16.02.2022

Class # 16

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

For a-polar material

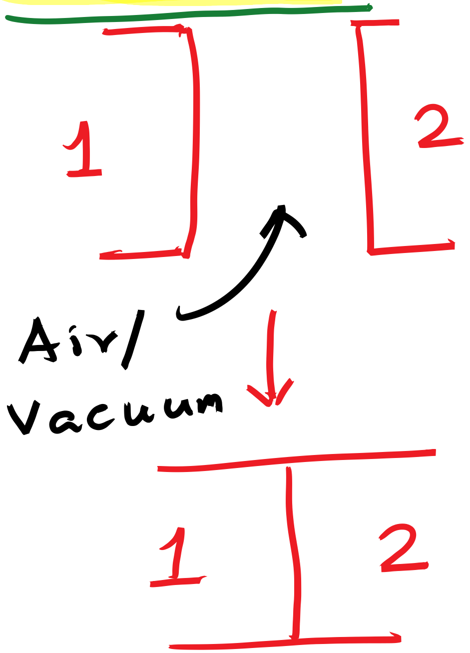
$$\gamma_{12}^{LW} = \gamma_1^{LW} + \gamma_2^{LW} + \Delta G_{12}^{LW}$$

$$= \gamma_1^{LW} + \gamma_2^{LW} - 2\sqrt{\gamma_1^{LW} \cdot \gamma_2^{LW}}$$

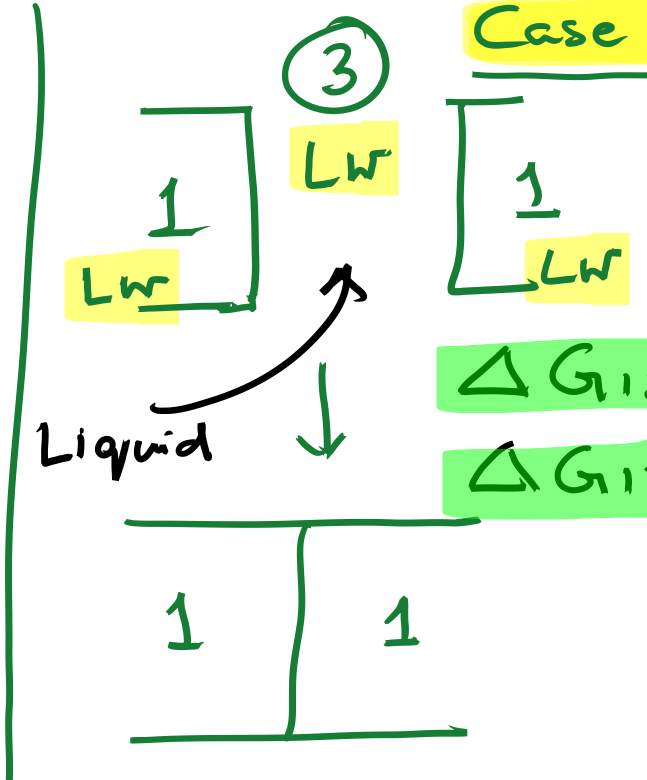
$$\gamma_{12}^{LW} = \left(\sqrt{\gamma_1^{LW}} - \sqrt{\gamma_2^{LW}}\right)^2$$

$\Rightarrow$ Consequence! γ_{12}^{LW} IS ALWAYS POSITIVE

Case 1:



Case 2



$$\Delta G_{131}^{LW} = \cancel{\gamma_1^{LW}}_{\to 0} - \left(\gamma_{13}^{LW} + \gamma_{13}^{LW}\right)$$

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

ΔG_{132} → 1 and 2 are coming $\bar{c}$ contact

ΔG_{131} → Two similar objects are coming $\bar{c}$ contact

Consequence: →

ΔG_{131}^{LW} = Always Negative

γ_{13}^{LW} → Always Positive

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

If both are a-polar

$$\Delta G_{12} = \Delta G_{12}^{lw}$$

$$\Delta G_{12}^{LW} = \gamma_{12}^{lw} - \left(\gamma_1^{lw} + \gamma_2^{lw}\right)$$

$$= \left(\sqrt{\gamma_1^{lw}} - \sqrt{\gamma_2^{lw}}\right)^2 - \left(\gamma_1^{lw} + \gamma_2^{lw}\right) = -2\sqrt{\gamma_1^{lw}\gamma_2^{lw}}$$

[ΔG_{12}^{lw} ALWAYS Negative]

Two a polar dis-similar objects $\bar{c}$ air will always adhere to each other.

VdW Component : Assumption/Rule we had:

$$\boxed{\gamma_{12}^{LW} = \sqrt{\gamma_{11}^{LW} \cdot \gamma_{22}^{LW}}} \leftarrow \underline{\gamma_{12}^{LW}}$$

Polar Component: (AB interaction) → Possible only

(Acid-Base Interaction) when Neighboring molecules have opposite polarity.

(Permanent Dipole/ Permanent Dipole Interaction)

- Two sets of Emperical Parameters are used to Quantify Polar Interaction

γ^- → Electron donor / Proton Acceptor Parameter
(Lewis Base) (Bronsted Base) ←

γ^+ → Electron Acceptor / Proton Donor Parameter.
(Lewis Acid) (Bronsted Acid) ←

The magnitude of the polar Component of Surface tension of any material $\gamma_1^{AB} = f(\gamma^{+}_{AB}, \gamma^{-}_{AB})$ ←

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

↑ Polar (Acid - Base) Component of Surface Tension of 1.

$\gamma_2^{AB} = 2\sqrt{\gamma_2^{+} \cdot \gamma_2^{-}}$

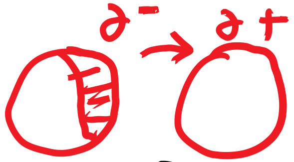
If either γ_1^{+} or γ_1^{-} is $= 0$ → Then $\underline{\gamma_1^{AB} = 0}$ $\quad \gamma_2^{AB} = 0$

Next assumption: →

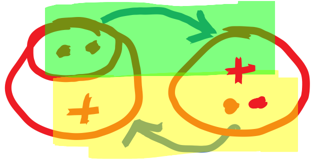
$$\Delta G_{12}^{AB} = -2\left[\sqrt{\gamma_1^{+}\gamma_2^{-}} + \sqrt{\gamma_1^{-}\gamma_2^{+}}\right]$$

$\gamma_2^{-} = 0$

$\gamma_2^{+}, \gamma_1^{+}, \gamma_1^{-}$ → Non Zero



AB

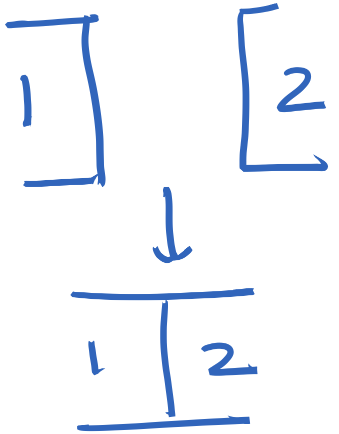


When is the Schematic Valid? → $\underline{\gamma^{+} \text{ and } \gamma^{-}}$

$\gamma_1^{+}, \gamma_2^{-}, \gamma_1^{-}$ and γ_2^{+} → All are Non Zero

Assumptions 1: $\gamma_1^{AB} = 2\sqrt{\gamma_1^+\gamma_1^-}$

Assumption 2: $\Delta G_{12}^{AB} = -2\left[\sqrt{\gamma_1^+\gamma_2^-} + \sqrt{\gamma_1^-\gamma_2^+}\right]$



$\rightarrow$ For the AB Component

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

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

$$\gamma_{12}^{AB} = 2\left[\sqrt{\gamma_1^+\gamma_1^-} + \sqrt{\gamma_2^+\gamma_2^-} - \sqrt{\gamma_1^+\gamma_2^-} - \sqrt{\gamma_1^-\gamma_2^+}\right]$$

$\leftarrow$ Polar component of Interfacial tension between 1 and 2

P.T.O

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

Cohesive Polar Int.

Adhesive Polar Interaction

$$= \left(\sqrt{\gamma_1^{LW}} - \sqrt{\gamma_2^{LW}}\right)^2 + 2\left[\left(\sqrt{\gamma_1^+\gamma_1^-} + \sqrt{\gamma_2^+\gamma_2^-}\right) - \left(\sqrt{\gamma_1^+\gamma_2^-} + \sqrt{\gamma_1^-\gamma_2^+}\right)\right]$$

<u>Conclusion?</u> $\gamma_{12}^{LW} \rightarrow$ has to be positive

$\gamma_i \rightarrow$ Always Positive

$\gamma_{ij} \rightarrow$ Can be positive or Negative

(Under what condition this can happen?)

It is possible to have negative Interfacial Tension.

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

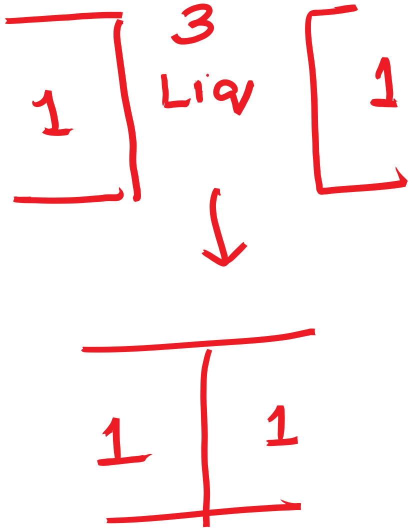
$\uparrow$ +ve

$\downarrow$ [(Cohesive) − (Adhesive)]

Necessary Condition for having negative γ_{12}

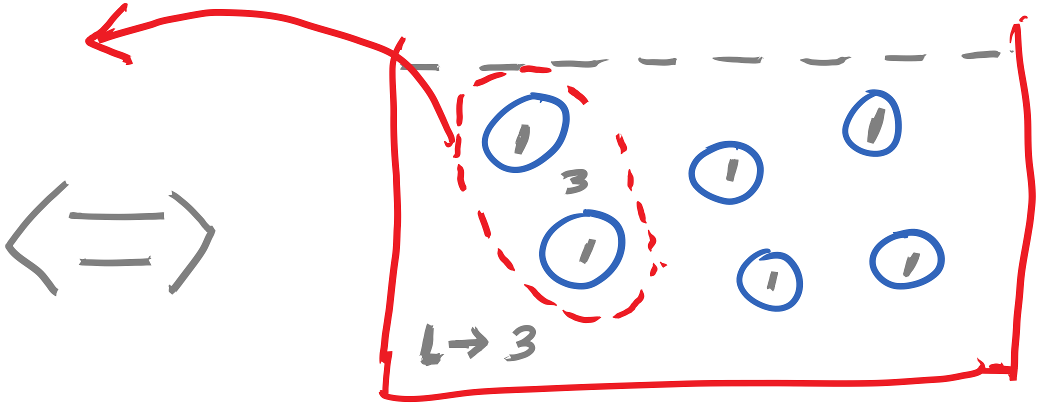
(Adh. Polar Interaction) > (Cohesive Polar Int) + (VDW Interaction)

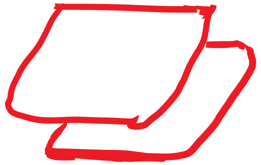
$\Delta G_{131} = -2\gamma_{13}$



Stable Colloidal Dispersion

Colloid → ? Small Particles





→ Sheet Like Colloids also.

At least one dimension ≃ μm range.

→ * Particles are dispersed in another medium / often a Liquid.

ΔG_{131} related to what?

$\Delta G_{131} = -ve$ → Two Particles of 1 will dislodge the liquid 3 between them and come in contact.
↳ Coagulation.

$\Delta G_{131} = +ve$ → The two particles of 1 will Fail to coagulate. Thermodynamically favored to remain dispersed.

BLOOD?

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

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

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

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

$$|C| < |A| + |B|.$$

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

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

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

3 Apolar: Most Organic Solvents

Nail Polish Remover

Pen Ink

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

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

→ 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 :

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

$\gamma^{-} \neq 0$

↓

We have a monopolar Solid & a Monopolar Liquid →