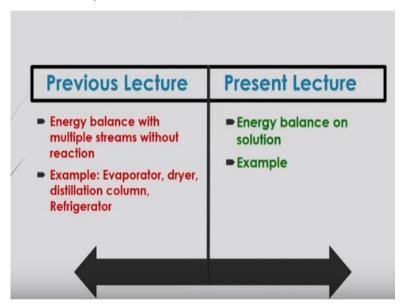
Basic Principles and Calculations in Chemical Engineering Prof. S. K. Majumder Chemical Engineering Department Indian Institute of Technology-Guwahati

Lecture - 23 Energy Balance on Heat of Solution

Welcome to massive open online course on Basic Principles and Calculations in Chemical Engineering. So we are discussing about energy balances on reactive processes and also nonreactive processes in our earlier lectures and under the module seven, we have discussed about this with ample of examples. Now in this lecture we will try to give more examples regarding that energy balance on you know heat of solution.

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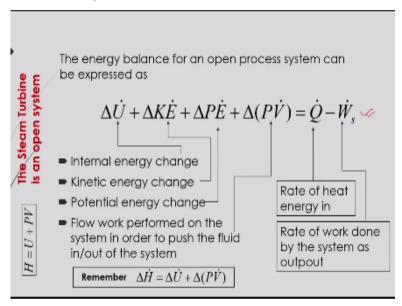


And we have this we have covered that energy balance with multiple streams without reaction, energy balance also you know with different you know streams in the specific you know chemical engineering operation like evaporator, drier, distillation column and also refrigeration processes. Now here also we have to find out that how actually that enthalpy balance can be helpful to analyze the solution basically for acid or other you know different type of solution.

Though we have discussed different aspects of that you know, mixtures and also how to calculate the enthalpy changes of mixtures in a particular process there and based on that, you know mixture specific heat capacity has also that temperature change, how those energy you know can be calculated. Based on that you know, internal energy change and also kinetic energy change inside the system.

So that solution also you know, can be considered as a mixture where that enthalpy change can be calculated based on that input and output streams and as well as you know that the different components enthalpy change based on their you know, formation and also how that sensitive heat changing during its you know phase change.

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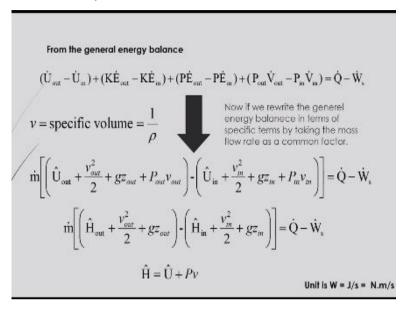


So we will extend this you know, enthalpy balance or energy balance equation for analysis some other problems here with solution. So before going to that, we have to look back that energy balance equation like we have actually described that energy balance equation in the form of you know, internal energy change, kinetic energy change, potential energy change and also flow work change based on that pressure change and volumetric flow rate change.

And those you know that energy as a sum that will be contributed by the net energy supplied to the system. Now that net energy supplied to the system basically comes from that heat energy supplied to the system and how much work is done by the system there so that you know balancing of that energy would be contributed to that internal energy, kinetic energy change and potential energy change.

Even if there is a pressure between these two you know streams of inlet and outlet if is there for the process then you have to consider that flow work change there for the energy balance.

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And based on that, you know continuous operation and also the continuous supply of mass, then how that internal energy, kinetic energy and also potential energy will be changed because of that flow wok and heat energy supplied to the system and that overall energy balance you know can be expressed based on that specific you know energy terms, just by multiplying that you know, the mass flow rate as a common factor in the common energy balance equation.

That also we have described earlier. So here in this slides also it is given that, this how that energy balance equation can be written based on that you know, specific energy terms with that mass flow rate.

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If there is no, Shaft work, no kinetic and potential energy, We can write
$$\begin{split} \dot{m} \Big(\hat{H}_{\text{out}} - \hat{H}_{\text{in}} \Big) &= \dot{Q} \\ \text{Or} \quad \dot{Q} &= \dot{m} \Delta \hat{H} \\ \text{Or} \quad \dot{Q} &= \Delta \dot{H} \end{split}$$
 $\Delta \dot{H} = \sum \dot{m}_{j} \hat{H}_{j} - \sum \dot{m}_{j} \hat{H}_{j} \end{split}$

$$\Delta \hat{H} = \sum_{\substack{Output \\ stream}} \hat{m}_j \hat{H}_j - \sum_{\substack{Input \\ stream}} \hat{m}_j \hat{H}_j$$

And finally, if you are considering that there is no you know shaft work, there is no kinetic energy change, there is no potential energy change, then you can simplify that energy balance equation as like this here Q dot will be is equal to delta H dot here and based on this you know enthalpy change you will be able to assess that what will be the you know heat energy required to you know change that operation or what would be the energy required for the you know actually that execute that process there in the system.

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Example 1:

Suppose in a closed constant pressure system of flask you are about to dilute 2.00 mol of 100% sulfuric acid with enough water to produce a 30 mole% aqueous solution. The acid and water are initially at 25°C.

- (a) How much heat would have to be removed to keep the final solution at 25°C? Given that heat of solution is -44.28 kJ/mole of H₂SO₄ at this condition
- (b) Suppose the flask has a mass of 150 g, and that the heat capacity of the flask and its contents is 3.30 J/(g °C). If the flask is sufficiently insulated to be considered adiabatic, what will be the final solution temperature?

So let us do an example with you know solution where that heat can be removed or may be added to keep that final solution at a certain temperature. Now in this case suppose in a closed constant pressure system of flask that you are about to dilute suppose two mole of 100% sulfuric acid with enough water to produce a 30 mole

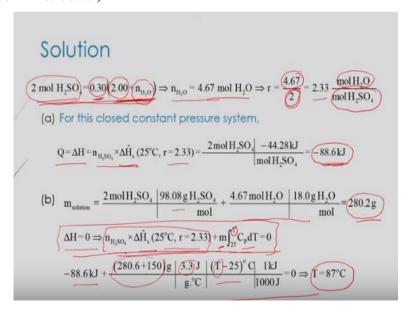
percent aqueous solution. In this case the acid and water are initially at a temperature of 25 degrees Celsius to be considered.

Now, in this case here see that there is a you know sulfuric acid solution of it is 2 mole capacity and which is mixed with that enough water to produce that 30 mole percent of aqueous sulfuric acid solution there. So in this case how much heat would be actually removed to keep that final solution at that 25 degrees Celsius because there you know that some heat energy to be removed to get this dilute solution of the sulfuric acid.

In this case that heat of solution is required and it is given that it will be amount of you know -44.28 kilojoule per mole of sulfuric acid at this condition. Another condition that if you supply that a mass of 150 gram of that, you know flask with the solution and the heat capacity of the flask is known to you and it contains its contents is you know 3.30 joule per gram degree Celsius.

And if the flask is sufficiently insulated, so that it will be, the system will be as a you know that adiabatic system and in that particular condition you have to find out what will be the final solution temperature. So this is the problem based on which you have to you know assess it by you know energy balance equation.

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Now, to solve this problem, first of all you have to calculate, you know what will be the amount of actually water to be mixed with that 2 mole of sulfuric acid to become it as a diluted 30% sulfuric acid solution. So for that 2 moles of you know, sulfuric acid to make it you have to add some water. That is not known to you. So for that if you consider that n mole of water is required for that, then we can write that you know, material balance for this solution as for this 2 mole of sulfuric acid that will come from that you know that whatever solution to be made up that would be 30%.

So 30% of that sulfuric acid, out of that total amount of solution will be is equal to here 2 moles of sulfuric acid plus n moles of water. So this is your total moles. So total moles, out of this total moles that 30% of you know this, you know moles will be sulfuric acid. That will be equals to 2 mole of sulfuric acid.

So if you write this equation of that mole balance of the sulfuric acid, you can you know calculate what should be the you know, moles of water to be required for getting that 30% sulfuric acid solution at its diluted condition of 25 degrees Celsius. And then, if you are getting this amount of water, that is as per calculation, it is coming as 4.67 mole of water.

In this case, then what will be our ratio of this sulfuric acid mole to the you know water mole. And based on which you can assess what will be the amount of you know, heat of solution to be required to get this you know of diluted solution at this 25 degree Celsius. So for that, what would be the ratio of that, water moles to that sulfuric acid. That is basically that 4.67 divided by 2 here.

4.67 is the mole of water and 2 is mole of sulfuric acid. So it is coming as 2.33. So at this ratio of the sulfuric acid and also that water here, you will see that at its 2.33 value that heat of solution at 25 degrees Celsius is around -44.28 kilojoule per mole of sulfuric acid. So in that case, what will be the total heat is actually you know to be removed from that system of this diluted sulfuric acid there.

So as per that energy balance equation you can write that here simply that there will be no shaft work. There is no kinetic energy change here. There is no potential energy change here. So finally, we can write that this energy balance will be is equal to Q. That will be equals to delta H that is enthalpy change there. So for that, that enthalpy

change for that solution at its ratio of 2.33 it is coming here delta H s hat, that is per mole of sulfuric acid is enthalpy change.

Now since there is you know 2 mole of sulfuric acid then total you know enthalpy change will be is equal to n of sulfuric acid into specific heat of solution at this 25 degree Celsius and the ratio of water to the sulfuric acid mole. So according to this finally after calculation you can get this -88.6 kilojoules of heat is to be you know removed from the solution.

Now this much heat is actually produced during that you know, addition of that sulfuric acid in you know water there. That is for making that solution, you will see there will be a heat generation and that heat should be removed by that you know, to the removed to the atmosphere so that certain dilution at a certain temperature it would be reached there.

So you have to then calculate what will be the final temperature of that solution there if you are you know removing this amount of heat from that solution. So for that you have to calculate what will be the you know mass of solution of that 30% sulfuric acid solution. So in this case you have to then add up of that what will be the mass of sulfuric acid and also what will be the mass of water in a solution.

So mass of sulfuric acid can be, you know calculated just by multiplying this 2 mole of sulfuric acid by a molecular weight of sulfuric acid. So it is coming as 2 mole of sulfuric acid into 98.08 gram of sulfuric acid per mole. And then what will be the mass of water that can be calculated again just by multiplying that mole of water by its you know that molecular weight.

So it is coming as here 4.67 mole of water multiplying by 18.0 gram of water, which is molecular weight of water. So finally after adding this, you can get this 280.2 gram of total solution. Since here again doing that enthalpy balance there in a solution, it is true that that in a net that enthalpy change will be is equal to zero. So finally, we can say that, at this 25 degrees Celsius, we can say that enthalpy change will be is equal to you know zero.

So what is the enthalpy basically, that is actually what will be the amount of sulfuric acid and what will be the heat of solution at that 25 degrees Celsius of the diluted solution. Plus, there will be a certain change of you know that temperature that is sensitive heat will be changed because of that change of temperature there. So that temperature you do not know, you have to find out.

So let us you know consider that temperature as T which is to be you know found out. So here if we multiply this mass of that solution and also that specific heat capacity of the solution at constant pressure and the temperature difference then you can get this you know sensible heat change there.

So what will be the heat of solution and what will be the sensible heat change there that you have to add it up to get that you know, total enthalpy change will be equals to zero. So we can write this equation here shown in the slides to you know balance that heat at its diluted solution of that amount here 280.2 gram. So after substitution of this value of here enthalpy this is you know simply what is that this value is already calculated here in part A.

So this is -88.6 kilojoule and this part here m is calculated as 280.2 and plus here 150 you know gram there total amount of this solution as well as there you know extra water is supplied for the dilution. For that you have to add it up So this is your total mass of that and then what will be the specific heat capacity that you have to multiply. This is basically 3.3 joule of the solution.

And temperature is you know changes T-25 because the initial temperature was 25 degree Celsius and when final temperature is you know that T. So T-25 degree Celsius, this will give you that you know, temperature change based on which that what would be the sensible heat change there. So finally, you can get after calculation that T will be is equal to here 87 degrees Celsius.

So you can say that if you add some water there you will see that solution temperature will be you know changed there. So accordingly you can say that, that how temperature will be changing because of the dilution or concentrating that solution also, accordingly you can calculate here as per this enthalpy balance equation.

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Example 2

Water is added to pure sulfuric acid in a well-insulated flask initially at 25°C and 1 atm to produce a 4.00-molar sulfuric acid solution (SG = 1.231). The final temperature of the product solution is to be 25°C, so that the water added must be chilled liquid (T < 25°C), or a mixture of liquid water and ice. Take as a basis of calculation one liter of the product solution and assume $Q = \Delta H$ for the process. If you need to know the heat capacity of ice, take it to be half that of liquid water.

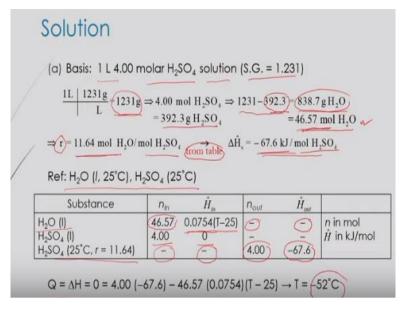
- (a) If only liquid water is added, what masses (g) of H₂SO₄ and H₂O should be mixed and what should be the initial temperature of the water?)
- (b) If a mixture of liquid water and ice is added, how many grams of each should be fed?

Now let us do another example, for assessing that energy balance equation with this example here. Let us consider that water is added to pure sulfuric acid in a well-insulated flask initially at 25 degrees Celsius and 1 atmosphere to produce a 4 molar sulfuric acid solution where specific gravity is given to you. The final temperature of the product solution is to be 25 degrees Celsius.

So that the water added must be chilled liquid at temperature less than 25 degrees Celsius or a mixture of you know liquid water and ice. Now in this case you have to consider a basis of calculation one liter of you know the product solution and assume Q will be is equal to delta H that is heat energy supplied that will be is equal to enthalpy change for the process.

Now if you need to know the heat capacity of ice and you can take it to be half that of a liquid water. Now in this case if only water is added what masses of sulfuric acid and water should be mixed and what should be the initial temperature of the water that you have to find out. And also if a mixture of liquid water and ice is added, then how many grams of each should be you know fed to the process.

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Now to solve this problem basically you have to consider that basis of that, you know problem your basis is one liter of 4 molar sulfuric acid solution is considered and specific gravity of that solution is 1.231 it is given to you. So one liter means here 1231 gram you have to multiply to this one liter so that you can get total you know of 1231 gram because the specific gravity is 1.231.

So what should be the density of that solution it will be simply 1231 gram per liter. So here in this way, you can calculate the mass of that solution is 1231 gram. Now, in this mass there will be 4 moles of sulfuric acid. That means here 1231 – 392.3 that will be your total amount of water. Here 392.3, this is basically that 4 moles of sulfuric acid how much it will give you that weight.

So in that case, if you subtract this amount of sulfuric acid from the total solution then you can get this what will be the amount of water there. And you can say that this water moles will be is equal to 46.57 mole of water because if you divide it by you know molecular weight of water you can get this you know, moles of water there.

So in this one liter of 4 molar sulfuric acid solution contains this gram of sulfuric acid, that is 392.3 gram of sulfuric acid and 46.57 mole of water or you can say 838.7 gram of water. In this case what will be the ratio of that water to sulfuric acid. It is simply as per this calculation here. 11.6 mole of you know water by mole of sulfuric acid here just by you know dividing this 46.57 mole of water divided by 4 moles of sulfuric acid then you can get it simply 11.64 mole of water per mole of sulfuric acid.

This is your ratio. Now, this ratio will give you the you know heat of solution. So this

heat of solution is coming as -67.6 kilojoule per mole of sulfuric acid. So you can get

it from a table what is given in your you know textbook there in the appendix that

how heat of solution can be changed to the ratio of you know, solid to you know

solvent there.

So in this case as per reference here it is given that water and sulfuric acid based on

which that heat of solution can be calculated. Now if you consider that in the solution

that on the water as a liquid substance then what will be the amount of this water is

coming into the you know system as it is 46.57 that we have calculated here, this

mole. So will be the enthalpy in the inlet?

That is simply you know that 0.0754 into T - 25, T is the temperature that you do not

know, that you have to find out there for that solution. Whereas, you know that what

will be the moles of water in the outlet condition. It is not known, because here this is

a simple you know, best process. There is no continuously supplying or that is

continuously outlet of that mole here, it is considered there.

So here in this case n out and H out to be you know nil. Similarly, sulfuric acid that

will be 4 mole and also you can say that here enthalpy will be is equal to zero. Now,

question is that why this 0.0754 it is coming because this is the mole ratio that you

have to consider there. And then what is that here sulfuric acid this ratio that n of

sulfuric acid nill and enthalpy change of that sulfuric acid is nil.

Whereas in output, there will be a sulfuric acid out at 4 mole and here this enthalpy of

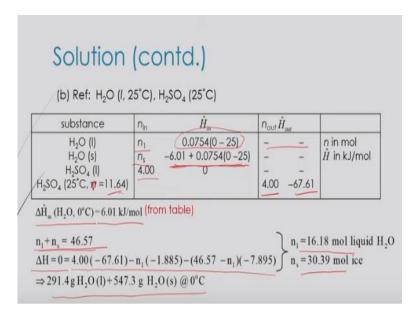
this outdate stream is -67.6. So finally, if you do that you know enthalpy balance

based on that earlier equation that we have given then we can have this you know

temperature as -52 point minus 52 degree Celsius as per after you know simplification

of this balance equation by substituting this various variable.

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Now at this you know, condition two whatever it is, you know given in the problem that water as a liquid that is coming in that will be is equal to n 1 that is not known to you that you are considering here it is n 1. Whereas in you know enthalpy at this inlet condition it is given as this. And in the outlet there will be no water. Similarly, for water solid in that case what will be the amount of solid there.

It is not known to you that you have to consider here as unknown and also enthalpy change for that solid water you can calculate by this simply you know that this amount, what is the heat of formation and then what will be the enthalpy of that you know or sulfuric acid because of this temperature change.

And then sulfuric acid as a liquid that is given to you that is 4 moles whereas in you know that sulfuric acid at 25 degree Celsius where this ratio of as per ratio here it is 11.64 at this ratio that you know that in total output of the sulfuric acid is 4 moles and enthalpy change at the outlet condition it will be is equal to -67.61.

So again you know that from the table of that solution, enthalpy of solution you can get this specific heat of solution for that amount of solution that you can calculate from that table, which is coming as 6.01 kilojoule per mole. Then total amount of liquid and solid that will be coming as you know as a material balance you can have this you know balance equation for this liquid and solid in inlet and outlet condition.

So based on this equation you can also solve this whenever the solution will be you know cooled down to a certain temperature by you know by supplying some you know sink heat sink like you know ice like that to what will be the amount of ice to be supplied and also what will be the water to be mixed with that you know acid solution to get its final temperature of you know T temperature like this.

Here in this case, this final temperature is considered as 25 degree Celsius. Accordingly, what will be the amount of heat is required that you how you can calculate and also from that heat balance and material balance you can calculate what will be the amount of liquid and also ice required for the making of solution.

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Example 3

An 8-molar hydrochloric acid solution [SG = 1.12, C_P = 2.76 J/(g.°C)] is produced by absorbing hydrogen chloride [HCl(g)] in water. Liquid water enters the absorber at 25°C and gaseous HCl is fed at 20°C and 790 torr (absolute). Essentially all of the HCl fed to the column is absorbed. Take one liter of product solution as a basis of calculation.

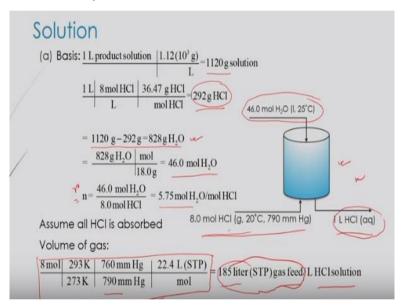
- (a) Estimate the volume (liters) of HCl that must be fed to the absorber.
- (b) Estimate the heat (kJ) that must be transferred from the absorber if the product solution is to emerge at 40°C.
- (c) Estimate the final solution temperature if the absorber operates adiabatically.

And another example let us do here. In this case an 8-molar hydrochloric acid solution the specific gravity of the solution is 1.12. And specific heat capacity at constant pressure is given 2.76 joule per gram degree Celsius is to be produced by absorbing hydrogen chloride as a gas in the water and liquid water enters the absorber at 25 degrees Celsius and gaseous hydrochloric acid is fed at 20 degrees Celsius and a pressure of 790 torr. That is one torr means one millimeter mercury pressure.

This is absolute pressure and in this case, you have to you know remember that, that all of the hydrochloric acid fed to the column is absorbed in the liquid system. And then take one liter of product solution as a basis of you know calculation here. So based on this you know problem you have to estimate the volume of hydrochloric acid that must be fed to the absorber.

And also you have to calculate the heat that must be transferred from the absorber if the product solution to emerge at 40 degrees Celsius. And also you have to estimate to the final solution temperature if the absorber operates adiabatically.

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So to solve this again you have to take that basis of one liter product solution and whose specific gravity is given and also you know that specific heat capacity is given. So as per that you can get this 1120 gram solution of that hydrochloric acid. Now, based on this you can calculate what will be the you know gram of you know hydrochloric acid there since here 8 mole of hydrochloric acid.

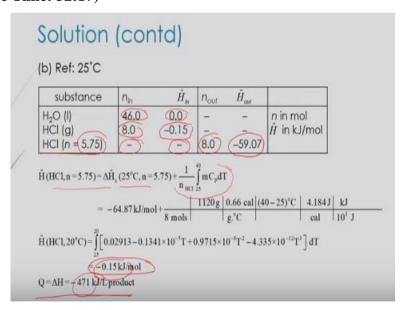
So if you multiply it by its molecular weight, then you can get what will be the mass of hydrochloric acid. So remaining amount will be you know that water that can be calculated here. It is as per this problem it is 828 gram of water. So in this case what will be the mole of water just dividing it by its molecular weight then you can get this mole of water.

And what will be the then ratio of that water to hydrochloric acid solution. It is coming as 5.75, this is as here, n or sometimes it is represented by r as ratio. Now assume all hydrochloric acid is to be absorbed in the absorber. So in this case, volume of gas that will be is equal to you know 8 mole of this you know hydrochloric acid hydrogen chloride gas to be absorbed.

So in this case 8 mole of hydrogen chloride at this temperature of you know 293 K as per problem and also the pressure of 790 millimeter mercury. Accordingly what will be the volume of that because per mole of gas will give you that 22.4 liter at STP condition. So as per that and also from the equation of state of gas, you can calculate that this 185 liter of gas feed per liter of hydrochloric acid solution which is to be you know, absorbed in the absorber here as shown in the slide.

So we can then calculate this amount of you know gas to be you know absorbed by this you know absorber there.

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Now, if we consider that reference temperature, what should be the enthalpy for that individual components in this absorber. What are the you know inlet and outlet of course, as per this schematic diagram, this is the amount of hydrochloric acid which is you know are going to that absorber and this is here aqueous you know hydrochloric acid solution.

So finally, you will see that you know this amount of hydrochloric acid aqueous solution of hydrochloric acid to be made if you absorb this you know, hydrochloric gas at 20 degree Celsius of 790 millimeter mercury there. And from this you know initial solution of 46.0 mole of water there. So accordingly what happened here this mole of water will be absorbing some hydrochloric acid gas and finally, you will see that one liter of hydrochloric acid to be made.

Now, in this case what will be the inlet what will be the outlet very interesting that this amount of hydrochloric gas or hydrogen chloride gas it will be in and this amount of water to be in and this is your outlet condition. So here two inlet and one outlet is there. So accordingly that inlet you will see that water inlet is 46 moles and enthalpy is zero.

Whereas hydrogen chloride gas inlet at 8 moles and also enthalpy change is -0.15. And in the solution you will see that heat of solution at this ratio that you can say that inlet condition there will be no you know hydrochloric acid solution at the inlet condition at this ratio. So that enthalpy and moles will be zero. Whereas it will come from this outlet whereas moles of that hydrochloric acid will be n out will be 8 moles and this enthalpy change will be -59.07.

Now according to that what will be the you know enthalpy specific enthalpy of the solution at this 25 degrees Celsius and how then you know sensible heat will be changing out of this hydrochloric acid from the temperature from 25 to 40 degrees Celsius. So if you substitute those values here, then finally you can get you know this value of you know 0.15 kilojoule per mole of this you know hydrochloric acid at 20 degree Celsius.

And then you know that according to that you know enthalpy balance or you can say that heat energy balance. So we can get this you know total enthalpy change will be is equal to if you multiply this minus you know 15 point kilojoule and the total mole of you know that hydrochloric acid solution there, then accordingly you can calculate here, this will be your amount of kilojoule or heat energy that is to be removed per liter of that hydrochloric acid solution.

So in this way you can calculate the enthalpy balance or you can do the enthalpy balance equation to calculate that what will be the amount of heat that is to be removed for its dilution or by absorption of even some gases by other liquid also.

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Solution (contd.)

(c)
$$Q = 0 = \Delta H = 8(\hat{H}) - 8(-0.15)$$

$$-0.15 = \hat{H} = -64.87 + \frac{1120g}{8 \text{mol}} \frac{0.66 \text{cal}}{g.^{\circ}\text{C}} \frac{(T - 25)^{\circ}\text{C}|4.184 \text{ J}| 1 \text{ kJ}}{\text{cal}} \frac{1000 \text{ J}}{1000 \text{ J}}$$

$$T = 192^{\circ}\text{C}$$

And from this you know heat balance or energy balance equation, you can say that at what temperature that solution will be you know reached there. So since the final solution will have that enthalpy change will be equals to zero. So accordingly if you consider that temperature is T then if you substitute that respective term here in this balance equation, you can get the final temperature of 192 degrees Celsius.

So we can solve this status of solution based on this energy balance equation for the assessment of you know what will be the amount of heat should be added or heat should be removed for making a certain you know, extent of dilution of that solution. So I think this problems will be helpful for you for further you know solving the problems related to this problem there.

And for this, you have to you know sometimes you know use the you know data that is given in you know tabulated for in appendix of this textbook. You have to consult that data otherwise the data to be given for your assessment in the problem so that you can solve the problem different you know problems related to this solution.

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Further reading.....

Text Books:

- R. M. Felder, Ronald W. Rousseau, Lisa G. Bullard, Elementary Principles of Chemical Processes, 4th Ed., John Wiley & Sons, Asia, 2017
- D. M. Himmelblau, J. B. Riggs, Basic Principles and Calculations in Chemical Engineering, 7/8th Ed., Prentice Hall of India, 2012.

Reference Books:

- N. Chopey, Handbook of Chemical Engineering Calculations, 4th Ed., Mc-Graw Hill, 2012.
- Olaf, K.M. Watson and R. A. R. Hougen, Chemical Process Principles, Part 1: Material and Energy Balances, 2nd Ed., John Wiley & Sons, 2004.

And its heat energy input and output to make this you know solution at its particular condition of temperature and pressure. So in the next lecture, we will start the you know new module where we will discuss more about that you know material balance and you know energy balance there. But that material balance or energy balance will be basically for the process where unsteady state you know operation will be there for chemical engineering processes.

So next lecture we will discuss the portion on unsteady state material balance. So thank you for your attention to this lecture.