Date: 23.02.22

Class 17

For vdw component of intermoleculer interaction, we have $\gamma_{12}^{LW} = \sqrt{\gamma_{11}^{LW} \cdot \gamma_{22}^{LW}}$ ← (A1)

This Leads to $\Delta G_{12}^{LW} = -2\sqrt{\gamma_1^{LW}\gamma_2^{LW}}$

And: $\gamma_{12}^{LW} = \left(\sqrt{\gamma_1^{LW}} - \sqrt{\gamma_2^{LW}}\right)^2$ Positive

For polar interaction: (1) $\gamma_1^{AB} = 2\sqrt{\gamma_1^{+} \cdot \gamma_1^{-}}$ ← (A2)

(2) $\Delta G_{12}^{AB} = -2\left[\sqrt{\gamma_1^{+}\gamma_2^{-}} + \sqrt{\gamma_1^{-}\gamma_2^{+}}\right]$ ← (A3)

$\Delta G_{12} = \Delta G_{12}^{LW} + \Delta G_{12}^{AB}$

$\Delta G_{12} = \gamma_{12} - (\gamma_1 + \gamma_2)$

1 2

1 | 2

Now $\Delta G_{12}^{AB} = \gamma_{12}^{AB} - (\gamma_1^{AB} + \gamma_2^{AB})$

$\Rightarrow \gamma_{12}^{AB} = \Delta G_{12}^{AB} + (\gamma_1^{AB} + \gamma_2^{AB})$

Cohesive Polar Int.

Adhesive Polar Interaction

$$\gamma_{12} = \gamma_{12}^{LW} + \gamma_{12}^{AB}$$

$$= \left(\sqrt{\gamma_1^{LW}} - \sqrt{\gamma_2^{LW}}\right)^2 + 2\left[\underbrace{\left(\sqrt{\gamma_1^+\gamma_1^-} + \sqrt{\gamma_2^+\gamma_2^-}\right)}_{\text{Cohesive Polar Comp.}} - \underbrace{\left(\sqrt{\gamma_1^+\gamma_2^-} + \sqrt{\gamma_1^-\gamma_2^+}\right)}_{\text{Adhesive Component}}\right]$$

$1]^3 \quad [1 \rightarrow 1 \,|^{3}\, 1$

$$\rightarrow \Delta G_{131} = \cancel{\gamma_{11}}^{\,0} - (\gamma_{13} + \gamma_{13})$$

$$= -2\gamma_{13}$$

$$\Delta G_{131} = -2\gamma_{13}$$

$$= -2\left[\gamma_{13}^{LW} + \gamma_{13}^{AB}\right]$$

$$= -2\left[\underbrace{\left(\sqrt{\gamma_1^{LW}} - \sqrt{\gamma_3^{LW}}\right)^2}_{A} + 2\underbrace{\left(\sqrt{\gamma_1^+\gamma_1^-} + \sqrt{\gamma_3^+\gamma_3^-}\right)}_{B} - 2\underbrace{\left(\sqrt{\gamma_1^+\gamma_3^-} + \sqrt{\gamma_1^-\gamma_3^+}\right)}_{C}\right]$$

$$\Delta G_{131} = -2\gamma_{13}$$
$$= -2\left[\gamma_{13}^{LW} + \gamma_{13}^{AB}\right]$$
$$= -2\left[\underbrace{\left(\sqrt{\gamma_1^{LW}} - \sqrt{\gamma_3^{LW}}\right)^2}_{A} + \underbrace{2\left(\sqrt{\gamma_1^+\gamma_1^-} + \sqrt{\gamma_3^+\gamma_3^-}\right)}_{B} - \underbrace{2\left(\sqrt{\gamma_1^+\gamma_3^-} + \sqrt{\gamma_1^-\gamma_3^+}\right)}_{C}\right]$$

3 Apolar: Most Organic Solvents
Nail Polish Remover
Pen Ink

Case 1: Both 1 and 3 Apolar → B = 0, C = 0, A = +ve

$\therefore$ $\Delta G_{131} = -ve$ → Coagulation.

Case 2: Everything Non Zero → Possibility of Getting Stable Colloid only when $|C| > |A| + |B| \Rightarrow \Delta G_{131} > 0$

→ It may be possible to have coagulation $|C| < |A| + |B|$.

$$\Delta G_{131} = -2\gamma_{13}$$

$$= -2\left[\gamma_{13}^{LW} + \gamma_{13}^{AB}\right]$$

$$= -2\Bigg[\underbrace{\left(\sqrt{\gamma_1^{LW}} - \sqrt{\gamma_3^{LW}}\right)^2}_{A} + \underbrace{2\left(\sqrt{\gamma_1^+\gamma_1^-} + \sqrt{\gamma_3^+\gamma_3^-}\right)}_{B} \underbrace{-2\left(\sqrt{\gamma_1^+\gamma_3^-} + \sqrt{\gamma_1^-\gamma_3^+}\right)}_{C}\Bigg]$$

Lets say 1 is a polar, 3 is polar.

$\gamma_1^+ = 0, \gamma_1^- = 0 \rightarrow$ 3 Polar terms = 0

Both C terms = 0

Case 3 : a-Polar Solid (1) in a Polar liquid (3),

3A / 3B

$\gamma_1^+ = 0, \quad \gamma_1^- = 0$ $\qquad \gamma_3^+ \neq 0, \quad \gamma_3^- \neq 0$

→ Coagulation. as

A = +ve

B = Exists because $\sqrt{\gamma_3^+\gamma_3^-}$, +ve

C = Does not Exist.

Polar Solid in an a Polar Liq

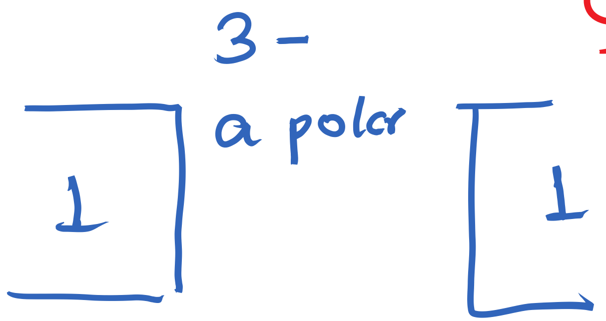
A = +ve, B = +ve, C = 0

Coagulation :

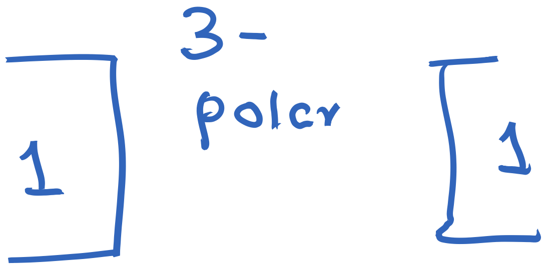
$\gamma_{13} = +ve$

ΔG_{131} is more Negative had been 1 and 3 a polar.

Case 1



Case2



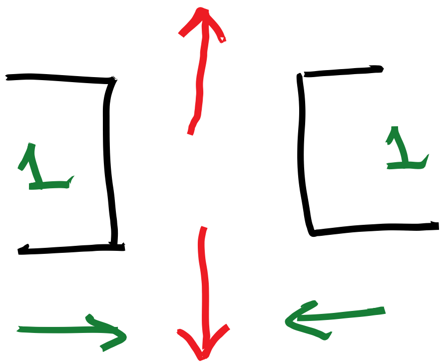
1 is a-polar. → Colloidal coagulation is Thermodynamically more favored in Case 2.

ΔG_{131} = Term 1 only

ΔG_{131} = Term 1 + One term of Term B

$\sqrt{\gamma_3^{+}\gamma_3^{-}}$

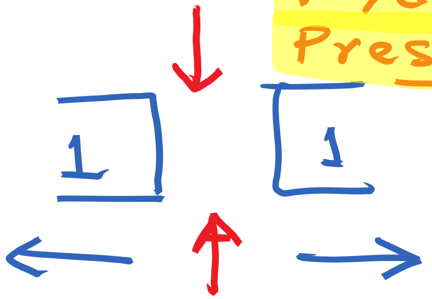
Hydrophobic Repulsion.



Squeezed out

Can you locate a flow?

Hydration Pressure



Case 4: Monopolar material → Either $\gamma^+ \neq 0$ or $\gamma^- \neq 0$

Polar material

We have a monopolar Solid & a Monopolar Liquid →

Uniqueness of monopolar material in terms of **Surface** & **interfacial Tension**.

$$\gamma_1^{AB} = 2\sqrt{\gamma_1^+\gamma_1^-} = 0$$

Surface Tension = LW component only.

$$\gamma_{13}^{AB} = 2\left[\left(\sqrt{\gamma_1^{LW}} - \sqrt{\gamma_2^{LW}}\right)^2 + \left(\underbrace{\sqrt{\cancel{\gamma_1^+}\gamma_1^-}}_{0} + \underbrace{\sqrt{\gamma_3^+\gamma_3^-}}_{\text{Depends on the Nature of } 3}\right) - \left(\underbrace{\sqrt{\cancel{\gamma_1^+}\gamma_3^-}}_{0} + \underbrace{\sqrt{\gamma_1^-\gamma_3^+}}_{\text{NOT ZERO}}\right)\right]$$

Let's say $\underbrace{\gamma_1^+ = 0,\ \gamma_1^- \neq 0}$

$$\Delta G_{131} = -2\gamma_{13}$$
$$= -2\left[\gamma_{13}^{LW} + \gamma_{13}^{AB}\right]$$
$$= -2\left[\underbrace{\left(\sqrt{\gamma_1^{LW}} - \sqrt{\gamma_3^{LW}}\right)^2}_{A} + 2\underbrace{\left(\sqrt{\gamma_1^+\gamma_1^-} + \sqrt{\gamma_3^+\gamma_3^-}\right)}_{B} - 2\underbrace{\left(\sqrt{\gamma_1^+\gamma_3^-} + \sqrt{\gamma_1^-\gamma_3^+}\right)}_{C}\right]$$

Coagulation is promoted ONLY by LW Component, AND NOT by the Cohesive Polar Component.

5 Special Case : Both 1 and 3 are mono-polar.

$$\left[\begin{array}{ccc} \gamma_1^+ = 0 & \text{or} & \gamma_1^- = 0 \\ \gamma_3^+ = 0 & & \gamma_3^- = 0 \end{array}\right]$$

Case 1

Both Term B and C = 0

Interfacial Tension entirely governed by LW interaction.

Case 2: MOST FAVORED Possibility of forming stable Colloid

$$\left[\begin{array}{ccc} \gamma_1^+ = 0 & \text{or} & \gamma_1^- = 0 \\ \gamma_3^- = 0 & & \gamma_3^+ = 0 \end{array}\right] \rightarrow$$

Both Terms of B = 0

one Term of C = 0 But one Term of C is NON ZERO.

The possibility of the formation of a stable colloidal dispersion is maximum when 1 and 3 are mono polar and have opposite polarity.

As, therm B is $= 0$

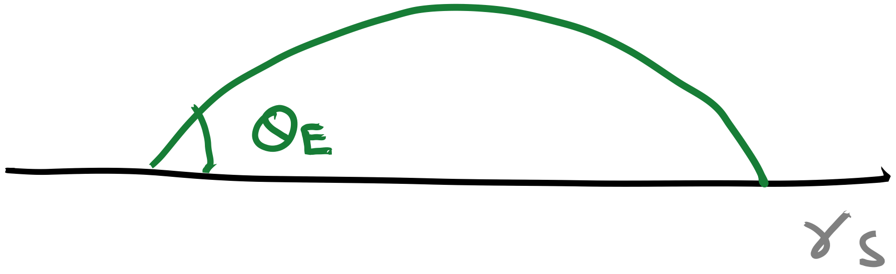
↳ The cohesive part of polar interaction, which favors coagulation is Absent.

So the adhesive polar interaction (c) just has to overcome the LW interaction (Term A).

Young's Equation: -

Contact Angle Goniometer.

It is possible to measure θ_E.



→ Conclusion: If the Liquid is Water → Whether the Surfece is Hydrophobic or Hydrophilic

$\theta_{E_1} = 105^\circ$ vs $\theta_{E_2} = 135^\circ$ → More Hydrophobic

It becomes possible to determine the Surfece Tension of an unknown Solid Sample → with the help of some Liquids.

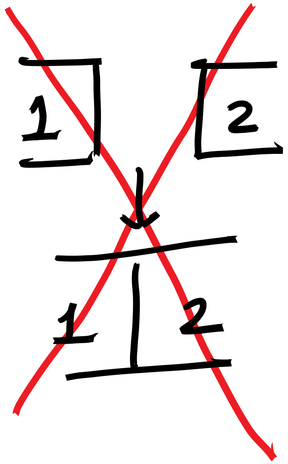
γ_s can be determined

$$\gamma_s = \gamma_s^{LW} + \gamma_s^{AB}$$

If γ_s^{LW}, γ_s^{+}, γ_s^{-} are known, then γ_s can be determined.

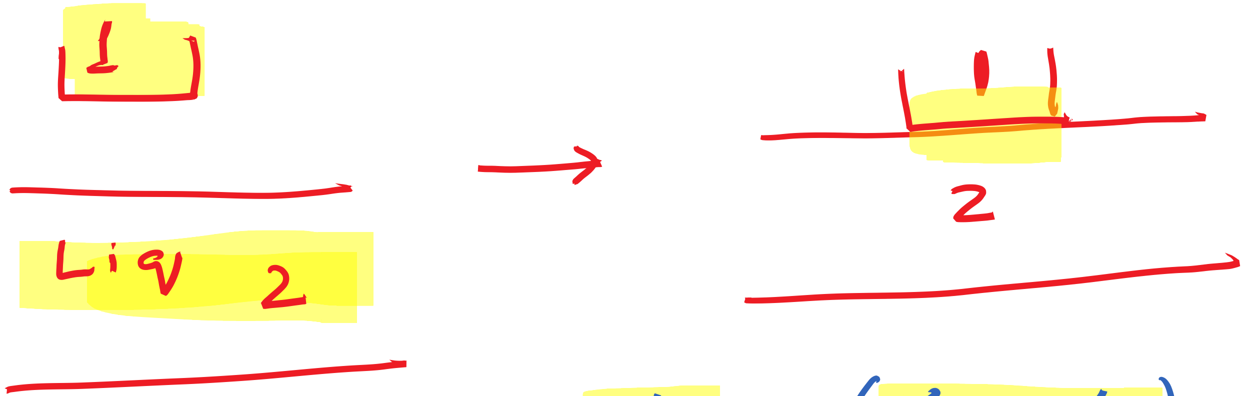
$$\gamma_s^{AB} = 2\sqrt{\gamma_s^{+}\gamma_s^{-}}$$

$$\Delta G_{12} = \gamma_{12} - (\gamma_1 + \gamma_2)$$ Generic

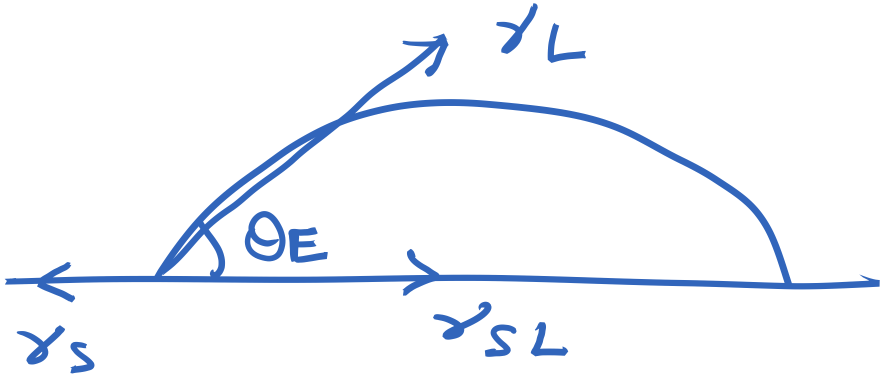


The above expression is not limited to this condition only.

It is valid for any interface between two non condensed phases.



$$\Delta G_{12} = \gamma_{12} - (\gamma_1 + \gamma_2)$$



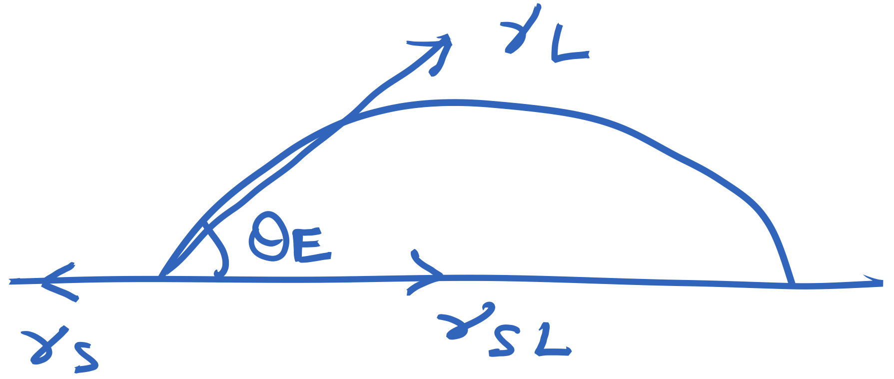
$$\gamma_S = \gamma_{SL} + \gamma_L \cos\theta_E$$

We can write

$$\Delta G_{SL} = \gamma_{SL} - (\gamma_S + \gamma_L)$$

$$\Rightarrow \gamma_{SL} = \Delta G_{SL} + (\gamma_S + \gamma_L)$$

$$\gamma_S = \gamma_{SL} + \gamma_L \cos\theta_E \quad — \; (1)$$



$$\Delta G_{SL} = \gamma_{SL} - (\gamma_S + \gamma_L)$$

$$\Rightarrow \quad \gamma_{SL} = \Delta G_{SL} + (\gamma_S + \gamma_L) \quad — \; (2)$$

Substitute γ_{SL} from (2) to (1), we get.

$$\gamma_S = \Delta G_{SL} + \gamma_S + \gamma_L + \gamma_L \cos\theta_E$$

$$\Rightarrow \quad \gamma_L(1 + \cos\theta_E) = -\Delta G_{SL} = -\left(\Delta G_{SL}^{LW} + \Delta G_{SL}^{AB}\right)$$

$$\rightarrow \quad \Delta G_{SL}^{LW} = -2\sqrt{\gamma_S^{LW} \cdot \gamma_L^{LW}}$$

$$\rightarrow \quad \Delta G_{SL}^{AB} = -2\left[\sqrt{\gamma_S^{+} \cdot \gamma_L^{-}} + \sqrt{\gamma_S^{-} \cdot \gamma_L^{+}}\right]$$

$$\underbrace{\gamma_L(1+\cos\theta_E)}= 2\left[\sqrt{\gamma_S^{LW}\gamma_L^{LW}} + \sqrt{\gamma_S^{+}\gamma_L^{-}} + \sqrt{\gamma_S^{-}\gamma_L^{+}}\right]$$

Young Dupre Eqn.

Objective: Is to determine γ_S^{LW}, γ_S^{+}, γ_S^{-}

What we do: We take 3 Liquids (probe Liquids),

for each one γ_L^{LW}, γ_L^{+}, γ_L^{-} is known

Put them on Solid surface.

Liquid 1	$\gamma_{L_1}^{LW}$	$\gamma_{L_1}^{+}$	$\gamma_{L_1}^{-}$	γ_{L1}	$\rightarrow \theta_{E_1}$
Liquid 2	$\gamma_{L_2}^{LW}$	$\gamma_{L_2}^{+}$	$\gamma_{L_2}^{-}$	γ_{L2}	$\rightarrow \theta_{E_2}$
Liq 3	$\gamma_{L_3}^{LW}$	$\gamma_{L_3}^{+}$	$\gamma_{L_3}^{-}$	γ_{L3}	$\rightarrow \theta_{E_3}$

Known

3 Linear Simultaneous eqns to $\sqrt{\gamma_S^{LW}}$, $\sqrt{\gamma_S^{+}}$, $\sqrt{\gamma_S^{-}}$

3 Linear Simultaneous eqns to

$\sqrt{\gamma_S^{LW}}$, $\sqrt{\gamma_S^{+}}$, $\sqrt{\gamma_S^{-}}$

Can obtain

γ_S^{LW}, γ_S^{+}, γ_S^{-}

Solid Surface

θ_E measured thrice with 3 diff liquid.

Eqlbm. Contact Angle of diiodomethane, water and glycerol on a solid surface are 39.4°, 60.9°, and 63.1°.

Following data is given: Determine the Surface Energy of the Solid.

Liq.	γ_L^{LW}	γ_L^{+}	γ_L^{-}	γ_L
Diiodomethane	50.8	0	0	50.8
Water	21.8	25.5	25.5	72.8
Glycerol	34.0	57.4	3.2	64.0

(mJ/m²)

$$\gamma_L(1+\cos\theta_E) = 2\left[\sqrt{\gamma_S^{LW}\gamma_L^{LW}} + \sqrt{\gamma_S^{+}\cdot\gamma_L^{-}} + \sqrt{\gamma_S^{-}\gamma_L^{+}}\right]$$

For Diiodomethane, $50.8(1+\cos 39.4°) = 2\sqrt{\gamma_S^{LW}\cdot 50.8}$

$$\Rightarrow \gamma_S^{LW} = 39.11 \text{ mJ/m}^2$$