Basic Thermodynamics

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Lecture - 29

Thermodynamics of Reacting System – III

Good morning. Today, we will be studying the application of second law to a chemical reaction. Last classes, we have studied in detail the application of first law of conservation of energy to a chemical reaction.

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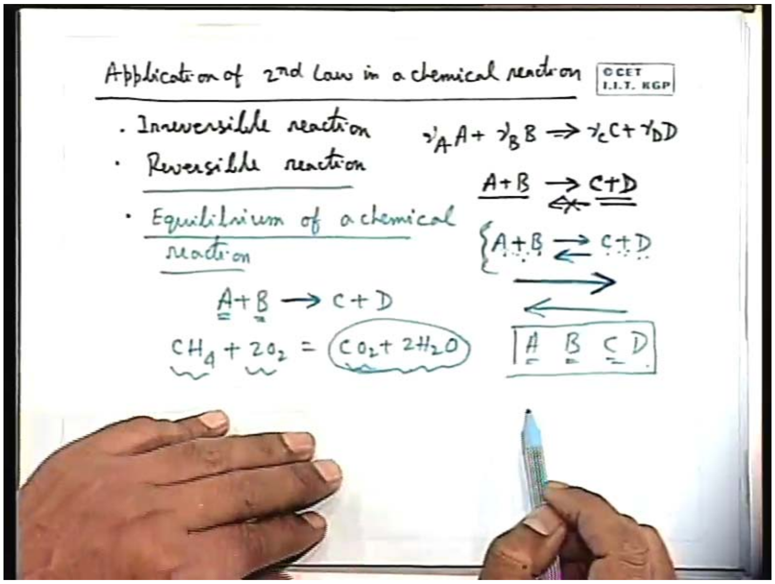

Application of 2nd Law in a chemical reaction

- Irreversible reaction
- Reversible reaction
- Equilibrium of a chemical reaction

$$\nu_A A + \nu_B B \Rightarrow \nu_C C + \nu_D D$$

$$\underline{A+B} \underset{\not\leftarrow}{\rightarrow} \underline{C+D}$$

$$\left\{ A+B \rightleftarrows C+D \right.$$

$$\longrightarrow$$

$$\longleftarrow$$

$$\boxed{A \quad B \quad C \quad D}$$

$$A+B \longrightarrow C+D$$

$$CH_4 + 2O_2 = CO_2 + 2H_2O$$

Let us see the application of second law in a chemical reaction. There are two types of reactions, one is irreversible reaction and another is reversible reaction. In the field of engineering science, there are many words which are repetitive. In fluid mechanics shock is used in compassable flow and also in turbo machines. Like that there are many words which are repetitive but they do not mean the same. These reversible and irreversible is not in our thermodynamic reversibility in reversibility.

This reversible and irreversible reaction means, if we consider a reaction like this, gamma$_A$A plus gamma$_B$B gives gamma$_C$C plus gamma$_D$D. It is not always necessary to give stoichiometric coefficient. You can write when you do not balance it as C+D. When this reaction proceeds in only one direction, that means only A and B produces C and D, the products cannot be converted back to the reactants that means opposite direction reaction is not possible. This is known as irreversible reaction. If you start with A+B as reactants we get C+D as products this products are not reverted back to the reactant that is known as irreversible reaction, reaction goes in one direction.

Under certain circumstances, the reaction takes place in both directions; that means, A + B converted to C + D and C D is converted to A B. Both the reactants give products and the product is again converted back to the reactant. This reaction is known as reversible reaction. One directional reaction is known as irreversible reaction and the reaction which can take place in both the directions. That means the products converted back to the reactants is known as irreversible reaction.

You need to know what is meant by equilibrium of a chemical reaction. When in a chemical reaction, the concentration of the species, temperature, pressure and everything remain invariant with time, this is known as equilibrium of a chemical reaction.

How the equilibrium takes place? In case of one directional or irreversible reaction C+D, if it is a one directional or irreversible reaction, then the equilibrium will be achieved when one of these reactants or both the reactants are totally consumed to produce C + D.

If the reactions take place in a stoichiometric coefficient then both the reactants will be consumed simultaneously. Otherwise, one of the reactants will be consumed first. For example, if you give excess air then the fuel will be consumed fast. That means, either one or both the reactants are consumed completely then the reaction stops. In that case, whatever is the constituents, the composition of pressure and temperature are fixed to attain equilibrium condition. For example, if we consider CH_4+ $2O_2$ is CO_2 + $2H_2O$ that means when both the reactants are consumed, the pressure and temperature will be fixed and this correspond to an equilibrium condition.

What happens when the reactions takes place in both the directions? That means A+ B converted to C + D and C + D will be converted to A + B. How will the reaction equilibrium take place? Before that one has to know that in this type of net reaction, the process continues where A, B, C, D all the constituting species vary in their concentration, which means that the reaction should proceed in one direction. The bulk reaction should proceed in only one direction. If it proceeds in left direction, the rate of reaction from left to right is more than the rate of reaction from right to left. There is net depletion of A and B and a net production of C and D.

When the reaction proceeds in the left direction, when A + B produces C + D, the rate is more than that of a reaction which takes place from C + D to A + B. Both the rates are balanced, that means neither reaction proceeds from left to right nor from right to left then the concentration of A, B, C, D are fixed. This corresponds to the equilibrium of chemical reaction.

Second law of thermodynamics deals with the two aspect. For a reversible reaction, the net reaction takes place in which direction, number one and number two if these attain equilibrium either on left or right, then there are three options. If the option is equilibrium that means the forward rate and reverse rate are same then what will be the equilibrium compositions of A, B, C, D? This is furnished by the second law of thermodynamics to the chemical reaction.

Let us consider a chemical reaction like this;

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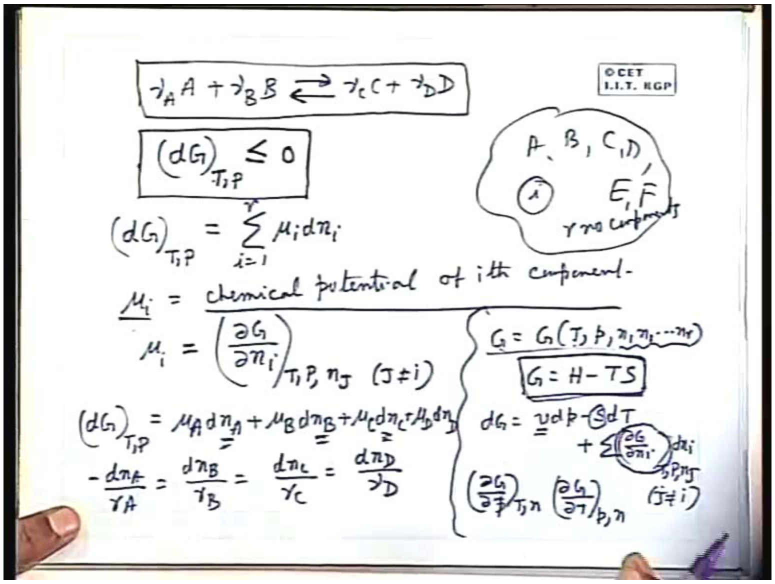

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$$\boxed{\nu_A A + \nu_B B \rightleftarrows \nu_C C + \nu_D D}$$

$$\boxed{(dG)_{T,P} \le 0}$$

$$(dG)_{T,P} = \sum_{i=1}^{r} \mu_i dn_i$$

A, B, C, D, E, F

ⓘ

r no components

μ_i = chemical potential of ith component.

$$\mu_i = \left(\frac{\partial G}{\partial n_i}\right)_{T,P,n_j} \quad (j \ne i)$$

$$G = G(T, P, n_1, n_2 \cdots n_r)$$

$$\boxed{G = H - TS}$$

$$dG = v\,dp - S\,dT + \sum \left(\frac{\partial G}{\partial n_i}\right)_{T,P,n_j} dn_i \quad (j \ne i)$$

$$\left(\frac{\partial G}{\partial P}\right)_{T,n} \quad \left(\frac{\partial G}{\partial T}\right)_{P,n}$$

$$(dG)_{T,P} = \mu_A dn_A + \mu_B dn_B + \mu_C dn_C + \mu_D dn_D$$

$$-\frac{dn_A}{\nu_A} = \frac{dn_B}{\nu_B} = \frac{dn_C}{\nu_C} = \frac{dn_D}{\nu_D}$$

nu$_A$A + nu$_B$B is a complete chemical reaction, but it is a reversible chemical reaction that means the products can be converted back to the reactants. The reaction can take place in both the directions. Let us consider the reaction to take place at a constant temperature and pressure.

We know that in this type of reaction, at constant pressure and temperature for equilibrium to be achieved, dG at constant temperature and pressure will be 0 which means for a physical process, the second law will be applied. Earlier, we discussed the Gibbs function. There are various ways, where we impose the directional constants as given by the second law. One of the ways is the entropy change of the universe, in a process that has to be greater than is equal to 0. In a cyclic process we know the cyclic integral of dq by t is less than equals to 0. In all the cases an equality sign represents the equilibrium conditions and inequality sign represents the feasibility condition.

Similarly, the Gibbs function at constant temperature and pressure should always be less than 0. For a process to be feasible that means for a physical process occurs in a particular direction the Gibbs function at constant temperature and pressure should be less than 0 and at equilibrium it should be equals to 0. By combining these two, we can write $(dG)_{TiP}$ less than equal to 0. We can write another stage. This is not so for taught to you that $(dG)_{TP}$, that is the change in the Gibbs function at any temperature and pressure for a multi component system having A,B,C,D,E,F…..r number of components. $(dG)_{TP}$ is given bysigma $mu_i dn_i$ i=1 to r, where mu_i represents the chemical potential of ith component.

The chemical potential of ith component, in a multi component system is defined like this: del G $deln_i$ with respect to the partial differential of Gibbs function with respect to the number of moles at constant temperature, pressure and other moles that means J not is equal to i. All other moles are fixed only the mole of that particular component is varied and the partial difference is defined as the chemical potential. mu_i is the chemical potential of the ith component. We consider G as a function of TP and mass, but in case of multi component system it is, n_1 n_2... n_r, the number of moles of all the components. If we make a total differential of it…. and using the definition G is equal to H minus $T_{S,}$ then you get the expression mu_i as del A del G del n_i.

If you get these, you will get dG is equal to vdp minus sdT plus sigma. If you write the equation; del G del ni at T, P, nJ where J not equals to i. If, it is del G then, you can write del G del p dp del G del s dT, here Tp del G del p dp del G del T dT, if you use this equation you get del G del T at del G del p at constant T and n.

From the definition, it will bedel G del T at constant p and n. If you make use of this, GH minus TS can be defined as the chemical potential of the ith component. I' am not going into much detail because, so far you have not been taught the chemical thermodynamics or thermodynamics of multi component system.

$(dG)_{T,P}$= $mu_A dn_A$+ $mu_B dn_B$+$mu_C dn_C$+mu_D dn_D, the change in the number of moles in a reactive multi component systems are not independent. There is another constraining equation with respect to this equation: dn_A by gamma A is equal to…..if we give a minus sign for one case that means the reactants have to give a plus sign, because these are the differentials we have to follow sign. Now, dn_C by $gamma_C$ is equal to dn_D by gamma D, which means another constraining equation for this change of moles are given by this. They are proportional to their stoichiometric coefficient, the change in the number of mole. If you use minus dn_B, then what results you get?

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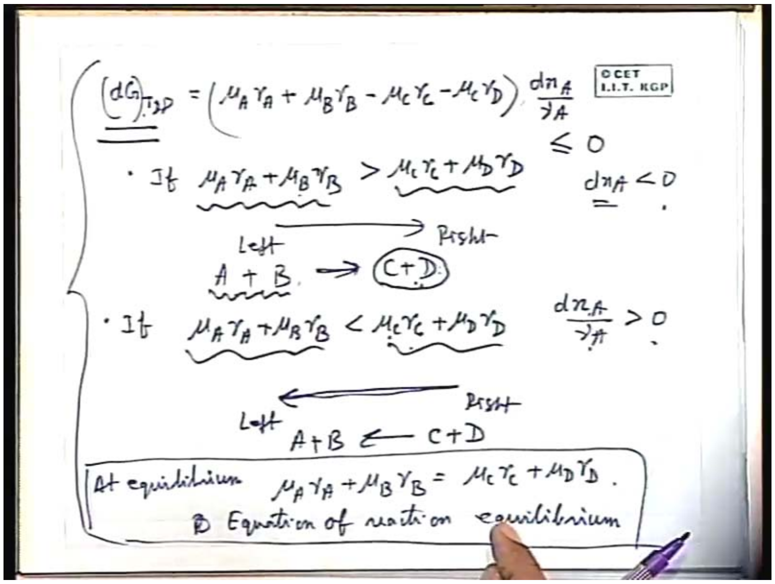

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$$(dG)_{T,P} = (\mu_A \gamma_A + \mu_B \gamma_B - \mu_C \gamma_C - \mu_C \gamma_D) \frac{dn_A}{\gamma_A} \leq 0$$

- If $\mu_A \gamma_A + \mu_B \gamma_B > \mu_C \gamma_C + \mu_D \gamma_D$ $\quad dn_A < 0$.

Left → Right

$A + B \rightarrow C + D$

- If $\mu_A \gamma_A + \mu_B \gamma_B < \mu_C \gamma_C + \mu_D \gamma_D$ $\quad \frac{dn_A}{\gamma_A} > 0$.

Left ← Right

$A + B \leftarrow C + D$

At equilibrium $\mu_A \gamma_A + \mu_B \gamma_B = \mu_C \gamma_C + \mu_D \gamma_D$.

B Equation of reaction equilibrium

You will get $(dG)_{T,P}$ at constant temperature and pressure is equal to mu_A $gamma_A$ plus mu_B $gamma_B$ minus mu_C $gamma_C$ minus mu_C $gamma_D$ times dn_A by $gamma_A$ means any of the reactants has to be there. I just replace dn_A dn_B dn_C dn_D by any of the term proportional to each other. I express everything in terms of dn_A by $gamma_A$ so that one dn_A by $gamma_A$ will come.

So, these quantities will be positive and this will be less than equals to 0, for the feasible process. There are two conditions, one condition is, if mu_A $gamma_A$ plus mu_B $gamma_B$ is greater than mu_C $gamma_C$ plus mu_D $gamma_D$ which means, some of the product of the chemical potentials and the stoichiometric coefficient of the reactants is greater than some of the products of the chemical potential and the stoichiometric coefficients of the products then the reaction should proceed from reactant to products that means from left to right, A + B gives C + D. In that case, dn_A has to be less than 0, to make it less than 0.

If mu_A $gamma_A$ + mu_B $gamma_B$ < mu_C $gamma_C$ + mu D gamma D, This quantity is already negative, that means dn_A $gamma_A$ has to be greater than 0. nA has to be produced from right to left. Net reaction will take place from C + D to A + B. It depends upon the relative magnitudes of these two sums. When mu_A $gamma_A$ plus mu_B plus $gamma_B$ is greater than this, it will proceed from, which means when some of the this is actually the chemical affinity. If this is more here then, it will go in this direction and dn_A is negative.

When this is more than mu$_C$ gamma$_C$ plus mu$_D$ gamma$_D$, some of the products of the chemical potential time and stoichiometric coefficients of this side is more than this side, hence the reaction will proceed from this to this. In that case dn$_A$ by gamma$_A$ has to be greater than 0 because the final constraining thermodynamic equation is $(dG)_{TP}$, which is less than 0. At equilibrium, mu$_A$ gamma$_A$ + mu$_B$ gamma$_B$ = mu$_C$ gamma$_C$ + mu$_D$ gamma$_D$. This is true for all reversible reactions and this is known as equation of reaction equilibrium.

In irreversible reactions, the products will never be converted back. The question may arise; why do not you write this equation for an irreversible reaction? For an irreversible reaction this is always greater than this one. This is true for all situations and we specially apply this for reversible reactions.

In unidirectional reaction equilibrium condition will come actually the chemical reactions is stopped. One of the reactants will be consumed. Which one will be consumed first, that reaction will stop. Sometimes, two may be consuming simultaneously if a stoichiometric coefficient is used, there was no reaction equilibrium. But, in a reversible reaction, there is a chemical equilibrium truly this is not equilibrium the process is taking place which means, reaction in both the directions are same at steady state mass in a controlled volume. Mass is invariant with time and control volume is steady with the mass. But, the mass flux processes are not seized, masses and are coming in and going out, thus balancing each other. This is the same concept for the reversible reactions.

We will find out an expression for the equation of reaction equilibrium.

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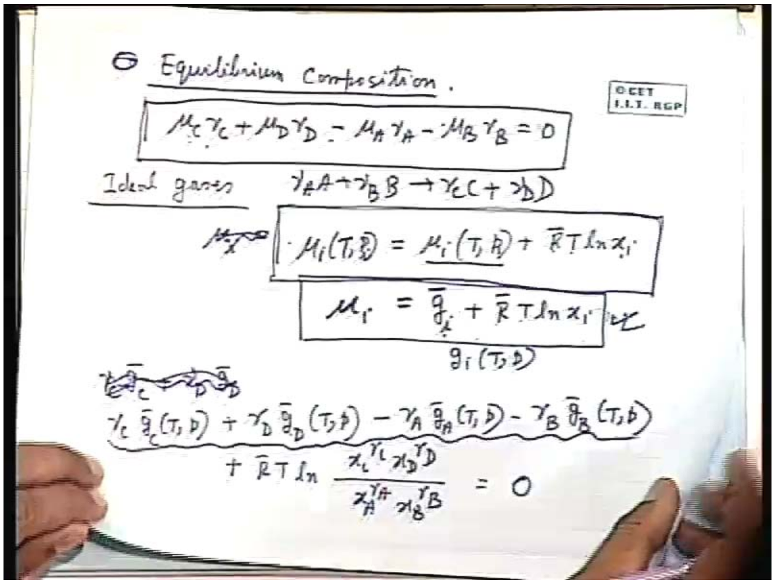

Equilibrium Composition.

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$$\boxed{\mu_C \gamma_C + \mu_D \gamma_D - \mu_A \gamma_A - \mu_B \gamma_B = 0}$$

Ideal gases $\gamma_A A + \gamma_B B \rightarrow \gamma_C C + \gamma_D D$

$$\boxed{\mu_i(T, p_i) = \underline{\mu_i(T, p)} + \bar{R} T \ln x_i}$$

$$\boxed{\mu_i = \underset{g_i(T,p)}{\bar{g}_i} + \bar{R} T \ln x_i}$$

~~$\gamma_C \bar{g}_C + \gamma_D \bar{g}_D$~~

$$\underbrace{\gamma_C \bar{g}_C(T,p) + \gamma_D \bar{g}_D(T,p) - \gamma_A \bar{g}_A(T,p) - \gamma_B \bar{g}_B(T,p)} + \bar{R} T \ln \frac{x_C^{\gamma_C} x_D^{\gamma_D}}{x_A^{\gamma_A} x_B^{\gamma_B}} = 0$$

Our final objective is to find out the equilibrium composition. We know that there is an instant, when the reversible reactions are in equilibrium, in both the directions the rates and chemical potentials are same. Therefore, to find out the equilibrium composition, we have to develop an expression for this reaction equilibrium. First, I write the reaction equilibrium equation; mu_C gamma_C - mu_D gamma_D - mu_A gamma_A - mu_B gamma_B = 0. The constituents will under equilibrium and this equation has to be valid.

If, we consider ideal gases, we can write, mu upon ideal gas ith component which is ideal gas with any temperature and pressure can be written as its value will be mu_i(T,P) plus RT ln x_i. This will not be reduced, if the thermodynamics of multi component system would have been studied. The chemical potential of an ith component in a mixture of multi component systems at temperature T, any component will be at the same temperature, as that of the mixture. At partial pressure, depending upon the constituent composition and the number of component can be written as the chemical potential at T and the total pressure of the mixture plus RTlnx_i. x_i is the mole fraction.

This can be written as the chemical potential of any component at the same pressure. The total pressure of the mixture and the temperature can be written as the molar Gibbs function of the ith component. This is R bar universal constant. When I deal with mole fraction, this will be universal. Therefore, mu$_i$ is the chemical potential of the ith component is equal to its molar Gibbs function at same temperature and pressure of the mixture.

Molar Gibbs function means the component will exist at the pure component at same temperature and pressure. What is molar Gibbs function? This is mu$_i$ is equal to g$_i$ bar plus R bar Tlnx$_i$. If you accept this equation and put this here, you get g and gamma$_C$ g bar c at temperature and presure plus gamma$_D$ g bar D at the same temperature and pressure of the mixture minus gamma$_A$ g bar A at the temperature and pressure minus gamma$_B$ g$_B$ T and P then the remaining part is R bar Tln, which is interesting that x$_C$ to the power gamma$_C$, x$_D$ to the power gamma$_D$ x$_A$ to the power gamma$_A$ x$_B$ to the power gamma B. For these 4 is equal to 0.

This is nothing but the change in the Gibbs function due to chemical reaction at T and P because, it is the Gibbs function of the product minus Gibbs function of the reactants. For a reaction gamma $_A$A plus gamma$_B$B gives gamma$_C$C plus gamma$_D$D. We just express this part as delta G$_R$ at T and P.

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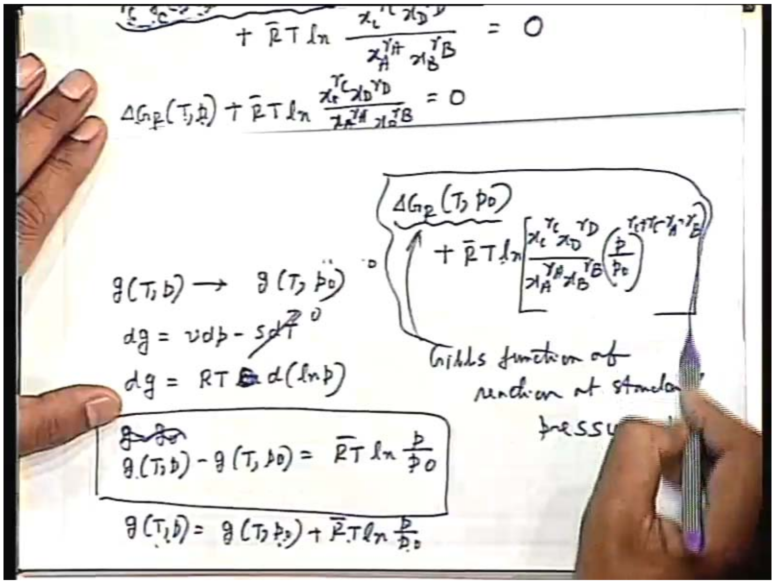

$$+ \bar{R}T \ln \frac{x_C^{\gamma_C} x_D^{\gamma_D}}{x_A^{\gamma_A} x_B^{\gamma_B}} = 0$$

$$\Delta G_R(T,p) + \bar{R}T \ln \frac{x_C^{\gamma_C} x_D^{\gamma_D}}{x_A^{\gamma_A} x_B^{\gamma_B}} = 0$$

$$\underbrace{\Delta G_R(T,p_0)} + \bar{R}T \ln \left[\frac{x_C^{\gamma_C} x_D^{\gamma_D}}{x_A^{\gamma_A} x_B^{\gamma_B}} \left(\frac{p}{p_0}\right)^{\gamma_C+\gamma_D-\gamma_A-\gamma_B} \right]$$

Gibbs function of reaction at standard pressu

$$g(T,p) \rightarrow g(T,p_0)$$

$$dg = v\,dp - s\,\cancel{dT}^{\,0}$$

$$dg = RT\, d(\ln p)$$

$$\boxed{g(T,p) - g(T,p_0) = \bar{R}T \ln \frac{p}{p_0}}$$

$$g(T,p) = g(T,p_0) + \bar{R}T \ln \frac{p}{p_0}$$

We can write, plus R bar Tln x$_C$ to the power gamma$_C$ X$_D$ to the power gamma divided by x$_A$ to the power gamma$_A$ x$_B$ to the power gamma$_B$ is equal to 0. delta G at TP is this plus this minus this minus this. I will just update g at T and P to g at T and some reference pressure P$_0$.

If you recollect your earlier definition; dg molar Gibbs function is vdp minus sdT. Molar Gibbs function for a pure component when the ith component is the pure component at constant temperature. I update pressure vdp and for an ideal gas, this dg is equal to RT d (lnp) dp by P is differential of lnp. This is the technique of writing these things. dg is RTlnp by p the dln. Therefore g of T and P minus g of T and P_0 that means you integrate this RTln p by p p_0.

The expression g(T,P) is 0 plus RTln p by p_0. If I substitute g at TP for all this C, D, A, B in terms of g(T, P_0) then this part will resemble with T_{P0} that means delta G_R(T,P) will be delta G_R(T, P_0). We can write delta G_R(T, P_0) but an extra term will come when I express RTln p by p_0, and will come out into gamma C RTln pby p_0 into gamma D RTlnp by $p_0$minus gamma A minus B. Ultimately, this will be added with R bar Tln x_C to the power gamma_C x_D to the power gamma_D. x_A to the power gamma_A x_B to the power gamma_B in top by p_0 to the power gamma_C plus gamma_D minus gamma_A minus gamma_B. I am expressing this at delta G at TP.

This will be gamma g_c bar, that is molar T, P_0 which is defined as delta G_R (T, P_0) which is the Gibbs function of reaction at standard state and standard pressure. Therefore, standard pressure or reference pressure P is 0. So, this will be an extra term and is R bar Tln p by P_0,which will be multiplied by the stoichiometric coefficient, positive and negative which is raised as power in ln because ln was already there they are clubbed together.

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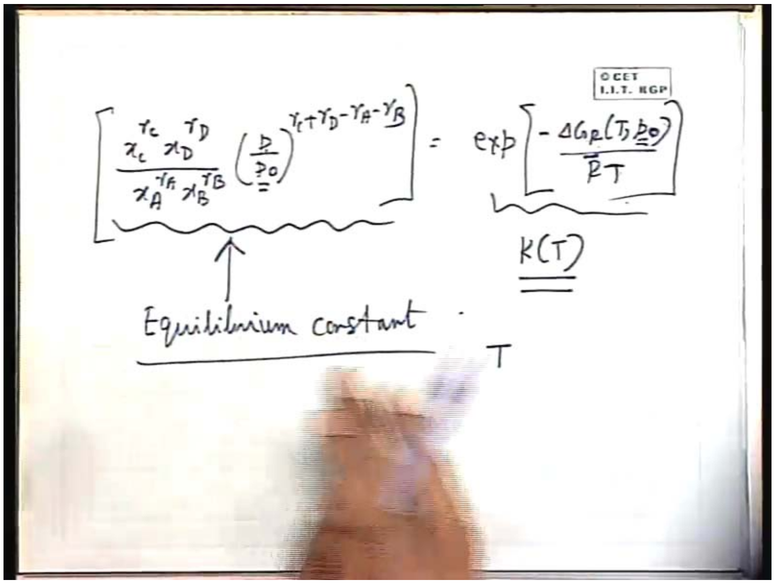

$$\underbrace{\left[\frac{x_C^{\gamma_C}\, x_D^{\gamma_D}}{x_A^{\gamma_A}\, x_B^{\gamma_B}}\left(\frac{p}{p_0}\right)^{\gamma_C+\gamma_D-\gamma_A-\gamma_B}\right]} = \underbrace{\exp\left[-\frac{\Delta G_R(T, p_0)}{\bar{R}T}\right]}_{K(T)}$$

Then x_C to the power gamma C, x_D to the power in a different fashion. This expression is equal to is always equal to 0 because I am writing this expression and substituting this 0 here. Therefore, gamma AxB gamma B into p by p0 to the power gamma C plus gamma D minus gamma A minus gamma B this thing is equal to exponential.

I am writing in other form minus delta G_R because this will go to other side of the equation divided by RT this is the final equation. Let the function of temperature be K(T) because, R bar T delta G_R(T, P) is 0. This is the standard reference pressure and it is a function of temperature.

Temperature and Gibbs function of equation reaction is fixed. Gibbs function of reaction, like enthalpy of reaction or internal energy of reaction is the change in the Gibbs function of the products minus reactant at that temperature. These are all functions of temperature. This part is a function of temperature and is known as equilibrium constant.

For a reaction at equilibrium, if the temperature and equilibrium constant is known from any tabulated value then this equilibrium constant equals to this. It gives a constraining equation. If I know the pressure of the equation and if it is an atmospheric or standard pressure, usually this is atmospheric pressure, and this part is 1. Otherwise, this will give a numerical value, which means, we get a constraining equation for the mole fractions of the equilibrium mixtures. I get constraining equations from the chemical equations and these two things are solved together to find out the values of x_C x_D x_A x_B. This theory will be made clearer if we follow this example.

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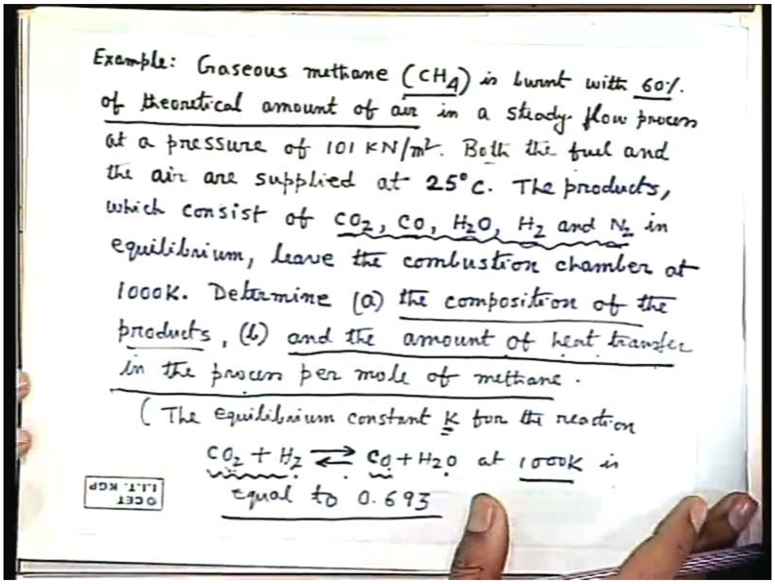

Example: Gaseous methane (CH_4) is burnt with 60% of theoretical amount of air in a steady flow process at a pressure of 101 kN/m². Both the fuel and the air are supplied at 25°C. The products, which consist of CO_2, CO, H_2O, H_2 and N_2 in equilibrium, leave the combustion chamber at 1000K. Determine (a) the composition of the products, (b) and the amount of heat transfer in the process per mole of methane.

(The equilibrium constant $\underline{K}$ for the reaction

$$CO_2 + H_2 \rightleftarrows CO + H_2O$$ at 1000K is equal to 0.693

Gaseous methane, CH_4 is burnt with 60 percent of theoretical amount of air. We have discussed earlier with 200 percent, 400 percent theoretical air. In a steady flow process at a pressure of 101 kilo Newton per meter square, both the fuel and the air are supplied at 25^0 Celsius. The products which consist of CO_2, CO, H_2O, H_2 and N_2 in equilibrium leave the combustion chamber at 1000 K. Determine the composition of the products and the amount of heat transfer in the process per mole of methane.

We want to know if this be the product of combustion then in equilibrium, CO_2, CO, H_2O, H_2, N_2 do not change in their composition and the compositions of the products are fixed. We have to find out the composition and the amount of heat transfer in the process per mole of methane.

The equilibrium constant K for the reaction is given that means this is the reaction which takes place. When carbon dioxide and hydrogen react with each other, they produce carbon monoxide and water vapor. Since, this is not a complete reaction. This reaction takes place, CO_2 + H_2 gives CO + H_2O that means always this reaction takes place in forward and backward direction at 1000K and the equilibrium constant is given as 0.693 for this reaction.

This will be clear if I proceed with this example. Enthalpy values are given like this.

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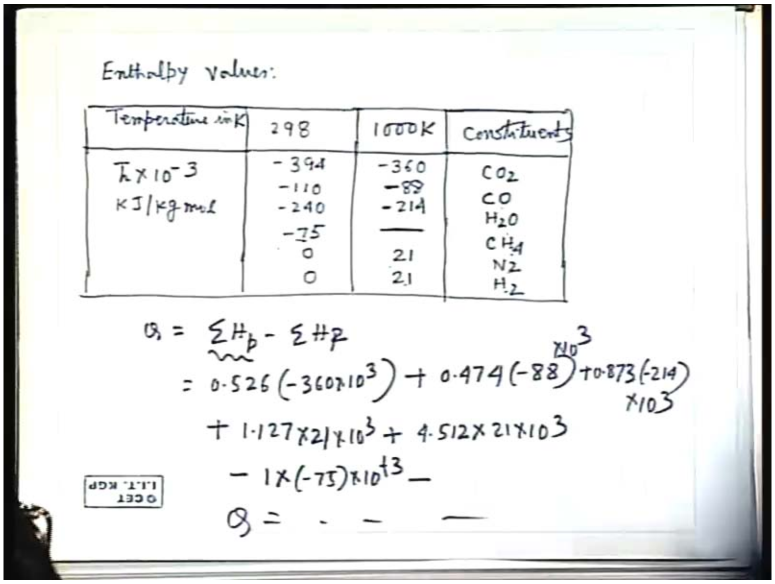

Enthalpy values:

Temperature in K	298	1000K	Constituents
$\bar{h} \times 10^{-3}$ KJ/kg mol	−394	−360	CO_2
	−110	−88	CO
	−240	−214	H_2O
	−75	—	CH_4
	0	21	N_2
	0	21	H_2

$$Q = \underset{\sim\sim}{\Sigma H_p} - \Sigma H_R$$

$$= 0.526(-360 \times 10^3) + 0.474(-88 \overset{\times 10^3}{)} + 0.873(-214) \times 10^3$$

$$+ 1.127 \times 21 \times 10^3 + 4.512 \times 21 \times 10^3$$

$$- 1 \times (-75) \times 10^{+3} -$$

$$Q = \; . \; - \; —$$

These are the different temperatures, 25 degree Celsius is the temperature at with the methane and air was supplied, 1000 K is the combustion products temperature and CO_2, H_2O, CH_4, N_2 are the constituents. Now you see how we proceed with this equation. First of all we have to write the chemical balance of these equations CH_4 + 0.6($2O_2$ + 2 × 3.76 N_2).

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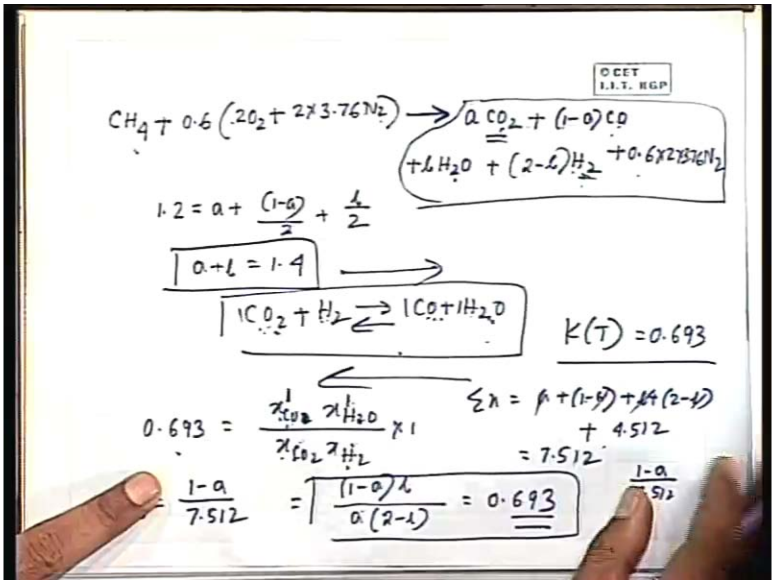

$$CH_4 + 0.6(2O_2 + 2 \times 3.76 N_2) \longrightarrow \boxed{a\,\underline{\underline{CO_2}} + (1-a)CO + b H_2O + (2-b)H_2 + 0.6 \times 2 \times 3.76 N_2}$$

$$1.2 = a + \frac{(1-a)}{2} + \frac{b}{2}$$

$$\boxed{a + b = 1.4} \longrightarrow$$

$$\boxed{1CO_2 + H_2 \rightleftarrows 1CO + 1H_2O}$$

$$\underline{K(T) = 0.693}$$

$$\Sigma x = \cancel{a} + (1-\cancel{a}) + \cancel{b} + (2-\cancel{b}) + 4.512 = 7.512$$

$$0.693 = \frac{x_{CO}^{1}\, x_{H_2O}^{1}}{x_{CO_2}\, x_{H_2}} \times 1$$

$$\frac{1-a}{7.512} = \boxed{\frac{(1-a)b}{a(2-b)} = 0.\underline{\underline{693}}}$$

$$\frac{1-a}{7.512}$$

Now, the question comes that why CO is coming? The complete formation of carbon monoxide, that hydrocarbon breaks but cannot completely form carbon di oxide. If this was 100 percent theoretical air, 200 percent no CO business.

CO2 +H_2, CO business is still there we will see afterwards because for a complete reaction it is not the amount that is required, it is the time we have to give. In a steady flow process, you will have to give the residence time. That means, the time for mixing and the time for the flow is important. If we consider time is sufficient then theoretical air or more than that we will give you carbon dioxide. Therefore, there is carbon dioxide and carbon monoxide.

Let us start with unknown carbon dioxide per one mole or methane. Then, carbon monoxide will be 1 minus…. I am trying to reduce the number of variables, if I write a mole of carbon is1…. Therefore 1 minus CO will be there. I will make the balance of O, from the left hand and right hand side. If b is, H_2Othen, probably you can follow 2 – b is H_2 because always I balance H_2 plus 0.6 into 2 into 3.76 N_2.

The entire CH_4 is burning means CH_4 is not there but it is converted to CO_2 and CO. If all the CH_4 is converted to CO_2 and H_2O, then I could have told this as complete combustion. When there is a CO_2 and H_2, from the enthalpy point of view this can again be burnt with oxygen to give water vapor and carbon dioxide because of which more heat will be generated, though it is not a correct term from thermodynamics point of view.

Temperature will be increased, that means some bonding elements remain, which is the reason for this type of burning reaction or combustion reaction is called incomplete. We can exploit enthalpy from this. Therefore, according to the concept; CO_2 and H_2O could have been there fully, if there was this thing or more than this.

When 0.6, with the deficient oxidizer, CO and H_2come into picture but concept lays else where I am writing the balanced equation, O_2, I get a plus b is 1.4. Nothing else is required to be balanced. Mass balance gives a relationship between the moles a plus b is 1.4. Now the concept is that the product, why are you making a complication, when the products are equilibrium? This is because there is a reaction which is possible, which is the products CO_2 + H_2 can react to give CO + H_2O and again CO + H_2.

We can understand that these constituents in the products are reacting and this reaction is possible. Hence, CO_2 + H_2 react with each other to produce CO and H_2O. Similarly, CO and H_2O have the affinity to react with each other to produce this. When one claims that, I get a product with fixed composition, it means that these reactions are in equilibrium. At the beginning of the problem, it is told that the equation defined by the reaction constant or equilibrium constant K(T) at that temperature of 1000K, where that is coming out is0.690.

Initially, it is difficult to appreciate, why these reactions come into consideration? In the product, this reaction is possible. If this reaction could have taken place in one of the directions, then one of the constituents: CO_2, H_2O could go on changing or four of the constituents go on changing, and not one so if it is going in this direction, they are depleted, and these are produced, increased vice versa but this is in equilibrium.

Now, I use the value 0.693 is equal to x_{CO} x_{H2O} x_{CO2} x_{H2}× 1.

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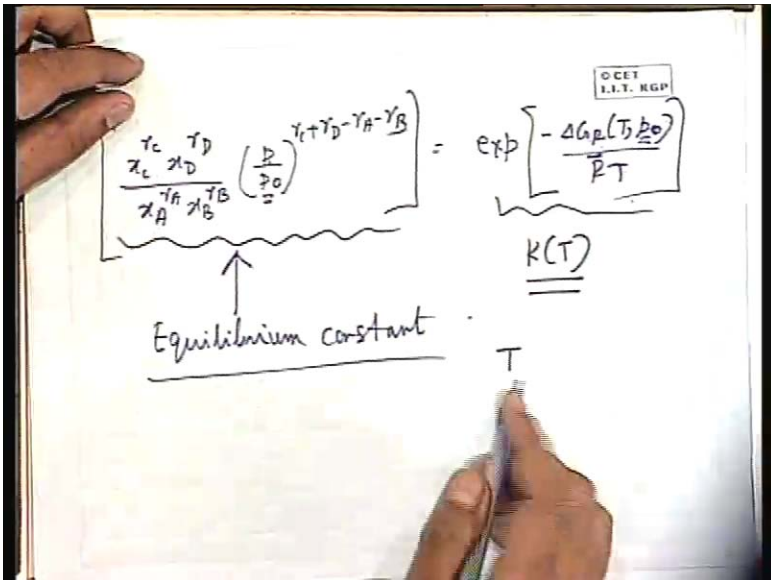

$$\underbrace{\left[\frac{x_C^{\gamma_C}\, x_D^{\gamma_D}}{x_A^{\gamma_A}\, x_B^{\gamma_B}}\left(\frac{p}{p_0}\right)^{\gamma_C+\gamma_D-\gamma_A-\gamma_B}\right]}_{\text{Equilibrium constant}} = \underbrace{\exp\left[-\frac{\Delta G_R(T, p_0)}{\bar{R}T}\right]}_{K(T)}$$

T

This is x_C gamma$_C$ x_D, these are the products: x_A x_B p by p0 is 1atmospheric pressure, 101 kilo Newton per meter square that is p0. Therefore, x of CO_2 to the power 1 is K (T). We have to find out x_{CO}, x_{H2O}, x_{CO2}, x_{H2}.

What is the total number of moles? a + (1 – a) + b +(2 – b) + …… This one is 4.512 and ultimately this becomes 7.512 because b, b cancels a, a cancels 2 + 137.512. Therefore, x_{CO} is 1–a/7.512. Actually you can cancel 7.512 because this is all to the power one only we can write the moles. A clever boy will write 1 – a × b ÷ a × 2 – b because denominators of all these are same, Total number of moles.

By stoichiometry, this is to the power 1. This is to the power 2. When the indexes are same, which means the number of moles cancels from the numerators and denominators. So, this is equal to 0.693 and you can find out one equation this and another equation.

You can find out values of a and b. Equilibrium composition is fixed, that means you can write the equation and tell the moles fractions. Now you require 7.512. For CO it is, 1 - a by 7.512. Now I write x_{CO2}.

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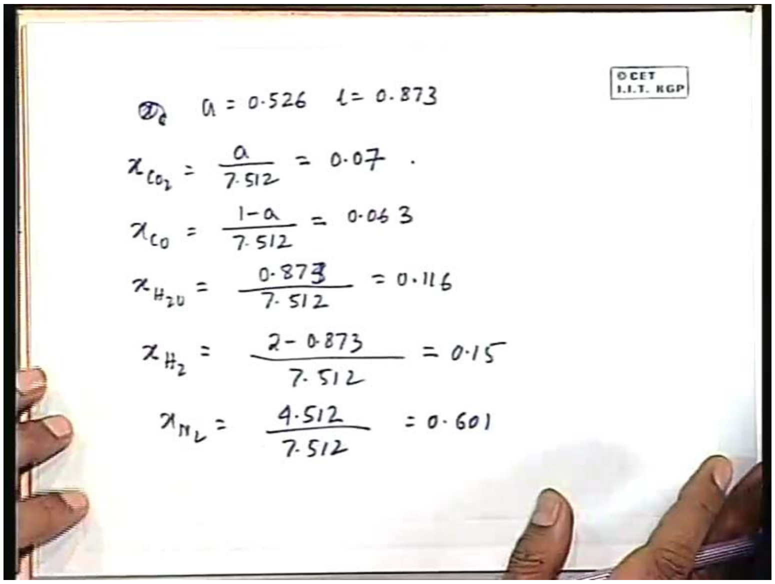

$a = 0.526 \quad b = 0.873$

$$x_{CO_2} = \frac{a}{7.512} = 0.07$$

$$x_{CO} = \frac{1-a}{7.512} = 0.063$$

$$x_{H_2O} = \frac{0.873}{7.512} = 0.116$$

$$x_{H_2} = \frac{2-0.873}{7.512} = 0.15$$

$$x_{N_2} = \frac{4.512}{7.512} = 0.601$$

a = 0.526 and b = 0.873, therefore the answer for x_{CO2} is a by 7.512. With the value of a, what is x_{CO2}? I do not know whether my calculations are correct or not. x_{CO} is 1 - a by 7.512 which comes to 0.063. Now, x_{H2O} = 0.873 ÷ 7.512 is 0.116.

xH_2= 2 – 0.873÷7.5 12= 0.15 and x_{N2} is 4.512, that is the number of moles of nitrogen on left hand side right hand side, same divided by 7.512. Now, you can write the chemical equation to find out the heat transfer.

The next part which is application of first law, the first part is the application of second law.

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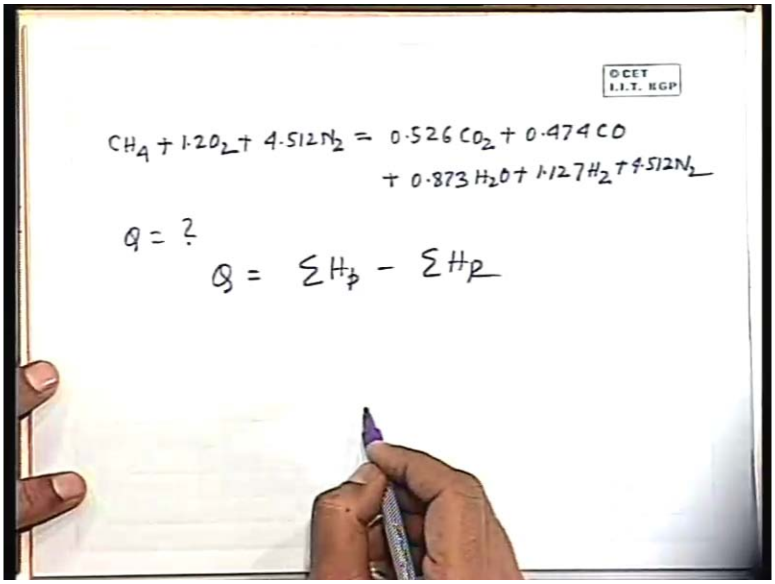

$$CH_4 + 1.2O_2 + 4.512N_2 = 0.526\,CO_2 + 0.474\,CO + 0.873\,H_2O + 1.127\,H_2 + 4.512\,N_2$$

$Q = ?$

$$Q = \Sigma H_p - \Sigma H_R$$

The equation will be CH_4 + 1.2 O_2 that is 60 percent of this, plus corresponding N_2. Initially it is equal to…. a is known 0.526 CO_2 + 0.474 CO + 0.873 H_2O + 1.127 H_2 + 4.512 N_2, these are chemical equation.

What is Q? Q is simply, sigma H_p minus sigma H_R. Sigma $H_p$is CH4.

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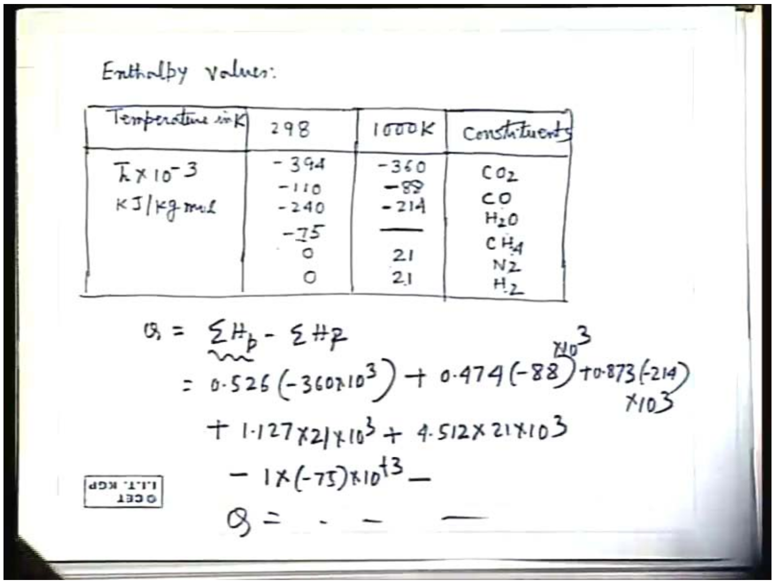

Enthalpy values:

Temperature in K	298	1000K	Constituents
$\bar{h} \times 10^{-3}$ KJ/kg mol	-394	-360	CO_2
	-110	-88	CO
	-240	-214	H_2O
	-75	—	CH_4
	0	21	N_2
	0	21	H_2

$$Q = \sum H_p - \sum H_R$$

$$= 0.526(-360 \times 10^3) + 0.474(-88)\times 10^3 + 0.873(-214)\times 10^3$$

$$+ 1.127 \times 21 \times 10^3 + 4.512 \times 21 \times 10^3$$

$$- 1 \times (-75) \times 10^{+3} -$$

$$Q = \cdot - \quad -$$

Q is equal to sigma H_p minus sigma H_R. You see that, sigma H_p is 0.526 CO_2. CO_2 is at temperature 1000K. You do not have to go to enthalpy of reaction, straight forward enthalpies are given. The enthalpy of CO_2 at 1000 K is -360×10^3interms of kilo joule plus 0.474 numbers of moles. The entire analysis is based on 1 mole of methane CH_4. CO is– 88 $\times 10^3$ very careful about putting the data and temperature, the products are at this temperature.

Therefore do not take the data from this column. H_2O is,0.873 (-214)$\times 10^3$ + (H_2)1.127 × 21these are all products, I am seeing the chemical equation and doing it 21× 10^3 + 4.512 ×(N_2) 21× 10^3, this is sigma H_p minus sigma H_R. What is H_R? CH_4 at temperature 25 degrees Celsius is not 0 that is its molar enthalpy of formation has to be there.

This reaction is at equilibrium in both the direction so for the entire theme of today's study is this that means this will react in forward and reverse direction. That is why, there are reactive species which can make reaction in both the directions and they are in equilibrium and this is the reason for which you get fixed composition of the constituent product.

If this reaction could have taken place in any of the net direction then could have been depleted or it could have been produced. It depends upon the condition that, mu_A $gamma_A$ + mu_B $gamma_B$ So this equality is greater than or less than mu_C $gamma_C$ plus mu_C $gamma_D$. If it is greater than this, in this direction, and less than this in this direction and equals reaction equilibrium from which we derived the expression for the equilibrium constant. This reaction is at equilibrium then only you will get a constant composition mixture.

This is the case where you get constant composition otherwise, you could not get either CO_2 was continuously depleted or H_2depleted and these are produced. Until and unless it is totally consumed the reaction is totally stopped. It continuously takes place, but it does not happen so when it takes place is just like other transport processes.

Some of the product of the chemical potential times the stoichiometric coefficient of one pair is going to be reduced and another pair are going to increase, so that at some condition they are balanced and this is the subject of chemical kinetics; it can be proved from chemical kinetics. The reaction equilibrium will occur when, the rate of reaction in the forward direction equals to the rate of reaction in the backward direction.

We conceive in this way, that both the reaction balances each other but they oppose in such a way that the reaction seizes toward. From the chemical rate equation or chemical kinetics, one can express the same result, which we have done from the consideration of thermodynamics; which is the expression for the reaction equilibrium.

Though there is a distant difference from chemical kinetics with thermodynamics, as I have told in the very first class of thermodynamics that classical thermodynamic deals with equilibrium system, they do not deal with the rate of transfer of energy, which is del for heat in heat transfer and del for momentum in the momentum transfer of fluid mechanics.

Similarly for chemical equation, the rate of equations is delta with the subject, chemical kinetics, which is as distinct from thermodynamics. But the concept of chemical equilibrium is still there and the same equation can be derived from the consideration of chemical kinetics, but we have derived it from the consideration of thermodynamics.

Therefore, second law tells under what condition the chemical equilibrium will exist for a reversible reaction, whether or not chemical equilibrium will be there, if chemical equilibrium does not exist, in which direction the reversible reaction will occur. So, these two things are very important or to be predicted by the second law of thermodynamics applied to a chemical reaction.

First law is the typical conservation of energy where you have to understand the enthalpy of formation. How do you define the enthalpy of formation or internal enthalpy formation? All elements having zero internal energy and zero enthalpy at the standard conditions 25^0 Celsius and one atmospheric pressure, 100 kilo Newton per meter square, say approximately 101 kilo Newton per meter square, whereas the compounds reveal some enthalpy, which is the enthalpy of the reaction by which the compounds has been formed from their elements at that standard conditions.

Thank you.