

Material and Energy Balances
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Lecture - 53
Mixing and Solution: Tutorials - 1

Welcome to today's lecture on mixing and solutions. In the last lecture we looked at the fundamentals associated with mixing and solutions and we performed some simple energy balance calculations where we had to account for mixing and formation of solutions as part of the energy balances that were being done. Today, we will perform a couple of more problems.

So this would be a tutorial session where we will look at two problems which I will try to explain step by step and this will help you understand how we would go about performing these calculations. So here is the first problem.

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Example #1

- Water is added to pure H_2SO_4 in a well-insulated flask initially at 25°C and 1 atm to produce one liter of 4 M H_2SO_4 solution (SG = 1.231). The final temperature is to be 25°C , so that the water added must be chilled liquid ($T < 25^\circ\text{C}$) or a mixture of liquid water and ice.
 - What are the masses of water and H_2SO_4 mixed?
 - Assuming only liquid water is added, calculate the initial temperature of water required. Is this process possible?
 - If a mixture of liquid water and ice is added, how many grams of each should be added?

Data: C_p of ice as half that of liquid water and $\Delta\hat{H}_s$ for preparing 4 M H_2SO_4 solution as -67.6 kJ/mol H_2SO_4

The first problem states that water is added to pure sulphuric acid in a well-insulated flask initially, at 25 degree Celsius and 1 atmosphere to produce 1 liter of 4 molar sulphuric acid solution. The specific gravity is given as 1.231. The final temperature is to be 25 degree Celsius so that the water added must be chilled liquid at temperature much less than 25 degree Celsius or a mixture of liquid water and ice.

What are the masses of water and sulphuric acid that need to be mixed? Assuming only liquid water is added, calculate the initial temperature of water required. Is this process feasible? If a mixture of liquid water and ice is added how many grams of liquid water and how many grams ice need to be added? You have been given that C_p of ice can be used as half of that of liquid water and $\Delta H_{s, cap}$ which is the heat of solution for preparing 4 molar sulphuric acid solution is given as -67.6 kJ/mol of H_2SO_4 dissolved in the solution.

So we have all these information. So let us see how we can go about solving this problem. So the first information which you are looking to find is the masses of water and sulphuric acid. So this is a simple material balance calculation that can be performed if we know the definition for molar AT.

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Example #1

$$\begin{aligned}
 &4 \text{ mol } \text{H}_2\text{SO}_4 \text{ in } 1 \text{ L of } \text{H}_2\text{SO}_4 \text{ (aq) soln.} \\
 &\text{MW of } \text{H}_2\text{SO}_4 = 98.1 \text{ g/mol} \\
 &\Rightarrow (4 \times 98.1) \text{ g in } 1 \text{ L soln.} \\
 &\boxed{392.4 \text{ g } \text{H}_2\text{SO}_4} \\
 &\text{Mass of } 1 \text{ L soln} = 1 \times 10^3 \times 1.231 \\
 &= 1231 \text{ g} \\
 &\Rightarrow \text{Mass of } \text{H}_2\text{O} = 1231 - 392.4 \\
 &= \boxed{838.6 \text{ g } \text{H}_2\text{O}}
 \end{aligned}$$

We have been given that the solution which is given to us is 4 molar sulphuric acid. This means that 4 moles of H_2SO_4 is present in 1 liter of H_2SO_4 aqueous solution. So this is what 4 molar means. So let us look at what is the molecular weight for sulphuric acid. So molecular weight of $\text{H}_2\text{SO}_4 = 98.1 \text{ g/mole}$. And this molecular weight would imply that 4 moles of sulphuric acid present in 1 liter means that 4 times 98.1 grams of sulphuric acid has to be dissolved in 1 liter of solution.

So our basis for the problem is 1 liter of 4 molar solution being prepared. So this means 4 times 98.1 grams of sulphuric acid is dissolved. This will be 392.4 grams of sulphuric acid dissolved in 1 liter of solution. So you need to use 392.4 grams of sulphuric acid and in the 1 liter solution it would be sulphuric acid and water that are present. So we know that the mass of sulphuric acid is 392.4 grams of sulphuric acid. So what is the mass of water?

So we know the volume of the solution and we know the specific gravity of the solution. So we can calculate the mass of the solution. So mass of 1 liter solution would be equal to 1 times 10 power 3 times 1.231 which equals 1231 grams. So 1 liter of H₂SO₄ solution, 4 molar H₂SO₄ solution would weigh 1231 grams. So this implies mass of water would be equal to 1231 – 392.4 grams which would be equal to 838.6 grams of water.

So you can prepare 4 molar H₂SO₄ solution 1 liter of it by mixing 392.4 grams of sulphuric acid and 838.6 grams of water. So for the next part of the problem we have been asked to calculate at what temperature this liquid water must be if it has to be mixed with sulphuric acid so that the final temperature will be 25 degree Celsius. So how do we go about doing this?

So we have to assume that liquid water at temperature T is being mixed with sulphuric acid which is initially at 25 degree Celsius. We want the final condition to also be 25 degree Celsius which means that you are going to have water less than 25 degree Celsius added because there is going to be heat generated while the solution is being formed. Therefore for this to maintain at 25 degree Celsius, the water added would have to be at a temperature which is significantly lower than 25 degree Celsius. Let us see how we would do this calculation.

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Example #1

$$R_{25}: \text{H}_2\text{O}(l, 25^\circ\text{C}), \text{H}_2\text{SO}_4(l, 25^\circ\text{C})$$

	n_{in}	\hat{H}_{in}	n_{out}	\hat{H}_{out}
$\text{H}_2\text{O}(l)$	46.57	$0.0754(T-25)$	-	-
$\text{H}_2\text{SO}_4(l)$	4	0	-	-
$\text{H}_2\text{SO}_4(aq)$	-	-	4	-676

$$\hat{H}_1: \text{H}_2\text{O}(l, 25^\circ\text{C}) \rightarrow \text{H}_2\text{O}(l, T)$$

$$\hat{H}_1 = \int_{25}^T C_p dT = 0.0754(T-25)$$

$$\hat{H}_2 = -67.6 \text{ kJ/mol H}_2\text{SO}_4$$

So the components which would be present in this system would be water liquid and sulphuric acid liquid, those two will be mixed to form sulphuric acid aqueous which will be the final condition. So we need to identify reference states for these components. So for any time we have a solution what we have looked at is we could use the reference state as the pure components. So that is what you would do.

So here we will take reference states as water liquid at 25 degree Celsius at 1 atmosphere and sulphuric acid again a liquid at 25 degree Celsius. So these are the pure components which are being taken as the reference states. So let us look at the number of moles of water and sulphuric acid which have to be supplied. So we will have to write this in terms of moles because the enthalpy terms are given in terms of kJ/mol.

So we will write the number of moles of water and sulphuric acid which is being present initially and finally. So you have n_{in} and \hat{H}_{in} , n_{out} and \hat{H}_{out} . So we know the mass of water which is being supplied which is 838.6. So converting this to moles it would be roughly 46.57. So you just divide it by molecular weight. We know that 4 moles of sulphuric acid is present in 1 liter of the solution that is why it is a 4 molar solution.

So H_2SO_4 is 4 moles and the final condition, you do not have any liquid H_2O and liquid H_2SO_4 present. You only have aqueous H_2SO_4 . So there is no aqueous H_2SO_4 entering into the

solution. The final condition of the outlet only has H₂SO₄ solution. So what would be the number of moles that we write here? If we look at the data given for heat of solution, it is given as kilo joules per mol of H₂SO₄.

So we should write the number of moles of H₂SO₄ present in the aqueous solution, not the total number of moles of the aqueous solution present. So this means you would write 4 as the number of moles of H₂SO₄ present and this should be multiplied with the enthalpy data to get the total change in enthalpy. The specific enthalpy times this will give you the total change in enthalpy. So now what are the enthalpy values for this?

So you have H₂SO₄ liquid which is present at 25 degree Celsius and 1 atmosphere which is the same as the reference state. Therefore this enthalpy would be, specific enthalpy would be 0. You have water liquid which will be coming in at a temperature T and the reference temperature here you have is 25 degree Celsius. So this would mean that this value you have for water which is the reference.

So the value, enthalpy value you have for water would be H₁ cap which needs to be calculated. And similarly there would be an enthalpy for aqueous solution of H₂SO₄ which would depend on the heat of solution. So let us say that is H₂ cap and the other parameters do not have to be accounted for. So now for H₁ cap what is the process? Water liquid at 25 degree Celsius which is the reference state goes to water liquid at temperature T.

So we have been told in the first part that we will be using only liquid water. So the liquid water would have to be at a temperature T for the cooling to happen. So for this process your H₁ cap would be equal to integral C_p dT where temperature changes from 25 to T. So if you were to use the C_p value in terms of kilo joules per mol degree Celsius then the units, the value for C_p is 0.0754.

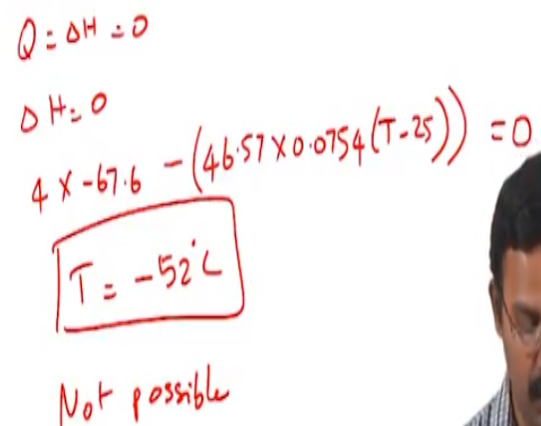
So you can convert the C_p in terms of joules per gram degree Celsius which is roughly 4.18 to the units of kilo joules per mol degree Celsius and check whether the value I have used is correct. So you have 0.0754 times T – 25 which is H₁ cap. H₂ cap is for what process? You

have pure components becoming the solution. The solution is at 25 degree Celsius. So this means the standard heat of solution which is obtained or the heat of mixing which is given in the problem can directly be used.

So this would mean you can use that value which is H_2 cap would be equal to the ΔH_s cap which has been given that is -67.6 kJ/mol of H_2SO_4 . So substituting these values here you would have H_1 cap as 0.0754 times $T - 25$ and H_2 cap would be -67.6 . So now with this we can start calculating the ΔH cap. We have been told that the system is perfectly insulated. This means it is basically a process where there is no heat being transferred from the surroundings or to the surroundings. So your Q would be equal to 0.

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Example #1



Handwritten equations and a note on a whiteboard:

$$Q = \Delta H = 0$$
$$\Delta H = 0$$
$$4 \times -67.6 - (46.57 \times 0.0754 (T - 25)) = 0$$

$T = -52^\circ C$

Not possible

So the equation actually would be $Q = \Delta H$ which would be equal to 0 because we do not have any shaft work or change in kinetic and potential energies. So you would end up with $\Delta H = 0$. So the ΔH can be calculated as 4 times $-67.6 - 46.57$ times 0.0754 times $T - 25 = 0$. So from here we can calculate the value for T . So T would be calculated as -52 degree Celsius. So this means that liquid water at -52 degree Celsius needs to be fed for the temperature of the final aqueous solution of H_2SO_4 to be 25 degree Celsius.

In other words this is not possible. You would not have liquid water at -52 degree Celsius and 1 atmosphere. It would be a solid. So this means we cannot use pure liquid water for the process to

continue. So not possible. So this is not possible. So now we need to look at what other alternatives are there. Third part of the problem asks us to find what if we used solid liquid mixture. So ice water mixture.

So if we were to use ice water mixture then what you would have is ice would have to melt and temperature would have to change so therefore there will be an effect because of this and therefore we might have to identify how much of ice and water has to be present so we will be able to get the 25 degree Celsius. How do we go about doing that?

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Example #1

Ref: $H_2O(l, 25^\circ C), H_2SO_4(l, 25^\circ C)$

	n_{in}	\hat{H}_{in}	n_{out}	\hat{H}_{out}
$H_2O(l)$	n_L	\hat{H}_1	-	-
$H_2O(s)$	n_S	\hat{H}_2	-	-
$H_2SO_4(l)$	4	0	-	\hat{H}_3
$H_2SO_4(aq)$	-	-	4	-

Again we will only have two chemical components which are water and sulphuric acid. So we need to identify the reference states considering that we still have to use the heat of solution given in the problem which is the standard heat of solution. We would use pure components at 25 degree Celsius as the reference state. Water liquid at 25 degree Celsius and sulphuric acid liquid at 25 degree Celsius would be our reference states.

Now what are the substances or components present in the system now. We said that we will have water liquid and water solid come in as a mixture. So we would have water H_2O liquid and H_2O solid both that need to be accounted for in the specific enthalpy table. You would have H_2SO_4 liquid and H_2SO_4 aqueous also in the system. So now again we will write n in \hat{H} cap in n out and \hat{H} cap out.

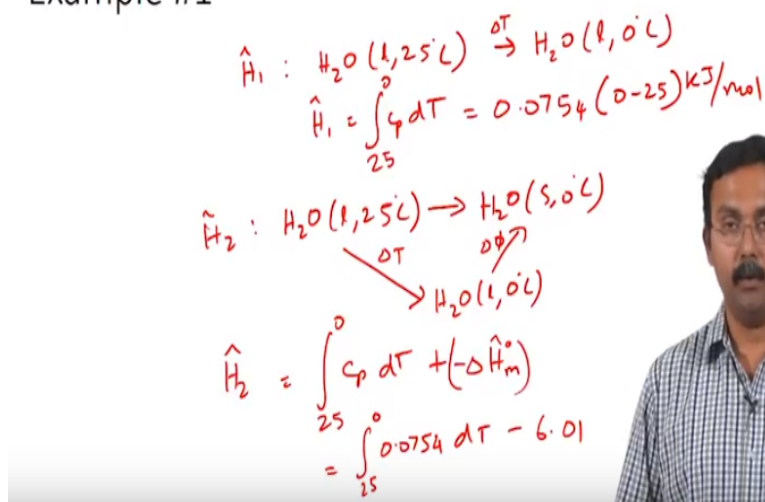
So for n in let us say it is n L for the amount of liquid water and n S for the amount of solid water or ice because that is what we need to calculate. We need to find the mass of liquid water and solid ice for the final answer. So we will take them as two variables. We know that 4 moles of sulphuric acid is present in the 4 molar solution which is of 1 liter. So this value is available to us. And we do not have any aqueous sulphuric acid coming in but we have sulphuric acid leaving as aqueous solution and we will again write only 4 moles.

As I already mentioned, we will be using the enthalpy of solution, heat of solution which is given as kilo joules per mol of H₂SO₄. So we will only write the number of moles of H₂SO₄ here. There is no liquid water solid water or sulphuric acid liquid as pure component leaving the system. So what are the enthalpies, which enthalpies do we have to calculate. So enthalpy of water has to be calculated because it is not coming in at 25 degree Celsius.

Similarly, enthalpy of ice also has to be calculated. Enthalpy of liquid sulphuric acid would be 0 because it is present at 25 degree Celsius and which is the reference state which we are using and this we do not have to worry about. These 3 we do not have to worry about and we have to identify the enthalpy associated with the formation of sulphuric acid aqueous. Now these are the terms which we have to identify.

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Example #1



In the last part of the problem, we were trying to identify the temperature. Here we have not been explicitly given the temperature. So what temperature do you think we would use? We have water and ice coexisting. This means the temperature would have to be 0 degree Celsius because it is 1 atmosphere. Water and ice will coexist at 0 degree Celsius and we will use that for performing the calculations.

So for H_1 cap we basically have a process where water from the reference state which is water liquid at 25 degree Celsius becomes water liquid at 0 degree Celsius. So all we have to do is identify this process and we will be able to calculate the enthalpy. So here it is only ΔT which is happening. So all we need to do is $\int C_p dT$ where temperature changes from 25 to 0. We already know the C_p for water. So for H_1 cap would be equal to $0.0754 \times (0 - 25)$.

This would be in terms of kilo joules per mol. Now let us calculate H_2 cap. So what is the process for H_2 cap? You have water liquid at 25 degree Celsius which is the reference state going to water solid at 0 degree Celsius. So now this actually has two steps where water liquid at 25 degree Celsius is cooled to water liquid at 0 degree Celsius and from here it solidifies to form water solid at 0 degree Celsius.

So this two steps are there, one where there is change in temperature and the other where there is change in phase. Now let us see how the total change in enthalpy which is H_2 cap can be calculated. H_2 cap would be for the first step it is $\int C_p dT$ from 25 to 0 + Δ heat of fusion, but here it is the solidification not melting. So you would have the negative of it. So you can use the standard heat of fusion and get this value.

So this would mean it is $\int_{25}^0 0.0754 dT - 6.01$ which is the heat of melting for water at 0 degree Celsius. You can look it up from any table available in your textbook or handbook. So this value can be calculated. So H_2 cap can be calculated from here and H_1 cap can be calculated from here. Now that we have H_2 cap and H_1 cap we can revisit the table.

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Example #1

$$\Delta H = 4(-67.61) - n_L \hat{H}_L - n_S \hat{H}_S = 0$$

$$n_L + n_S = 46.57$$

$$4(-67.61) - n_L(-1.885) - (46.57 - n_L)(-7.895) = 0$$

$$n_L = 16.18 \text{ mol H}_2\text{O}$$

$$\Rightarrow n_S = 30.39 \text{ mol ice}$$

$$m_L = 291.48 \text{ H}_2\text{O} \left. \vphantom{m_L} \right\} \text{at } 0^\circ\text{C}$$

$$m_S = 547.39 \text{ ice}$$

So from the specific enthalpy table so delta H would be equal to 4 times -67.61 – n L times H 1 cap – n S times H 2 cap. So this is what we have. Now we need, we have already calculated H 1 cap and H 2 cap. We need to calculate n L and n S. So we already know the number of moles of water which needs to be fed. We know the mass is around 838.6 grams. So this would mean that the number of moles would be 46.57 so implying n L + n S = 46.57.

So now this can be substituted back into the equation we have for delta H. We know that delta H = 0 because Q is 0 for this process and there is no change in kinetic energy, potential energy or shaft work. So using this equation we would end up having 4(-67.61) – n L(-1.885) – (46.57 – n L) -7.895 = 0. So from here we can calculate n L as 16.18 moles of water and therefore n S would be equal to 30.39 moles of ice.

So mass of liquid water would be 291.4 grams of water and mass of ice would be 547.3 grams of ice. So both would be at 0 degree Celsius. So this is what we would have and if were to add this masses to the H2SO4 solution, 4 moles of H2SO4 at 25 degree Celsius and we have a process where there is no heat being transferred, we would finally end up with 25 degree Celsius temperature for a 4 molar H2SO4 aqueous solution. Let us move on to the next problem.