Fundamentals Of Combustion (Part 1)

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Lecture - 07
Thermodynamics of Combustion (Contd.)

In the last lecture we discussed about, the basic definition of thermodynamics and we learnt about the energy and as I told earlier the energy is an enticing property or entity, that governs all the activity of the entire universe and today also in the towards end we discuss about, ideal gas law and we will have to see, how these actual gas will be deviating from the ideal gas law for that, we need to look at basically.

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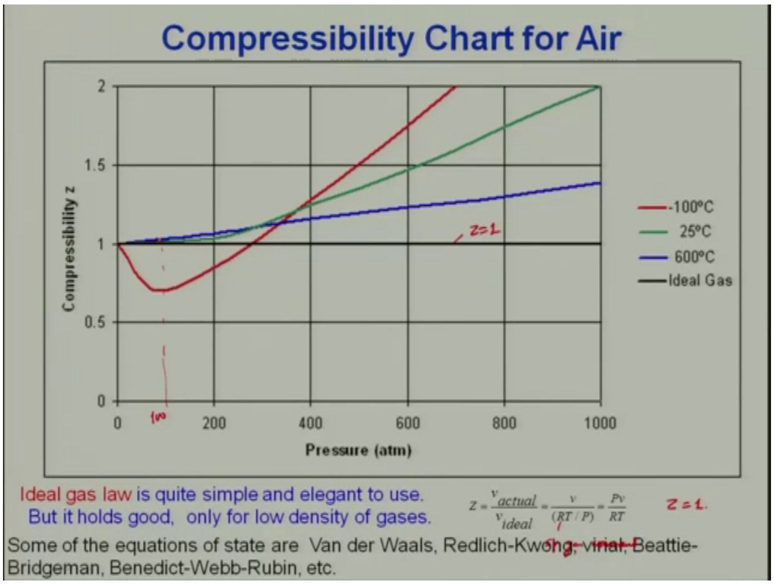

Compressibility Chart for Air

Ideal gas law is quite simple and elegant to use.
But it holds good, only for low density of gases.

$Z = \frac{v_{actual}}{v_{ideal}} = \frac{v}{(RT/P)} = \frac{Pv}{RT}$ $Z = 1.$

Some of the equations of state are Van der Waals, Redlich-Kwong, ~~virial,~~ Beattie-Bridgeman, Benedict-Webb-Rubin, etc.

Compressibility factor or the this thing which is Z, Z is basically V actual divided by V ideal and V ideal I can write down RT by P keep in mind this R is basically the specific gas constant, right? This is specific gas constant, right? And these Z, if it is Z is equal to 1 then, what will happen if Z is equal to 1; that means, it is an ideal gas if it is different than 1 it will be real gas. So, if you consider this Z the compressible chat verses the atmospheric or the sorry pressure in atmosphere unit at different temperature, right? 100 degree minus 100 degree Celsius 25 degree and 600 degree Celsius, right? And if you look at ideal gas this will be Z is equal to 1.

So, this is corresponding to ideal gas, right? But, if it is you know different from the one like it will be real gas. So, if you consider this region, which is something 200 atmospheric pressure even like if I consider the you know 600 even the ambian temperatures right, green colour you see that there is not much change, but if I take something 100 atmospheric pressure, right? The Z is for all this temperature is very, very low, right?

So, therefore in this region if the pressure is around 100 atmospheric pressure, right? For air and of course, we can consider this fuel, then you can happily consider it as an ideal gas, that does not mean that you know there would not be error, but that error will be very negligibly small, right? So, that you can apply; so, in all practical purposes what will be doing will be basically, using the ideal gas law.

But; however there are several other you know gas laws are being deviced, which can be utilized for the real gas for example, for you know some of them are basically like Van der Waals, Redlich-Kwong and Beattie-Bridgeman, Benedict and Webb Rubin laws, right? But, we will be using ideal gas law for our calculation because, it is quite simple and elegant to use. And it holds good for only for the low-density gases and for the combustion problem the temperature being very high and the pressure would not be that high, if it is within 100 atmosphere we can happily use ideal gas law for our calculation in combustion.

So, question arises how to handle the gas mixture, right? Because, whenever saying the combustion basically it is not the one gas or the component of the gas will be not one like, even in air you are having nitrogen and oxygen majority, but there might be some other gases we are not considering them for our calculations.

And the product of course, there will be several carbon dioxide, carbon monoxide, water and then unburned hydrocarbon, sox, nox several other things will be coming to be; that means, it will be you know basically, number of gases in the combustion product and during the combustion will be very high. Now, how will handle those things that is the question for that you know.

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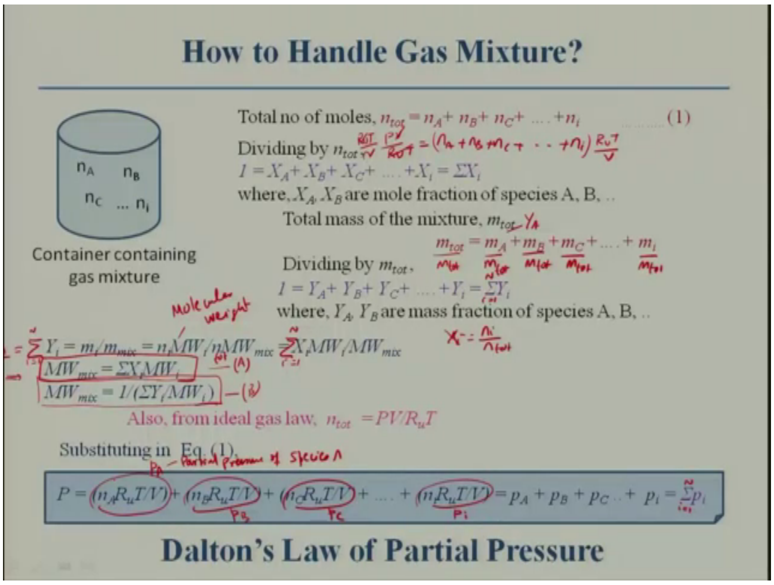

How to Handle Gas Mixture?

Container containing gas mixture

Total no of moles, $n_{tot} = n_A + n_B + n_C + \dots + n_i$ ……… (1)

Dividing by n_{tot} $\frac{R_uT}{PV}$ $\frac{PV}{R_uT} = (n_A + n_B + n_C + \dots + n_i)\frac{R_uT}{V}$

$1 = X_A + X_B + X_C + \dots + X_i = \Sigma X_i$

where, X_A, X_B are mole fraction of species A, B, ..

Total mass of the mixture, m_{tot} Y_A

$$\frac{m_{tot}}{m_{tot}} = \frac{m_A}{m_{tot}} + \frac{m_B}{m_{tot}} + \frac{m_C}{m_{tot}} + \dots + \frac{m_i}{m_{tot}}$$

Dividing by m_{tot},

$1 = Y_A + Y_B + Y_C + \dots + Y_i = \sum_{i=1}^{N} Y_i$

where, Y_A, Y_B are mass fraction of species A, B, ..

$X_i = \frac{n_i}{n_{tot}}$

Molecular weight

$1 = \sum_{i=1}^{N} Y_i = m_i/m_{mix} = n_i MW_i/n_{tot} MW_{mix} = \sum_{i=1}^{N} X_i MW_i/MW_{mix}$

$\boxed{MW_{mix} = \Sigma X_i MW_i}$ — (A)

$\boxed{MW_{mix} = 1/(\Sigma Y_i/MW_i)}$ — (B)

Also, from ideal gas law, $n_{tot} = PV/R_uT$

Substituting in Eq. (1),

p_A – Partial pressure of species A

$$\boxed{P = \underbrace{(n_A R_u T/V)}_{p_A} + \underbrace{(n_B R_u T/V)}_{p_B} + \underbrace{(n_C R_u T/V)}_{p_C} + \dots + \underbrace{(n_i R_u T/V)}_{p_i} = p_A + p_B + p_C \dots + p_i = \sum_{i=1}^{N} p_i}$$

Dalton's Law of Partial Pressure

Let us, consider a container which contains like nA moles of species A, nB moles of species B, nC moles of species C and let us say ni moles, then i can write down, that total number of moles is basically nA plus nB plus nC and it goes on till the i th species, right? And if I divide this by the n total, right? And each by n total, right? What I will get this become corresponding to 1, right? What will be this nA by n total, what it would be mole fraction; that means, if I look at these will be I can write down 1 is equal to nA by n total, right?

This is nothing but your XA right plus like XB plus XC plus Xi, right? And that is basically, you can write down that basically summation of Xi, Xi is your mole fraction of is species XA is your mole fraction of species A, XB is your basically mole fraction of species B and so on. So, 4th right, but this is about mole, but if you consider the mass right, then it is total mass will be mass of A plus mass of B plus mass of C it goes on till i th mass. I can do in the similar fashion, that is I will divide this m total right and this is nothing but your mass fraction of A and of course, this will be mass fraction of B and mass fraction of C it goes on, right?

So, what it says the summation of all the species i is equal to 1 to n, right? I can 1 to n whatever it may be right, that is equal to 1 so; that means, mass fraction of species in a container is equal to 1. Similarly, the mole fractions of all this species in a container is equal to 1. So, if I look at basically I want to now, relate this mass fraction with the mole fraction if you look at by definition Yi is equal to mi divided by m of the m mixtures and what is mi, mi is nothing but ni into nWi this is basically end of this is a molecular weight, and there mass of mixture is nothing but, n into MW mixture right and we know this Xi is equal to ni by n, in this case n means basically n total you can say this is n total according to the avow you know like notation.

So, this is nothing but your Xi mi divided by MW mixture is nothing but your mass fraction. So now, if I sum it up right, if I sum it up here. So, what will happen when I sum it up this one this will be nothing but, here equal to 1 yes or no; that means, if I look at; that means, MW mixture is nothing but, some of Xi MWi; that means, this is the by this way I can find out the molecular weight of the mixture, right? If I know the molecular weight of individual species plus mole fraction of individual species in a mixture.

If I know, I can find out the molecular weight of a mixture, is that clear and similarly you can find out the molecular mixtures in terms of mass fraction, that is basically 1 divided by summation of Yi divided by nWY what I suggest that, please you know derive yourself this expression let us say, this is your equation 1, I can say equation 2 I would suggest that you derive that expression and which is very easy what you do then for doing that, here you have summit with the starting with the definition of mass fraction, in that case you will start with definition of mole fraction and then you will get, are you getting it is very easy you can do that.

Now of course, also from the ideal gas law we know the n total is equal to PV by RuT this is we know, what will do we will basically you know use this expression for the n total, right? In the eq I am sorry this is basically I can say this is equation I can say equation A, this may be I can say equation B like. So, this is your equation 1 right, and I can substitute this values, if I substitute this values in this equation 1 right here, what I will get in this expression if I put this thing this will be PV by RuT, right? And equal to nA plus nB plus nC plus ni yes or no, what I will do I will find out this P is basically I will take all those thing into here, what I will do I will put, RuT by V and I will multiplied here, RuT by V. So, this will cancel it out this is nothing but your P.

So, when will do that, what I will get, I will get this expression, right? I will get what nA nA RuT by V is nothing but, your what this I say nA RuT by V this expression is what you call this is a PA, and this PA am using a small p is known as partial pressure of a species A, this is partial pressure of species A similarly, this will be PB, this will be PC, this will be Pi and this is nothing but here, summation of partial pressure of i th species i equal to 1 to n it can be right and what you mean by partial pressure of you know for a particular species from these definition you can see that, if it will occupy the entire volume, right?

At the same temperature then you call it as basically partial pressure of that species, right? And this relationship is known as Dalton's law of partial pressure, right? Sometimes people say Gibbs Dalton's law of partial pressure, right?

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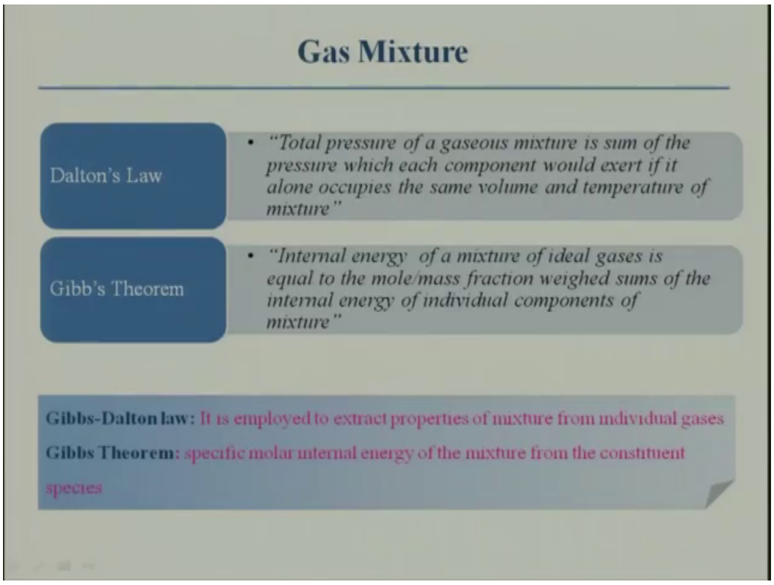

Gas Mixture

Dalton's Law	• *"Total pressure of a gaseous mixture is sum of the pressure which each component would exert if it alone occupies the same volume and temperature of mixture"*
Gibb's Theorem	• *"Internal energy of a mixture of ideal gases is equal to the mole/mass fraction weighed sums of the internal energy of individual components of mixture"*

Gibbs-Dalton law: It is employed to extract properties of mixture from individual gases

Gibbs Theorem: specific molar internal energy of the mixture from the constituent species

So, and Daltons law of partial pressure is basically if you look at total pressure of a gaseous mixture is sum of pressure, which is component would exert if it alone occupies same volume and the temperature of the mixture; that means, same temperature of the mixture, right? And of course, by these we you can really connect you know your properties, basically the mole fractions right and if you know the mole fraction you can connect to the mass fractions, we have learnt how to we can connect the mole fraction with a mass fraction of individual species and also the mixture we can calculate but, we need to also handle the internal energy of the mixture and also by knowing the species or vice versa right? If I know, the some of the what you call species and mixture internal energy or the enthalpy I know, but I can find out one of them, right? That way; so, according to Gibbs theorem the internal energy of a mixture of ideal gases, right? Is equal to the mole or the mass fraction of weighted sums of the internal energy of individual component of mixture, right?

And this is basically by a you know Gibbs theorem, which is you know helps us to calculate. As I told that, Daltons law is also known as Gibbs Daltons law it is employed to extract properties of mixture from individual species and vice versa right and whereas, the Gibbs theorem helps us to basically calculate the specific molar internal energy enthalpy, you know entropy and others of the mixture from the constituent species, right? So, am doing this laws we can really handle the mixtures of various components of gases.

So, let us now, look at enthalpy and internal energy am my question might be coming to your mind what do you mean by internal energy? Any idea or enthalpy right how it is related? Internal energy you know like, it is basically microscopic form of energy due to vibration, conscillation, rotation of the molecules right, that is corresponding to internal energy, right?

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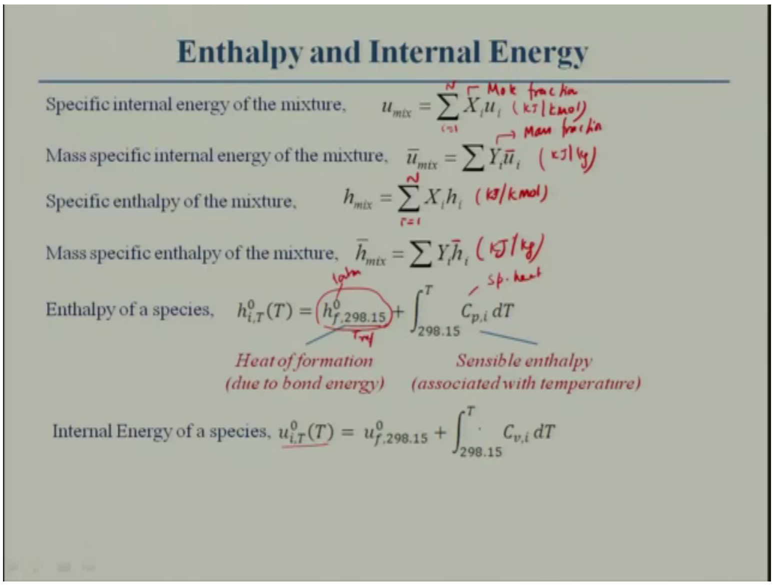

Enthalpy and Internal Energy

Specific internal energy of the mixture, $u_{mix} = \sum_{i=1}^{N} X_i u_i$ (kJ/kmol)

Mole fraction

Mass specific internal energy of the mixture, $\bar{u}_{mix} = \sum Y_i \bar{u}_i$ (kJ/kg)

Mass fraction

Specific enthalpy of the mixture, $h_{mix} = \sum_{i=1}^{N} X_i h_i$ (kJ/kmol)

Mass specific enthalpy of the mixture, $\bar{h}_{mix} = \sum Y_i \bar{h}_i$ (kJ/kg)

Enthalpy of a species, $h^0_{i,T}(T) = \boxed{h^0_{f,298.15}} + \int_{298.15}^{T} C_{p,i}\, dT$

form, Tref, Sp. heat

Heat of formation (due to bond energy)

Sensible enthalpy (associated with temperature)

Internal Energy of a species, $u^0_{i,T}(T) = u^0_{f,298.15} + \int_{298.15}^{T} C_{v,i}\, dT$

And of course, the specific internal energy of a mixture if you look at u mixture is equal to sum of Xi ui where, i is equal to 1 to n, right? And this is what will be unit of this ui? Or what will be u this will be joule per mole, right? And mass specific internal energy of the mixture will be Yi by ui right, and this is there should be A bar also right, and this unit will be basically joule per kg this will be, I can say kilo joule per kg and this is of course, without any unit this is some number ratio, right? The mass fractions X is your mole fraction, this is kilo joule per kilo mole per unit.

Similarly, the specific enthalpy of a mixture can be you know hB is equal to summation of Xi hi and i is equal to 1 to n and this is again will be kilo joule per kilo mole and mass specific enthalpy of mixture will be kilo joule per kg now, a question might be coming to your mind, right? When I will be using internal energy, when I will be using enthalpy, what is enthalpy? Right? You are having any doubt ui bar is basically am trying to separate the specific internal energy based on the mole to specific internal energy based on the mass, right? Because, both are different nA right, specific means what per unit something 1 is per unit mole other is per unit mass.

So, therefore, you will have to difference it nA is not it otherwise, you will be mixed up nA. So now, enthalpy of species is basically you can say hiT and 0 is the basically i th species I can be any species i is just the symbol am using, i can be nitrogen, it can be methane, it can be oxygen and which is basically function of temperature, this enthalpy is basically function of temperature is having hf at the reference temperature this is your T reference, right? 298.150 and this is known as the heat of formation this portion, right? Plus, the Cp,i, Cp is your specific heat into dT, right? And integrated over 298.15 to by some set temperature it can be anything, you know different than that 298.15 and this is known as a reference standard temperature and standard pressure STp what you call, right?

Is basically the reference, which being taking and this portion is your what you call sensible enthalpy, right? This is your sensible enthalpy associated with temperature, due to temperature it will be change will be keep it in mind, that this Cp is a function of what? Is a also a function of temperature. It will be dependent on also the species, but at the same temperature Cp of methane will be different then cp of oxygen.

And this is heat of formation due to the bond energy, right? There will be some bond and that, energy which is you know there with during the formation of bond whether, it will be released or it will be what you call absorb depending on that, we call the heat of formation and this is always being used as a standard right, 298.15 Kelvin and atmosphere this 0 corresponding to what? 1 atmospheric pressure right.

So, and sometimes this is also known as delta h basically, heat of formation I will put it here hf 298, but this is a delta h now, internal energy of the species also you can write down in a similar fashion, right? Keep in mind that this internal energy is a at a particular temperature, if it is happens to be 298 what will happen? This will be 0 this side sensible enthalpy will be 0, right? But, if it is different than the reference temperature it will be this sensible enthalpy will be certain value. Now, I had asked this question when will be using internal energy? When you will be using enthalpy? Is that clear, is that question you been answered you know.

When the system is closed you will be using internal energy, but when the system is open you will be using enthalpy, but why it is. So, but why in the open system you are using that form why not internal energy? That is a mathematical you know like some algebra, but physically yes he is saying the right the flow of work which will be taking that; that means, flow is already taking place right you will have to pump. So, therefore, that is taken care it will be easier to handle that is all, but; however, internal energy is already embedded into the system through the enthalpy. So now, we will have to basically look at enthalpy of formation.

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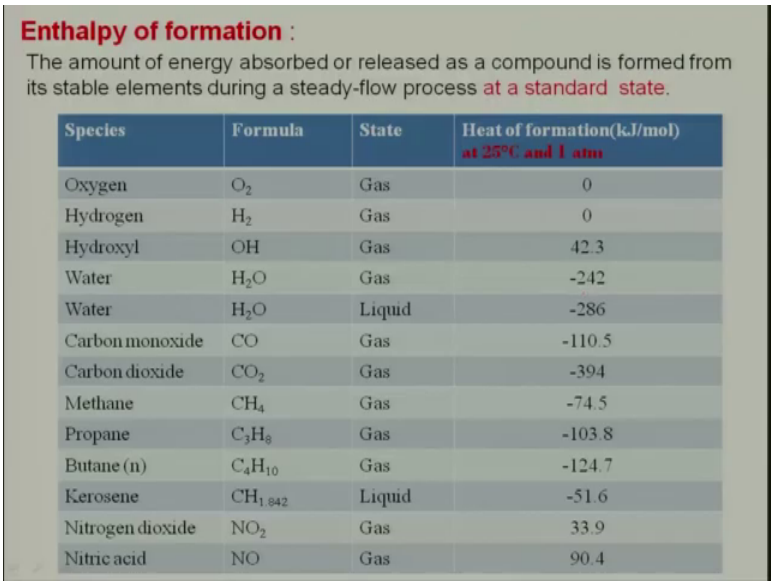

Enthalpy of formation :

The amount of energy absorbed or released as a compound is formed from its stable elements during a steady-flow process at a standard state.

Species	Formula	State	Heat of formation(kJ/mol) at 25°C and 1 atm
Oxygen	O_2	Gas	0
Hydrogen	H_2	Gas	0
Hydroxyl	OH	Gas	42.3
Water	H_2O	Gas	-242
Water	H_2O	Liquid	-286
Carbon monoxide	CO	Gas	-110.5
Carbon dioxide	CO_2	Gas	-394
Methane	CH_4	Gas	-74.5
Propane	C_3H_8	Gas	-103.8
Butane (n)	C_4H_{10}	Gas	-124.7
Kerosene	$CH_{1.842}$	Liquid	-51.6
Nitrogen dioxide	NO_2	Gas	33.9
Nitric acid	NO	Gas	90.4

And enthalpy of formation, if you look at the amount of energy absorbed or released, when a compound is found from a stable elements during a steady flow process or at a standard state, right? Because, if you look at enthalpy we are talking about therefore, we will be talking about the flow system, are you getting and standard state means 298.15 Kelvin and 1 atmospheric pressure which is equal to 101325 Pascal.

And how what is the meaning of that this enthalpy of formation, if you look at let us say, there is a 1O atom there is another O atom is coming together, right? And then the O2 is formed and then you know like, there will be some kind of energy will be there which will be taken care am like will be supplied or will be removed you know like depending upon whether, the heat of formation is exothermic or is endothermic like if it released basically exothermic.

So, if it is absorbed it is endothermic right heat being. So, that is known as the enthalpy of formations and various enthalpy of formation right, in you know I have given here, if you look at oxygen of the gas is 0 how it is being done? Because, the whichever is the standard state people assume to be 0, right? And similarly, the hydrogen is 0, but whereas, the water it is 242 kilo joule per mole provided if it is gas, if it is liquid 286 kilo joule per mole the difference is basically heat of what? Vaporization right. So, therefore, one has to very carefully use this heat of formation whenever, you are handling combustion this thing you will have to see whether, it is a gaseous state or liquid state depending on the temperature. So, of course, the others are given here, these values you need not to remember, but; however, one has to be very careful to use it, right?

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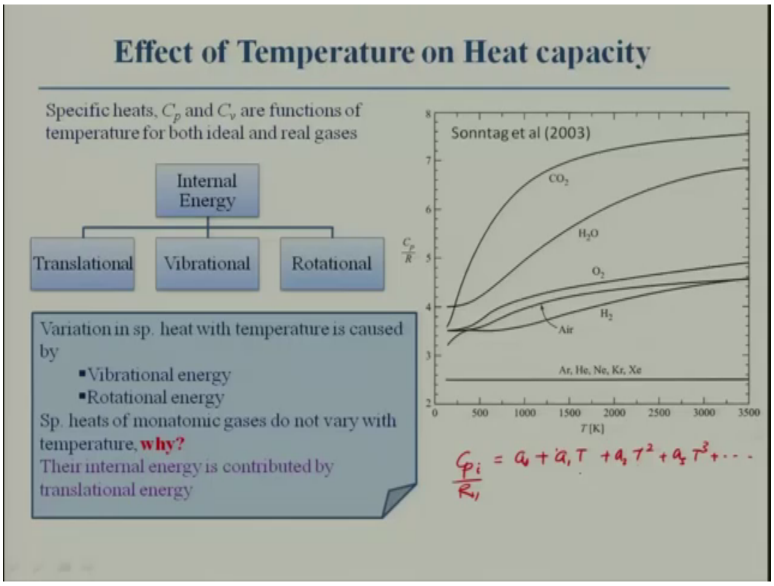

Effect of Temperature on Heat capacity

Specific heats, C_p and C_v are functions of temperature for both ideal and real gases

Internal Energy

Translational

Vibrational

Rotational

Variation in sp. heat with temperature is caused by

- Vibrational energy
- Rotational energy

Sp. heats of monatomic gases do not vary with temperature, **why?**

Their internal energy is contributed by translational energy

$$\frac{C_{pi}}{R_i} = a_0 + a_1 T + a_2 T^2 + a_3 T^3 + \cdots$$

And let me look at now, the how this you know whenever you are looking at this heat of formations at particular temperature little different than that of the reference temperature or away from the temperature will have to look at sensible enthalpy. When you talk about sensible enthalpy, then we will have to look at specific heat, right?

When we are dealing with internal energy will have to look at specific heat at constant volume, and when you are dealing with enthalpy we will have to work with the specific heat constant pressure, and for an ideal gas even for the real gas right there will be function of temperature, right? But in our calculation in thermodynamics generally we do not consider to be the function of temperature simplicity, right? But; however, you cannot except certain cases for example, if you consider if you are using argon, helium, neon, krypton, xenon, all those gases you need not to bother about Cp as a function of temperature because, it is remaining constant is a monatomic gas, right? So, therefore, it is really does not depend on their temperature means, the Cp values and then you know both the specific heat constant pressure and constant volume does not depend on the temperature.

But however, if it is a di atomic molecules like hydrogen, oxygen, heat is you know depend on the; that means, it increase temperature and it is what you call non-linear it is not that linear fine and when you go the triatomic gases like water, carbon dioxide, heat also changes, right? So now, this if I look at this I was asking this question internally, that internal energy basically contributed to the translational, vibrational and rotational energy of the molecule, right? And the temperature specific heat temperature is caused by vibrational and rotational, right? And translational is does not contribute to that and of course, the argon, helium, neon and other thing they will translation there will be motion.

But; however, it would not really contribute to the temperature and therefore, the internal energy of monoatomic does not vary with their temperature, right? Because, there internal energy contributed by translator I have earlier discussed this thing right. Now, how it has to be dealed with if you look at some properties kind of things one can use the table, right?

Another way the people have used also the semi ampherical formulas, right? So, if you look at they will be using Cp,i right and is equal to n not plus a not a 1 T plus a 2 T 3 by R, right? T 3 sorry, cube plus goes on like that will be several coefficient will be and knowing the coefficient and this is corresponding to various species also this coefficient will be changing with respect to species, right? And then, you can get these values and then you can calculate, but; however, it will be easier if you prepare a table and then you know you can calculate, right?

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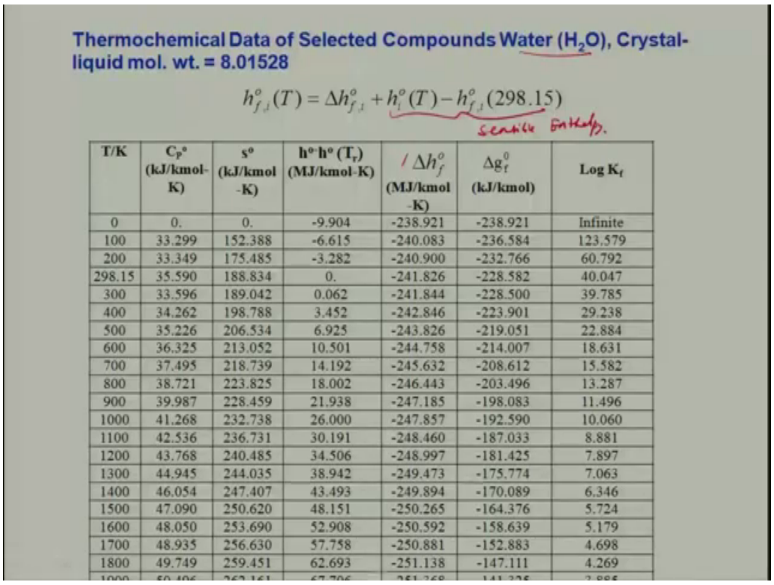

Thermochemical Data of Selected Compounds Water (H_2O), Crystal-liquid mol. wt. = 8.01528

$$h^o_{f,i}(T) = \Delta h^o_{f,i} + \underbrace{h^o_i(T) - h^o_{f,i}(298.15)}_{\text{sensible Enthalpy.}}$$

T/K	C_p^o (kJ/kmol-K)	s^o (kJ/kmol-K)	h^o-h^o (T_r) (MJ/kmol-K)	Δh_f^o (MJ/kmol-K)	Δg_f^0 (kJ/kmol)	Log K_f
0	0.	0.	-9.904	-238.921	-238.921	Infinite
100	33.299	152.388	-6.615	-240.083	-236.584	123.579
200	33.349	175.485	-3.282	-240.900	-232.766	60.792
298.15	35.590	188.834	0.	-241.826	-228.582	40.047
300	33.596	189.042	0.062	-241.844	-228.500	39.785
400	34.262	198.788	3.452	-242.846	-223.901	29.238
500	35.226	206.534	6.925	-243.826	-219.051	22.884
600	36.325	213.052	10.501	-244.758	-214.007	18.631
700	37.495	218.739	14.192	-245.632	-208.612	15.582
800	38.721	223.825	18.002	-246.443	-203.496	13.287
900	39.987	228.459	21.938	-247.185	-198.083	11.496
1000	41.268	232.738	26.000	-247.857	-192.590	10.060
1100	42.536	236.731	30.191	-248.460	-187.033	8.881
1200	43.768	240.485	34.506	-248.997	-181.425	7.897
1300	44.945	244.035	38.942	-249.473	-175.774	7.063
1400	46.054	247.407	43.493	-249.894	-170.089	6.346
1500	47.090	250.620	48.151	-250.265	-164.376	5.724
1600	48.050	253.690	52.908	-250.592	-158.639	5.179
1700	48.935	256.630	57.758	-250.881	-152.883	4.698
1800	49.749	259.451	62.693	-251.138	-147.111	4.269

So, these are the temperature which is given here, and this is mean for water, right? And this is the Cp values are given here, and entropies you can find out it is not only the Cp you can also use for the what you call entropy Gibbs free energy and this is basically delta h, this is delta hf which will heat of formation which is there for the gaseous and if you look at this is nothing but heat of formation and this is a sensible enthalpy, right? So, similar way you can find out I will stop over this and we will be discussing more about the thermochemistry part in next lecture.

Thank you very much.