Good morning, in the last few classes we have been talking of chemical propellants. (Refer Slide Time: 00:15)

We have been trying to find out what are the characteristics we must look for in chemical propellants. Let us take a quick let us take a stock of what we have done so far. Suppose, I have propellant like let us say HNO$_3$; we said it is an oxidizer because it consists more of oxygen than a fuel. And then I react it with something like hydrogen which we say is a fuel. We get products and these products could be H$_2$O could be something like N$_2$ and so on.

These are the completed oxidized products of combustion. But if the temperature is high these could dissociate into let us say H, OH may be H$_2$ could form, may be O$_2$ could also combine with N$_2$ to give NO and so we could get a number of species. Therefore, to be
able to find out the products and the number of moles of each of the species in the products that means, the concentration of the different species in the products, we define the Gibbs free energy. And for a given temperature which would be the flame temperature at the given pressure we said all these species will be in equilibrium and that is what we did.

We also went ahead and defined something known as K equilibrium, which tells us the condition that the product of the partial pressures of each of these species are in equilibrium and we defined this as K equilibrium. And using K equilibrium we found out what will be the products and mind you there is dissociation with a number of specious in the products. Because the energy liberated in a reaction depends on the total heat of formation of the products minus the total heat of formation of the reactants with a negative sign, and since we have dissociated specious, we may not get that much of energy as with completed products of combustion and the flame temperature or the adiabatic temperature would be smaller.

(Refer Slide Time: 02:37)

Therefore, to illustrate the procedure, we calculated the result for H₂ going to H plus H. And we use the Gibbs free energy, which was available and we calculated the value of K equilibrium at two temperatures of 300 Kelvin and 4000 Kelvin. We found that at higher temperature we get more of H. Because the K equilibrium value was higher and we were able to write out let us say K equilibrium is equal to p_H squared that is the partial
pressure of hydrogen squared to $p_{H_2}$, partial pressure of hydrogen. Based on the value of K equilibrium, we could calculate the proportion of the partial pressures.

Through this example we did see the importance of dissociation. This is important because in any chamber let us say I have a rocket chamber like this and at the exit of the chamber I have the nozzle, which is expanding the products of combustion. This is at a pressure let us say $p_C$, which is quite high let us say may be 22 MPa or may be 200 bar or 300 bar or so. I can always calculate the flame temperature which we called as the combustion temperature. To be able to calculate the combustion temperature I need to know precisely what are the products of combustion? We decided this earlier and we said well if it the composition is stoichiometric, we would have completed combustion products and I can calculate the value of heat release $q$.

Once we know the value of $q$, since the specific heat of the product species are known, we can calculate the temperature. We can also calculate the phase changes the temperature change from the initial value to the boiling point at that phase and again boiling temperature to flame temperature for each of the cases. Therefore, we know how to determine these quantities for stoichiometric propellant combinations? When we said fuel rich we made an assumption saying that if the propellant combination is fuel rich, first the nitrogen in the fuel or oxidizer being inert gets converted to $N_2$ in the products and it does not really give any heat. Then the hydrogen reacts with oxygen and we get $H_2O$. And then the balance oxygen goes to react with carbon and this is how we proceeded. And it was an approximate way of finding out what is the number of moles of $CO_2$ and what is the value of the number of moles of CO.
But then if I can do the same problem by assuming let us say that the products of combustion are at a pressure $p_c$, and if we assume that the products of combustion are at a temperature $T_f$ or $T_C$? And then we went ahead for each of the species in the products and for a combination of species, we related them through some chemical reactions. We found out the value of $K$ equilibrium, which we said is equal to minus delta into Gibbs free energy for the reaction divided by $R_0$, the universal gas constant into the particular temperature. The value of Gibbs free energy at any temperature is available in literature and in books and for the assumed temperature of the products $T_f$ we can calculate $K$ equilibrium. And using this $K$ equilibrium I can now calculate the products and the mole numbers of the products.

But we have assumed this temperature; therefore, we have to check whether this temperature is possible. For this purpose, we do the enthalpy balance. What is the enthalpy balance? The energy released by the propellants would be minus the heat of formation of the reactants with a negative sign. This would be the same as the thermal capacity into the rise in temperature of the products. The heat release divided by the $C_p$ must give us back this value of temperature of the combustion products which was assumed earlier. If it does not give us the assumed value; well the assumed value is wrong and I must iterate and redo it. Let me illustrate this through the example with which we had got started in the last class.
We in this particular reaction considered one mole of hydrogen with a1 moles of oxygen. Now, this reaction between one mole of hydrogen and a1 moles of oxygen gives me b1 moles of steam in the gas phase, b2 as hydroxyl radical b3 moles of H atom and b4 moles of O atom. I just assumed these products; you could have assumed something else for the products. This is to illustrate how we calculate the products?

Using the products of a reaction we go ahead and calculate the flame temperature and this what I want to illustrate. Therefore, what is it that we first have to do? I must calculate the value of b1, b2, b3 and b4. With this I can calculate the heat of formation of the products. We know the heat of reactants of this reaction and I subtract this value from the heat of formation of the products which gives the heat of combustion for the reaction.

If I know the specific heat of each of these constituents multiplied by the moles, which if I use the molar specific heat I can get the temperature and this is what we want to do. Therefore, to do this problem, we first need to know what must be my value of a1 and how do we get a1? Mixture ratio is specified and is mass of oxidizer to mass of fuel and we saw this in the last class. That the mixture ratio for a reaction such as involving H2 plus a1 moles of O2, the mass of oxygen is 32 into a1 divided by 2, which is the molecular mass of hydrogen. We get it as 16 into a1 for the mixture ratio. Since the mixture ratio is specified, let us say mixture ratio must generally be fuel rich, we get the value of a1.
The stoichiometric mixture ratio for hydrogen oxygen is 8. Let us say that the mixture ratio is 5; therefore, this value is equal to 16 a1 and we get the value of a1. Whatever, be the mixture ratio I can do this problem. Now, to be able to get b1, b2, etc., we must be able to get the atoms on the left hand side to be equal to the atoms on the right hand side. And therefore, we have two atoms of hydrogen, which on the right hand side I get two b1 plus 1 atom here b2 plus 1 atom here b3 this is the atom balance equation for H.

Similarly, for O we have two a1 on the reactant side and I have 1 of b1 plus 1 of b2 plus 1 of b4. Therefore, we get two equations that connect the moles of my products, which we have assumed to be b1, b2, b3 and b4 with the moles in the reactants. And which we want to determine for a given value of a1 and therefore, we get these two equations. But then we find that a1 is known we just say for a mixture ratio of 5, a1 is 5 by 16 and therefore, now I need to know what is going to be my value of b1, b2, b3 and b4.
We have 4 unknowns, but only two equations and therefore, I need two more equations to solve for the values of $b$. To get the other two equations, we use the value of the equilibrium constants and how did we do it? If we assume that $\text{H}_2\text{O}$ could have dissociated into $\text{OH}$ and $\text{H}$ then the value of equilibrium constant for this reaction is equal to partial pressure of $\text{OH}$ into partial pressure of $\text{H}$ divided by partial pressure of $\text{H}_2\text{O}$. We said we could also express the equilibrium constant in terms of concentrations, which is denoted by $K_c$ i.e., terms of concentrations of $\text{OH}$, $\text{H}$ and $\text{H}_2\text{O}$, but we said let us use partial pressure itself.

And from this equation we get $\text{pH}$, which is from the right hand side we take it over here to give $K_p1$ into $\text{pH}_2\text{O}$ divided by $\text{pOH}$. We know the now the value of $\text{pH}$ in terms of $\text{pH}_2\text{O}$ and $\text{pOH}$. Similarly, we would also like to get the partial pressure of oxygen and for that we use the following three equations. $\text{H}_2$ could have got dissociated to $2\text{H}$, $\text{O}_2$ could have got dissociated to $2\text{O}$. For this particular reaction $\text{H}_2$ to $2$ $\text{H}$, we get $K_p2$ is equal to $\text{pH}$ squared divided by $\text{pH}_2$; that means, we have $\text{pH}$ squared as $K_p2$ into $\text{pH}_2$. Similarly, $\text{O}_2$ going to $2\text{O}$, if we can write the reaction rate constant for this cycle as equilibrium constant $K_p3$ gives $K_p3$ as equal to $\text{pO}$ squared divided by $\text{pO}_2$ over here.

I have one more equation, $\text{H}_2$ plus half $\text{O}_2$ is equal to $\text{H}_2\text{O}$ in gas phase. For this reaction we take the equilibrium constant as $K_p4$. And $K_p4$ is equal to partial pressure of $\text{H}_2\text{O}$ over here, divided by $\text{pH}_2$ and half $\text{O}_2$ means $\text{pO}_2$ half. Therefore, we look at these three
equations and from this second equation we get the value of may be $p_{H2}$ is equal to $Kp2$ by $p_H$ squared. I get the value of $p_{O2}$ is equal to $Kp3$ by $p_O$ squared. I substitute it in this particular equation four and we get $p_O$ is equal to $p_{H2O}$ into $Kp2$ into $Kp3$ to the power half divided by $Kp4$ into $p_H$ squared.

Let us take a look at what has been derived. We have $p_H$ squared here and one by $p_{H2}$ is equal to $Kp2$ by $p_H$ squared. We also have in this case $p_O$ from this reaction as equal to $p_{O2}$ to the power half into $Kp3$ to the power half. Substitute these in equation four gives $p_O$ equal to partial pressure of steam into $Kp2$ into $Kp3$ to the power half divided by $Kp4$ divided by $p_H$ squared. Now, what is it we have done? Of the products we had in the products, $H_2O$, OH, H and O, we have expressed these four species in terms of two of them.

We have expressed $p_O$ in terms of $p_H$ squared and $p_{H2O}$ that is $p_H$ and $p_{H2O}$. We also related $p_{H2}$ in terms of $p_H$. Essentially therefore, though we had four species; what were the four species? $b_1$ moles of $H_2O$, $b_2$ of OH, $b_3$ of H and $b_4$ of O. We are now able to relate two of them to the remaining two of them and therefore, now I can close my set of four equation because I have two more equations.

(Refer Slide Time: 13:17)

![TO CONVERT PARTIAL PRESSURE TO MOLES]

And therefore, let us put it together again. However, we need to put partial pressures in terms of $b_1$, $b_2$, $b_3$ and $b_4$ since we have determined partial pressure of $H_2O$, partial
pressure of OH, partial pressure of H and partial pressure of O. Now, how do we convert partial pressure of H_2O to b1? Let us do it on the board.

(Refer Slide Time: 13:42)

Let me again repeat. I have H_2O, I have OH, I have H, and I have O in the products. And according to the equation we have b1 moles of this, b2 moles of OH, b3 moles of H and b4 moles of O. Through equilibrium constant, we expressed the partial pressure of H_2O as so much the partial pressure of OH as so much the partial pressure of H and so much the partial pressure of O atom. Now, I have the atom balance equation in terms of b1, b2, b3 and b4 but we have equilibrium relations in terms of partial pressure. How do we convert p in terms of b?

If we can find out the total number of moles in the products, then we can always go back and determine this dependence? Let us say that the total numbers of moles in the product are let us say n_T total number of moles. And now the total number of moles of H_2O in gas phase is b1 by total number of moles n_T is equal to partial pressure of steam divided by the total pressure in the chamber. And therefore, I get b1 as equal to partial pressure of water – steam - divided by the total pressure multiplied by the total number of moles n_T.

Therefore, if I can determine the total number of moles it will be possible for me convert the partial pressure of each of these species into their respective number of moles is it. Now, to do that i.e., the total number of moles in the products, we need to know the
values of the bs: b1 plus b2 plus b3 plus b4 over. But we still do not know the value of any b; and the total number of moles is not known. Therefore, we make an assumption. Let us assume that the reaction is stoichiometric. And based on this the products are completed combustion products. We find that the total number of products, which are formed, is not very different from the stoichiometric condition and the value can be corrected.

(Refer Slide Time: 16:27)

Let us take the same reaction again: we said H₂ plus a₁ O₂ if it is stoichiometric combustion complete products of combustion would have been formed. Therefore, we would have got H₂O plus what is it? We had two of a₁ O of which have consumed one O and we are left with 2 a₁ minus 1 of O. Therefore, the amount of oxygen left in this reaction as per this relation should be plus 2 a₁ minus 1 of O, but I would like to put it in terms of O₂, which is left after the stoichiometric reaction. If I were to assume that this reaction is stoichiometric, I get one mole of H₂O and I get the balance that is 2 a₁ minus 1 divided by 2 is what is left of oxygen O₂.

Therefore, the total number of products which are formed or total number of moles of products, according to this reaction if stoichiometric is going to be one plus 2 a₁ minus 1 divided by 2, which is equal to a₁ plus half and this is the total number of moles in the products. Mind you this assumes stoichiometric reaction; but the generally, if you do as
number of problems the number of moles are not very much different, but then we will go back and correct it as we go along as we shall observe.

Therefore, to begin with we will assume that the total number of moles what we are going to get is going to be $a_1$ plus half. If this is so we know now, the total number of moles over here and therefore, we can calculate $p_{\text{H}_2\text{O}}$ as equal to $b_1$ into $p$ divided by $n_T$. And therefore, what is that we get? $b_1$ is equal to $p_{\text{H}_2\text{O}}$ divided by the total pressure into the total number of moles. Therefore, we can get the value of $b_1$.

(Refer Slide Time: 19:01)

Similarly I get the value of $b_2$ as the partial pressure of OH into the total number divided by the total pressure; $b_3$ in terms of $p_H$ into the total number of moles divided by the total pressure and $b_4$ partial pressure of oxygen atom into total number of moles divided by the pressure. And what is it we have done? We have converted partial pressure of $\text{H}_2\text{O}$, in the gas phase, partial pressure of OH, partial pressure of H and partial pressure of O into $b_1$, $b_2$, $b_3$ and $b_4$. 
But we already had the relation between $b_1$, $b_2$, $b_3$ and $b_4$ and this was the relation we had from atom balance. We had $2b_1 + b_2 + b_3$ is equal to 2; we also had $b_1 + b_2 + b_4$ was equal to 2 $a_1$. Therefore, we can use these two relations and we substitute for $b_1$, $b_2$, $b_3$ and $b_4$ in terms of the partial pressures. We therefore get $2p_{H_2O}$ plus $p_{OH}$ plus $p_H$ divided by this particular conversion viz., $p$ divided by $a_1$ plus half and this gives when moved to the right hand side 2 divided by $a_1$ plus half into $p$. And similarly, we get from this relation $p_{H_2O}$ plus $p_{OH}$ plus $p_O$ is equal to the value of 2 $a_1$ divided by $a_1$ plus half into the value of $p$ over here.

That means, we have succeeded in putting the atom balance equations which were in moles in terms of the partial pressure of $H_2O$, $OH$, $H$ and $O$. Mind you we also had two other relations for $p_H$ in terms of $p_{H_2O}$, $p_{OH}$ through the equilibrium constant and we derived the relation for $p_O$ in terms of $p_{H_2O}$ and $p_H$ squared. Therefore, we have four equations in four unknowns. And what are the four unknowns? These were the partial pressure of $H_2O$ in gas phase, partial pressure of $OH$, partial pressure of $H$ and partial pressure of $O$. We can solve these four equations and determine the value of $p_H$, $p_O$, $p_{OH}$ and $p_{H_2O}$. Mind you the equations are not linear, but we can always use some scheme like the Newton Raphson method or some other scheme to be able to solve the equations easily.
Once we determine the value of the partial pressures, we must go back and determine the value of $b_1$, $b_2$, $b_3$ and $b_4$. For this, we go back substitute it again in the equations for $b_1$, $b_2$, $b_3$ and $b_4$, which we had here. That means, we know the number of moles of $H_2O$, we know the number of moles of $OH$, we know the number of moles of $H$ and we know the number of moles $b_4$ of $O$. But we have assumed the total number of moles was equal to a 1 plus half.

But the actual number of moles in the products is $b_1$ plus $b_2$ plus $b_3$ plus $b_4$. If this is going to be different from this assumed value, well we assume this sum to be the total number of moles and redo the calculations till $b_1$ plus $b_2$ plus $b_3$ plus $b_4$ converges and that will be the final value of the $b$s. That is number of moles of $H_2O$, number of moles of $OH$, number of moles of $H$ and number of moles of $O$ in the products are now known.
What is it we have done? We got b1 of H₂O, b2 of OH, b3 of H and b4 of O. To be able to do that we assume the total number of moles to be stochiometric and then we determine b1, b2, b3 and b4. Then we said summation of b i’s as i goes from 1 to 4 must be the same as total number of moles, which we have assumed. If it is not so, let us again assume n_T is equal to summation of b i’s is equal to 1 to 4. And again repeat the calculation till I get consistent or converged value for b1, b2, b3 and b4.

However, all the equilibrium constants were calculated at a given temperature. We write out the enthalpy balance equation and check if the assumed value of temperature is correct. What is the enthalpy equation? We need to check whether the summation of the heat of formation of the products viz., b1 moles of water plus b2 moles of OH plus is b3 moles of H and b4 moles of O would give the assumed value of temperature of the products. While doing this the heat required to change the liquid hydrogen to it is boiling point then the phase change plus the change from the boiling point to the to the standard condition of 298 in the reactants has to be accounted.

Similarly, for oxygen from the liquid state to the boiling state to the latent heat and then the sensible heat or heat of the gas from the boiling temperature to 298 Kelvin. Similarly, for steam: liquid water to boiling point, vaporization and sensible heat which is the specific heat into the number of moles into Tf minus boiling temperature and sensible heat for the other species. And this must be satisfied if I have to if my values of b1, b2,
b3 and b4 are correct at the temperature, which I have assumed. If my assumed temperature is not correct then the enthalpy balance will not be satisfied. We need to assume a new value of temperature, calculate the value of Kp1, Kp2, Kp3 and Kp4 at the new temperature again; determine the new converged values of b1, b2, b3 and b4 and check for enthalpy balance till the final temperature converges; this convergence temperature is the flame temperature.

(Refer Slide Time: 25:46)

Let me repeat this procedure on the board with respect to the two convergences and the iterations. What are we looking for? We have K equilibrium for a number of may be four steps that we had. We had K equilibrium one for a reaction of H2 to form H and H. K equilibrium we said is equal to minus of Gibbs free energy divided by R naught into temperature T. To be able to get the equilibrium condition, we need to the value of temperature because K equilibrium is a function of temperature. First we assume the temperature of the products to be let us say 2000 Kelvin.

Therefore, we evaluate delta G at 2000 Kelvin for the particular reaction just the same way as we did for the reaction in the last class. H2 is equal to H plus H and we evaluated it at 300 Kelvin we evaluated at 4000 Kelvin. Similarly, we get the value of delta G at the assume value of 2000 Kelvin. We have R naught as 8.314 Joule per kg Kelvin into temperature 2000 Kelvin. We get the K equilibrium for the reaction. Similarly, we get K
equilibrium for reaction two, and similarly $K$ equilibrium 3 and $K$ equilibrium 4 at the assumed a temperature $T_f$.

(Refer Slide Time: 27:02)

Let us now put these two iterations together. We first assume the value of $T_f$, then we determine the values of $K$ equilibrium. Then once we have determined $K$ equilibrium, we again assume the value of total number of products, which are available based on stoichiometric reaction and calculate the value of $b_1$, $b_2$, $b_3$ and $b_4$. Then we check whether the assumed value of the total number of moles $n_f$ is correct. If so, we get the correct values of $b_1$, $b_2$, $b_3$ and $b_4$ at this particular temperature. Thereafter, we use these $b_1$, $b_2$, $b_3$ and $b_4$ in the enthalpy balance.

In the enthalpy balance we sum up the heat of formation of the total products that means, we multiply by $b_i$ into delta $H_f$ for the products minus the net heat of formation of the reactants. And where it is this part of this heat go? It goes into taking the reactants to the standard condition at 298 Kelvin and the products from the standard condition to the flame temperature $T_f$. This is because, the initial state may not be the standard condition and part of this heat goes into the enthalpy required to convert the condition of let us say hydrogen from it is original condition to the standard condition. That means, if we have hydrogen in the liquid phase, we have to supply the latent heat for phase change and have the vapor phase to be heated to the standard condition. Therefore, we require heat for $H_2$ to reach the standard condition.
Similarly, I have for the oxygen. And again what happens is the balance of heat goes into sensible heat for the products and also, latent heat as applicable for H$_2$O, which I do not explicitly mention. Using the enthalpy balance, we get the new value of temperature. We had assumed T$_f$ to be 2000 Kelvin and the energy balance may give us a new temperature of 2500K. We now assume another value of T$_f$, which is in between the two and repeat the process till two successes iterations give us T$_f$ around the same number.

If I am interested in a very accurate value of temperature, the number of iterations would be higher. If I am not interested in such a close values, one may be satisfied with a fewer iterations. The first set of iterations is with respect to moles at an assumed value of T$_f$ and then in the second set of iterations we calculate for the value of T$_f$ and this is the iterative procedure followed. I like this method of equilibrium constants, because you can see physically what is happening as you are proceeding with the problem. I will also discuss about another method. Therefore, let us again repeat; we determine the moles from the atom balance equations for an assumed temperature, again check for the total number of moles till this is satisfied.

But then for this we had assumed a particular temperature since the equilibrium constants were required; but the temperature was not known. To determine the temperature, we do the enthalpy balance and then find out the revised value of temperature based on the assumed value and repeat it till two successive iterations show near about the same value of T$_f$. At each value of T$_f$, we calculate the moles of the products. Each of us will do for one specific project for a given propellant combination using a computer coding.
But then, it is also possible that some of the species could be in different phases such as water and water vapor i.e., liquid and vapor phase.

Let us take an example. We considered mono methyl hydrazine. I will talk about it in the next class. You have hydrazine N₂H₄, you take one of the H and substitute it by methyl radical this is known as mono methyl hydrazine. It is used in many of the rockets it is a liquid fuel. And if this is going to react with another oxidizer we will consider it in the next class again N₂O₄. The products of combustion could be CO₂ if my temperature is
very high maybe I could get CO, may be if the temperature is still high maybe I could also get C in the gaseous phase, but if my temperature is not so high I could also get some solid form of carbon C.

Therefore, how do we distinguish between a gas phase and a solid phase and estimate how much of solid and gaseous carbon is formed? This also, can be done using equilibrium analysis.

We illustrate it through an example of water being formed. And let us say liquid phase of H₂O, which is water and gaseous phase, which is steam. We take the reaction H₂ plus half O₂ is equal to H₂O. Therefore, we get the total number of moles of H₂O should be the total number of moles in the gas phase and in the liquid phase for this reaction. However, we can write the equilibrium constant Kp as equal to p$_{H2O}$ in the gas phase divided by p$_{H2}$ and p$_{O2}$ to the power half. The partial pressure of H₂O would correspond to the steam i.e., H₂O in the vapor phase.

We can also from the temperature, which is either assumed or calculated, always calculate how much of steam will be there? Because steam is saturated at that particular temperature I can get the partial pressure from vapor pressure table. And once we know the proportion of steam from the vapor pressure table, we can go back and determine what is the balance of H₂O left? And this is in the liquid phase. This is how we calculate the proportion of phases?

And different phases are present especially in the products of combustion of solid propellant rockets. We will consider solid propellants in the next class again. We have aluminum as fuel and aluminum forms Al₂O₃. This Al₂O₃ could be in a liquid phase or could be as a solid phase. And we know all the different phases have different energy in them. Therefore, we must be able to calculate the phases of the species in the products. Those of you who do a project using solid propellant must be able to differentiate it, but the procedure is straightforward.
This is all about calculation of the species in the products. But there is also another method which is normally followed in many of the computer codes such as NASA SP 273, available for calculating the temperatures.

Instead of going ahead and finding out the equilibrium constants from Gibbs free energy and then finding the temperature, what they do is minimize the Gibbs free energy, which corresponded to equilibrium. We defined at constant pressure and temperature, the Gibbs free energy as equal to $n_j \mu_j$. With $b_1$, $b_2$, $b_3$ and $b_4$ being the species and $\mu$
being their chemical potential, we can write the total Gibbs free energy of the products as equal to the let us say in the in our particular case where we had b1 of H₂O, b2 of OH, b3 of H and b4 of O into their respective value of mu.

(Refer Slide Time: 35:10)

Therefore, the total Gibbs free energy is equal to mu of H₂O into b1 plus mu of OH into b2 plus mu of H into b3 plus mu of O into b4. This is the total Gibbs free energy. And what will be the condition for moles of the species to be in equilibrium at the given temperature and pressure? When Gibbs free energy is a minimum that is equilibrium. Therefore, if we put G as a minimum or rather if I were to put dG as equal to 0, we should be able to find out the value of b1, b2, b3 and b4. And this is a very direct procedure, but it is little involved.

Let us see what is involved in it? But for this set of dG equal to 0 must also obey the constraint that the atoms must be conserved. Here we had H₂ plus half O₂ and what were our atom balance equations.

These atom balance equations were for hydrogen atom 2 is equal to or let us put the right hand side first two b1 plus b2 plus b3. We could also state it as 2 of b1 plus b2 plus b3 minus 2 is equal to 0. For O balance we had b1 plus b2 plus b4 minus if we had into two of a1 is it not? H₂ plus a1 oxygen is present in the reactants. Therefore, I have this quantity b1 plus b2 plus b4 minus 2 a1 equal to 0. We determined a1 based on mixture
ratio. Therefore, these were the two equations which have to be satisfied because I cannot create atoms in a reaction and therefore, we call this as the constraint equation.

Even though I have to minimize the value of Gibbs free energy i.e., $dG$ equal to 0 this constraint condition must also be obeyed. We therefore use the method of Lagrangian multipliers, which is what I show in the following: We define an arbitrary quantity known as Lagrangian $L$, which is equal to $G$ plus this is the summation of the constraints into the Lagrangian multiplier lambda. We have two constraint equations and therefore we have two Lagrangian multipliers lambda1 and lambda2. On differentiating $L$, we get delta $L$ to be given by the variables $db$ (db1, db2, db3 and db4) and dlambda (dlambda$1$ and dlambda$2$).

(Refer Slide Time: 38:09)

\[
\begin{align*}
L &= G + \lambda_1 \left( b_1 + b_2 + b_3 - 2 = 0 \right) \\
&\quad+ \lambda_2 \left( b_4 - 2g = 0 \right) \\
&\quad+ \alpha \lambda_1 \left[ \right] \\
\end{align*}
\]

And therefore, this plus this in other words let us put it back again. We define $L$ as equal to $G$ plus lambda into I have this constraint equation coming over here. We have lambda I and lambda 2 and accordingly we have four dbs and two dlamdas. These cannot be zero and we get the term within brackets as zero for the first and second terms of dL.

Since the differentiation of the moles of the products, cannot be 0 and the Lagrangian multiplier is a free multiplier cannot be 0 and therefore, we get this is equal to 0 we get this is equal to 0. We get a set of equations, which we solve for the values of $b_1$, $b_2$, $b_3$ and $b_4$. May be you should learn to use both the methods. I have never really used the multiplier method, but I when I went through the SP 273 manual and I found it is quite
simple. I personally like the method of equilibrium constant because I am able to see everything come through the equilibrium constants. In the Gibbs free energy minization metod we sole for the set of matrices to give us the values of b1, b2, b3 and b4.

(Refer Slide Time: 39:56)

This is how we determine the products of combustion. And once the products of combustion are known, the heat of reaction can be determined. You can find out the temperature Tf. We can find out the value of Cp for the mixture and also the value of Cv for the mixture of the products. We can find out the gamma and thus determine the performance coefficient C*.
And now let us take a look at the results that I did present earlier. Let us understand the variations of the flame temperature changes with mixture ratio for a hydrogen oxygen reaction. Mixture ratio 8 is stoichiometric and as we said we always operate in the fuel rich region. Now, at higher pressure we find a higher value of temperature than at lower pressure. Why is it? At higher pressure you know the gases cannot dissociate because you are compressing the gases in a region. They cannot readily multiply in view of the resistance offered.

And therefore, you get more completed products of combustion at higher pressure and therefore, the temperature is higher. As pressure reduces, I come to something like 10 bar that is 1 MPa, the temperatures are much lower than at thousand MPa. Therefore, I find higher pressure the dissociation is less and I can get a higher value of flame temperature. See we are able to interpret the results now we have understood the problem.
Let us take a look at the molecular mass of the products? You find over here the molecular mass of the products increases as the pressure increases. At 1 MPa it is a little bit lower while at a higher value of pressure we get a higher molecular mass. Why is it? Because I get more completed products of combustion, which cannot readily dissociate at higher pressure. Therefore, the molecular mass also increases as the pressure increases. But we do find if we go back to our previous slide that the change in temperature is quite substantial whereas the change in molecular mass is very much less.
Therefore, the ratio of let us say under root $T_C$ by the molecular mass will still be large and will still be higher at higher pressures. Therefore, a higher pressure gives us a higher value of performance. Let us take a look at some more parameters. Let us take a look at gamma, the ratio of specific heats. We had said for the simple species like a mono atomic species it was 1.67. For more complex species like $\text{CCl}_4$ it was lower at 1.12 or something of this order. We find that at higher pressure we have more complex products and therefore, the gamma is smaller. As the pressure reduces, the value of gamma increases, which is again in the direction.

(Refer Slide Time: 42:47)

With the value of $T_C$, molecular mass and gamma, we can calculate the value of $C^*$ or equivalently the Isp. We find at higher values of pressure like what is shown hundred MPa, we get a higher value of specific impulse compared at a lower pressure. But something more important is to be noted? The peak values is somewhere, over here at hundred MPa, at as the pressure decreases, we get a more fuel rich gives a higher value. That means, the choice of the mixture ratio will depend on the chamber pressure. Which mixture ratio gives us the maximum performance also depends on pressure because of the dissociation. I think these are the important conclusions which we draw from these particular slides.

Let us now go back and try to understand the last part as to why we do the equilibrium analysis? There certain things which we need to understand further.
When we showed the Isp values in that particular plot, it is Isp at sea level. Isp will change between sea level where the ambient pressure is one atmosphere and at high altitudes where the ambient pressure is less. A comparison of $C^*$ would have been more appropriate.

Now, let us consider the last part of the dissociation before we can look at the chemical propellants and their characteristics. We have a combustion chamber wherein the pressure is $p_C$ the temperature is $T_C$ and we now know how to calculate $T_C$, which we said is adiabatic flame temperature. We also know at this adiabatic temperature what is going to be the proportion of the product $b_1$, $b_2$, $b_3$ and $b_4$ and so on?

All these products are formed in the combustion chamber. I deliberately use a chamber configuration as shown, because let us not get let us not think that the rocket chamber should always be a cylinder. This is the combustion chamber and this feeds the hot gas into the nozzle. The nozzle is as shown; over here is the converging part of the nozzle, this is the throat after the convergent and this part is the diverging part of the nozzle. We have determined the products of combustion that is moles of the products, the flame temperature as the gases enter the nozzle.

Now, what is going to happen what is going to happen to the flow in the nozzle? Based on the values of $b_1$, $b_2$, $b_3$ and $b_4$ here, we calculated the value of gamma, the molecular mass of the gas and the value of $T_C$ and using the relations we got Isp. In other words, we
assumed that the composition remains the same everywhere, the value of gamma remains the same everywhere. The value of molecular mass remains the same everywhere. That means the flow is taking place flow through the nozzle as if the composition were frozen. And what did we determine for flow through a nozzle? Let us plot it.

We determined the variation of let us say temperature from the adiabatic flame temperature, which we have just calculated. As the flow progresses the temperature drops. Therefore, let us take a section here now let me take a section over here, let us call it as section one let me take section two over here, just to illustrate the phenomena.

That means, I take this this is my section one of the nozzle that means, I take it in the convergent. I again go ahead take a section in the divergent this is 2. At section one the temperature is let us say T1, at section two the temperature is T2. Now, what is it we find? We find the temperature T1 at section 1 is less than the flame temperature.

(Refer Slide Time: 47:09)

That means, in the convergent at section 1 the temperature is T1 which is less than the flame temperature Tf. If the products are going to be equilibrium at this section 1, well the proportion will not be b1, b2, b3 and b4 as we calculated at Tf, but since it is cooler perhaps the composition will be much different. It will be b1 corresponding to the new value of T1; similarly, b2 corresponding to the new temperature T1 and so on. In other words in practice at as the temperature gets lower, I will get a new composition. When it has expanded quite a bit, say at section 2, the composition will be totally different.
In other words the composition of the products b1, b2, b3 and b4 and whatever the heat release will keep on changing as the flow takes place. Therefore, I say in practice composition of the gases or the molar composition which we are considering will keep changing. As the gas expands I am going to get a new value of equilibrium constant and that is going to lead to different values of the moles of the products. In other words the composition keeps shifting and such type of flow in which at each point the composition shifts is known as shifting flow or shifting equilibrium flow. Because the equilibrium shifts I call it as shifting equilibrium flow.

Well to solve this is extremely simple? We go to the next section and find out what will be the temperature for this particular expansion assuming the values of gamma corresponding to the earlier section. We can find out at this point the value of the moles of species and we can calculate the revised temperature again and revise products again and so on. I can do this with a shifting equilibrium. And what happens in shifting equilibrium? Because the temperature drops I get more of the products, which are not dissociated, because at low temperatures a gas cannot get dissociated. As a result recombination takes place and heat gets released.

(Refer Slide Time: 49:31)

And therefore, heat release takes place along the length of the nozzle. We did not consider heat release at all earlier whenever we calculated the temperature distribution in the nozzle. The actual temperature will therefore increase. And therefore, because the
temperature has increased the Isp corresponding to shifting equilibrium will be greater than Isp corresponding to frozen flow. Is this point clear? This is important. But now how do we determine which is the value frozen or shifting equilibrium to be used?

In the convergent the flow is subsonic and therefore, we have lot of time for reactions to occur. In my divergent that the flow is supersonic there may not be much time for equilibrium to take place. And the general practice is well you could assume equilibrium flow or shifting equilibrium flow up to the nozzle throat and frozen thereafter and this seems to give, the value of specific impulse to be near the values what are experimentally measured. But this is not always true. It depends on the type of gas and the type of dissociation. But for hydrogen oxygen as the propellants; there has been published work such as Bray model which gives reasonable estimates for Isp with flow shifting till the throat and frozen thereafter.

(Refer Slide Time: 51:18)

In other words, in a nozzle convergent followed by divergent, we have in the convergent shifting equilibrium flow and in the divergent frozen flow and this assumption tends to give me a reasonable value of Isp. If not what is going to happen to me? How to predict the performance?
And if we were to plot specific impulse; this is my stoichiometric value, this is fuel rich region and in the fuel rich region we will get the maximum specific impulse. This lower curve is for frozen flow. For shifting equilibrium flow we will get a higher value. The actual value will be in between the two. And this mean value somewhat matches with equilibrium flow in the convergent followed by frozen in the divergent.

This is all about dissociation of gases and the performance characteristics of propellants. In the next class, we will take a look at the different types of propellants.