Lecture - 12

First Law and Second Law of Thermodynamics Applied to Combustion - Part 04

Chemical Equilibrium

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We saw that in the calculation of adiabatic flame temperature, we need the product composition. The product composition should be determined properly in order to get accurate value of the flame temperature.

For example, consider methane reaction with air; $CH_4 + 2(O_2 + 3.76N_2)$ giving $CO_2 + 2H_2O + 7.52N_2$, complete combustion is assumed here. The major products dissociate due to high temperatures. We have seen that CO_2 dissociates to $CO + \frac{1}{2} O_2$; H_2O dissociates to $H_2 + \frac{1}{2} O_2$. So, the product mixture will have CO, H_2 and O_2 in addition to what we actually assume as a complete combustion product. So, if you see the product mixture, it will have some moles of CO_2, say a moles, b moles of CO and c moles of H_2O, d moles of H_2 and e moles of O_2.

$$CH_4 + 2(O_2 + 3.76N_2) \rightarrow aCO_2 + bCO + cH_2O + dH_2 + eO_2 + 7.52N_2.$$

But you can also add several species in this and you can extend the list as we want. To determine these unknowns here, the number of moles a, b, c, d, e, you need five equations; but you have only three equations by carbon, hydrogen and oxygen balance. So, two more equations are required.

These two more equations are actually derived from equilibrium equations. So, CO_2 dissociate into $CO + ½ O_2$ or H_2O dissociating to $H_2 + ½ O_2$, these two equations are called equilibrium equations. They are molecular level equations; one CO_2 molecule dissociates to CO and O_2.

These two equilibrium equations should be used somehow and the two more equations which are required to complete the set of equation should be produced. Three atom balances will produce the remaining three equations.

So, two more equations from these two equations can be generated so that five equations can be generated with the five unknowns a, b, c, d and e so that you can solve that to get the product information. But please understand that this product, the number of moles of this is dependent on temperature itself.

So, that is a main problem here. That means your iterative process becomes more complex. Previously we saw that for adiabatic flame temperature, even if the product composition is known, then we have to first guess the temperature and find H_P, compare it with H_R and see whether they are equal or else you have to re guess and iteratively solve for this temperature.

But in this case, you have additional steps, you first guess the value of product temperature T_P, then you calculate equilibrium products a to e, you have to calculate by using 3 atom balance equations plus 2 equilibrium equations given here and then calculate H_P, the enthalpy of the product mixture.

If it is same as that of H_R or the difference between H_P and H_R is negligible, then its fine. If it is non-negligible, then you have to assume another value of T_P, then additional step is again you have to calculate the equilibrium products at that temperature. That means, this equilibrium products are dependent on temperature. For that, you we need what is called second law concepts.

So, that is what we are going to see further.

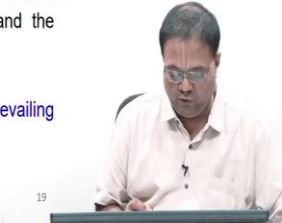(Refer Slide Time: 04:03)

Chemical Equilibrium

Equilibrium products are calculated using second law based concept called chemical equilibrium.

When a major product such as CO_2 is at high temperature, say 2000 K, it undergoes a dissociation reaction given as, $CO_2 \leftrightarrow CO + 0.5\ O_2$.

The system or control volume has these three species in some proportions, which is dependent on prevailing temperature and pressure. The reaction is reversible. As it is written above, forward (dissociation) reaction is endothermic and absorbs heat and the reverse reaction is exothermic.

The extent to which the reaction occurs depends on prevailing temperature and pressure.

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So, chemical equilibrium allows us to determine the equilibrium products as a function of temperature and pressure. Now, consider this equation, dissociation of CO_2 which is a one of the major products. When a temperature of 2000 K or this order comes, then you can see the dissociation of CO_2 occurring.

At lower temperatures, it may not occur. This equation is a reversible equation. $CO + \frac{1}{2}\ O_2$ can form CO_2; CO_2 can also dissociate to form $CO + \frac{1}{2}\ O_2$ and based upon the temperature either the forward reaction, which is dissociation can occur or the backward reaction can occur. Even if you maintain temperature as constant, then to some extent these reactions will occur.

The rate at which these reactions occur in the forward and backward direction will be the same at a given temperature. You have to find what it is. Based upon the temperature, the extent will be varying. Now, if you fix the temperature and pressure of the combustion chamber which may be a system or control volume, then based upon this some amount of CO_2 will dissociate and the reverse reaction will also be frozen. Both will be at the same rate so that you get in the products all the three species in some proportions. How to find the proportions at a given temperature and pressure? for that, you need second law concepts.

Chemical Equilibrium

At the given pressure and temperature, let α kmol of CO_2 dissociate from its initial value of 1 kmol. Then as per the reaction, α kmol of CO is formed and $\alpha/2$ of O_2 is formed. Then, the mixture has $(1 - \alpha)$ kmol of CO_2, α kmol of CO and $\alpha/2$ kmol of O_2.

An important property related to II law is entropy. This property is used to determine the feasibility of a process. In this case, it can be used to check up to which extent the reaction can proceed.

Entropy of a species depends on both temperature and pressure. It has a value at T_{ref} = 298 K. Its value increases due to an increase in temperature from T_{ref} to T. Its value also changes depending upon the value of the partial pressure of the species.

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Now, let us assume that α kilomoles of CO_2 dissociate. If α kilomoles of CO_2 dissociates number of kilomoles of CO formed is α and $\alpha/2$ kilomoles of O_2 is be formed

So, initially if CO_2 is say 1 kilomole, then in the mixture, you will get $1-\alpha$ kilo mole of CO_2, α kilomole of CO and $\alpha/2$ kilomoles of O_2. So, this is the mixture you have. We have to find α.

This α is determined at a given temperature and pressure. So, this is a function of temperature and pressure. For a given temperature and pressure, this may be evaluated by using the 2nd law concepts.

An important property which is derived using the 2nd law is the entropy. Entropy will tell about the feasibility of a process whether the process can occur or not. The direction of the process, direction of flow and several things, it is very useful and for calculating irreversibility.

So, entropy is a very important property. In this case, we are going to use entropy to derive few more properties which are going to be helpful for us in determining the chemical equilibrium.

Now, let us just see how entropy of a species is first calculated. Entropy of a species depends both on temperature and pressure. Unlike enthalpy, which is only dependent on temperature, because we are assuming that the mixture of reactants or products should be ideal gas. For ideal gas enthalpy is only a function of temperature; on the other hand, entropy is a function of both temperature as well as pressure.

So, it has a value at standard reference temperature 298 K and its value increases due to increase in temperature from 298 K to any temperature T where we are going to fix the system or control volume.

Similarly, it has a certain value at atmospheric pressure; if the total pressure of combustion varies, partial pressure of species also will vary. Depending upon the partial pressure of the species, the value of entropy will change. So, entropy depends both on temperature and pressure.

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We can write the specific entropy in molar unit J/kmol-K, we can write this for any species i; so, s_i is the entropy of any species at a given temperature T and p_i is the partial pressure of species. It is not equal to atmospheric pressure. So, even if the combustion occurs at atmospheric pressure since the partial pressure of the species is different than the atmospheric pressure, you will have a pressure dependence. Now, you split the term into two. The first term is the standard entropy value of the species i.

$$\bar{s}_i(T, p_i) = \bar{s}_i(T_{ref}, p_0) + \int_{T_{ref}}^{T} \bar{c}_{p,i} \frac{dT}{T} - R_u \ln \frac{p_i}{p_0} = \bar{s}_i(T, p_0) - R_u \ln \frac{p_i}{p_0}$$

So, it is calculated at the reference temperature of 298 K and atmospheric pressure p_o. You can put p superscript 0 or a p subscript 0. Both represent atmospheric pressure. T reference is 298 K.

Now, if the temperature is different than the reference temperature, then you have to integrate this. So, the second term is got by integrating $c_p dT / T$ from T_{ref} to T. So, integrating the second term from T_{ref} to T will give you the change in entropy due to temperature change.

So, that should be added to this. Similarly, pressure is different than the atmospheric pressure or any operating pressure. Operating pressure may be p, it may not be equal to atmospheric pressure always. So, partial pressure will be different.

Since the pressure is different than the atmospheric pressure p_0. This is the pressure dependence term, $-R_u$ natural log of partial pressure of the species i divided by the atmospheric pressure. These additional terms are added to get the entropy of a particular species at a particular temperature T and its partial pressure p_i. Now, the first two terms are clubbed as this.

Entropy of these species at the given temperature T, but at atmospheric pressure; then add the pressure dependence here $-R_u \ln(p_i/p_0)$. So, this is the way you calculate the entropy of a given species at a particular temperature and particular partial pressure. Now, once you know the entropy of all the species. Then the entropy of the mixture is calculated at any temperature.

It may be a flame temperature or any other temperature and the operating pressure is p. Now, you please see that this is the total pressure at which the combustion chamber is operated when you sum up all the partial pressures of species, you will get the total pressure.

Now the entropy of the mixture at a given temperature and pressure is nothing but the entropy of the particular species multiplied by the number of moles.

$$S_{mix}(T_f, p) = \sum_i N_i \bar{s}_i(T_f, p) = (1-\alpha)\bar{s}_{CO_2} + (\alpha)\bar{s}_{CO} + (\alpha/2)\bar{s}_{O_2}$$

You do the same thing what we do for enthalpy. So, in this case, if 1-α moles of CO_2 is present, then $S_{CO2} \times$ 1-α is the entropy of CO_2 calculated at that temperature. Similarly, α × S_{CO} and α/2 × S_{O2} are the entropy of CO and O_2, respectively. Please understand that when you do the calculation, pressure should be partial pressure of the species. So, you calculate the entropy of the mixture.

Now, once you know the entropy of the mixture, when you have an isolated system or an isolated control volume, there is no heat interaction or work interaction; especially when there is no heat interaction, entropy cannot change.

So, entropy can change either due to heat interaction or reversibility. Any irreversible process occurring in the system will change the entropy or if heat is transferred to the system, it will change the entropy. If heat is rejected by the system, it will also change the entropy.

So, entropy can change due to heat interaction or irreversibility. When I say its isolated system, there is no heat interaction, so, entropy cannot change due to heat interaction, it can change only due to irreversibility.

When there is an irreversibility, entropy always increases. If there is no irreversibility, entropy will be same. So, isentropic process is nothing but a process where entropy remains constant. So, dS = 0. So, either dS = 0 or can be greater than 0, if there is any irreversibility.

Obviously, in this case reaction is going to take place; chemical reaction its highly irreversible. So, we expect dS to be greater than 0. When the equilibrium condition prevails, the reaction stops; that means, there is no irreversibility anymore and there is no heat transfer also. In that case, dS will be equal to 0.

So, that is the chemical equilibrium condition dS = 0. That means, at that particular point, S_{mix} should become maximum. So, if you want to evaluate the equilibrium condition, the entropy should be at its maximum value.

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Now, entropy cannot be always used for our calculations, for example, when I say dS = 0, there is something we should write dS at a constant U, constant V and constant mass equal to 0, for equilibrium. That means, internal energy is constant, at a given internal energy, volume and mass this dS = 0. We cannot find the condition like this everywhere. Actually, what happens is when you assume a constant volume process is in equilibrium, if entropy is specified to be constant, then internal energy assumes the minimum value.

On other hand, if internal energy is specified to be constant, then dS = 0; that means, entropy assumes a maximum value. But we cannot have internal energy to be a constant, it is not possible for us to make internal energy to be constant; in fact, it will not be.

So, if neither S nor U is constant; then, what happens? Then, a quantity called U - TS will assume a minimum value. Minimum value, please understand it is not a maximum value.

This quantity U - TS is called a free energy, it is called Helmholtz free energy and it is given as letter A; capital A.

So, when there is a constant volume combustion occurring, if the quantity U - TS which is the Helmholtz free energy, A, assumes a minimum value, then equilibrium is said to be prevailed; chemical equilibrium is attained. Now, for constant pressure process you define enthalpy like this $H = U + pV$.

Even though its derived from constant pressure process, it is a property at a state point basically a state function. Now, similar to that we can derive Gibbs free energy, that is G, $G = H - TS$.

So, here $U + pV - TS$, that is the G. You can derive the G just like how you derive the value of H. Now, this Gibbs free energy is used for constant pressure process and this Gibbs free energy attains a minimum value at the equilibrium for a constant pressure process.

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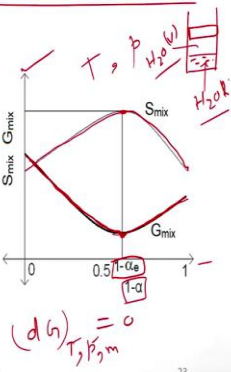
So, similar to constant volume process, where Helmholtz free energy attains a minimum value, in a constant pressure process, Gibbs free energy attains a minimum value at equilibrium. This is an important point.

So, as I told you, we are deriving two more properties; one is called Helmholtz free energy corresponding to a constant volume process or Gibbs free energy for the constant pressure process, both involving entropy in it; so, TS. H - TS is the Gibbs free energy and U - TS is the Helmholtz free energy.

Now, since entropy is involved in this, Gibbs free energy is a function of both temperature as well as pressure because you can see H is temperature dependent only for ideal gases; but since S is dependent on pressure, G will also be dependent on pressure.

For instance, if the mixture entropy and mixture Gibbs free energy are plotted like this; here in this plot in the y axis, I plot mixture entropy and mixture free energy on different scales and I plot the extent of reaction in the x axis.

So, if I am just saying I am plotting the number of moles of CO_2, 1-α. See it varies from 0 to 1. So, when I say it is varying from 0 to 1, for example, then the plot goes like this. Now, you can see that the entropy increases and turns like this.

That means, any particular reaction is taking place either in a forward or backward reaction, when it reaches a maximum, you reach the equilibrium condition. So, S_{mix} attaining a maximum value or dS equal to 0 represent the equilibrium condition. This is the mole the number of moles of CO_2 at the equilibrium 1-α_e.

Similarly, a backward reaction can occur starting from here and it may reach a maximum value. Here, equilibrium is set to prevail. Now, this is for a given temperature T and pressure p, total pressure is p please understand that. So, when you vary the temperature or pressure, this maximum value will shift; that means, 1-α_e value will shift according to the pressure and temperature.

Similarly, when you take G; G shows a decreasing trend that means that some reaction is taking place and it reaches a minimum value, where the equilibrium condition is reached.

This is for the reverse; reverse of the reaction and this. So, both can take place. For example, if you have a piston cylinder arrangement in which water and water vapor is there.

So, its fully water, this is liquid and this is vapor. So, in its own vapor, liquid water is prevailing and it is a piston cylinder arrangement so that pressure p is maintained at a whatever value you want. Now, the temperature is T. So, what happens now under this condition? the mass will not change; mass is remaining constant.

So, constant mass, temperature is constant, pressure is constant; that means, Gibbs free energy should be constant. The Gibbs free energy of the liquid water will be equal to the Gibbs free energy of the vapor. This is called phase equilibrium. That means, the dG totally is equal to 0. So, we can write at equilibrium dG at a given temperature, pressure and the mass will be equal to 0.

So, this is the phase equilibrium. In this case phase equilibrium defines the condition that the number of molecules leaving the liquid to the vapor phase will be equal to the number of molecules leaving the vapor to the liquid phase.

So, that is a dynamic system. It can be seen that the vaporization is occurring at a same rate as the condensation; but the number of moles or the energy level of the liquid and the energy level of vapor is preserved in terms of Gibbs free energy.

Similar to that, the forward reaction can occur when there is a decrease in the Gibbs free energy; reverse reaction can also occur. But once this minimum value is reached, there equilibrium prevails.

So, for a given temperature and pressure, there is a definite equilibrium value for the products that is $1-\alpha_e$ for CO_2 that means, the others will have α_e CO and $\alpha_e/2$ O_2. So, this is the equilibrium value.

So, that is dependent on pressure. The condition for that is dG = 0 at a given temperature and pressure. So, how to do that? You know how to calculate enthalpy, you know how to calculate entropy, combining this you can calculate the Gibbs free energy.

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Now, Gibbs free energy change. So, we are interested in the Gibbs free energy change dG that should be equal to 0 for equilibrium. So, how to calculate dG? Let us first take a non-reactive system. Number of moles of any species does not change. If the number of moles of species does not change, we do not even require to get that into the equation.

So, G = H - TS; that means, dG = dH - TdS - SdT. Now, you can use the TdS relationship. TdS = dH - Vdp. So, use this equation and you get dG = -Vdp – SdT. So, this is the equation which we can use to find the change in the Gibbs free energy for a non-reactive system.

Now, you can say that G is a function of p and T.

$$dG = \left(\frac{\partial G}{\partial p} \right)_{T,n} dp + \left(\frac{\partial G}{\partial T} \right)_{p,n} dT$$

So, dG is nothing but dou G by dou p at constant T,n dp plus dou G by dou T at constant p,n dT. Now, we can see that dou G by dou p is nothing but -V.

Similarly, dou G by dou T at constant p,n is nothing but -S. From this you can equate this and see. Now, if there is any reaction or any phase change the number of moles is going to change, then we want to add few more terms here.

$$\mu_1 = \left(\frac{\partial G}{\partial n_1} \right)_{p,T,n_2}$$

$$\mu_2 = \left(\frac{\partial G}{\partial n_2} \right)_{p,T,n_1}$$

See for example, in a reactor system having some n_1 kilomole of reactants and n_2 kilomole of products. Let us group the reactants into one species say reactant species, and product into product species. So, when reactants are consumed, product will be formed. Let the n_1 kilomole of reactant be present, n_2 kilomole of product be present. Now the n_1 and n_2, they are not going to be constant. So, initially n_1 maybe some number and n_2 may be 0 Now, as the reactants are consumed n_1 decreases and n_2 increases ok. That is what you have to take into account here. Now the change in the number of moles of the reactants is dn_1, change in number of moles of products is dn_2. -V corresponds to dou G by dou p at constant T.

Similarly, μ_1 here will correspond to partial change of G with respect to n_1 when temperature, pressure and n_2 is constant. Now, since there are other variables, when one variable varies partially, if you want differentiate, then another variable should become constant.

So, μ_1 is nothing but dou G by dou n_1 when pressure, temperature and the product moles remaining constant.

So, this is called a chemical potential. How the free energy varies with respect to number of moles of the reactant that is called chemical potential or partial molal Gibbs function with respect to a particular species; reactant species for example. So, this is the way you write this. Similarly, μ_2 will be equal to dou G by dou n_2 when pressure temperature and n_1 or held constant.

Now, $\mu_1 \times dn_1$ will give you the change which happens when there is a change in the number of moles of reactant species. Similarly, $\mu_2 \times dn_2$ will give the change in the Gibbs free energy, when there is a change in the n_2 or number of moles of product species. Now, at a constant pressure and temperature these term dp and dT goes to 0.

So, you can write this like this. I am just now changing μ_1. So, this is nothing but I am saying it is $\bar{g}_1$. So, dou g by dou n_1, partial molal change I am writing as $\bar{g}_1$. Similarly, this is $\bar{g}_2$.

Now, I can say that $dG = \bar{g}_1 \times dn_1 + \bar{g}_2 \times dn_2$ So, how to calculate these g's that is what is going to be next step.

Partial Molal Free Energy Function

$$dG = \bar{g}_1 dn_1 + \bar{g}_2 dn_2$$

Therefore, the condition for equilibrium for constant pressure process is given by dG = 0. The **partial molal Gibbs function** may be estimated at any temperature and pressure as,

$$\bar{g}(T, p) = \bar{h}(T, p) - T \bar{s}(T, p)$$

$$\bar{g}_i(T, p_i) = \bar{h}_i(T) - \left(T \times \bar{s}_i(T, p_0) - R_u T \ln \frac{p_i}{p_0} \right) = \bar{g}_i(T, p_0) + R_u T \ln \frac{p_i}{p_0}$$

For a constant volume process, partial molal Helmholtz function of a species is calculated from the partial molal Gibbs function as,

$$\bar{a}_i(T, p_i) = \bar{g}_i(T, p_i) - p_i \bar{V}$$

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Let us now calculate the value of $\bar{g}_1$ and $\bar{g}_2$ bar. Now, for that what we try to use is the definition of g.

$$\bar{g}(T, p) = \bar{h}(T, p) - T \bar{s}(T, p)$$

$$\bar{g}_i(T, p_i) = \bar{h}_i(T) - \left(T \times \bar{s}_i(T, p_0) - R_u T \ln \frac{p_i}{p_0} \right) = \bar{g}_i(T, p_0) + R_u T \ln \frac{p_i}{p_0}$$

So, g at any temperature T and p can be calculated as h at the given temperature and pressure, for ideal gases pressure dependence will not be there for enthalpy, so, $\bar{h}$ (T) - T$\bar{s}$ (T, p).

Now, entropy will be dependent on both temperature as well as pressure. Let us try to do for given species, then we can apply the mixture rule mixing rule for this. So, take the ith species which is at temperature T and partial pressure p_i; i^{th} species has a partial pressure of p_i that is x_i into p.

The enthalpy of the species is $\bar{h}_i$ (T) which is nothing but the formation enthalpy $\bar{h}_{fi}$ (298 K) + $\Delta \bar{h}_i$ (T), that is the sensible enthalpy. We can calculate and you know how to calculate this. So, $\bar{h}_i$ (T) will be the enthalpy of the ith species at given temperature. Now, coming to the entropy, entropy has two terms; $\bar{s}_i$ (T, p$_o$).

This means $\bar{s}_i$ of the ith species is calculated at temperature of T, but atmospheric pressure p$_0$ and the pressure dependence comes by the second term -R$_u$ln(p$_i$/p$_0$). So, that will be the pressure dependence of this particular term. When you combine this, you can see that T $\times$ [$\bar{s}_i$ (T, p$_0$) - R$_u$ln(p$_i$/p$_0$)] that will be the entropy.

Now, let us gather the first two terms; $\bar{h}_i$(T) - T $\times$ $\bar{s}_i$ (T, p$_0$). So, these two terms I tried to gather and put it as $\bar{g}_i$(T, p$_0$); this is nothing but the Gibbs function of the ith species at the given temperature T calculated at atmospheric pressure p$_0$. So, that is the first term. Then, pressure dependency of the Gibbs function which is arising due to the pressure dependency of the entropy will be given in the second term R$_u$ ln(p$_i$/p$_0$) $\times$ T.

So, that is the second term which is coming here. When you try to calculate the Gibbs function for a particular species at a given temperature and its partial pressure, we split that into two terms; $\bar{g}_i$ of the particular species i, $\bar{g}_i$(T, p$_0$), which is calculated atmospheric pressure plus the pressure dependency coming due to this second term R$_u$T ln(p$_i$ /p$_0$).

Now, you can use tables which directly give the Gibbs function of the particular species as a function of temperature and calculate the first term or you can calculate the enthalpy of ith species at a temperature and use the formula $\bar{h}$ - T$\bar{s}$ to calculate $\bar{g}$.

So, entropy also we can take from the tables and you can calculate $\bar{g}$. So, either way you can calculate the value of $\bar{g}$ at a given T, but calculated at the atmospheric pressure p$_0$ and the second term is obvious, you know the mole fraction of the particular species. From that, you can calculate the partial pressure. Mole fraction into total pressure will be the partial pressure. So, use that to calculate this. So, both temperature and pressure control the value of $\bar{g}$. Now, for constant volume process, you need partial molal Helmholtz function A.

So, we calculated internal energy by first calculating the enthalpy. So, using the definition of the enthalpy, H = U + pV, we calculated U as H - pV. Similar to that, I calculate the Helmholtz free energy or Helmholtz function as a function of Gibbs free energy and pV here.

$$\bar{a}_i(T, p_i) = \bar{g}_i(T, p_i) - p_i V$$

So, I can write $\bar{a}_i$ which is the molal based Helmholtz free energy at a given temperature and partial pressure of the ith species will be equal to Gibbs function which I calculated above at the given temperature and the partial pressure minus p$_i$ into V for a constant volume process. So, we can calculate the Helmholtz free energy. So, we illustrate this for Gibbs free energy, then we use the Gibbs free energy to calculate the Helmholtz free energy like we first calculated enthalpy, and then calculated internal energy.