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Course Title

Environmental Degradation of Materials

Lecture – 38
Broad Subject: Thermodynamics of Oxidation, Ellingham diagram, Oxidation kinetics and laws

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So we have seen that the partial pressure of oxygen which is needed for the formation of oxide would be decided from the free energy change for the process of oxidation, and also we have seen that if the pressure which is the partial pressure of oxygen external oxygen partial pressure in contact with the, and that is basically the partial pressure of oxygen in contact with the metal, if that is greater than external or actual, is greater than partial pressure of oxygen at equilibrium then oxidation would be favored, so oxidation would be possible for that metal but if this is less than this, if this is more than this that case oxidation will not happen because Del GT at that condition Del G PT is positive, positive for this reaction, so if it has to go this way Del G PT should be negative and which is possible in this situation so oxidation would happen, and if the situation is like this where the partial pressure of oxygen which is in contact with the metal is less than the partial pressure of oxygen that is needed to reach equilibrium at that particular temperature T so that case Del G PT, PT means partial pressure and temperature constant that overall pressure and temperature are constant so that condition this forward reaction would not happen rather if we consider the reverse reaction that time Del G PT would be negative, would be this is greater than 0 or positive and here it is negative or less than 0, this is for forward reaction, and this reaction and if we consider this reaction which is backward, backward reaction that case this is negative, so what would happen? The oxide would like to go to this side that means it is a basically dissociation. Again, so that means here dissociation of oxide would happen.

And another important information from this relation which is Del G0 equal to RT Ln PO2 so this relation the partial pressure of oxygen which is found out at a particular temperature T from the free energy value, standard free energy value, that value that means from that you can calculate PO2 equilibrium = Del G0 / RT equal to and that can be exponential this value from that value we can find out what is this pressure and this pressure is also known as dissociation pressure of oxide, dissociation pressure of oxide, so from this concept we can also find out what is the dissociation pressure of oxide at a particular temperature T, at a particular temperature T from if we know this value. Now this Del G0 can be also found out from this relation which is, so this 0, so this relation which is - T Del S0, so this is for a particular temperature T, this is for particular temperature T, this is also for particular temperature T, now from this relation also we can find out what is the free energy change from the standard enthalpy change as well as standard entropy change for that particular process.

Now if we would like to plot this relation shows and, shows basically a sort of linear plot between Del G0 and temperature, okay, or we can relate it to like this RT Ln PO2 and this time instead of putting equilibrium, let me put it as dissociation = Del H0 T - T Del S0, so this relation also tells you sort of reliable if this if we plot Ln RT Ln PO2 with temperature it would show a straight line and the plot would be, and this plot would be a linear plot and if we plot this, if we plot this for example this is temperature and this is RT Ln P O2 dissociation, let's say for a particular oxide M for this particular oxide, if we see this particular oxide we can plot a straight line with respect to temperature where the slope would give the value of Del S0 and the intercept will give the value of Del H0, so this intercept with respect to temperature at a 0 Kelvin it would give the value of Del H0, so we see that the intercept would give the value of Del H0 and the slope would give the value of Del S0, now from this we can see that if there is, and then we can find out a plot with that plot for different oxides we can also have a, we can also plot RT Ln PO2 as a function of temperature for different oxides we can get different slopes for example this one for M1, this one for M2, this one for M3 like this we can have a different slopes and then this plot would be termed as Ellingham diagram, so Ellingham diagram would give you an idea that at different temperature what would be the dissociation pressure of oxygen for the formation of oxide or for the dissociation of oxide. So now let's say if I would like to find out what would be the dissociation pressure of oxygen, dissociation pressure of oxygen for that particular oxide let's say at that case this is my value of, let's say this value is - X and this is temperature is T1, now we can find out the value of dissociation pressure of oxygen so - X = RT1 Ln PO2 dissociation and from this we can find out the PO2 dissociation pressure.

Now in the Ellingham diagram you might find that this is my, if this is my 0 point which is Del G0 = 0 and from that you might find a scale which is running like this and from that this point and this point if you connect, if you connect and extend it like this you will see that there is a small line like this, small line like this, so this line, the straight line connecting this, this, and then extending it wherever this the straight line is connecting or crossing this line which is nothing but the PO2 line that is basically the value of dissociation pressure of oxygen of that oxide at that particular temperature, so this is basically the Ellingham diagram and from that we can find out what could be the tendency of that oxide at that particular temperature with respect to the value of PO2.

Now in the Ellingham diagram you might find that there is a slope change whenever there is a melting phenomena of, melting of metal is taking place and if there is melting of, melting of that oxide then you will find that the slope is again decreasing, and if there is a boiling of metal slope again would increase and if there is a boiling of oxide slope again would decrease, so this is basically melting of oxide and this is boiling of metal, this is again boiling of oxide like that the slope would change that means whenever you have, we have melting phenomena of this metal from solid to metal that time the entropy increases, so that's our slope increases because the slope indicates the change in entropy, and then if this one melts that means the entropy again decreases because the liquid, there is a liquid and now here we have liquid so the entropy overall entropy is decreasing so the slope would decrease and if there is a boiling of this metal so then also the entropy would again increase the slope would increase like that the slope would change as per the melting phase transformation of different of metal as well as oxide. So this gives you the overall thermodynamic picture what would be the possibility of that metal to get oxidized in the presence of oxygen and at the same time it would also be dependent on the partial pressure of oxygen what is there in contact with the metal.

Now once we know this then we have to see that what could be the kinetics of the process, now thermodynamics would give you the idea that whether oxidation would take place or not but we have to also find out whether actually oxidation is taking place or not, so for that we have to study the kinetics of the process, so if we see that, now let us find out what would be the oxidation kinetics, so we see that the kinetic actually decides whether the oxidation would actually happen or not, so by now whenever we consider oxidation kinetics we have to see that what are different laws that would decide the kinetics of that process. Now when we come to the laws of oxidation kinetics there are the simplest law would be one is linear plot, linear law where we can say that D Del W DT equal to a constant, now from this since this is a linear plot that’s why let me put it as KL, now here Del W is basically the weight gained by area, and why you are considering the weight gain per area? Let's say we are considering this cube of that metal which is getting oxidized that means whenever we are seeing the oxidation process actually the six phases are exposed to the oxygen exposed to oxygen and that’s what those surfaces are getting oxidized and on the surface gradually you have oxide growth, similarly this way you can have oxide growth and this way you can have oxide growth or this way you can have oxide growth, so like that six surfaces are getting oxidized and the thickness of the oxide is gradually increasing as well as whenever we are considering the thickness of the oxide that is gradually increasing we are assuming that the oxide layer is sticking to the surface, so that means if we increase the area overall weight would increase but if we divide it by area for a particular metal at a particular temperature if we consider that oxidation process that would remain same, because if that oxidation process is following the linear law at a particular temperature T it should have a constant relation, the change in or weight should be same changing weight that time per unit time would be same even if you start from T, T equal to one minute or T equal to ten minutes, so that is the linear law and we see that the area if we divide it by area that would give you the actual picture of oxidation process or the rate at which oxide is growing.

Now so this is from this we can also say that this Del W would be equal to KLT + C, so here KL is nothing but the rate constant, rate constant for the oxidation at that temperature T where the oxidation is taking place, C is another constant which is coming due to the integration process and T is time. Now we also see that this Del W is nothing but the weight gain per unit area in order to depict the oxidation process properly since if we consider only the weight then it will not give you the actual picture because weight if we consider a larger area or smaller area let’s say this small area is considered, that time weight gain would be, weight would be more, weight would be less compared to this but actually the weight gain per unit area if this is also taking place at temperature T would be same if this is following the linear law at that particular temperature. And same thing happen in case of other cases other laws, for example this is linear law and this can happen, the example of linear law is basically sodium potassium where we see that the linear layer law is followed and that case we generally see that the R value which is the pilling bedworth ratio is less than 1. Now that time we have also seen that if R is less than 1 that means the volume of metal oxide is not sufficient to cover up the entire surface so the metal surface is exposed to the oxygen all the time and so the oxygen can oxidize the metal in a linear fashion.

Now in this case also, in the linear rate law would be possible if the metal oxide is not a, metal oxide is not forming sufficiently on the metal surface which is decided by R and this can also be possible in case of niobium, niobium this is possible and that time we see that R is very high, very, very high and it is close to around 2.5 and which tells you that if the R value is very large that means the volume of oxide is very, very high compared to the metal which is volume of metal which is getting oxidized, so there could be a possibility of compressive stress that is generated on the metal surface so metals generate on the oxide layer and that oxide layer might get cracked and this cracking would allow the oxygen to get into the, get through the metal oxide and come in contact with the metal surface, so that means linear law is possible and we have seen the example where linear law can be possible. And now we see that R less than 1 and R is much higher than 1 those cases we have the problem of having good protection due to the oxide formation, but if R is equal to close to 1 or little higher than 1 it should not be less than 1 or little higher than 1 that time we would see that the oxidation resistance would be relatively good, for example aluminum where the R value is around 1.28 and that's what the metal oxide would be protective throughout the metal surface and it will form throughout the metal surface uniformly and that’s what aluminum gives you very good oxidation resistance in normal condition, in atmospheric condition.

Now let us find out what are the other laws then we have parabolic law. In this process we see that Del W = KP T + C and this case the change in weight per unit area of that oxide or the square of that change in weight of that oxide layer would be proportional to time, and that time it is called parabolic law and from this we would find that the oxidation rate is gradually decreasing as the time is increasing. Now if we would like to plot the with time and Del W so that case if it is linear that time from zero time if we consider it would be linear like this that means the linear law is followed but if it is parabolic law then this will be like this, so this is linear and this is parabolic, fine, so that means with the parabolic law we see the gradual decrease in the rate of oxidation as the weight gain is increasing or other way around if you can you can see from this that as the oxidation is progressing you see that there is a gradual increase in the thickness of oxide layer, so this is my thickness of the oxide layer so another way if we consider this metal so you have the thickness this is my MO oxide layer, so gradually this is the oxide layer thickness, gradually the thickness is increasing, so if we increase the thickness, if the thickness of the oxide is increasing that means the weight gain is also increasing.

Now from this point if the rate of oxidation is taking place we can see that weight gain per unit area as the time is passing per unit time, so weight gain per unit, this is my weight gain per unit area so as the time is passing or the time increases that time Del W by T would be decreasing, so that means initially it would be very fast rate of weight gain and later on the rate of weight gain would decrease. Now this is also happening at a particular temperature T, now if we see that the temperature this temperature let’s say at T1 is happening the oxidation, parabolic oxidation is happening at T1, this is let’s say T1, and then second case if I would like to do it at a different temperature which is T2, and if T2 is less than T1 so your rate of weight gain would be less compared to the oxidation, oxidation that is happening at T1 so this is at T2.

Now secondly if we consider T3, this is T3, so this is also would be below and then if we consider another temperature which is T4, if we consider this is T4, then we can also find out from this simple experiment, we can also find out what is the value of activation energy, how would we do that? Let’s say I have one furnace, I have one furnace which is the vertical furnace let’s say this is my vertical furnace and these are my coils which basically heat of the furnace, now you have a weighing machine, this is weighing machine WM or and here we have the bottom weighing facility and from that I'll put sample of metal, this is my metal sample in the constant temperature zone of the furnace and that time once, and the furnace temperature is taken to let’s say temperature T1 and that means if this is my constant temperature zone that point that there my temperature is maintained at T1 and that we can measure with a thermocouple, with the thermocouple we can measure and then once we put the sample we will tire this digital, let’s say if this weighed machine is, we can maintain, we can start from zero weight gain, so if we plot zero weight gain from the zero weight gain and as a function of time at temperature T1 let’s say this is 00 and then let’s say at 10 minutes time I have weight gain at this point and then I can have weight gain at this point after 20 minutes like that, like that if we plot all those weight gain and then connect them like this I could get a plot like this, and which is the plot at T1. Now we change the T1 temperature to T2 we can get another plot of weight gain as a function of temperature even if we change it to T3 we can again get a plot like this and like that we have all those four plots.

Now from this what is my rate constant? This is my rate constant, and this P means for the parabolic rate law, now if we once we have this data then we can calculate what is the activation energy for that thermally activated oxidation process, now from this graph we can also plot one more graph which is time as a function of Del W square which is the weight gain per unit area square, and if it is following a parabolic rate law then it should give you a straight line for a particular temperature T1, second case it would give a straight line like that. Now once we have all the straight lines that means I can have, I can calculate what is the value of KP at that temperature, so this is KP T1 which is basically the slope of the line this slope would give you the KP at temperature T1, now like that we can find out other rate constants at other temperatures so we see that at different temperatures we can find out the KP value or the parabolic rate constant for the oxidation process if we plot Del W square as a function of temperature T, now if we plot this then we get all the four KP values and then four KP values can enable to find out what is the rate constant, what is the activation energy for the oxidation process. Now once we get all the KP values we can plot a table like thi,s this is for example temperature and this is time, time in this axis, temperature in this axis, so we can find out T1, T2, T3, T4 and then t4 and then so at different times this is time T1, T2, T3, T4, T5, T6 and finally we can have a value of KP, this table if we make then let’s say the half part this is del W and the below half if we plot Del W square like this if we continue like this and then we can also find out what is the value of KP1, KP let’s say we can plot it as 1 which is at T1, KP2, KP3, KP4, so all the values of KP at different temperatures and since it is thermally activated process we can relate KP via Arrhenius equation exponential – Q by RT, if either where Q is the activation energy for the oxidation process.

Now if we plot KP, Ln KP now if we take logarithm, log of both the ends Ln KP would be equal to Ln K0 - Q / RT, now if we plot Ln KP as a function of 1/T we will see that this relation gives a linear plot, now if we plot Ln KP as a function of 1/T it will give you linear plot let us connect it so these are all the points after doing linear fitting we see that the slope would give you the value of – Q/R, so we find out the slope and equate it to Q/R this would be equal to slope and from that putting the value of R as 8.314 joule, 8.314 joule per Kelvin per mole which is R we can get the value of Q in the form of joule per mole so Q, so from this process we can find out the value of Q and this process is actually called isothermal technique, this entire technique is called isothermal technique because we are carrying out oxidation at a particular temperature that means isothermally we are seeing what is the weight gain of that metal when it is exposed to the metal, was exposed to the oxygen environment at different time intervals, so this is a parabolic oxidation law which has been put forward by a famous scientist called Wagner.

Now we can also have a simplistic proof of this parabolic law let us also see what is the simplistic proof of that oxidation law, simplicity proof of parabolic oxidation law, so we can also have a simplistic proof of this parabolic oxidation law which has been put forward by famous scientist called C Wagner and let us see that what is the synchronistic proof. Now in case of oxidation let's say this metal is getting oxidized and let's say that this surface only is getting oxidized, this surface is getting oxidized other surfaces are coated somehow with some, let's say this entire surface is outside the oxygen environment only this surface is exposed to the oxygen environment. Now we have gradually the oxidation happening on this surface and the thickness is gradually increasing, thickness is gradually increasing, this is my thickness X, now if we assume that this increase in thickness is, if we assume that increase in thickness is proportional to the flux of the species that is either coming out or going in, and the flux of species is basically means, fluxes species mean which is J it means that either outward diffusion of metal ion or inward diffusion of oxygen and ion or combination of this two this is basically the flux which is basically the mass flow rate per unit area per unit time, now that could be proportional to the increase in thickness or in other way around we can also see that if we consider this graph that as we increase the time for oxidation we see the rate of weight gain is decreasing, so that means the rate of weight gain is proportional to inverse of thickness Y because as you increase the time your thickness is increasing, as the thickness, as you increase the time the rate of oxidation is decreasing or the rate of weight gain is decreasing or the rate at which thickness increases that would also decrease so it means that rate of thickness increase would decrease so that means if we consider rate of weight gain is proportional to 1/X then the rate of thickness increase also would be proportional to 1/X.

Now rate of thickness increase means DX DT would be equal to K or some constant by X and if we integrate this then we would get X square = 2KT + C so that means we see that it is almost similar form like this and where Del W is actually proportional to the thickness of the oxide layer, so this parabolic oxidation can be proved through this simplistic approach and there are many assumptions here one assumption is we are assuming that the mass flow rate is steady state, that means the steady state diffusion of either metal ion or oxygen ion is taking place through the oxide layer so we see that this is a simplistic approach to proof parabolic oxidation law, and where we can find this parabolic oxidation law? For example in case of iron, copper, cobalt, all those cases at high temperature we always find that oxidation law is governed by the parabolic rate law, so this is a parabolic rate law, we can also find the oxidation law obeying logarithmic fashion or logarithmic expression, so we can also have logarithmic oxidation law where Del W which is the weight gain per unit area would be equal to K log, K log means the rate constant when the process is logarithmic oxidation law, when the oxidation is following a logarithmic law, so that time this would be equal to K log which is basically the rate constant for the oxidation process T + A, so this is A constant and this is logarithmic rate constant. Now again we can also have inverse logarithmic law, inverse logarithmic law it says that 1/ Del W would be equal to K log inverse log T plus some constant let's say B, so again this is my rate constant for the oxidation process when it is falling inverse logarithmic law, and the example is for example aluminum, copper at ambient temperature, ambient temperature they would follow this logarithmic oxidation law, and of course ambient temperature or little higher than ambient temperature, it will higher than a main temperature.

Now we can also have one more law that is called cubic law, cubic oxidation law in some cases for example in case of zirconium this cubic oxidation law is followed where it says that Del W which is a weight gain per unit area cube would be equal to K cubic T + some constant let say D, so this is another constant and this is nothing but the rate constant when the law is cubic in nature or the oxidation law is cubic and this process in this case it can this cubic law can happen or can be followed by a particular metal during oxidation when two processes are simultaneously happening, one is diffusion controlled growth of oxide layer and second thing is simultaneous dissolution of oxygen in metal, when these two things are combinedly happening, two things are combinedly taking place then we can have a cubic rate law. Now we have seen the plot of cubic plot of linear as well as parabolic we can also see the plot of cubic and logarithmic rate law, so this is T this is either Del W or Del W, okay so this plot is Y axis is Del W this is T we see that the linear plot is like this parabolic let me put parabolic like this, this is parabolic, then we can have a cube with logarithmic, logarithmic is, logarithmic and then we can also have, just a minute let me plot it properly, this is logarithmic, this is linear, this is parabolic, and there could be cubic one, so cubic one could be like this, so we can have cubic, this is cubic, so we can have a different plots for different laws.

Now in case of metals and alloys if we have parabolic or logarithmic or cubic we find that those are very good for high temperature application, why? Because for high temperature application if that oxide is sticking to the surface we see that the rate of oxidation is decreasing as we, as we see that the time is increasing. Now in case of aluminum one particular example is aluminum in case of aluminum if we consider the temperature or which is close to the ambient temperature, ambient temperature that time we see that the aluminum has got a very good oxidation resistance, why? Because that time the rate law that is being followed by aluminum is for the oxidation process is logarithmic and in case of logarithmic we see that the increase in thickness or increase in weight as we cross this time, this time if you go to the right side is almost constant there is no change, so that means the oxidation is almost are stopped, okay, so the oxidation stopping and after few days this will stop in the ambient condition so it would have a very good oxidation resistance, so since it is following logarithmic rate law, so this is about the oxidation kinetics there are mainly five kinetics which have been discussed here one is linear then parabolic which is very common, then we have logarithmic or even inverse logarithmic is possible, then we have cubic rate law.

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