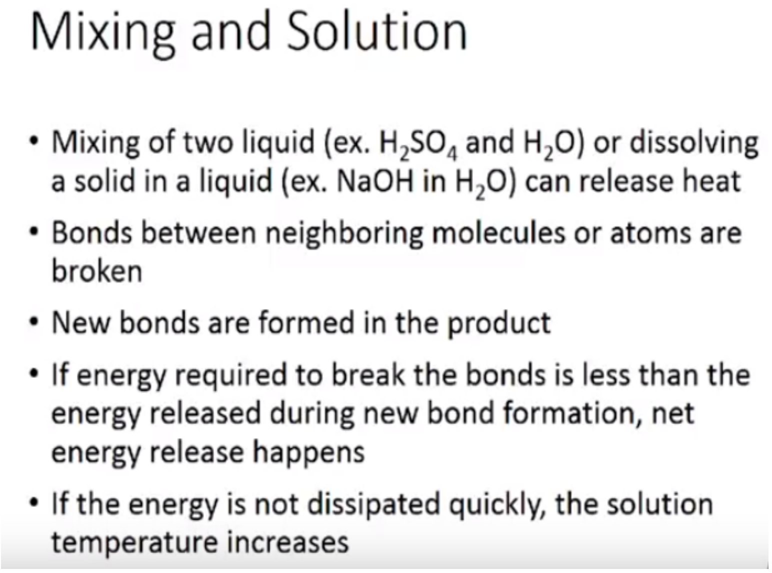
Material and Energy Balances
Prof. Vignesh Muthuvijayan
Department of Biotechnology
Indian Institute of Technology-Madras

Lecture - 52
Mixing and Solution

Hello everybody. Welcome back to the course on Material Energy Balances. Today we will talk about mixing and solutions. So what is the importance of this? So until now we have been assuming ideal mixing and solutions behavior. Now let us look at how we can account for non-ideality in these scenarios.

(Refer Slide Time: 00:39)



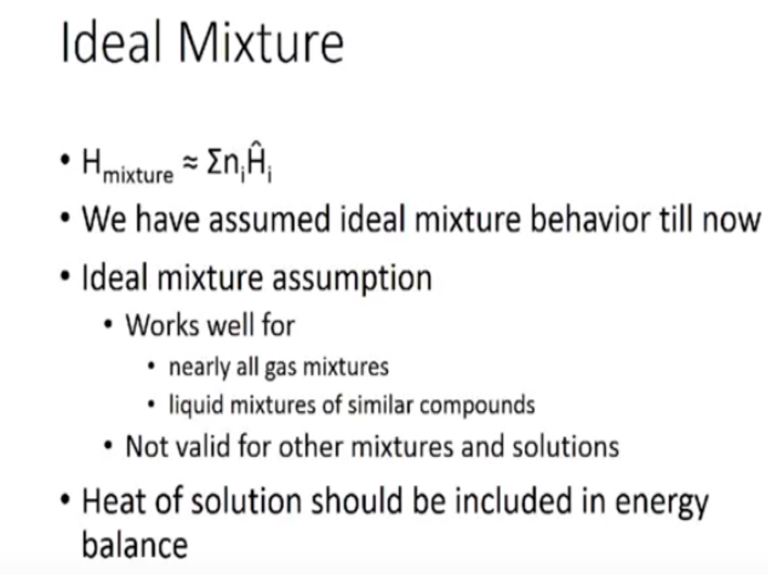
Mixing and Solution

- Mixing of two liquid (ex. H_2SO_4 and H_2O) or dissolving a solid in a liquid (ex. NaOH in H_2O) can release heat
- Bonds between neighboring molecules or atoms are broken
- New bonds are formed in the product
- If energy required to break the bonds is less than the energy released during new bond formation, net energy release happens
- If the energy is not dissipated quickly, the solution temperature increases

So what is the importance of mixing and solution in energy balances? Mixing of two liquids for example sulphuric acid and water or dissolving a solid in a liquid can actually release heat or absorb heat. Bonds between neighboring molecules or atoms are broken and new bonds are formed in the product. So this means there is going to be energy associated with this process.

If the energy required to break the bonds is less than the energy released during the bond formation then the net energy release happens. If you have it the other way, then energy is absorbed. If this energy which is released is not dissipated quickly then the solution temperature will also increase.

(Refer Slide Time: 01:23)



Ideal Mixture

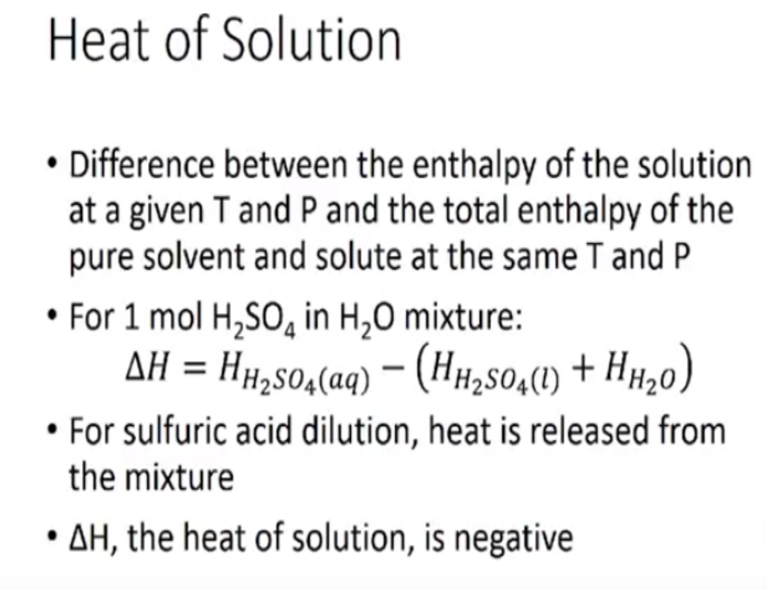
- $H_{mixture} \approx \Sigma n_i \hat{H}_i$
- We have assumed ideal mixture behavior till now
- Ideal mixture assumption
  - Works well for
    - nearly all gas mixtures
    - liquid mixtures of similar compounds
  - Not valid for other mixtures and solutions
- Heat of solution should be included in energy balance

In an ideal mixture what happens is the enthalpy of the mixture is equal to the summation of the contributions of enthalpy of individual components. So until now we have been assuming ideal mixture behavior. So that is why we have just been calculating the total enthalpy of a mixture as the summation of the enthalpies of individual components present in the mixture.

So the ideal mixture assumption works well for merely all gas mixtures because we are anyways operating under idea gas behavior most of the times and for those kind of conditions this assumption is reasonably valid. It also works for liquid mixtures of similar compounds. So if you have methanol and ethanol getting mixed, this would not be a problem. However, it is not valid for other mixtures and solutions.

Heat of solution should be included while you are performing energy balance calculations to account for the energy which is either lost or energy change because of the formation of this mixture and solution.

(Refer Slide Time: 02:27)



Heat of Solution

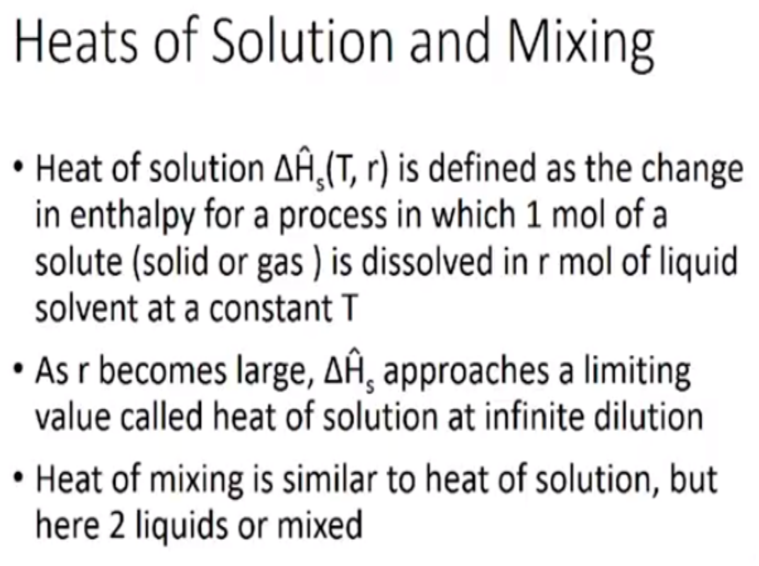
- Difference between the enthalpy of the solution at a given T and P and the total enthalpy of the pure solvent and solute at the same T and P
- For 1 mol H_2SO_4 in H_2O mixture:
$$\Delta H = H_{H_2SO_4(aq)} - \left(H_{H_2SO_4(l)} + H_{H_2O}\right)$$
- For sulfuric acid dilution, heat is released from the mixture
- ΔH, the heat of solution, is negative

What is heat of solution? The difference between the enthalpy of the solution at a given temperature and pressure and the total enthalpy of the pure solvent and the solute at the same temperature and pressure is defined as the heat of solution. So this is quite simple. So think of this as having an initial and final condition. So initial condition is where the pure solvent and the solute are existing separately at a particular temperature and pressure.

Now, the final condition is the solution which has formed. So just like how we have been looking at phase change, here the process is formation of solution. So just like how phase change has to happen at the constant temperature and pressure for us to identify the enthalpy associated with the phase change, here for identifying the heat of solution the formation of solution or mixture has to happen at the constant temperature and pressure.

For 1 mol of sulphuric acid in water mixture, what you would have is the change in enthalpy which is the heat of solution can be given as the enthalpy of the aqua sulphuric acid minus the summation of the enthalpy of liquid sulphuric acid and enthalpy of water at that particular temperature and pressure. For sulphuric acid dilution, heat is released from the mixture and because of this delta H cap which is the delta H which is the heat of solution is negative.

(Refer Slide Time: 03:55)



Heats of Solution and Mixing

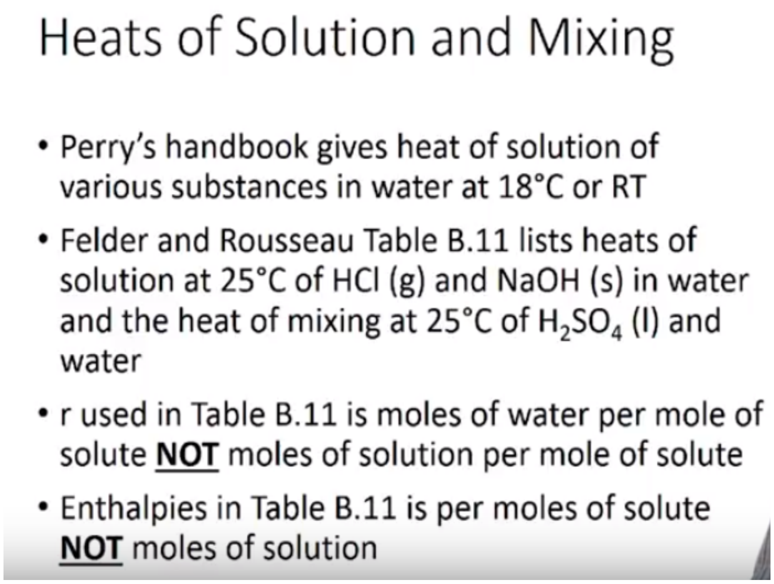
- Heat of solution $\Delta\hat{H}_s(T, r)$ is defined as the change in enthalpy for a process in which 1 mol of a solute (solid or gas) is dissolved in r mol of liquid solvent at a constant T
- As r becomes large, $\Delta\hat{H}_s$ approaches a limiting value called heat of solution at infinite dilution
- Heat of mixing is similar to heat of solution, but here 2 liquids or mixed

So now heat of solution also has another parameter which is the r term. So what you have here is delta H s cap T, r is defined as the change in enthalpy for a process in which 1 mol of a solute is dissolved in r mol of liquid solvent at constant temperature. See just like how you have a process where two components are mixing, so here now what happens is depending on the concentration of one component, you are going to have a different effect on the enthalpy change and this needs to be accounted for using the r term.

So this is the term which defines the level of dilution or concentration of the solute in the solvent. So if r becomes very large then what happens is delta H s cap approaches a limiting value which is called as the heat of solution at infinite dilution. So as r keeps increasing, the concentration of the solvent goes up to a very large level.

And the concentration of solute is infinitesimally small in that kind of a situation and this is called as an infinite dilution and the heat of solution then reaches a plateau and it remains a constant which is called as the heat of solution at infinite dilution. Heat of mixing is similar to heat of solution except here you have two liquids that are mixed instead of a solid being dissolved in a liquid.

(Refer Slide Time: 05:30)



Heats of Solution and Mixing

- Perry's handbook gives heat of solution of various substances in water at 18°C or RT
- Felder and Rousseau Table B.11 lists heats of solution at 25°C of HCl (g) and NaOH (s) in water and the heat of mixing at 25°C of H_2SO_4 (l) and water
- r used in Table B.11 is moles of water per mole of solute **NOT** moles of solution per mole of solute
- Enthalpies in Table B.11 is per moles of solute **NOT** moles of solution

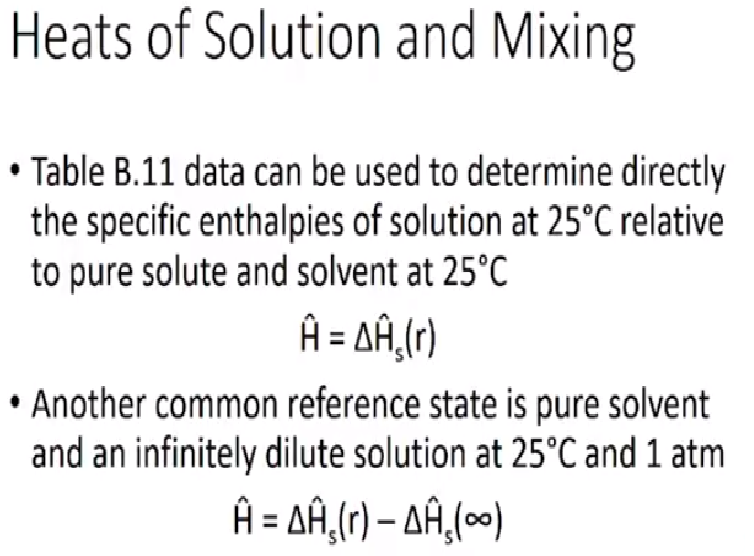
Perry's handbook gives you an extensive list of a heat of solution for various substances in water at 18 degree Celsius at room temperature. You can also get this information from one of the prescribed text books which is Felder Rousseau Table B.11 where you have the heat of solution at 25 degree Celsius for HCl gas and sodium hydroxide solid in water and the heat of mixing for 25 degree Celsius of H2SO4 liquid and water.

R is used in the table B.11 in terms of moles of water per mole of solute. It is not moles of solution per mole of solute. So r is usually represented as the number of moles of the solvent which is water per mole of solute okay. So use that appropriately because when we write the enthalpy table, so just like how we saw with psychrometric charts. If you remember, when we did psychrometric charts we filled the enthalpy table with only the dry air.

We did not write the mass of humid air because the enthalpy term was obtained for the dry air. It was given in terms of kilo joules per kilogram of dry air. So the component multiplied with the specific enthalpy term has to be the mass of dry air. Similarly, here this value would have to be accounted for appropriately so that we use the moles of water and not the moles of solution. Enthalpies in the table are also given as moles of solute, not moles of solution.

Again, using the same concept when you prepare the enthalpy table you would have to use the appropriate moles for the moles in and moles out or the moles initial and final.

(Refer Slide Time: 07:17)



Heats of Solution and Mixing

- Table B.11 data can be used to determine directly the specific enthalpies of solution at 25°C relative to pure solute and solvent at 25°C

$$\hat{H} = \Delta\hat{H}_s(r)$$

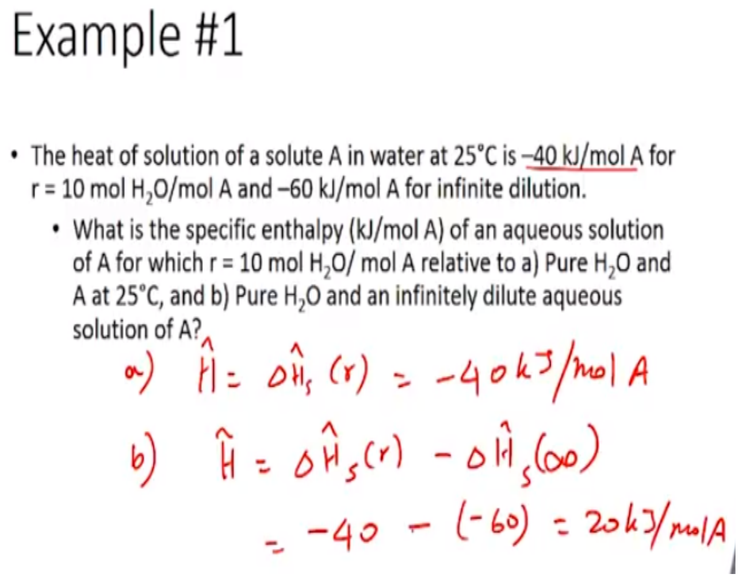
- Another common reference state is pure solvent and an infinitely dilute solution at 25°C and 1 atm

$$\hat{H} = \Delta\hat{H}_s(r) - \Delta\hat{H}_s(\infty)$$

Table B.11 data can be used to determine directly the specific enthalpies of solution at 25 degree Celsius relative to pure solute and solvent at 25 degree Celsius which indirectly means that the reference state which is used is pure solute and solvent at 25 degree Celsius. So this is given as H cap = delta H cap s at r where r is the level of dilution. Another common reference state which is used which is pure solvent and an infinitely dilute solution at 25 degree Celsius and 1 atmosphere.

Instead of using pure solute and solvent you can also use pure solvent and an infinitely dilute solution as the reference states. If you were to do this, then what you have is the actual enthalpy which you would be looking at would be the enthalpy you get from the table B 1 minus the enthalpy at infinite dilution.

(Refer Slide Time: 08:14)



Example #1

- The heat of solution of a solute A in water at 25°C is –40 kJ/mol A for r = 10 mol H_2O/mol A and –60 kJ/mol A for infinite dilution.
  - What is the specific enthalpy (kJ/mol A) of an aqueous solution of A for which r = 10 mol H_2O/ mol A relative to a) Pure H_2O and A at 25°C, and b) Pure H_2O and an infinitely dilute aqueous solution of A?

a) $\hat{H} = \Delta\hat{H}_s(r) = -40 \text{ kJ/mol A}$

b) $\hat{H} = \Delta\hat{H}_s(r) - \Delta\hat{H}_s(\infty)$

$= -40 - (-60) = 20 \text{ kJ/mol A}$

So here are a few example problems which would help us understand the fundamentals associated with mixing and solutions. The heat of solution of a solute A in water at 25 degree Celsius is -40 kJ/mol A. For r = 100 moles water per mol of A and -60 kJ/mol of A for infinite dilution. What is the specific enthalpy in terms of kJ/mol A of an aqueous solution of A for which r is 10 moles of water per mol of A relative to pure water and A at 25 degree Celsius.

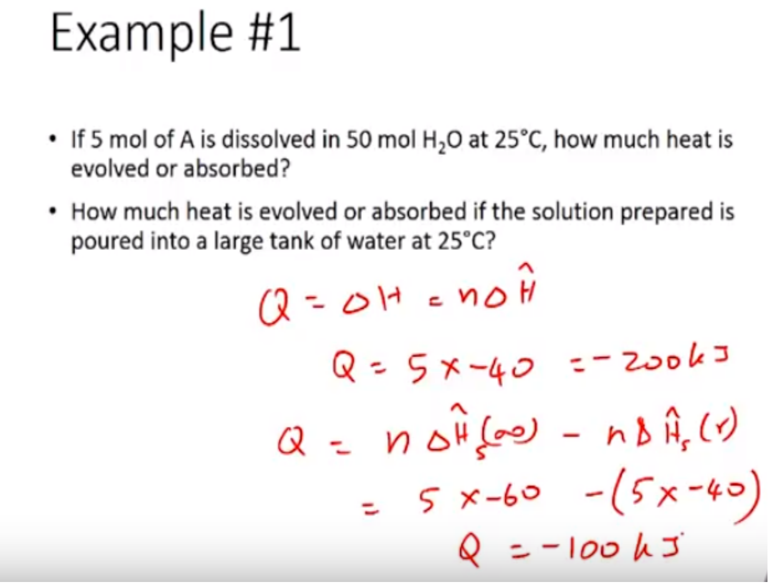
And the second component is pure water and an infinitely dilute aqueous solution of A. So what do you have in the problem is you have the heat of solution given. So one is the heat of solution using pure solute and solvent as the reference states which is given to you with a particular r value and you also have the infinite dilution heat of solution. Now we need to calculate what the change in specific enthalpy would be for preparing such a solution.

So for the first aspect we need to calculate the specific enthalpy of an aqueous solution of A with r of 10 moles of water per mol of A with relative to pure water and the solute A at 25 degree Celsius. So this means the value we have here directly -40 kJ/mol of A would give us the enthalpy associated with this. So our H cap would be equal to delta H s cap at r and the r is 10 moles of water per mol of A so we can directly use this value which is -40 kJ/mol of A.

So the next reference state which is used is pure water and an infinitely dilute aqueous solution. So in the previous slide we looked at how we would calculate this. So your H cap would be delta

H s cap at r - delta H s cap at infinity. So this is the infinite dilution. So what you would have here is -40 – (-60) giving you 20 kJ/mol of A. So depending on the reference states we get two different values.

(Refer Slide Time: 10:50)



Example #1

- If 5 mol of A is dissolved in 50 mol H_2O at 25°C, how much heat is evolved or absorbed?
- How much heat is evolved or absorbed if the solution prepared is poured into a large tank of water at 25°C?

$$Q = \Delta H = n\Delta\hat{H}$$

$$Q = 5 \times -40 = -200 \text{ kJ}$$

$$Q = n\Delta\hat{H}_s(\infty) - n\Delta\hat{H}_s(r)$$

$$= 5 \times -60 - (5 \times -40)$$

$$Q = -100 \text{ kJ}$$

Now let us look at the next few parts of the problem. If 5 moles of A is dissolved in 50 moles of water at 25 degree Celsius how much heat is evolved or absorbed. So first thing we need to know is what is the r value. So we have defined r value as the number of moles of water per mol of A. So here we have 5 moles of A dissolved in 50 moles of water. So 50 moles of water divided by 5 moles of A would give us an r value of 10 which means we can use the value given for heat of solution in the problem directly.

So the Q would be equal to delta H so which is equal to n delta H cap. So here we are assuming no change in kinetic energy, potential energy and shaft work. So this would mean this equation simplifies for the open system to Q = n delta H cap. So this would mean Q = 5 times -40 which is -200 kJ. So Q here is less than 0 which means heat is not supplied, heat is removed from the system or released from the system.

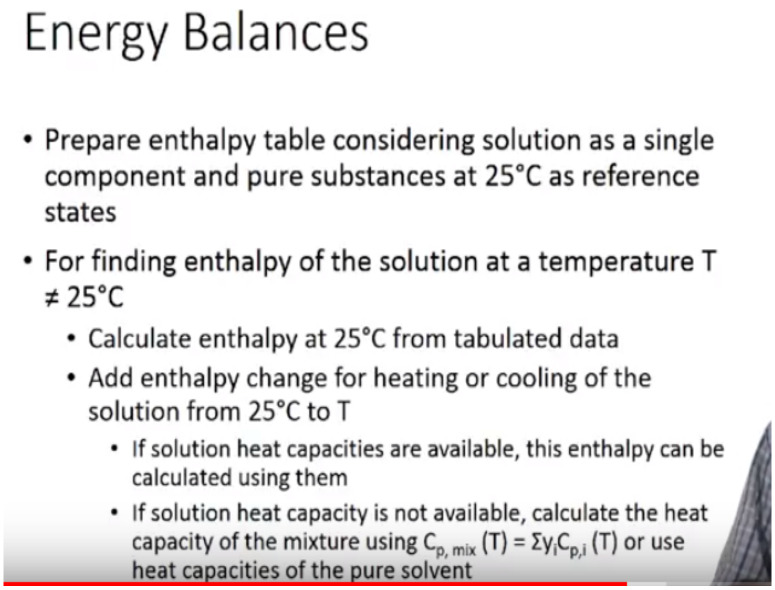
You have 200 kJ of heat which is released from the system while the solution is being prepared. So this is the second part. So now for the third part we are asked to identify how much heat is evolved or absorbed if the solution prepared is poured into a large tank of water at 25 degree

Celsius. Now what you have is the initial condition is 5 moles of A dissolved in 50 moles of water.

The final condition is what this solution being thrown into a huge tank of water which would eventually mean the final condition would be at infinite dilution. So now what we have is the final condition is infinite dilution. Initial condition we already know. So let us try to identify what the change in enthalpy would be. So Q = n times delta H cap s infinity - n times delta H cap s r which = 5 times -60 - 5 times -40 giving you Q = -100kJ.

So 100 kJ would be released if this mixture, if the solution is poured into a large tank of water at 100 degree, at 25 degree Celsius. So with this we have done some simple calculations to try and understand what this heat of solution represents.

(Refer Slide Time: 13:36)



Energy Balances

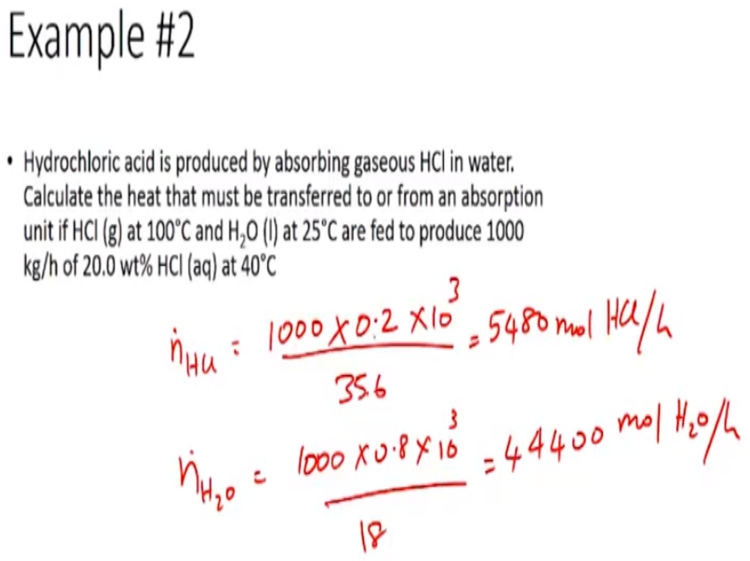
- Prepare enthalpy table considering solution as a single component and pure substances at 25°C as reference states
- For finding enthalpy of the solution at a temperature T ≠ 25°C
  - Calculate enthalpy at 25°C from tabulated data
  - Add enthalpy change for heating or cooling of the solution from 25°C to T
    - If solution heat capacities are available, this enthalpy can be calculated using them
    - If solution heat capacity is not available, calculate the heat capacity of the mixture using $C_{p,\,mix}(T) = \Sigma y_i C_{p,i}(T)$ or use heat capacities of the pure solvent

We will also look at more example problems which would help us perform energy balances using heat of solution. So how would we perform energy balances when we account for solutions? First thing we need to do is we will be preparing the enthalpy table which would consider the solution as a single component and pure substances at 25 degree Celsius as the reference state.

By doing this we would actually have a process where the pure components which are the reference state goes to the final condition which is there in the enthalpy table which would be the solution of these two components. So for finding the enthalpy of a solution at a temperature which is different from 25 degree Celsius what you would do is you would calculate the enthalpy at 25 degree Celsius from the tabulated data.

You would add enthalpy change for heating or cooling of the solution from 25 degree Celsius to temperature T. If solution heat capacities are available, this can be used directly for calculating the change in enthalpies. If not what you do is when you have to calculate the heat capacity of the mixture using CP of the mixture or use heat capacity of the pure solvent depending on the, pure solvent and solute or the pure solvent alone depending on the level of dilution.

(Refer Slide Time: 14:55)



Example #2

- Hydrochloric acid is produced by absorbing gaseous HCl in water. Calculate the heat that must be transferred to or from an absorption unit if HCl (g) at 100°C and H_2O (l) at 25°C are fed to produce 1000 kg/h of 20.0 wt% HCl (aq) at 40°C

$$\dot{n}_{HCl} = \frac{1000 \times 0.2 \times 10^3}{35.6} = 5480 \text{ mol HCl/h}$$

$$\dot{n}_{H_2O} = \frac{1000 \times 0.8 \times 10^3}{18} = 44400 \text{ mol } H_2O/h$$

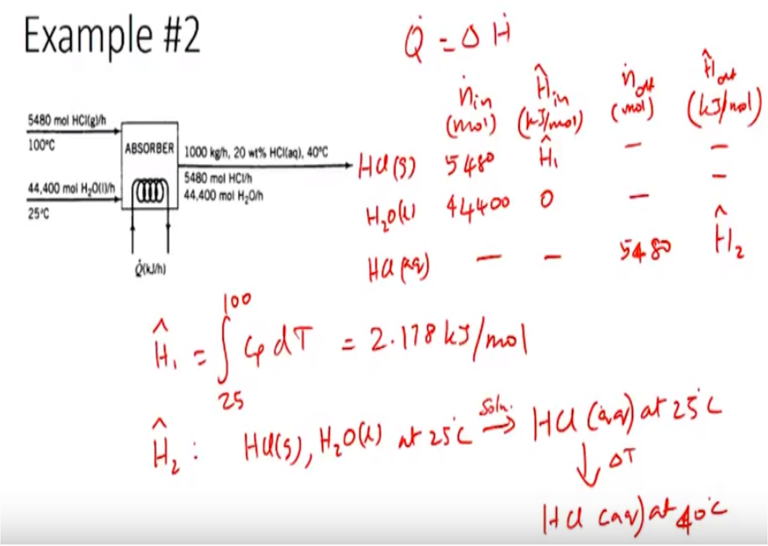
Here is an example problem where we will be preforming energy balances accounting for heat of solution as well. Hydrochloric acid is produced by absorbing gaseous hydrochloride in water. Calculate the heat that must be transferred to or from an absorption unit if HCl gas at 100 degree Celsius and H2O liquid at 25 degree Celsius are fed to produce 1000 kg/h of 20 weight percent HCl aqueous at 40 degree Celsius. Let us now look at how to solve this problem.

As the H cap values are available to us in terms of kilo joules per mole we first need to identify the number of moles of HCl and water in the system. So the molar flow rate n dot HCl for the HCl would be given as 1000 times 0.2 times 10 power 3/35.6. So this gives us 5480 moles of

HCl per hour. So we can also calculate the molar flow rate for water as 1000 times 0.8 times 10 power 3/18 giving us 44400 moles of H2O per hour.

So what you have here is the mass of the solution times the mass fraction of the component times 10 power 3 to convert it into grams divided by the molecular weight to finally get the number of moles of HCl or H2O which is present in the system.

(Refer Slide Time: 16:41)



Example #2

$\dot{Q} = \Delta \dot{H}$

	$\dot{n}_{in}$ (mol)	$\hat{H}_{in}$ (kJ/mol)	$\dot{n}_{out}$ (mol)	$\hat{H}_{out}$ (kJ/mol)
HCl(g)	5480	$\hat{H}_1$	—	—
H_2O(l)	44400	0	—	—
HCl(aq)	—	—	5480	$\hat{H}_2$

$$\hat{H}_1 = \int_{25}^{100} C_p \, dT = 2.178 \text{ kJ/mol}$$

$$\hat{H}_2 : \text{HCl(g)}, H_2O(l) \text{ at } 25^\circ C \xrightarrow{\text{Soln.}} \text{HCl(aq) at } 25^\circ C$$

$$\downarrow \Delta T$$

$$\text{HCl(aq) at } 40^\circ C$$

Now that we have the system, we have drawn the flow chart. So as you see 5480 moles of HCl gas at 100 degree Celsius and 44400 moles of H2O liquid at 25 degree Celsius are entering to finally form 1000 kg/h of 20 weight percent HCl aqueous leaving at 40 degree Celsius. Now, let us see how to perform the energy balance calculations. Here no material balances are required. So we can start performing the energy balance calculations.

So here it is an open system which means the equation would be Q dot = delta H dot assuming there is no change in kinetic and potential energies and no moving parts indicating shaft work = 0. So because of this we can use this as the equation for the general energy balance. Now we need to identify the reference states for performing the calculations. So before we build the enthalpy table, we need to identify what would be the reference states.

As we have to use the enthalpy of solution, we will have to use the reference states from the table which is listed. So the enthalpy table would have HCl gas H2O liquid and HCl aqueous. So as I had already mentioned, the aqueous solution is listed as a separate component so that we can account for the enthalpy change from the reference states. So the reference state should be the pure components as given in the table.

So n in dot which would be in terms of moles and you would have H cap in in terms of kJ/mol and n dot out in terms of moles and H cap out in terms of kJ/mol. So you have 5480 moles of HCl gas and 44400 moles of water liquid entering into the system. So now you do not have any HCl gas leaving the system or water liquid leaving the system. All you have is the aqueous HCl which is leaving the system.

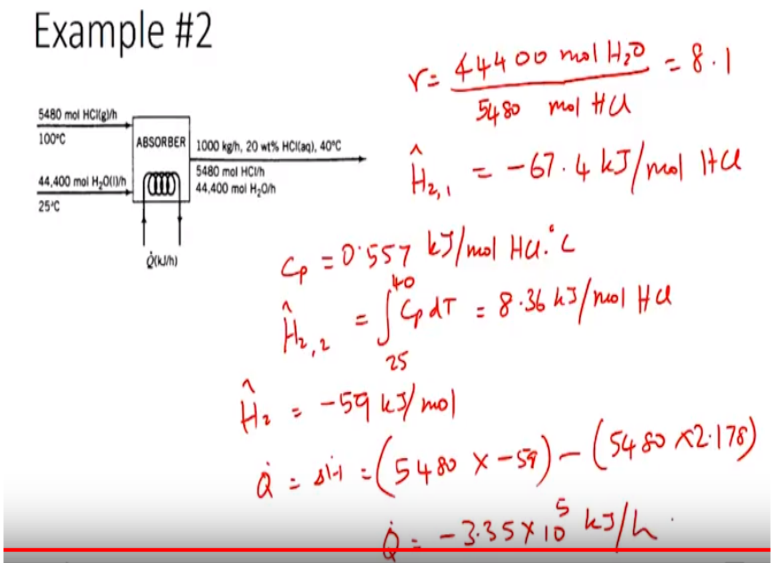
However, when we are writing the component in the aqueous HCl, we will not write the total number of moles. We will only write the number of moles of HCl because the enthalpy is given in terms of per mole of solute. So when we use the enthalpy value from the table we can use only the mass of the solute or the moles of the solute to be multiplied. So we will account only for the moles of HCl here for performing the calculations. So this is 5480.

So this would have an H 1 cap. So you have water liquid coming in at 25 degree Celsius which is the same as the reference state. So this would have a 0 enthalpy and this would have another enthalpy which is H 2 cap. Now we need to calculate H 1 cap and H 2 cap. H 1 cap is simple. H 1 cap is basically integral C p dT where C p is the specific heat capacity of HCl gas and the condition goes from 25 degree Celsius which is the reference state to 100 degree Celsius which is the temperature at which HCl is coming in.

So using the Cp value for Hcl gas we can calculate H 1 cap as 2.178 kJ/mol. Now the next step is to identify H 2 cap. How do we do that? H 2 cap is basically for the process where you have 2 steps. The first step is you have HCl gas and water liquid at 25 degree Celsius forming HCl aqueous at 25 degree Celsius. From here it goes to HCl aqueous at 40 degree Celsius. So this is the process. We have two steps.

The first step is the formation of the solution and the second step is the heating of the solution. So this would mean this is delta T and this is the solution formation. So for the first step we can get the change in enthalpy rate using the table which lists the heat of solution.

(Refer Slide Time: 21:14)



Example #2

$r = \frac{44400 \text{ mol } H_2O}{5480 \text{ mol HCl}} = 8.1$

$\hat{H}_{2,1} = -67.4 \text{ kJ/mol HCl}$

$C_p = 0.557 \text{ kJ/mol HCl}\cdot{}^\circ C$

$\hat{H}_{2,2} = \int_{25}^{40} C_p \, dT = 8.36 \text{ kJ/mol HCl}$

$\hat{H}_2 = -59 \text{ kJ/mol}$

$\dot{Q} = \Delta H = (5480 \times -59) - (5480 \times 2.178)$

$\dot{Q} = -3.35 \times 10^5 \text{ kJ/h}$

For identifying the heat of solution from the table we need to know the r value. So r would be equal to number of moles of water per mol of HCl. So we have 44400 moles of water for 5480 moles of HCl which implies r is roughly 8.1. So for the first step which is the formation of the solution from HCl pure component and water pure component we can look up the table B.11 in the text book Felder Rousseau.

Or you can use any other reference book and you will be able to get this value as H 2, 1 cap = -67.4 kJ/mol of HCl. For the next value which is heating the aqueous HCl to from 25 degree Celsius to 40 degree Celsius you need to identify the Cp value for HCl aqueous. So this value can be obtained from Perry's handbook. So according to Perry's handbook the Cp for HCl solution is equal to for the given mol fraction = 0.557 kJ/mol HCl degree Celsius.

So using this we can calculate the change in enthalpy for the second step which is integral C p dT where temperature is increased from 25 to 40 degree Celsius. So this would be equal to 8.36 kJ/mol of HCl. So the total change which is H 2 cap would be equal to the sum of these two giving us a value of -59 kJ/mol. So from here we can substitute the value back into the enthalpy table and calculate Q dot. So Q dot which is equal to delta H dot would be equal to 5480 times -59 which is the enthalpy of the aqueous HCl leaving the system minus the inlet HCl which is coming in which is 5480 times 2.178.

So this value would be Q dot would be equal to -3.35 times 10 power 5 kJ/h. So this is the rate at which heat must be removed for the process to happen. So with this we have performed an energy balance problem using heat of solution as well. In the next lecture we would have a tutorial session to solve a few more problems which use mixing and solution and this will help us get familiarized with these concepts and it will help us in applying these concepts directly while we perform energy balance calculations. Thank you.