Material and Energy Balance Computations

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Lecture-55
Energy Balance with Chemical Reactions-V

Welcome back to the last lecture of 11th week. We are now sort of nearing the end of the course which I am sure you are quite happy to be. And though it is easy course but pretty heavy. We have learnt a lot of new things which you must admit and appreciate. So, last couple of lectures we have been broadly talking about heat of reaction and we also came across terms like heat of formation, heat of combustion etcetera.

The primary objective what we have been looking into what is the major difference from the initial part of the course where we were talking about energy balance; we were actually looking at energy balance of non reacting system. For example, when a steam was condensing on a steam chest or you were taking or breaking a pool ample of liquid in an excavated tank, there was no chemical reaction.

And now the moment you talk about chemical reaction, you need to consider the thermo chemistry or the thermal effects of chemical reactions and which we have been learning. So, one specific term that we have already encountered is heat of combustion which is nothing but essentially the heat of reaction of combustible material. In today's lecture if you look into the title we will be talking about heat of neutralization.

Now heat of neutralization is nothing but the neutralization reaction you all know that there is neutralization reaction that takes place between acids and bases and so essentially when an acid reacts with a base it is called the neutralization reaction because the base neutralizes the acidity or the acid neutralizes the basicity and stuff like that.

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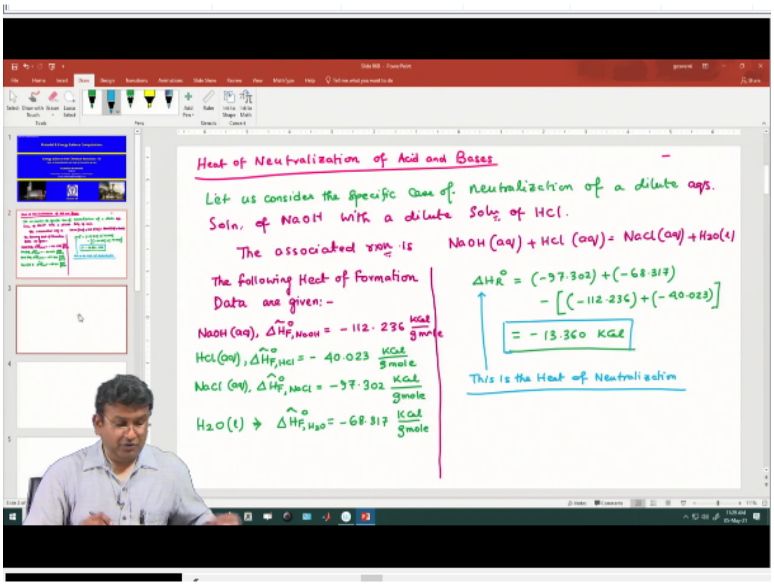

So, what is heat of neutralization? It is essentially the heat of reaction, or a neutralization reaction between an acid and base. So, let us consider a specific case of neutralization of a dilute aqueous solution of NaOH with a dilute solution of HCl and I am going to show you something very interesting.

So, the associated chemical reaction is

$$NaOH\ (aq) + HCl\ (aq) = Nacl\ (aq) + H_2O\ (l)$$

So, there is nothing exceptional or great in this whole concept as we all know about it. Now there is some additional data such as the following heat of formation data are given,

NaOH (aq), $\Delta H_{F,\ NaOH}{}^{0}$ cap = - 112.236 Kcal/gmole

HCl (aq), $\Delta H_{F,\ HCl}{}^{0}$ cap = - 40.023 Kcal/gmole

NaCl (aq), $\Delta H_{F,\ NaCl}{}^{0}$ cap = - 97.302 Kcal/gmole

H_2O (l), $\Delta H_{F,\ H2O}{}^{0}$ cap = - 68.317 Kcal/gmole

Since all the heat of formations data are known therefore the heat of reaction for this particular reaction can be easily found out and it turns out to be -13.360 kilo calories as shown in the above slide. So, you get some value for the heat of neutralization. So, this heat of reaction is actually nothing but the heat of neutralization. And it turns out that this particular number is quite interesting, let us see how? So, we now understand what is heat of neutralization? So, heat of neutralization can be directly measured actually based on calorimetric measurements, how you do that? you can read the texts, I would not go into the details of the experimental procedure. You can always open an experimental chemistry textbook and find out how it is done. So, agreeing to that let us now look into the heat of neutralization of some other acids and base.

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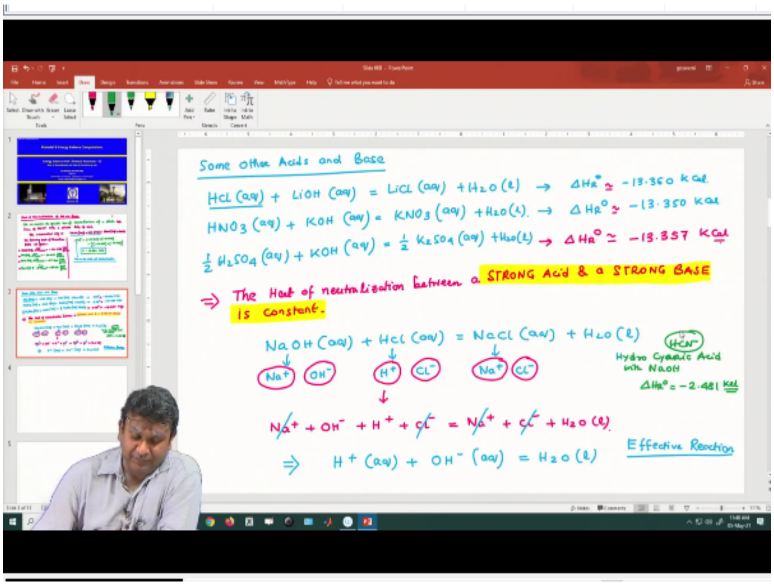

Let us say if we are talking about the neutralization between hydrochloric acid and lithium hydroxide (LiOH), you get LiCl and H_2O. You can have neutralization between nitric acid and potassium hydroxide which leads to KNO_3 and H_2O. You can also have let us say neutralization between sulfuric acid and potassium hydroxide or sodium hydroxide.

And theoretically, you can calculate or in principle based on all the discussion we have had so far you can calculate the heat of neutralization in each case provided you know the heat of formation of each of the constituents. Well there is the crux, it turns out that the heat of reaction for this particular neutralization reaction is -13.36 kilo calorie. This aprox. -13.350 kilo calorie or maybe I will use an approximately equal to sign to be absolutely clear because the data may vary from case to case.

If I provide the heat of formations of these compounds and ask you to find out the heat of neutralization on any one of the reactions. It turns out so here is a take home message about the heat of neutralization. So, what is the take home message? The take home message is the heat of neutralization between a strong acid and a strong base is constant. I guess all of you remember what a strong acid and/or a strong base is. And in this particular case the right question is why? What exactly is happening amongst all different combinations of strong acid and strong bases that their heat of reaction or the heat of neutralization is constant. So, what exactly is happening is actually attributed to the property of strong acids and strong base and what is that property?

Strong acids and strong base in an aqueous solution we all know remain fully dissociated. So, whenever you are taking HCl and NaOH; what we actually have? And a salt of a strong acid and a strong base which is sodium hydroxide in this particular case in an aqueous solution will also remain fully dissociated. So, this NaOH actually remains in the form of Na^+ and

OH^-; HCl remains in the form of H^+ and Cl^-, Nacl remains in the form of Na^+ and Cl^-. So, therefore, when you put this acid and base together, the actual chemical reaction that is happening is $Na^+ + OH^- + H^+ + Cl^- = Na^+ + Cl^- + H_2O$ (l).

All the ions exist in aqueous medium and what we actually understand that that Na^+ and Cl^- cancels out each other at the both side of the equation. The net effective reaction that actually takes place is $H^+ + OH^- = H_2O$ (l) and Na^+ and Cl^- remain dispersed as ions. So, what is the genesis of Na^+? Na^+ comes from NaOH but once it enters the aqueous medium it now is in the form of Na^+.

Though effectively it forms NaCl by reacting with HCl; why does it actually form? Because in the ionic state or within the aqueous medium it forms Na^+ and OH^-; HCl forms H^+ and Cl^-. Now, as the OH^- and H^+ are gone. They are combining to form water as you can see in the effective reaction. So, essentially the 2 charged species that are actually left are Na^+ and Cl^-. And when you remove the water, it forms NaCl.

So, for all the reactions that we have written above if you write them or if you consider the dissociation of the acid, the salt, the base and the effective reaction that actually happens in each of the case of this neutralization is a reaction which is $H^+ + OH^- = H2O$ (l) and therefore in all cases there is now no doubt I guess all of you understand why in all cases the heat of neutralization is same. Does it mean that it is universally valid for all types of acids and bases? The answer to that is 'no'. It is only valid for strong acid and strong base which fully dissociates in an aqueous medium. So, anything we can conclude if you have a weak base, weak acid or whatever so you can have either a weak base and a weak acid or you can have a weak base or a strong acid or whatever. The moment you have one of the components which is weak it does not fully dissociate; it undergoes partial dissociation. And, the moment there is partial dissociation; either the supply of the cation or the anion is restricted and therefore you cannot have a complete reaction of all the H^+ ions and OH^- ions reacting to form H_2O. So, therefore the numerical value of the heat of neutralization for any neutralization reaction which involves at least one weak component either a weak base or a weak acid is going to be numerically lower than 13.36.

It does not really matter whether you have both or just one weak component in the neutralization reaction. Because whichever is going to be the weak one that is going to limit the supply of the cation or anion. And that limits the extent of water molecules that will form. So, essentially as we were talking in the context of a reaction with the partial completion, the moment you have a weak acid or a weak base.

So, it is something like that. So, this is what I wanted to talk about, so one can look into the neutralization reaction of hydrocyanic acid (HCN) for example. this you do not have to remember again let me tell you just for the sake of completeness. The heat of neutralization for neutralization reaction between HCN and NaOH is -2.481 kilo calorie. And now, I guess you all understand what the reason is? Why you have a lower value of the heat of neutralization.

So, it is very interesting that the heat of neutralization between all strong acids and strong bases have exactly the same value. Next what we talk about is another very interesting case that is essentially the thermo neutrality of salt solution.

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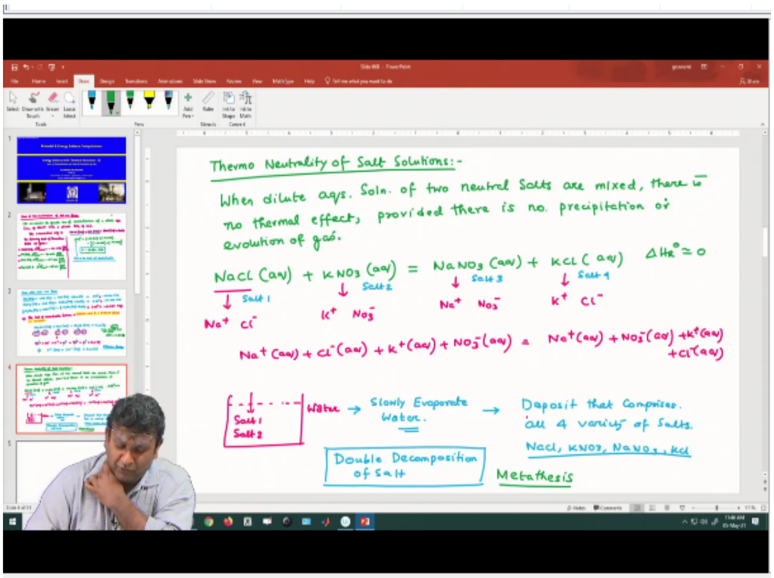

So, it is also something many of you actually know, so essentially when dilute aqueous solution of 2 neutral salts are mixed, there is almost no thermal effect. The reason for that we will understand in a minute's time, provided there is no precipitation or evolution of gas. So, it is something like let's say $NaCl\ (aq) + KNO_3(aq) = NaNO_3(aq) + KCl(aq)$

and the reason for this occurrence is exactly what we discussed in the previous context. And the heat of reaction is nearly equal to 0. So, what type of salt is NaCl? It is a salt of a strong base and a strong acid. So, therefore in an aqueous medium this will remain fully dissociated as Na^+ and Cl^-. And, same with KNO_3, it will remain dissociated as K^+ and NO_3^-. So, if you look into the ionic reaction what happens is

$Na^+\ (aq) + Cl^-\ (aq) + K^+\ (aq) + NO_3^-\ (aq) = Na^+\ (aq) + NO_3^-\ (aq) + K^+\ (aq) + Cl^-\ (aq)$

And you can see there is actually no reaction. So, therefore obviously the heat of reaction gets '0' and if you treat this as an algebraic reaction you cancel the terms from both the sides you actually get an identity 0 = 0. So, this is what is known as 'thermo neutrality' of salt solutions. So, when you mix two salts which are both the salts of strong acid and strong base there is no thermal effect.

Of course, again if you have a salt of a weak base or a weak acid into the system, there will be some small thermal effect, you understand that because there will be some partial dissociation. Now one interesting question if you have a salt mixture like this which is in an aqueous solution and the water is slowly evaporated or you dry the salt. So, you have this in a bath of water, you have a mixture of salt 1 and salt 2.

Now, let's assume here NaCl is salt 1; KNO_3 is salt 2; $NaNO_3$ is salt 3 and KCl is salt 4. So, what do you expect if you slowly evaporate water? You get deposit that comprises all 4 variety of salts; So, you have NaCl, KNO_3, $NaNO_3$ and KCl. And, this phenomenon is called 'Double decomposition of salt' or 'Metasthesis'.

I guess it is obvious and very clear to all of you. So, we have learnt about heat of neutralization between acids and base and we have also learnt about the thermo neutrality of salts. Now what I am going to pick up and if I am unable to finish it in today's this particular class we will continue till the next class. It is a hypothetical but very useful concept which is known as the 'heat of formation of ions'.

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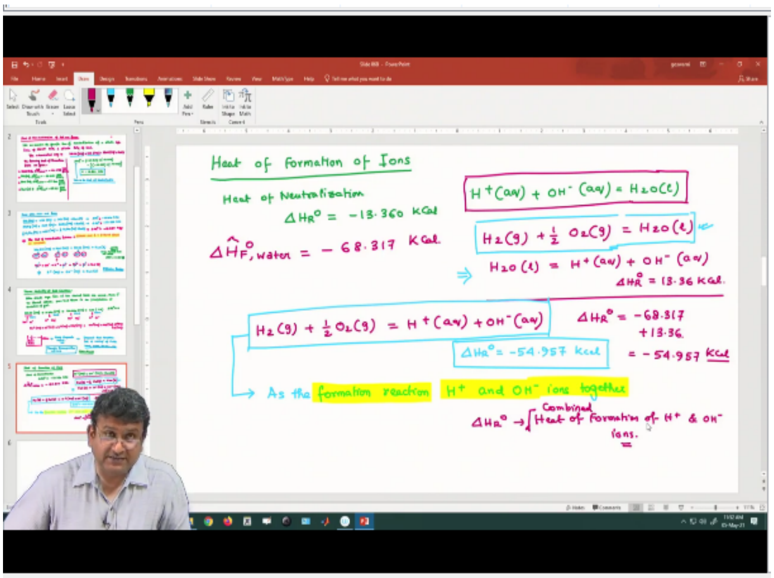

So, let me repeat its a hypothetical concept but it does not really matter because your whole business of heat of reaction, heat of formation actually rests on the fact that all elements have in their natural form have heat of formation is equal to 0. So, there is already lot of assumptions. So, again there are going to be some assumptions when we talk about the heat of formation of ions.

Let us have a look how it goes. So, what we have got is from the previous lesson that the heat of neutralization or in even simpler terms:

the heat of reaction -13.360 kilo calorie for this reaction [$H^+ + OH^- = H_2O$ (l)] and

the heat of reaction of this particular reaction [H_2 (g) +1/2 O_2 (g) = H_2O (l)] is -68.317 kilo calorie.

Now if we just combine these two equations, again Hess law coming into the picture. So, we have H_2 + 1/2 O_2 = H_2O and $H_2O = H^+ + OH^-$ as if it is dissociating. So, this is exactly the situation like the way we calculated the heat of formation of carbon monoxide in the previous class. So, the neutralization reaction we write like this then obviously from Hess law we understand that its heat of reaction is going to be -13.36 kilo calorie.

And if you now join them up following Hess law, you get this particular equation and its heat of reaction turns out to be (-68.317 +13.36). So, it turns out to be -54.957 kilo calorie. So, what exactly is this value? So, we can consider this reaction as the formation reaction of H + and OH - ions together.

Why? because as per this particular reaction these two ions H^+ and OH^- are getting generated from their constituent elements in their standard form. I repeat though we are running out of time I will repeat. See here when we talk about the formation reaction of water, we are essentially talking about generation of water from their constituent elements in their standard form.

Then we applied Hess law essentially over here and we have got this reaction which sort of gives us the feeling that it is the formation reaction as I have written here clearly it is the formation reaction of H^+ and OH^- ions together from their constituents in their standard form. So, here I stop this particular lecture at this point of time and continue in the next class. Here as if we now have the combined value of heat of formation of H^+ and OH^- ions. So, I stop here and finish the remaining part of the heat of formation of ions in the next class, thank you very much.