Indian Institute of Science Education and Research, Pune
National Programme on Technology on Technology Enhanced Learning
Medicinal Chemistry
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Tutorial – 02
Basic Concepts of Thermodynamics and Kinetics

Welcome to the tutorial session so in today's tutorial session we will look at two very important aspects of chemistry which is thermodynamics and kinetics so again this are some concepts that have been done in the past in your previous classes but we will go over some of this things in detail in some details so that we can recap some of the important concepts. So thermodynamics as we know involves basically in equilibrium between let's say A and B.

So you have delta G on one co-ordinate and reaction co-ordinate is on the x-axis right. So this is a fundamental aspect of equilibrium and kinetics deals with basically the height of this barrier which is delta G double dagger or activation energy so with this broad sort of picture let's look at some specific examples so the first example that will look at.

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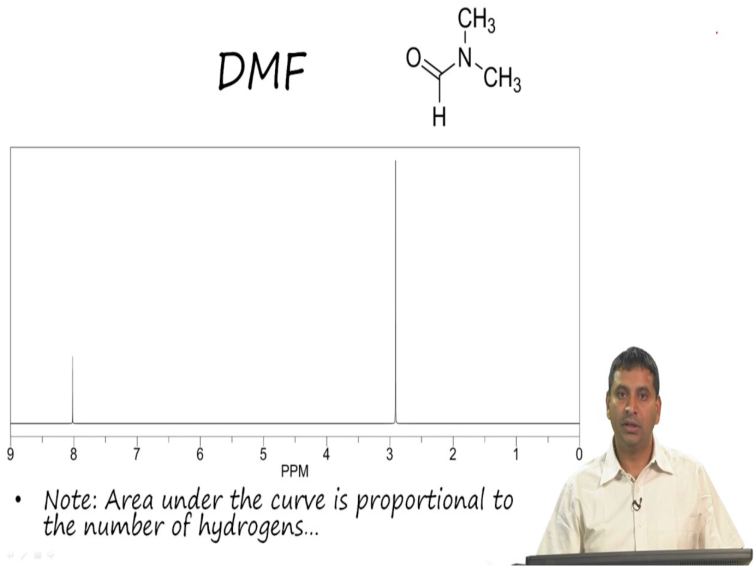
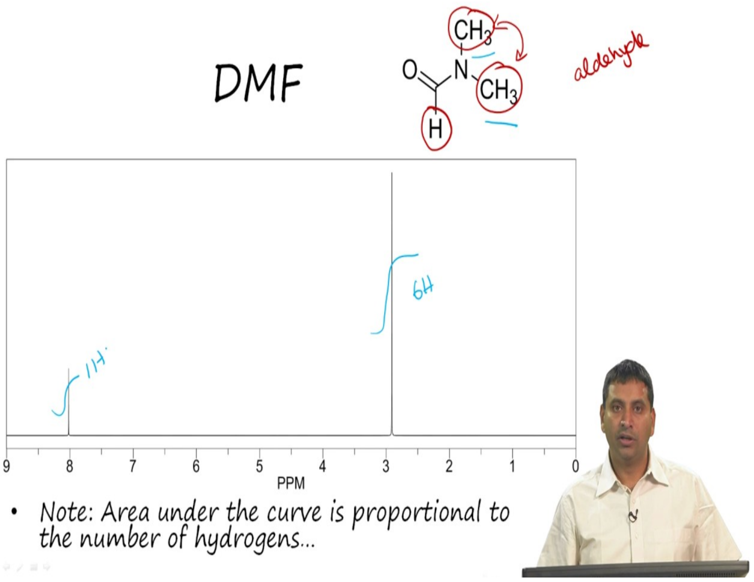


- Note: Area under the curve is proportional to the number of hydrogens...



- Note: Area under the curve is proportional to the number of hydrogens...

Is dimethylformamide so dimethylformamide whose structure is shown here has seven hydrogens as shown here and one of the hydrogen belongs to an aldehyde or a carbonyl and the other hydrogen are attached to two methyl groups which is again in turn attached to a nitrogen.

So fundamentally the chemical properties or the properties of this hydrogens would be different that is the six hydrogens would be identical and this hydrogen would be different so if you want to measure an NMR spectrum an NMR spectrum of a proton which is basically hydrogen which is again a concept that you guys have looked at previously. Theoretically, since this hydrogens are identical what you would expect is that you will see one signal which is shown here of 6 hydrogen each so if you integrate this you get 6 hydrogens and if integrate this you get one hydrogen so this is what I would expect as a theoretical NMR spectrum so as you already know from basic NMR spectroscopy that area under the curve is proportional to the number of hydrogens so it's very simple situation right.

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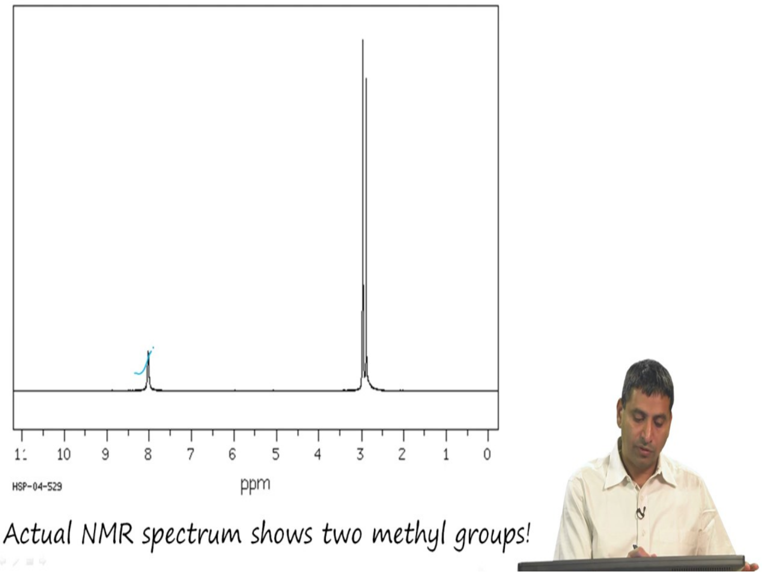
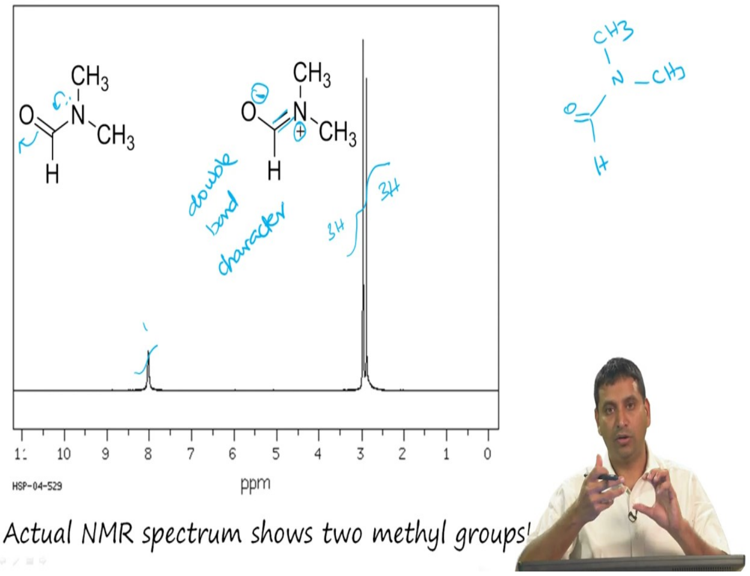


Actual NMR spectrum shows two methyl groups!



Actual NMR spectrum shows two methyl groups!

However in practice if you record this NMR spectrum you get a single peak which integrates to 1 but actually you get 2 peaks here which integrates to 3 hydrogens each so just to recap the structure that we are dealing with here is NCH3CH3 C double bond OH so the two methyl groups which we were thinking as identical to be identical are actually showing up as to separate peaks in the NMR spectrum.

So this suggests that the two methyl groups are actually not the same. So how do we understand this so what we know from the prior lectures on amide is that the lone pair on the nitrogen can delocalise into the carbonyl so once this happens it generates a form of Nitrogen where there is a positive charge on nitrogen there is a double bond right and O minus so together what it does is that it makes a for a resonance hybrid.

So once you have this molecule they could be restricted rotation around the carbon nitrogen bond there is substantial double bond character of the carbon nitrogen bond which contributes to restricted rotation right.

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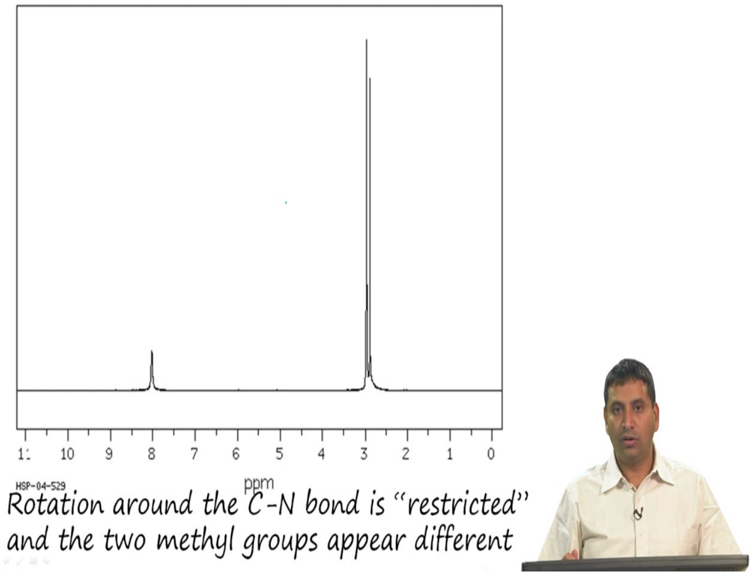
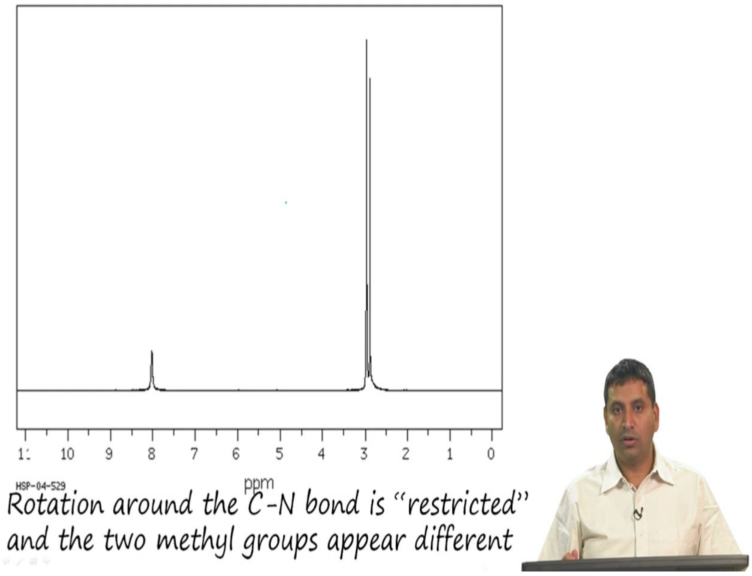


Rotation around the C-N bond is “restricted” and the two methyl groups appear different



Rotation around the C-N bond is “restricted” and the two methyl groups appear different

So therefore with this restricted rotation the two methyl groups actually appear different because you have this carbon this hydrogen here which is right next to to the O minus where as this hydrogen here is next to a aldehydic hydrogen so the chemical environment around and the magnetic environment around the hydrogen is actually different and so you start seeing those differences in the NMR spectrum.

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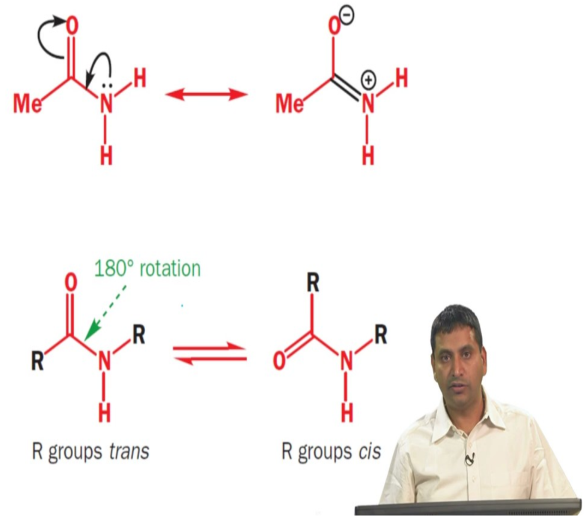

But in order to understand this, let's look at some stereochemical aspects so if you have this lone pair instead of going here and instead of looking at dimethylformamide, we are going to look at another amide just for a basic understanding. So now in this case you have NH and NH and these 2 hydrogens are again going to experience a very different chemical environment.

But when you have a functional group R attached to add you actually have two isomers which are trans and sis and they are going to be in equilibrium with one another.

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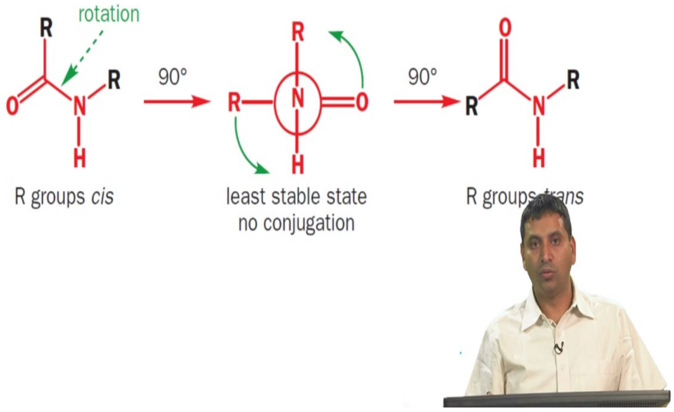

So if I have to look through one of these nitrogen carbon bonds then it would look in the following way. So if you draw the Newman projection so then the R is on top that is this the hydrogen is on the bottom and this carbonyl is going to be at 90 degrees from the RNH plane and this R group is also going to be 90° because it is it is over here right. So now, if I rotate this and if you go to the other confirmer or other isomer you will get the trans group.

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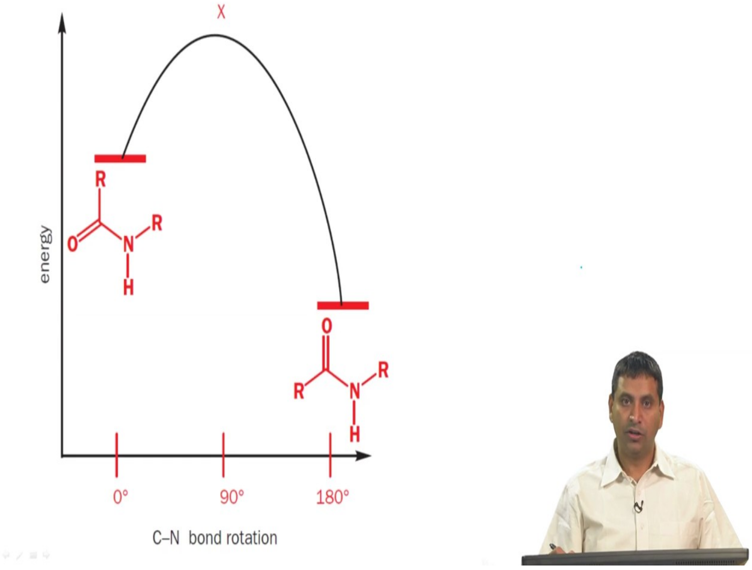

So if I have to do draw an equilibrium the what we would draw out is the structure such as this and this here on top must be a high energy configuration or high energy conformation there is going to be very little overlap of the orbitals.

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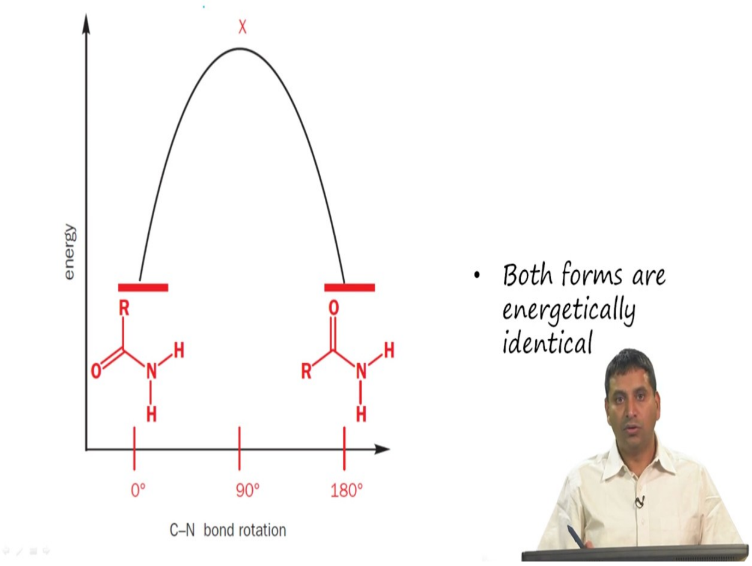

- Both forms are energetically identical

So if we start with the 2 hydrogens instead we can imagine that both the forms are going to energetically identical but there would still be a form wherein there is going to be least conjugation between the two groups.

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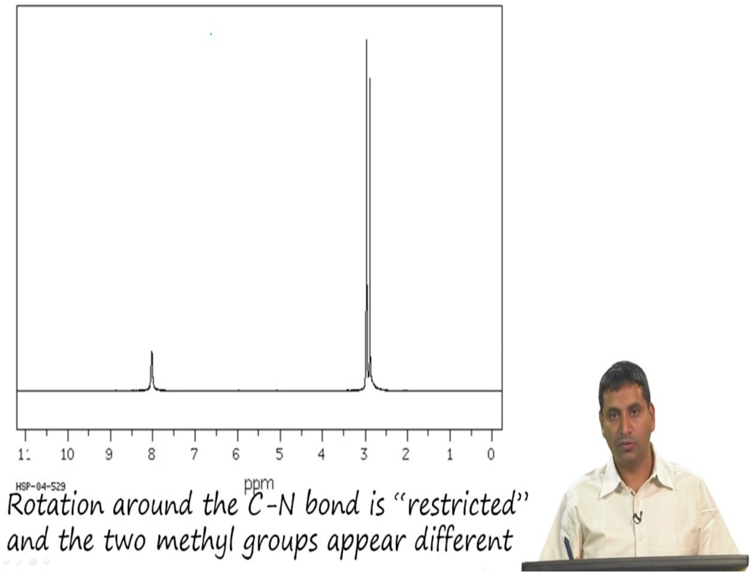
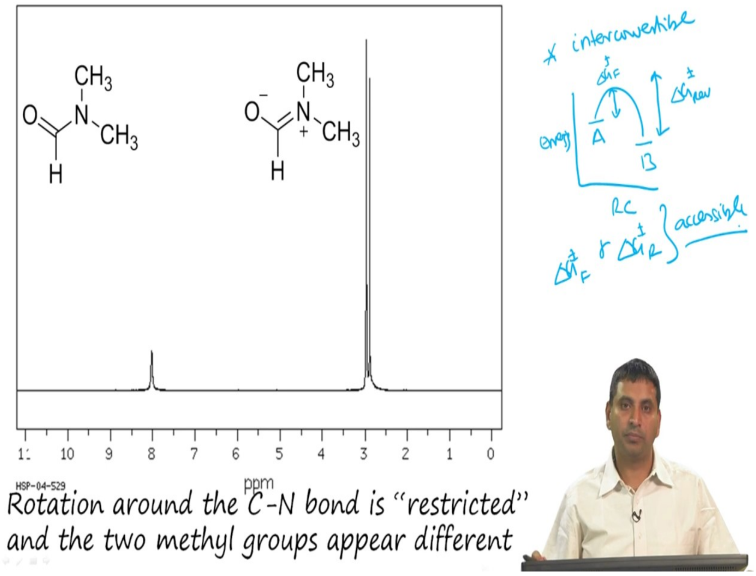


Rotation around the C-N bond is "restricted" and the two methyl groups appear different



Rotation around the C-N bond is "restricted" and the two methyl groups appear different

So therefore rotation of the carbon hydrogen bond can be understood to be restricted and therefore there are two methyl groups that appear and they are appearing to be different this is an example of how we can understand equilibria. So equilibria means that they are interconvertible ok which means that the barrier of A going to B is not so high that it is not accessible right.

So this barrier that is the forward barrier and the reverse barrier so this is delta G double dagger forward and this is delta G double dagger reverse so delta G double dagger forward and delta G double dagger reverse are both accessible okay. If they are not if one of them is not accessible at room temperature then the population would move towards that particular confirmation and it would not revert.

So when we observe an equilibrium it is quite likely or it is important for us to understand that both the barriers that is a forward barrier as well as the reverse barrier are both accessible and then the equilibrium constant would be dependent on the stability of the particular species that is involved in equilibrium.

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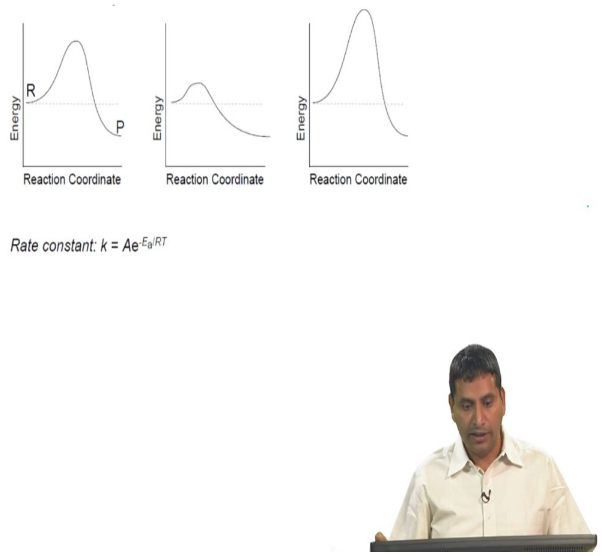

Rate constant: $k = Ae^{-E_a/RT}$

Now if you look at kinetics we can draw an energy profile which we have seen in several examples previously. So you have a reactant going to product and you can also have a situation where the reactant and product are situated like this and you have very small barrier that is separating the 2 we can also have a situation where the reactant and product have a very high energy gap between the two.

So these heights of these barriers as we have seen here will determine what the rate of the reaction is or in another words the rate of the reaction is dependent on the heights of the barrier and this is defined by the Arrhenius equation which is shown here which is K is A into E power minus E_a by RT. E_a is defined as activation energy or the energy required for the reactant to cross the barrier to give you the product so there is a situation here on top where in there is a very high energy species that is produced which we call as transition state and then it collapses to give you the product.

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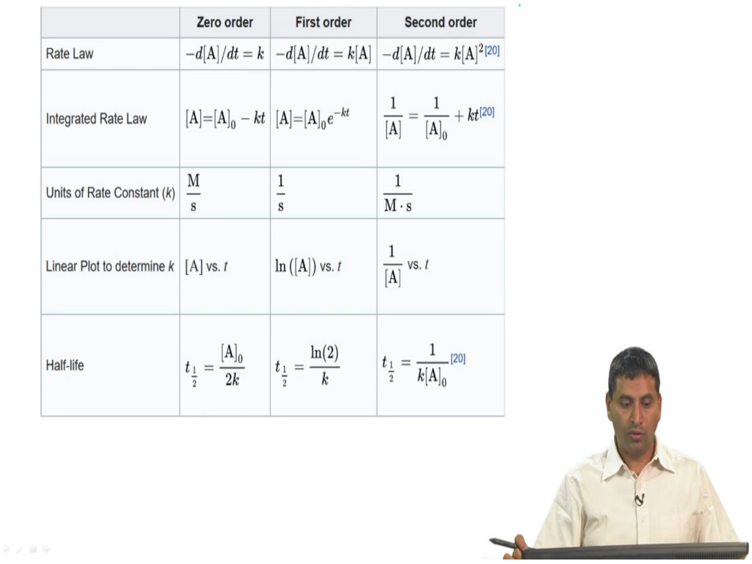

	Zero order	First order	Second order
Rate Law	$-d[\mathrm{A}]/dt = k$	$-d[\mathrm{A}]/dt = k[\mathrm{A}]$	$-d[\mathrm{A}]/dt = k[\mathrm{A}]^2$[20]
Integrated Rate Law	$[\mathrm{A}]=[\mathrm{A}]_0 - kt$	$[\mathrm{A}]=[\mathrm{A}]_0 e^{-kt}$	$\frac{1}{[\mathrm{A}]} = \frac{1}{[\mathrm{A}]_0} + kt$[20]
Units of Rate Constant (*k*)	$\frac{\mathrm{M}}{\mathrm{s}}$	$\frac{1}{\mathrm{s}}$	$\frac{1}{\mathrm{M} \cdot \mathrm{s}}$
Linear Plot to determine *k*	$[\mathrm{A}]$ vs. t	$\ln([\mathrm{A}])$ vs. t	$\frac{1}{[\mathrm{A}]}$ vs. t
Half-life	$t_{\frac{1}{2}} = \frac{[\mathrm{A}]_0}{2k}$	$t_{\frac{1}{2}} = \frac{\ln(2)}{k}$	$t_{\frac{1}{2}} = \frac{1}{k[\mathrm{A}]_0}$[20]

So now here is a table that shows you the various parameters and will look at this in some detail now.