

Interfacial Engineering

Dr Manigandan S.

Department Chemical Engineering

Indian Institute of Technology, Ropar

Lecture-13

Girifalco-Good Fowkes equation; Tutorial

Girifalco-Good-Fowkes equation; dispersion component

Welcome back.

So, in today's video lecture, we will look at the molecular interpretation of surface tension. So, how I mean we will understand the role of surface tension when we want to determine the you know work required to pull the molecule near the interface you know to the interface right. So we have a couple of equations, a famous equation proposed by Girifalco and Fowkes, right But that involves the use of the London dispersion force. Because it involves the use of London dispersion force, we will also look at, along the line, we will also look at other types of physical forces as well. So in today's video lecture, we will look at the different types of physical forces, you know, with addition to the London dispersion force and we will look at the Girifalco Fowkes equation to understand the role of surface tension from the molecular perspective.

(Time:01:40)

Girifalco-Good Fowkes equation Tutorial **Molecular interpretation of surface tension** NPTEL

❖ Several broad categories of molecular interactions are listed below.

Electronegative **Hydrogen bonding**

Physical state of a compound determines the strength of a hydrogen bond.

The force of attraction between hydrogen and fluorine

Intermolecular hydrogen bonding:
Hydrogen bonding that exists between the different molecules.
Boiling point of H_2S is -60°C
E.g. Water

Intramolecular hydrogen bonding:
Hydrogen bonding that exists within the same molecules.
Boiling point of H_2O is 100°C
E.g. Ethylene glycol

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Let's begin. yeah so as just now we described so we will understand the different types of forces because we want to know what is a London dispersion force but as we you know talk about London dispersion force we can also look at the other types of forces as well so let's first start with the the hydrogen bonding okay let's understand what is hydrogen bonding and we have you know metallic bonding and we have you know London dispersion force and we also have you know dipole-dipole force right. So, first you just look at the hydrogen bonding. So, hydrogen bonding occurs there are at A couple of, you know, the two types of hydrogen bonding that, you know, from the molecular perspective.

One is the intermolecular hydrogen bonding. Here, the hydrogen bonding exists between the molecules, right? Two different molecules. The other type is the intramolecular hydrogen bonding. This happens within the molecule, okay? It shares the hydrogen bonding. within the same molecule.

So we can see, let's take an example of the hydrogen fluoride. So how the hydrogen bonding takes place in this case is, you got hydrogen and you have fluorine. Because it has got, you know, number of valence electrons, that is seven. So it hawks electron from the hydrogen so that it can, you know, complete its valency. right, so because fluorine is highly electronegative, okay, and the electron cloud, because it hawks electrons from the hydrogen towards it, the electron cloud will shift from the hydrogen to fluorine, and the probability of electron cloud seen in the fluorine end will be, you know, high, so because of which the fluorine will gain you know net negative charge whereas hydrogen will gain net positive charge okay and because of this hawking tendency fluorine will always gain net negative charge and hydrogen will gain net positive charge and there exists

electrostatic interaction attraction between these two atom within the same molecule right and this is one type of hydrogen bonding So there are some examples for intramolecular hydrogen bonding.

So this hydrogen bonding is very crucial in determining the, you know, physical properties. You can take an example of the, let's say if you take an example of intramolecular hydrogen bonding, let's say ethylene glycol, okay. And intermolecular hydrogen bonding, the example that we can, you know, give is water, right It's the simplest example of intermolecular hydrogen bonding. Hydrogen bonding that exists between the molecules, right Different molecules, okay So you can understand the role of hydrogen. Just if you look at the hydrogen sulfide and the hydrogen, sorry, water in itself, because of the hydrogen bonding, okay in the water molecule, you can see that the physical property is drastically changed.

The boiling point of H_2S and boiling point of water they are, you know, significantly different. It is because of the, you know, presence of hydrogen bonding, okay. So this is one type of, you know, physical force. The other one is metallic bonding. So this exists between metal atoms, okay.

(Time:06:00)

❖ *Metal atoms are neutral in its physical state: An attraction between a sea of valence electrons and metal contributes to the metallic bonding in bulk samples.*

Metallic bonding

❖ **Metallic bonds result from the electrostatic attraction between metal cations and delocalized electrons.**

Examples: Na, Mg, etc.

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So usually these metal atoms are covered by the C-F valence electrons, okay. and there will be, because of the delocalized electron, another atom will gain positive charge and there will be, you know, the attraction between, you know, electrostatic attraction between this metal cation and the delocalized electrons due to which you can expect metallic bonding between the metal atoms. This is another type of physical force we can

say. Here this London dispersion force this is always exist no matter whether the atom is charged or neutral. Because this is I mean this London dispersion force is part of Van der Waals force which we may see in very I mean see in detail when we cover the module 4.

So this London dispersion force is due to the electron fluctuation, the fluctuation in the electron density distribution. So, because electrons are constantly jumping around, okay, you know constantly jumping around that exist, you know difference, I mean there will be density, I mean there will be a fluctuation in the electron density distribution which will result in the net positive and net negative charge. Because the electron density distribution is constantly changing, that will actually cause the atom to gain partial positive and partial negative charges, depending on the cloud of the electrons. you know that are constantly jumping around. So you can expect because this atom gains partial negative and partial positive that can be electrostatic in attraction between positive charge and negative charge due to which you can expect the physical force between these neutral atoms that is due to London dispersion force.

(Time:08:45)

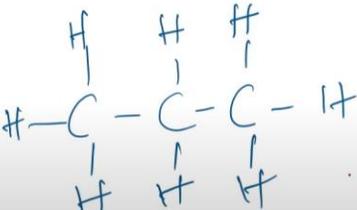
☰ Girifalco-Good Fowkes equation: Tutorial NPTEL

Molecular interpretation of surface tension

Permanent dipole interactions

❖ *Polar molecules have relatively positive and negative regions. Regions of opposite charge on different molecules result in an attraction between these molecules.*

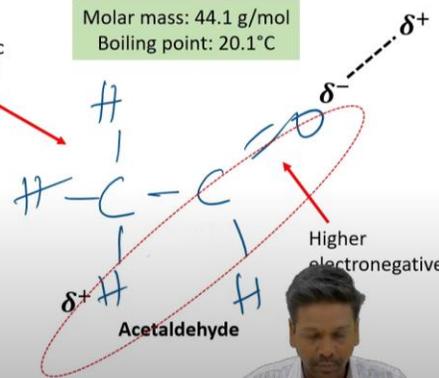
Molar mass: 44.1 g/mol
Boiling point: -42.1°C



Propane

Asymmetric Compound

Molar mass: 44.1 g/mol
Boiling point: 20.1°C



Acetaldehyde

Higher electronegative

☐ Increase in dipole moment increases boiling point of a compound

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So this type of force is called London dispersion force. You also have what is known as permanent dipole interactions. This is also part of Van der Waals interaction. The beauty of this interaction, if you see, it, I mean, the measure, I mean, it is mainly due to the difference in the polarity, right? So this is usually the case for polar molecules, okay So you look at this two chemical compounds, one is propane and the other one is acetone. Although the molar mass of these two chemical compounds is same, you see the physical property, let's say boiling point is drastically different because of the polarity.

So, dipole-dipole interaction, permanent dipole interactions. So, this happens because in this case, this molecule has got oxygen atom, which is a highly negative atom. So, which will hawk electron from the hydrogen, right. So, because this polarity the dipole moment shifts towards the oxygen atom because it hawks electron, right So this end will gain negative charge and the other end will gain the net positive charge. okay, due to which you can expect electrostatic attraction between the molecules.

So this is also one of the Van der Waals forces which we will cover in module 4. Now what we will do is we will try to understand So what we have to do is, our objective for today's lecture is, okay, let's say if I got one molecule here, which is type A, very near to the interface, there's another molecule here, which is type B, okay, and you also have a molecule, sorry, you also have molecules in the bulk, right the molecules in the bulk these molecules are always surrounded by the neighbors right neighboring molecules so you can expect the interaction you know from 360 degree angle so you will have interaction everywhere okay and it is very difficult to separate the molecule from the bulk Whereas here you have the molecule very near to the interface type A molecule and type B molecule. So there can be interaction between these two molecules as they are very near to the interface. So if A-B interaction sometime can overcome the A-A interaction. In such case you can expect that this molecule can be pulled towards the interface, right So this is the, you know, the objective.

So what is the work required to, so we have, so this Girifalco equation is going to tell us about what is the work required to bring this molecule to the interface and form the interface, right So in such case, so how it can be defined is, so we know the Girifalco equation, Okay, so it says that, so you need to calculate individually that is work, okay, required to bring the molecule A, which is nothing but, you know, γ_A . So why γ_A is because there will be interfacial surface tension, right So one has to supply force equivalent of that so that this molecule can work on the surface engine, which is acting downward and can be brought to the interface, right And in addition to it, you also have the interaction rate that is due to A to B, AB interaction. So this energy is actually a bonus for us because this is available naturally for us. So you don't need to supply this energy. So you can subtract this energy so that you can understand what is the energy required to pull this molecule towards the interface.

So this is one way. So this ΔE is associated with the London dispersion force, as we described when we talked about the various types of forces. This is actually given as the geometric mixing rule, which is:

$$\Delta E_{AB} = (\phi_A \gamma_A + \phi_B \gamma_B)^{1/2}$$

This is different from the general mixing rule we often employ, which is:

$$\Delta E_{AB} = \sum \phi_i \gamma_i$$

So in general, the geometric mixing rule is found to be very suitable for this kind of application. That's why it was proposed. Okay, so if I have to use the same for, I mean, for bringing molecule A to the interface, then we need the same work to bring molecule B to the interface. So that is nothing but:

$$\gamma_B - \Delta E_{AB}$$

(Time:14:55)

The screenshot shows a video player with a whiteboard background. The equations written on the board are:

$$(Work)_A = \gamma_A - (\Delta E)_{A-B}$$

$$(\Delta E)_{A-B} = \sqrt{(\phi_A \gamma_A)(\phi_B \gamma_B)} \quad \sum_i \phi_i \gamma_i$$

$$(Work)_B = \gamma_B - (\Delta E)_{A-B}$$

$$(Work)_{total} = \gamma_A + \gamma_B - 2 \sqrt{(\phi_A \gamma_A)(\phi_B \gamma_B)}$$

The video player interface includes a title bar with 'Girifalco-Good Fowkes equation; Tutorial', a progress bar at the bottom showing 14:55 / 20:35, and a small inset video of a man in the bottom right corner.

Right. A, B. All right. So what is the total work then? The total work is going to be the work for A and work for B. So, which means that you have:

$$Work_{total} = \gamma_A + \gamma_B - 2(\phi_A \gamma_A \cdot \phi_B \gamma_B)^{1/2}$$

This is also denoted usually as γ_{AB} , and it is interchangeably used with work total or γ_{AB} . This is known as the Girifalco equation.

However, Fowkes approximates this as the following way. That means the work total is:

$$Work_{total} = \gamma_A + \gamma_B - 2(\gamma_A^{dispersion} \cdot \gamma_B^{dispersion})^{1/2}$$

In this approximation, you need not worry about the ϕ_A and ϕ_B components because Fowkes uses the London dispersion force based on his proposed method. So, he has proposed γ_{AD} and γ_D for several molecules based on this method. The advantage of this method is that γ_D is the same as γ for hydrocarbons.

(Time:16:45)

Unit 16: Girifalco-Good Fowkes equation; Tutorial

NPTEL

γ_{AB}
Fowkes

$$(W_{\text{work}})_{\text{Total}} = \gamma_A + \gamma_B - 2 \sqrt{\gamma_A^d \gamma_B^d} \rightarrow$$

$\gamma = \gamma$ for hydrocarbons

$$(W_{\text{work}})_{\text{Total}} = \gamma_{AB} = \gamma_A + \gamma_B - 2 \sqrt{\gamma_A^d \gamma_B^d}$$

16:45 / 20:35

So, now we know that the total work γ_{AB} is given by:

$$\gamma_{AB} = \gamma_A + \gamma_B - 2(\gamma_{AD} \cdot \gamma_{BD})^{1/2}$$

This is the Girifalco-Fowkes approximation, right. So we will try to solve one problem, you know as part of tutorial today and so then we will use this equation and try to solve the problem, right. Yeah, so here we have got a problem where we need to understand the Girifalco-Good Fowkes, so what we saw right now is the Girifalco-Good Fowkes equation, okay.

So here, so we have been given the interfacial tension, right, for obtained water, obtained mercury, right, and we got water and mercury. So what we are asked to find out is the, you know, gamma D for water and mercury, right. So let's understand this, you know, let's calculate this gamma D for water. And I leave it to you to calculate, sorry, we calculate gamma D for mercury. You can calculate gamma D for water reversal.

So now we know the equation that is gamma AB, which is nothing but, you know, gamma A plus gamma B minus two root over gamma AD and gamma BD, right Right. So let's take the octane problem here. We have the extent is octane mercury. Okay. So, and then we can try to solve the gamma D for mercury.

(Time:18:25)

Estimation of interfacial tensions using the Girifalco-Good-Fowkes equation

The following are the interfacial tensions for the various two-phase surfaces formed by n-octane (O), water (W), and mercury (Hg): for n-octane-water, $\gamma = 50.8 \text{ mJ m}^{-2}$; for n-octane-mercury, $\gamma = 375 \text{ mJ m}^{-2}$; and for water-mercury, $\gamma = 426 \text{ mJ m}^{-2}$. Assuming that only London forces operate between molecules of the hydrocarbon, use Equation described below to estimate γ^d for water and mercury. Do the values thus obtained make sense?



So for octane mercury, we know the equation that is 375, right? Millijoule per meter square. Okay. So let's use that.

Yeah. So we know this one. This is 375 octane mercury. And octane is 22, right? Plus mercury is also given. If I'm correct, it is 465. I think this is 465 minus 2. And so since we said gamma d is also nothing but gamma, you know, you can take as it is, this one as it is, so which is 22, right? Okay, into, and this we need to calculate, right? Okay, so in this case, you can calculate then, you know, So we have this one, gamma B, D, okay, 1 by 2, right? So this you can say that 375 minus 22 minus 465 divided by, you have, you know, 22 into 2, so 22 power 1 by 2, right? Yeah, into 2.

(Time:20:05)

Unit 10: Surface Tension - Good Fowkes equation; Tutorial

NPTEL

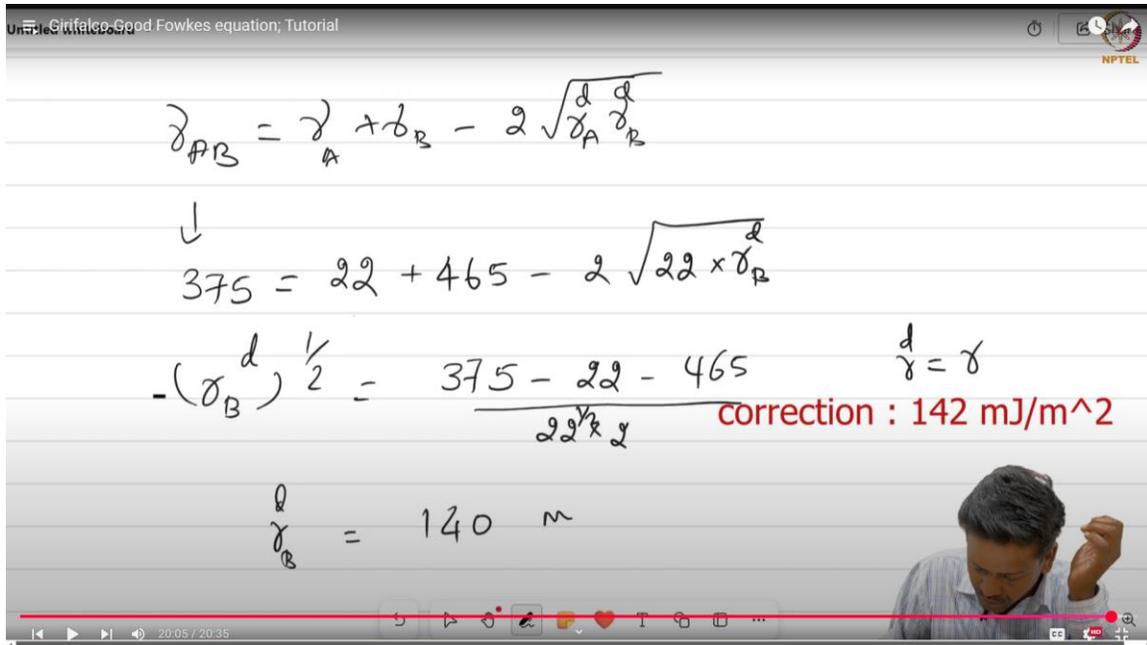
$$\gamma_{AB} = \gamma_A + \gamma_B - 2\sqrt{\gamma_A^d \gamma_B^d}$$

$$\downarrow$$

$$375 = 22 + 465 - 2\sqrt{22 \times \gamma_B^d}$$

$$-(\gamma_B^d)^{\frac{1}{2}} = \frac{375 - 22 - 465}{2 \times 22} \quad \frac{d}{\gamma} = \gamma$$

correction : 142 mJ/m²

$$\gamma_B^d = 140 \text{ mJ/m}^2$$


So, you can check, I think this is simply 140 millijoules per meter square. You can check this one, okay? Similar way, you can calculate the gamma d for water, right So that I have given to you as an exercise for you to do yourself.

We will stop here. We will continue from the next lecture.

Thank you.