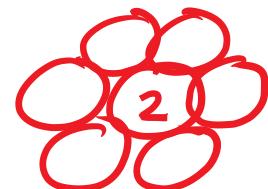
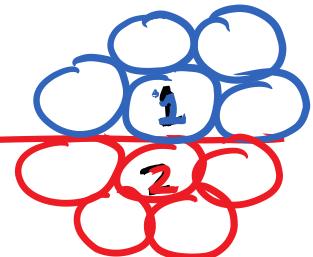
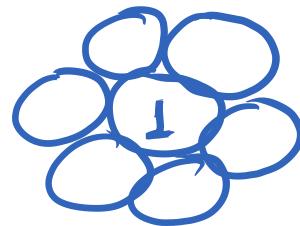


Components of Surface Tension:-

1



2

in the total

Difference [Energy of interaction of 1 molecule of (1) and 1 molecule of (2), When they were in bulk vs. When they are at the interface.]

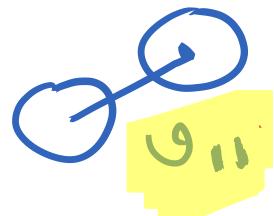
$$\gamma_{12} = (\text{Energy of interaction of a pair of molecule at surface}) - (\text{Energy of Interaction of the same pair when in Bulk})$$

$$\gamma_{12} = E_s - E_b$$

Components of Surface Tension:-

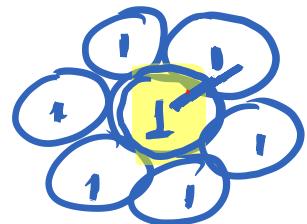
$\sigma_{11}, \sigma_{22}, \sigma_{12}$

1



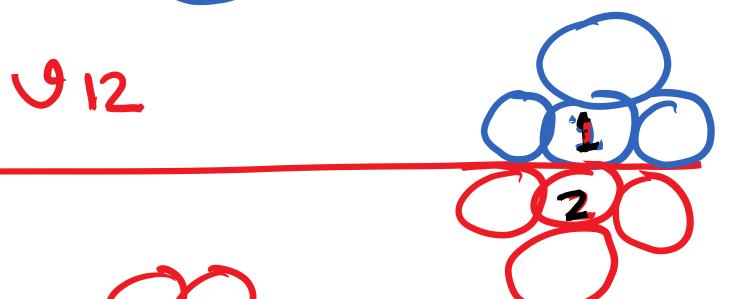
$Z_{11} = \text{Co-ordination No. in Phase 1}$

$Z_{22} = \text{Co-ordination No. in Phase 2.}$



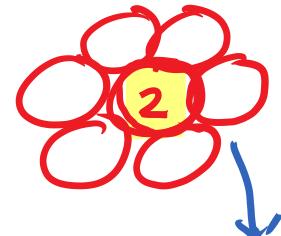
$\sigma_{11} = \text{Pair wise interaction potential between two molecules of 1}$

(vdW, may include Polar Int, Steric interaction)



$$\sigma_{11} = \underbrace{\sigma_{11}^{\text{LW}}}_{\text{Van der waal Present Always.}} + \underbrace{\sigma_{11}^{\text{AB}}}_{\text{Polar}} + \underbrace{\sigma_{11}^{\text{ST}}}_{\text{Steric Int (Polymer)}} + \dots$$

2



Total intermolecular Interaction It is highlighted
mol of 2 is subject to $\sigma_{22} Z_{22}$

Van der waal
Present Always.

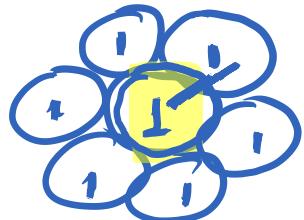
Polar
Acid-Base Int

Components of Surface Tension:-

$\sigma_{11}, \sigma_{22}, \sigma_{12}$

Z_{11} = Co-ordination No. in Phase 1

1



Z_{22} = Co-ordination No. in Phase 2.

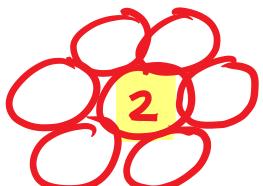
σ_{11} = Pair wise interaction potential between two molecules of 1

Z_{11S}

Z_{12}

Z_{22S}

Z_{21}



$\sigma_{22}, \sigma_{12} = \sigma_{21}$

$\underbrace{Z_{11S}}, \underbrace{Z_{22S}}, \underbrace{Z_{12}}, \underbrace{Z_{21}}$

$$E_b = -Z_{11} \sigma_{11} - Z_{22} \sigma_{22}$$

$$\underline{P_{12} = E_s - E_b}$$

$$E_s = -\sqrt{Z_{11S} \sigma_{11}} - \sqrt{Z_{12} \sigma_{12}} - \sqrt{Z_{22S} \sigma_{22}} - \sqrt{Z_{21} \sigma_{21}}$$

2 Interaction is attractive.

$$E_b = -Z_{11} \varphi_{11} - Z_{22} \varphi_{22} = -Z(\varphi_{11} + \varphi_{22})$$

$$E_s = -Z_{11s} \varphi_{11} - Z_{12} \varphi_{12} - Z_{21} \varphi_{21} - Z_{22s} \varphi_{22} = \frac{Z}{2} (\varphi_{11} + \varphi_{22} + 2\varphi_{12})$$



Assumptions: $\varphi_{12} = \varphi_{21}$

$$Z_{11s} = \frac{1}{2} Z_{11} \quad Z_{12} = \frac{1}{2} Z_{11}$$

$$Z_{22s} = \frac{1}{2} Z_{22} \quad Z_{21} = \frac{1}{2} Z_{22}$$

and $Z_{11} = Z_{22} = Z$



$$P_{12} = E_s - E_b = -\frac{Z}{2} (\varphi_{11} + \varphi_{22} + 2\varphi_{12}) - [-Z(\varphi_{11} + \varphi_{22})]$$

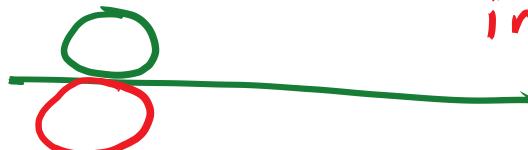
$$P_{12} = \frac{Z}{2} (\varphi_{11} + \varphi_{22} - 2\varphi_{12})$$

$$P_{12} = \frac{z}{2} (\vartheta_{11} + \vartheta_{22} - 2\vartheta_{12})$$

↳ Pair wise excess Energy ←

For one pair of molecules at the interface, the Excess energy

is Known.

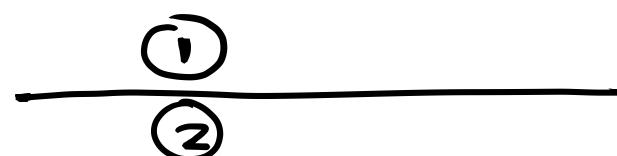


↳ Can γ_{12} be determined from P_{12} .

$$\gamma_{12} = P_{12} \cdot N$$

N = No. of Pair of molecules Per unit area

↳ This N is NOT AVOGADRO's Number.



$$\gamma_{12} = \frac{z}{2} (\vartheta_{11} + \vartheta_{22} - 2\vartheta_{12})$$

$$\begin{aligned} z_{11} &= z_{22} = \bar{z} \\ z_{11s} &= \frac{1}{2} z_{11} \\ z_{22s} &= \frac{1}{2} z_{22} \\ z_{12} &= z_{21} = \frac{1}{2} z_{11} = \frac{1}{2} \bar{z} \end{aligned}$$

$$\gamma_{12} = \frac{ZN}{2} (\vartheta_{11} + \vartheta_{22} - 2\vartheta_{12}) \quad \text{--- (1)}$$

1
2

$$\boxed{\gamma_2 = \frac{ZN}{2} \vartheta_{22}} \xrightarrow{\text{Eqn 2}} \leftarrow$$

By Considering ② to be a rectified phase,

$$(\vartheta_{22} = 0, \vartheta_{12} = 0) \quad \underline{\gamma_1 = \frac{ZN}{2} \vartheta_{11}}$$

Let's say ① is now a Non-Condens or a Rectified Phase.

Air / vacuum.
2

Consequence?:

$$\vartheta_{11} = 0, \vartheta_{12} = 0, \underline{\gamma_{12} = \gamma_2}$$

Eqn (1)

$$\gamma_{12} = \frac{ZN}{2} \vartheta_{11} + \frac{ZN}{2} \vartheta_{22} - ZN \vartheta_{12}$$

$$\gamma_{12} = \gamma_1 + \gamma_2 - ZN \vartheta_{12}$$

$$\gamma_{12} = \gamma_1 + \gamma_2 - zN\vartheta_{12} \quad (3)$$

$$\Rightarrow \underbrace{\gamma_{12} - (\gamma_1 + \gamma_2)}_{\text{Red Box}} = -zN\vartheta_{12}$$

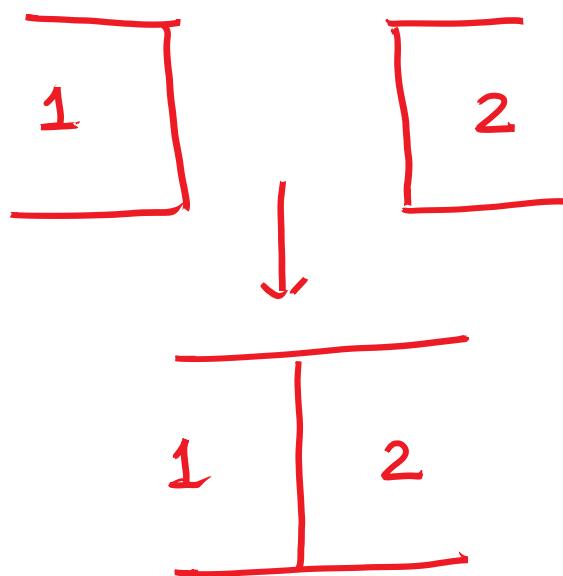
$\therefore \underbrace{\Delta G_{12} = -zN\vartheta_{12}}_{\text{Red Box}}$

$$\rightarrow \underbrace{\Delta G_{12} = \Delta G_{12}^{\text{LW}} + \Delta G_{12}^{\text{AB}} + \dots}_{\text{Yellow Box}}$$

ϑ_{12} = Total Pairwise interaction.

$$= \vartheta_{12}^{\text{LW}} + \vartheta_{12}^{\text{AB}} + \underbrace{\vartheta_{12}^{\text{ST}}}_{\text{Neglected}}$$

$$\approx \underbrace{\vartheta_{12}^{\text{LW}} + \vartheta_{12}^{\text{AB}}}_{\text{Yellow Box}}$$



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

Now Let's say ① and ② are
a-polar. $\rightarrow \underbrace{\vartheta_{12}^{\text{AB}} = 0}_{\text{Red Box}}$

$$\underbrace{\vartheta_{12} = \vartheta_{12}^{\text{LW}}}_{\text{Yellow Box}}$$

\leftarrow only vdw
Interaction.

Assumption.

$\vartheta_{12} \rightarrow$ depends on? $\rightarrow f(\vartheta_{11}, \vartheta_{22})$

For vdw interaction: $\vartheta_{12}^{LW} = \sqrt{\vartheta_{11}^{LW} \vartheta_{22}^{LW}}$

$$\Delta G_{12} = -NZ\vartheta_{12}$$

When we have only vdw interaction

$$\vartheta_{12} = \vartheta_{12}^{LW}$$

$$\begin{aligned}\Delta G_{12} &= \Delta G_{12}^{LW} \\ &= -NZ\vartheta_{12}^{LW} \\ &= -2\sqrt{\frac{N^2 Z^2}{4} \vartheta_{12}^{LW}}\end{aligned}$$

$$= -2\sqrt{\frac{Z^2 N^2}{4} \cdot \vartheta_{11}^{LW} \cdot \vartheta_{22}^{LW}}$$

$$= -2\sqrt{\left(\frac{NZ}{2} \vartheta_{11}^{LW}\right) \left(\frac{NZ}{2} \vartheta_{22}^{LW}\right)} = -2\sqrt{\gamma_1^{LW} \gamma_2^{LW}}$$

(Expt 2, Slide 6)

We have $\gamma_{12} = \gamma_1 + \gamma_2 + (\Delta G_{12})$ From eqn(3) - slide 2.

For α -polar material

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

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

$$\gamma_{12}^{\omega} = (\sqrt{\gamma_1^{\omega}} - \sqrt{\gamma_2^{\omega}})^2$$

\Rightarrow Consequence!

γ_{12}^{ω} is ALWAYS POSITIVE