Combustion in Air Breathing Aero Engines
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Lecture – 02
Chemical Equilibrium – I

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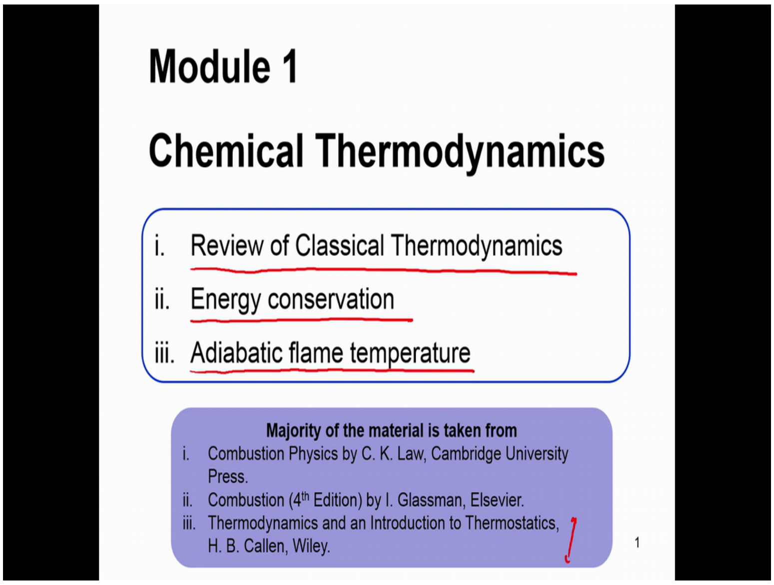

Module 1

Chemical Thermodynamics

i. Review of Classical Thermodynamics
ii. Energy conservation
iii. Adiabatic flame temperature

Majority of the material is taken from
i. Combustion Physics by C. K. Law, Cambridge University Press.
ii. Combustion (4th Edition) by I. Glassman, Elsevier.
iii. Thermodynamics and an Introduction to Thermostatics, H. B. Callen, Wiley.

So, welcome back, as we discussed in the introduction our module one will cover topics of a chemical thermodynamics and here we will talk about we will basically review some parts of classical thermodynamics will go into energy conservation, and using energy conservation we will show how adiabatic flame temperature is can be obtained and the material of this talk or of this lecture is mainly taken from combustion physics by C.K Law, combustion by glassman and also combustion and an introduction to thermo by an thermodynamics and an introduction to Thermostatics by H. B Callen. Now this is a very classic text in thermodynamics which you might be aware of.

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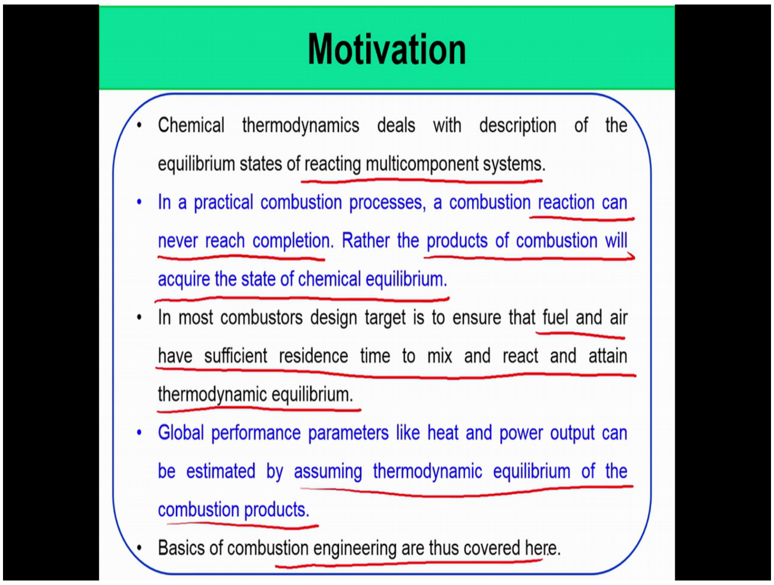

Motivation

- Chemical thermodynamics deals with description of the equilibrium states of reacting multicomponent systems.
- In a practical combustion processes, a combustion reaction can never reach completion. Rather the products of combustion will acquire the state of chemical equilibrium.
- In most combustors design target is to ensure that fuel and air have sufficient residence time to mix and react and attain thermodynamic equilibrium.
- Global performance parameters like heat and power output can be estimated by assuming thermodynamic equilibrium of the combustion products.
- Basics of combustion engineering are thus covered here.

So, why do we need to understand the chemical thermodynamics and combustion? Now chemical thermodynamics deals with the description of equilibrium states of reacting multicomponent systems. Now as you would recognize a combustion is essentially is deals with reacting multicomponent systems of course, there is reactions and because of reaction you have heat release and of course, it is multicomponent because you have fuel you have oxidizer and you have different kinds of products right and also might be intermediates. So, it is a study, to understand that what are the equilibrium states of combustion, we need to know chemical thermodynamics.

Now, in a practical combustion process or in any process as such most process as such the reactions the chemical reactions especially combustion reactions cannot reach completion; rather the products of combustion will acquire the state of chemical equilibrium. So, to understand the composition and the temperature of the combustion products, which is governed by chemical equilibrium we need to understand chemical thermodynamics.

Now, then you have on to ask if a does in the most practical combustors is chemical equilibrium reached. Now the target is to ensure that the chemical equilibrium is reached’ now we need to design combustors such that fuel and air have sufficient residence time to mix and react and attain thermodynamic equilibrium. But depending on the flow on the speed of the flow thermodynamic equilibrium may or may not be reached will come to that for example, in a gas turbine combustor your residence times are large flow residence times, flow residence times you can simply are obtain by the length of the combustor divided by the velocity of the of the fuel air mixture of the air flows speed that is mean air flow speed that is inside the combustor. So, this you can define as the residence time.

Now, in a gas turbine combustor this is large for example, in a scram jet combustor this can be very small, because in a scramjet combustor your use is very very large; right. So, in a scramjet combustor you may not have thermodynamic equilibrium, in a gas turbine combustor you may or may not have thermodynamic equilibrium, but the target is to a ensure that it is reached.

Now, when you do a first cut design an engineering design, you do not need to go into the different things like how a flame looks like inside a combustor, how the flame structure looks like, how does the flow look like? When the first of course, those are needed for optimizing the combustor of the optimizing the engine, but for the first cut analysis you need to know what is the heat and the power output that you can obtain from the combustor and that can be estimated by assuming thermodynamic equilibrium of the combustion products.

So, that is why you in thermodynamic equilibrium or and chemical equilibrium is a very important tool that we must know for combustion engineering. So, the basics of combustion the basics of the combustion engineering are thus covered here.

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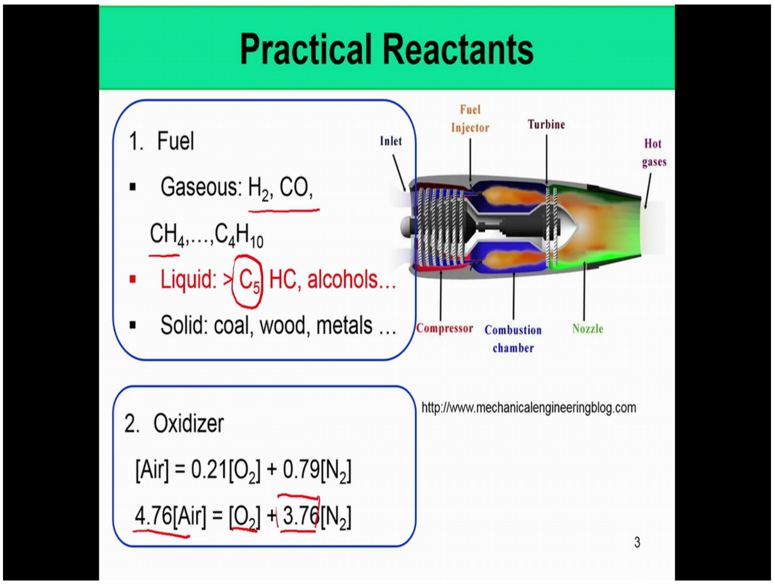

Practical Reactants

1. Fuel
- Gaseous: H_2, CO, CH_4,…,C_4H_{10}
- Liquid: > C_5 HC, alcohols…
- Solid: coal, wood, metals …

2. Oxidizer

$[Air] = 0.21[O_2] + 0.79[N_2]$

$4.76[Air] = [O_2] + 3.76[N_2]$

http://www.mechanicalengineeringblog.com

So, now practical reactants what should come what should undergo combustion and the product of what should be in chemical equilibrium fuels. So, what are the question is, what are the fuels gaseous fuels can be hydrogen carbon mono oxide, Methane, ethane propane butane. If it is greater than 5 is the number of carbons is greater than 5 typically they are equate and in the previous introduction introductory lecture we have seen the importance of liquid fuels because of their very high energy densities; and then we also have alcohols and for other purposes for power generation purpose we might have coal woods etcetera metals which is not of importance in this course.

So, fuels liquid fuels and gaseous fuels are of primary importance in this course in which are mainly hydrocarbons now oxidizer. Now the great thing about the most important thing about air breathing combustion air breathing engines as such is that, here of course your carrying the fuel in the fuel tank, but the oxidizer you are taking from the air from the atmosphere. So, these as a great benefit that you are not carrying the oxidizer with you which reduces the payload of which allows you to carry some other things, and also you do not spend money to get the oxidizer it comes free.

So, that is the hallmark of your breathing propulsion that we are not carrying oxidizer and it comes free from the atmosphere. So, we only have to spend money for the fuel only the fuel costs. So, how does what is the composition of air? We know that for every point we know that air is composed of 21 percent volumes of oxygen and approximately

79 percent nitrogen and the rest are there were also some amount of small amount of carbon dioxide and also inert gases etcetera.

So, for every; we can write that for every 4.76 moles of air, there is one mole of oxygen and then there is 3.76 moles of nitrogen. Now please note this number 3.76 it essentially is comes from dividing 0.79 by 0.21, now this we will use this number very often because mostly lightly because a as we the topic of the title of the this course is a b ring essentially combustion in air breathing engines. So, we will only deal with hydrocarbon bonding in air. So, we will frequently encounter this number of 3.76 moles of nitrogen.

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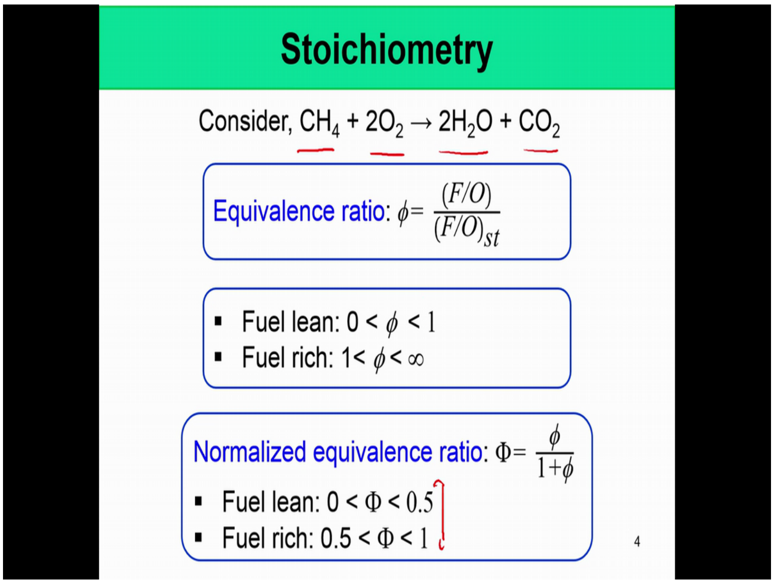

Stoichiometry

Consider, $\underline{CH_4} + \underline{2O_2} \rightarrow \underline{2H_2O} + \underline{CO_2}$

Equivalence ratio: $\phi = \frac{(F/O)}{(F/O)_{st}}$

- Fuel lean: $0 < \phi < 1$
- Fuel rich: $1 < \phi < \infty$

Normalized equivalence ratio: $\Phi = \frac{\phi}{1+\phi}$

- Fuel lean: $0 < \Phi < 0.5$
- Fuel rich: $0.5 < \Phi < 1$

So, let us consider the overall combustion reaction of methane in which this is methane and this is oxygen, and it produces 2 moles of water and one mole of CO2.

So, first we define something like an equivalence ratio. Equivalence ratio is the fuel to oxidize a ratio the actual fuel to oxidize a ratio divided by the stoichiometric fuel to oxidize the ratio which you probably already know the fuel lean of course, if it is between 0 and 1 it is fuel lean, and if it is between one and infinity it is fuel rich. Of course, you see that this fuel lean and fuel rich definitions are not very not do not occupy the equal ranges in it do not occupy equal ranges. So, we can also define a normalized equivalence ratio phi capital which is divide which is defined as phi divided by 1 plus phi, and this gives a more symmetric definition for fuel lean and fuel rich. Of course, you must remember that if it is this with though we define phi from 0 to 1 this does not mean that combustion happens between phi from 0 to 1it only happens between certain range of phi and which we will let define us flammability.

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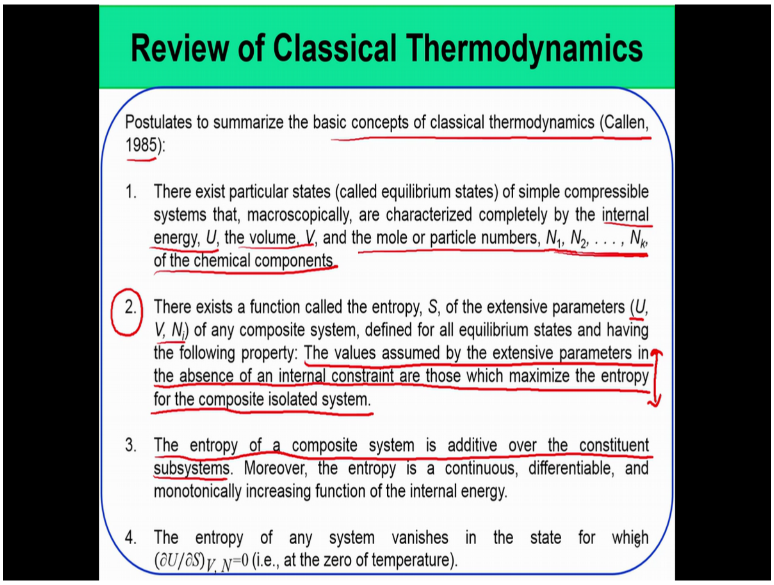

Review of Classical Thermodynamics

Postulates to summarize the basic concepts of classical thermodynamics (Callen, 1985):

1. There exist particular states (called equilibrium states) of simple compressible systems that, macroscopically, are characterized completely by the internal energy, U, the volume, V, and the mole or particle numbers, $N_1, N_2, \ldots, N_k$, of the chemical components.
2. There exists a function called the entropy, S, of the extensive parameters (U, V, N_i) of any composite system, defined for all equilibrium states and having the following property: The values assumed by the extensive parameters in the absence of an internal constraint are those which maximize the entropy for the composite isolated system.
3. The entropy of a composite system is additive over the constituent subsystems. Moreover, the entropy is a continuous, differentiable, and monotonically increasing function of the internal energy.
4. The entropy of any system vanishes in the state for which $(\partial U/\partial S)_{V,N}=0$ (i.e., at the zero of temperature).

So, now with this we need to review the concepts of classical thermodynamics. Now let us go slowly over this it might appear little bit new, but this is important to introduce some the classical thermodynamics in a in the slightly different manner and this is mainly taken from this the concepts are basically taken from this book Harvard b Callen thermodynamics and an introduction to Thermostatics. So, what are the postulates? There are basically four postulates and there conceive is be several corollaries which will not go into that. The postulates states that there exist particular states call equilibrium states which you might be aware of equilibrium states in thermodynamics where basically all the motivation is to find out this equilibrium states and the characteristics of this equilibrium states.

So, this says that there exists particular states called equilibrium states of simple compressible systems, that macroscopically are characterized completely by the internal energy U this is internal energy U, volume V and the mole of the particle numbers are mole numbers N 1, N 2, N k that is if you have different species in your system like methane oxygen etcetera. So, the mole numbers of them of the chemical components. So, a state can be essentially characterized by the internal energy U, the volume V and the particles number of the mole number. Then it states that there exists a function called the entropies which is a function of these extensive parameters U V and N. Now remember; what are extensive parameters extensive parameters are those that depends on the size of the system, right. And if you say double the size of the system the magnitude of the parameters also gets doubled or if you triple the size of the system the magnitude of the parameters also get tripled.

So, S is a function of these extensive parameters; of any composite system define for all equilibrium states and having the following property. The values assumed by the extensive parameters in the absence of internal constraints are those that maximize entropy for the composite isolated system. So, this says that these parameters this extensive parameters U, V, N i will act in a such a manner that your entropy is maximized in these equilibrium states and the entropy of a composite system is additive this is the third postulate that entropy of a composite system is additive over the constituent subsystems, moreover the entropy is a continuous differentiable and monotonically increasing function of internal energy, and this is the fourth which is not really important now it is called the fourth third law of thermodynamics that is the entropy of any system vanishes in the state for which d partial d U, d S, V, N equal to 0 at the 0 that is at the when temperature is equal to 0. These first 3 postulates are very important then we lose them to essentially review chemical thermodynamics.

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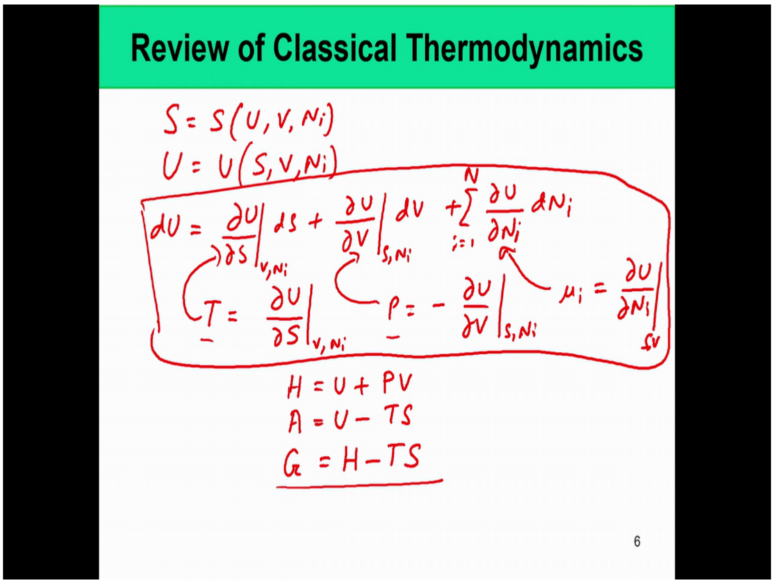

Review of Classical Thermodynamics

$S = S(U, V, N_i)$

$U = U(S, V, N_i)$

$$dU = \left.\frac{\partial U}{\partial S}\right|_{V,N_i} dS + \left.\frac{\partial U}{\partial V}\right|_{S,N_i} dV + \sum_{i=1}^{N} \frac{\partial U}{\partial N_i} dN_i$$

$$T = \left.\frac{\partial U}{\partial S}\right|_{V,N_i} \qquad P = -\left.\frac{\partial U}{\partial V}\right|_{S,N_i} \qquad \mu_i = \left.\frac{\partial U}{\partial N_i}\right|_{SV}$$

$H = U + PV$

$A = U - TS$

$G = H - TS$

So, if you see if you go to this second postulates it is says that S is the function of U, V and N i. U is the internal energy V is the volume and N i are the mole numbers right. So, we can also write the internal energy is a function of S, V and N i. If so, we can write d U is equal to partial d U d S, d V over all species i is equal to 1 to N say there are total N species . So, this we can write.

Now, we can define using this we can define certain quantities, that is we can say T is equal to temperature we define it as this way partial d U partial d S when V and N i is constant we can define P is equal to minus d U d V when S and N i are constant and we can define out the new quantity called chemical potential which is defined as d partial d U partial d, N i when S and V are constant.

Now, we can show that these definitions that we have defined actually correspond to our known definitions of temperature pressure and chemical potential. Using this you can show that that if you define it like this this quantity T will immerge as that quantity which will determine with the thermal equilibrium is attained that this quantity T will determine when or when or in other words when this T this quantity say T in 2 different components of a system, which was separated by non-adiabatic wall when this 2 quantities are equal there will be no heat flow.

Similarly, when this in that in 2 composite in a system which is a separated into 2 parts by a flexible wall which can move in these 2 components if this pressure P are equal then you will see that it can be shown that mechanical equilibrium is attained; similarly for chemical potential you will see that once again if you define if you have a composite system which is divided into 2 parts, and if mu 1 and mu 2 are equal that is the chemical potential of the of the one system is equal to the chemical potential of the other systems, and if this 2 systems are separated by permeable wall then you will see that the matter flow will stop when chemical potential that is mu 1 equal to mu 2.

So, temperature determines some equilibrium pressure determines mechanical equilibrium and mu chemical potential determines whether matter will flow from one system to other system when they are separated by a permeable wall. So, these then corresponds it can be shown in this way. So, this then corresponds to our known definitions of temperature pressure and chemical potential will not go into show how this can be obtained actually. But now we can even define new quantities which is enthalpy which is equal to U plus P V, we can define Helmholtz free energy a is equal to U minus TS and we can define Gibbs free energy is equal to H minus TS. Now this quantity is you will see that is very important for determining chemical equilibrium.

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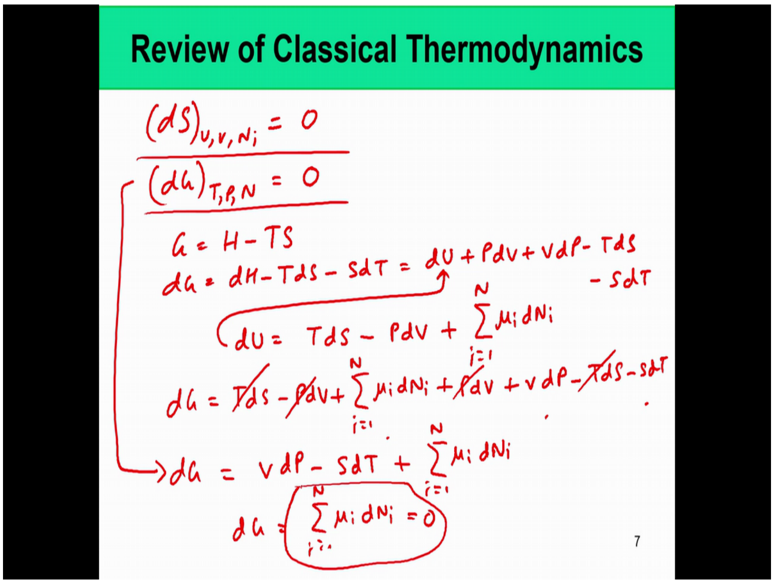

Review of Classical Thermodynamics

$$(dS)_{U,V,N_i} = 0$$

$$(dG)_{T,P,N} = 0$$

$$G = H - TS$$

$$dG = dH - TdS - SdT = dU + PdV + VdP - TdS - SdT$$

$$dU = TdS - PdV + \sum_{i=1}^{N} \mu_i dN_i$$

$$dG = \cancel{T}dS - \cancel{P}dV + \sum_{i=1}^{N} \mu_i dN_i + \cancel{P}dV + VdP - \cancel{T}dS - SdT$$

$$dG = VdP - SdT + \sum_{i=1}^{N} \mu_i dN_i$$

$$dG = \boxed{\sum_{i=1}^{N} \mu_i dN_i = 0}$$

Now, if you go to the third postulate or the let us go back yes if you go to the second postulate itself you have seen that this part says that the values of extensive parameters in absence of an internal constraints are those that maximize the entropy for the composite isolated systems. So, we can write that means, that the equilibrium criteria for a isolated system from the second postulates emerges as d S when u, v, N is equal to 0 and it you can also be shown that the corresponding equilibrium criteria in terms of Gibbs free energy will be d G for T, P, N is equal to 0.

Now, when T and so what was the definition of; so, we define that we defined G is equal to H minus T S. So, what does this this mean actually? So, this means that. So, we can write and of course, we have defined that G is equal to H minus T S. So, we can define d G is equal to d H if we differentiate as equal to minus T d S minus S d T and that is equal to d U plus P d V that is if you differentiate H itself; where H is equal to is equal to U plus P V.

Now, let us go back to what we define U S. We defined U as d U that is if you go to this thing this is d U is equal to T d S minus P d V plus summation i is equal to 1 to N mu i d N i right this is what we obtained that is this is if you substitute this things here, if you substitute this things here, if you substitute this thing here this is what you get and now if you substitute this thing into this what you get is d G is equal to T d S minus P d V plus summation i is equal 1 to N, mu i d N i plus P dv, plus V d P, minus T d S minus S d t. So, you see that P d V P d V cancels T d S T d S cancels, and you are left with this this and this. So, we define we can d G is equal to V d P minus S d T plus summation i is equal to 1 to N mu i d N i right. So, now, if you apply the equilibrium criteria that is this on to this at T and P is equal to constant what we get is d G is equal to summation i is equal to one to N mu i d N i is equal to 0 now please remember this is a very important thing we lose this to arrive at more important concepts in a in chemical thermodynamics.

Now, let us again go back to the to the concept that you itself is an extensive parameter no as I said that it depends on the extensive means that it depends on the size of the system before you double the size, it is the magnitude of the parameter also gets doubled.

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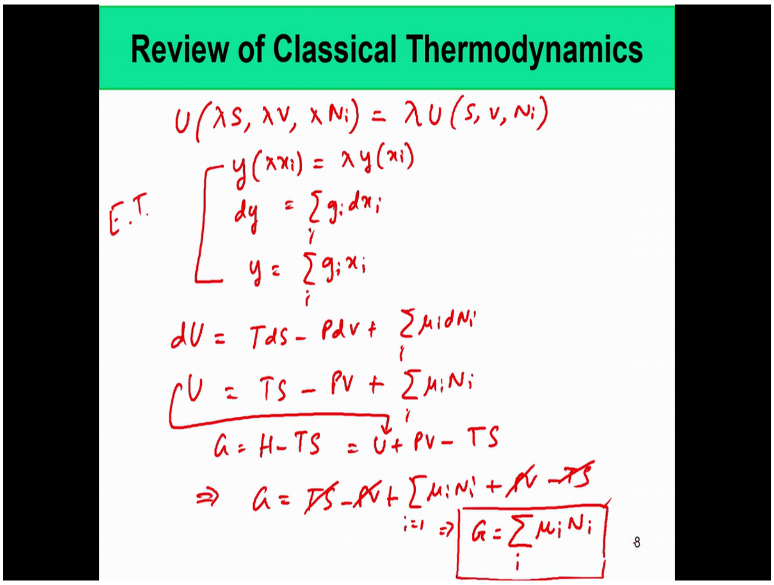

Review of Classical Thermodynamics

$$U(\lambda S, \lambda V, \lambda N_i) = \lambda U(S, V, N_i)$$

$$\text{E.T.}\quad \left[\begin{aligned} y(\lambda x_i) &= \lambda y(x_i) \\ dy &= \sum_i g_i\, dx_i \\ y &= \sum_i g_i x_i \end{aligned}\right.$$

$$dU = TdS - PdV + \sum_i \mu_i dN_i$$

$$U = TS - PV + \sum_i \mu_i N_i$$

$$G = H - TS = U + PV - TS$$

$$\Rightarrow G = \cancel{TS} - \cancel{PV} + \sum_{i=1} \mu_i N_i + \cancel{PV} - \cancel{TS}$$

$$\Rightarrow \boxed{G = \sum_i \mu_i N_i}$$

So, mathematically what this means is that that if you define U is equal to lambda S, lambda V, lambda N i then we can write lambda U is equal to S, V, N I. Now mathematically these mean that these are first order homogeneous quantities extensiveness essentially implies that first order homogeneous.

Now, we can then invoke Euler’s theorem and we can go into a first ordered equation of the form if we write lambda x i y is equal to lambda x i which can be any variable as such and l y is equal to lambda x i just like we have written we have written internal energy if we can write it for general variable y dependent variable y and general dependent variable x i we can if you write this just like we have written for internal energy and then whose differential is given by d y is equal to summation I, g I, d x i then by Euler's theorem y is given by summation I, g I, x i.

So, this is what it is. So, then it means that the all the differentials that we have obtained for internal energy we can remove and obtain the function of the parameter itself. So, this we can allow us to simply remove all the differentials in G etcetera we can remove the differentials of internal energy and we can write it as internal energy as H U is equal to TS it was essentially d U is equal to T d S minus P d V plus summation i mu i d N i.

So, by this things by this Euler's theorem we can write U is equal to TS minus P V plus summation I, mu I, N i and now you can use this 2 substituting the in the Gibbs free energy. So, which is essentially G is equal to we know is equal to H minus TS is equal to U plus P V minus T S. So, we can substitute here this here and this implies G is equal to TS minus P V minus plus summation i is equal to mu i N I, plus P V minus T s. So, this this cancels this this cancel. So, this implies G is equal to summation I, mu i that is all one second this implies G is equal to summation N i.

So, then this becomes the definition of G; now the reason why I have gone through all these things is that in many books you will find that this is defined in a little bit convoluted manner and it is this comes arbitrarily, now i myself could not understand this things and it took me some amount of time to understand how this is arrived from d G how you can arrive at G is equal to summation mu I, N i. Now these are very important and very fundamental concepts which we need to be which needs to be clarified.

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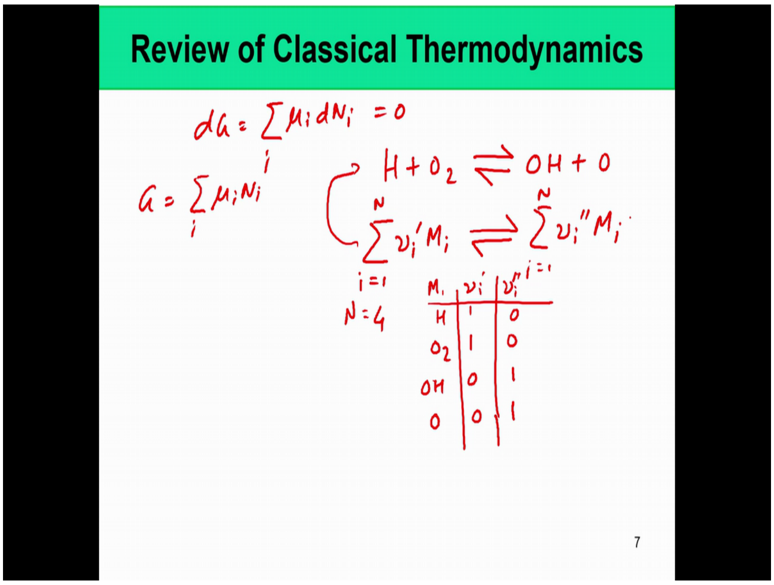

Review of Classical Thermodynamics

$$dG = \sum_i \mu_i dN_i = 0$$

$$G = \sum_i \mu_i N_i$$

$$H + O_2 \rightleftharpoons OH + O$$

$$\sum_{i=1}^{N} \nu_i' M_i \rightleftharpoons \sum_{i=1}^{N} \nu_i'' M_i$$

$N = 4$

M_i	ν_i'	ν_i''
H	1	0
O_2	1	0
OH	0	1
O	0	1

Now, so we have obtained this and let us it has these things. So, now,. So, will go back will just have obtain to very important things that is for equilibrium we have obtained d G is equal to summation i mu I, d N i is equal to 0 and we have obtained the definition of G which is given by summation I, mu i N i, but remember the difference is at this is differential this is actual G parameter itself quantity itself.

So, now let us go and apply this to a real chemical reaction and see how we can what we can what property we can obtain for that chemical reaction. So, in general you can say or suppose you are having chemical reaction like H plus O 2 going to O H plus O. Now of course, you know that this is one chemical reaction which is very simple. So, this all this stoichiometric coefficient this is one this is one this is one this is one right and of course, there can be a numerous kinds of chemical reactions. So, we need to have a general representation and the general representation for this can be like something like you can write like or you can write a general reaction like y is equal to 1 to N nu i dash m I; nu i dash is the stoichiometric coefficient for the reactant mi is the name of the species which goes to summation i is equal to 1 to N, nu i dashed m i and this is the name of the product and this is the stoichiometry coefficient of the product.

Now, it goes to 1 to N in both sides. So, if we apply this to now this equation N is equal to then is 4, because in the total reaction we have four species hydrogen atom oxygen one hydroxyl radical and one oxygen right. So, these things. So, that it is not confusing alright. So, here if you see that our new i dashed for H, if i write the name of the species and new i dashed and new i double dash and this is say our m i. So, for H we have new i dash is equal to one new i double dash is equal to 0 because it does not appear on the products. So, we concise the stoichiometric coefficient of H in the product side is 0 for o 2 we have 1 we have 0, for o H, we have new i dashed is equal to 0 and for this is one and for o we have this is equal to 0, this is 1.

So, this I hope explains you the principle by which you are writing this generalized equation. Now this is just for demonstration purpose and a, but this is I mean the reason for introducing this kind of notation is that this is if you are suppose writing a going to read a code commercial code or research code and you are going to read the manual or going to read literature, you will find that there this the it is reactions are represented in this generalized manner are not really in the this manner. So, it is important to get familiar with the with the state of the art notations also.

So, that is why I have introducing this kind of notations alright. So, now, say this is our generalized reaction which will use throughout this kind of generalized reaction notation.

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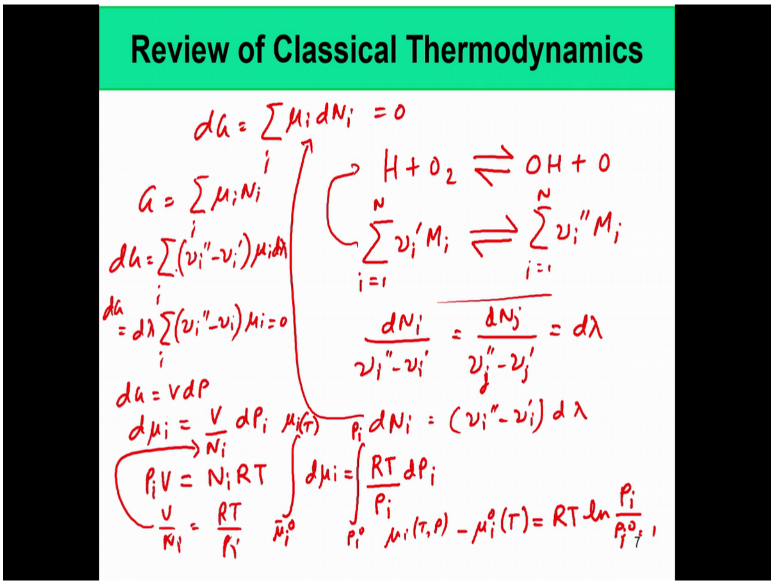

Review of Classical Thermodynamics

$$dG = \sum_i \mu_i dN_i = 0$$

$$G = \sum_i \mu_i N_i$$

$$dG = \sum_i (\nu_i'' - \nu_i') \mu_i d\lambda$$

$$dG = d\lambda \sum_i (\nu_i'' - \nu_i) \mu_i = 0$$

$$H + O_2 \rightleftarrows OH + O$$

$$\sum_{i=1}^{N} \nu_i' M_i \rightleftarrows \sum_{i=1}^{N} \nu_i'' M_i$$

$$\frac{dN_i}{\nu_i'' - \nu_i'} = \frac{dN_j}{\nu_j'' - \nu_j'} = d\lambda$$

$$dN_i = (\nu_i'' - \nu_i') d\lambda$$

$$dG = VdP$$

$$d\mu_i = \frac{V}{N_i} dP_i$$

$$P_i V = N_i RT$$

$$\frac{V}{N_i} = \frac{RT}{P_i}$$

$$\int_{\bar{\mu}_i^0}^{\mu_i(T)} d\mu_i = \int_{P_i^0}^{P_i} \frac{RT}{P_i} dP_i$$

$$\mu_i(T,P) - \mu_i^0(T) = RT \ln \frac{P_i}{P_i^0},$$

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And now the now by element conservation we can say that we can write essentially d N i divided by nu i doubled dash by nu i dash is equal to d N j divided by nu i nu j double dash by nu j dash and that we can represent by a progress variable lambda which is the reaction progress. So, far this d lambda amount of reaction progress this amount of N i is can be produced or consumed depending on the sign, and the this is proportional to their stoichiometry coefficients, rather the change in the stoichiometry coefficients between the product side and the reactant side alright.

So, you can write d N i is equal to nu i double dash minus nu i dashed times d lambda. So, we can now substitute this here. So, the condition of equilibrium becomes d G is equal to summation i, nu i double dash minus nu i dash times nu i times d lambda. Now d lambda does not depend on i so that can go out. So, this is it this is equal to 0 for equilibrium.

Now, will come back to this let us remember this and we will come back to this very soon. Now let us consider a single ideal gas at constant temperature need not be in equilibrium. So, for that we can write d G is equal to V d P and for the ith pure component of the ideal gas we can write d mu i is equal to V by N i d P i, i will not derive how you do this and this is left as a little small exercise to you. So, you can check how you can basically go from that therefore, a system not in equilibrium how this can be arrived at this is very simple just you have take my you have to take the differentiates.

Now, for an ideal gas we know that P we can know that P i V whereas, P i is essentially the partial pressure of the gas is equal to N i times R T right. So, V by N i is equal to R T by P i. So, substituting this here we get d mu i is equal to R T d P i. And now we can integrate on both sides from a given reference state from P i 0 we will actually define this reference state to be P i equal to 1 that is which can be like 1 bar P i, and this gives mu i T minus mu i 0 T is equal to R T l n P i by P i 0. P i 0 is equal to be considered always 1; 1bar or and that is our; this is equal to 1.

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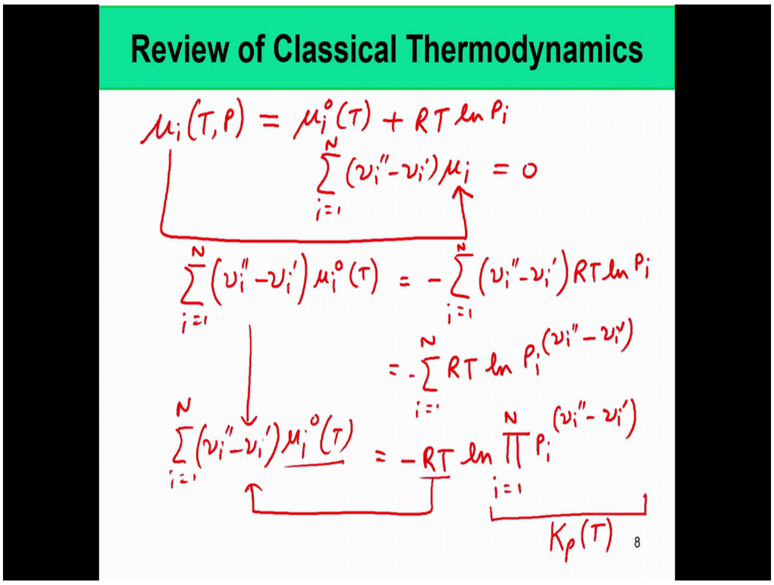

Review of Classical Thermodynamics

$$\mu_i(T,P) = \mu_i^0(T) + RT \ln P_i$$

$$\sum_{i=1}^{N} (\nu_i'' - \nu_i')\mu_i = 0$$

$$\sum_{i=1}^{N} (\nu_i'' - \nu_i')\mu_i^0(T) = -\sum_{i=1}^{N} (\nu_i'' - \nu_i') RT \ln P_i$$

$$= -\sum_{i=1}^{N} RT \ln P_i^{(\nu_i'' - \nu_i')}$$

$$\sum_{i=1}^{N} (\nu_i'' - \nu_i')\underline{\mu_i^0(T)} = -\underline{RT} \ln \underbrace{\prod_{i=1}^{N} P_i^{(\nu_i'' - \nu_i')}}_{K_p(T)}$$

So, the equation we have obtained is essentially mu I, T it is actually is also a function of pressure of course, as you see because it depends on the reference pressure which is it is arrived ya a. So, this is a function of pressure also fine.

Now, if we go back to a definition of equilibrium you have already obtained d G is equal to d lambda summation i is equal to 1 to N nu i double dash minus nu i dash that is a difference of the stoichiometry coefficience from the product side to the reactant side mu i is equal to 0. Now of course, z lambda is arbitrary so, we do not need it. So, this is the equation that you obtain now what we can do is that you will basically substitute this thing here. So, if you do that you obtain summation i is equal to 1 to N, we can take this part on the right hand side this is equal to because of the properties of the logarithm and this quantity is called the equilibrium constant K P in terms of pressure, equilibrium constant in terms of pressure which is only a function of temperature. Why is it only a function of temperature? Because what do you have on this side is essentially if you bring this down here.

So, if you take this here in the denominator. So, this is the function of temperature alone this is the function of temperature alone. So, this is l n K P can be only be a function of temperature alone. So, you must always remember that though it is K P it is only a function of temperature. So, and of course, you see what it is essentially it is a product of the different partial pressures raise to their stoichiometric factors stoichiometric proportionality stoichiometry constants for the given reaction. So, that is what K P is and this is a very important tool to understand to estimate why we have we got this. These are very important quantity which can you can find in different kind of tables where given reaction of other things using the K P we can find out what is the composition of chemical equilibrium that is what is the what is if you are interested in understanding what is the composition of the combustion products that is given by K P . So, that is why it is a very very important constant better remember always that it is the function of temperature alone.

So, what we have obtained is that we have obtained this thermodynamic function.

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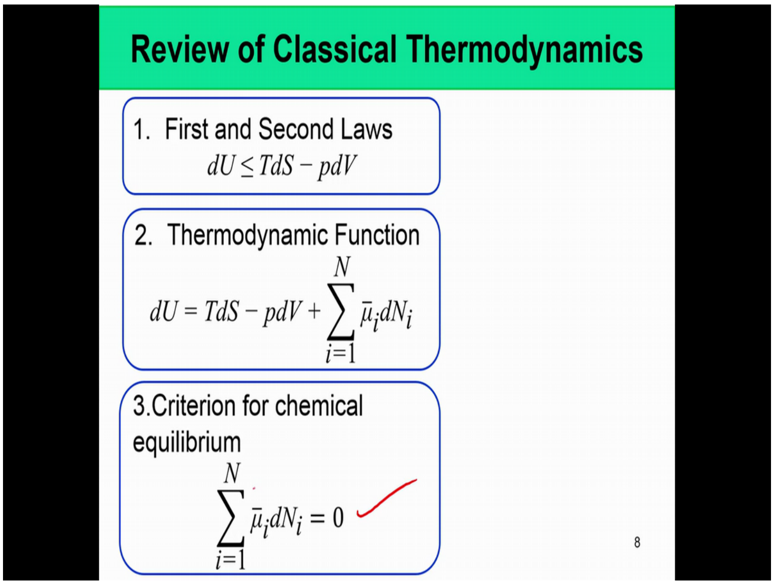

Review of Classical Thermodynamics

1. First and Second Laws

$$dU \le TdS - pdV$$

2. Thermodynamic Function

$$dU = TdS - pdV + \sum_{i=1}^{N} \bar{\mu}_i dN_i$$

3.Criterion for chemical equilibrium

$$\sum_{i=1}^{N} \bar{\mu}_i dN_i = 0 \checkmark$$

We have to obtain this criteria for chemical equilibrium mu i d N i here the (Refer Time: 38:12) essentially represents when it is terms of moles which we have also used.

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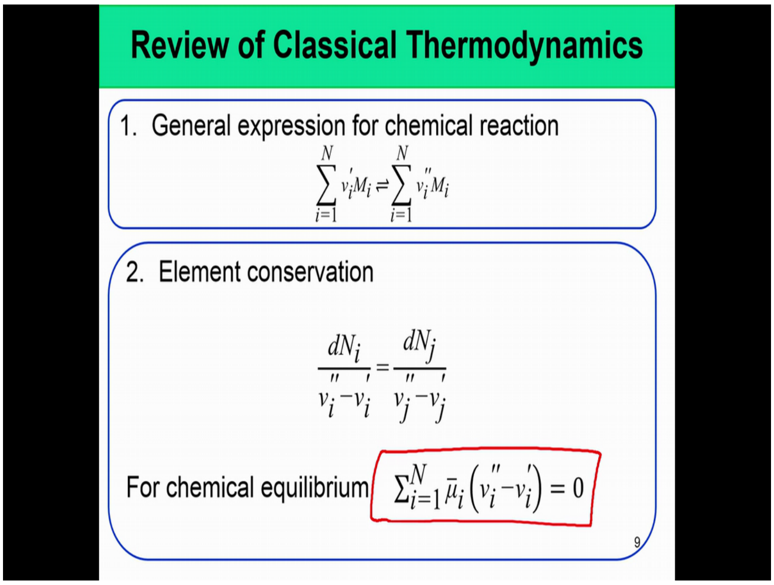

Review of Classical Thermodynamics

1. General expression for chemical reaction

$$\sum_{i=1}^{N} v_i' M_i \rightleftharpoons \sum_{i=1}^{N} v_i'' M_i$$

2. Element conservation

$$\frac{dN_i}{v_i'' - v_i'} = \frac{dN_j}{v_j'' - v_j'}$$

For chemical equilibrium $\boxed{\sum_{i=1}^{N} \bar{\mu}_i \left(v_i'' - v_i'\right) = 0}$

So, we have obtained the general expression for chemical reaction and by implementing applying element conservation we obtained the criteria for chemical equilibrium to be this.

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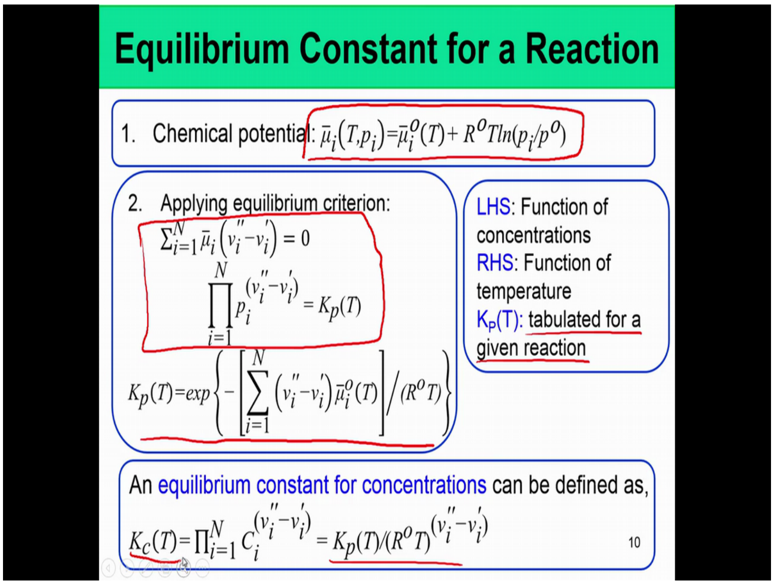

Equilibrium Constant for a Reaction

1. Chemical potential: $\boxed{\bar{\mu}_i(T,p_i) = \bar{\mu}_i^o(T) + R^o T ln(p_i/p^o)}$

2. Applying equilibrium criterion:

$$\boxed{\begin{gathered}\sum_{i=1}^{N} \bar{\mu}_i \left(v_i'' - v_i'\right) = 0 \\ \prod_{i=1}^{N} p_i^{(v_i'' - v_i')} = K_p(T)\end{gathered}}$$

$$\underline{K_p(T) = exp\left\{ - \left[\sum_{i=1}^{N} \left(v_i'' - v_i'\right) \bar{\mu}_i^o(T) \right] / (R^o T) \right\}}$$

LHS: Function of concentrations

RHS: Function of temperature

$K_p(T)$: tabulated for a given reaction

An equilibrium constant for concentrations can be defined as,

$$\underline{K_c(T)} = \prod_{i=1}^{N} C_i^{(v_i'' - v_i')} = \underline{K_p(T)/(R^o T)^{(v_i'' - v_i')}}$$

And we have obtain derived the y chemical potential should be in this manner whereas, P 0 is 1 and then we have obtained the equilibrium constant K P which is given by this.

So, this is what we have obtained and the final expression for K P as given here is this one. So, now, as i said that you can see it is written here that the K P can be at a given temperature can be tabulated for a given reaction or alternatively one can also find right define an another equilibrium constant because you can relate partial pressure and concentrations and with that you can define K C and K P and k c are also related in the following manner. And also will see later that this can be utilized for estimating a red constant of a backward reaction if a forward reaction is known. So, this is got multiple use.

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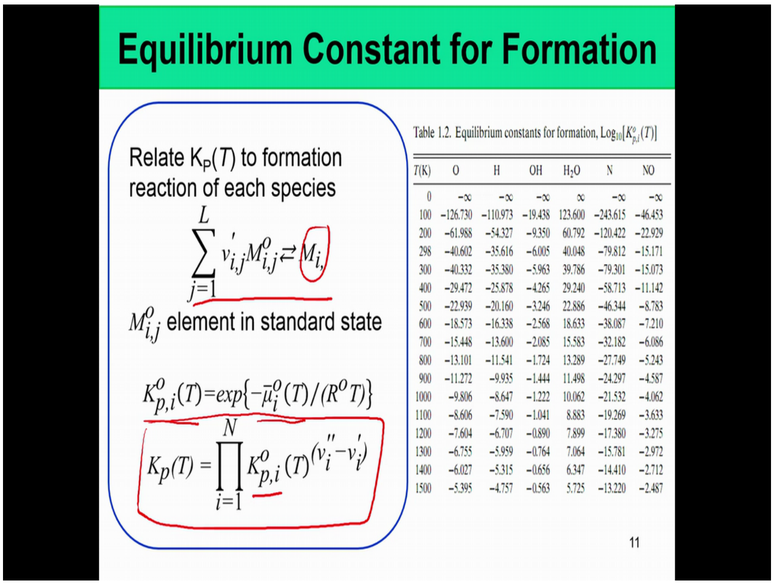

Equilibrium Constant for Formation

Relate $K_P(T)$ to formation reaction of each species

$$\sum_{j=1}^{L} v'_{i,j} M^{o}_{i,j} \rightleftarrows \boxed{M_{i,}}$$

$M^{o}_{i,j}$ element in standard state

$$K^{o}_{p,i}(T) = exp\{-\bar{\mu}^{o}_{i}(T)/(R^{o}T)\}$$

$$\boxed{K_p(T) = \prod_{i=1}^{N} K^{o}_{p,i}(T)^{(v''_i - v'_i)}}$$

Table 1.2. Equilibrium constants for formation, $Log_{10}[K^{o}_{p,i}(T)]$

T(K)	O	H	OH	H_2O	N	NO
0	−∞	−∞	−∞	∞	−∞	−∞
100	−126.730	−110.973	−19.438	123.600	−243.615	−46.453
200	−61.988	−54.327	−9.350	60.792	−120.422	−22.929
298	−40.602	−35.616	−6.005	40.048	−79.812	−15.171
300	−40.332	−35.380	−5.963	39.786	−79.301	−15.073
400	−29.472	−25.878	−4.265	29.240	−58.713	−11.142
500	−22.939	−20.160	−3.246	22.886	−46.344	−8.783
600	−18.573	−16.338	−2.568	18.633	−38.087	−7.210
700	−15.448	−13.600	−2.085	15.583	−32.182	−6.086
800	−13.101	−11.541	−1.724	13.289	−27.749	−5.243
900	−11.272	−9.935	−1.444	11.498	−24.297	−4.587
1000	−9.806	−8.647	−1.222	10.062	−21.532	−4.062
1100	−8.606	−7.590	−1.041	8.883	−19.269	−3.633
1200	−7.604	−6.707	−0.890	7.899	−17.380	−3.275
1300	−6.755	−5.959	−0.764	7.064	−15.781	−2.972
1400	−6.027	−5.315	−0.656	6.347	−14.410	−2.712
1500	−5.395	−4.757	−0.563	5.725	−13.220	−2.487

Now, how do you obtain K P you can obtain of course, there are numerous kinds of reactions that are possible. So, is very difficult to write down the K P for each of them. So, the best idea is to is to basically estimate it somehow. So, we can write that we can state that that the K P we can define a K P for the formation reaction of each species that is we can if you have concern with the species m i which can be say like a CO2 we can write the formation of CO2 like formation of c plus o 2 goes to CO2 and you can basically define the K P of that reaction itself that is the reaction of formation of the K P i, and the purpose is basically to obtain is to basically have a relationship of K P i is 0 and this chemical potential at the standard state and by substitution you can obtain the K P this one.

So, often you will find that the instead of the K P of the reactions, the K P of this of the formation of the species is given and then using this kinds of (Refer Time: 40:59) the K P

0 for the individual species you can estimate the K P of a reaction involving those species alright so this is how you can estimate the equilibrium constant.

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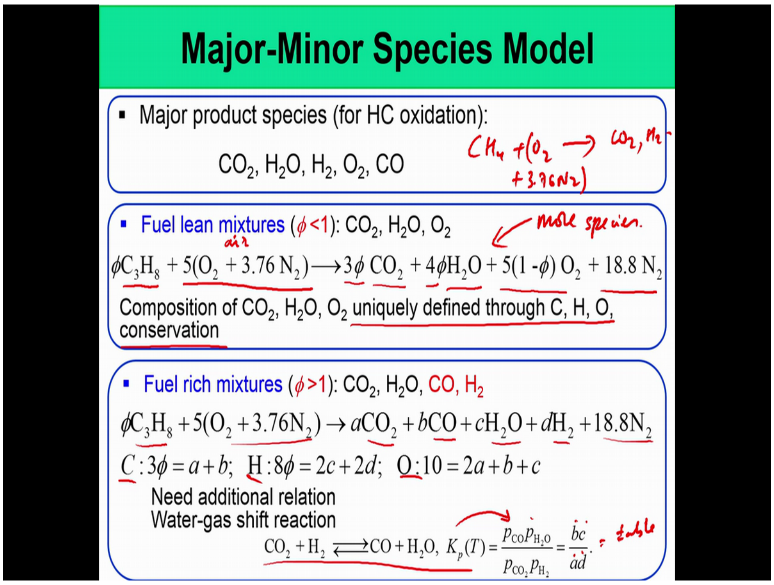

Major-Minor Species Model

- Major product species (for HC oxidation):

CO_2, H_2O, H_2, O_2, CO

$CH_4 + (O_2 + 3.76N_2) \rightarrow CO_2, H_2$

- Fuel lean mixtures ($\phi<1$): CO_2, H_2O, O_2

more species.

air

$$\phi C_3H_8 + 5(O_2 + 3.76\,N_2) \longrightarrow 3\phi\, CO_2 + 4\phi H_2O + 5(1-\phi)\, O_2 + 18.8\, N_2$$

Composition of CO_2, H_2O, O_2 uniquely defined through C, H, O, conservation

- Fuel rich mixtures ($\phi>1$): CO_2, H_2O, CO, H_2

$$\phi C_3H_8 + 5(O_2 + 3.76N_2) \rightarrow aCO_2 + bCO + cH_2O + dH_2 + 18.8N_2$$

$$C: 3\phi = a+b;\quad H: 8\phi = 2c+2d;\quad O: 10 = 2a+b+c$$

Need additional relation

Water-gas shift reaction

$$CO_2 + H_2 \rightleftarrows CO + H_2O,\ K_p(T) = \frac{p_{CO}p_{H_2O}}{p_{CO_2}p_{H_2}} = \frac{bc}{ad}. = \text{table}$$

Now, why is it useful what do you do with the K P? As I said the K P is used for basically identifying or finding out the composition for the products which are in chemical equilibrium. Now for hydrocarbon oxidation that is if you say methane oxidation CH4 plus oxygen that goes with this 2 methane bonds in oxygen as well as in some amount of nitrogen and if we assume that the nitrogen is not participating in the reaction.

So, the main products that you will get is CO2 water and if it is lean then you can have some left over oxygen, and if it is rich you do not have any leftover fuels, but you have basically co carbon monoxide and hydrogen as the which were also some amount some kind fuels essentially. So, you can use this to basically find out the equilibrium the composition now for fuel lean mixtures; there is no problem actually for fuel lean mixtures that is suppose it is propene bonding in air this is air right. So, for bonding one mole of propane you need a five moles of air, and phi is essentially the equivalence ratio in front which is obvious something between 0 and 1 and you will see that there will be for phi moles of a propane there will be 3 phi C 3 phi moles of CO2 there will four phi meals of moles of water and you will have some left over oxygen in this form and in this is constant because it does not participate in every action.

So, this is predetermined, this is you do not need equilibrium constants to find out the composition of CO2 water and oxygen because these are uniquely defines through element conservation that is just by looking at the reaction ,and by looking at how the 3 modes of a c the 3 molecules of c in a propane and 8 8 3 atoms of C and 8 atoms of H in propane how they are how it is the formula for propane and the formula for oxygen and nitrogen etcetera, you can find out how many what will be the proportionality constants for what will be the stoichiometry constants for CO2 what will be the stoichiometry constants for water and for oxygen and nitrogen so on and so forth.

So, this is uniquely defined. The problem arises when you have rich mixtures or in other some places when you actually include more species then to cannot basically if you include most species in your equilibrium in your in your products of course, there are these are not the only species that is produced that is at equilibrium in a combustion reaction you can have some hydroxyl, you can have some co some trace amount of co etcetera and many other molecules that are that are being formed.

So, few include more species you will actually cannot determine the equilibrium composition through just these elemental balance, and this problem is clearly identified here when you have fuel rich mixture that is when you burn propane in oxygen and when phi is greater than one then of course, you produce CO2, but you also produce co you also produce some water you also produce hydrogen and you also produce nitrogen. So, how do you know that, how many moles will go to co and how many moles how many what will be the how many what will be b and what will be a which are the stoichiometric coefficients and how may what will be c and what will be d.

Now, by applying element conservation we can basically form of by applying element conservation we did not C H and O which of the only elements which are participating in the reaction through different molecules, we can 3 equations, but as you can see we have four unknowns. So, where will the other unknown come from. So, the for that we need a additional reaction that is a water gas shift reaction and for that we need to know the K P of that. So, using that the K P of that will be define by this because if you immediately apply the derivation of K P that we have obtained in terms of the partial pressure raise to the stoichiometry coefficients for this water gas shift reaction you will immediately find that K P is this formed and then you can find b c b you can find this will be a proportional to b times c times divided by a and d if you can get this from the table, you can get this from that is fellow from the table and we can find the additional equation that was missing to derive the 4 unknowns.

So, like this using K P you can find out the equilibrium composition the product the equilibrium composition of the products of combustion reactions alright. So, this class ends here next we will see how we can apply energy conservation to basically obtain the temperature of the adiabatic flame temperature in for a combustion reaction.

Thank you.