Colloids and Surfaces
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Lecture-12
Molecular Origin of Van Der Waals Forces

Okay.

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Module 2
Van der Waals Interactions
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So, we will start with the module 2 which is going to be on what are called as van der Waals interactions.

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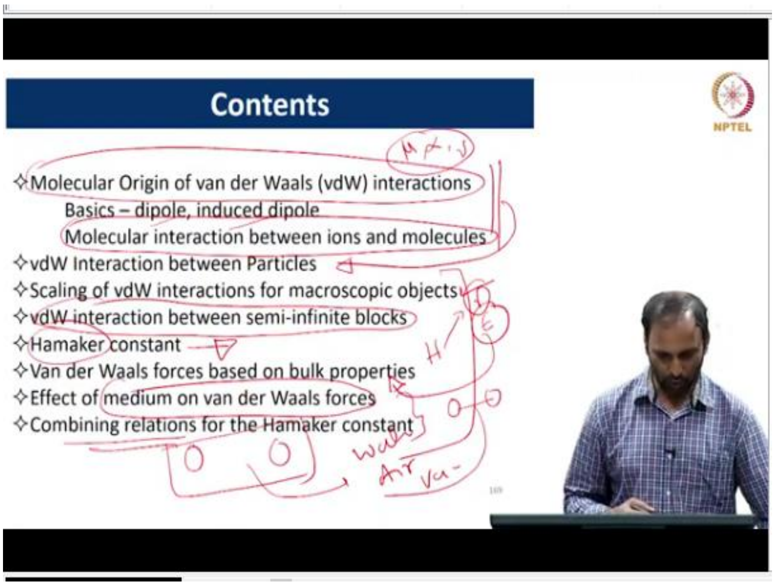

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- Van der Waals forces based on bulk properties
- Effect of medium on van der Waals forces
- Combining relations for the Hamaker constant

So, this is going to be the content that I would most likely you know follow throughout you know this module. We will start with talking about molecular origin of van der Waals interactions. So, that would need you know you know little bit of intro to dipoles, induced dipoles , then we will talk a little bit about you know molecular interaction between ions and molecules.

That is important for us to have a background because we are going to extend that concept to van der Waals interaction between particles later okay. So, therefore we will start with talking about van der Waal forces in molecules and atoms and then we will try and see how can we extend those concepts to talk about van der Waals interaction between particles. Then we have bunch of things which concern van der Waal's interaction between particles we will you know discuss a little bit about scaling of van der Waals interactions.

And derive an expression for van der Waals interaction between you know different objects. We will introduce a concept of Hamaker constant because when we talk about van der Waals interaction between atoms and molecules we need information about you know dipole moment we need information about something called as a polarizability, we need to know something about you know the frequency of vibration of atoms and molecules okay

All of that are required for you to estimate what is the van der Waals interaction between atoms and molecules. Now in order to calculate van der Waals interaction between molecules all the physical parameters okay are kind of clubbed together into a constant what is called as a Hamaker constant, we will try to tell you a little bit about how does this come about . Then so, followed by.

So, there are some theories that people have developed okay which are useful in obtaining the van der Waals forces. For example we are going to touch upon a theory where we are going to show that this Hamaker constant on which the van der Waals you know forces depend on you know you can obtain that from bulk properties of the materials like by measuring surface tensions or by measuring you know the dielectric constants you know.

So, we will try and relate the Hamaker constant to some measurable you know properties of the materials and then we will see how you know that can be used for obtaining van der Waals interactions. Finally we will talk about it turns out that the you know when we say that the van der Waals interaction between 2 particles , it is also important in which medium you are putting the particles, is the medium in which the particles are present is it water, is it air, you know or is it vacuum right.

So, the medium in which the particle dispersed is also important. So, in that context we will talk a little bit about what is the effective medium on van der Waals interactions, how is the presence of a medium affect the van der Waals interactions and then finally we will end with talking something about combining relations. These combining relations are useful when you have information about the van der Waals interaction between 2 atoms or molecules or particles in vacuum I can use that information to obtain van der Waals interaction between the particles in any medium okay.

So, therefore these combining relations become important**.** So, this is what is going to be the flow of you know this particular module.

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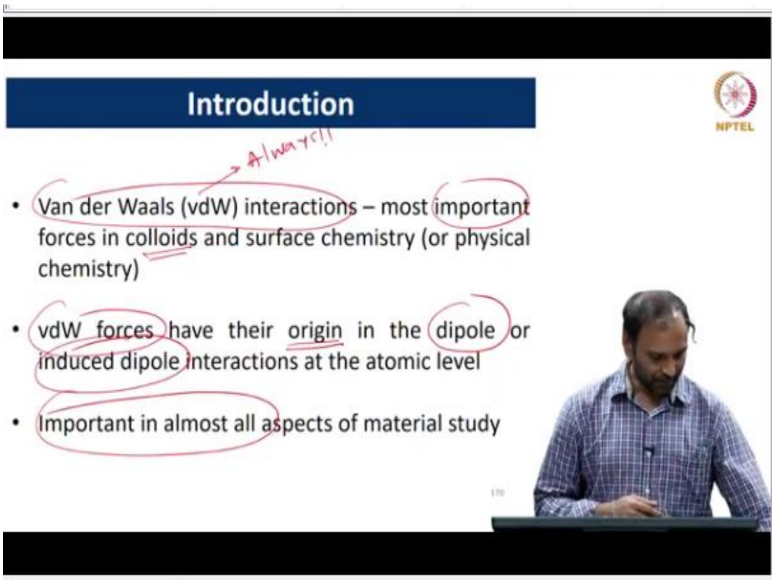

Introduction

- Van der Waals (vdW) interactions – most important forces in colloids and surface chemistry (or physical chemistry)
- vdW forces have their origin in the dipole or induced dipole interactions at the atomic level
- Important in almost all aspects of material study

Just a bit of introduction one thing that you should be aware is that the van der Waals interactions are always present okay, you take any colloidal system be it particles in a fluid you know association colloids in a fluid or any colloidal dispersions you talk about the van der Waals interactions are always going to be there. Okay that is okay they are the most important forces in colloids and surface chemistry or physical chemistry or colloids and interfacial science.

So, these van der Waals forces have their origin, they originate because every atom or a molecule will have some dipoles and induced dipoles which are inherent to you know these molecules or atoms , we will again discuss some of these you know terms as we go along and therefore such interactions they are really important when you want to really look at any aspects of material study okay.

Whether you are trying to look at formulating new materials, whether you are trying to tailor some properties of you know material. So, these become very, very important.

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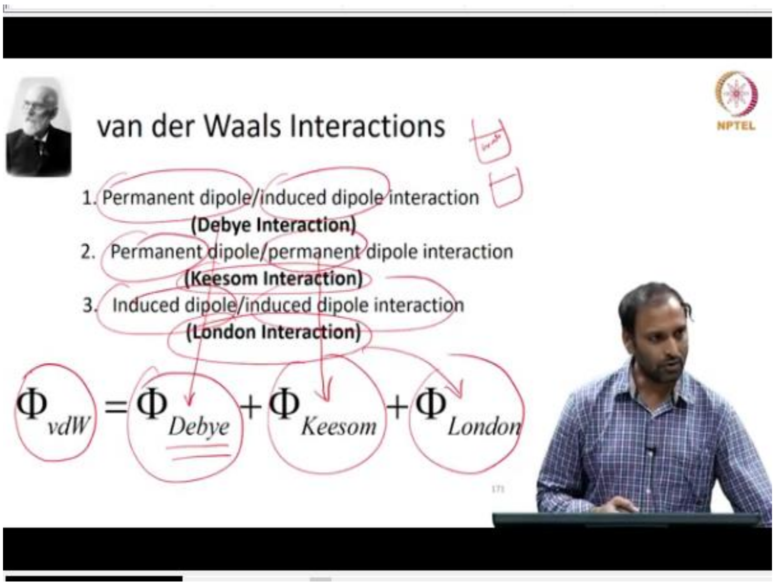

van der Waals Interactions

1. Permanent dipole/induced dipole interaction **(Debye Interaction)**
2. Permanent dipole/permanent dipole interaction **(Keesom Interaction)**
3. Induced dipole/induced dipole interaction **(London Interaction)**

$$\Phi_{vdW} = \Phi_{Debye} + \Phi_{Keesom} + \Phi_{London}$$

In a nutshell there are actually 3 sub class of interactions which contribute to van der Waals okay. That means if you have a total van der Waals interaction, it has contributions from something called as a Debye interactions. This Debye interactions are interactions between 2 permanent dipole and a induced dipole okay. That is the Debye interactions. And something called a Keesom instructions which is interaction between 2 permanent dipoles okay.

If you have 2 permanent dipoles and the interaction between them would be phi Keesom and what is called the London dispersion forces or London interactions which is interaction between induced dipole and induced dipole okay. You take any material you know it could be like say you know if you have a container with water okay or any you know liquid or any you know condensed phases okay.

You will see that there will always be van der Waals interaction and this interaction would be combination of the interactions that come because of what are called as Debye interactions, Keesom interactions and London dispersion forces or London interactions okay. So, before we talk a little bit about each of these things we will try and do a very quick intro to dipoles and induced dipoles okay.

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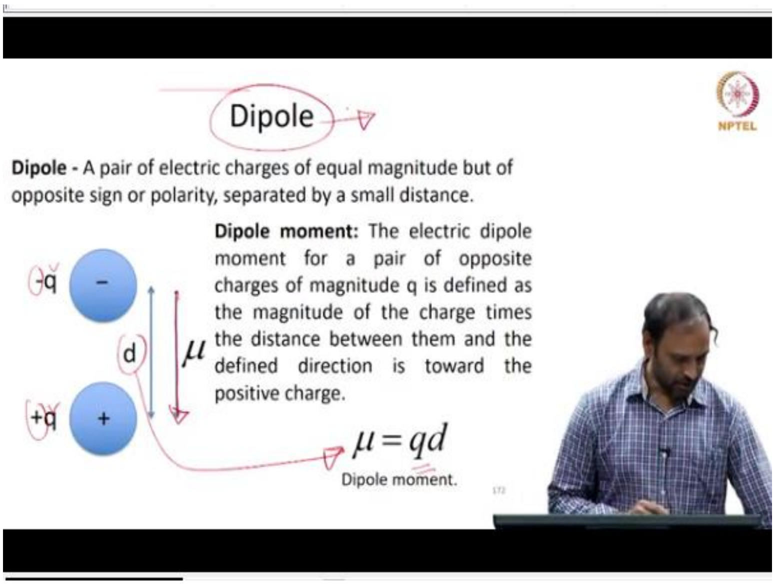

Dipole

Dipole - A pair of electric charges of equal magnitude but of opposite sign or polarity, separated by a small distance.

Dipole moment: The electric dipole moment for a pair of opposite charges of magnitude q is defined as the magnitude of the charge times the distance between them and the defined direction is toward the positive charge.

$$\mu = qd$$

Dipole moment.

So, all of you already know a dipole, it is essentially a pair of electric charges okay which are of equal magnitude okay, but they have opposite sign and they are separated by some distance d and for that you define something called as a dipole moment which essentially is the product of the magnitude of the charge multiplied by the distance right. That is what is a dipole.

And typically whenever you represent dipole you start with you know a line starting from the negative charge and you kind of draw an arrow and the arrow typically points from the negative to positive okay. That is a typical convention that people use, that is what is called as a dipole okay.

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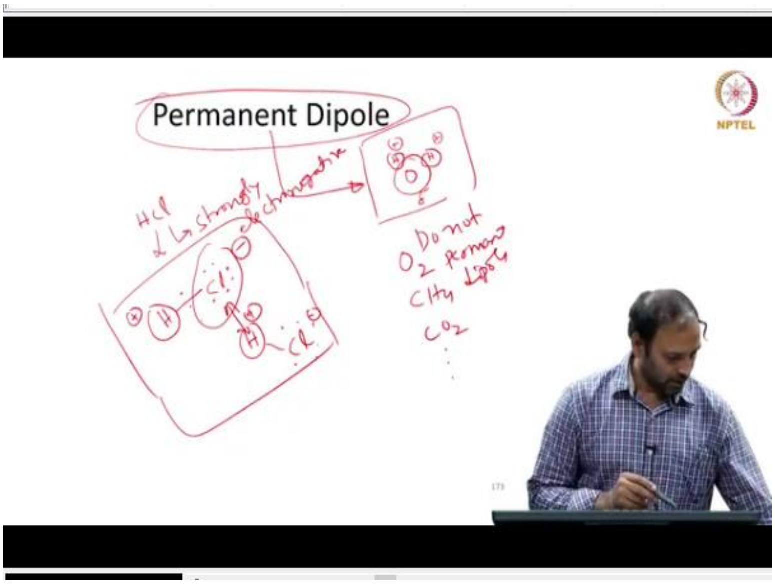

Let us talk a little bit about what is called as a permanent dipole okay, any thoughts what is a permanent dipole some thoughts, water molecules yeah. So, water molecule has a permanent dipole right, whenever you are seen you know water molecules people represent something like this okay. That is your oxygen and that is your hydrogen okay, people typically say you know oxygen end will have some negative charge.

And okay the hydrogen end will have some positive charge right okay, that is an example of a molecule which has a permanent dipole okay. So, the of course you can think about other examples right HCl is another example hydrochloric acid okay. So, typically permanent dipoles are found in molecules in which one of the atom is strongly electronegative okay, when one of the atom is strongly electronegative okay.

If you take the case of HCl it turns out that its chlorine has 7 electrons in the outermost shell, chlorine has 7 electrons in the outermost shell and it wants to share an electron with hydrogen okay. So, that you know it can complete its outer layer more shell right. So, therefore typically what will happen is when you talk about sharing of electrons we talk about a covalent bonds right.

In covalent bonds it is you know and the electron that are shared they kind of belong to both the atoms right and because you know chlorine is a strongly electronegative you know atom what it does is, it will pull the electrons a little bit towards itself okay. So, because of which you know the end of the molecule which has a stronger electronegative atom you know acquires a partial negative charge.

And the end which has a less electronegative atom will basically you know achieve a you know it will have a slight positive charge okay. So, therefore whenever you have many such molecules you know what will happen is there is going to be. So, if I take for example another you know HCl molecule, again I can write a similar configuration this end is going to be slightly positively charged.

This is going to be slightly negative charge and there is going to be a attraction between the 2 molecules which have permanent dipole okay. So, therefore and so typically molecules which have similar symmetry. For example in oxygen, methane, CO2, all these molecules do not have permanent dipoles okay, one of the requirement for a molecule to have a permanent dipole is one of the atom or molecule has to be more electronegative than the other molecule okay. That is what is called as a permanent dipole okay.

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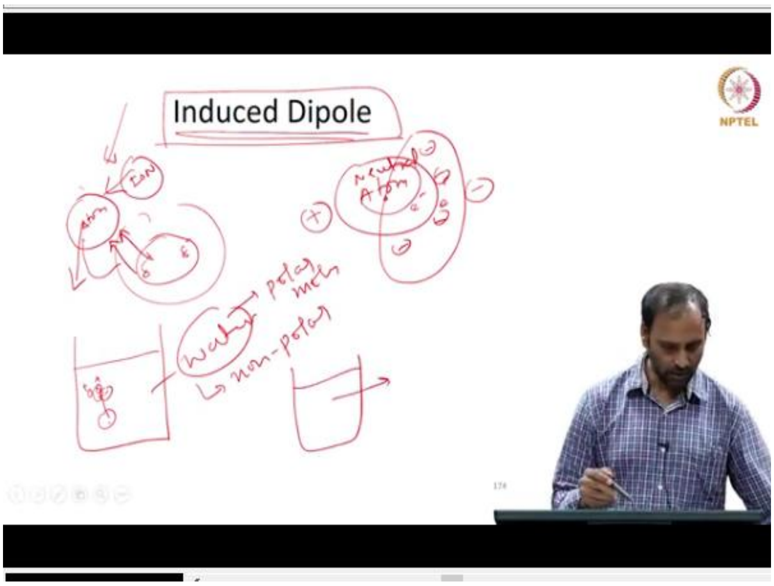

Induced Dipole

So, then what is called as induced dipole. So, induced dipoles what I can do is there could be an atom or a molecules which is a neutral atom or a molecule now. So, if an ion approaches you know such a neutral atom or a molecule or if I have a molecule which has a dipole if that approaches a neutral atom what will happen is. So, it will disturb the electron cloud around the neutral atom.

So, because of which you know the neutral atom can also be polarized it can also acquire either positive or negative charge depending upon whether it is approached by a cation or an anion or which end of the permanent dipole is near to the neutral atom okay. That is what you know then what I would say that you know this there is a dipole that is induced in the neutral atom okay.

The other ways by which you know you can have an induced dipole is that even if you take a neutral atom okay we know that you know if you look at electronic structure you have in a nucleus okay then you have different orbitals right and you know the electrons are kind of revolving around these you know orbitals right. Now what will happen is but of course because they are continuously they are not fixed in space right.

They are changing their position what will happen is momentary there could be a case there could be some imbalance in the distribution of electrons you know in these you know orbitals because of which one end of the atom can have a more number of you know electrons on one side compared to the other side okay and that depends on you know it is probabilistic process right.

So, therefore what could happen is even in a neutral atom at momentarily there could be a case where one region of the atom is slightly negatively charged and correspondingly the other end will have a positive charge okay. So, therefore induced dipole can be either can occur if you have a neutral atom and if an ion or a permanent dipole approaches a neutral atom or the fluctuations in the electron position you know can also lead to induced dipole ok.

So, therefore we go back to again now these interactions, now we know each of these terms. So, therefore this Debye interactions are the interaction between a permanent dipole and a induced dipole okay, you could think about a case like this right. There was a permanent dipole okay and then in the case of a neutral atom okay you could have. So, one way to think about this would be that let us think about a case.

See water has a permanent dipole right. Now if you look at some organic species okay which is say sparingly soluble in water okay. So, we know that you know typically organic molecules will not have a permanent dipole right. There what are called as non polar right and water is an example of a polar molecule. If you have cases like that then you have some molecules which have a you know a permanent dipole right okay.

And some non polar species which does not have any charge okay. Therefore you can think about an interaction between a permanent dipole and an induced dipole right or if I take an example where I have only non polar molecules okay, then what will happen is they will have what are called as induced dipole, induced dipole interactions okay. That will be the more dominant interactions.

Correspondingly if you take something like water molecule which has known to have a permanent dipole, then the permanent dipole, permanent dipole interactions are going to be more common okay.

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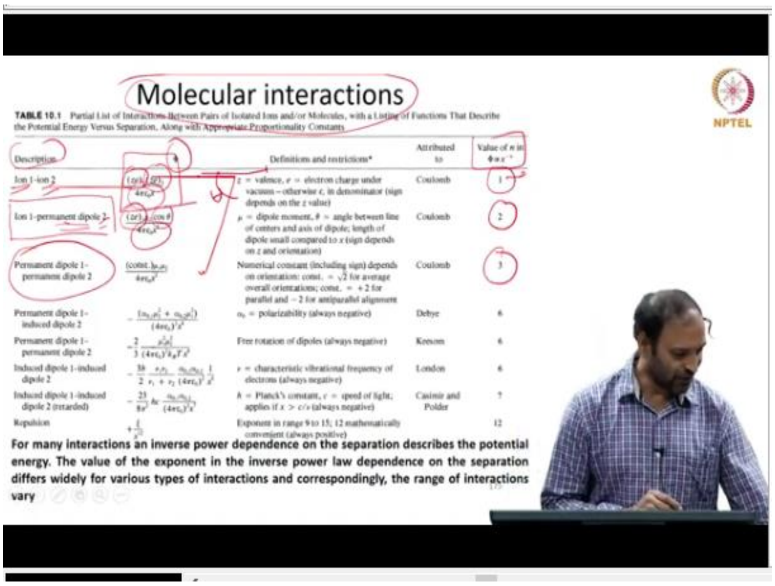

Molecular interactions

TABLE 10.1 Partial List of Interactions Between Pairs of Isolated Ions and/or Molecules, with a Listing of Functions That Describe the Potential Energy Versus Separation, Along with Appropriate Proportionality Constants

Description	ϕ	Definitions and restrictions*	Attributed to	Value of n in $\phi \propto x^{-n}$
Ion 1-ion 2	$\frac{(z_1e)(z_2e)}{4\pi\varepsilon_0 x}$	z = valence, e = electron charge under vacuum – otherwise ε, in denominator (sign depends on the z value)	Coulomb	1
Ion 1-permanent dipole 2	$\frac{(ze)\mu\cos\theta}{4\pi\varepsilon_0 x^2}$	μ = dipole moment, θ = angle between line of centers and axis of dipole; length of dipole small compared to x (sign depends on z and orientation)	Coulomb	2
Permanent dipole 1-permanent dipole 2	$\frac{(\text{const.})\mu_1\mu_2}{4\pi\varepsilon_0 x^3}$	Numerical constant (including sign) depends on orientation: const. = $\sqrt{2}$ for average overall orientations; const. = +2 for parallel and −2 for antiparallel alignment	Coulomb	3
Permanent dipole 1-induced dipole 2	$-\frac{(\alpha_{0,1}\mu_2^2+\alpha_{0,2}\mu_1^2)}{(4\pi\varepsilon_0)^2 x^6}$	α_0 = polarizability (always negative)	Debye	6
Permanent dipole 1-permanent dipole 2	$-\frac{2}{3}\frac{\mu_1^2\mu_2^2}{(4\pi\varepsilon_0)^2 k_B T x^6}$	Free rotation of dipoles (always negative)	Keesom	6
Induced dipole 1-induced dipole 2	$-\frac{3h}{2}\frac{\nu_1\nu_2}{\nu_1+\nu_2}\frac{\alpha_{0,1}\alpha_{0,2}}{(4\pi\varepsilon_0)^2}\frac{1}{x^6}$	ν = characteristic vibrational frequency of electrons (always negative)	London	6
Induced dipole 1-induced dipole 2 (retarded)	$-\frac{23}{8\pi^2}hc\frac{\alpha_{0,1}\alpha_{0,2}}{(4\pi\varepsilon_0)^2 x^7}$	h = Planck's constant, c = speed of light; applies if $x > c/\nu$ (always negative)	Casimir and Polder	7
Repulsion	$+\frac{1}{x^{12}}$	Exponent in range 9 to 15; 12 mathematically convenient (always positive)		12

For many interactions an inverse power dependence on the separation describes the potential energy. The value of the exponent in the inverse power law dependence on the separation differs widely for various types of interactions and correspondingly, the range of interactions vary

So, this is a table uh which lists all the molecular interactions okay between atoms you know or ions okay or the molecules that constitute matter right. So, I will just quickly go through this table that is a description it will tell you what is the interaction between in this case this is a interaction between ion 1 and ion 2 and that is an expression for the interaction potential okay.

So, ion 1 has charge ze okay, the valency multiplied by the charge in the electron of 1 you know ion similarly ze2 that is a valency again multiplied by e for the second one and 4 pi epsilon 0 x okay. That is the interaction potential for 2 ions right and. So, therefore this goes as 1 over x okay you know. So, the general form is phi going as x power – n, n for this case is 1 because you have 1 over x here right.

Similarly you can think about interaction between an ion and a dipole okay. In this case the ion will have a charge ze1 again, a mu 2 is it permanent dipole, it is a dipole moment of the dipole 2 okay. Therefore this mu 2 here and cos theta is the angle right. For example I could have a you know dipole here okay and my ion could be here right, you know that the theta refers to the angle right and.

So, it has a 4 pi epsilon 0 x square dependence, therefore your exponent is going to be 2 okay. So, I can go on so on and so forth okay. I can derive an expression again for the interaction between 2 permanent dipoles in that case it will go as mu 1 mu 2 divided by x cube where exponent is 3 right.

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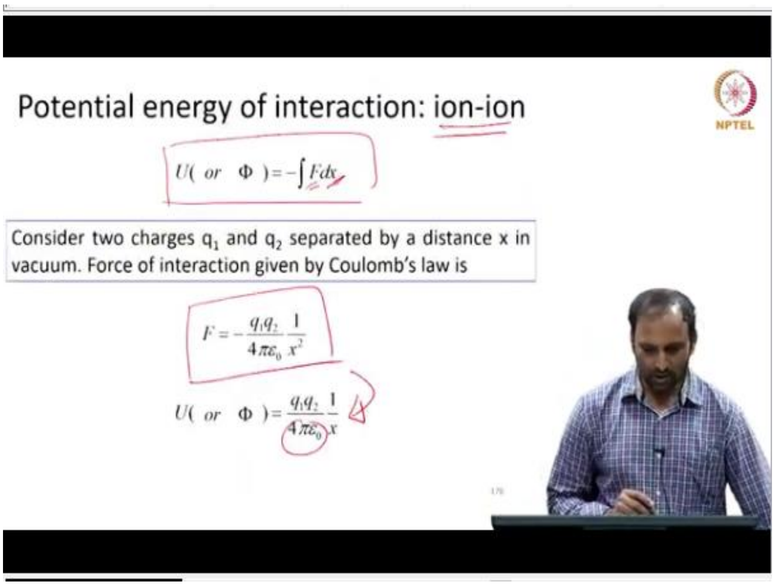

Potential energy of interaction: ion-ion

$$U(\ or\ \ \Phi\ ) = -\int F dx$$

Consider two charges q_1 and q_2 separated by a distance x in vacuum. Force of interaction given by Coulomb's law is

$$F = -\frac{q_1 q_2}{4\pi\varepsilon_0}\frac{1}{x^2}$$

$$U(\ or\ \ \Phi\ ) = \frac{q_1 q_2}{4\pi\varepsilon_0}\frac{1}{x}$$

So, we have done these exercise already right, one exercise we have done in the class right. So, if you look at the potential energy of interaction between 2 ions okay. So, I said that the interaction potential if you want to calculate is the negative integral of the force times the distance right. The force you know if you take 2 ions it goes as q 1 q 2 divided by 4 pi epsilon 0 into 1 over x square.

So, if I you know integrate that out right you get U to be q 1 q 2 divided by 4 pi 1 over x right. This is exactly the first entry okay. So, if I rub this up right, that is actually your first entry, only thing is q 1 you know q 1 is ze 1 and q 2 is ze 2 and you have 4 pi epsilon 0 that this one and you know 1 over x right.

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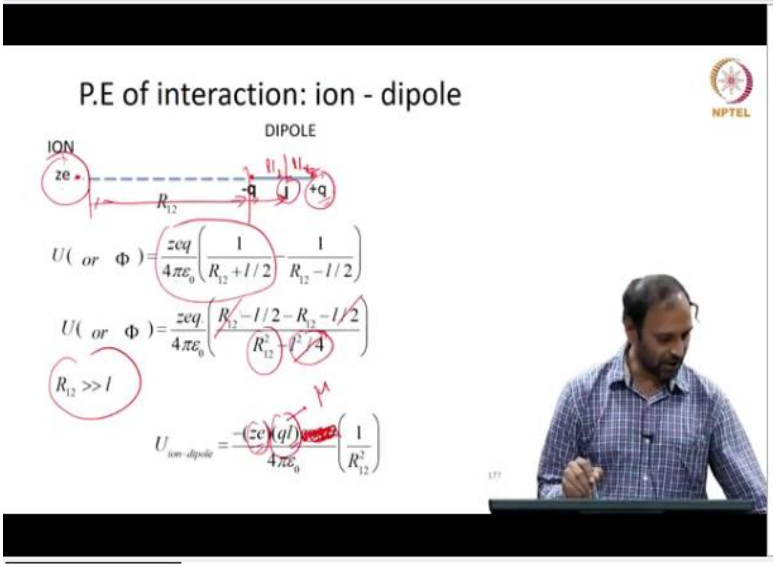

P.E of interaction: ion - dipole

$$U(\ or\ \Phi\ ) = \frac{zeq}{4\pi\varepsilon_0}\left(\frac{1}{R_{12}+l/2} - \frac{1}{R_{12}-l/2}\right)$$

$$U(\ or\ \Phi\ ) = \frac{zeq}{4\pi\varepsilon_0}\left(\frac{\cancel{R_{12}}-l/2-\cancel{R_{12}}-l/2}{R_{12}^2-\cancel{l^2/4}}\right)$$

$R_{12} >> l$

$$U_{ion-dipole} = \frac{-(ze)(ql)}{4\pi\varepsilon_0}\left(\frac{1}{R_{12}^2}\right)$$

I can do the similar thing for potential energy of interaction between an ion and a dipole right. So, I have a ion whose charge is ze okay and there is a dipole okay, you know something which you know in which you have 2 charges of equal magnitude opposite sign separated by some distance in this case l okay and the this distance is okay R 12 right. So, I can write a similarly I mean this first term you know.

So, this is ze times q okay, ze times q divided by 4 pi epsilon 0 into 1 over distance between the 2 right, this is R 12 ok plus l by 2 because if you say that l is a you know the distance between. So, this distance is going to be l by 2 l by 2 right okay. So, therefore this is going to be l right. This is small mistake right this is going to be right, because if you look at what is it R 12 would be yeah.

So, yeah, yeah that is true, let us do like that okay. So, now if I look at this okay. Let us do that right yeah. So, if I say that R 12 is the distance of the center of the dipole okay from okay, this is the distance from the center of the dipole to the ion. Therefore your the distance that the q + q is from the ion is R 12 + l by 2 right. Similarly this is going to be at a distance R 12 - l by 2 right.

And I can simplify this a little bit. So, I can just do the right. So, therefore your denominator becomes R 12 square - l square by 4 okay and this, this gets cancelled okay. So, - l by 2 - l by 2 that is l okay and there is ze times q q times l is club because that is a dipole moment okay cos theta . Now in this case what will happen is because you have okay. This is for a case where I have a okay let us not for a moment consider this is not there okay.

So, your I have ze here right, that is this term q times l and negative sign that comes because of the you know there was a - l here right and 4 pi epsilon 0, now if you consider a case where you know this R 12 is much, much larger than l I can kick this out therefore it becomes 1 over distance square okay.

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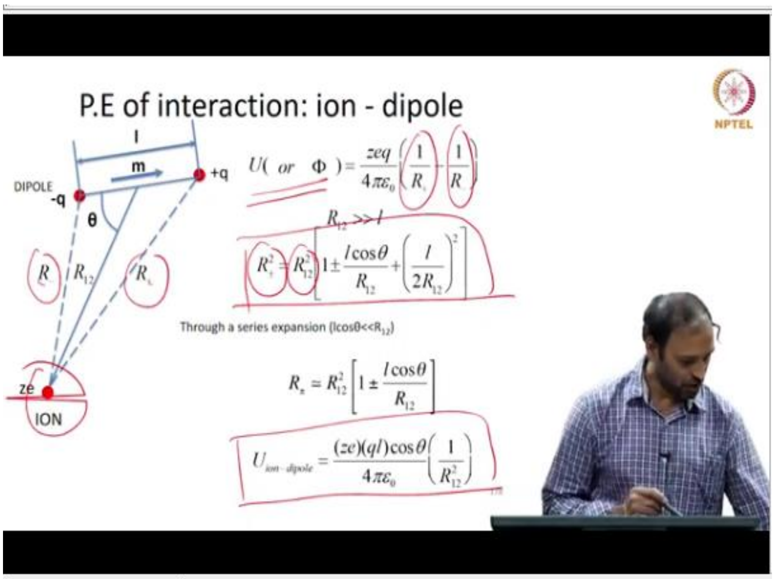

P.E of interaction: ion - dipole

$$U(\ or\ \Phi\ ) = \frac{zeq}{4\pi\varepsilon_0}\left(\frac{1}{R_+} - \frac{1}{R_-}\right)$$

$R_{12} >> l$

$$R_\pm^2 = R_{12}^2\left[1 \pm \frac{l\cos\theta}{R_{12}} + \left(\frac{l}{2R_{12}}\right)^2\right]$$

Through a series expansion ($l\cos\theta << R_{12}$)

$$R_\pm = R_{12}^2\left[1 \pm \frac{l\cos\theta}{R_{12}}\right]$$

$$U_{ion-dipole} = \frac{(ze)(ql)\cos\theta}{4\pi\varepsilon_0}\left(\frac{1}{R_{12}^2}\right)$$

Now I can do a similar exercise, but for a case where it is an oriented dipole right, you know this dipole is oriented at a particular angle to the ion that I have okay, then this theta becomes important you know I could similarly if R - and R + are the distance of these 2 you know charges which make up the dipole I can actually write the total interaction energy is zeq divided by 4 pi epsilon 0 into 1 over R + - 1 over R -.

These are just these 2 separation distances right okay and of course I can you know derive an expression that connects these distances to R 12 right. I can do that, again if you use the approximation if you do some simplification it turns out that you know the interaction between the ion and the dipole for any arbitrary orientation okay goes as zeq l cos theta divided by 4 by epsilon 0 into 1 over distance square okay.

So, that is the this term right. So, similarly I could do a construction and I can actually also get what is the interaction between the 2 right, if you want to think about you know I could take 2 dipoles + q - q okay, again other you know + q - q right and I can get the separation distance to be x okay. If this is the l and l are you know distance between the ions that form the dipole.

I can either take a fixed dipole, that dipoles are fixed in space I can calculate what is the total energy of interaction exactly the similarly right. So, you can do that right, you know how to do that right. So, if you go back here. So, when we did the 2 dipoles is the interaction between this plus the interaction between this right. Similarly if you have a dipole, dipole interaction is the interaction of these 2 plus these 2 okay.

These two plus these two, there will be 4 terms right, you can simplify that if you do that then you will end up with a expression wherein you will have 1 over x power 3 dependence okay.

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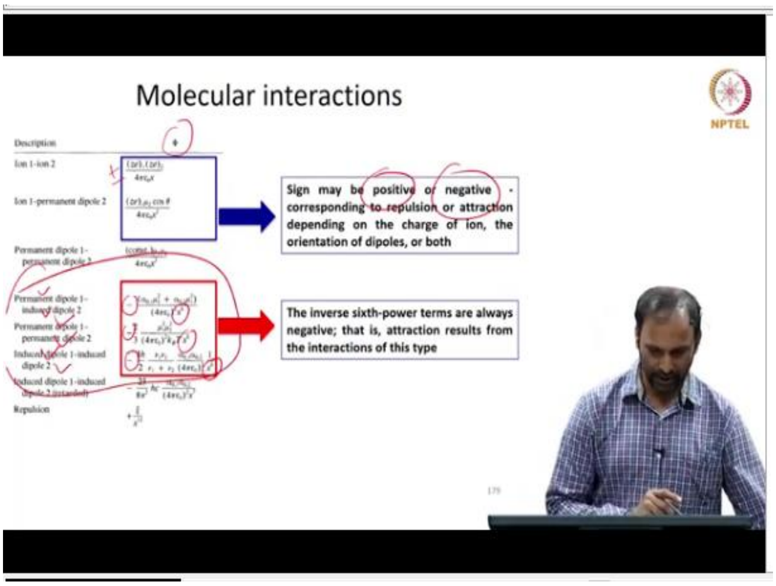

Molecular interactions

Description	Φ
Ion 1-ion 2	$\frac{(ze)_1(ze)_2}{4\pi\epsilon_0 x}$
Ion 1-permanent dipole 2	$\frac{(ze)_1\mu_2\cos\theta}{4\pi\epsilon_0 x^2}$
Permanent dipole 1-permanent dipole 2	$\frac{(\text{const.})\mu_1\mu_2}{4\pi\epsilon_0 x^3}$
Permanent dipole 1-induced dipole 2	$-\frac{(\alpha_{0,1}\mu_2^2+\alpha_{0,2}\mu_1^2)}{(4\pi\epsilon_0)^2 x^6}$
Permanent dipole 1-permanent dipole 2	$-\frac{2}{3}\frac{\mu_1^2\mu_2^2}{(4\pi\epsilon_0)^2 k_B T x^6}$
Induced dipole 1-induced dipole 2	$-\frac{3h}{2}\frac{\nu_1\nu_2}{\nu_1+\nu_2}\frac{\alpha_{0,1}\alpha_{0,2}}{(4\pi\epsilon_0)^2}\frac{1}{x^6}$
Induced dipole 1-induced dipole 2 (retarded)	$-\frac{23}{8\pi^2}hc\frac{\alpha_{0,1}\alpha_{0,2}}{(4\pi\epsilon_0)^2 x^7}$
Repulsion	[illegible]

Sign may be positive or negative - corresponding to repulsion or attraction depending on the charge of ion, the orientation of dipoles, or both

The inverse sixth-power terms are always negative; that is, attraction results from the interactions of this type

Now okay. So, this is again the same table right. So, if you look at you know the expressions for phi right. This phi can be either positive or negative. That means the interaction can be either repulsive or attractive depending upon whether you know you are dealing with ions of same charge or you know. So, therefore in the table that I showed there are some entries which sign may be positive or negative.

It depends on the kind of ionic species that you are dealing with okay. However, there are a few entries okay which are marked here okay, that is a permanent dipole, induced dipole interaction and a permanent dipole, permanent dipole interactions and induced dipole induced dipole interactions you know they are always attractive okay and all of them have 1 over x power 6 dependence okay.

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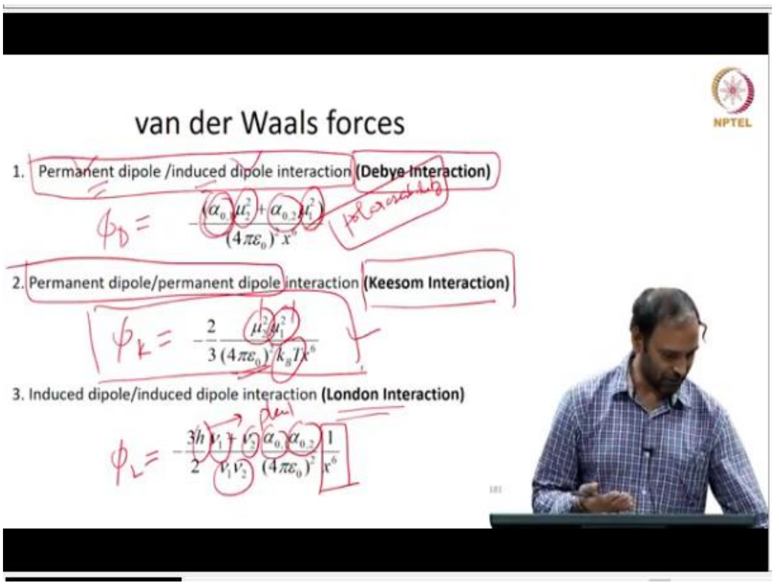

van der Waals forces

1. Permanent dipole /induced dipole interaction **(Debye Interaction)**

$$\phi_D = -\frac{\alpha_{0,1}\mu_2^2 + \alpha_{0,2}\mu_1^2}{(4\pi\varepsilon_0)^2 x^6}$$

polarizability

2. Permanent dipole/permanent dipole interaction **(Keesom Interaction)**

$$\phi_K = -\frac{2}{3}\frac{\mu_2^2\mu_1^2}{(4\pi\varepsilon_0)^2 k_B T x^6}$$

3. Induced dipole/induced dipole interaction **(London Interaction)**

$$\phi_L = -\frac{3h}{2}\frac{\nu_1 + \nu_2}{\nu_1\nu_2}\frac{\alpha_{0,1}\alpha_{0,2}}{(4\pi\varepsilon_0)^2}\boxed{\frac{1}{x^6}}$$

So, these 3 entries which are always attractive and which have 1 over 6 dependents are what are called as van der Waals forces okay. So, that is your phi Debye okay phi Keesom and phi London okay. So, because let us look at this right, this is a interaction between 2 permanent dipoles of course you know it should depend on the magnitude of the dipole moments okay.

And this is you know 1 over 4 pi epsilon 0 that comes from the electrostatics right and you have kB T, the thermal energy and 1 over x power dependence. So, therefore the terms which have only dipole moments they are the Keesom interactions because they are the interaction between the permanent dipoles okay and if you look at the Debye interactions which are interaction between the permanent dipole and the induced dipole.

So, you have these are the dipole moments okay, then this alpha 0 1 and alpha 0 2, these are what are called as polarizability okay which tells you something about I talked about you know this induced dipole right.

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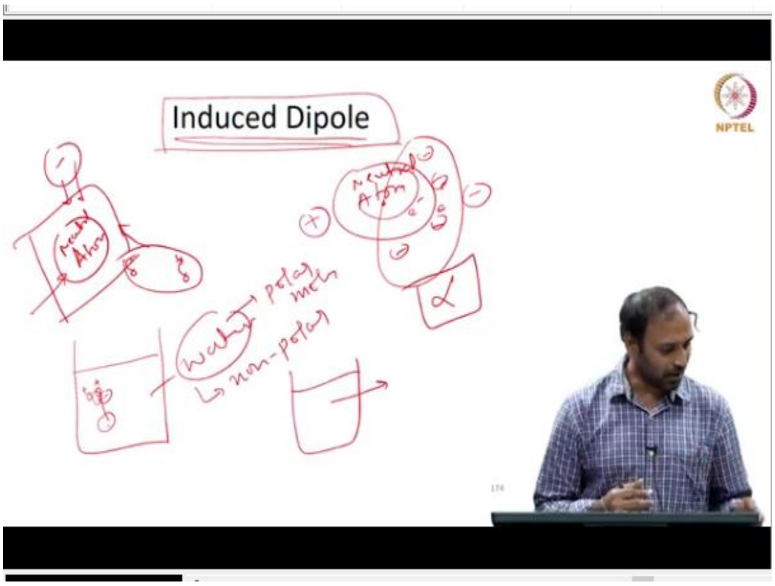
Induced Dipole

So, I said that okay I say that no I have a neutral atom okay and I said that if I have you know if a charged species approaches a neutral atom or if a permanent dipole approaches you know this neutral atom you know I say this can acquire okay, this can be polarized right okay. The extent to which the approaching atom you know or a molecule or a charge species can influence the electron distribution okay or distribution of electrons in the cloud okay is basically measured by alpha okay.

So, higher you know. So, for some molecules it may be easier to influence the distribution okay. So, we say that they are highly polarisable, but for some it may be very difficult to you know influence the electron distribution okay. They are less polarizable okay. So, alpha tells you something about the polarizability okay. So, therefore the term that have you know the polarizability and the dipole moments would be the Debye by interactions.

Because that is the interaction between a permanent dipole and a induced dipole okay and the third contribution London dispersion forces . So, we know what is alpha now okay, again 1 hour x power 6 dependence h is, what is h Planck’s constant right. yeah Planck’s constant and this nu 1 and nu 2 okay, that what are called as the frequency of vibration okay of the atoms and the molecules okay.

Now for a given atom or a molecule if you know all these you know parameters I can plug in all of them and I can actually estimate what is the van der Waals force of interaction okay.

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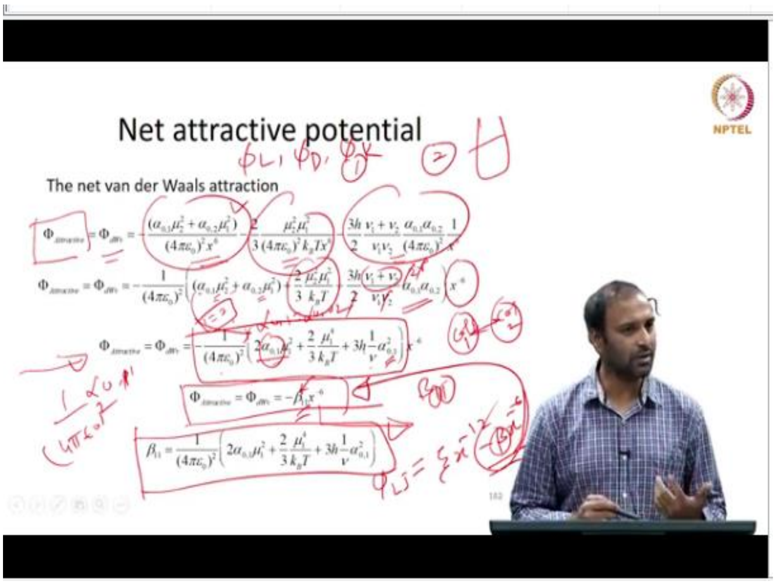

Net attractive potential

The net van der Waals attraction

$$\Phi_{attractive} = \Phi_{vdW} = -\frac{(\alpha_{0,1}\mu_2^2 + \alpha_{0,2}\mu_1^2)}{(4\pi\varepsilon_0)^2 x^6} - \frac{2}{3}\frac{\mu_2^2\mu_1^2}{(4\pi\varepsilon_0)^2 k_B T x^6} - \frac{3h}{2}\frac{\nu_1+\nu_2}{\nu_1\nu_2}\frac{\alpha_{0,1}\alpha_{0,2}}{(4\pi\varepsilon_0)^2}\frac{1}{x^6}$$

$$\Phi_{attractive} = \Phi_{vdW} = -\frac{1}{(4\pi\varepsilon_0)^2}\left((\alpha_{0,1}\mu_2^2 + \alpha_{0,2}\mu_1^2) + \frac{2}{3}\frac{\mu_2^2\mu_1^2}{k_B T} + \frac{3h}{2}\frac{\nu_1+\nu_2}{\nu_1\nu_2}\alpha_{0,1}\alpha_{0,2}\right)x^{-6}$$

$$\Phi_{attractive} = \Phi_{vdW} = -\frac{1}{(4\pi\varepsilon_0)^2}\left(2\alpha_{0,1}\mu_1^2 + \frac{2}{3}\frac{\mu_1^4}{k_B T} + 3h\frac{1}{\nu}\alpha_{0,1}^2\right)x^{-6}$$

$$\Phi_{attractive} = \Phi_{vdW} = -\beta_{11}x^{-6}$$

$$\beta_{11} = \frac{1}{(4\pi\varepsilon_0)^2}\left(2\alpha_{0,1}\mu_1^2 + \frac{2}{3}\frac{\mu_1^4}{k_B T} + 3h\frac{1}{\nu}\alpha_{0,1}^2\right)$$

So, we have done that. So, there is phi attractive or phi van der Waals is essentially the summation of the 3 okay, because everything has 1 over x power you know - 6 dependence I have taken x power - 6 out here okay and this 1 and 2 right 1 and 2 correspond to you know 2 atoms or 2 molecules right. Now if I have identical atoms, if I talk about just water molecule for example.

Then you know your 1 is equal will be 2 right because you know we are talking about interaction between same atoms or same molecules okay, you know this expression is for 2 atoms and molecules which are not identical, but if I have identical atoms and molecule for example if I am worried about the van der Waals interaction between water molecules okay in a container which has only water.

Then you know your 1 is equal to 2 right because you are talking about interaction between like atoms or like molecules. Therefore your alpha 0 1 will be equal to alpha 0 2 right. Therefore I have written this as 2 times alpha 0 1, again mu 1 is equal to mu 2 because the dipole moment of water will be the same right. Therefore this becomes 2 times alpha 0 1 mu 1 square.

Similarly this term will you know simplify to 2 by 3 mu 1 power 4 right divided by k B T + 3 h by 2, this becomes 2 nu and 2, 2 gets cancelled right and then I have nu square here again 1 nu 1 nu gets cancelled. Therefore you have 1 over nu and you have alpha 01 alpha 02 which will be alpha 0 1 square right okay. Now this pre factor is actually you know called is given like beta 11 right.

1 1 because again it is a interaction between same identical molecules and that has x power - 6. Now you should think about in a similarity of this attractive part to phi Lenard Jones, remember we wrote this as x bar - 12 - beta x power - 6 right. This part essentially is the van der Waals interactions right okay. So, now we know where does this come from right. This essentially comes from the van der Waals attractions okay which has 3 parts okay London dispersion forces, Keesom interactions and Debye interactions.

We kind of we did not derive expression for this, we kind of know how they come about and you should be able to identify each of these terms to have an idea as to which one is you know phi l which one is phi D and which one is phi K.

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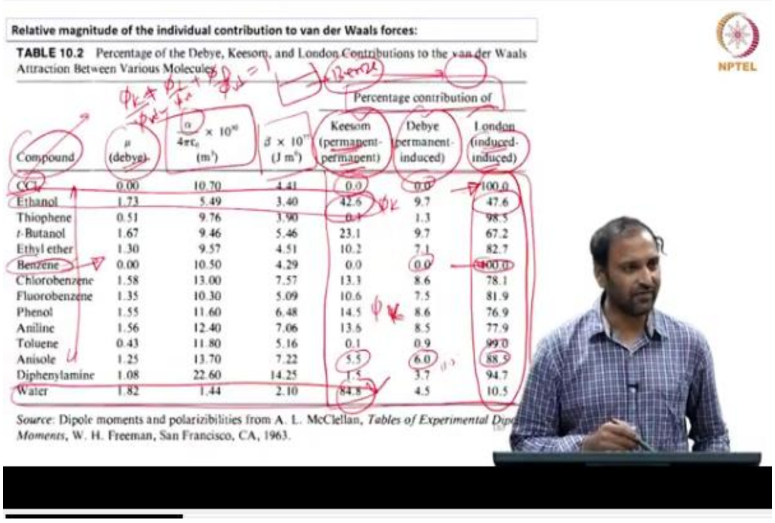

Relative magnitude of the individual contribution to van der Waals forces:

TABLE 10.2 Percentage of the Debye, Keesom, and London Contributions to the van der Waals Attraction Between Various Molecules

Compound	μ (debye)	$\frac{\alpha}{4\pi\varepsilon_0} \times 10^{30}$ (m^3)	$\beta \times 10^{77}$ ($J\ m^6$)	Percentage contribution of Keesom (permanent-permanent)	Debye (permanent-induced)	London (induced-induced)
CCl_4	0.00	10.70	4.41	0.0	0.0	100.0
Ethanol	1.73	5.49	3.40	42.6	9.7	47.6
Thiophene	0.51	9.76	3.90	0.1	1.3	98.5
t-Butanol	1.67	9.46	5.46	23.1	9.7	67.2
Ethyl ether	1.30	9.57	4.51	10.2	7.1	82.7
Benzene	0.00	10.50	4.29	0.0	0.0	100.0
Chlorobenzene	1.58	13.00	7.57	13.3	8.6	78.1
Fluorobenzene	1.35	10.30	5.09	10.6	7.5	81.9
Phenol	1.55	11.60	6.48	14.5	8.6	76.9
Aniline	1.56	12.40	7.06	13.6	8.5	77.9
Toluene	0.43	11.80	5.16	0.1	0.9	99.0
Anisole	1.25	13.70	7.22	5.5	6.0	88.5
Diphenylamine	1.08	22.60	14.25	1.5	3.7	94.7
Water	1.82	1.44	2.10	84.8	4.5	10.5

Source: Dipole moments and polarizibilities from A. L. McClellan, *Tables of Experimental Dipo… Moments*, W. H. Freeman, San Francisco, CA, 1963.

So, I just want to . So, this is a table, this is a really good table I think you can learn a lot about van der Waals forces from this particular table. So, this is a compound okay the molecules of interest to you and that is mu dipole moment you know its units is Debye right and if you look at like say. So, if you look at this term right, if you look at this expression you have 1 over 4 pi epsilon 0 whole square.

And there is alpha 0 1 right alpha 0 1. So, it is actually this term okay. So, right. So, alpha. So, basically this will give you what is alpha okay, the polarizability right and that is beta okay, that is this term right beta 11 and this tells you about the percentage contribution okay and we said that there are 3 contributions okay, what is the individual contributions to the total van der Waals force of interaction okay.

That is the Keesom interaction, that is between permanent dipoles okay, that is London induced dipoles and Debye between the permanent and induced okay, what can you say about this table, look at these numbers, I want you to make a comment about what can you say about this table, this is a unique feature over the number that you have you okay, that feature is that look at this entry, it is always non-zero okay**.**

That means you take any atom or any molecule London dispersion forces are always present okay right, that is one thing and if you look at the other 2 terms right, there are cases where this 0 here 0 here 0 here right. So, therefore depending upon the molecules that you work with okay, this Keesom and Debye interactions may be there, may not be there but the London dispersion forces are always present okay.

And let us look at cases where if you look at London dispersion forces here right, here for these 2 molecules which are benzene and CCl 4, again CCl 4 is again another example of a symmetric molecule right, symmetric molecule where only induced dipoles would be present okay. So, the cases where for the non polar molecules okay, for non-polar molecules you will see that the contribution of London dispersion forces would be highest.

Examples are benzene and CCl 4 okay. However, on the other hand if you take molecules which have permanent dipoles, for example water right or if you take even ethanol right okay, they are example of polar molecules right and if you look again the numbers it turns out that the contribution of the permanent dipole permanent dipole interactions is highest for such molecules right.

So, if I look at water. So, 84.8% is the phi K okay and if you take ethanol you will see that again of course London dispersion was also important but there are significant contributions from the phi K itself right. So, therefore so I can say that you know this phi K + phi L + phi D divided by the total phi right, phi total or phi van der Waals. Phi van der Waals should be equal to 1 right.

That is what it will turn out right. So, if you look at this number, this 5.5 + 6 right that is going to be 11.5 + 88.5, that is going to be 100% right okay. So, that is yeah. So, this induced dipole I talked about 2 ways in which you know this induction can occur right, one is if I have a container you know which has a mixture of both you know neutral molecules and charge molecules okay right.

That is one example, but even in cases where I have only neutral molecules okay the disturbance you know to the distribution of ions you know the electrons in the cells that can also lead to induced dipoles. For example if you look at like say benzene right benzene. So, you see I mean everything comes from the induced dipole interactions ok. That means if I have like say a container which has benzene right.

Now we will have only you know every benzene molecule will only see other benzene molecules right. But the fact that they are also neutral okay you know yeah, it is not because it is not that you know one benzene molecule will come near another benzene molecules and it will induce a dipole you know it will induce the formation of the dipole okay.

Yeah yes, yeah right, that is what if I have a neutral atom if a charged species comes near it of course it can disturb the distribution of ions in around the yeah, it does not have a a permanent dipole yeah okay. I am thinking if 2 benzene molecules come together yeah, then both are getting induced, that is why it is called induced, induced intervals. No what will happen is this right okay. Let me just make that point that is clear. So, that is a good point. So, what he is trying to say is this.

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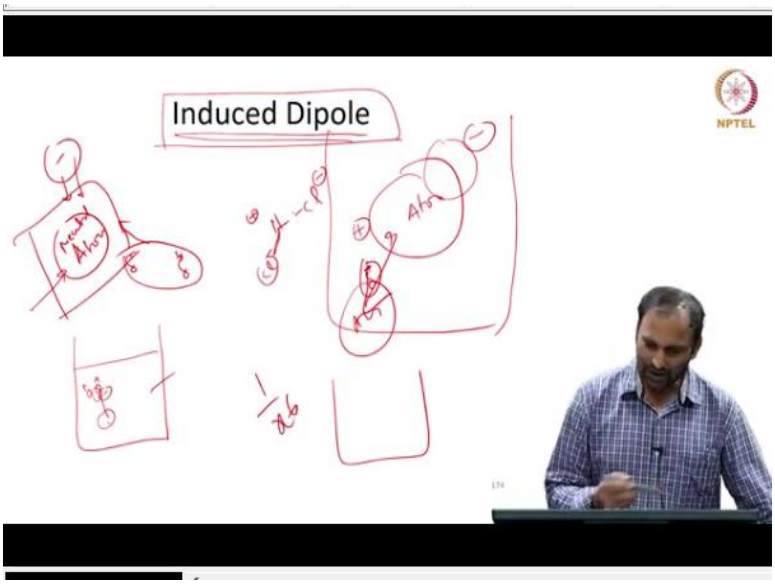

See one thing that is important is that you know see for the induced dipole interactions you know to occur the orientation of the molecule is also important right, ok the orientation of the you know for example if I have like say HCl molecule ok which is say this is slightly negative, this is slightly positive right. Now you know if only if Cl - end comes near H +, there is going to be attraction right okay.

So, anyway. So, in the case of induced dipole what will happen is this right. Now I said that because of the fact that the electrons are not mobile they are moving around, there is going to be a fluctuation in the electron density right, that means if I take you know even a neutral atom or a molecule ok. If you look at some regions of the atom at some particular instant in time they may have a higher density of electrons compared to other regions okay.

So, therefore so the region where there are more electrons will acquire a negative charge and the region where you know there is less electrons will acquire a positive charge. Now this will happen for as I said right this only occurs momentarily and this can happen for may happen may not happen is a statistical process right, it can happen for a large number of molecules which may be in a container.

Now if the orientation of the molecules are such that ok, if there is another you know again a neutral atom which has been polarized because of the change in the fluctuation right**.** Therefore so if there is a negative end and there is going to be. So, if you sum up all the interactions such interactions it will turn out that okay, the overall interaction is going to be attractive okay.

It will go as 1 over x power 6 dependence okay yeah, if you can read up a little bit about it okay. So, what I will do is I mean so yeah so maybe I will just stop here okay. So, we have kind of talked about the van der Waals interaction between you know atoms and molecules. I have introduced you different terms, we know where the van der Waals interactions come about now okay.

So, we will try and extend these concepts to van der Waals interaction between colloidal particles okay. If I have colloidal particle 1, colloidal particle 2 okay. So, we will see how do we think about van der Waals interaction between particles in the next class okay.