Chemical principles 2 Dr. Arnab Mukherjee Department of Chemistry Indian Institute of Science Education Research, Pune Module 06 Lecture 36 Tutorial Problem – 07

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True or False?

 $U = C \sqrt{dT}$ H= CpdT 1. For a fixed amount of a perfect gas
 \sqrt{d} \overline{U} and H each depend only on T . $\frac{1}{2}$ (b) $\frac{1}{2}$ is a constant.
(c) P dV = nR dT for every infinitesimal process. (d) $C_{P,m}$ - $C_{V,m}$ = R.
(e) $dU = C_V dT$ for a reversible process.

Okay so we will continue with the problem solving session and today will continue some problems of true false type and short answer and also if and long answer type of questions on the second law of thermodynamics so first will start with the true false problem the first question is that for a fixed amount of a perfect gas U and H each depend on the on temperature so is it true or not? So we know that for ideal gas system U is CV DT and CV for an ideal gas is nothing but three by two R which does not depend on universal gas constant that will does not depend on temperature so CV does not depend on temperature and U then only depends on temperature and H is nothing but CP DT and we know that CP is nothing but CP plus R so therefore CP also will not depend on temperature and therefore H will only depend on temperature.

So this first one is true CP is a constant we already discuss that CP is nothing but CM plus R and ideal gas system actually CP is nothing by three by two R plus which is five by two R so it is a constant and because a constant PDV equal to NRDT for every infinite thermal process, so the question is that for a fixed amount of perfect gas now for a fixed amount of perfect gas N is a constant R is a constant, and so whenever we do PDV.

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So let us say the equation is we will just go here to write it equation is PV equal to NRT now if I take a differential amount so it will be DPV equal to D of NRT which means D P DV plus VDP is equal to NRDT because in a N and R for are constant this is the equation that we have to follow so therefore only PDV equal to NRDT is true only when pressure is constant or DP equal to zero.

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True or False? $U = C\sqrt{dT}$ H = Cod T For a fixed amount of a perfect gas 160 U and H each depend only on T. \sqrt{b} \sqrt{c} is a constant. $Q(e) \rightarrow e$ is a constant.
 $Q(e) P dV = nR dT$ for every infinitesimal process.
 $Q(e) P dV = nR$
 $Q e/dV = C_V dT$ for a reversible process. 2. For a reversible process in a closed system, ΔS must be zero. $\sqrt{}$. For a reversible process in a closed system, ΔS_{univ} must be zero. For a process in an isolated system, AS cannot be negative. X⁵. For a closed system, equilibrium has been reached when S has been maximized. 6. In every cyclic irreversible process, the final and initial states of the system are the same and the final and initial states of the surroundings are the same. 7. Q is zero for every cyclic process. 8. ΔS for an irreversible change of 1 mol of N₂(g) from 10L to 20L at 25°C must be the same as ΔS when 1 mol of $N_2(g)$ goes reversibly from 10L to 20L at the same temperature.

So therefore this is going to be false now forth one CP minus CV for a one mole of gases R which is true we know and D equal to CVDT for a reversible process now of course we know that for an ideal gas system D equal to CV DT but for real gas system is not true, so the second question for a reversible process in a closed system delta S must be zero so we know that delta S is the DQ reversible by T, so for a reversible process we know that the entropy of the system is equal and opposite of the interrupt the surroundings so therefore entropy of the universe will be equal to zero, however for the system it depends on the type of the system weather the delta S will be zero or not.

So therefore we cannot say for sure this particular question for a reversible process in a closed system delta universe must be equal to zero and that just now we have discussed that is true for a process in an isolated system delta S cannot be negative now any process in an isolated system we know that if it is spontaneous process or for example any process that happens in an isolated system there is no external influence for example you talked about our universe is an isolated system and in that any process that happens and has to happen spontaneously because there is no influence from outside and therefore if that happens we know that entropy has to be always positive.

So therefore it cannot be negative is a right statement for a closed system next question for a closed system equilibrium has been reached when S has been maximized, now we know that for an isolated system when the system reaches to equilibrium the entropy becomes maximum however for a closed system it may not be true because in a closed system it depends on both the energy and entropy we will understand that later that something else rather than free energy will be negative or maximum negative in this particular situation where it becomes it liberated.

So we will discuss about that later on, that the however for this it is not true in every cyclic irreversible process the final and initial states of the system are same and the final and initial states of the surrounding are same now when I talk about cyclic process then the final and initial states of the system has to be the same because the process we are talking about the state function of the system which will become the same many system will come back however something else happened to the universe in every cycle irreversible process the final and initial states of the system are saying however the surrounding is not the same, Q is zero for every cyclic process which is not true we know that Q is not a path function so Q may not be zero and again for Carnot cycle you know that Q is Q1 minus Q2 for that cyclic process Carnot cycle delta is for an irreversible change of one mole of nitrogen from 10 liter to 20 liter at 25 degree centigrade must be same as delta S when one mole of nitrogen gas goes reversible from 10 to 28 liter at the same temperature so the question is that whether or not and irreversible process going from A to B and a reversible process going from A to B will have same entropy or not.

So remember we discuss that even the processes words in irreversible we have to construct the corresponding reversible path and calculate the entropy, so therefore even for the irreversible path the entropy is calculated from the reversible path so they have to be the same because the calculation itself will depend on the reversible path so this is a true statement and also you should know that you know that the entropy is the state function so therefore it does not matter whether the process is reversible and irreversible as long as the initial and final states are the same.

True or False?

Thermodynamics cannot calculate ΔS for an irreversible process. 10 Increasing the temperature of the hot reservoir of a Carnot-cycle engine must increase the efficiency of the engine. $\eta = 1 -$ 11 Decreasing the temperature of the cold reservoir of a Carnot-cycle engine must increase efficiency of the engine. $\sqrt{12}$. The work done in a Carnot cycle is zero.

Next question thermodynamics cannot calculate delta S for an irreversible process again we know that in order to calculate such entropy we have to construct reversible path and therefore you will be able to calculate that as long as we have well defined initial and final states this is wrong increasing the temperature of the hot reservoir of a Carnot cycle engine must increase the efficiency of the engine so we know the efficiency of the engine formula efficiency of the engine is one minus T2 by T1 so where T2 is the temperature of the cold reservoir, T1 temperature is a temperature of hot reservoir what is the question increasing the temperature of the hot reservoir which means we increase the T1, what will happen if you increase T1, T2 by T1 will becomes smaller efficiency will increase.

So increasing the temperature the hot reservoir the Carnot cycle must increase the efficiency of the engine which is right decreasing the temperature in the cold reservoir again if we decrease the T2 what will happen T2 by T1 will become smaller $(0)(08:07)$ will increase must increase the efficiency of the engine which is also true the work done in a Carnot cycle is zero which is not true because you remember the work done in a Carnot cycle is actually area enclosed by the curve which is also the heat change in the Carnot cycle process which will only be zero if there is no area left and that is only possible if there is no adiabatic process happens because you need the whole path and only when the temperature are same or rather the first isothermal serve is traced back then only work done will be zero otherwise it is not a right answer so now we finish the true false type of questions so you see this similar type of questions will come and have to

use the logic the same logic that we have used in order to answer this particular questions remember the logic behind each question and think physically to understand what is going on that and that is what we are trying to explain during explanation of each and every answer for this question.

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Now we are going to come to some simple short questions just to lose this type of questions can be understood if you know the formula and if you can catch the right place for example let us see this one which state function must remain constant on joules explained this is a knowledge based questions so you do not now that internal energy U remain constant which state function must remain constant in joule Thomson you know that it is the enthalpy, so this is something that you have to know, second one container is filled gas at pressure 1.5 atmosphere the gas is compressed isothermally to one fourth of his original volume what will be the new pressure of the gas, so initial pressure.

So now you see we are talking about an ideal gas so you have to use an ideal gas equation PV equal to NRT or 1 V1 equal to P2V2 and we know that initial pressure is 1.5 atmosphere and the gas is compressed isothermally to one forth, one forth means we know that V2 by V1 is one forth which means P2 by four, so what will be the pressure, pressure will be 1.5 into four is six atmosphere third question the state of an ideal gas was changed three times at three different temperatures let me just erase this one, so that you can see that this is a figure that is given here

the state of an ideal gas was changed three times at three different temperature the diagram represent three different isothermal curves, what can you tell about the temperature of the graph now you see PV equal to constant is the equation of ideal gas however there is something you know therefore if you draw P against V you will get something like is called the rectangular hyperbola equation which go like each equation will go like this however you have a temperature associate this one which means that if we increase the temperature your PV value will increase, so which means that let us say for when you increase your temperature for any given volume because let us say you can write P as in our T by V.

So when you increase your temperature for any given volume if the volume is fixed your pressure will increase now let us talk about this particular volume then in this case the pressure is smaller but in this case the pressure is higher in this case the pressure is even higher which means this must be T3 must be greater than T2 and T2 must be greater than T1, find the molar volume of an ideal gas at 20 degree centigrade and one bar pressure now molar volume of an ideal gas at 20 degree centigrade in one bar pressure, so how do you know that so again we are going to the equation ideal gas equation PV equal to NRT.

Now we need to find out molar volume so which means we need to find out V by N V bar to RT we have the value of R we have the value of temperature 20 degree centigrade and we have the value of pressure, so we have to get the volume molar volume RT by V now we have to simply put the value which is 8.314 multiplied by temperature is 20 degree now there is a catch here because it is not centigrade we have to use Calvin unit which means 20 degree means 293 Kelvin divided by one atmospheric pressure, now what is the unit here so for example here you need is joule per kelvin.

So I need to go there so V bar equal to RT by P, so now pressure is one bar pressure so one bar pressure is so you have to convert everything in joule and Kelvin so you have to convert the one bar into joule per liter pressure this is 100 joule per liter giving rise to 8.314 multiplied by 293 by 100 liter and let us calculate that how much that comes let me use a calculator is 24.36 liter so that will be the answer, next question calculate the temperature change of one mole of an ideal diatomic gas contained in a piston where Q is 65 Joule hand W is 210 joule.

Short Questions

1. Which state function must remain constant in the Joule's experiment? (b) Which state function must remain constant in the Joule-Thomson experiment? 2. A container is filled with of an ideal gas at pressure 1.5 atm. The gas is compressed isothermally to 1/4th of its original volume. What will be the new pressure of the gas? 3. The state of an ideal gas was changed three times at three different temperatures. The diagram represents
three different isothermal curves. What can you tell about the temperatures from the graph? 4. Find the molar volume of an ideal gas at 20 $^{\circ}$ C and 1 bar pressure. (R = 8.314 J/K) 5. Calculate the temperature change of 1 mole of an ideal diatomic gas contained in a piston, q = 65J and w EXECUTE AND $dU = \frac{QV}{V} = \frac{275 \text{ J}}{\frac{2V}{V}} = \frac{275 \text{ J}}{\frac{2V}{Z}} = 13.23 \text{ K}$
 $= 65 \text{ J} \pm 210 \text{ J}$
 $= 65 \text{ J} \pm 210 \text{ J}$
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We know in first law of thermodynamics U equal to Q plus W is actually change in internal energy U and we know Q is 65 Joule and W is 210 joule, which is 275 Joule now we will use the formula of you SCV delta T, delta T is the change in the temperature and CV is the specific heat of a diatomic ideal gas so therefore delta T will be equal to delta U by CV which is 275 joule by CV, now CV for a diatomic gas is 5 by 2R so which is 275 joule divided by 5 by 2 into 8.314 joule per kelvin which will be equal to let us do the calculation so 275 divided by 5 by 22.5314 which is giving us 13.23 kelvin, so 13.23 kelvin is the answer that much temperature change you will happen.

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Short Questions

- 1. Which state function must remain constant in the Joule's experiment? (b) Which state function must remain constant in the Joule-Thomson experiment?
- 2. A container is filled with of an ideal gas at pressure 1.5 atm. The gas is compressed isothermally to 1/4th of its original volume. What will be the new pressure of the gas?
- 3. The state of an ideal gas was changed three times at three different temperatures. The diagram represents three different isothermal curves. What can you tell about the temperatures from the graph?
- 4. Find the molar volume of an ideal gas at 20 $^{\circ}$ C and 1 bar pressure. (R = 8.314 J/K)
- 5. Calculate the temperature change of 1 mole of an ideal diatomic gas contained in a piston, $q = 65J$ and w $= 210J$
- 6. If an electric motor produced 15 kJ of energy each second as mechanical work and lost 2 kJ as heat to the surroundings, then calculate the change in the internal energy of the motor each second. $\ddot{\bullet}$

Next question if an electric motor produces 15 kilo joule of energy each second as mechanical work and lost 2 kilojoule heat to the surrounding then calculate the change in internal energy of the motor each second go here so it is 15 kilo Joule so we know that delta U equal to U plus W o when W is minus 2 kilo joule minus and it is a work done by the system so there is minus 15 kilo Joule each second so it is minus 17 kilo joule each second so that is answer to the question.

Short Questions

- Which state function must remain constant in the Joule's experiment? (b) Which state function must remain $\mathbf{1}$. constant in the Joule-Thomson experiment?
- 2. A container is filled with of an ideal gas at pressure 1.5 atm. The gas is compressed isothermally to 1/4th of its original volume. What will be the new pressure of the gas?
- 3. The state of an ideal gas was changed three times at three different temperatures. The diagram represents three different isothermal curves. What can you tell about the temperatures from the graph?
- 4. Find the molar volume of an ideal gas at 20 $^{\circ}$ C and 1 bar pressure. (R = 8.314 J/K)
- 5. Calculate the temperature change of 1 mole of an ideal diatomic gas contained in a piston, $q = 65J$ and w $= 210J$
- 6. If an electric motor produced 15 kJ of energy each second as mechanical work and lost 2 kJ as heat to the surroundings, then calculate the change in the internal energy of the motor each second.
- 7. A mole of water vapour initially at 200°C and 1 bar undergoes a cyclic process for which w=338 J. Find q $9 - 3382$ for this process.
- 8. Determine the heat to be supplied to a Carnot engine operating between 400°C and 15°C and producing 200 kJ of work.
200 kJ of work.
 Q_1 Q_2 T_1 Q_3 Q_4 Q_5 Q_7 and producing
 $/\omega = 8$, -8 ₂ = 2 ω CJ 288

Next one a mole of water vapor initially at 200 degree centigrade and 1 bar undergoes a cyclic process in which the work done is 338 joule find Q in the process, so here again we have to use the first law- of thermodynamics so water vapor that is initially at this temperature so it goes a cyclic process, so if it goes through acyclic process we know that internal energy remains constant and if that is case then Q will be nothing but minus Q so therefore we do not have to do any calculation we can say that the Q will be minus 338 joule, determine the heat to be supplied to a Carnot engine operating between 400 degree centigrade and 15 degree centigrade and producing 200 kilo joule of work.

So we know that in Carnot engine the heat input by heat output is proportional to the ratio two today over site so T1 by T2 where Q1 is the heat input to the engine Q2 is the heat output from the engine T1 is the temperature of the hot reservoir T2 is the temperature of the cold reservoir now as you can see here we have been given the temperatures here which is 400 degree centigrade means 400 plus 273 is 673 and 15 degree plus 400 is 288 kelvin and now producing in 200 kilo joule of work so and we have been also given the work which is Q1 minus Q2 to be 200 kilo joule now we have two information one is that Q1 minus Q2 is 200 kilo joule we need a little bit more space.

So we will go there so Q1 by Q2 is 673 by 288 and Q1 minus Q2 is 200 so this are the two information's given and this is a like two unknown two equation it is scenario so we can always right Q1 equal to 200 plus Q2 we can put in that in equation 1 so 200 plus Q2 by Q2 is 673 by 288 so 200 by Q2 plus 1 is 673 by 288 so 200 by Q2 is 673 by 288 minus one is how much 385 by 288 so Q2 by 200, 288 by 385 so giving rise to Q2 equal to 288 into 200 by 385 will just do that is in calculator 288 into 200 divided by 385 you are getting 149.61 and naturally we are going to get Q1 equal to 349.61 that is kilo joule and this is also kilo joule, so you got that so heat to be supplied will be 349 so that we got.

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Now continuing is this short questions a body at 200 degree centigrade undergoes a reversible isothermal process the heat energy the removed in the processes 7875 joule determine the change in the entropy of the body so now what kind of problem you know it is basically that it is an isothermal process and so and the heat energy removed in the process is also given so heat is given temperature is given calculate the entropy now we know the formula, formula of entropy is delta S is equal to DQ reversible by T and we have been given the DQ, which is 7875 provided of course this is reversible is mentioned here that undergoes a reversible isothermal process so we are just taking into video first of all we do not have to do anything here.

So this is joule per kelvin because the standard you need we have to use so for 200 will converted into kelvin which is 273 plus 200 is 473 kelvin and value will come out to be 7875 divided by 473 is 16.65 approximately, 16.65 joule per kelvin see this is the unit of entropy however joule per kelvin that you have to remember next one helium stored in a container under pressure 10 mega Pascal starts to leak I will just remove this answer start to leak slowly through a broken valve until this pressure drops to the atmospheric pressure of this much the whole precedes isothermally at room temperature 20 degree centigrade find the change in the entropy for this ideal gas of weight 1.0 kg, now what are the approaches one can take in this particular process first thing to note down is that the process is isothermal process so if you remember and of course we all do we have taken helium gas but we said that for this ideal gas meaning take the helium gas to be an ideal gas.

So we have to know the formula for calculating the entropy for an ideal gas system now if you remember the formula for calculating entropy for an ideal gas system is NRLN V2 by V1 where V2 is the final volume, V1 is the initial volume, N is number of moles our gas constant and things like that now also we know that so but here though we have not the question does not give you the initial and final volume but initial and final pressure so you also know that only P1V1 equal to P2V2 for an ideal gas therefore V2 by V1 is nothing but PP1 by P2 which means initial pressure by final pressure so we can write in our LN P1 by P2, P1 and P2 are given R is known but we have to still calculate the N, N is number of moles for that what is given is this particular thing 1 kg so we know that molecular weight of helium is for so therefore number of moles here is 1kg which is 1000 gram divided by 4 which is will be 250.

So now we have to put the initial pressure and final pressure we do not have to care about the unit only thing to make sure that they are on the same unit, so we know the number of moles will be 250, R is 8.314 into LN of 10 mega Pascal is 10 to the power 7 Pascal by 101325, now let us calculate how much that comes so 250 into 38.314 into LN of 98.6923 giving us 9544.48 or 49 joule per kelvin that is what we get.

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Short Questions

9. A body at 200°C undergoes a reversible isothermal process. The heat energy removed in the process is 7875J. Determine the change in entropy of the body. 10. Helium stored in a container under pressure 10 MPa starts to leak slowly through a broken valve until its pressure drops to the atmospheric pressure 101 325 Pa. The whole process proceeds isothermally at room temperature 20°C.
Find the change in entropy for this ideal gas of weight 1.0 kg. 11. A refrigerator operates on a reversed Carnot cycle. Determine the power required to drive refrigerator between temperatures of 42°C and 4°C if heat at the rate of 2 kJ/s is extracted from the low temperature region 315
 $\frac{9}{2}$
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 215
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So we will go to the next question, a refrigerator operates on reverse Carnot cycle determine the power required to drive refrigerator between temperature 42 degree centigrade and 4 degree centigrade if heat at the rate of 2 kilo joule per second is extracted from the low temperature region, now in order to understand this question particular question let us draw this so in refrigerator operates on a reverse Carnot cycle so Carnot cycle is has to be reversed which means that now it will take the heat from low temperature reservoir and through the heat to the high-temperature reservoir let us call it T1 and T2 and we know that we need work done otherwise it is not possible, so power is nothing but work done and par time work by time is the power so power required.

So first we have to calculate then the work done right so power required to drive the this thing between the temperatures 42 degree and 4 degree centigrade if heat at the rate of 2 kilo joule per second is extracted we know that Q2 equal to 2 kilo Joule per second we have to know what is the Q1 and the temperature have been given so we know from Carnot cycle is Q1 by Q2 is T1 by T2 now what is Q1 we do not know Q2 we know as to be two so I will put that value as two T1 is the high temperature which is 273 plus 42 degree and this one is to 723 plus 4 degree giving us 315 by 277 so Q1 is 315 by 277 into 2 so which is 635 by 277 which is if I do the calculator I

will see that 630 divided by 277 is 2.274 kilo joule per second there is Q1 so therefore W equal to Q1 minus Q2 which is 2.274 minus 2 kilo joule per second or W by no power rather power equal to W power time which is 0.274 kilo joule per second, so we have done that.

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Next question is oxygen is compressed reversibly and isothermally at 27 degree centigrade from 125 kilo Pascal pressure to a final pressure of 375 kilo Pascal determine the change in entropy of the gas we have already discuss a similar problem that if that happens isothermal process then entropy changes in NRLN P1 by P2 initial pressure by the final pressure now N is given N so here it is saying that so N is not given so we will just assume to be you know one mole and then it only boils down to 8.314 multiplied by LN of final pressure is 375 initial pressure is 125 so 125 by 375, so then you can do the calculation and solve that straight forward.

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Short Questions

9. A body at 200°C undergoes a reversible isothermal process. The heat energy removed in the process is 7875J. Determine the change in entropy of the body.

10. Helium stored in a container under pressure 10 MPa starts to leak slowly through a broken valve until its pressure
drops to the atmospheric pressure 101 325 Pa. The whole process proceeds isothermally at room temperatu Find the change in entropy for this ideal gas of weight 1.0 kg.

11. A refrigerator operates on a reversed Carnot cycle. Determine the power required to drive refrigerator between
temperatures of 42°C and 4°C if heat at the rate of 2 kJ/s is extracted from the low temperature region.

12. Oxygen is compressed reversibly and isothermally at 27°C from 125 kPa pressure to a final pressure of 375 kPa. Determine the change in the entropy of gas?

13. Determine the change in the entropy of the universe if a copper block of 1 kg at 27°C is dropped from a height of 200 m in the sea water at 27°C. (Heat capacity for copper= 0.393 kJ/kg K)

Next question determine the change in entropy of the universe if a crop or block of 1 kg at 27 degree centigrade is dropped from a height of 200 meter in the sea water at 27 degree centigrade when it is the same temperature and heat capacity is given now you see when you drop a copper block from certain height you know the potential energy of the block will hit the ground a little convert to the kinetic energy and then when you hit the ground will convert to the heat so we have to know basically what is the potential energy of the system and then we will be able to will assume that all are converted to the heat and then we will able to calculate the change in the entropy of the process.

So one thing just I would like to tell you that this process is not a reversible process however we are calculating the entropy change of the universe so here is a catch I will just I will come to that this about this particular question first let us calculate the heat that is going to the universe, so here the DQ is nothing but DU which is mass MGH M into G into height, so mass of the block is 1 kg G is 9.8 meter per second square and H is a 200 meter, so that will give rise to a value in joule, which is 196 and then 200 so 196 joule that is the DQ we get like Q we can say Q we get and then we the temperature 27 degree centigrade now it is an irreversible process, because the

Q so fallen block will never come back it is an irreversible process but universe is very big even a process that is happening irreversible within the system and there is a change in the Q it is taken to be a reversible process for the universal for example I talked about a system there and let us say there is an irreversible process going on from A to B let us say and let us say there is change DQ irreversible DQ.

So therefore we will not be able to calculate from this process alone the entropy change for the system however that let us say this change in the Q and it throws away Q amount of heat to the universe irreversibly for the system however we take that to be a reversible change for the universe and we will be able to calculate the entropy change so delta is here will be nothing but the Q by T now Q is 1960, T is 27 degree, which is 300 kelvin that is the joule per kelvin entropy change, so that is an important point that we have to remember and because of that only we can see that an irreversible process the entropy of the universe will be positive otherwise it will not be positive.

So the fact that is small is reversible change or for a system a large change is extremely small for the universe because you see whenever there is a change in the heat we have to see how much change that happens for a particular you know for our universe for example if I take out a glass of water from the ocean is very extremely small change for the ocean however for a system bottle of water this is a huge change so that analogy is used so whenever you talked about an infinitesimal change it is with respect to the system alone if the system is big than the change can be infinitesimal even if it is finite for a smaller system that is what we have to understand.