

**Chemical and Biological Thermodynamics: Principles to Applications**  
**Prof. Nand Kishore**  
**Department of Chemistry and Biochemistry**  
**Indian Institute of Technology, Bombay**

**Lecture – 17**  
**Tutorial session**

Let us continue with our discussion on solving some more numerical problems and today, we will further discuss on calculation of changes in entropy under different conditions.

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**Question :** Calculate the change in entropy when 200g of  
 (a) water at 0<sup>o</sup> C  
 (b) Ice at 0<sup>o</sup> C is added to 200g of water at 90<sup>o</sup> C in an insulated container

**Solution:**

$$T_f = \frac{n_1 T_{i,1} + n_2 T_{i,2}}{n_1 + n_2} = \frac{T_{i,1} + T_{i,2}}{2} \text{ (if } n_1 = n_2) = 318 \text{ K}$$

$$\Delta S = n_1 C_{p,m} \ln \frac{T_f}{T_{i,1}} + n_2 C_{p,m} \ln \frac{T_f}{T_{i,2}} = n_1 C_{p,m} \ln \frac{T_f^2}{T_{i,1} T_{i,2}} \text{ (because } n_1 = n_2)$$

$$\Delta S = \left( \frac{200 \text{ g}}{18.02 \text{ g mol}^{-1}} \right) \times 75.3 \text{ J K}^{-1} \text{ mol}^{-1} \times \ln \left( \frac{318^2}{273 \times 363} \right) = +16.9 \text{ J K}^{-1}$$

Let us first take up this question which is calculate the change in entropy when 200 gram of water at 0 degree Celsius and in the second experiment, ice at 0 degree Celsius is added to 200 gram of water at 90 degree Celsius in an insulated container. If we look at the statement very carefully, what is being done is in 1 case, we are adding 200 gram of water which is at 0 degree Celsius to 200 gram of water which is at 90 degree Celsius. So, in this case you are just mixing 2 liquid forms of water which are at different temperatures.

In the second case that is part b, what we are doing is, we are adding 200 gram of ice at 0 degree Celsius and this is being added to 200 gram of water which is at 90 degree Celsius. The point to be noted here is, here we are adding ice to water. Therefore, there

has to be a phase change in this mixing and we have to account for that, but first let us take up case number 1.

When we are adding 200 gram of water at 0 degree Celsius to 200 gram of water at 90 degree Celsius, so obviously 1 part of the water which is at 0 degree Celsius will be gaining heat and the other part of water which is at 90 degree Celsius will be losing heat, and overall heat change, heat gained plus heat lost has to be 0.

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The image shows a handwritten derivation of the final temperature formula for mixing two substances. The equations are as follows:

$$n_1 C_{p,m} (T_f - T_{i,1}) + n_2 C_{p,m} (T_f - T_{i,2}) = 0$$
$$n_1 T_f - n_1 T_{i,1} + n_2 T_f - n_2 T_{i,2} = 0$$
$$T_f (n_1 + n_2) = n_1 T_{i,1} + n_2 T_{i,2}$$
$$T_f = \frac{n_1 T_{i,1} + n_2 T_{i,2}}{n_1 + n_2}$$

In the bottom left corner of the slide, there is a logo for NPTEL (National Programme on Technology Enhanced Learning).

So, that is what we are going to now use the information on let us say, we are taking  $n_1$  moles of any substance and let us say the heat capacity is  $C_p$ , I will put  $C_{p,m}$  into  $T_f$  minus  $T_{i,1}$  plus  $n_2$  times  $C_{p,m}$ . If it is the same substance,  $T_f$  minus  $T_{i,2}$  has to be 0. That is heat gained plus heat loss has to be equal to 0 and the heat gain or heat loss is given by this formula  $n$  is number of moles times heat capacity times the temperature difference.

Now, since here the heat capacities are same, these will get cancelled. So, what we have? We have  $n_1$  times  $T_f$  minus  $n_1$  times  $T_{i,1}$  plus  $n_2$  times  $T_f$  minus  $n_2$  times  $T_{i,2}$  has to be equal to 0. Let us take  $T_f$  outside. Inside what we have is,  $n_1$  plus  $n_2$ . This is going to be equal to  $n_1 T_{i,1}$  plus  $n_2 T_{i,2}$ . Rearranging this we can calculate the final temperature as  $n_1 T_{i,1}$  plus  $n_2 T_{i,2}$  divided by  $n_1$  plus  $n_2$ .

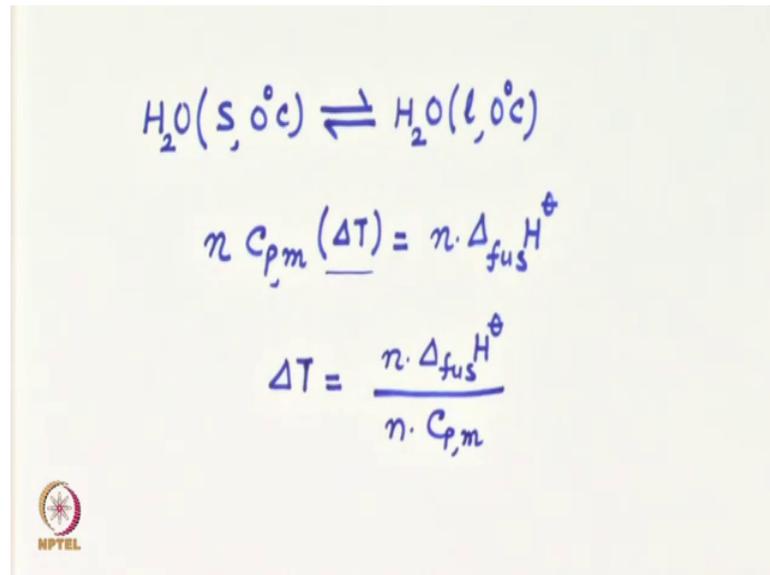
Now, let us go to the slide. This is the formula  $T_f$  is equal to  $n_1 T_{i1} + n_2 T_{i2}$  over  $n_1 + n_2$ . This is the formula that we just derived. Now, if you mix equal amounts, for example, in the given question you are adding 200 gram to 200 grams. So, same number of moles and then,  $n_1$  is equal to  $n_2$ . If you put  $n_1$  is equal to  $n_2$ , this solves out to  $T_{i1} + T_{i2}$  divided by 2. That is the temperature will become half of the addition of 2 since one sample of water is at 0 and other sample of water is at 90 degree Celsius divided by 2, and this 90 divided by 2 is 45 in Kelvin. This will turn out to be 318 Kelvin.

So, you see what we had. We had water at 0 degree Celsius, we had water at 90 degree Celsius and the final temperature is 318 Kelvin. Since we know the final temperature, we can calculate the entropy change by using the well established equation that we derived earlier that is for the first sample of water  $\Delta S$ . For the first sample, it is  $n_1$  times molar heat capacity into  $\log T_{\text{final}} / T_{\text{initial}}$  plus for the second sample  $n_2$  times  $C_{pm}$  times  $\log T_{\text{final}} / T_{\text{initial}}$ . In fact, if you combine these two logarithmic terms, this is you know  $n_1$  is equal to  $n_2$ . So, if  $n_1$  is equal to  $n_2$ ,  $n$  will come out or  $n_1$  you can substitute  $C_{pm}$  will come out. So, it is  $\log a + \log b$  times.  $\log a + \log b$  is equal to  $\log a$  into  $b$ . So, when you combine the final form is  $n_1$  into  $C_{pm}$  into  $\log T_{\text{final}}^2 / T_{i1} T_{i2}$ , this is because  $n_1$  is equal to  $n_2$ .

So, now if I have the information on the number of moles, molar heat capacity and initial and final temperatures, I can easily calculate the value of  $\Delta S$ . The heat capacity of water is 75.3 Joules per Kelvin per mole and we know how to calculate number of moles. It is weight divided by molecular weight and once you substitute these numbers, where  $T_{i1}$ , see it was at 0 degree Celsius, so you put 273. For second sample, it was 90 degree Celsius. So, we put 363 and final temperature is 318 Kelvin and when you solve it the answer comes out to plus 16.9 Joules per Kelvin.

Now, we take a look at the second part. Now, you are adding 200 gram of ice to 200 gram of water.

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Therefore what is happening, we are taking 200 gram of ice solid form which is at 0 degree centigrade and this is being added to water same amount 200 gram which is at 90 degree centigrade. Next since we are adding two ice, first of all this phase equilibria will be set up that is the solid form has to be molten to liquid form and some heat will be required for this phase transition. How do we calculate this heat required?

This will be number of moles into  $C_{p,m}$  molar heat capacity into  $T_{\text{final}} - T_{\text{initial}}$ . Let me put  $\Delta T$  from where this heat will come, number of moles times enthalpy of fusion. The enthalpy of fusion, we know the value of water and if we move, if we know the molar heat capacity of ice, we can easily calculate how much is the change in temperature. Now, let us go back look at the slide.

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Heat required for melting:  $n\Delta_{\text{fus}}H = (11.1 \text{ mol}) \times (6.01 \text{ kJ mol}^{-1}) = 66.7 \text{ kJ}$

The decrease in temperature of hot water as a result of melting:

$$\Delta T = \frac{q}{C_{p,m}} = \frac{66.7 \text{ kJ}}{(11.1 \text{ mol}) \times (75.3 \text{ J K}^{-1} \text{ mol}^{-1})} = 79.8 \text{ K}$$

At this stage, the system has 200 g water at 0°C and 200 g water at (90-79.8)°C = 10°C

$$\Delta S = \frac{n\Delta_{\text{fus}}H}{T_f} + nC_{p,m} \ln \frac{283}{363}$$

$$\Delta S = \frac{11.1 \text{ mol} \times 6.01 \text{ kJ mol}^{-1}}{273 \text{ K}} + 11.1 \text{ mol} \times 75.3 \text{ J K}^{-1} \text{ mol}^{-1} \times \ln \frac{283}{363} = +35.3 \text{ J K}^{-1}$$



Heat required for melting  $n$  times  $\Delta H$  fusion  $n$  is 11.1 mol and  $\Delta H$  is 6.01 kilo Joules per mole. It turns out to be 66.7 kilo joule. So, by using this information and the formula that we just derived,  $\Delta T$  is equal to  $q$  by  $C_{p,m}$  which is same as this. From here we write  $\Delta T$  is equal to  $n$  times  $\Delta H$  fusion  $n$  because it is a constant pressure. I can write it as  $q$  also divided by  $n$  times  $C_{p,m}$ . So, you can include  $n$  into this or you can just cancel  $n$  and use 6.01. Whatever way you want to use  $\Delta T$ , by this calculation comes out to around 79.8 Kelvin which is approximately 80 Kelvin.

The change in temperatures is 80. It does not matter whether you count it in degree Celsius or you count it in Kelvin because the change  $\Delta$  will remain same. Initial temperature was 90 degree Celsius and the change in temperature is 80 degree Celsius or 80 Kelvin, which is same.

Therefore, the final temperature is going to be 90 minus 80 which is equal to 10 Kelvin or 10 degree centigrade, not 10 Kelvin 10 degree Celsius. So, up to this that is up to the point, where ice has molten into liquid water at 0 degree Celsius, the temperature of the water which was at 90 degree Celsius has fallen down to 10 degree Celsius. So, there is an entropy change. How do we calculate that entropy change? Let us take a look at it.

Entropy change for the phase transition is equal to enthalpy of fusion divided by the freezing point that we have discussed many times. This is the entropy change associated with the melting of ice at 0 degree Celsius and then, since the final temperature is 10

degree Celsius, we have to now calculate the entropy change associated with the sample of water which was earlier at 90 degree Celsius and for that, we will use  $n C_p \log \frac{T_{\text{final}}}{T_{\text{initial}}}$ .  $T_{\text{final}}$  is 283 which is 10 degree Celsius and  $T_{\text{initial}}$  was 90 degree Celsius which is 363 Kelvin.

So, once you substitute these numbers for enthalpy of fusion number of moles heat capacity, the change in entropy is plus 35.3 Joules per Kelvin. This is the change in entropy associated with the melting of ice and the decrease of temperature of water which was from 90 degree centigrade; it has come down to 10. So, what you have now? You have water at 0 degree Celsius, water liquid form at 0 degree Celsius and you have water liquid which is decrease in temperatures from 90 degree Celsius to 10 degree Celsius, 200 gram of each.

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The final temperature is :

$$T_f = \frac{273 + 283}{2} = 278 \text{ K}$$

$$\Delta S = n_1 C_{p,m} \ln \frac{T_f}{T_{i,1}} + n_2 C_{p,m} \ln \frac{T_f}{T_{i,2}} = n_1 C_{p,m} \ln \frac{T_f^2}{T_{i,1} T_{i,2}} \quad (\text{because } n_1 = n_2)$$

$$\Delta S = 11.1 \text{ mol} \times 75.3 \text{ J K}^{-1} \text{ mol}^{-1} \times \ln \left( \frac{278^2}{273 \times 283} \right) = +0.27 \text{ J K}^{-1}$$

$$\text{Total } \Delta S = (35.3 + 0.27) \text{ J K}^{-1} = +36 \text{ J K}^{-1}$$

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So, when these two further mix the final temperature by the same arguments that we just discussed because the number of moles are same. The final temperature is going to be the average of the two which is 0 plus 10 degree Celsius divided by 2 or 278 Kelvin which is 5 degree Celsius. So, therefore now I can easily calculate the entropy change which is associated with 200 gram of water which was at 0 degree centigrade and reaching 278 Kelvin and 200 gram of water which was at 10 degree Celsius and it is now reaching 5 degree Celsius.

So, that is why  $n_1 C_{p,m} \log \frac{T_f}{T_{i1}}$  plus  $n_2 C_{p,m} \log \frac{T_f}{T_{i2}}$ . When you make a further rearrange this, you get this expression  $T_{i1}$  and  $T_{i2}$ . Both are known because initially one of the sample was at 0 degree Celsius; other was at 10 degree Celsius and giving a final temperature of 5 degree Celsius converting into Kelvin and after substitution of the values, we see that the change in entropy now is 0.27 Joules per Kelvin.

Therefore, the total entropy change is the entropy change in part 1. This part 1 what means, this is associated with the melting of ice and the lowering of temperature of water 200 gram of water from 90 degree centigrade to 10 degree centigrade and this contribution is now when the water at 0 degree centigrade is further mixing with water at 10 degree centigrade reaching a final temperature of 5 degree centigrade. The total  $\Delta S$  is plus 36 Joules per Kelvin.

So, although the problem is bit lengthy, but it does explain how to account for the changes in a entropy. Remember that during the process of mixing of ice with water which is at higher than room temperature, the first step is that the ice has to melt. It has to go to liquid water and that is a phase transition and we should not miss any phase dimension. This is a point which is worth remembering that while calculating the changes in entropy if there is any phase transition, let us not miss that. We must calculate the entropy change corresponding to phase transition plus the entropy changes which could be due to changes in temperature.

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**Question :** Calculate (a) the maximum work and (b) the maximum non-expansion work that can be obtained from the freezing of super cooled water at  $-5^{\circ}\text{C}$  and 1.0 atm. The densities of water and ice are  $0.999$  and  $0.917\text{ g cm}^{-3}$ , respectively at  $-5^{\circ}\text{C}$ .

**Solution:**

$$W_{\text{max, non-pV}} = \Delta G(T) = \Delta H(T) - T\Delta S(T)$$
$$\Delta G(T) = \left(\frac{T}{T_f} - 1\right) \Delta_{\text{fus}} H(T_f) - \Delta C_{p,m} \left(T - T_f - T \ln \frac{T}{T_f}\right)$$
$$\Delta G(268\text{K}) = \left(\frac{268}{273} - 1\right) \times (6.01\text{ kJ mol}^{-1}) - (37.3\text{ J K}^{-1}\text{ mol}^{-1}) \times \left(268 - 273 - 268 \ln \frac{268}{273}\right) = -0.11\text{ kJ mol}^{-1}$$

**Maximum non-expansion work =  $\Delta G = -0.11\text{ kJ mol}^{-1}$**



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Now, let us take another type of question which is calculate the maximum work and maximum non-expansion work that can be obtained from freezing of super cooled water at minus 5 degree Celsius and one atmosphere. The densities of water and ice are  $0.999$  and  $0.917$  gram per centimeter cube respectively at minus 5 degree centigrade. Let us try to examine the question and see what is being asked and how we should approach answering such questions.

We are asked to calculate the maximum work. Maximum work means we have to calculate delta a and then, we have been asked to calculate maximum non-expansion work. Maximum non-expansion work means we have to calculate delta G. So, this should be very clear that what should be calculated for maximum work and what should we calculate for maximum non-expansion and it is freezing of super cooled water at minus 5 degree Celsius and one atmosphere pressure. Take a look at the slide.

Let us first calculate the maximum known pressure volume work. The reason for calculating the maximum known pressure volume work first is that if we have the information on delta G, it is easy to then calculate delta a from the given information and to calculate delta G, we need information on delta H and we need information on delta S at minus 5 degree centigrade.

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$$\begin{aligned} \Delta H(T) &= \Delta H(T_f) + \Delta C_p(T - T_f) \\ \Delta S(T) &= \frac{\Delta H(T_f)}{T_f} + \Delta C_p \ln \frac{T}{T_f} \\ \Delta S(T) &= \frac{\Delta H(T_f)}{T_f} + \Delta C_p \ln \frac{T}{T_f} \\ \Delta G(T) &= \Delta H(T) - T \Delta S(T) \\ \Delta G(T) &= \Delta H(T_f) + \Delta C_p(T - T_f) - T \left\{ \frac{\Delta H(T_f)}{T_f} + \Delta C_p \ln \frac{T}{T_f} \right\} \\ \Delta G(T) &= \Delta H(T_f) \left\{ 1 - \frac{T}{T_f} \right\} + \Delta C_p \left\{ T - T_f - T \ln \frac{T}{T_f} \right\} \end{aligned}$$

The question is now how do we get the information at minus 5 degree centigrade? Let us see delta H. At any temperatures let us say I can calculate from the knowledge of delta H, let us say at freezing point plus delta C p into T minus T f, where T is any general temperature. Now, the second information that we need is on delta S. Delta S at any temperature I can calculate. From the knowledge of delta S, again let me use the freezing point plus delta C p log T by T f.

Please remember that this is the entropy of phase transition. So, therefore I can use delta S at any temperature is equal to this will be 1. This will be enthalpy delta H at freezing point. This is enthalpy of fusion divided by the freezing point plus delta C p log T by T f. Now, I make use of this equation delta G at any temperature is equal to delta H at any temperature minus T into delta S at any temperature and I will now substitute delta H and delta S at any temperature, what do I get. Delta G at any temperature is equal to delta H at any temperature is delta H at freezing point that is enthalpy of fusion plus delta C p into T minus T f minus T delta S minus T into delta S.

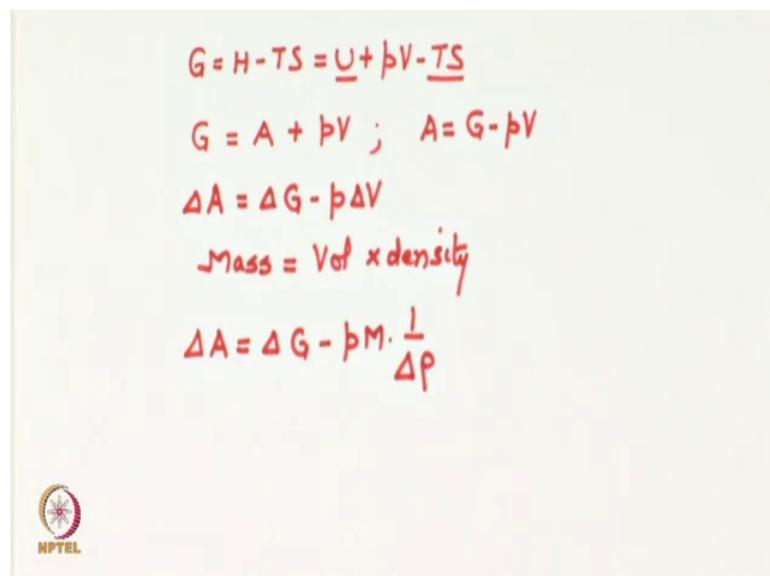
I will put the entire thing over here which is delta H at T f over T f plus delta C p log T by T f and now, if you further rewrite delta G at any temperature T is equal to delta H at T f, if I take out as common, it is 1 minus T by T f from here and here, then plus delta C p. Let us take out common. It is T minus T f minus T log T by T f. This is the equation

that can be used. Now, please remember that we are talking about that this T is minus 5 degrees Celsius and this is the freezing point, right.

So, we have to calculate delta G which is obtained from freezing of super cooled water at minus 5 degree Celsius. It is a freezing of water, right. So, the equation to be used now is actually negative of this because here what we are using is this T is any general temperature, T is this, T f is the freezing of water, a freezing point of water. So, maximum work that can be obtained from freezing of super cooled water at minus 5 degree Celsius and one atmosphere is actually going to be negative of this and that is why the equation that we are using over here is actually negative of what we have derived is the same equation that we just derived, but with a negative sign because we are talking about freezing liquid to solid.

Once you substitute the numbers, the answer comes out to be minus 0.11 kilojoules per mole, right. So, let us now comment on this minus 0.11 kilojoules per mole. That is the maximum non-expansion work because delta G is a measure of maximum non-expansion work which is equal to minus 0.11 kilojoules per mole.

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The image shows a slide with handwritten equations in red ink. The equations are:

$$G = H - TS = U + pV - TS$$
$$G = A + pV ; A = G - pV$$
$$\Delta A = \Delta G - p\Delta V$$
$$\text{Mass} = \text{Vol} \times \text{density}$$
$$\Delta A = \Delta G - pM \cdot \frac{1}{\Delta \rho}$$

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Now, we have the information on delta G and it is easy to calculate delta A. How do we do that? G is equal to H minus TS which is equal to U plus p V minus TSU minus TS is A. So, therefore G is equal to A plus p V.

This allows me to write  $\Delta A$  is equal to  $\Delta G$  minus pressure into volume and since pressure is constant, I will write  $\Delta A$  is equal to  $\Delta G$  minus  $p$  times  $\Delta V$  and since mass is equal to volume times density. So, I can write now  $\Delta A$  is equal to  $\Delta G$  minus  $p$  if I know the molecular weight. What I need to know is,  $1$  over  $\Delta \rho$ .  $\Delta \rho$  is the density we are talking about freezing.

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$$\Delta A = \Delta G - p\Delta V = \Delta G - pM\Delta\left(\frac{1}{\rho}\right)$$

$$\Delta A = (-0.11 \text{ kJ mol}^{-1}) - (1.013 \times 10^5 \text{ Pa}) \times 18.02 \times 10^{-3} \text{ kg mol}^{-1} \times \left( \frac{1}{917 \text{ kg m}^{-3}} - \frac{1}{999 \text{ kg m}^{-3}} \right) = -0.11 \text{ kJ mol}^{-1}$$

**Thus both maximum work ( $\Delta A$ ) and maximum non-expansion work are about 0.11 kJ mol<sup>-1</sup> each.**




So, therefore what we will do is, we will substitute for the values liquid to solid, that is what we are talking about and therefore,  $\Delta \rho$  has to be  $1$  over density of solid minus  $1$  over density of liquid and minus  $0.11$  kilojoules per mole is the value of  $\Delta G$ . Pressure has to be in Pascal's and molecular weight of water is  $18.02$  into  $10$  to the power minus  $3$  kilogram per mole.

So, we have to take care of the units and then, put the densities of ice and density of liquid water. The answer still comes out to be minus  $0.11$  kilojoules per mole. So, you see both  $\Delta A$  and  $\Delta G$  are coming out to be minus  $0.11$  kilojoules per mole. So, therefore the comment is both maximum work. Maximum work is in terms of  $\Delta A$  and maximum non-expansion work which is  $\Delta G$  are about  $0.11$  kilojoules per mole each. So, this is the amount of work which is available from freezing of super cooled water at minus  $5$  degree Celsius.

So, I hope that these examples have cleared several questions that might have arisen when we were deriving these equations, and the application of these equations make us

understand these concepts in a better way. We will further continue solving numerical problems in few other sessions, where the concepts of  $\Delta G$   $\Delta A$  be again be used.

Thank you very much.