

Interfacial Engineering

Dr Manigandan S.

Department Chemical Engineering

Indian Institute of Technology, Ropar

Lecture-09

Contact angle for ideal and non-ideal cases; Application of Young-Dupre

Contact angle for surfaces with chemical heterogeneities and roughness; Cassie-Baxter; Wenzel state

Welcome back. So in today's video lecture, we will look at the contact angle for non-ideal cases. Okay. In a couple of lectures ago, we have looked at the Young-Dupré equation derived for, you know, ideal case, right? So in today's equation, we will look at the the contact angle for non-ideal case and along with that we will also look at the application of Young-Dupré equation. So these are going to be the learning objectives of this lecture. Let's begin.

(Time : 01:10)

☰ Contact angle for ideal and non-ideal cases; Application of Young-Dupre

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(i) Contact angle for non-ideal cases

(ii) Applications of Young-Dupre

Young-Dupre

$$\cos\theta = \frac{\gamma_{SG1} - \gamma_{SL}}{\gamma_{LV}}$$

Assumpt

As I just mentioned, we will look at the contact angle for non-ideal cases. Okay. Contact angle for non-ideal cases. Right.

And apart from that, we will also look at the application of Young-Dupre equation in this lecture. All right. So we know that the contact angle of Young-Dupré equation can be described in this way. So, this we have already looked at in previous lecture. So, this equation describes this phenomenon.

Whenever you place a droplet of liquid on a smooth surface, okay the droplet may wet or retract depending on the nature of the solid right solid surface right and this behavior is captured by this Young-Dupré so this is nothing but so using Young-Dupré equation one can understand the nature of the surface by, you know, evaluating the three-phase contact angle. Three-phase contact angle is given in this schematic also. This is nothing but three-phase contact angle because at this juncture, all three phases exist like, you know, solid-gas, solid-liquid and solid, you know, I mean liquid gas, right. That's why we call it theta you know, measured at this juncture as three-phase contact angle. So, remember when we derived this equation, we made some assumptions, which means that this equation is applicable, only these assumptions are made, right.

So, the first and foremost assumption that we mentioned was equilibrium is attained. So, this theta that we measure is equilibrium contact angle. Okay, so that is our first assumption. The second and third assumptions are it is applicable for surfaces with homogeneous you know and surfaces I mean surfaces with which are chemically homogeneous and which are you know which are smooth right. So, which means that they are not, this equation is not applicable for surfaces which are homogeneous, okay, sorry, which are heterogeneous and surfaces with roughness, right.

So, these two, how do we encounter whenever, you know, we face this kind of a situation, how we can, you know, revisit the equation. Is that, I mean, that is what exactly we are going to look at. and the last one is nothing but the no absorbing of liquid by the surface. So well this part we will cover in the following lecture but in today's lecture we are only going to look at How we can tackle when we deal with surface with heterogeneous and surface with roughness. So we have got two models.

(Time:04:50)

Contact angle for ideal and non-ideal cases; Application of Young-Dupre

Assumptions:

- ✓ (i) Equilibrium is attained.
- ✓ (ii) For surfaces which are homogeneous
- ✓ (iii) Not valid for surfaces with roughness
- ✓ (iv) No absorption of liquid by the surface

Two Models:

- (i) Cassie-Baxter
- (ii) Wenzel state.

One is nothing but Cassie-Baxter. The other one is Wenzel state. Okay, so this Cassie-Baxter model comes from the Cassie's law itself. Okay, so what does this law says is that whenever you have surface with, you know, which is porous in nature, right? So in such case, let's say I can draw a schematic, right? Okay, let's say we have a surface where we have a type I impurity and we have you know okay we have let's say we have type I impurity at the same time we also consider surface with porous you know porosity right. In that case you have a segment where you have surface corresponds to type I okay and and zone where you will have a zone which is filled with air pockets.

So in this case this particular zone is filled with air pockets because of the you know, the factor that we mentioned, right, just now, which is the surface which has high porosity, right? So in this case, so what will happen is whenever we spread a droplet, in this zone, because this zone is filled with, I mean, air pockets, water, it doesn't allow water to penetrate inside this door, right? So, in such case, we can assume that theta will be, you know, 180 degree, which means that it will completely the water molecule cannot enter into this zone so that the theta in this case will be you know the droplet in this case will not be spread at all will not spread at all so in such case we can say theta we can denote theta as you know 180 degree okay so whenever we deal with a combination of you know you know, properties, right? So we always have used what is known as lever rule. Whenever we deal with, you know, mixture or whenever we deal with a combination of properties, right? So, in this case, we know the Young-Dupré equation. I denote Young-Dupré equation with the theta. We do γ as in the in the subscript.

Well, okay. Along with the θ so that this is nothing but theta for the Young-Dupré case, right? So, which is nothing but

$$\theta = \frac{\gamma_{SG} - \gamma_{SL}}{\gamma_{LG}}$$

We know that the same θ will not be applicable here, but whenever we want to measure θ in this case as a property, whenever we deal with a mixture or a combination of several properties, in such cases, we use the lever rule, which is something like, So, in this case, since we deal with the surface, we can call it as fraction 1. So 1 represents type 1, right? So the fraction of type 1 molecule which is F_1 multiplied by $\cos\theta_2 \cos\theta_1$. Right, because this θ corresponds to type 1 surface. Then you can say $F_2 \cos\theta_2$. Okay. Because for brevity, we're only considering two kinds of surfaces, right? One is the air pocket itself, another one is a type I surface. So, in this way, you can also simplify this equation in this way:

$$F_1 \cos\theta_1 + (1-F_1) \cdot (-1)$$

Since just now we mentioned that the air pocket will not allow the water molecule to penetrate inside, so we can theoretically assume θ to be 180 degrees, which means that $\cos 180 = -1$. So we can simply write this equation as minus 1 minus F_1 epsilon.

(Time:09:55)

The screenshot shows a video lecture interface. At the top, there is a title bar with the text "Contact angle for ideal and non-ideal cases: Application of Young-Dupre" and a handwritten note " $\theta \approx 180^\circ$ ". The main content is handwritten on a white background with horizontal lines. It starts with the text "Lever rule" underlined. Below it, the equation $\cos \theta = \frac{\gamma_{SG} - \gamma_{SL}}{\gamma_{LG}}$ is written. Further down, the equation is modified to $\cos \theta = f_1 \cos \theta_1 + f_2 \cos \theta_2$, which is then simplified to $= f_1 \cos \theta_1 + (1-f_1)$. At the bottom right, a small video inset shows a man in a light blue shirt looking down. The video player controls at the bottom show a progress bar at 9:55 / 28:09.

So this is how the equation can be modified. So in this way, I want to denote theta... with the subscript c, which represents Cassie's model.

So this equation, we can obtain a compact equation from the Young-Dupré Equation that we just now shown, which I have just now shown. So now, this is nothing but Cassie's law itself. Right now, what is Cassie Baxter? So that is what we have to look at. What is

Cassie Baxter? OK, so this is the modified version of Cassie's law itself. So in Cassie Baxter, what we consider is instead of considering the air pockets, we consider, you know, different types of surfaces, right? I mean, we consider different types of surfaces instead of, you know, air pockets, right? So let's say you have a surface which has got different chemical heterogeneity, right? Okay.

Right. So you have, let's say in this case, we have type 1 impurity and type 2 impurity. So we considered two types of impurities in this case. Just to understand, to get, you know, for brevity we have just considered two types of surfaces, but one can have numerous types of surfaces as well. We will see how, you know, we can you know, obtain equation, you know, for cases where we deal with numerous types of surfaces. For now, we will consider only a surface which has two different types of chemical heterogeneities okay one is type one and another one is type two so in this case the same lever can be applied so in this case i will use $\cos \theta$ as C_b which represents cassie baxter. So this can be written in this way, which is nothing but:

$$F_1 \cos \theta_1 + F_2 \cos \theta_2$$

Right.

And so sometimes you might deal with the surface, okay, with numerous, you know, chemical heterogeneities. In such case, you can simply represent, you know, the Cassie-Baxter model in this way, which is simply nothing but:

$$\sum_i f_i \cos \theta_i$$

Right? Because when you have numerous types of surfaces, you can simply represent the Cassie-Baxter model in this fashion, right? So the next comes the surface with roughness, okay? So we have seen Cassie's law, you know, whenever the surface, so you consider in this case, surface with porosity. The second one we dealt with was Cassie-Baxter. In this case, you have to consider, you know, a surface with numerous types of, you know, heterogeneities, right? The next one that we will deal with is a surface with roughness, right? So in this case, what we will have is the Wenzel model, right? Wenzel's state, okay?

Okay, so what does it say? Let's say you have a surface with roughness, right? Something like this, right? So this roughness indicates that the interfacial area is more than the surface area of the smooth surface itself, right? So because it has got more exposure, the roughness factor will amplify the nature of the surface. Say for example, if the surface is hydrophilic, the roughness will make the surface more hydrophilic.

It is because this interfacial area is more significant than the surface with the smooth surface, right? So on the other hand, if the surface is originally hydrophobic, the roughness makes the surface more hydrophobic, okay, than the previous case. So that's what we need to understand in this case whenever we deal with a surface with roughness, okay. So Wenzel state says that, you can use the Young's equation as it is, right, but with some correction factor which is nothing but β . So β is nothing but the ratio of actual area to the projected area.

$$\beta = \frac{A_{actual}}{A_{projected}}$$

So β is always greater than 1 because the actual area in the case of a surface with roughness is higher than the projected area. So this factor will enhance the nature of the surface. If the surface is hydrophobic, the roughness will make the surface more hydrophobic. If the surface is hydrophilic, the roughness will make the surface more hydrophilic.

Right? So in these modifications help us revisit the Young-Dupre equation and use the modified equation derived from the Young-Dupre. depending on the situations, you know, we deal with. Right Right. So these are some deviations that we have seen so far. And one other, I mean, the other deviation that we have not looked at in this lecture is that what if the surface is imbibing in nature? If the surface is absorbing some amount of liquid, for such case, we will have to use a different equation what is known as Washburn equation, which you will see in the, you know, not in today's lecture, but in following lecture we will see.

So now we move on to the second aspects of our learning objective. That is nothing but the application of Young-Dupre. Application of Young-Dupre. So consider whenever we, especially in pharmaceutical industries or healthcare industries, whenever we deal with dry solid or dry powder and mix, I mean, whenever you mix these dry powder or dry solids with the liquid, okay, it always generates some amount of heat, right? As a result of, you know, the mixing, right soaking the dry powder into liquid it releases some amount of heat right so although the fraction of heat that is released out of this process is you know not very significant whenever we deal with product like you know API drug products are drug products, even a small amount of heat released from the this and from this process, we make the product with, you know, we'll deteriorate the product, right? So we'll affect the product quality. So that's why sometimes it is very important to understand, okay, so whenever we, you know, deal with mixing, and those operations, are we adding right amount of dry powder, you know, or are we mixing, are we soaking these dry powders with the right amount of liquid.

So these questions we often ask so that we can you know we can quantify the amount of heat released and if and then say that you know this and this factor will not affect the quality of the product. So that is the exact objective of this exercise. So First, let us understand how this application of Young-Duprey can be utilized. So, let's say we are talking about a scenario where you have dry solid, okay, and soaking that with liquid and it becomes wet solid, okay. So, in this process, it releases some amount of heat, okay.

So, what will happen is the, let's say if you are calculating the delta H immersion, okay, which is nothing but H, you know, enthalpy of wet solid minus enthalpy of dry solid. . You expect that in this case, some amount of heat is released, right? So this is what is our problem statement. Okay, so how do we calculate this $\Delta H_{\text{immersion}}$? So that is the question that we are trying to address, right? So before that, let's understand, you know, what is the The fundamental equation that we know in terms of Gibbs free energy, which is nothing but

$$G = H - TS$$

where S is the entropy here and T is the temperature. And we also know Gibbs free energy in differential form, which is nothing but:

$$dG = -S dT + V dP$$

Okay? Right? So at constant pressure, we know that:

$$\left(\frac{\partial G}{\partial T}\right)_P = -S$$

(Time:22:41)

Handwritten equations on a whiteboard:

$$G = H - TS$$
$$dG = -S dT + V dP$$
$$\left(\frac{\partial G}{\partial T}\right)_P = -S$$
$$\frac{G}{A} = \delta$$
$$G = H - TS$$

The video player interface at the bottom shows a progress bar at 22:41 / 28:09 and various control icons.

Okay, right. So sometimes we also, you know, refer to the Gibbs excess free energy as G/A itself, which is Gibbs free energy measured per unit area. This is also nothing but γ , which is surface tension. This notation is sometimes used without the differential form. So, G/A gives the energy measured per unit area, is nothing but surface tension, right? So, what we can do is, we can revisit the equation that we mentioned here, that is $G = H - TS$. I can also, you know, slightly modify this equation so that, you know, I can bring in, bring this γ into this equation, right? So what I will do is I will simply mention G as superscript S , which represents excess Gibbs free energy measured per unit area. Right? So you can also represent in the same way, you can also represent entropy superscript S as $-T * (\partial G^S / \partial T)_P$.

Okay? So what it represents is we have normalized each term with respect to area. Okay? So in this case, I can simply write G^S as γ itself, okay? In this way, I could bring γ into this equation. Then you have $H^S - T * (\partial \gamma / \partial T)_P$, right?

So we know, you can also write this as γ , right? $G^S = \gamma$. So you can write as:

$$H^S = \gamma - T * (\partial \gamma / \partial T)_P$$

(Time:25:31)

The video frame displays the following handwritten equations:

$$H^S = \gamma - T \left(\frac{\partial \gamma}{\partial T} \right)_P$$

$$\Delta H_{imm}^S = H_{SL}^S - H_{SG}^S$$

$$\Delta H_{imm}^S = \left[\gamma_{SL} - T \left(\frac{\partial \gamma_{SL}}{\partial T} \right)_P \right] - \left[\gamma_{SG} - T \left(\frac{\partial \gamma_{SG}}{\partial T} \right)_P \right]$$

So we know then what is H^S , which is nothing but $\gamma - T \frac{d\gamma}{dT}$, right? So this we know, we have obtained from this equation. Now we know for H^S , but we're talking about ΔH_{imm} , which is nothing but H_{wet} , wet means SL , right? Subscript SL , then H_{dry} solid, which is nothing but SG , right? So, if I can, so then I specify ΔH_{imm}^S , then I will use the

notation same for all the term. In this way, I can rewrite this equation in this way that is nothing but:

$$H_{SL} = \gamma_{SL} - T * (\partial\gamma_{SL}/\partial T)_P$$

$$H_{SG} = \gamma_{SG} - T * (\partial\gamma_{SG}/\partial T)_P.$$

(Time:27:36)

Handwritten equations from the video:

$$-\Delta H_{imm}^S = \gamma_{LG} \cos\theta + T \cos\theta \left(\frac{\partial \gamma_{LG}}{\partial T} \right)_P + T \gamma_{LG} \left(\frac{\partial \cos\theta}{\partial T} \right)_P$$

$$-\Delta H_{imm}^S \Rightarrow$$

So we know that:

$$\gamma_{SL} - \gamma_{SG}$$

Okay, so this is nothing but $\gamma_{SL} - \gamma_{SG}$, and if I take out the T, then this is nothing but:

$$\gamma_{SG} * (\partial\gamma_{SG}/\partial T)_P - \gamma_{SL} * (\partial\gamma_{SL}/\partial T)_P$$

Okay, so we know that if I apply the minus everywhere, then I will be having this will be:

$$\gamma_{SG} - \gamma_{SL} = \gamma_{LG} * \cos(\theta) + T * (\partial(\gamma_{LG} * \cos(\theta)) / \partial T)_P$$

So if you expand this further, so you will have:

$$\gamma_{LG} * \cos(\theta) + T * \cos(\theta) * (\partial\gamma_{LG}/\partial T)_P + T * \gamma_{LG} * (\partial\cos(\theta)/\partial T)_P$$

So if you see all you need to know is what is the γ_{LG} and the regression of γ_{LG} and $\cos(\theta)$ on T, right? In this way, you can calculate what is the ΔH_{imm} of, you know, solid, dry solid, you know, whenever it is soaked with liquid, right, immersed with liquid, what is the amount of heat released from the process? That is exactly what we

calculate using this equation. So, this equation has been verified. Although we have complemented, I mean, we have several sophisticated techniques, okay, like calorimetric technique to measure this small amount of heat that is released, you can use this equation to complement the research, calorimetric research, right? You know, to validate the research, right? So in this way, this equation can be used to compute the amount of heat released from the process, right? The quenching process, right? So we'll stop here. We'll continue from the next lecture. Thank you.