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Chemistry 1
Introduction to Quantum Chemistry and Molecular Spectroscopy

Lecture 31
Beer – Lambert Law

Prof. Mangala Sunder Krishnan,
Department of Chemistry,
Indian Institute of Technology Madras

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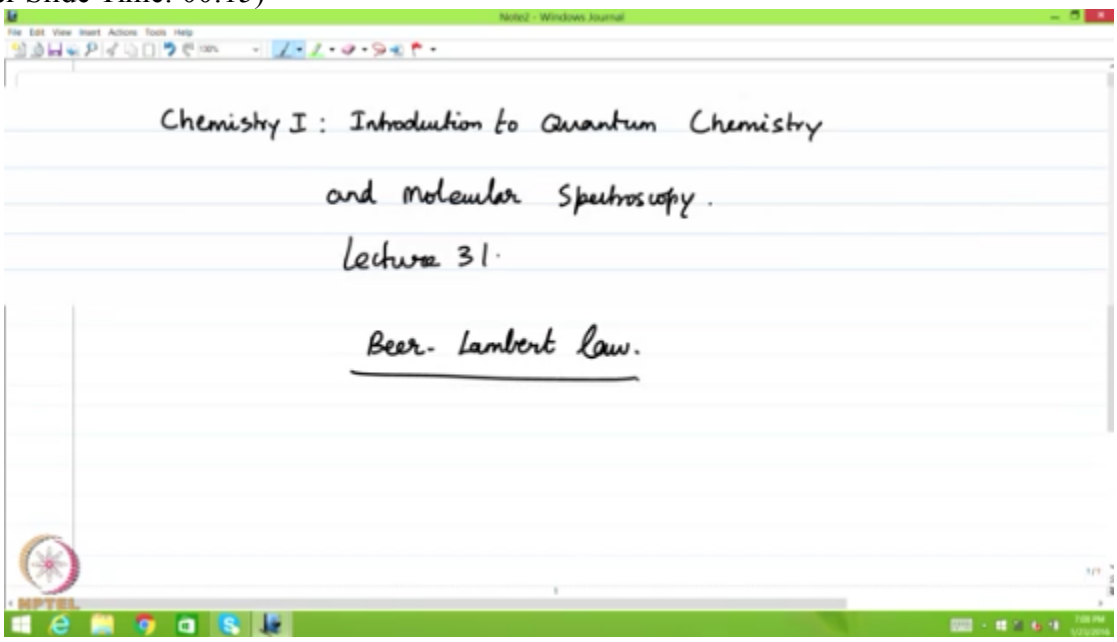

Welcome back to the lecture on spectroscopy, the introduction to molecular spectroscopy and chemistry 2. This is a very short lecture on an important quantitative law lowness of Beer Lambert law which is used to study the fluorescence properties and also determined concentrations of compounds which are show fluorescence character districts in samples, therefore it's a quantitative law used to measure concentrations of species through fluorescence basically absorption of light, absorption of visible light.

And I shall just write down the law in a simple form,
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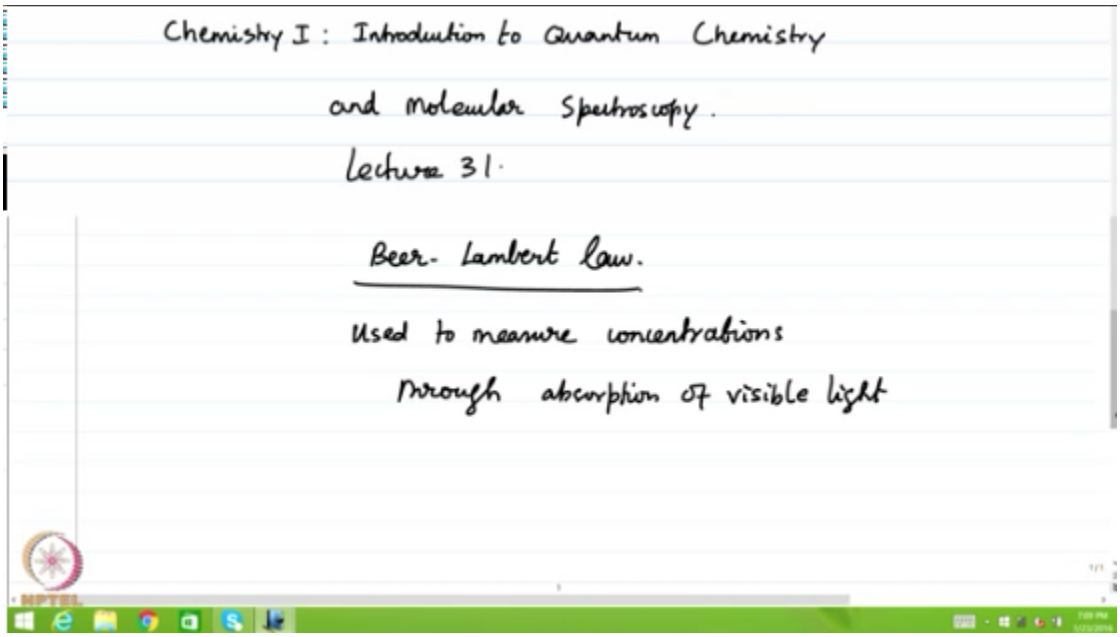

we'll say more of it when we study electronic spectroscopy with some applications and properties of molecules and so on, in a very simple and elementary form the Beer Lambert law goes like this. Suppose we have light falling on a sample tube containing the sample, and let the concentration be C moles per liter, and let the length of the spectroscopic cell the photometrically spectrophotometer the cell but which we use to measure the absorption and also take the spectrum,

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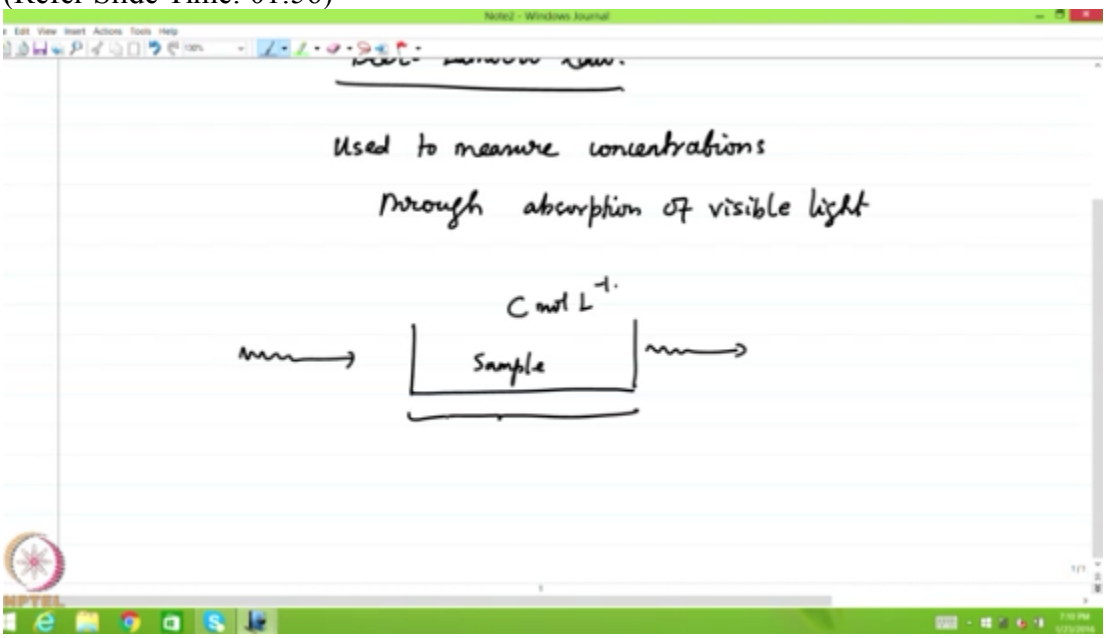

this is the cell of length say L centimeters, so usually 1 centimeter or even less than that.

And if light with a certain initial intensity I naught visible light falls on the sample and light with the intensity IF is emitted obviously IF is less than I naught, okay, that means that the sample has absorb some light

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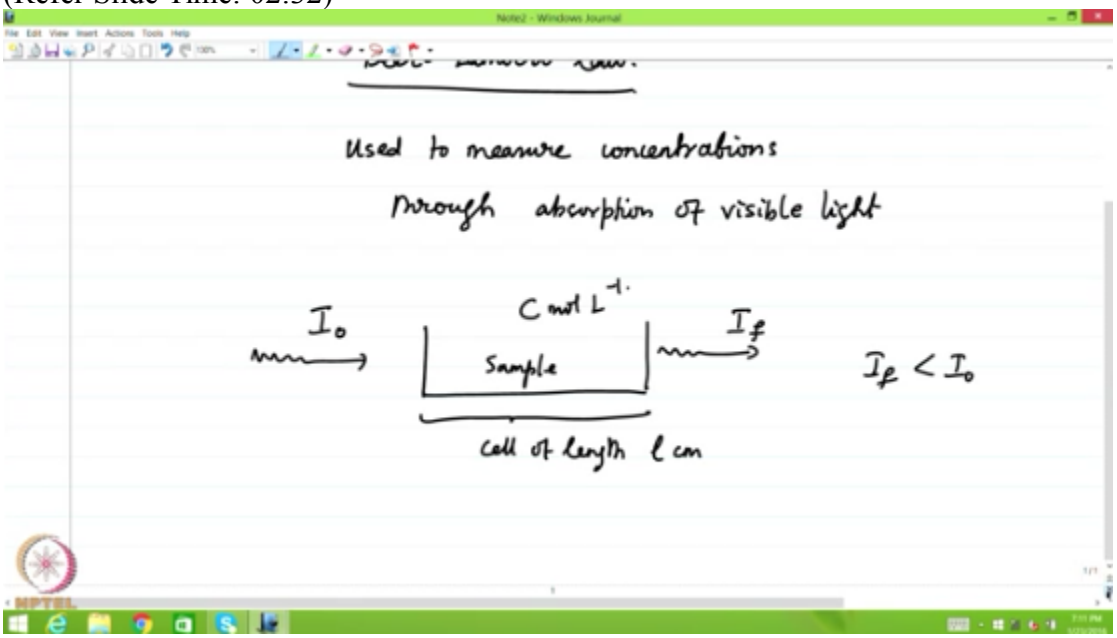

and this phenomenon for certain small concentrations and reasonably low intensities of light absorptions, small concentrations C like millimoles per liter kind of concentrations or even less, okay, typical example.

And then for light of moderate intensity, satisfies the law that log I naught/IF = a constant times the concentration of the substance and there is the length of the cell and this constant is called the molar extinction coefficient or molar absorption coefficient, and this is called absorbance,

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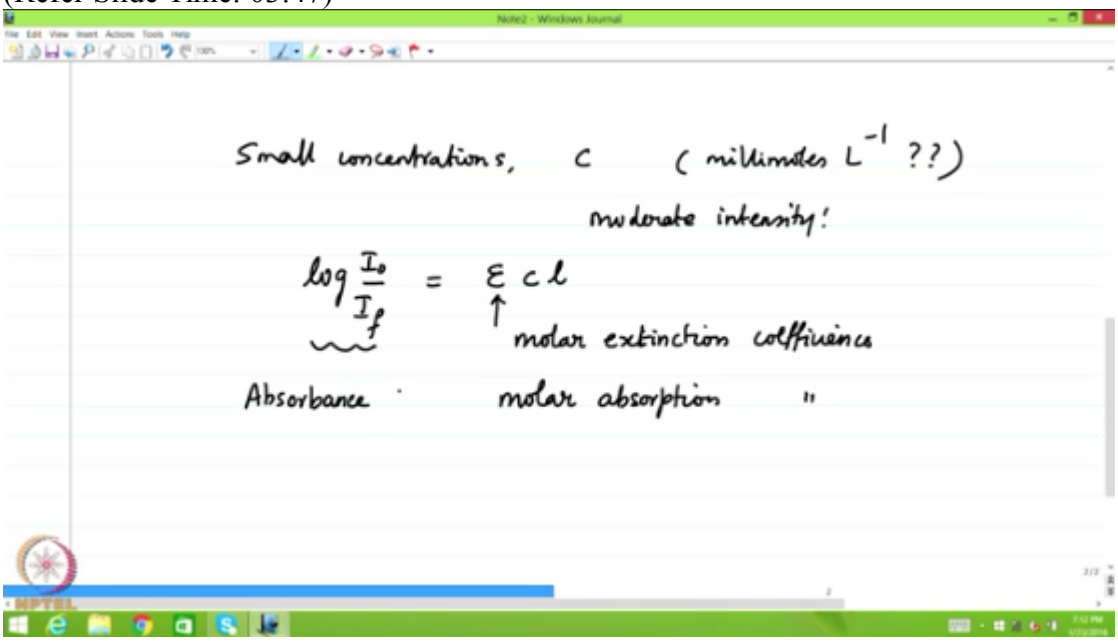

you can also write this in the form of transmitted radiation, and so this can be written in the form of light that is, this is the light that is transmitted therefore this ratio the logarithm of I naught/IF

gives a constant associated with each system, each chemical species and one important is that this epsilon is actually a function of the wavelength of light, lambda B the wavelength.

So typically if a species absorbs light and so function of the lambda and you write the epsilon, as a function of epsilon lambda you choose that value of epsilon for which the absorption is the maximum, that is, that value of the light, lambda, so you choose that lambda and perform the 6 pyramid,
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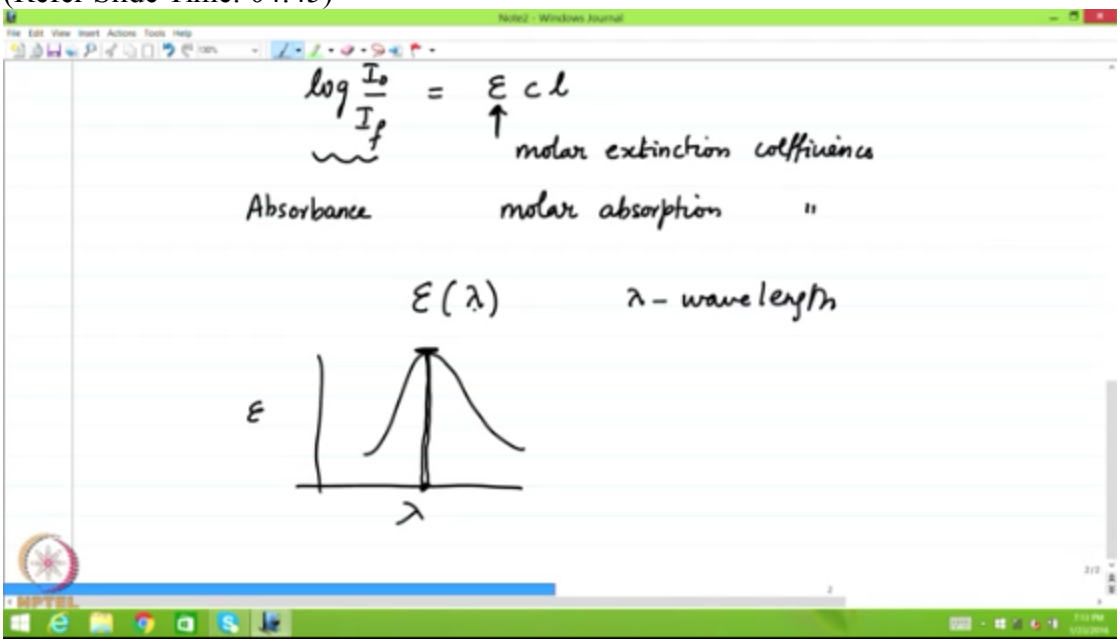

and these are tabulated in all electronics spectra textbooks and also in analytical chemistry textbooks.

Now how do we get this law? Log I naught/IF is equal to this constant epsilon times concentration and length, okay, so very simple argument that if you have a cell of length L consider a small, and extremely small what is known infinite simile small DL, because at that level you can imagine that most things will be linear,
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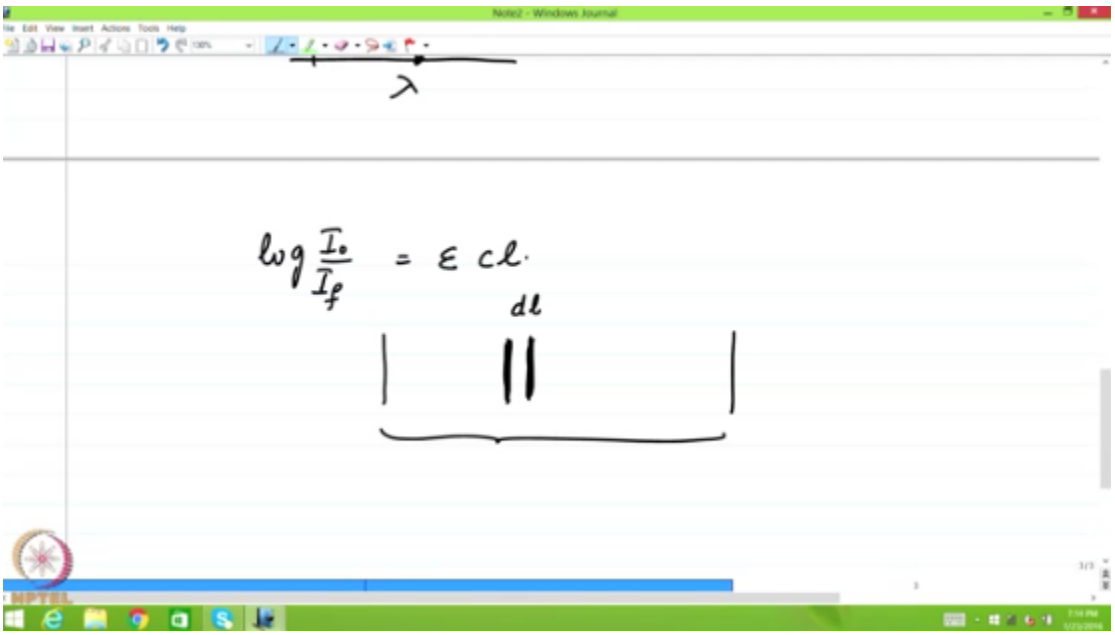

if there is an absorption that absorption will be roughly proportional to the concentration in that region and the absorption, I mean if there is more species obviously that will be more absorption that linear law can be obtained from starting with this kind of infinite decimals, therefore if you do that the DL which is also a very small length tells you that the absorption is dependent on DL itself, if DL is slightly more, more absorption and so on.

So what you do is you take the differential if I is the intensity at this point and I – DI is the intensity of light that is emitted passing through DL then you can write the –DI as roughly proportional to the concentration and proportional to the DL, and obviously also proportional to the intensity of light that all format.

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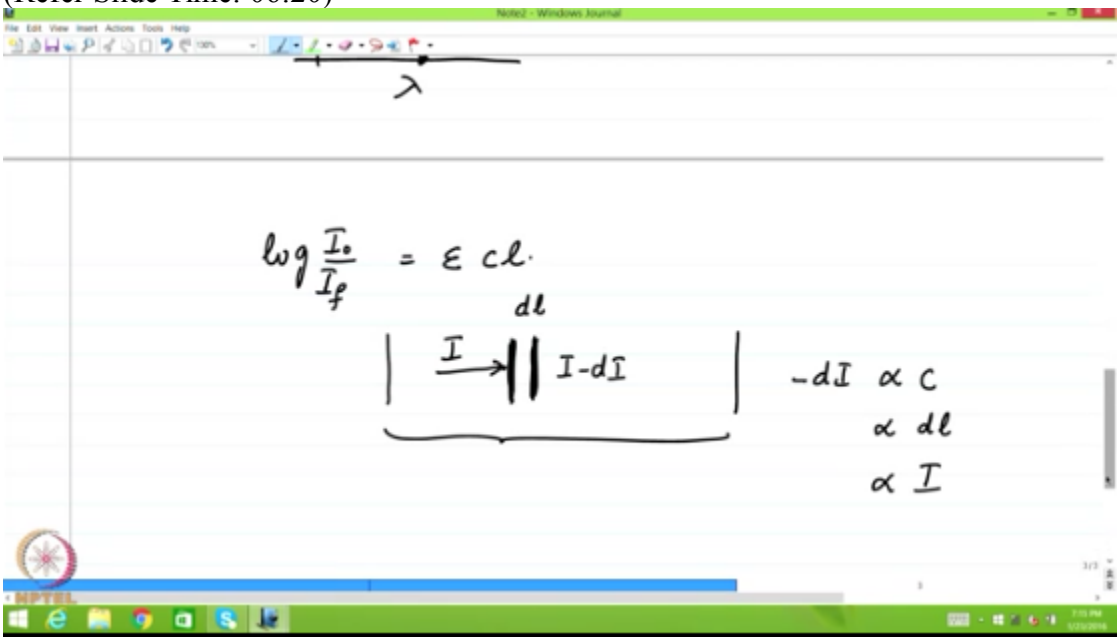

Therefore if you write this the linear law simply gives you –DI is some constant which I'll write as say kappa, okay some K times C times DL times I and so you can write –DI/I is a kappa, a constant C DL, and now you extend this argument that this is what happens throughout and therefore if you start with I naught here as the initial intensity and if you end up with IF as the intensity of light emitted at the other side of the cell

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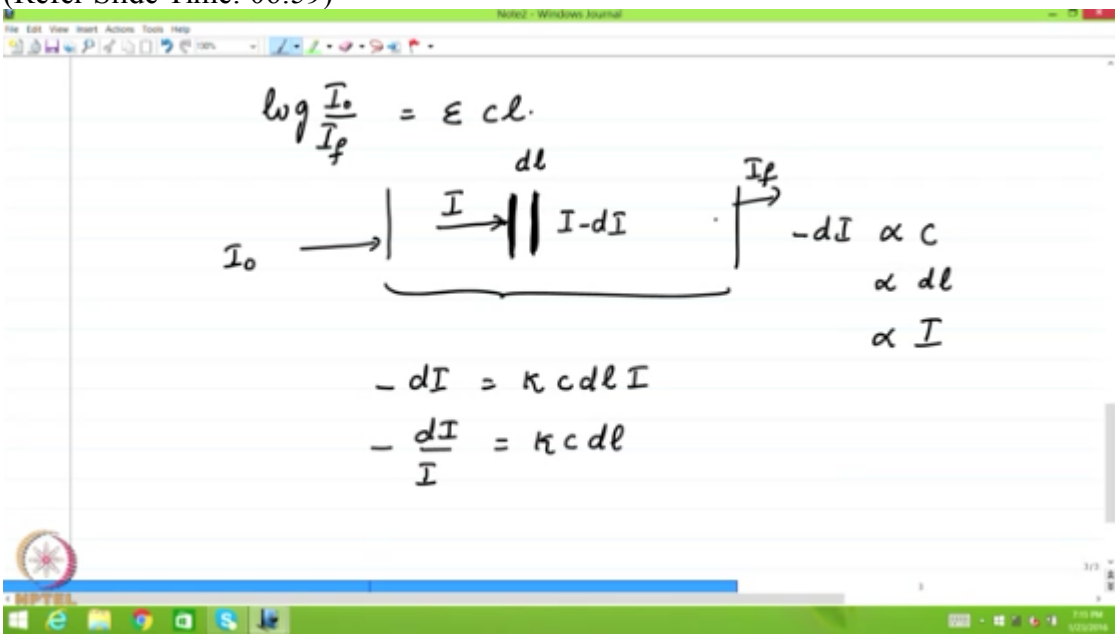

then you know when you integrate this equation you integrate it between the limits I naught and IF, you can write DI/I and write that as the length being also integrated it is kappa times say DL, starting from the length 0 here to the length L, so this gives you immediately L and I between the limits I naught and IF is kappa C L, between the limits 0 and L,

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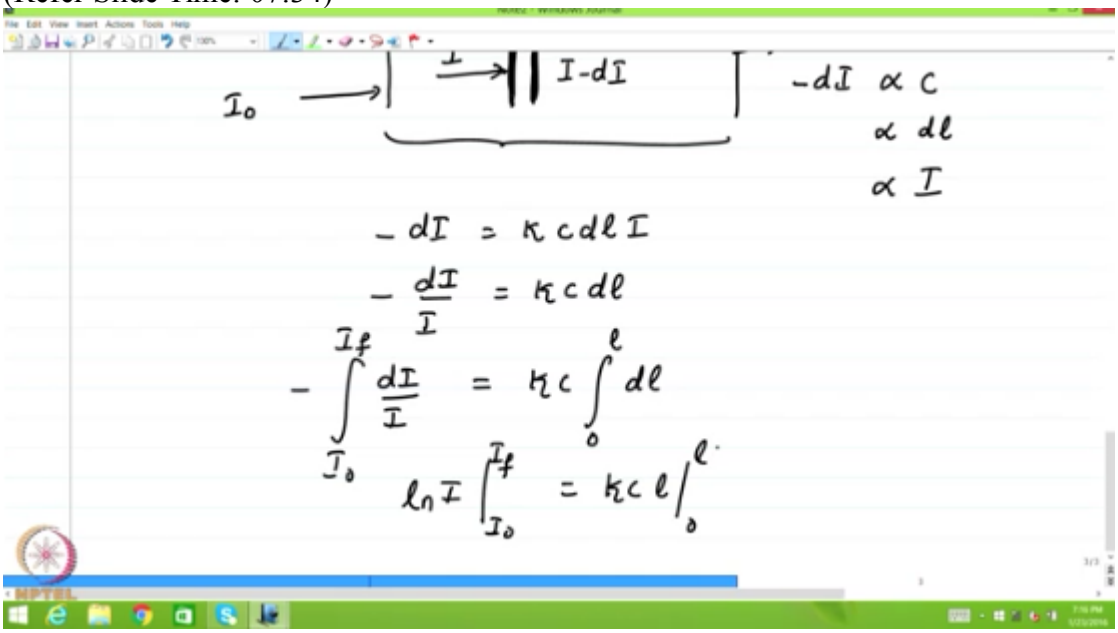

and therefore you know immediately that you get L and I naught by IF is kappa times C times L, and LN is off course 2.303 times logarithm to the base 10 of I naught/IF and that's equal to

kappa times CL and so you write logarithm of to the base 10 I naught/IF is equal to kappa/2.303 which is again a constant times CL, and this is what is called the epsilon or the molar extension coefficient.

And by dimension please remember this is dimension less because they both refer to intensities, so this is left hand side is dimensionless, right hand side is moles per liter, and usually L is expressed in centimeter therefore epsilon is liter per mole per centimeter,
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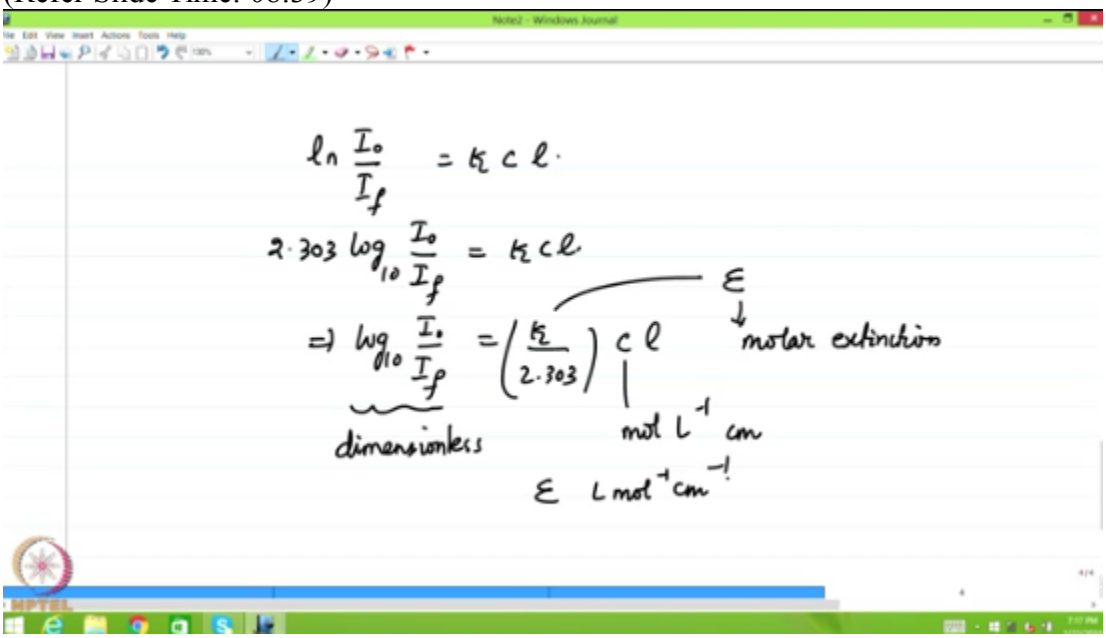

and at low concentrations and low intensities epsilons are additives, so if you have two substances the differing concentrations then the absorption or that frequency of or the wavelength of light by both the substances is roughly additive that the absorbance of the first one and the absorbance of the second one and in the logarithmic ratio and here they add in terms of the concentration times the molar extinction coefficient, some small numerical problems will give you how to do this in a, and how to do this for different concentrations and also sometimes determine the unknown concentration of the substance that you want to find out in by a fluorescence experiment, this is an important rule and we shall see more of it, but I just wanted to introduce this as something to remember before we do the electronic spectroscopy.

From the next lecture onwards we shall start with the microwave and then the vibrational and the electronic spectroscopy. And also talk about the molecular properties like dipole moment, the polarizabilities, the moments of inertia as we start looking up microwave spectroscopy, that will be some numerical problems given on this in some pure assignments to make you familiar with some of these elementary concepts, okay. We'll continue this with the subsequent lectures on rotational spectroscopy, until then thank you very much.

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