

Concepts of Chemistry for Engineering
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Lecture – 60
Problems from Thermodynamics

Welcome back to the final segment of this thermodynamics discussion. In the previous sections we have discussed about the important thermodynamic properties like energy, work and heat. How they are connected together to form the basics of the first law of thermodynamics. Then we derived the important parameters like enthalpy and entropy; and redefine the second law of thermodynamics.

And from there we understand when a reaction becomes spontaneous; from there we even go to the third law of thermodynamics. After that we look into the free energy parameters, the Helmholtz free energy and Gibbs free energy; and how they are connected with respect to the work done by the system.

And from there we actually extrapolate that to different applications with respect to the electrochemical cell, with respect to acid-base equilibria, with respect to solubility equilibria. And at the end we have also discussed little bit on corrosion, which is also can be understood better with the extension of the thermodynamics. So, after we cover all these processes, in this final part we will do a few problems; and this problem set will help you to understand the underlying concept of thermodynamics better. So, let us start the problem set.

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1. An electric motor produces 15 kJ of energy as mechanical work & loose 2 kJ of heat to the surrounding. Calculate the change in internal energy of the motor?

$\Delta E, w, q$

$\Delta E = q - w$

$\Delta E = -q - w = -2 \text{ kJ} - 15 \text{ kJ} = -17 \text{ kJ}$

(heat is lost) (system is doing work)

The image shows a digital notepad with a yellow background. At the top, it says 'Thermodynamics'. The problem is written in black ink. A diagram shows a circle labeled 'motor' with an arrow pointing out labeled '15 kJ of work' and another arrow pointing out labeled '2 kJ heat'. A third arrow points into the circle labeled '-q'. Below the diagram, the equations are written out. The final answer is underlined.

So, over here I am going to write the different problems first, explain it and solve it. So, the first problem says that there is an electric motor, which produces 15 kilojoule of energy, as mechanical work and lose 2 kilojoules of heat to the surrounding. Now, we need to calculate the change in internal energy of this motor.

So, over here there is electric motor is present there; so, say this is defining the motor. It actually produces 15 kilojoules of mechanical work; so, it itself has done 15 kilojoule of work. And at the same time, it lose 2 kilojoule of heat to the surrounding. We have to measure what is the overall change in internal energy during this process.

So, this is nothing but we have to measure the delta E, the internal energy change. We have given the work done; we have given the heat exchange. So, these three parameters comes together and play well in the first law of thermodynamics, which says $\Delta E = q - W$.

Now, again the problem is easy, but over here the important factor is the sign of these parameters. Over here it is said that the heat is actually lost to the surrounding; so that means the heat is coming from the system to the surrounding. So, that means heat is lost; so that sign of heat will be negative, when you talking with respect to the system or the motor in this case.

So, when you are talking about ΔE , this will be $-q$; because heat is lost; now, the next is W , the work. The work when the system does work on its own, then it is taken as negative; and that is

exactly what is happening. The electric motor produces 15 kilojoule of energy as mechanical work; that means it is doing the work itself. So, it will remain as negative sign, because the system itself is working. Now, once the signs are actually figured out, the rest is simple; the heat is -2 kilojoule, work is -15 kilojoule. All together -17 kilojoule; so that much of energy change is happening.

So, it is negative, which is saying that in the final state the motor is 17 kilojoules lower compared to when it started this process. And why it is so? Because 15 kilojoule is lost for doing the work and 2 kilojoule is lost as a heat. So, again the important factor is the signature; if heat is lost from that system to the surrounding, it is negative. And if work is done by the system, it is negative; so that is the first problem. Let us go to the next one.

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2. A spring is suppressed with 100 kJ of work. During this process 15 kJ of heat escapes the system. What is the change in internal energy?

$\Delta E = q - W$

$\Delta E = -q + W$
 (heat is lost from the system) (work is done on the system)

$= -15 \text{ kJ} + 100 \text{ kJ}$
 $= 85 \text{ kJ}$

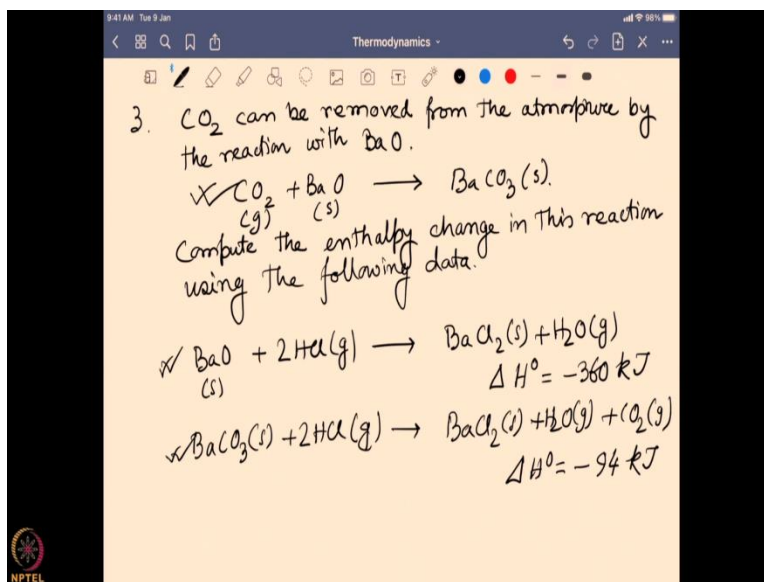
The diagram shows a spring on the left. An arrow points from the spring to the right, labeled $-q$. A checkmark is next to the spring. An arrow points down to the spring, labeled $+W$. Below the spring, it says "work is done on the system".

The next problem says there is a spring made out of steel is suppressed with 100 kilojoules of work. During this process 15 kilojoule of heat escapes the system. Again, the question remains the same what is the change in internal energy. So that is the question. So, over here we have a spring in the beginning and then it is pressed; so, during this pressing a work is done on the system. So, over here the work is done on the system. So, that is why now the work will be having a positive sign; because work is done on the system not by the system. And at the same time some heat escapes from the system to the surrounding.

So, it will be negative because heat is going out of the system. So, looking back into the first law of thermodynamics, we can redefine over here. For this particular system ΔE is $-q$, because heat is lost from the system; and $+W$ because work is done on the system. So, if we combine this thing together, then straight forward just put the values -15 kilojoule $+ 100$ kilojoule; so altogether 85 kilojoule. So, it says now the system has more energy compared to where it starts; and that is quite obvious by looking into the picture. Now, it is suppressed it has more capacity to do work, which is defined as the energy.

So, again first law of thermodynamics be very careful while you are looking into the signatures. Heat: if the heat is going out of the system, it is negative; if it is coming to the system it is positive. Work: work if it is done by the system, it is negative; work is done on the system, it is positive. So, with respect to that will go to the next set of the question.

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The next question is it is said carbon dioxide can be removed from the atmosphere, by the reaction with barium oxide. How? So, carbon dioxide and barium oxide can you can put together; where carbon dioxide is a gas, barium oxide is a solid. And you can produce barium carbonate, carbon salt is formed and you can remove the carbon dioxide.

The question is compute the enthalpy change in this reaction using the following data; the following data's are as follows. Barium oxide solid plus 2HCl which is a gas, producing BaCl_2

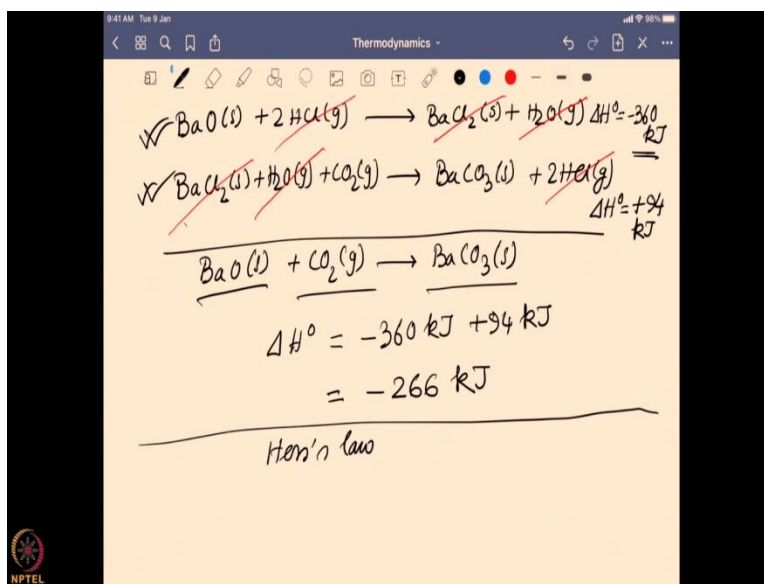
solid plus H₂O is a gas. And ΔH is 0 value; that means the reaction is considered the standard state; and standard enthalpy change for this reaction is -360 kilojoule.

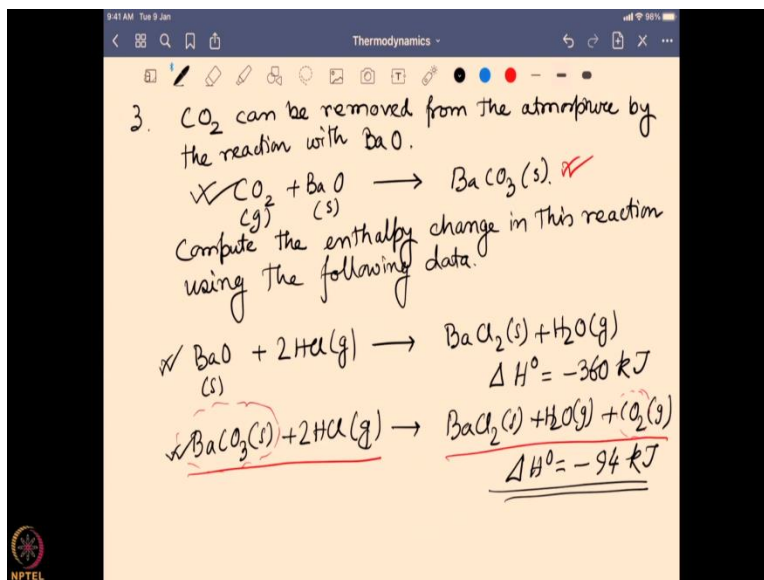
There is another reaction given over there. Barium carbonate solid plus 2 HCl in the gaseous form, barium chloride in solid form, H₂O in gaseous and carbon dioxide in gaseous form. The standard enthalpy change for this system is -94 kilojoule; these are the two equations given.

And now I have to find out the enthalpy change for this reaction; so, this is nothing but an example of Hess's law. In Hess's law, we discussed that we can combine a particular unknown reaction to the known reaction, such a way that we can just subtract or add the enthalpy values. And we can get enthalpy value for the reaction we are looking for.

So, basically over here what you need to do reorganize these two reactions such a way that combining them, I can get this, the reaction given in this question. So, how to do that? Let us take a look.

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So, I have barium oxide solid plus 2 HCl gas; it is giving me barium chloride solid plus H_2O gas, so that is fine. It is given now at the end result what I need is barium oxide solid, plus carbon dioxide gas to barium carbonate solid. So, that means the other reaction I have to balance such a way that I have a barium carbonate on the right hand side, and carbon dioxide on the left hand side. And if we look to this particular reaction over here, it is such a way that the carbon dioxide is on right hand side and barium carbonate on the left hand side. Now, I need to do the opposite so what I need to do? I just need to shift the reaction other way. So, what we did is the following.

Barium chloride solid plus H_2O gas, plus carbon dioxide gas, is equivalent to barium carbonate solid plus 2 HCl gas. Now, we have turned the reaction on the opposite way; so what will be the effect on the ΔH value? It will be exactly same value, but opposite sign. So, now it will be plus 94 kilojoule. Why? Because look into this equation, before it was minus 94 when the reaction is barium carbonate to barium chloride and carbon dioxide. And now we put barium chloride and carbon dioxide together to form barium carbonate; so it is actually opposite. Whereas, the first reaction it is written in the same way as the values are given; so it remains minus 360 kilojoule.

Now, if we combine these two reactions together, you can see the barium chloride and barium chloride getting cancelled; H_2O , H_2O get cancelled, HCl HCl get cancelled. So, it is just simple additions which leave us with only barium oxide, carbon dioxide and barium carbonate. So, the overall ΔH for this particular reaction will be minus 360 kilojoule for the first reaction; and plus 94 kilojoule, because we have reversed the reaction the second one. And all together if you put it

all together, it is going to be -266 kilojoule. So, you can see over there by using the Hess's law we actually recombine some known reaction, such a way that we can go to an unknown reaction by simple addition and subtraction.

And find out what will be the enthalpy value of this reaction; that is the beauty of Hess's law. Because the enthalpy change can be used in this particular manner; and we can find out the enthalpy change even for some unknown reactions.

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4. Calculate the entropy of fusion of ice if its heat of fusion (ΔH_{fus}) is 6.01 kJ/mol @ 273 K .

Ans. Entropy change for a phase transition can be expressed as

$$\Delta S = \frac{\Delta H_{\text{fusion}}}{T_{\text{melting}}} = \frac{6.01 \text{ kJ mol}^{-1}}{273 \text{ K}}$$

absolute temperature \rightarrow T_{melting}

$$= \frac{6010 \text{ J mol}^{-1}}{273 \text{ K}}$$
$$= 22.01 \text{ J K}^{-1} \text{ mol}^{-1}$$

Next, we go to the next problem which says calculate the entropy of fusion of ice, if its heat of fusion is nothing but ΔH_{fusion} is 6.01 kilojoule per mole at 273 Kelvin. So, to calculate the entropy, the heat of fusion is given, temperature is given; you have to find it out. So, as we know the entropy change for a phase transition can be expressed as ΔS is equal to ΔH_{fusion} in this curricular case, and temperature of melting. So, over here ΔH_{fusion} is given 6.01 kilojoule per mole, temperature is 273 Kelvin. So, be careful even if it is given 0 degree centigrade, you have to convert that to absolute temperature; because this is absolute temperature.

So, you have to put that in Kelvin scale; so that is very important factor, and then we have to do this calculation. So, it is kilojoule we can break it down to joule; so, it will be 6010 joule per mole inverse, divided by 273 Kelvin. And if you do calculation, you will find it will be very close to 22.01 joule per Kelvin inverse into mole inverse. So, the two important factors of doing this problem is, make sure you are going to use the absolute temperature over here; otherwise, it

will not work, do not divided that by 0 degree centigrade and 0. It will be undividable and you will get not the correct answer.

Over here the other important factor is the unit; so, you can see the enthalpy values are generally in the kilo joule unit. Whereas, the ΔS value are generally the joule unit; that is because it is multiplied by this particular temperature when we are considering the ΔH , which is t times ΔS . So, ΔS is divided by the temperature and this temperature has a huge value. So, it divides the factor by at least three orders of magnitude; and that is why this joule and kilojoule factor is particularly present there.

So, while you are doing this calculation make sure you want to do this calculation such a way that the kilojoule to joule transformation, you multiply the thousand in the proper way. Next, we will do an another problem of the same sort.

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5 // Calculate the increase in entropy when 1 mol of water evaporates @ 100°C. Latent heat of vaporization $\approx 540 \text{ Cal/g @ } 100^\circ\text{C}$.

Answer: 1 mol of water = 18.0 g water
Latent heat of vaporization = $540 \text{ cal g}^{-1} \times 18.0 \text{ g}$
 $q_{\text{rev}}(\text{vaporization}) = 9720 \text{ Cal mol}^{-1}$

$\Delta S = \frac{q_{\text{rev}}}{T} = \frac{9720 \text{ Cal mol}^{-1}}{373 \text{ K}}$
 $100^\circ\text{C} \rightarrow 373 \text{ K}$
 $= 26.06 \text{ Cal K}^{-1} \text{ mol}^{-1}$

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4. Calculate the entropy of fusion of ice if its heat of fusion (ΔH_{fus}) is 6.01 kJ/mol @ 273 K .

Ans. Entropy change for a phase transition can be expressed as

$$\Delta S = \frac{\Delta H_{\text{fusion}}}{T_{\text{melting}}} = \frac{6.01 \text{ kJ mol}^{-1}}{273 \text{ K}}$$

absolute temperature \rightarrow T_{melting}

$$= \frac{6010 \text{ J mol}^{-1}}{273 \text{ K}}$$

$$= 22.01 \text{ J K}^{-1} \text{ mol}^{-1}$$

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So, the question is calculate the increase in entropy when 1 mole of water evaporates at 100 degree centigrade. And what is given is the latent heat of vaporization and that is 540 calorie per gram at 100 degree centigrade. So, the question is very similar to the last time; but it is a little bit different, because right now I have to ask to measure the entropy change for an amount of water. In previous case we just asked to add the entropy of fusion; so we calculated that with respect to per mole unit. Over here it is given like how much water is there. So, sometime instead of water it can given like the amount of water, the volume, or the weight; so you have to do that perfectly.

So, first I need to find out what is the overall heat of vaporization; because it is given 540 calorie per gram not per mole. So, I have to calculate the mole of the water to the gram, so transform it that; and then calculate the overall heat exchange during that process. So, to do that what we will do?

First, we will calculate what is 1 mole of water? That is nothing but 18 gram of water. Now, the total latent heat of vaporization that is involved in this case is equal to 540 calorie per gram into 18 gram; because 18 gram of water is present there. So, they cancel each other the unit, and I get 540 into 18 calorie, which you find it out close to 9720 calorie. So, this much of calorie is heat is exchanged.

So, this is nothing but this q reversible during this vaporization. And as we know ΔS is q reversible divided by T ; so this is going to be 9720 calorie divided by temperature. Temperature

is 100 degree centigrade, but again the 100 degree centigrade should be converted to Kelvin scale first. So, it goes to 373 Kelvin.

So, you have to divide it with 373 Kelvin, and we get the value close to 26.06 calorie per Kelvin; and you can write it per mole unit now, this is gram per mole unit, so I should have write that mole unit; so, that mole unit is coming over here. So, the important factor is to when it is given the amount of water in presence of volume or in terms of grams; you have to multiply it or consider it properly.

Then the temperature you have to consider it with respect to the absolute temperature; and only then you can go to the right calculation. So, then we go to the next question where we go to some of the application part of these overall calculations.

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6 // Calculate the free energy & entropy change per mole of liquid water when it boils at 1 atm. pr. $\Delta H_{\text{vaporization}} = 2.0723 \text{ kJ g}^{-1}$

Ans Enthalpy change (ΔH) = $2.0723 \text{ kJ g}^{-1} \times 18 \text{ g mol}^{-1}$
 $= 37.30 \text{ kJ mol}^{-1}$

because it is happening at $100^\circ\text{C} \rightarrow 373\text{K}$

Entropy change (ΔS) = $\frac{\Delta H_{\text{vap}}}{T} = \frac{37.30 \text{ kJ mol}^{-1}}{373 \text{ K}}$
 $= 0.1 \text{ kJ K}^{-1} \text{ mol}^{-1}$
 $= 100 \text{ J K}^{-1} \text{ mol}^{-1}$

So, the question is calculate the free energy and entropy change per mole of liquid water, when it boils at 1 atmospheric pressure. And the other data given over there enthalpy of the vaporization and that is given in the unit of 2.0723 kilojoule per gram. So, that is the heat of vaporization of enthalpy change of vaporization is given.

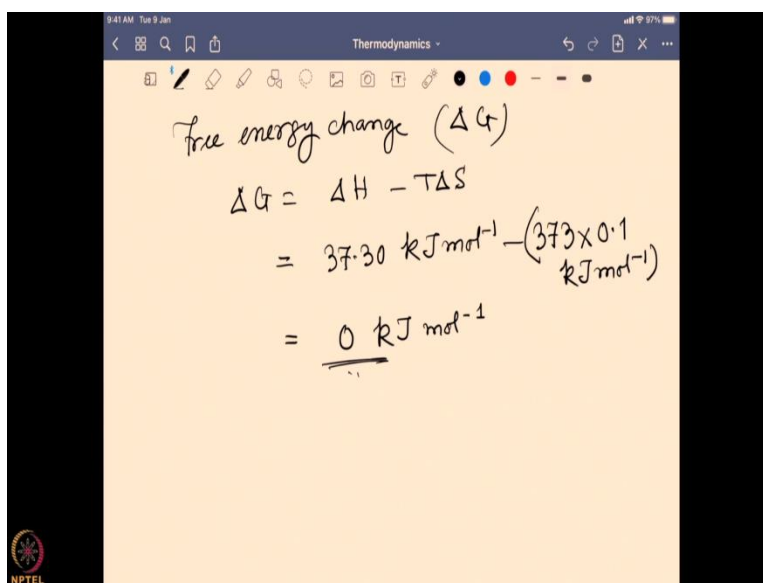
So, now enthalpy of vaporization if I want to carry, because we have 1 mole of liquid water; that means again 18 gram of water comes here. So, the overall enthalpy change for this process will

be the following, 2.0723 kilojoule per gram into 18 gram per mole. Because that is 1 mole of water weighs and all together you get 37.30 kilojoule per mole; that is overall enthalpy change.

And the process what you are talking about it is happening at 100 degree centigrade; that means 373 Kelvin. Because it stays as this boiling condition; so that means is the 100 degree centigrade temperature. So, the entropy change will be ΔS , ΔH vaporization divided by T delta H vaporization of enthalpy, we have already calculated over here.

So, it is 37.30 kilojoule per mole divided by 373 Kelvin, which comes out to be 0.1 kilojoule per Kelvin per mole inverse. Or, if you want to convert it to the joule unit, it is 100 joule per Kelvin per mole inverse; so that is the overall entropy change. Now, we have to also calculate the free energy change.

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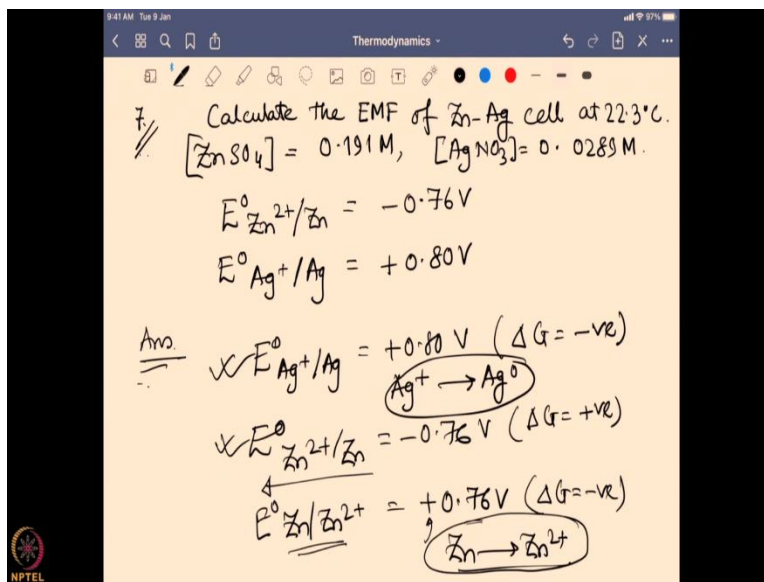
Free energy change (ΔG)

$$\Delta G = \Delta H - T\Delta S$$
$$= 37.30 \text{ kJ mol}^{-1} - (373 \times 0.1 \text{ kJ mol}^{-1})$$
$$= \underline{0 \text{ kJ mol}^{-1}}$$

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So, the free energy change for this system is ΔG , which is given by $\Delta H - T\Delta S$. So, ΔH we know it is 37.30 kilojoule per mole inverse; T is 100 K sorry, I am doing the same mistake; 373 Kelvin into 0.1 kilojoule per mole inverse. So, you can see it will cancel out and give you 0 kilojoule per mole inverse is the overall Gibb's free energy change. It is coming to this particular figure, because it is in the equilibrium during the vaporization of the system of the water. So, that is how you calculate the energy and enthalpy changes accordingly using the free energy conversions; now, the penultimate problem.

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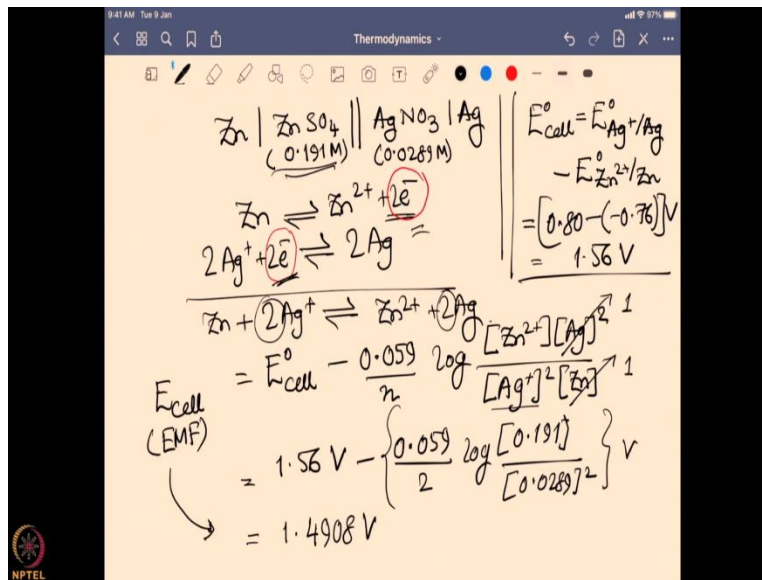
There is a zinc silver cell and we have to calculate the electromotive force of this zinc silver cell, which is operating at 22.3 degree centigrade. Over here it is given zinc sulphate is present there; its concentration is 0.191 mole. Silver nitrate is present there; its concentration is 0.0289 moles. To other standard reduction potential values are given, Zn⁺² to Zn; it is given minus 0.76 volt.

And Ag⁺ to Ag, is given as plus 0.80 volt. So, now I have to calculate the emf for this whole system. So, now which side the reaction will first go that we have to calculate. And you can see the E^o value of Ag⁺ to Ag is plus 0.8, which is a positive; so, ΔG is negative for this particular system.

Whereas, Zn⁺² to Zn is negative value; so ΔG is positive for this particular direction. So, by looking into that we can say the first process will be spontaneous; this process will be not the opposite process will be spontaneous. Because the opposite process will be E^o value of Zn to Zn⁺² the oxidation; that will be plus 0.76 volt that will be spontaneous; because the redox potential values are mostly given in the reduction site. So, when you are talking about oxidation, the value remains same; only the sign changes, because it is exactly the opposite reaction.

So, we can say Ag⁺ will go to silver that reaction will happen; and here this reaction becomes negative then, so, zinc will go to Zn⁺². So, now we know the direction of the reaction in this electrochemical cell; silver will get reduced, zinc is going to get oxidized. So, now we will create the cell.

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So, zinc is going to get oxidized to zinc sulphate and its concentration is given 0.191 molar. The other part of the cell, this double line signifies the separation of the two half cells; is Ag^+ ion in the present in the form of silver nitrate is going to silver zero. And this is present in 0.0289 molar; so, this overall cell. So, now the overall reaction is the following, zinc is going to $\text{Zn}^{2+} + 2e^-$ (electron). And now there are two Ag^+ has to act over here to balance the overall electrons; it is going to be 2 Ag, because there are 2 electrons are released by the zinc during oxidation.

And these two electrons will reduce 2 Ag^+ , because one Ag^+ goes to Ag with taking with one electron. After balancing the reaction, we find the reaction is $\text{Zn} + 2\text{Ag}^+ \rightarrow \text{Zn}^{2+} + 2\text{Ag}$.

Now, we are going to use the E cell which is nothing but the emf value we need to measure. It is going to be the E° cell at the standard condition; and by using the Nernst equation, we can write

$0.059/n \left(\log \frac{[\text{Zn}^{2+}][\text{Ag}]^2}{[\text{Ag}^+]^2[\text{Zn}]} \right)$. And there are two silver, so it will be squared; the reactant side is

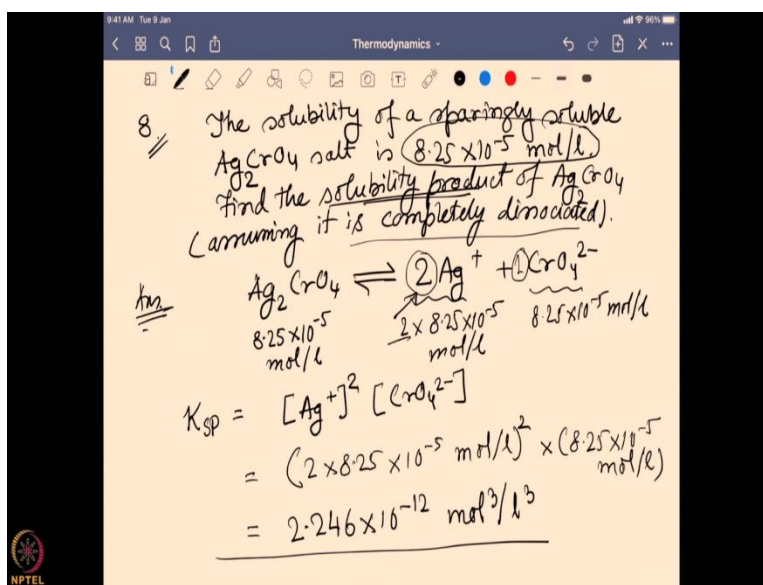
silver plus squared and zinc. The square terms coming; because their stoichiometric coefficient is two for both the silver.

E° cell, E° cell is nothing but the difference between the $E^{\circ}_{\text{Ag}^+/\text{Ag}} - E^{\circ}_{\text{Zn}^{2+}/\text{Zn}}$. It is already given in minus, so do not need to convert it to Zn to Zn^{2+} again. So, this value will be $0.80 - (-0.76)$ volt, so 1.56 volt; so that is the E° cell value. So, you are going to write it over there 1.56V - $0.059/n$, n is the number of electrons involved here; there are two electrons involved. So, it will

be 2 log scale of Zn^{+2} solution is given value 0.191. Silver is in the solid state, so activity is 1; zinc in solid state, activity is 1; so you do not need to consider Ag^+ concentration is 0.0289 then squared.

And if you do all the calculations, this is also given in the value of volt; all together it comes to 1.4908 volt, and this is the emf of the cell. So, that is how you use the standard reduction potential and the Nernst equation to find out the overall emf of an electrochemical cell; now, the last problem.

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So, here is a solubility equilibrium problem. The solubility of a sparingly soluble silver chromate salt Ag_2CrO_4 salt is 8.25×10^{-5} mole per liter; so that is the solubility, it is found experimentally. Now, our question is we need to find the solubility product of this particular salt Ag_2CrO_4 assuming.

So, there is assumption that the salt is completely dissociated; so considering these assumptions we have to find out the K_{sp} or the solubility product of this salt. So, let us look into the equation first; so, it is Ag_2CrO_4 . So, when it splits out, it is going to give me 2 Ag^+ ion and 1 CrO_4^{2-} . So, now you can see the solubility is given over here; so how much it is actually present as the salt and it is 100 percent dissociating.

So, the concentration present in the solution is 8.25×10^{-5} mole per liter. So, when it dissociates it completely dissociates, so hundred percent of it goes to silver ion and chromate ion. It is going to create two equivalent of silver and one equivalent of chromate ion. So, it will be $2 \times 8.25 \times 10^{-5}$ mole per liter silver ion present; and 8.25×10^{-5} mole per liter chromate ion present there. So, that is we know the ion concentration. Now what is the solubility product? As we know it is going to be the $[\text{Ag}^+]^2$; because it has two coefficients over there, and CrO_4^{2-} .

The coefficient is one, so there is no other thing coming into here. And now what we need to do, we have to just put the concentration we just figured it out. So, it will be $(2 \times 8.25 \times 10^{-5} \text{ mole per liter})^2 \times 8.25 \times 10^{-5} \text{ mole per liter}$. And if you all do the calculations around, it comes out $2.246 \times 10^{-12} \text{ mole}^3 \text{ per liter}^3$; so that is the solubility product. So, if you find this kind of problems coming into your way, you have to first find out what is the ion concentration; and that is given by the solubility.

And over there very careful about how much equivalent of ions you are producing here; because that is going to be multiplied with respect to the solubility. And that is also going to be coming over here as the power of the system with respect to the stoichiometric coefficient. So, this is all the application part we discussed with respect to the problem solving; and that is the concluding section of the thermodynamics. I hope that is quite an enjoyable segment for you in the near future. Thank you very much.