Chemical Principles II
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Module 06
Lecture 34
Tutorial Problem - 05

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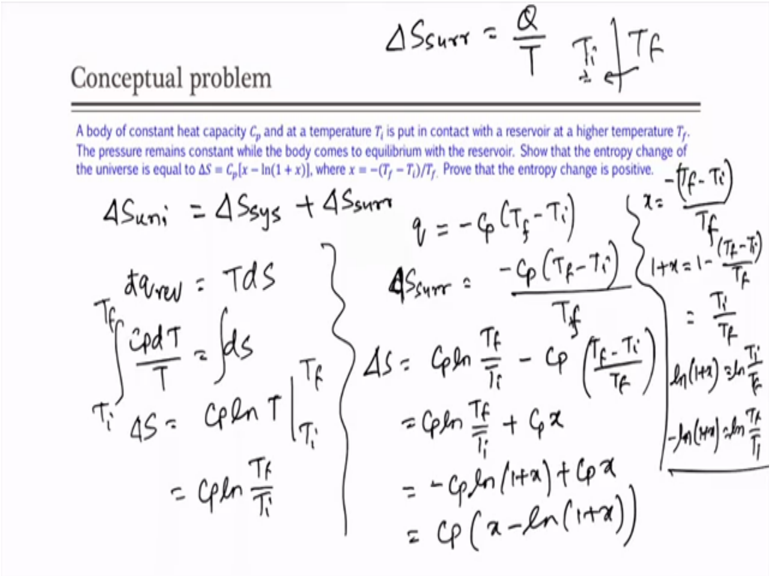

Conceptual problem

A body of constant heat capacity C_p and at a temperature T_i is put in contact with a reservoir at a higher temperature T_f. The pressure remains constant while the body comes to equilibrium with the reservoir. Show that the entropy change of the universe is equal to $\Delta S = C_p[x - \ln(1+x)]$, where $x = -(T_f - T_i)/T_f$. Prove that the entropy change is positive.

$\Delta S_{surr} = \frac{Q}{T}$ $T_i \,|\, T_f$

$\Delta S_{uni} = \Delta S_{sys} + \Delta S_{surr}$

$dq_{rev} = TdS$

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

$\Delta S = C_p \ln T \Big|_{T_i}^{T_f}$

$= C_p \ln \frac{T_f}{T_i}$

$q = -C_p(T_f - T_i)$

$\Delta S_{surr} = \frac{-C_p(T_f - T_i)}{T_f}$

$\Delta S = C_p \ln \frac{T_f}{T_i} - C_p\left(\frac{T_f - T_i}{T_f}\right)$

$= C_p \ln \frac{T_f}{T_i} + C_p x$

$= -C_p \ln(1+x) + C_p x$

$= C_p(x - \ln(1+x))$

$x = \frac{-(T_f - T_i)}{T_f}$

$1 + x = 1 - \frac{(T_f - T_i)}{T_f}$

$= \frac{T_i}{T_f}$

$\ln(1+x) = \ln \frac{T_i}{T_f}$

$-\ln(1+x) = \ln \frac{T_f}{T_i}$

So now this is an interesting question, conceptual problem also. A body of a constant heat capacity Cp and at a temperature T i is put in contact with a reservoir at a higher temperature T f. The pressure remains constant while the body comes to equilibrium with the reservoir. Show that the entropy change of the universe is equal to this one. Now you see we are talking about entropy change of the universe. So entropy change of the universe is equal to entropy change of the system plus entropy change of the surrounding. And we have to calculate both of them.

So here the heat capacity Cp and temperature is T i is in contact with a high temperature T f. So what is the change in the heat that we see reversible heat? How does the, so it is a constant pressure process, right? So how does the heat change in a constant pressure process? So we know that dQ reversible is TdS, we start from there. dQ reversible is CpdT for a constant pressure process, is dS. So therefore S is Cp ln T but we are doing an integration, right? We are doing an integration from T i to T f. So S will be or change in rather, change in S will be, because we are talking about change from initial to final, so delta S that is why I have given, it is CpdT going from T i to T f.

So it is Cp ln T f by T i, okay, so this part is okay. So this is the part, the system's entropy change, how did I do that? We calculated the dQ reversible and we know that dQ reversible is TdS. dQ reversible we know CpdT, so CpdT and then put the T down, it is Cp ln T f by T i. This is the formula for constant pressure process when to calculate the entropy of the system. Now what will be the entropy of the surrounding? So surrounding however gives away the heat dQ, right? And it is temperature does not change, the surrounding is a reservoir.

Reservoir's temperature does not change, so Q that is gone out of the reservoir is minus Cp T f by T i. Is it okay? What do you think? What is the dQ? dQ is Cp dT, right? How much heat is going out? Heat is going out according to heat capacity and temperature difference. How much heat was going into the system? System's was Cp delta T. Now what is the entropy that system is, the surrounding is going to lose? Cp T f minus T i by T f, because T f is the temperature of the reservoir. What is the formula for entropy? dQ by T, right?

What is dQ? Cp dT, so we did Cp dT. And we did by T f. Now what is the total change? The total change in entropy will be Cp ln T f by T i minus Cp T f minus T i by T f. Now what is X given here? X is minus T f minus T i by T i. So it is this particular quantity, minus, this is particular quantity, so we can write it is Cp ln T f by T i plus minus T f, minus, so plus Cp into X. Now let us simplify this one little bit more? 1 plus X, so I add 1 on both sides, so this is T f sorry, 1 plus X if I add, then it will be 1 plus 1 minus T f minus T i this one, which will give us T f minus T i plus Ti, so T i by T f.

Now ln of 1 by X, ln of 1 plus X will be ln of T i by T f. Now for ln you know that if I take negative sign, it will be just the opposite. So minus ln of 1 by X, 1 plus X sorry, is ln of T f by T i which is here. So this is minus Cp ln 1 plus X plus Cp X. Now Cp is common, X minus ln of 1 plus X, and that is what is proved. Is it clear?

So why in this case we did not integrate and we have done that, right? So surrounding temperature was always T f, surrounding is losing some amount of heat Q, so we are only calculating how much surrounding is losing the heat. So system is receiving the heat in a slow manner and its temperature is also changing. That is why the integration is required on the left hand side. The integration, you see the T is under the integration sign, dT by T, because at every instance the temperature of the system is changing from T i to T f slow manner.

But the temperature of the surrounding is always kept at T f, it is just giving away some heat. How much heat it is giving away, that is what we are calculating here. Once we calculate the heat, we are dividing by the temperature. And for the surroundings since it is so big, we do not really care. Remember the entropy of the surrounding is just Q by T, nothing else. Just calculate the Q, divide it by T, will be the entropy change of the surrounding. So we are calculating how much heat is lost which is Cp delta T divided by T. There is no change in the temperature for the surrounding. However there is a change in the temperature for the system.

System is gaining the temperature slowly from T i to T f and that is why we have to do the integration from T i to T f which is not required for the right hand side. You asked, now is it clear? That is the big difference between system and surrounding. I have a system which is I kept T i and this is T f and heat is coming in, dQ heat is coming in. System temperature slowly changes, increases to T f. Surrounding temperature does not change, surrounding is losing some amount of heat. So that is why it is just heat by T and the left hand side we have to do an integration because the process in which the temperature increases.

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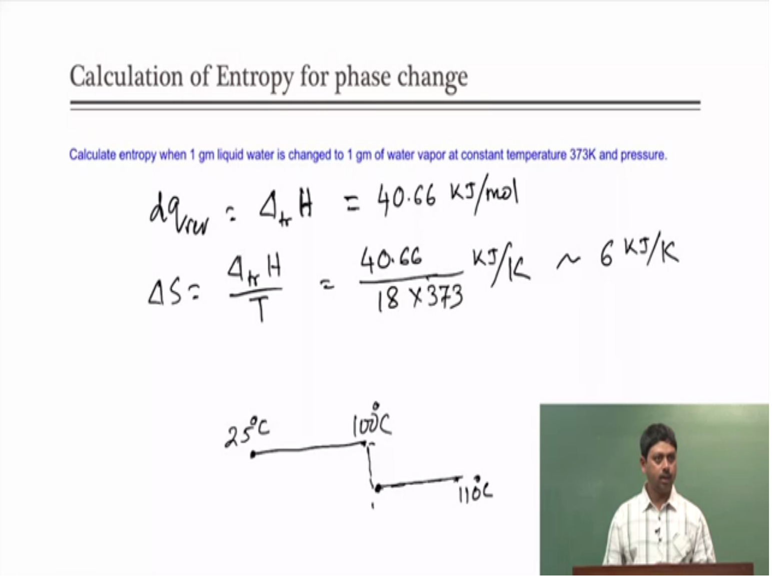

Calculation of Entropy for phase change

Calculate entropy when 1 gm liquid water is changed to 1 gm of water vapor at constant temperature 373K and pressure.

$dq_{rev} = \Delta_{tr}H = 40.66$ KJ/mol

$\Delta S = \frac{\Delta_{tr}H}{T} = \frac{40.66}{18 \times 373}$ KJ/K ~ 6 KJ/K

So calculate the entropy for phase change, which is very simple, so the question is that calculate entropy when one gram liquid water is changed to 1 gram of vapor at constant temperature of 373. So at 373, you know the liquid and vapor will coexist. So all that we need, so what is the dQ? dQ reversible or dQ is nothing but delta the enthalpy for transition. So enthalpy for transition is typically we know that in thermochemistry we have talked about it, 40.66 kilo joules per mole. That is the heat of transition, so what will be the change in entropy? It will be nothing but this by temperature.

Now we have to calculate the transition enthalpy for 1 gram, we know that 1 mole contains 18 gram, so it is 40.66 by 18 kilo joule and then you have to multiply by 373, then you will get Kilo Joule per Kelvin. This value will come out to be approximately 6 Kilo Joule per Kelvin if you do the calculation. So here it is very simple because we, so we know that this transition's enthalpies are calculated at constant pressure, so and we know that heat at constant pressure is nothing but enthalpy. All that we are doing is that we are calculating the total change in heat, we are assuming that it is going very slowly.

And the temperature is not changing, so it is just an isothermal process. Temperature is not changing, so no integration, nothing is required. So whenever you are heating the system, we do Cp ln T f by T i. But if there is no heating, no change in temperature takes place, all that we need is the heat change divided by the temperature, will give you the change in the entropy. Now let us say you have to take the system from 15 degree centigrade, water at 25 degree centigrade let us say we want to calculate the entropy for the system when it is water at 110 degree centigrade.

So we have to calculate the entropy change from water going from 25 degree centigrade to 100 degree centigrade in a slow manner by using Cp ln T formula. At 100 degree centigrade we will have to now add the transition enthalpy that is the vaporization, the latent heat of vaporization or transition enthalpy. And then again there will be a Cp dT, we need the specific heat of the vapor and that will take us from 100 degree centigrade to 110 degree centigrade. So by three steps we can calculate the overall entropy change going from 25 degree centigrade water to 110 degree centigrade water vapor. Okay, is it okay? This part?

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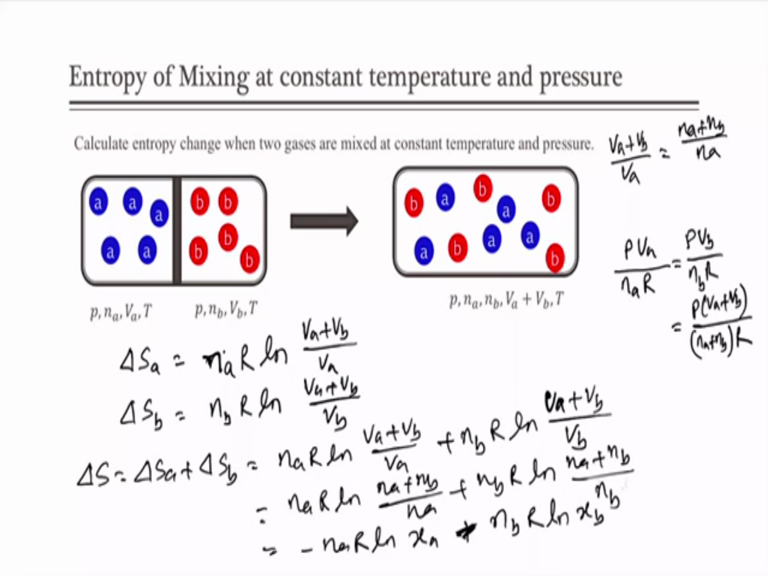

Entropy of Mixing at constant temperature and pressure

Calculate entropy change when two gases are mixed at constant temperature and pressure.

$$\frac{V_a+V_b}{V_a} = \frac{n_a+n_b}{n_a}$$

$$\frac{PV_a}{n_aR} = \frac{PV_b}{n_bR} = \frac{P(V_a+V_b)}{(n_a+n_b)R}$$

$$\Delta S_a = n_a R \ln \frac{V_a+V_b}{V_a}$$

$$\Delta S_b = n_b R \ln \frac{V_a+V_b}{V_b}$$

$$\Delta S = \Delta S_a + \Delta S_b = n_a R \ln \frac{V_a+V_b}{V_a} + n_b R \ln \frac{V_a+V_b}{V_b}$$

$$= n_a R \ln \frac{n_a+n_b}{n_a} + n_b R \ln \frac{n_a+n_b}{n_b}$$

$$= -n_a R \ln x_a + n_b R \ln x_b$$

So now let us calculate the entropy of mixing. So let us say initially some A molecules are confined to a volume V a at some temperature T and pressure P. N a number of molecules are there. And on the other side or in a different box also you can say n b molecules are there and suddenly they are mixed or at some point they are mixed. And then the total volume becomes V a plus V b, total pressure becomes P and temperature remains the same. So it is isothermal mixing. So what is the change in entropy for both the systems?

So we can say, we can calculate that by changing the, change in entropy of system a, so system a if you see if you just do not look at the part V, we do not look at this part, then it is going from V a to V a, a plus V b. So what is the formula for that expansion? Is minus or it is minus, it is plus n a R ln V a plus V b by V a. Change in entropy for b is n b R ln V a plus V b by V b. We can call that overall volume as V also.

So now total change in entropy will be delta S a plus delta S b giving us n a R ln V a plus V b by V a, n b R ln V a plus V b by V b. Now we can simplify this further by using, since it is an ideal gas mixture or perfect gas mixture, we can simplify it further by knowing that if I use the relation that P is the pressure, V a, PV equal to nRT. So n a R equal to T, equal to temperature which is same for the other system also, P V b, n b R. So equal to P V a plus V b by n a plus n b R.

Now if I use this relation, then we can get, P, P cancels of course and then we get V a plus V b by V a equal to n a plus n b by n a. So we can write as n a R ln n a plus n b by n a, plus n b ln n a plus n b by n b. Now just take the, since it is the logarithm, we can take the minus sign.

So minus n a R ln, n a by n a plus n b, which is nothing but fractions of this thing, let us call it Xa, plus again take minus n b R ln X b, same manner. Let us remove this part.

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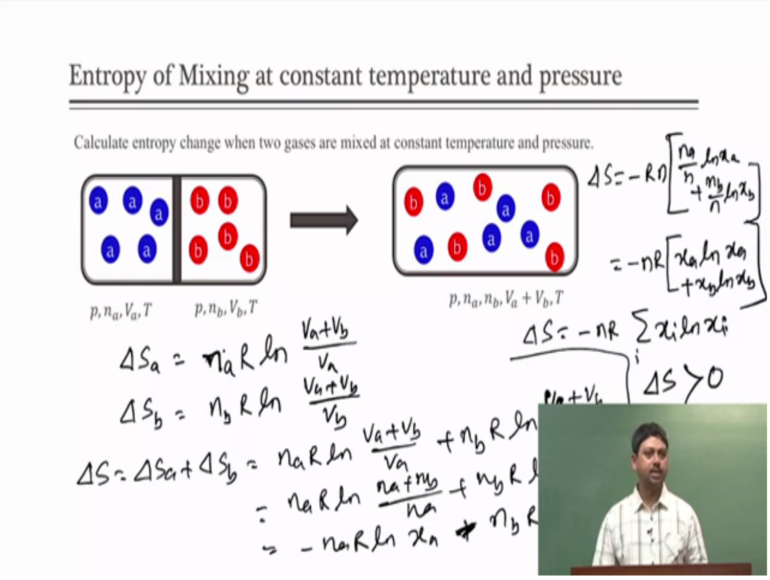

Entropy of Mixing at constant temperature and pressure

Calculate entropy change when two gases are mixed at constant temperature and pressure.

p, n_a, V_a, T p, n_b, V_b, T $p, n_a, n_b, V_a + V_b, T$

$\Delta S_a = n_a R \ln \frac{V_a+V_b}{V_a}$

$\Delta S_b = n_b R \ln \frac{V_a+V_b}{V_b}$

$\Delta S = \Delta S_a + \Delta S_b = n_a R \ln \frac{V_a+V_b}{V_a} + n_b R \ln$

$= n_a R \ln \frac{n_a+n_b}{n_a} + n_b R$

$= -n_a R \ln x_a + n_b R$

$\Delta S = -Rn\left[\frac{n_a}{n}\ln x_a + \frac{n_b}{n}\ln x_b\right]$

$= -nR\left[x_a \ln x_a + x_b \ln x_b\right]$

$\Delta S = -nR \sum_i x_i \ln x_i$

$\Delta S > 0$

$V_a + V_b$

And write it here, delta S then, now let us take R common, minus R common and n common. We will get n a by n which is of course mole fraction, ln X a plus n b by n ln X b. n a by n a is also X a, right? So minus n R, I am just simplifying it, X a ln X a plus X b ln X b. That is the entropy of mixing formula. Now this we can generalize to multiple mixers as well. So let us say there are multiple gas molecules are mixing, then overall we can write as n R, sum over i, X i ln X i, minus n i.

So we can see that if X i are half, then we will get a famous formula, half ln half, will give n R ln too. So that is mixing of entropy when like volume goes just the double of that. No, so the, yeah, that is the good question. So minus n R X i ln X i but X i is a fractional quantity. So since ln X i, X i is a fractional quantity, ln X i is a negative quantity, so negative and negative will become positive. So basically delta S is greater than zero, because ln X i is negative. Good that you asked.

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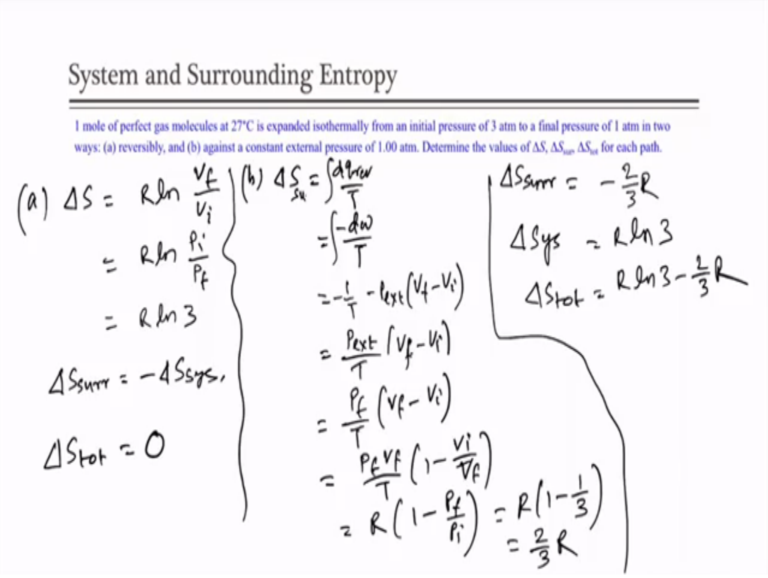

System and Surrounding Entropy

1 mole of perfect gas molecules at 27°C is expanded isothermally from an initial pressure of 3 atm to a final pressure of 1 atm in two ways: (a) reversibly, and (b) against a constant external pressure of 1.00 atm. Determine the values of ΔS, ΔS_{sur}, ΔS_{tot} for each path.

$$(a)\ \Delta S = R\ln\frac{V_f}{V_i} = R\ln\frac{P_i}{P_f} = R\ln 3$$

$$\Delta S_{surr} = -\Delta S_{sys},$$

$$\Delta S_{tot} = 0$$

$$(b)\ \Delta S_{su} = \int\frac{dq_{rev}}{T} = \int\frac{-dw}{T} = -\frac{1}{T}\cdot -p_{ext}(V_f - V_i) = \frac{P_{ext}}{T}(V_f - V_i) = \frac{P_f}{T}(V_f - V_i) = \frac{P_f V_f}{T}\left(1 - \frac{V_i}{V_f}\right) = R\left(1 - \frac{P_f}{P_i}\right) = R\left(1 - \frac{1}{3}\right) = \frac{2}{3}R$$

$$\Delta S_{surr} = -\frac{2}{3}R$$

$$\Delta S_{sys} = R\ln 3$$

$$\Delta S_{tot} = R\ln 3 - \frac{2}{3}R$$

Now again we are going to do one more calculations on system and surrounding to get handle, let us understand it little bit better. One mole of perfect gas molecule say 27 degree centigrade isothermally expands, expands isothermally from an initial pressure 3 atmosphere to a final pressure of 1 atmosphere in two ways: reversibly and against a constant external pressure of 1 atmosphere. Calculate delta S meaning delta S of the system surrounding and the total for each part. So let us do for the reversible case. So it is an isothermal expansion from 3 atmosphere to this thing.

So what will be the system's entropy? So we know that system's entropy is from the formula n R ln V f by V i, now we know from ideal gas system is that P i V i by T is P f V f by T because it is an isothermal one which means that V f by V i, V f by V i will be P i by P f. Do not make that mistake. So it is n R ln P i by P f, what is P i? We know that P i is 3 atmosphere, initial pressure and this is one. So this is n R ln 3. And one mole of gas, so just take n to be 1. Just take n to be 1, R ln 3 is the answer. That is a system entropy.

What will be the surrounding entropy? Now it is a reversible process, so in the case of reversible process delta S surrounding is just minus delta S of the system because surrounding is changing the same way. For example, remember an isothermal expansion for Carnot Cycle, the heat changes, isothermally it is very slow, so both the system and the surroundings are at the same temperature. So therefore the changes are reversible. It can go back to the same value. So the surrounding is exactly same as a system, negative of the system.

So delta S total is going to be 0. So reversible, the idea to show this problem, idea that the problem shows is that for a reversible isothermal processes the total change in the entropy is zero, because system and surroundings are negative. You are going to see that is not the case when it does at a constant pressure. So that is the in the problem number b. So it says that what happens when it expands at a constant external pressure of 1 atmosphere. So now in that case system entropy how do we calculate that? It is an isothermal process, temperature is nto changing. So we know that dS is dQ by T, dQ reversible by T.

So what is dQ reversible here? It is a constant pressure process changing. So our dQ we can get from, dU is zero, because the temperature is not changing. So dQ is minus dW. What is minus dW? dU is minus dW by T. Now what is the minus dW or rather I should the integration of that. So minus 1 by T dW. Now what is dW? dW is the work done at the constant pressure is just P V2 minus V1. So minus P external V final minus V initial. Now let us write down, so P external divided by T, V f minus V i.

Now we have to calculate what is V f and what is V i? Again we will use the ideal gas formula. So P f V f by T is 1 minus V i by V f. That is also fine. P f V f by T is R, that is also fine, 1 minus V i by V f. What is V i by V f? P f by P i. We can do otherwise this one, P i V i by T is P f V f by T. T, T cancels. Then V i by V f is P f by P i, just the opposite of that. Now we know the values, R 1 minus, what is P f?

P f is the final pressure, 1; initial pressure this thing, so we are going to get 2 by 3 R. Is it okay? All the steps? So this I said that b is having at a constant external pressure and I calculated the changes this way at a constant pressure. But will that be system's entropy?

Student is answering: No.

Correct. So it cannot be system's entropy because even if the process is happening irrecoverably to calculate the entropy of the system we have to always choose the reversible path. So that is the idea of this particular problem. See in the first case, the problem number a, it is happening reversibly. So both system and surrounding's entropy are the same. But the second step, it is happening irreversibly. But in case of an irreversible process to calculate the entropy of the system we have to choose a reversible path which means in the case of b, the system entropy, the same one as R ln 3, but surroundings entropy is negative of this particular quantity.

So the thing is that the calculation that we showed is that the surrounding entropy is whatever we calculated just now, is minus 2 by 3 R because it is negative value because it is losing that amount of this entropy. And the system entropy is whatever we calculate by a reversible way which is R ln 3, which we already calculated for the reversible state. So remember again that entropy calculation for the system has to be always a reversible path, it cannot be irreversible path. So even if the process is happening irreversibly one has to calculate the corresponding reversible path.

The second example when it is happening at a constant pressure that to the final constant pressure the process is irreversible. However entropy calculation we have to consider a reversible path which is already done in the problem a, so system entropy still remains as R ln 3. However surrounding's entropy first of all it will be negative, and secondly it is calculated the way I have shown here which is, So now the total entropy, so let me just, so this surrounding entropy, system entropy is R ln 3 for the second problem, problem b. So the total entropy is R ln 3 minus 2 by 3 R. So here what we are calculating actually is surrounding entropy.