can use the Fick’s law to quantify this mass diffusion. But in addition to that if there are temperature gradients then we may have thermal or Soret diffusion.

There is also the diffusion that results due to gradient in the pressures. So, we call this as a pressure diffusion, there are possibilities of unequal body force among the species so these are called force diffusions. So, out of this four; the first two terms are most important in the conventional combustion systems and the pressure diffusion terms is normally not too large to be taken into account in counter of with respect to ordinary or thermal diffusions.

And, force diffusion term will come only when in a reaction instead of species if these species are in the form of ions. So, when I say ions; obviously, it is a positive or negative charge particles for example, a chemical reaction that takes place in an electric environment, so we expect there may be formation of ions. So, when such a thing happens then the unbalanced body force needs to be taken into account and such diffusion process we will call it as a force diffusions.

So, in general when you add all these terms, we can define diffusion mass flux and diffusion velocities. And these velocities are nothing but the combinations of all these components which can be expressed in the vectorial form and also each term and in particular if you neglect this pressure term and force terms.

Then there are two important terms mass and velocity diffusion due to the concentration gradient and mass and velocity component due to the temperature gradient. And in particular they can be expressed in the form of mixture pressure, temperatures, molecular weight of the species and with summation of all the species.

$$\vec{m}''_{i,diff,\chi} = \left(\frac{p}{\bar{R}T}\right)\left(\frac{MW_i}{MW_{mix}}\right)\left(\sum_{j=1}^{N} MW_j D_{ij} \nabla \chi_j\right)$$

$$\vec{v}_{i,diff,T} = -\left(\frac{D_i^T}{\rho Y_i}\right)\left(\frac{1}{T}\right)\nabla T$$

So, here if you look at this term the term that is going to be introduced here is D_{ij} which is effective diffusion coefficients and that arises due to this concentration gradient. Similarly, due to this concentration gradient, we have the velocity component of diffusion species, but while talking about the thermal components we have a term D_i^T which arises thermal diffusion coefficients. But however, in our preliminary study we will only focus on the diffusion components due to concentration only.

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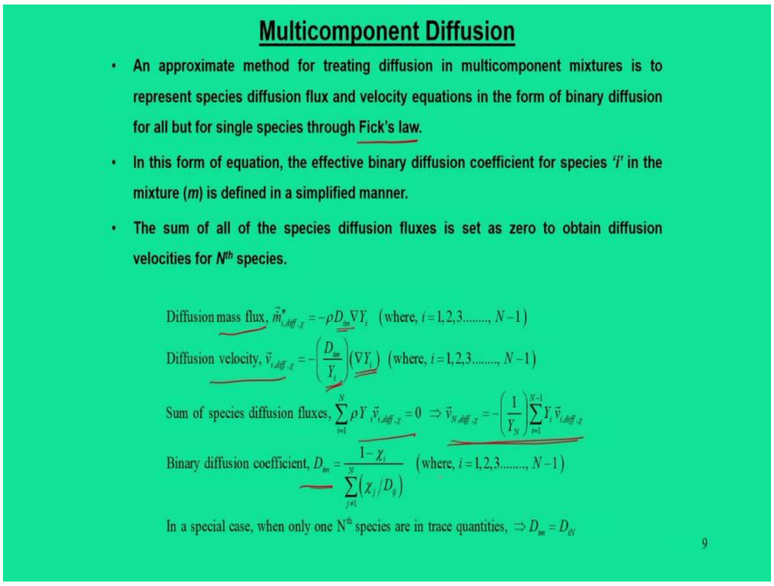

Multicomponent Diffusion

- An approximate method for treating diffusion in multicomponent mixtures is to represent species diffusion flux and velocity equations in the form of binary diffusion for all but for single species through Fick's law.
- In this form of equation, the effective binary diffusion coefficient for species '*i*' in the mixture (*m*) is defined in a simplified manner.
- The sum of all of the species diffusion fluxes is set as zero to obtain diffusion velocities for N^{th} species.

Diffusion mass flux, $\vec{\dot{m}}''_{i,diff,\chi} = -\rho D_{im} \nabla Y_i$ (where, $i = 1,2,3........, N-1$)

Diffusion velocity, $\vec{v}_{i,diff,\chi} = -\left(\frac{D_{im}}{Y_i}\right)(\nabla Y_i)$ (where, $i = 1,2,3........, N-1$)

Sum of species diffusion fluxes, $\sum_{i=1}^{N} \rho Y_i \vec{v}_{i,diff,\chi} = 0 \Rightarrow \vec{v}_{N,diff,\chi} = -\left(\frac{1}{Y_N}\right) \sum_{i=1}^{N-1} Y_i \vec{v}_{i,diff,\chi}$

Binary diffusion coefficient, $D_{im} = \frac{1-\chi_i}{\sum_{j\neq i}^{N} (\chi_j / D_{ij})}$ (where, $i = 1,2,3........, N-1$)

In a special case, when only one N^{th} species are in trace quantities, $\Rightarrow D_{im} = D_{iN}$

So, to do that one simplest analysis that can be made or it can be considered as an approximate method is a multi-component mixtures with species diffusion flux and velocity equations to be represented in the form of binary diffusion coefficients and for which we can recall Fick's law.

So, basically what we are trying to find out that we need to evaluate this effective binary diffusion coefficient for species i in the mixer m in a simplified manner. And the sum of all the species of diffusion coefficient is set to zero to obtain the diffusion velocity of n species, this is as per the Fick's law.

Now when you do that, we can write these two terms mainly diffusion mass flux and diffusion velocities, so here we write instead of ij we write i,m; i stands for species, m is with respect to mixture; so the mixture may have many species. So, accordingly we have mole fractions Yi and gradient of this mole fractions. So, this is how we write these equations for diffusion mass flux and diffusion velocity.

$$\text{Diffusion mass flux}, \vec{\dot{m}}''_{i,diff,\chi} = -\rho D_{im} \nabla Y_i (\text{where}, i = 1,2,3 \ldots \ldots .., N-1)$$

$$\text{Diffusion velocity}, \vec{v}_{i,diff,\chi} = -\left(\frac{D_{im}}{Y_i}\right)(\nabla Y_i)(\text{where}, i = 1,2,3 \ldots \ldots .., N-1)$$

By setting the sum of species diffusion flux to be 0 we can find an another expressions like diffusion velocities for N species and for all these equations the binary diffusion coefficients with respect to mixture is defined in this manner D_{im}; i stands for species, m stands for mixture. So, j can be other components in the mixture. So, j is not equal to 1, but it starts from second third and fourth onwards.

$$D_{im} = \frac{1-\chi_i}{\sum_{j\neq 1}^{N}\left(\frac{\chi_j}{D_{ij}}\right)}$$

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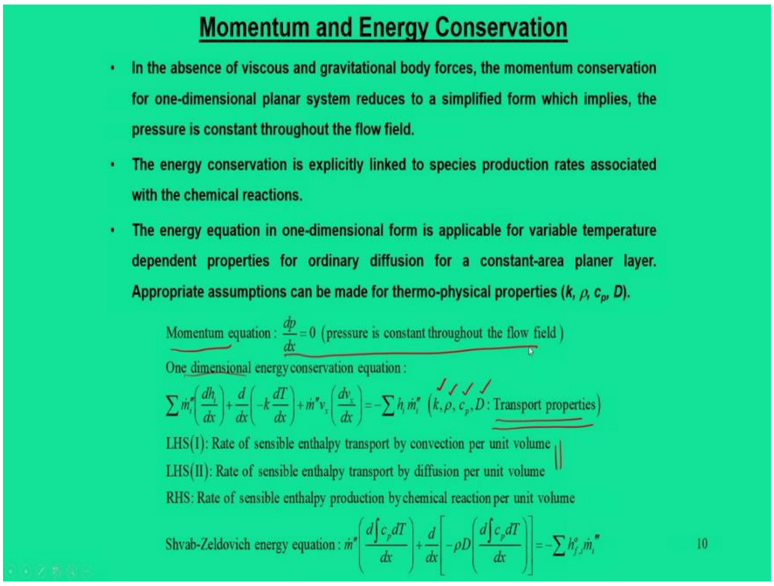

Momentum and Energy Conservation

- In the absence of viscous and gravitational body forces, the momentum conservation for one-dimensional planar system reduces to a simplified form which implies, the pressure is constant throughout the flow field.
- The energy conservation is explicitly linked to species production rates associated with the chemical reactions.
- The energy equation in one-dimensional form is applicable for variable temperature dependent properties for ordinary diffusion for a constant-area planer layer. Appropriate assumptions can be made for thermo-physical properties (***k***, *ρ*, **c**$_p$, ***D***).

Momentum equation : $\frac{dp}{dx}=0$ (pressure is constant throughout the flow field)

One dimensional energy conservation equation :

$$\sum \dot{m}_i''\left(\frac{dh_i}{dx}\right)+\frac{d}{dx}\left(-k\frac{dT}{dx}\right)+\dot{m}''v_x\left(\frac{dv_x}{dx}\right)=-\sum h_i\dot{m}_i''' \quad (k,\rho,c_p,D:\text{Transport properties})$$

LHS(I): Rate of sensible enthalpy transport by convection per unit volume

LHS(II): Rate of sensible enthalpy transport by diffusion per unit volume

RHS: Rate of sensible enthalpy production by chemical reaction per unit volume

Shvab-Zeldovich energy equation : $\dot{m}''\left(\frac{d\int c_p dT}{dx}\right)+\frac{d}{dx}\left[-\rho D\left(\frac{d\int c_p dT}{dx}\right)\right]=-\sum h^o_{f,i}\dot{m}_i'''$

Then for the continuity sake we will just briefly discuss about the momentum and energy conservation equations. If you write the entire equations of energy or momentum then it will be a huge task and for this course it is almost beyond the scope.

So, what I have written is that I have written two simple equations what says is that momentum equations which says that pressure is constant throughout the flow field. That means; unless and until there is a pressure gradient exist during reactions and the reaction process is something like independent of pressure.

Other thing is that we are writing one dimensional energy equations in this particular form which says that the sum of rate of sensible enthalpy transport by convection per unit volume plus the rate of sensible enthalpy transport by diffusion per unit volume. So, this sum is equal to rate of sensible enthalpy productions by the chemical reaction per unit volume.

So, this is the general expressions that are used here and here the term that are frequently important is thermal conductivity k, ρ is the density, c_p is the specific heat, D is the diffusion coefficient. And all these properties are regarded as transport properties and one of the forms of this one-dimensional equations is Shvab Zeldovich energy equations which is written in the integral forms. So, more details we can go through the fundamental books, we are not going to discuss further on this aspect.

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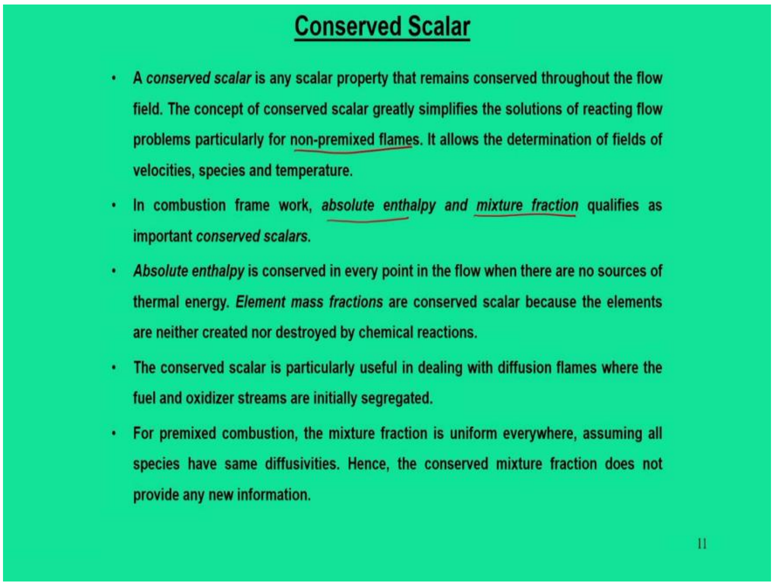

Conserved Scalar

- A *conserved scalar* is any scalar property that remains conserved throughout the flow field. The concept of conserved scalar greatly simplifies the solutions of reacting flow problems particularly for non-premixed flames. It allows the determination of fields of velocities, species and temperature.
- In combustion frame work, *absolute enthalpy and mixture fraction* qualifies as important *conserved scalars.*
- *Absolute enthalpy* is conserved in every point in the flow when there are no sources of thermal energy. *Element mass fractions* are conserved scalar because the elements are neither created nor destroyed by chemical reactions.
- The conserved scalar is particularly useful in dealing with diffusion flames where the fuel and oxidizer streams are initially segregated.
- For premixed combustion, the mixture fraction is uniform everywhere, assuming all species have same diffusivities. Hence, the conserved mixture fraction does not provide any new information.

The most important aspect of this lecture is to define quantities which are regarded as conserved scalar. So, normally we have two quantities scalar quantity and vector quantities, but conserved scalar comes as a word; that means, any scalar quantity which remains conserved during the reaction process.

So, if you look at reaction globally normally reactants vanish, products are formed. But what we can see is that when the reactant vanishes, there is some origin of certain fuel component that have traces throughout the reaction process. And if you want to calculate a particular information about that species then that conserved scalar is one of the good approach and two such important conserved scalars are absolute enthalpy and mixture fractions.

So, in a combustion reaction there are many such conserved scalar is possible. But only absolute enthalpy and mixture fractions are very important conserved scalar. And in fact, where this conserved scalar concept is important. This is mainly when we have non premixed flame means fuel are oxidized, species they come separately, but when they come separately not necessarily it forms an homogeneous mixture.

So, it is heterogeneous kind of mixture, but whereas, in a premixed situation it is a homogeneous mixture and of course, the conserved scalar does not provide any extra information. Because we already have mass fractions, mole fractions all these terms and this conserved scalar will also fall in the similar line. But where it becomes importance when there is a non premixed flames; that means, fuel and oxygen streams comes separately.

So, with this view point we say that in the combustion framework absolute enthalpy and mixture fractions qualifies as the importance conserved scalar. Why absolute enthalpy is conserved? Because it is conserved in every point during the flow where there is no sources of thermal energy, absolute enthalpy remains constant everywhere. Because there is no source of thermal energy also enthalpy can change, but absolute enthalpy cannot change that is throughout the process.

Element mass fractions are conserved scalar. Because the elements are neither created or nor destroyed by the chemical reactions. Because fuel and oxidizer both comes and after reactions they form another species. So; that means, the species are neither created nor destroyed during the chemical reaction.

Another important aspect is that the conserved scalar is a very particularly useful in dealing with diffusion flames where fuel and oxidizer streams are initially segregated. But however, in premixed combustion situations the conserved mixture fraction does not provide any new information.

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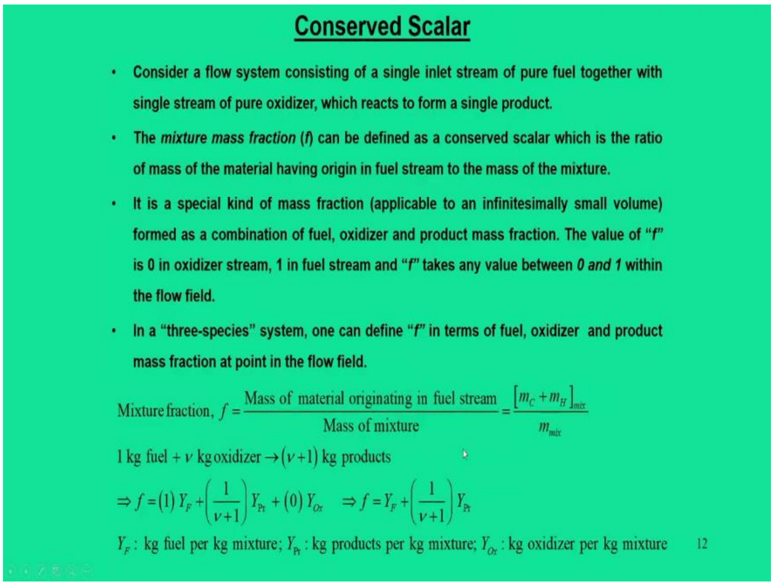

Conserved Scalar

- Consider a flow system consisting of a single inlet stream of pure fuel together with single stream of pure oxidizer, which reacts to form a single product.
- The *mixture mass fraction* (*f*) can be defined as a conserved scalar which is the ratio of mass of the material having origin in fuel stream to the mass of the mixture.
- It is a special kind of mass fraction (applicable to an infinitesimally small volume) formed as a combination of fuel, oxidizer and product mass fraction. The value of "*f*" is 0 in oxidizer stream, 1 in fuel stream and "*f*" takes any value between *0 and 1* within the flow field.
- In a "three-species" system, one can define "*f*" in terms of fuel, oxidizer and product mass fraction at point in the flow field.

$$\text{Mixture fraction, } f = \frac{\text{Mass of material originating in fuel stream}}{\text{Mass of mixture}} = \frac{[m_C + m_H]_{mix}}{m_{mix}}$$

$$1 \text{ kg fuel} + \nu \text{ kg oxidizer} \rightarrow (\nu+1) \text{ kg products}$$

$$\Rightarrow f = (1)\,Y_F + \left(\frac{1}{\nu+1}\right) Y_{Pr} + (0)\,Y_{Ox} \quad \Rightarrow f = Y_F + \left(\frac{1}{\nu+1}\right) Y_{Pr}$$

Y_F : kg fuel per kg mixture; Y_{Pr} : kg products per kg mixture; Y_{Ox} : kg oxidizer per kg mixture

Now let us see how you want to calculate the mixture fraction f and which is typically considered as a conserved scalar. So, for which we take a flow systems that consist of single inlet stream of pure fuel together with single stream of pure oxidizer. And when you do that what we see is that 1 kg of fuel when it mixes with ν kg of oxidizer it gives $\nu + 1$ kg of products. Of course, prior to this we defined mass fractions, mole fractions of fuel and oxidizer of each species.

But this conserved scalar definition says that this mixture fraction f is equal to mass of material originating from the fuel streams. For example, in hydrocarbon fuels the mass of the materials are carbon and hydrogen. So, the presence of total mass of carbon and hydrogen in the mixture divided by the mass of the mixtures, so the mass of the mixtures can consist of fuel stream species oxidizer stream species and so on.

So, what we can say that this number f when we calculate in oxidizer stream this number is 0, when we calculate in a fuel stream this number is 1. And during the flow field or during the combustion process this value can take any number between 0 to 1. So, in three species systems, we can define f in terms of fuel and oxidizers and the product mass fraction in the flow fields.

So, for these reactions when we say 1 kg of fuel plus ν kg of oxidizer gives $\nu + 1$ kg of products. Then the mixture fraction f can be defined

$$f = (1)Y_F + \left(\frac{1}{\nu+1}\right)Y_{\mathrm{Pr}} + (0)Y_{Ox} \Rightarrow f = Y_F + \left(\frac{1}{\nu+1}\right)Y_{\mathrm{Pr}}$$

Y_F stands for kg of fuel per kg of mixture, Y_{Pr} stands for kg products per kg mixture, Y_{Ox} is kg oxidizer per kg mixture.

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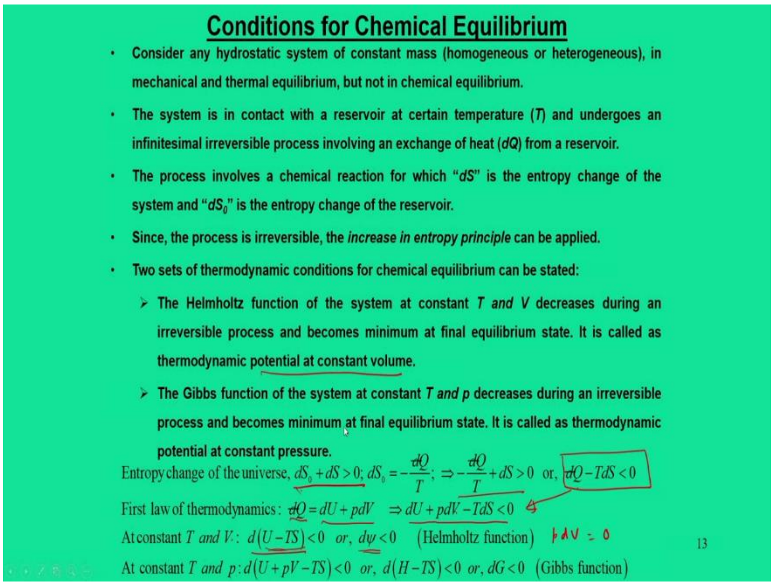

Conditions for Chemical Equilibrium

- Consider any hydrostatic system of constant mass (homogeneous or heterogeneous), in mechanical and thermal equilibrium, but not in chemical equilibrium.
- The system is in contact with a reservoir at certain temperature (*T*) and undergoes an infinitesimal irreversible process involving an exchange of heat (*dQ*) from a reservoir.
- The process involves a chemical reaction for which "*dS*" is the entropy change of the system and "*dS₀*" is the entropy change of the reservoir.
- Since, the process is irreversible, the *increase in entropy principle* can be applied.
- Two sets of thermodynamic conditions for chemical equilibrium can be stated:
  - The Helmholtz function of the system at constant *T and V* decreases during an irreversible process and becomes minimum at final equilibrium state. It is called as thermodynamic potential at constant volume.
  - The Gibbs function of the system at constant *T and p* decreases during an irreversible process and becomes minimum at final equilibrium state. It is called as thermodynamic potential at constant pressure.

Entropy change of the universe, $dS_0 + dS > 0;\ dS_0 = -\frac{đQ}{T};\ \Rightarrow -\frac{đQ}{T} + dS > 0$ or, $\boxed{đQ - TdS < 0}$

First law of thermodynamics: $đQ = dU + pdV \quad \Rightarrow dU + pdV - TdS < 0$

At constant T and V: $d(U - TS) < 0$ or, $d\psi < 0$ (Helmholtz function) $pdV = 0$

At constant T and p: $d(U + pV - TS) < 0$ or, $d(H - TS) < 0$ or, $dG < 0$ (Gibbs function)

And after saying so the last component of discussion in this module is the conditions for chemical equilibrium. So, all these times we have talked about the total thermodynamic equilibrium consists of 0 unbalanced force, no change in the temperatures, the system is in thermal equilibrium, system is in mechanical equilibrium. Another part segment is that the system should be in chemical equilibrium.

Now, to satisfy the conditions of chemical equilibrium we recall a simple hydrostatic system of constant mass which may be homogeneous or heterogeneous, they are in mechanical as well as thermal equilibrium, but not in chemical equilibrium. And when they are not in chemical equilibriums, so we expect that there has to be some irreversible process that is going on due to chemical reactions.

And this irreversible change can be defined as the entropy productions which involves due to the chemical reactions and the entropy change for the reservoir; that means, when the reaction is in contact with a reservoir, so, you can say the change in the entropy for the reservoir. So, for that things we can find out the total change in the inverse is $dS_0 + dS > 0$ that is law of entropy.

$$dS_0 = -\frac{\text{đ}Q}{T}; \Rightarrow -\frac{\text{đ}Q}{T} + dS > 0 \text{or}, \text{đ}Q - TdS < 0$$

Now, if you recall the first law of thermodynamics we say $\text{đ}Q = dU + pdV$. So, we write this equation in the form now $dU + pdV - TdS < 0$.

So, this equation now represented in this part. Here you take a stand that when you are looking at a constant temperature and volume systems at for constant temperature and volume situations, we write this equations $pdV = 0$ which means $d(U - TS) < 0$and what is this, $U - TS$ is nothing but Helmholtz function $d\psi < 0$.

So, what it says is that in a constant temperature and volume system Helmholtz functions should must be less than 0. ~~So, U plus p V is nothing but H enthalpy. So, u H minus TS is equal to 0 and H minus TS is~~ $d(U + pV - TS) < 0or, d(H - TS) < 0or, dG < 0$. So, change in the Gibbs function is less than 0.

So, there are two sets of thermodynamic conditions for chemical equilibrium by considering the principle of increasing the entropy. So, first one is the Helmholtz function for a system at constant T and V decreases during an irreversible process and it becomes minimum at final equilibrium state. So, it is called as thermodynamic potential at constant volume.

Another term that comes in is Gibbs function for the system at constant T and p decreases during an irreversible process and it becomes minimum at the final equilibrium state. So, Gibbs function is minimum at the final equilibrium state, Helmholtz function is minimum at final equilibrium state. So, this is called as thermodynamic potential of constant pressure when the Gibbs function becomes minimum at the final equilibrium state.

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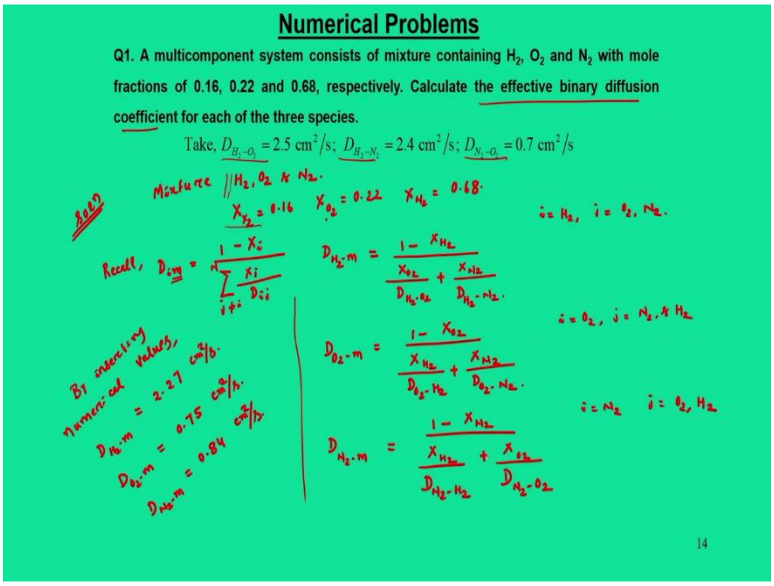

Numerical Problems

Q1. A multicomponent system consists of mixture containing H_2, O_2 and N_2 with mole fractions of 0.16, 0.22 and 0.68, respectively. Calculate the effective binary diffusion coefficient for each of the three species.

Take, $D_{H_2-O_2} = 2.5\ cm^2/s$; $D_{H_2-N_2} = 2.4\ cm^2/s$; $D_{N_2-O_2} = 0.7\ cm^2/s$

Sol^n

Mixture || H_2, O_2 & N_2.

$X_{H_2} = 0.16$ $X_{O_2} = 0.22$ $X_{N_2} = 0.68$.

Recall, $D_{im} = \dfrac{1 - X_i}{\sum_{j \neq i}^{N} \dfrac{X_j}{D_{ij}}}$

$i = H_2$, $j = O_2, N_2$.

$D_{H_2 \cdot m} = \dfrac{1 - X_{H_2}}{\dfrac{X_{O_2}}{D_{H_2 \cdot O_2}} + \dfrac{X_{N_2}}{D_{H_2 - N_2}}}$.

$i = O_2$, $j = N_2$, & H_2

$D_{O_2 - m} = \dfrac{1 - X_{O_2}}{\dfrac{X_{H_2}}{D_{O_2 - H_2}} + \dfrac{X_{N_2}}{D_{O_2 \cdot N_2}}}$.

$i = N_2$ $j = O_2, H_2$

$D_{N_2 \cdot m} = \dfrac{1 - X_{N_2}}{\dfrac{X_{H_2}}{D_{N_2 - H_2}} + \dfrac{X_{O_2}}{D_{N_2 - O_2}}}$

By inserting numerical values,

$D_{H_2 \cdot m} = 2.27\ cm^2/s$.

$D_{O_2 \cdot m} = 0.75\ cm^2/s$.

$D_{N_2 \cdot m} = 0.84\ cm^2/s$.

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So, this is all about this lecture. Now today we will solve some numerical problems based on the understanding of our lecture. So, the first problem is about a multi component system the mixture contains this H_2, O_2 and N_2 and for which they are mole fractions we $X_{H_2} = 0.16, X_{O_2} = 0.22, X_{N_2} = 0.18$.

We need to calculate the effective binary diffusion coefficients. To find this effective binary coefficient, you recall this expression

$$D_{im} = \frac{1 - \chi_i}{\sum_{j \neq 1}^{N} \left(\frac{\chi_j}{D_{ij}}\right)};\ D_{H_2 m} = \frac{1 - \chi_{H_2}}{\frac{\chi_{O_2}}{D_{H_2 O_2}} + \frac{\chi_{N_2}}{D_{H_2 N_2}}};\ D_{O_2 m} = \frac{1 - \chi_O}{\frac{\chi_{H_2}}{D_{O_2 H_2}} + \frac{\chi_{N_2}}{D_{O_2 N_2}}};$$

$$D_{N_2 m} = \frac{1 - \chi_{N_2}}{\frac{\chi_{O_2}}{D_{N_2 O_2}} + \frac{\chi_{H_2}}{D_{N_2 H_2}}}$$

So, here the terms like $D_{H_2 N_2}, D_{O_2 H_2}, D_{N_2 O_2}$ is given and we also know $X_{H_2} = 0.16, X_{O_2} = 0.22, X_{N_2} = 0.18$. So, by inserting values numerical values we can find out effective binary diffusion coefficients $D_{H_2 m} = 2.27 cm^2/s$, $D_{O_2 m} = 0.75 cm^2/s$, $D_{N_2 m} = 0.84 cm^2/s$. So, this is how a simple system process tells that in a three-component system how to calculate effective binary diffusion coefficients. So in fact, if there are more number of species then this summation has to be further extended.

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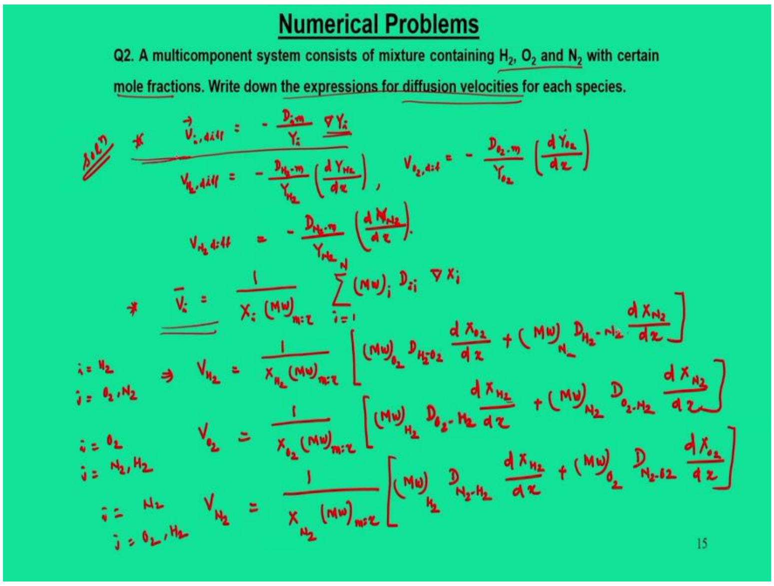

Numerical Problems

Q2. A multicomponent system consists of mixture containing H_2, O_2 and N_2 with certain mole fractions. Write down the expressions for diffusion velocities for each species.

Soln * $\vec{V}_{i,diff} = -\frac{D_{im}}{Y_i}\nabla Y_i$

$V_{H_2,diff} = -\frac{D_{H_2-m}}{Y_{H_2}}\left(\frac{dY_{H_2}}{dx}\right)$, $V_{O_2,dif} = -\frac{D_{O_2-m}}{Y_{O_2}}\left(\frac{dY_{O_2}}{dx}\right)$

$V_{N_2,diff} = -\frac{D_{N_2-m}}{Y_{N_2}}\left(\frac{dN_{N_2}}{dx}\right)$.

* $\bar{V}_i = \frac{1}{X_i (MW)_{mix}} \sum_{i=1}^{N} (MW)_j D_{ij} \nabla X_j$

$i = H_2$, $j = O_2, N_2$ $\Rightarrow$ $V_{H_2} = \frac{1}{X_{H_2}(MW)_{mix}}\left[(MW)_{O_2} D_{H_2-O_2}\frac{dX_{O_2}}{dx} + (MW)_{N_2} D_{H_2-N_2}\frac{dX_{N_2}}{dx}\right]$

$i = O_2$, $j = N_2, H_2$ $\quad V_{O_2} = \frac{1}{X_{O_2}(MW)_{mix}}\left[(MW)_{H_2} D_{O_2-H_2}\frac{dX_{H_2}}{dx} + (MW)_{N_2} D_{O_2-H_2}\frac{dX_{N_2}}{dx}\right]$

$i = N_2$, $j = O_2, H_2$ $\quad V_{N_2} = \frac{1}{X_{N_2}(MW)_{mix}}\left[(MW)_{H_2} D_{N_2-H_2}\frac{dX_{H_2}}{dx} + (MW)_{O_2} D_{N_2-O_2}\frac{dX_{O_2}}{dx}\right]$

And the next problem is that the same multi component systems involving H_2, O_2 and N_2 with certain mole fractions and we basically know their mole fractions and we have to write the expression for diffusion velocity. So, diffusion velocities can be written by two expressions and here it is mainly with respect to concentrations. $\vec{v}_{i,diff,\chi} = -\left(\frac{D_{im}}{Y_i}\right)(\nabla Y_i)$. So, Yi is the mole fractions gradient, Y will talk about the concentration gradient.

$$\vec{v}_{H_2,diff} = -\left(\frac{D_{H_2m}}{Y_{H_2}}\right)\left(\frac{dY_{H_2}}{dx}\right);\ \vec{v}_{O_2,diff} = -\left(\frac{D_{O_2m}}{Y_{O_2}}\right)\left(\frac{dY_{O_2}}{dx}\right);$$

$$\vec{v}_{N_2,diff} = -\left(\frac{D_{N_2m}}{Y_{N_2}}\right)\left(\frac{dY_{N_2}}{dx}\right)$$

This is one way we write the diffusion flux. There is another expressions which also can be written diffusion coefficient in the form of molecular weight $\vec{v}_{i,diff,\chi} = \left(\frac{1}{\chi_i MW_{mix}}\right)\left(\sum_{j=1}^{N} MW_j D_{ij} \nabla \chi_j\right)$.

$$\vec{v}_{H_2,diff,\chi} = \left(\frac{1}{\chi_{H_2} MW_{mix}}\right)\left(MW_{O_2} D_{H_2O_2}\frac{d\chi_{O_2}}{dx} + MW_{N_2} D_{H_2N_2}\frac{d\chi_{N_2}}{dx}\right)$$

$$\vec{v}_{O_2,diff,\chi} = \left(\frac{1}{\chi_{O_2} MW_{mix}}\right)\left(MW_{H_2} D_{O_2H_2}\frac{d\chi_{H_2}}{dx} + MW_{N_2} D_{O_2N_2}\frac{d\chi_{N_2}}{dx}\right)$$

$$\vec{v}_{N_2,diff,\chi} = \left(\frac{1}{\chi_{N_2} MW_{mix}}\right)\left(MW_{O_2} D_{N_2O_2}\frac{d\chi_{O_2}}{dx} + MW_{H_2} D_{N_2H_2}\frac{d\chi_{H_2}}{dx}\right)$$

So, this is how we can write the expression for diffusion velocities for each species and one method we can write this way, other method we can write in this form.

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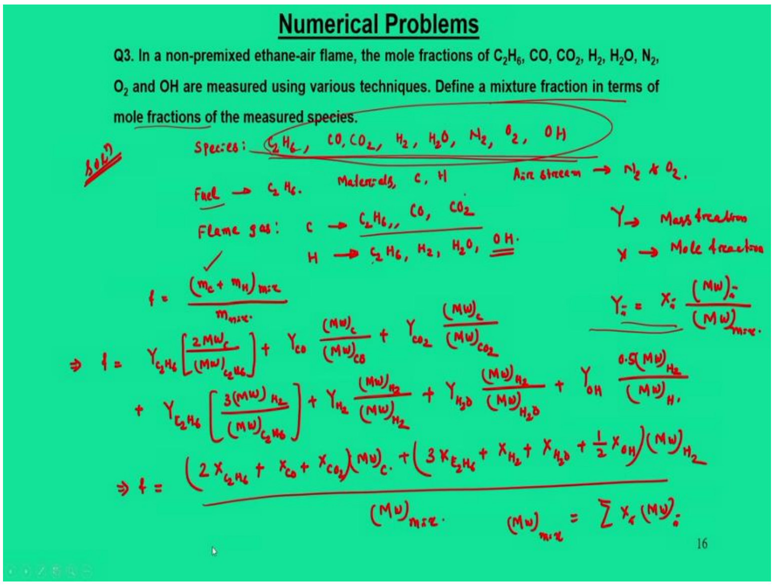

Numerical Problems

Q3. In a non-premixed ethane-air flame, the mole fractions of C_2H_6, CO, CO_2, H_2, H_2O, N_2, O_2 and OH are measured using various techniques. Define a mixture fraction in terms of mole fractions of the measured species.

Sol^n

Species: C_2H_6, CO, CO_2, H_2, H_2O, N_2, O_2, OH

Fuel → C_2H_6. Materials, C, H

Air stream → N_2 & O_2.

Flame gas: C → C_2H_6, CO, CO_2

H → C_2H_6, H_2, H_2O, OH.

Y → Mass fraction

X → Mole fraction

$$f = \frac{(m_C + m_H)_{mix}}{m_{mix}}$$

$$Y_i = X_i \frac{(MW)_i}{(MW)_{mix}}$$

$$\Rightarrow f = Y_{C_2H_6}\left[\frac{2MW_C}{(MW)_{C_2H_6}}\right] + Y_{CO}\frac{(MW)_C}{(MW)_{CO}} + Y_{CO_2}\frac{(MW)_C}{(MW)_{CO_2}}$$

$$+ Y_{C_2H_6}\left[\frac{3(MW)_{H_2}}{(MW)_{C_2H_6}}\right] + Y_{H_2}\frac{(MW)_{H_2}}{(MW)_{H_2}} + Y_{H_2O}\frac{(MW)_{H_2}}{(MW)_{H_2O}} + Y_{OH}\frac{0.5(MW)_{H_2}}{(MW)_{H}}.$$

$$\Rightarrow f = \frac{(2X_{C_2H_6} + X_{CO} + X_{CO_2})(MW)_C + (3X_{C_2H_6} + X_{H_2} + X_{H_2O} + \frac{1}{2}X_{OH})(MW)_{H_2}}{(MW)_{mix}}$$

$$(MW)_{mix} = \sum X_i (MW)_i$$

See the last problem is we are talking about the conserved scalar and which is nothing but your definition which is the mixture fraction and it is expressed in terms of mole fractions. So, to solve this problem first thing that we need to understand is that what are the species the species that are available at any instant is during a combustion process it is C_2 H_6, CO, CO_2, H_2, H_2O, N_2, O_2 and OH. At any instant of time, we find these is the species available.

Now, if you look at the fuel stream fuel stream consist of C_2H_6 and it consist of the compounds or materials which is carbon and hydrogen. Now air stream it consists of N_2 and O_2 and here you do not see any kind of fuel components and flame gas and when we talk about flame gas flame gases are this. Here what is the source of fuel streams? So, carbon is present in C_2H_6; second is CO, third is CO_2, hydrogen is present where in C_2H_6, in H_2, in H_2O, and in OH.

So, basically $f = \frac{(m_C + m_H)}{m_{mix}}$. Now let us see how do you find out this. So, this can be represented as this, but let us first talk about carbon then we will talk about hydrogen. So, carbon is present in C_2H_6; second is CO, third is CO_2. So, we write in terms of their mass fraction as Y; Y stands for mass fraction X stands for mole fractions.

$$f = Y_{C_2H_6}\left[\frac{2MW_c}{MW_{C_2H_6}}\right] + Y_{CO}\left[\frac{MW_c}{MW_{CO}}\right] + Y_{CO_2}\left[\frac{MW_c}{MW_{CO_2}}\right] + Y_{C_2H_6}\left[\frac{3MW_{H_2}}{MW_{C_2H_6}}\right] + Y_{H_2}\left[\frac{MW_{H_2}}{MW_{H_2}}\right] + Y_{H_2O}\left[\frac{MW_{H_2}}{MW_{H_2O}}\right] + Y_{OH}\left[\frac{0.5MW_{H_2}}{MW_{OH}}\right]$$

$$Using\ Y_i = X_i(MW)_i/(MW)_{mix}$$

$$f = \frac{\left(\left(2X_{C_2H_6} + X_{CO} + X_{CO_2}\right)MW_c + \left(3X_{C_2H_6} + X_{H_2} + X_{H_2O} + 0.5X_{OH}\right)MW_{H_2}\right)}{MW_{mix}}$$

$$MW_{mix} = \sum X_i(MW)_i$$

So, this is how we define the mixture fractions which is basically a conserved scalar in a situation in a non premixed ethane air flame which contains C_2 H_6, CO, CO_2, H_2, H_2O, N_2, O_2 and OH. So, this is all about module 7, with this we will conclude this lecture as well as this module.

Thank you for your attention.