Chemical and Biological Thermodynamics: Principles to Applications

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Lecture - 09

Entropy and Second Law: Applications

In this lecture, we will further discuss the entropy and connected with several applications in terms of numerical problems.

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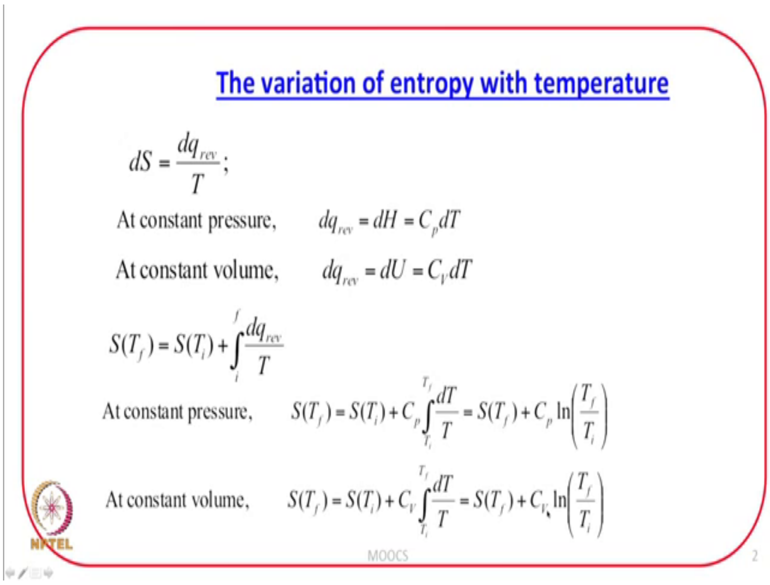

The variation of entropy with temperature

$$dS = \frac{dq_{rev}}{T};$$

At constant pressure, $dq_{rev} = dH = C_p dT$

At constant volume, $dq_{rev} = dU = C_V dT$

$$S(T_f) = S(T_i) + \int_i^f \frac{dq_{rev}}{T}$$

At constant pressure, $S(T_f) = S(T_i) + C_p \int_{T_i}^{T_f} \frac{dT}{T} = S(T_f) + C_p \ln\left(\frac{T_f}{T_i}\right)$

At constant volume, $S(T_f) = S(T_i) + C_V \int_{T_i}^{T_f} \frac{dT}{T} = S(T_f) + C_V \ln\left(\frac{T_f}{T_i}\right)$

Variation of entropy with temperature: the temperature dependence of any thermodynamic property is very, very important because it will allow you to understand the process in details as a function of temperature. But you remember that the parameter a thermodynamic parameter or a property which is required to connect any thermodynamic property from one temperature to another temperature is heat capacity, and here we will connect the heat capacity and entropy.

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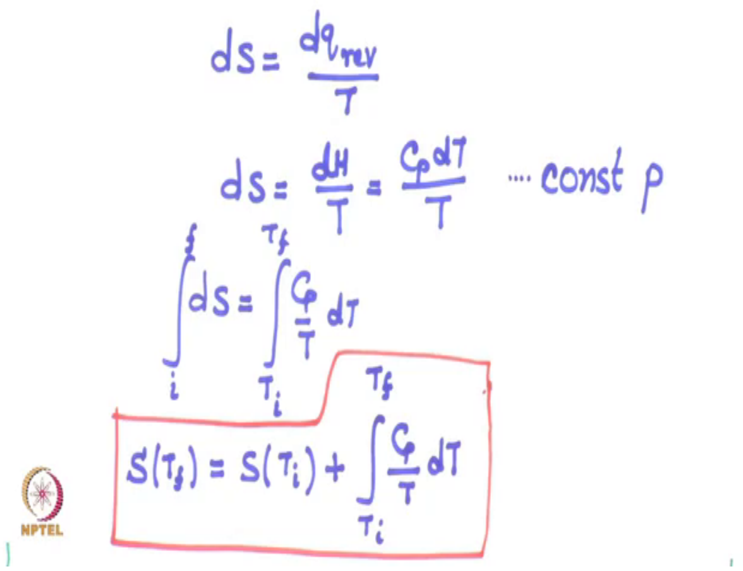

$$dS = \frac{dq_{rev}}{T}$$

$$dS = \frac{dH}{T} = \frac{C_p dT}{T} \quad \text{.... const } p$$

$$\int_i^f dS = \int_{T_i}^{T_f} \frac{C_p}{T} dT$$

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

So, let us begin again with the definition of change in entropy mathematical definition of change in entropy d S is equal to d q reversible by T d S is equal to d q reversible by T. And at constant pressure d q reversible is equal to d H is equal to C p d T. And that I will substitute over here d S is equal to d H by T at constant pressure, this is equal to C p d T by T, and remember that we are talking about constant pressure. Therefore, if I write now like this d S is equal to C p by T d T initial to final from T initial to T final, I can write this as entropy at a final temperature is equal to entropy at initial temperature plus integration T i to T f C p by T dT, very important relation.

So, how do we determine experimentally determine the value of entropy? What kind of experiments we need to design we need to do? According to this equation entropy of a substance at a given temperature can be determined if I am able to measure the heat capacity of that system. And how do you measure the heat capacities heat capacities are determined by using calorimeters this also we will discuss later on that how calorimeters can be use to determine the heat capacity of a system.

So, if I know the entropy at any reference temperature and then the integration of this from initial reference temperature to the temperature of choice will allow us to determine the value of S T f. Now, let us go back to this slides if we talk about constant volume then in place of d q reversible I will use d U because constant volume d q is equal to d U and d U is equal to C v d T.

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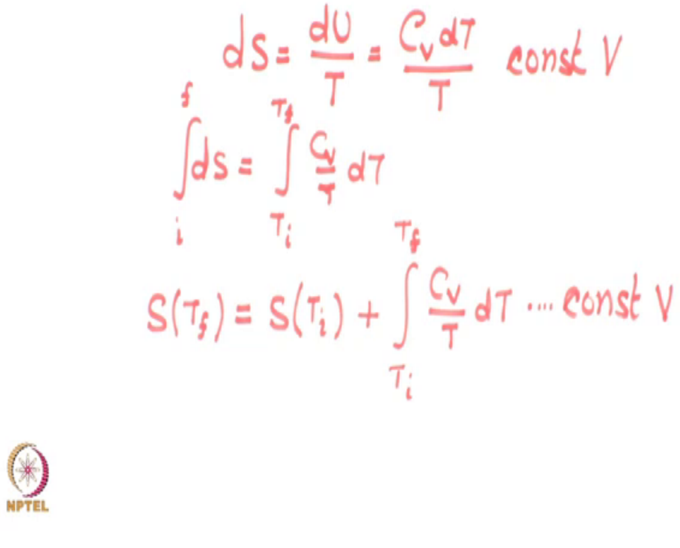

$$dS = \frac{dU}{T} = \frac{C_v dT}{T} \quad \text{const } V$$

$$\int_i^f dS = \int_{T_i}^{T_f} \frac{C_v}{T} dT$$

$$S(T_f) = S(T_i) + \int_{T_i}^{T_f} \frac{C_v}{T} dT \cdots \text{const } V$$

Then if I put that d S is equal to d U by T is equal to C v d T by T at constant volume. Then by the same arguments d S, I go for initial state to final state is equal to T I to T f C v by T d T, I have S at the final temperature is equal to S at an initial temperature plus integration T i to T f C v by T d T. This is at constant volume. So, here again the measurement of entropy requires the measurement of the heat capacity. And heat capacities can be measured by using calorimeter. Going back to the slides, if heat capacity is independent of temperature, you can always take it out of integral then S T f is equal to S T I plus C p log T f by T i at constant pressure. And in place of C p, it will be C v; everything else remains the same when it is at a constant volume.

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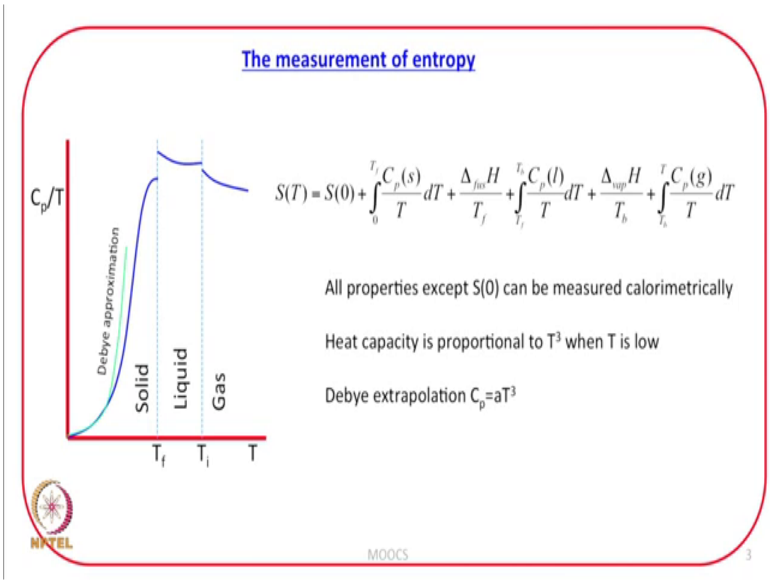

The measurement of entropy

$$S(T) = S(0) + \int_0^{T_f} \frac{C_p(s)}{T} dT + \frac{\Delta_{fus}H}{T_f} + \int_{T_f}^{T_b} \frac{C_p(l)}{T} dT + \frac{\Delta_{vap}H}{T_b} + \int_{T_b}^{T} \frac{C_p(g)}{T} dT$$

All properties except S(0) can be measured calorimetrically

Heat capacity is proportional to T^3 when T is low

Debye extrapolation $C_p = aT^3$

Let us now apply it: measurement of entropy. Let us say I am interested in experimentally measurement of entropy of any substance A in gaseous form at any temperature T. This is the assignment, experimental measurement of the entropy of a substance A in the gaseous form at temperature T.

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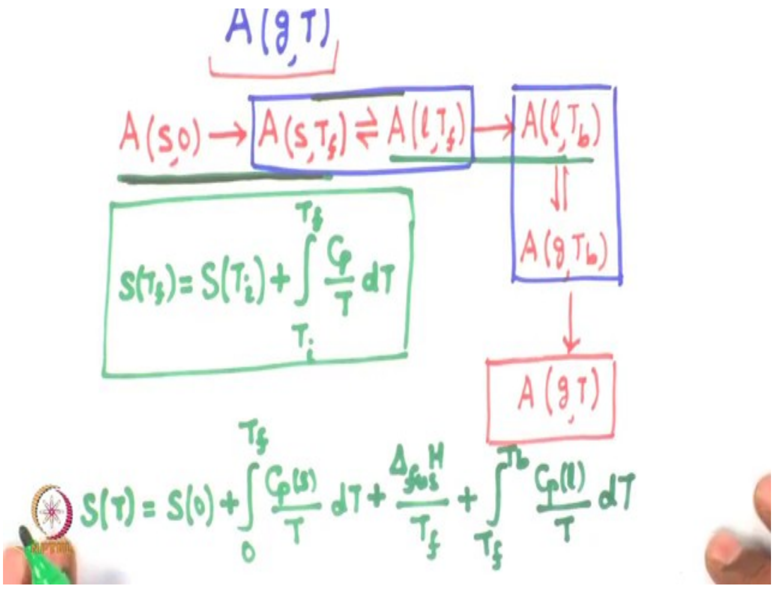

Now, let me consider from 0 Kelvin onwards. A will be in solid form at 0 Kelvin. When I heat it, A solid form and T f is its multi point or freezing temperature, where there will be a phase transition and A will become liquid, but the temperature will not change. Further heating, you will have A in the liquid form at boiling point; and then further heating, A will become vapor at boiling point; and then if further heat, A in gaseous form at general temperature. This is my interest, I want to know the entropy of A that is you remember this was the target in gaseous form at temperature T.

So, what information do I need? We have just discussed that entropy at a final temperature is equal to entropy at an initial temperature plus integration T i to T f C p by T d T, this equation we need to use. And we need to choose an appropriate reference temperature T i; and here initial we will choose as 0 Kelvin. So, what experimental information do I need, I need to know how the heat capacity varies with temperature of the solid, how the heat capacity varies with temperature of the liquid and of the gas. On the way, you see there are phase transition, we cannot ignore that this phase transition, this is one phase transition we cannot ignore; this is another phase transition we cannot ignore and sometime there is a phase transition within a solid we cannot ignore those. And the entropy of the phase transition have to be added in this expression.

So, how do I know go about this the entropy of A at temperature T, I will say T will be equal to entropy at 0 that is my reference plus for this process - the first one, I need to add this integration that is 0 to T f C p of solid divided by T dT. So, I have taken care now of this step. Now, I need to consider this step phase transition. And we already know that the entropy of phase transition is delta fusion divided by freezing point. Entropy of phase transition is enthalpy of freezing divided by the freezing point plus now the next one this one this one will be from T f to T b, it will be C p of liquid divided by temperature d T.

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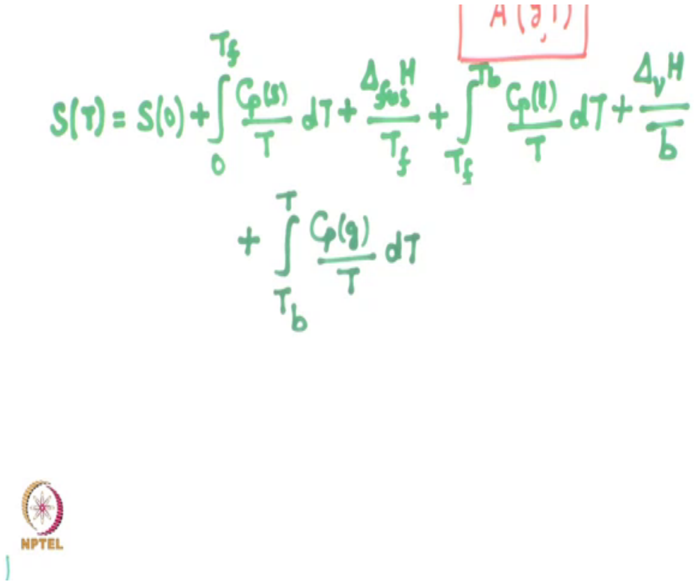

$$\boxed{A(s,l)}$$

$$S(T) = S(0) + \int_0^{T_f} \frac{C_p(s)}{T} dT + \frac{\Delta_{fus} H}{T_f} + \int_{T_f}^{T_b} \frac{C_p(l)}{T} dT + \frac{\Delta_v H}{b}$$

$$+ \int_{T_b}^{T} \frac{C_p(g)}{T} dT$$

Then next one I need to account for the phase transition and that will be delta vaporization H by boiling point. And there is one more term that we need to add for this that will be plus integration T b to T C p of gas divide by temperature d T. Now, let us go back the same thing I will show on the figure, figure I will discuss a bit later, but let me just show you this equation, which we just derive S T is T is the final temperature, 0 is the initial temperature 0 Kelvin. Then 0 to freezing point C p of solid by T d T then there is a phase transition, so entropy of phase transition. Then from freezing point to boiling point we need to use this value of integral; and then again a phase transition and then again the value of integral till the temperature of interest.

Now, the question is how do we evaluate this integral one is numerical integration or biographical method

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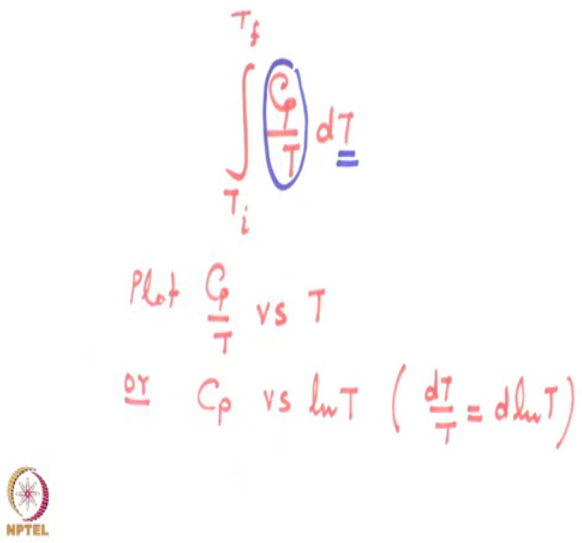

$$\int_{T_i}^{T_f} \left(\frac{C_p}{T}\right) dT =$$

Plot $\frac{C_p}{T}$ vs T

or C_p vs $\ln T$ $\left(\frac{dT}{T} = d\ln T\right)$

What we have is we need to integrate let us from T i to T f C p versus T d T these integrals we have to be evaluating. So, a graphical method will be I plot C p by T versus T or you plot C p versus log T, because d T by T is equal to d log T. So, an easy way can be I plot C p by T against T that means I need experimental measurement of heat capacity at constant pressure, and that is what is shown in the figure. This is experimental determination of heat capacity C p, and you plot C p by T against T. This is the nature, this is for the solid, and this area is for the liquid, and this is for the gas. And you know the integral can be solved if you can, for example, if you look at this T f and T b you plot C p by T against T and area under the curve within the limits T f to T b that will be the value of integral. This is to be write as T b.

Now, the question is this needs experimental determination of heat capacity up to 0 Kelvin, is it possible to determine experimentally the value of heat capacity at 0 Kelvin? Experimentally, it is not possible because even the third law says that you cannot achieve 0 Kelvin, we will discuss third law later on, but according to third law it is not possible to arrive at 0 Kelvin infinite numbers of steps. Then what is done is the value of heat capacity, let us look at the figure, experimentally you determine the value of heat capacity down to as low temperature as possible let us say up to this temperature. And then beyond which there are good theoretical grounds to assume that heat capacity is proportional to the third power of T, C p is proportional to T cube, C p is equal to a T cube, where a is the proportionality constant and this a depends on the properties of the material.

Now, you fit whatever data you have at low temperature to this equation and extrapolate down to 0. What we have done this is we use the Debye extrapolation. C p varies direct proportional to the third power of temperature or C p is equal to a T cube this is called the T by extrapolation. So, Debye extrapolation is used for the variation of heat capacity at constant pressure at very, very low temperature.

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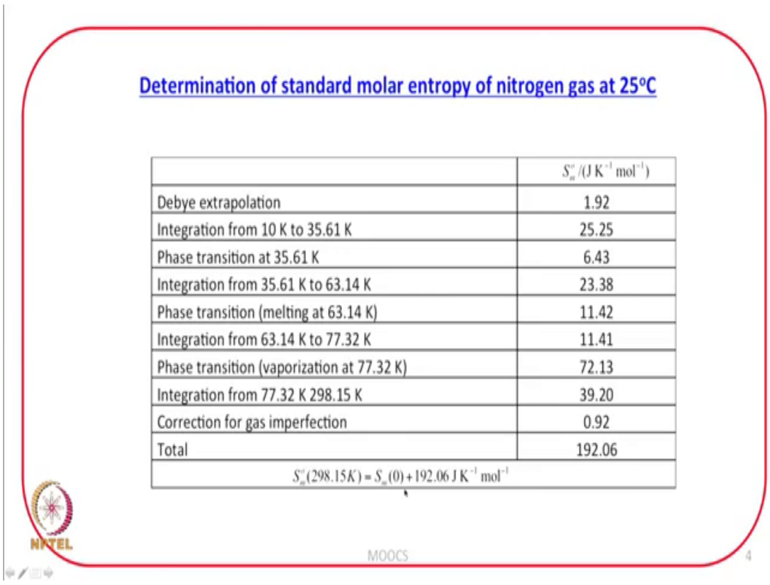

Determination of standard molar entropy of nitrogen gas at 25°C

	$S_m^\circ/(\mathrm{J\,K^{-1}\,mol^{-1}})$
Debye extrapolation	1.92
Integration from 10 K to 35.61 K	25.25
Phase transition at 35.61 K	6.43
Integration from 35.61 K to 63.14 K	23.38
Phase transition (melting at 63.14 K)	11.42
Integration from 63.14 K to 77.32 K	11.41
Phase transition (vaporization at 77.32 K)	72.13
Integration from 77.32 K 298.15 K	39.20
Correction for gas imperfection	0.92
Total	192.06

$S_m^\circ(298.15K) = S_m(0) + 192.06\ \mathrm{J\,K^{-1}\,mol^{-1}}$

Let us take a look at this table I just described that we need to measure the value of heat capacity from 0 Kelvin and keep on measuring up to the temperature of interest. And according to the previous equation for nitrogen, the Debye extrapolation contribution is 1.92 joules per Kelvin per mol integration from 10 Kelvin to 35.61 Kelvin for nitrogen. This is 25.25 joules per Kelvin per mol. Then in nitrogen, there is a phase transition at 6.43 at 35.61 Kelvin, the contribution that is 6.43. Then further integration in the solid form 35.61 to 63.14 that contribution is 23.38 joules per Kelvin per mol.

Then phase transition contribution is 11.42, further integration 11.41. Again there is a phase transition vaporization 72.13, then further integration up to 25 degree Celsius 39.20. And there is a correction for gas imperfection required which is 0.92 joules per Kelvin per mol, you will study in another topic why this gas imperfection correction is required basically due to the failure of hard sphere model. The total value total when added the molar heat capacity at 298.15 K comes out to be 192.06 joules per Kelvin per mol.

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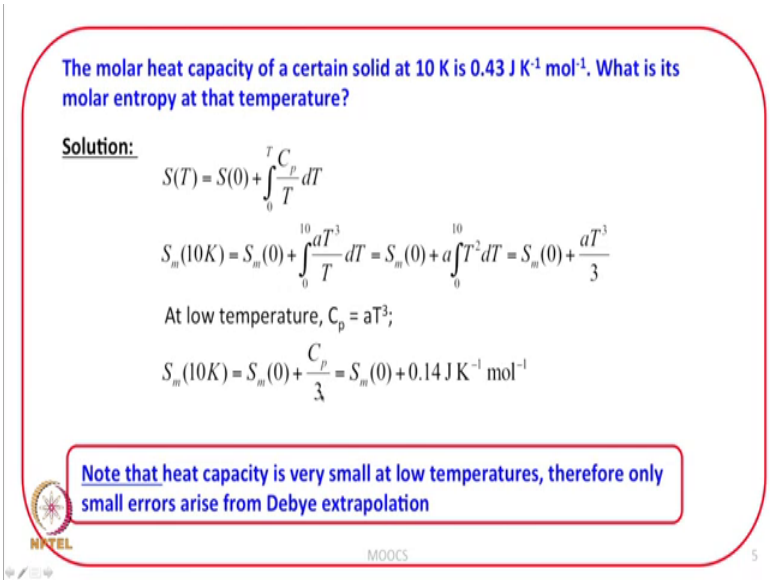

The molar heat capacity of a certain solid at 10 K is 0.43 J K^{-1} mol^{-1}. What is its molar entropy at that temperature?

Solution:

$$S(T) = S(0) + \int_0^T \frac{C_p}{T} dT$$

$$S_m(10K) = S_m(0) + \int_0^{10} \frac{aT^3}{T} dT = S_m(0) + a\int_0^{10} T^2 dT = S_m(0) + \frac{aT^3}{3}$$

At low temperature, $C_p = aT^3$;

$$S_m(10K) = S_m(0) + \frac{C_p}{3} = S_m(0) + 0.14\,\mathrm{J\,K^{-1}\,mol^{-1}}$$

Note that heat capacity is very small at low temperatures, therefore only small errors arise from Debye extrapolation

These is how one can experimentally determine the entropy, but remember that we are talking about the molar entropy at a certain temperature we have not yet discussed about the molar entropy at 0 Kelvin that we will take up in the third law of thermodynamics. Let us apply the various concepts that we have developed so far in solving some numerical problems. The molar heat capacity of a certain solid at 10 Kelvin is 0.43 joules per Kelvin per mol. What is the molar entropy at that temperature? The information given to us is the molar heat capacity, and obviously that is what you need to calculate the entropy that is nothing else given to us.

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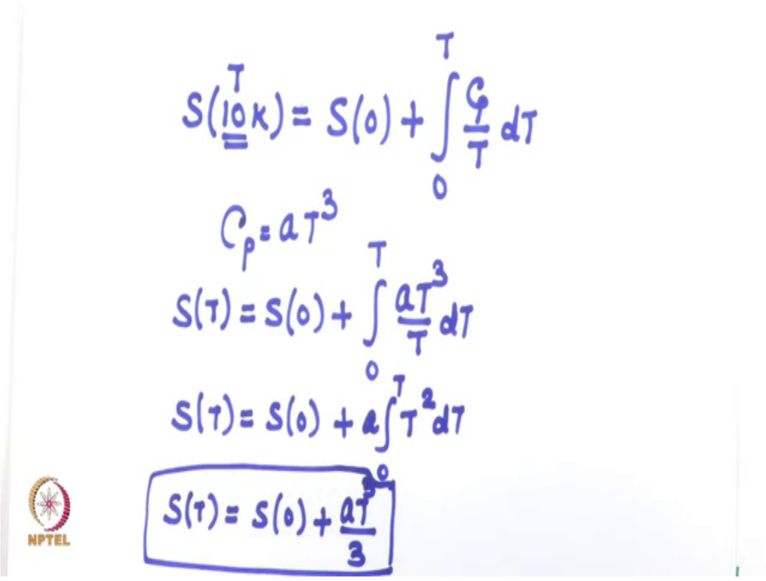

$$S(\overset{T}{\underline{\underline{10}}}K) = S(0) + \int_0^T \frac{C_p}{T}\, dT$$

$$C_p = aT^3$$

$$S(T) = S(0) + \int_0^T \frac{aT^3}{T}\, dT$$

$$S(T) = S(0) + a\int_0^T T^2\, dT$$

$$\boxed{S(T) = S(0) + \frac{aT^3}{3}}$$

And I will straight away start with that I am ask to calculate entropy at 10 Kelvin. I will write entropy at 0 plus 0 to T, where T, I will put 10 later on; at this point, I will not write is C p by T d T. I am deliberately not putting 10 over here because ten the temperature is very low and at this temperature we can conveniently use Debye extrapolation or Debye third power law which is C p is equal to a T cube. Now, let me substitute over here. So, S at very low temperature will be equal to S at 0 plus 0 to T a T cube by T d T or S T is equal to S 0 plus integration 0 to T, if I take out a out it is T square d T. Or S T is equal to S 0 plus a T cube by 3, this is what I get from this integration.

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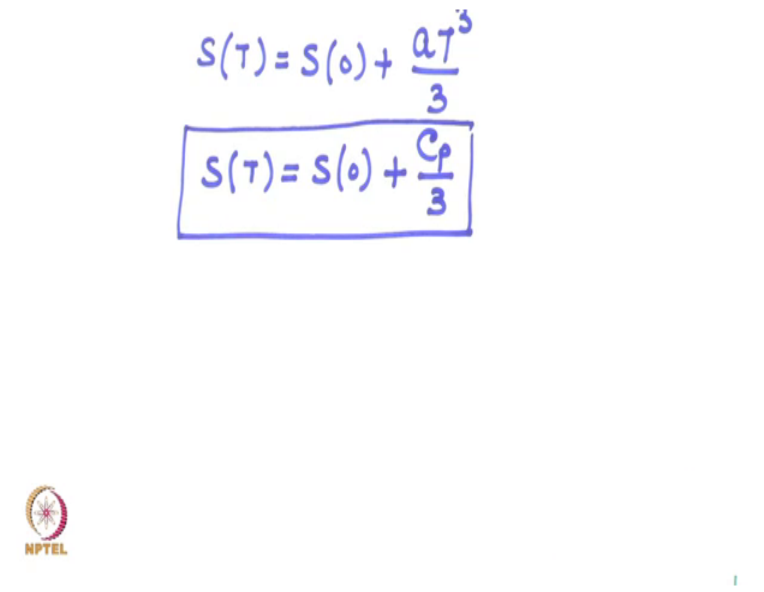

$$S(T) = S(0) + \frac{aT^3}{3}$$

$$\boxed{S(T) = S(0) + \frac{C_p}{3}}$$

So, what I have is now S at T is equal to S at 0 plus a T cube by 3. I can further write this as S at T is equal to S at 0 and instead of a T cube I will write C p, because C p is equal to a T cube. And since C p is give to me, now I can calculate. So, let us now go back to the slide. We will use this equation and as I just discussed, you solve this integral. And what you have is now the entropy at 10 Kelvin can be calculated, if I know entropy at 0 Kelvin plus a T cube by 3; instead of a T cube let us write C p. And you substitute the value of C p which is given to us as 0.43 joules per Kelvin per mol the answer comes out to be 0.14 joules per Kelvin per mol.

So, molar entropy at 10 Kelvin is equal to molar entropy at 0 plus 0.14 joules per Kelvin per mol. There is a comment to be made here that since the heat capacity is very small you see here heat capacity at 10 Kelvin is just 0.43 joules per Kelvin per mol. So, when you divide by three it further goes down the contribution further goes down that is why we mentioned here that note that heat capacity is very small at low temperature therefore, only small errors arise from Debye extrapolation.

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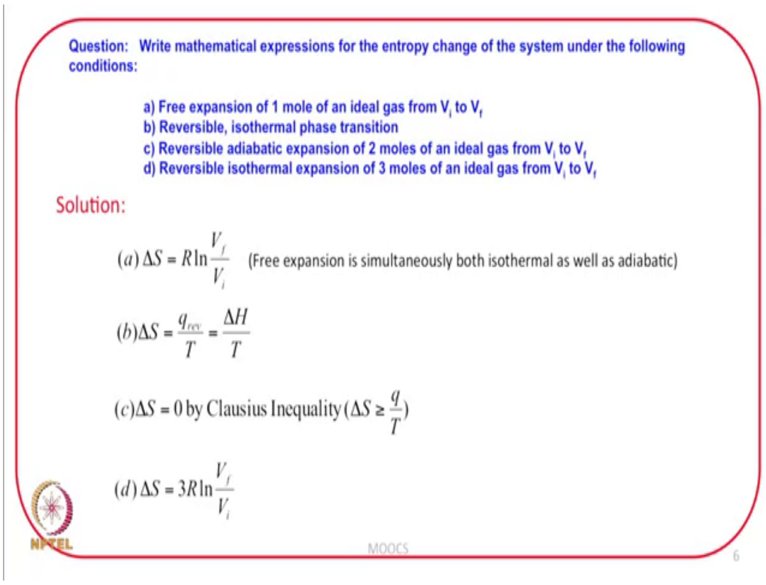

Question: Write mathematical expressions for the entropy change of the system under the following conditions:

a) Free expansion of 1 mole of an ideal gas from V_i to V_f
b) Reversible, isothermal phase transition
c) Reversible adiabatic expansion of 2 moles of an ideal gas from V_i to V_f
d) Reversible isothermal expansion of 3 moles of an ideal gas from V_i to V_f

Solution:

$$(a)\,\Delta S = R\ln\frac{V_f}{V_i}$$ (Free expansion is simultaneously both isothermal as well as adiabatic)

$$(b)\Delta S = \frac{q_{rev}}{T} = \frac{\Delta H}{T}$$

$$(c)\Delta S = 0 \text{ by Clausius Inequality} \left(\Delta S \geq \frac{q}{T}\right)$$

$$(d)\,\Delta S = 3R\ln\frac{V_f}{V_i}$$

Let us take a look at another question. Write mathematical expressions for entropy changes of the system under the following conditions. This is the very simple question. A free expansion of 1 mol of an ideal gas from V i to V f, free expansion. Again, recall free expansion is simultaneously both adiabatic as well as isothermal.

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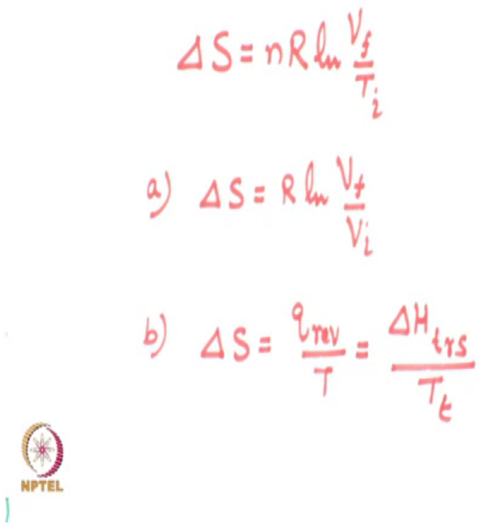

$$\Delta S = nR \ln \frac{V_f}{T_i}$$

a) $$\Delta S = R \ln \frac{V_f}{V_i}$$

b) $$\Delta S = \frac{q_{rev}}{T} = \frac{\Delta H_{trs}}{T_t}$$

So, as long as I get the key word isothermal and the gas is perfect, I will have to use this equation delta S is equal to n R log V final by V initial that I have to use as long as it is isothermal. Therefore, for answering part a n is equal to 1, so delta S will be equal to R log V final over V initial. Now, let us take a look at b, reversible isothermal phase transition reversible isothermal phase transition. Whenever process is a phase transition, it has to be reversible then in that case simply delta S is equal to q reversible by T of obviously, at constant pressure, this is equal to delta H of transition divide by T transition. The delta H is the enthalpy change for the phase transition. Part c reversible adiabatic expansion of 2 moles of an ideal gas from V i to V f. Note, carefully reversible adiabatic expansion, reversible adiabatic expansion.

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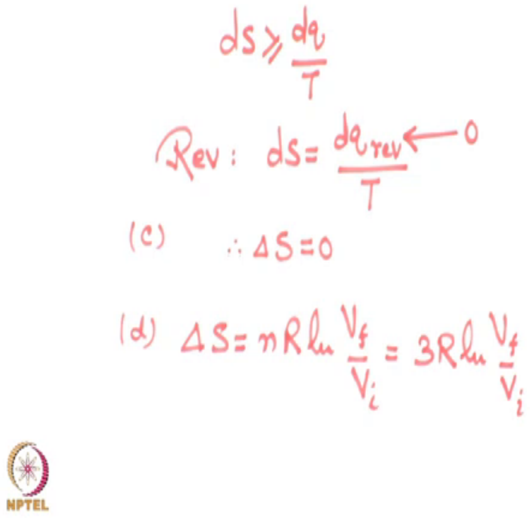

$$ds \geq \frac{dq}{T}$$

Rev : $ds = \frac{dq_{rev} \longleftarrow 0}{T}$

(c) $\therefore \Delta S = 0$

(d) $\Delta S = nR\ln\frac{V_f}{V_i} = 3R\ln\frac{V_f}{V_i}$

So, immediately Clausius inequality will help in answering this question that is d S is greater than or equal to d q by T. And if the process is reversible then d S is equal to d q reversible by T; and if the process is adiabatic then d q reversible is equal to 0, therefore, delta S will also be equal to 0, and this is for part c. And finally, reversible isothermal expansion, reversible isothermal expansions of 3 moles of an ideal gas from V i to V f here isothermal. Isothermal means I will again immediately go back and use this equation delta S is equal to n R log V final by V initial which is equal to n is equal to 3, I will say 3 R log V final over V initial.

So, through this numerical problems, it should be clear that which equation to use when the process is isothermal, which equation to use how to address this problem when the process is adiabatic. And also it is important to understand whether the process is reversible or irreversible, because depending upon the reversible or irreversible process the method that use for calculation may change.

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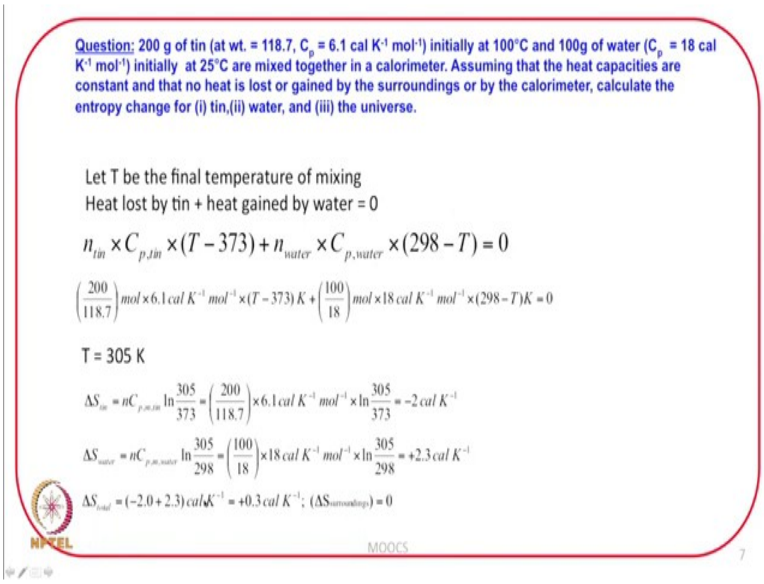

Question: 200 g of tin (at wt. = 118.7, C_p = 6.1 cal K^{-1} mol^{-1}) initially at 100°C and 100g of water (C_p = 18 cal K^{-1} mol^{-1}) initially at 25°C are mixed together in a calorimeter. Assuming that the heat capacities are constant and that no heat is lost or gained by the surroundings or by the calorimeter, calculate the entropy change for (i) tin,(ii) water, and (iii) the universe.

Let T be the final temperature of mixing
Heat lost by tin + heat gained by water = 0

$$n_{tin} \times C_{p,tin} \times (T-373) + n_{water} \times C_{p,water} \times (298-T) = 0$$

$$\left(\frac{200}{118.7}\right) mol \times 6.1\, cal\, K^{-1}\, mol^{-1} \times (T-373)\, K + \left(\frac{100}{18}\right) mol \times 18\, cal\, K^{-1}\, mol^{-1} \times (298-T) K = 0$$

T = 305 K

$$\Delta S_{tin} = nC_{p,m,tin} \ln\frac{305}{373} = \left(\frac{200}{118.7}\right) \times 6.1\, cal\, K^{-1}\, mol^{-1} \times \ln\frac{305}{373} = -2\, cal\, K^{-1}$$

$$\Delta S_{water} = nC_{p,m,water} \ln\frac{305}{298} = \left(\frac{100}{18}\right) \times 18\, cal\, K^{-1}\, mol^{-1} \times \ln\frac{305}{298} = +2.3\, cal\, K^{-1}$$

$$\Delta S_{total} = (-2.0+2.3)\, cal K^{-1} = +0.3\, cal\, K^{-1};\ (\Delta S_{surroundings}) = 0$$

Let us take look at this question now. 200 gram of tin atomic weight 118.7 heat capacity is given 6.1 calorie per Kelvin per mol, initially at 100 degree Celsius and 100 gram of water C p is given 18 calorie per Kelvin per mol, initially at 25 degree Celsius are mixed together in a calorimeter. Assuming that the heat capacity is are constant and that no heat is lost or gained by the surroundings or by the calorimeter calculate the entropy change for tin water and the universe.

What is the information given to us, let us first of all take a look at. There is a mixing of tin which is at 100 degree Celsius with water which is at 25 degree Celsius. So obviously, there will be heat loss by tin and heat gained by water. Tin is initially at 100 degree centigrade and water is initially at 25 degree centigrade, and since there initial amount different therefore, we will have to calculate the actual amount of heat loss actual amount of heat gain, heat loss has to be equal to heat gain and then calculate the final temperature.

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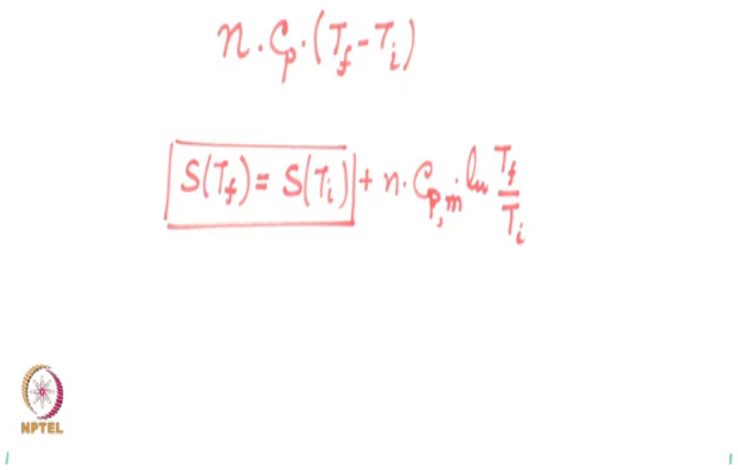

$$n \cdot C_p \cdot (T_f - T_i)$$

$$\boxed{S(T_f) = S(T_i)} + n \cdot C_{p,m} \ln \frac{T_f}{T_i}$$

How do we calculate heat loss or heat gain? Let T b the final temperature of mixing. We will use this equation that heat lost by tin plus heat gained by water is equal to 0. And heat lost or heat gain can be calculated from number of moles into heat capacity into T final minus T initial. So, depending upon whether it is positive or negative it will either heat lost or heat gained. So, let us use that for tin, it is number of moles of tin heat capacity of tin, and since T tin is going to lose heat its temperature will fall. So, final temperature T minus 373, this is the amount of heat lost plus the amount of heat gained here instead of T minus 298, I will write 298 minus T, because I am writing here as heat gained if I add the two that has to be equal to 0.

And once you substitute the numbers 200 gram divided by the atomic weight, these many moles multiplied by the heat capacity multiplied by T minus 373 and 100 divided by 18. 18 is the molecular weight of water 100 divide by 18 is number of moles of water into heat capacity into the temperature difference is this addition it should be equal to 0. And according to this temperature comes out to be 305 K.

So, once I know the final temperature, once I know the initial temperature, then I use the equation that we just derived that delta S has to be equal to n time C p m time block T f minus T i. This is from S T f is equal to S T i plus n times C p m into log T f by T i. So, what I am calculating is S T f minus S T I which is being shown over there, the delta S is equal to n times C p m, here I am talking in terms of molar heat capacity that is why n is written over here.

So, once you substitute the value of n delta and C p and the log 305 by 373 which is the final and initial temperature the change in entropy is minus 2 calorie per Kelvin. And since heat is gained by water, if we do the calculations for water by substituting the appropriate numbers, it will come out to be plus 2.3 calorie per Kelvin. And the total delta as total will be this plus this which is minus 2 plus 2.3, and this turns out to be 0.3 calorie per Kelvin. There is a net small gain in entropy by water. And since it is being done in an insulated container, the entropy change in the surrounding is 0. So, total entropy changes system plus surrounding is still positive and that is what is driving the process.

So, when calculating the values of entropy change, the knowledge of heat capacity, the values of heat capacities are very, very important. And the heat capacity you know is connected to the properties of the system, how strong the system is, a well hydrogen bonded system will have a different heat capacity then a non hydrogen bonded system. So, obviously, whenever there are changes, the amount of disorder generated or order generated will be different.

So therefore, these thermodynamic parameters like heat capacity, like entropy changes provided lot of information not only just in terms of numbers, but their sign as well as magnitude give a lot of information about the properties of the material and about the intermolecular interactions. We will further solve numerical problems based on entropy and connect with the different examples later on.

So, I hope that the second law of thermodynamics is very clear. And if still there are any questions and queries, we will address those during tutorial sessions or during help sessions.

Thank you very much.