it known as adsorption isotherme.

Gibb's adsorption isotherm:

J. willard Gibb's & J. J. Jamson derived a relationship between adsorption and surface tension its known as Gibb's adsorption isotherm.

It is considered γ is the interfacial tension. The free energy G is given by

$$G = \mu_1 n_1 + \mu_2 n_2 \text{ ——— } (1)$$

where n_1, n_2 are no. of molecule. μ_1, μ_2 chemical potential of two species

The γs may added in calculating the free energy

thus, $G = \gamma s + \mu_1 n_1 + \mu_2 n_2$ ——— (2)

on differentiation equation (2).

$$dG = \gamma ds + s d\gamma + \mu_1 dn_1 + n_1 d\mu_1 + \mu_2 dn_2 + n_2 d\mu_2 \quad \text{—— (3)}$$

The value of dG obtained by the use of thermodynamic function by adding the surface entropy.

$$dG = -SdT + VdP + \gamma ds + \mu_1 dn_1 + \mu_2 dn_2 \quad \text{—— (4)}$$

by comparing equation (3) & (4)

$$SdT - VdP + sd\gamma + n_1 d\mu_1 + n_2 d\mu_2 = 0 \quad \text{—— (5)}$$

at constant temperature and pressure is 0.

$$sd\gamma + n_1 d\mu_1 + n_2 d\mu_2 = 0 \quad \text{—— (6)}$$

This equation is an analogous to Gibb's-Duhem equation. This equation wholed goods for surface phase but the bulk phase is quite free from surface phase and therefore only Gibb's Duheme equation wholes good.

Let n_1, n_2 be the no. of molecule in surface phase while n_1°, n_2° be the no. of molecules in bulk phase.

For the bulk phase the following relationship may be given.

$$n_1^\circ d\mu_1 + n_2^\circ d\mu_2 = 0 \quad \text{—— (7)}$$

The above equation does not contain γs term. Since its free from surface effect.

on equation (7) $\times \frac{n_1}{n_1^\circ}$ and subtracting with equation (6).

$$n_1 d\mu_1 + \frac{n_1 n_2^\circ}{n_1^\circ} d\mu_2 = 0 \quad \text{—— (8)}$$

(6) − (8)

equ (6) − equ (8)

$$sd\gamma + n_2 d\mu_2 - \frac{n_1 n_2^\circ}{n_1^\circ} d\mu_2 = 0 \quad \text{—— (9)}$$

$$-sd\gamma = n_2 d\mu_2 - \frac{n_2^\circ}{n_1^\circ} n_1 d\mu_2 \quad \text{—— (10)}$$

$$-sd\gamma = \left(n_2 - \frac{n_1 n_2^\circ}{n_1^\circ}\right) d\mu_2 \quad \text{—— (11)}$$

$$-\frac{d\gamma}{d\mu_2} = \left[\frac{n_2 - \frac{n_1 n_2^{\circ}}{n_1^{\circ}}}{s} \right] \quad (12)$$

The R.H.S of equation (12) is called concentration of solute and represented by S_2.

$$\therefore S_2 = -\frac{d\gamma}{d\mu_2} \quad (13)$$

we know that $\mu_2 = \mu_2^{\circ} + RT \ln a_2$ — (14)

where a_2 is activity of solute and constant temperature

differenating equ (14)

$$d\mu_2 = RT\, d\ln a_2 \quad (15)$$

Substitute the values in equation (13) we get $\left(\therefore d\ln a_2 = \frac{da_2}{a_2}\right)$

$$S_2 = \frac{-d\gamma}{RT\, d\ln a_2}$$

$$S_2 = \frac{-a_2\, d\gamma}{RT\, da_2}$$

This equation known as Gibb's adsorption isotherm equation

* If the value of $\frac{d\gamma}{da_2} = -ve$ surface tension increase with increasing the concentration. (i-e) there is an excess solute present at the inter phase.

* If $\frac{d\gamma}{da^2}$ is positive S_2 is +ve it means further addition of solute decrease the surface tension of the solution.