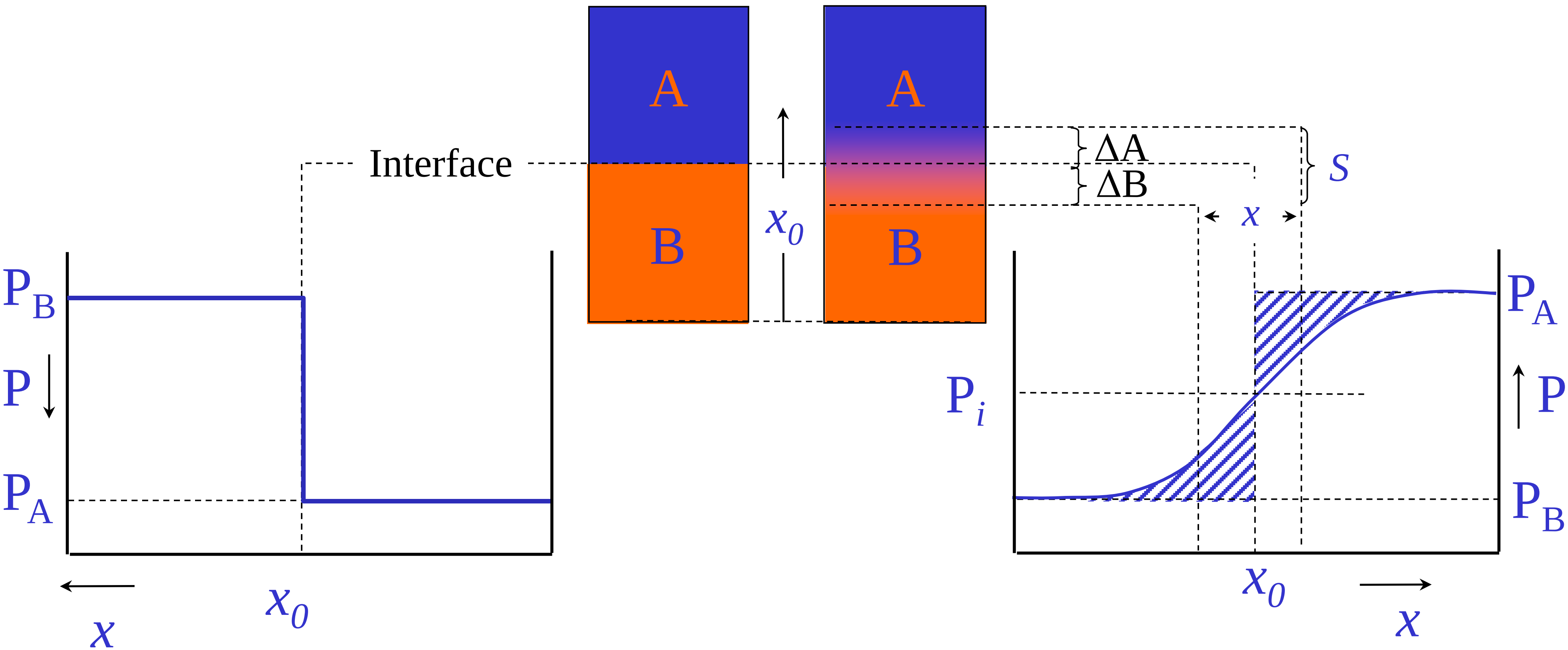
Gibb's Adsorption Isotherm

SURFACE EXCESS



A Property, P, of system vary across the interface (of thickness S) from that of phase 'A' and 'B'

If P_i is the value of the Property P at the ideal border of the interface, then:

- Area left of x_0: represents underestimated value of P_i
- Area right of x_0: represents overestimated value of P_i

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SURFACE EXCESS (Cont.)

- X_0 - may be selected such that two shaded areas are equal

  -may divide the profiles of other properties differently

- Property which is least convenient to handle mathematically can be eliminated by selecting its surface excess to be zero.
- Note - dividing surface only a Reference Level rather than a physical boundary.

  - Surface excess can be positive or negative.

THE GIBBS ADSORBION EQUATION

- Amount of surfactant adsorbed per unit area can be calculated from surface or interfacial tension measurements

$$d\gamma = -\sum_i \Gamma_i d\mu_i$$

Where, $d\gamma$ = change in surface tension

Γ_i = surface excess concentration of 'i'

$d\mu_i$ = change in chemical potential of 'i'

$$d\mu_i = RTd\ln a_i$$

At equilibrium

where a_i = activity of 'i' in bulk phase

= mole fraction x activity coefficient

THE GIBBS ADSORBION EQUATION

Therefore

$$d\gamma = -RT\sum_i \Gamma_i d\ln a_i$$

- For dilute solutions containing one non-dissociating surfactant

Where C = molar concentration of surfactant in bulk

$$d\gamma = -RT\sum_i \Gamma_i d\ln C$$

- At constant temperature

$$\Gamma = -\frac{1}{RT}\left(\frac{d\gamma}{d\ln C}\right)_T$$

- Surface excess given by slope of plot of γ versus log C
- Knowing Γ, area per molecule at the interface can be calculated.

AREA PER MOLECULE AT THE INTERFACE

- Important in assessing
  - Degree of packing
  - Orientation of adsorbed molecules
- a = area per molecule (in $Å^2$) at interface, given by

$$a = \frac{1 \times 10^{20}}{N\,\Gamma}$$

Where N = Avogadro number

Γ = Surface excess in moles/m^2

APPLICATION OF GIBBS ADSORPTION

- Surface tension of aqueous solution of the nonionic surfactant $CH_3(CH_2)_9(OCH_2CH_2)_5OH$ at 25^0C is as given:

C ($x10^{-1}$) mol/m^2	0.1	0.3	1.0	2.0	5.0	8.0	10.0	20.0	30.0
γ(mN/m)	63.9	56.2	47.2	41.6	34.0	30.3	29.8	29.6	29.5

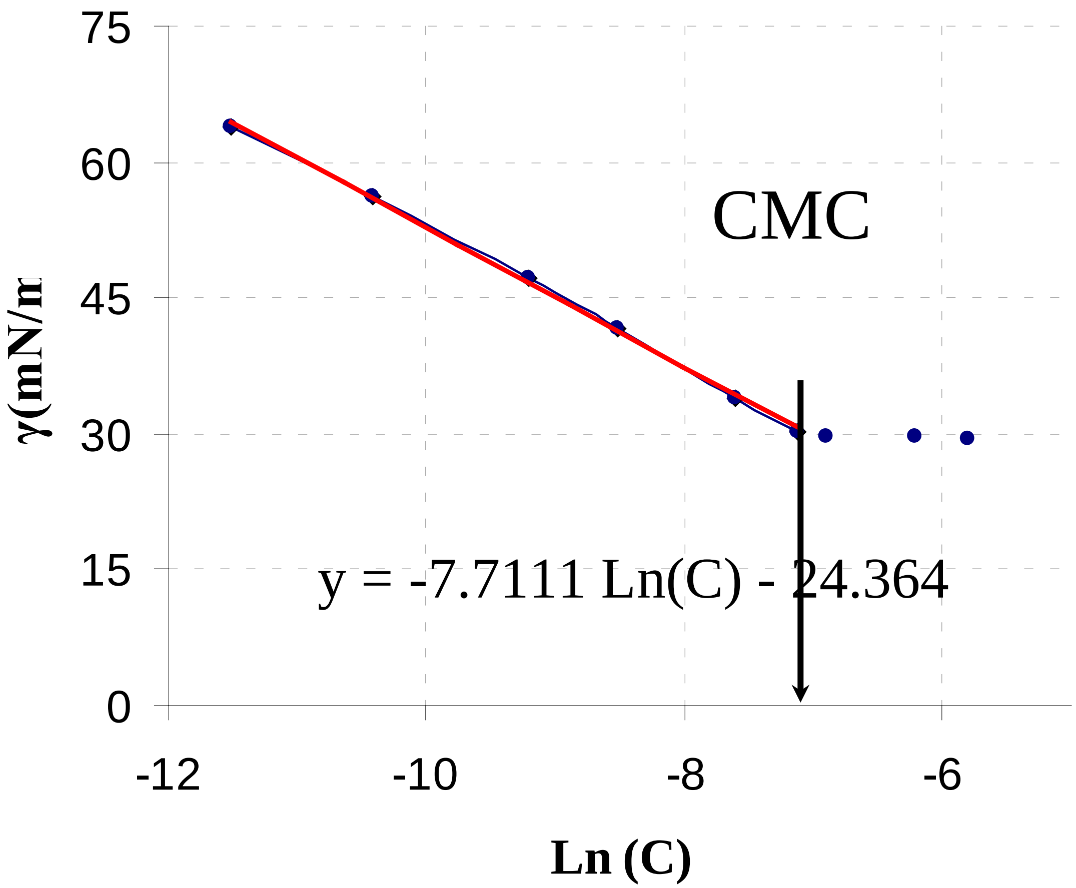
APPLICATION OF GIBBS ADSORPTION

- Surface excess is given by:

$$\Gamma = -\frac{1}{RT}\left(\frac{d\gamma}{d\ln C}\right)_T$$

$$\Gamma = -\frac{-7.711\cdot 10^{-3}}{8.314\cdot 298} =$$

$$= 3.11\cdot 10^{-6}\, mol/m^2$$



- Average area occupied by each molecule,

$$a = \frac{1\times 10^{20}}{3.11\times 10^{-6}\times 6.023\times 10^{23}} = 53.4\,\overset{o}{A}^{2}$$

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