Chemical and Biological Thermodynamics: Principles to Applications

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Lecture - 16
Tutorial session

Let us discuss some numerical problems in this session. We have now discussed a lot about Gibbs Energy, we have discussed about Helmets Energy Entropy; as well as we have started discussing about Deviations from Ideality at least in terms of Fugacity. Just in the previous lecture, we developed an equation for the Fugacity coefficient for a real gas.

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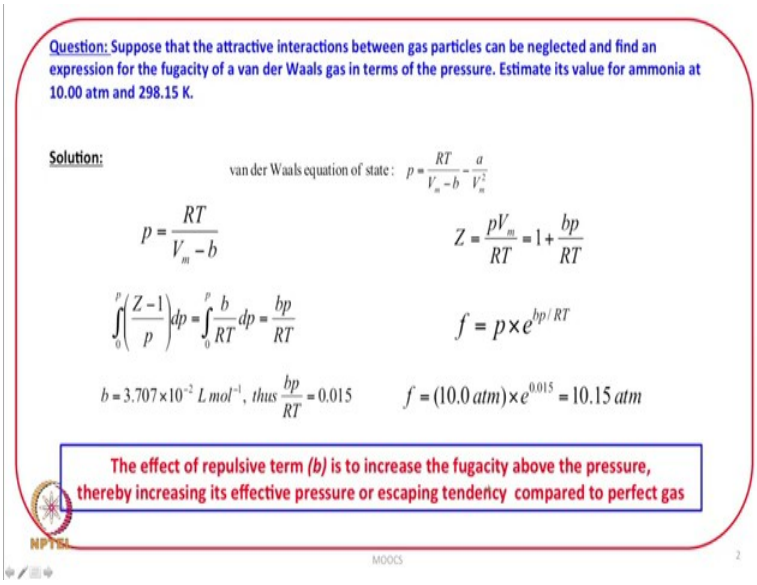

Question: Suppose that the attractive interactions between gas particles can be neglected and find an expression for the fugacity of a van der Waals gas in terms of the pressure. Estimate its value for ammonia at 10.00 atm and 298.15 K.

Solution:

van der Waals equation of state: $p = \frac{RT}{V_m - b} - \frac{a}{V_m^2}$

$$p = \frac{RT}{V_m - b}$$

$$Z = \frac{pV_m}{RT} = 1 + \frac{bp}{RT}$$

$$\int_0^p \left(\frac{Z-1}{p}\right) dp = \int_0^p \frac{b}{RT} dp = \frac{bp}{RT}$$

$$f = p \times e^{bp/RT}$$

$$b = 3.707 \times 10^{-2}\ L\,mol^{-1},\ thus\ \frac{bp}{RT} = 0.015$$

$$f = (10.0\,atm) \times e^{0.015} = 10.15\,atm$$

The effect of repulsive term *(b)* is to increase the fugacity above the pressure, thereby increasing its effective pressure or escaping tendency compared to perfect gas

Let us take up this question. Suppose that the attractive interactions between gas particles can be neglected and find an expression for the fugacity of a van der Waals gas in terms of the pressure estimate, its value for ammonia at 10 atmosphere and 298.15 Kelvin. Let us examine the question very carefully. It says that suppose that the attractive interactions between the gas particles can be neglected. So, you are neglecting the attractive interactions. So, if the attractive interactions are neglected, that means the molecules will not be sticking to each other.

So, just before beginning answering the question, we know that the fugacity is not going to be less than pressure because attractive interactions are missed and since we are also given this information that the gas behaves that van der Waals equation which is p is equal to R T by V m minus b minus a by V m square. That is the van der Waals equation of statement, where a includes information on attractive interactions and, b includes information on repulsive interactions and what we have been asked is to get rid of a. We can just ignore this a by V n square because we are told that attractive interactions can be ignored.

So, what is the remaining part? Now, only the first part p is equal to R T by V m minus b. This is the equation of State for the Gas that we are going to use and in order to evaluate for the fugacity coefficient or fugacity, we need the information on compression factor z. Z is equal to p V m by R T. If you now manipulate this p is equal to R T of a V m minus b, we rearrange and get p V m by R T. You will see that z terms out to be equal to 1 plus b p by R T. It is just by rearranging this and obviously, from this z minus 1 over p z minus 1 over p is going to be equal to b o b over R T and that is what we are interested in because the fugacity can be determined from this integration z minus q over p by d p z minus 1 over p from this expression is b over R T.

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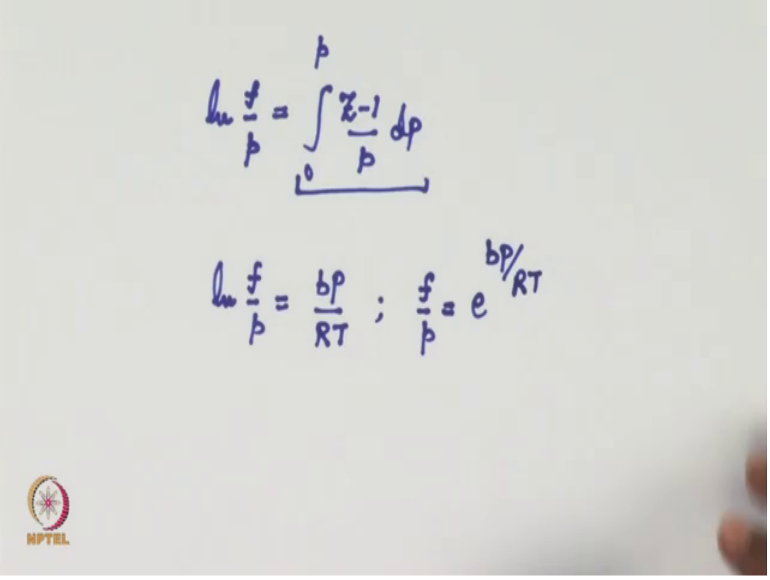

$$\ln\frac{f}{p} = \underbrace{\int_0^p \frac{z-1}{p}\,dp}$$

$$\ln\frac{f}{p} = \frac{bp}{RT} \; ; \; \frac{f}{p} = e^{bp/RT}$$

Now, when you evaluate this integral, it is very easy. It is b p by R T therefore, if I now recall that log f upon p is equal to 0 to p z minus 1 over p d p and we have evaluated this and obtained log f over p is equal to b p by R T, which means f upon p is equal to exponential b p upon R T. Let us go back to the slide. Now, therefore, f is equal to p into exponential b p by R T. Now, if I know the values of b p r and t, I can calculate the fugacity.

All the information is given. The value of b is 3.707 into 10 is to the power minus 2 liter per mole and when use substitute in b p over R T r and t in suitable units, it can be substituted because if you are putting pressure in atmosphere, then it is better to use r in liter atmosphere per Kelvin per mole and when you calculate, it will turn out to be 0.015 and then, now if you substitute in this f is equal to pressure into exponential b p over R T, we know pressure is 10 atmosphere b p over R T is 0.015. The answer comes to be 10.15 atmosphere and this is what we were expecting because the attractive interactions between the gas particles are being neglected. We are only accounting for repulsion.

Repulsion means the molecules will tend to repel each other and therefore, the escaping tendency of the gas molecules will be more. Fugacity will be more than pressure and that is what we see that fugacity is 10.15 atmosphere, whereas the given pressure was 10 atmosphere. So, escaping tendency is more and that is what is commented over here that the effect of repulsive term b is to increase the fugacity above the pressure, thereby increasing its effective pressure or escaping tendency compared to the perfect gas.

Now, let us go to another question. This will be on the maximum non expansion work.

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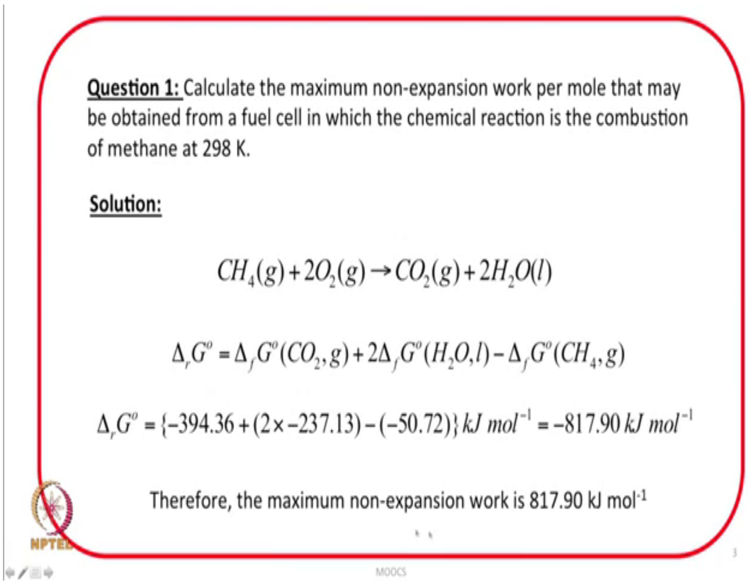

Question 1: Calculate the maximum non-expansion work per mole that may be obtained from a fuel cell in which the chemical reaction is the combustion of methane at 298 K.

Solution:

$$CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(l)$$

$$\Delta_r G^o = \Delta_f G^o(CO_2, g) + 2\Delta_f G^o(H_2O, l) - \Delta_f G^o(CH_4, g)$$

$$\Delta_r G^o = \{-394.36 + (2 \times -237.13) - (-50.72)\}\ kJ\ mol^{-1} = -817.90\ kJ\ mol^{-1}$$

Therefore, the maximum non-expansion work is 817.90 kJ mol^{-1}

The question is calculate the maximum non-expansion work per mole that may be obtained from a fuel cell in which the chemical reaction is the combustion of methane at 298 Kelvin. The question that is asked is on maximum non-expansion work. When we talk about work, two things come to our mind. One is the change in Helmets Free Energy and the other is changing Gibbs Energy. We have also discussed that if we are interested in determining maximum work inclusive of pressure volume and pressure volume work, then we have to act on the change in Helmets Free Energy and if we have to only target non expansion or extra work or other work, then we have to act upon delta G.

So, here since we have been asked to calculate the maximum non expansion work, we will calculate delta G. The chemical reaction is combustion of methane. This reaction represents combustion of methane, methane plus 2 moles of oxygen forming carbon dioxide plus 2 moles of water and we are interested in knowing delta G for this reaction.

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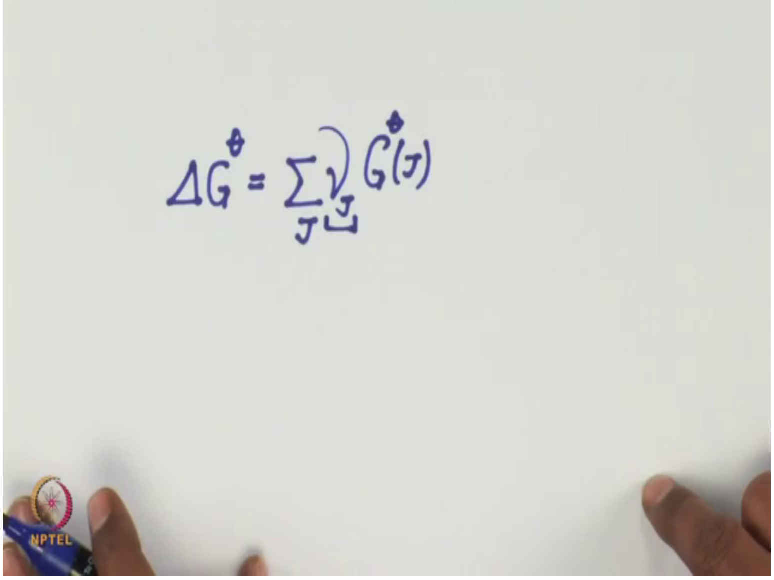

$$\Delta G^{\ominus} = \sum_{J} \nu_{J} G^{\ominus}(J)$$

Remember that we have earlier discussed in the Standard Molar Gibbs Energy that delta G naught; we can calculate from summation J nu J G J naught, where this psychometric number is positive for products and negative for reactors.

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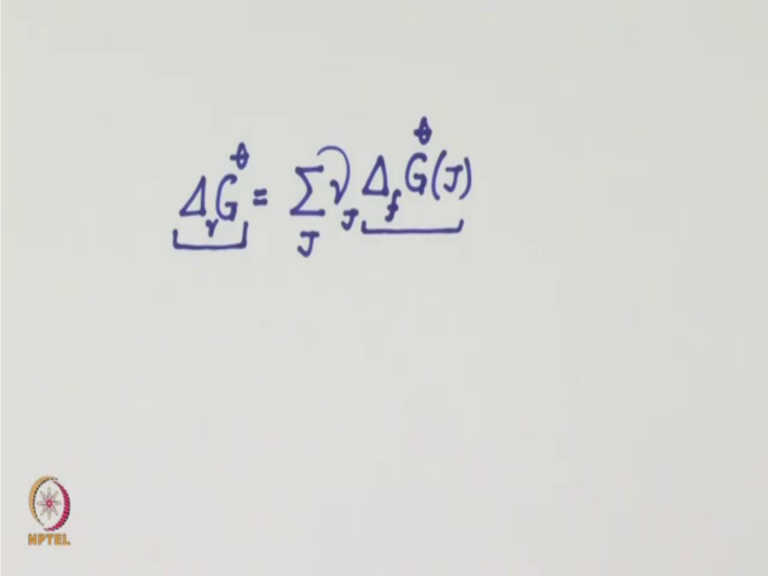

$$\underbrace{\Delta_r G^\ominus} = \sum_J \nu_J \underbrace{\Delta_f G^\ominus(J)}$$

So, remember that we have earlier discussed that the change in reaction Gibbs Energy can be calculated from summation J nu J delta f. F is formation G J.

If I have the information on free energy of formation of reactants and products, I can immediately calculate the free energy change for the reaction. So, therefore for the given question here, I need to have information on free energy of formation of water, free energy of formation of carbon dioxide, free energy of formation of oxygen and free energy of formation of methane. Oxygen is an element. So, immediately we can say that the free energy of formation of oxygen must be 0.

Therefore, we need the data on free energy of formation of water, carbon dioxide and methane. Once I have this, then I can use this expression that the reaction keeps energy is equal to free energy of formation of carbon dioxide. Here you see plus 2 moles of water are being formed. So, twice free energy of formation of water liquid minus free energy of formation of methane gas and for oxygen, we will put a value of 0, and using the free energy of formation data which is for carbon dioxide, it is minus 394.36. For water liquid, it is minus 237.13 and for methane gas, it is minus 50.72 and by this addition and subtraction, we find out that the overall value of reaction Gibbs Energy is minus 800 and 17.9 kilojoules per mole and this change in delta G is equal to maximum non expansion work that the system can do and that is what is over commented over here.

Therefore, the maximum non-expansion work is 817.9 kilojoules per mole.

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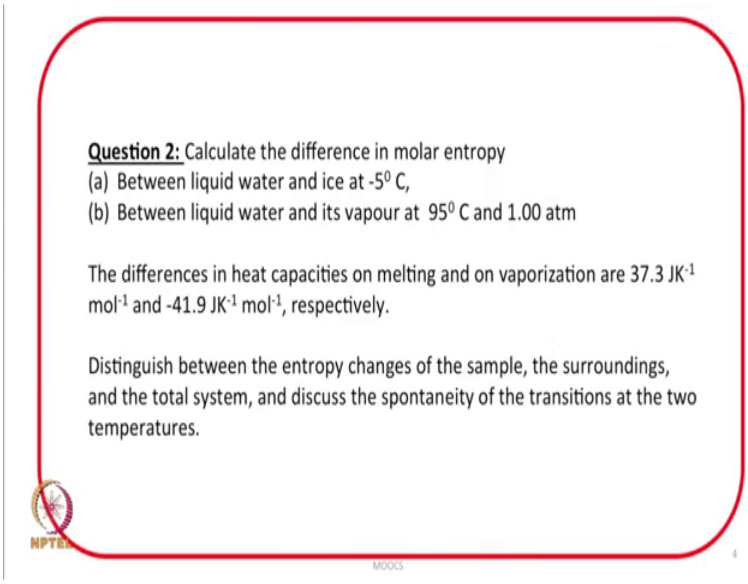

<u>Question 2:</u> Calculate the difference in molar entropy

(a) Between liquid water and ice at -5^0 C,

(b) Between liquid water and its vapour at 95^0 C and 1.00 atm

The differences in heat capacities on melting and on vaporization are 37.3 JK^{-1} mol^{-1} and -41.9 JK^{-1} mol^{-1}, respectively.

Distinguish between the entropy changes of the sample, the surroundings, and the total system, and discuss the spontaneity of the transitions at the two temperatures.

Now, let us move to another question; these questions are on entropy and please try to understand this question a little more carefully because it involves understanding of several different concepts.

The question is calculate the difference in molar entropy between liquid water and ice at minus 5 degree Celsius and part b, between liquid water and its vapour at 95 degree Celsius and one atmosphere. The information given to us is the differences in heat capacities on melting and on vaporization are 37.3 joules per Kelvin per mole and minus 41.9 joules per Kelvin per mole respectively. Distinguish between entropy changes of the sample, the surroundings and the total system and discuss the spontaneity of the transitions at the two temperatures. What is being asked in this question is to calculate the value of delta s, when water freezes at minus 5 degree centigrade. We know that metastable state of water, liquid water can exist at minus 5 degree centigrade and a slight disturbance will lead to its freezing.

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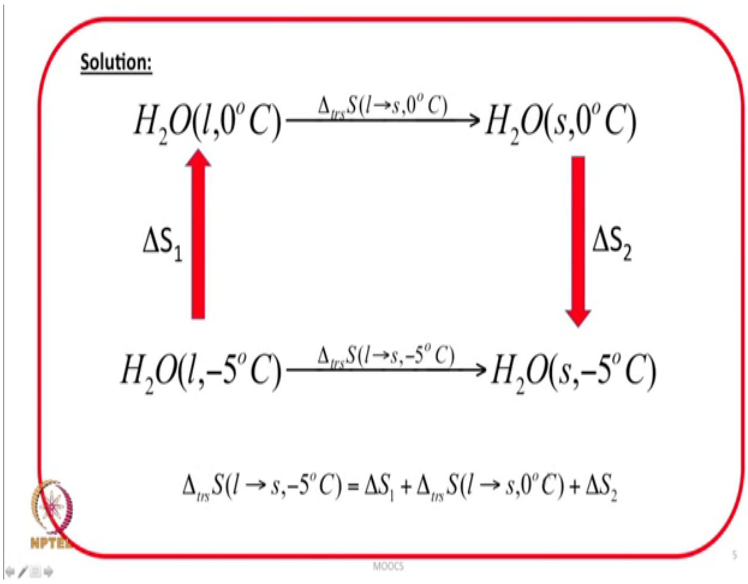

Solution:

$$\begin{tikzcd}
H_2O(l,0^oC) \arrow[r, "\Delta_{trs}S(l\rightarrow s,0^oC)"] & H_2O(s,0^oC) \arrow[d, "\Delta S_2"] \\
H_2O(l,-5^oC) \arrow[u, "\Delta S_1"] \arrow[r, "\Delta_{trs}S(l\rightarrow s,-5^oC)"] & H_2O(s,-5^oC)
\end{tikzcd}$$

$$\Delta_{trs}S(l \rightarrow s,-5^oC) = \Delta S_1 + \Delta_{trs}S(l \rightarrow s,0^oC) + \Delta S_2$$

So, let us see how to solve this question. Let us try to understand this cycle very carefully. This is the desired process. This is the asked question that water liquid form at minus 5 degree Celsius is freezing at minus 5 degree Celsius, what is the entropy change for this transition? Entropy is a state function. It appears difficult to directly get information on this transition. Alternatively we can devise another path. Path 1, when water in the liquid state minus 5 degree Celsius is taken to 0 degree Celsius and the corresponding change in a drop is delta S1, and then there is a phase transition. Let the liquid solidify at 0 degree Celsius. That is a normal phase transition and then, you reduce the temperature to minus 5 degree Celsius and the corresponding change in entropy is delta S2.

Therefore, we need to calculate delta S1. We need to calculate delta S for these transition and we need to calculate delta S2. We have already discussed how to calculate entropy change. For each of these steps, let us carefully see what information do we need to solve or to get delta S1 and delta S2. For this step, water remains as liquid. It is only the temperature changing, right. So, therefore, the information that I need entropy at some final temperature is equal to entropy at some initial temperature plus integration T i to T f C p by T d T.

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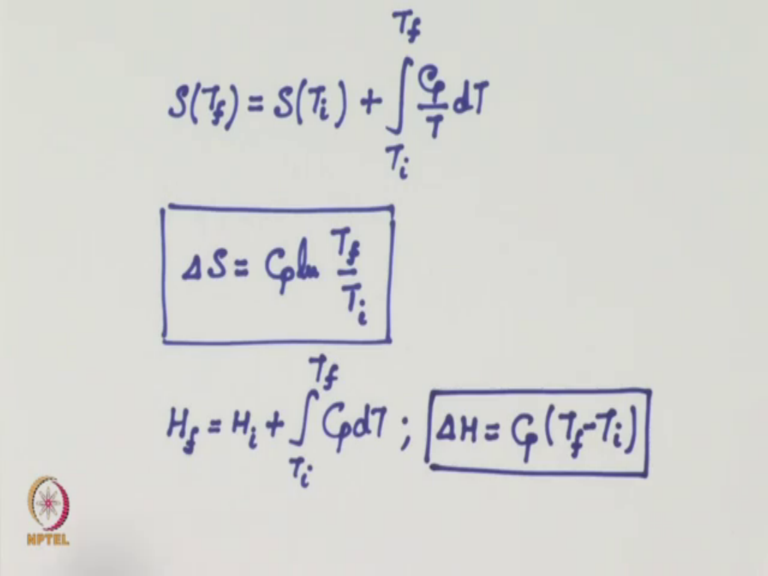

$$S(T_f) = S(T_i) + \int_{T_i}^{T_f} \frac{C_p}{T}\, dT$$

$$\boxed{\Delta S = C_p \ln \frac{T_f}{T_i}}$$

$$H_f = H_i + \int_{T_i}^{T_f} C_p\, dT \; ; \; \boxed{\Delta H = C_p (T_f - T_i)}$$

This is the equation that I will use and if heat capacity is independent of temperature, then I can write delta S is equal to C p log T final over T initial. This is the expression that I can use.

So, let us go back to slide and discuss further. In order to get this delta S for transition from l to S at minus 5 degree Celsius, I need information on delta S1, I need information on this phase transition which is occurring at 0 degree Celsius corresponding to this process and I need information on delta S2.

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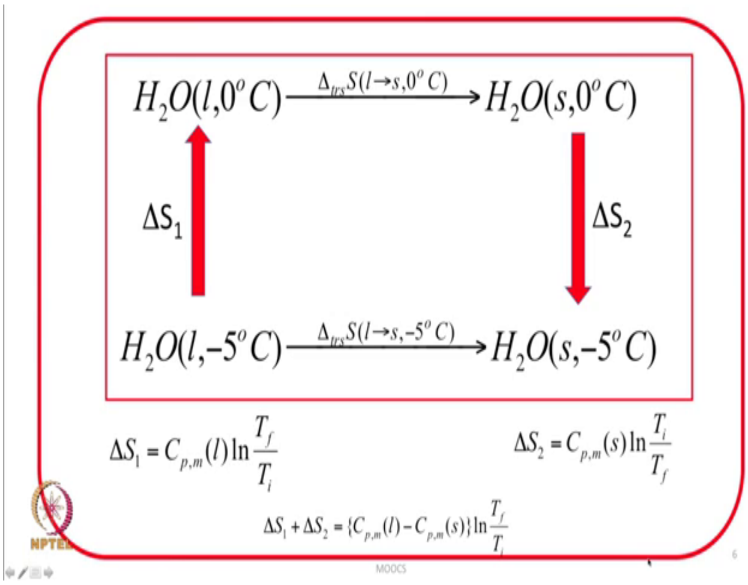

$$\begin{tikzcd}
H_2O(l,0^o C) \arrow[r, "\Delta_{trs}S(l\rightarrow s,0^o C)"] & H_2O(s,0^o C) \arrow[d, "\Delta S_2"] \\
H_2O(l,-5^o C) \arrow[u, "\Delta S_1"] \arrow[r, "\Delta_{trs}S(l\rightarrow s,-5^o C)"] & H_2O(s,-5^o C)
\end{tikzcd}$$

$$\Delta S_1 = C_{p,m}(l)\ln\frac{T_f}{T_i} \qquad \Delta S_2 = C_{p,m}(s)\ln\frac{T_i}{T_f}$$

$$\Delta S_1 + \Delta S_2 = \{C_{p,m}(l) - C_{p,m}(s)\}\ln\frac{T_f}{T_i}$$

For this process, as we just discussed we can use C p of liquid into log T final. Final here is this, freezing. This f here means freezing point T final over T initial. T initial we will substitute later as minus 5 degree Celsius. Similarly, delta S2 will be heat capacity of solid into log. Here T final is actually T i which is minus 5, because this is the final state. An initial state is T f. Please remember here T i and T f are being used as initial temperature which is minus 5 degree Celsius and f is the freezing point.

When you add these two up, what you have is delta S1 plus delta S2 will be equal to C p of liquid minus C p of solid into log T f by T, T i this. This is by addition of the two after having this information.

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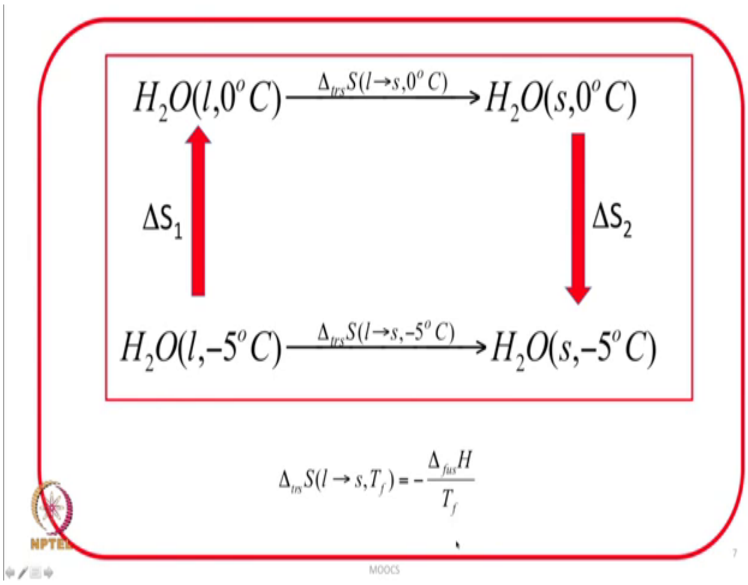

$$\begin{tikzcd}
H_2O(l,0^o C) \arrow[r, "\Delta_{trs}S(l\rightarrow s,0^o C)"] \arrow[d, phantom] & H_2O(s,0^o C) \arrow[d, "\Delta S_2"] \\
H_2O(l,-5^o C) \arrow[u, "\Delta S_1"] \arrow[r, "\Delta_{trs}S(l\rightarrow s,-5^o C)"] & H_2O(s,-5^o C)
\end{tikzcd}$$

$$\Delta_{trs}S(l \rightarrow s, T_f) = -\frac{\Delta_{fus}H}{T_f}$$

Now, we would like to calculate delta S. For this phase transition, it is a simple phase transition at 0 degree Celsius for water liquid to water solid and the phase transition if you remember, the entropy of phase transition is equal to enthalpy divided by transition temperature that we have discussed and since liquid to solid is a reverse of fusion process. So, therefore the negative sign will come and then, you put enthalpy of freezing or enthalpy of fusion divided by the freezing point.

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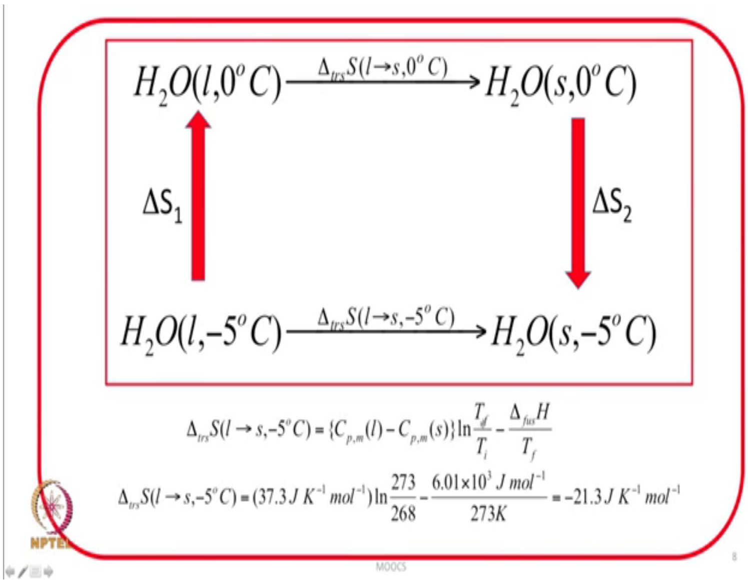

$$\begin{tikzcd}
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\end{tikzcd}$$

$$\Delta_{trs}S(l \rightarrow s,-5^oC) = \{C_{p,m}(l) - C_{p,m}(s)\}\ln\frac{T_f}{T_i} - \frac{\Delta_{fus}H}{T_f}$$

$$\Delta_{trs}S(l \rightarrow s,-5^oC) = (37.3\,J\,K^{-1}\,mol^{-1})\ln\frac{273}{268} - \frac{6.01\times10^3\,J\,mol^{-1}}{273K} = -21.3\,J\,K^{-1}\,mol^{-1}$$

Now, what we will do is, we will add up all the three and if you add delta S1 plus delta S2 plus this, we will end up with this relation as we just derived in the previous two slides. Substituting the numbers, this information is given to us 37.3 Joules per Kelvin per mole. This is given to us T f freezing point is 273 Kelvin. Initial is minus 5 degree Celsius which is 268 Kelvin and enthalpy of fusion or freezing is 6.01 kilojoules per mole. Convert that into joule and put the freezing point which is 273 Kelvin. The answer is minus 21.3 joules per Kelvin per mole. This is the entropy change for the system.

Let us just take a relook at what we have done. We had asked, we have been asked to calculate entropy change for the freezing of water at minus 5 degree centigrade. This process what we did, we devised another path. We took the water liquid at minus 5 degree Celsius to 0 degree Celsius and then, allowed it to freeze. This is an equilibrium process and then, we reduce the temperature of solid to minus 5 degree centigrade. We calculated delta S1 and we just saw how to calculate that. It is C p log T final over T initial.

We calculated delta S2 which is also C p log T final over T initial and this was simply a phase transition. For the phase transition, the entropy change is equal to enthalpy divided by the transition temperature. So, from these considerations, we got an enthalpy of phase transition or entropy of phase transition. Entropy of this transition, this phase transition for liquid to solid at minus 5 degree Celsius as minus 21.3 joules per Kelvin per mole and as liquid is forming solid, it is expected that the value should be negative, the entropic decreases.

Now, how do we calculate? For this surrounding for system, we have calculated and if you remember that the entropy change in surrounding is to be calculated from the knowledge of the actual amount of heat has been transferred to the surrounding divided by the temperature.

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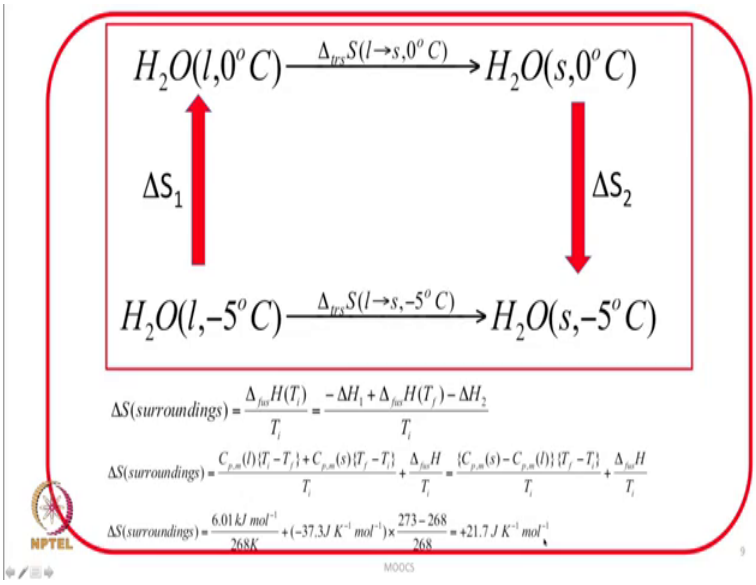

$$\begin{tikzcd}
H_2O(l,0^o C) \arrow[r, "\Delta_{trs}S(l\rightarrow s,0^o C)"] & H_2O(s,0^o C) \arrow[d, "\Delta S_2"] \\
H_2O(l,-5^o C) \arrow[u, "\Delta S_1"] \arrow[r, "\Delta_{trs}S(l\rightarrow s,-5^o C)"] & H_2O(s,-5^o C)
\end{tikzcd}$$

$$\Delta S(surroundings) = \frac{\Delta_{fus}H(T_i)}{T_i} = \frac{-\Delta H_1 + \Delta_{fus}H(T_f) - \Delta H_2}{T_i}$$

$$\Delta S(surroundings) = \frac{C_{p,m}(l)\{T_i - T_f\} + C_{p,m}(s)\{T_f - T_i\}}{T_i} + \frac{\Delta_{fus}H}{T_i} = \frac{\{C_{p,m}(s) - C_{p,m}(l)\}\{T_f - T_i\}}{T_i} + \frac{\Delta_{fus}H}{T_i}$$

$$\Delta S(surroundings) = \frac{6.01\, kJ\, mol^{-1}}{268K} + (-37.3 J\, K^{-1}\, mol^{-1}) \times \frac{273-268}{268} = +21.7\, J\, K^{-1}\, mol^{-1}$$

So, we begin we need to know the total delta H corresponding to surrounding and the temperature. So, that means we again go back to this step, this step, this step and since we are talking about the surroundings, that means we will talk about negative of this step, negative of this step and negative of this step because whatever is there for the system and if there is a thermal equilibrium between system and surrounding, the negative effect will be there for the surrounding.

That is what is mentioned in this that delta S surroundings can be calculated if I know the total enthalpy of fusion. For this process which we trying to get through, these 1 2 3 for first process is minus of delta H1 minus because we are talking about surroundings and this will be actual fusion for freezing enthalpy because freezing enthalpy is the corresponding to solid to liquid. So, we will put the positive number over here and for this, the negative of the enthalpy change for solid at 0 degree to minus 5 degree and here, we will make use of this expression that enthalpy H f is equal to H i plus integration T i to T f C p d T which can be written as delta H is equal to C p. If I assume to be independent of temperature, I make use of this expression and this is what I will use here for delta minus delta H1. It will turn out to be C p m of liquid into T i minus T f. You can actually figure out from there C p of liquid into because we are talking about the reverse process. T i has to be first and T f has to be later plus C p m of S into T f minus T i and then, the remaining term is delta H fusion by T i.

Rearrange this substitute, the numbers and get the answer. The answer turns out to be plus 21.7 joules per Kelvin per mole. Remember that we are talking about the freezing process. Freezing is exothermic and this heat liberated goes out to the surroundings and increases the entropy of the surroundings. So, when you calculate the total for surroundings it was 21.7 joules per Kelvin per mole, for system it is minus 21.3 joules per Kelvin per mole and when you take the total delta S system plus delta S surrounding, it turns out to be 0.4 joules per Kelvin per mole.

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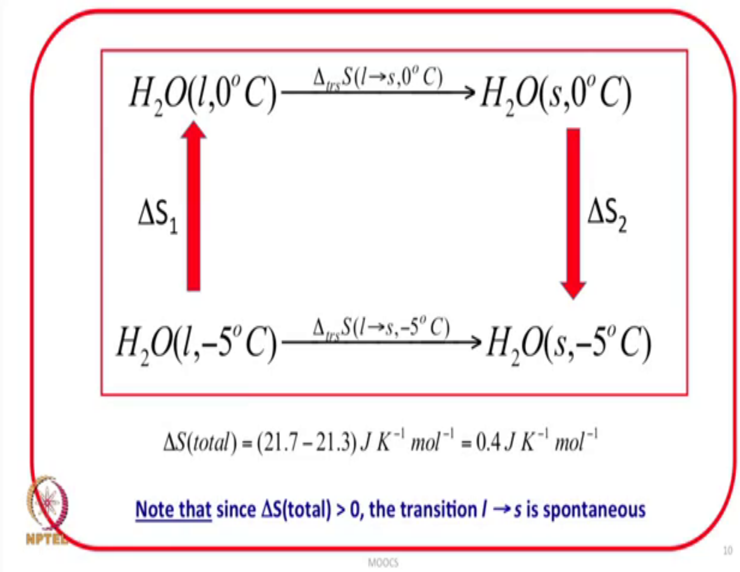

$$\begin{tikzcd} H_2O(l,0^oC) \arrow[r, "\Delta_{trs}S(l\to s,0^oC)"] & H_2O(s,0^oC) \arrow[d, "\Delta S_2"] \\ H_2O(l,-5^oC) \arrow[u, "\Delta S_1"] \arrow[r, "\Delta_{trs}S(l\to s,-5^oC)"] & H_2O(s,-5^oC) \end{tikzcd}$$

$$\Delta S(total) = (21.7 - 21.3)\,J\,K^{-1}\,mol^{-1} = 0.4\,J\,K^{-1}\,mol^{-1}$$

Note that since $\Delta S(total) > 0$, the transition $l \to s$ is spontaneous

So, once again the point to be noted here that the total entropy, entropy change in the system plus entropy change in the surrounding turns out to be positive. Therefore, the process must be spontaneous and that is what is commented over here that since delta S total is greater than 0, the liquid to solid transition is spontaneous. So, this problem once again highlights the significance of second law of thermodynamics in establishing in demonstrating this spontaneity of a process. It also highlights that if we want to demonstrate that, a process is spontaneous in terms of second law of thermodynamics, then we need to calculate the change in entropy of the system. We need to calculate the change in entropy of the surrounding, add up the two and if this term turns out to be positive, then the process is spontaneous in that direction. More numerical problems we will take up in the next lecture.

Thank you very much.