2.5 The liquid surface :

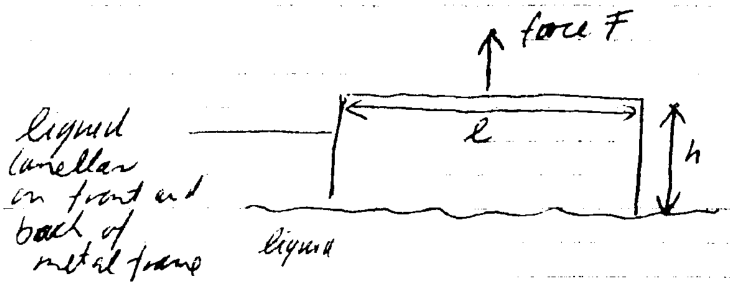
- surface tension γ :
  - liquids such as water to minimize their air-fluid surface (e.g. for water molecules no hydrogen bonding with air makes surface unfavourable) ⇒ leads to droplets
  - work needed to change the surface area σ

$$\boxed{dW = \gamma\, d\sigma} \underset{\substack{V=const\\T=const}}{\overset{}{=}} dA$$

Helmholtz energy

- $[\gamma] = \frac{J}{m^2} = \frac{N}{m}$ "2-dimensional pressure"

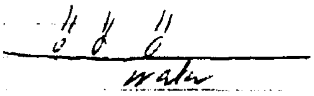
- film balance.

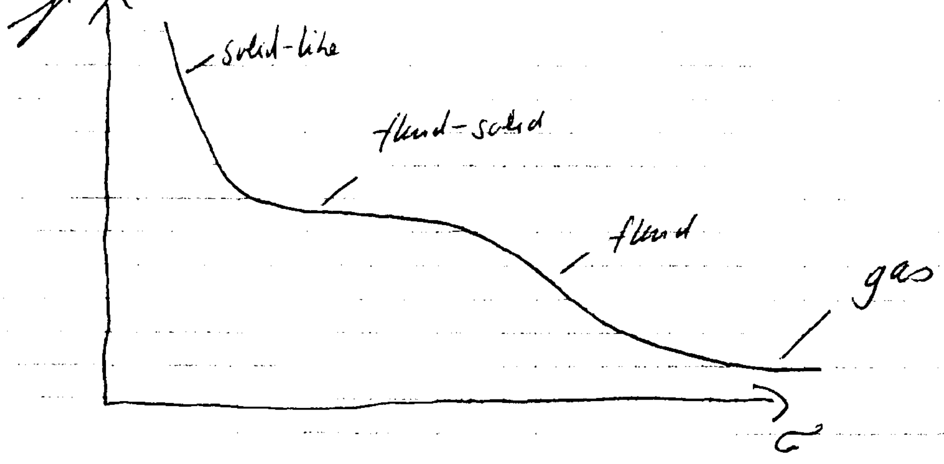


$W = 2\gamma hl \Rightarrow F = 2\gamma l$

total area change: $2hl$

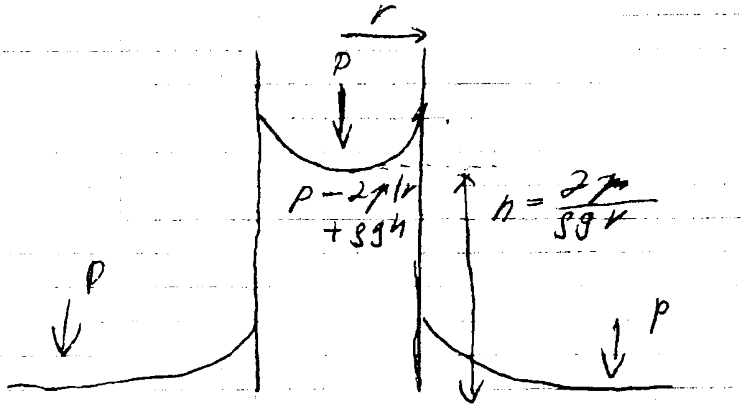
⇒ lipid monolayers:



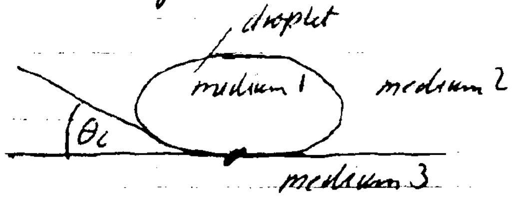


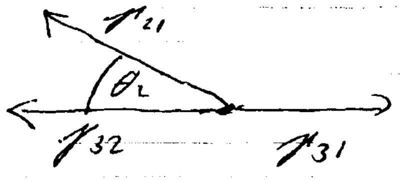
- Capillary action

liquid that has a tendency to adhere to walls



- contact angle θ_c





$$\gamma_{31} = \gamma_{32} + \gamma_{21} \cos\theta_c$$

$$\Rightarrow \cos\theta_c = \frac{\gamma_{31} - \gamma_{32}}{\gamma_{21}}$$

adhesion work of medium 1 to medium 3:

$$W_{ad} = \gamma_{31} + \gamma_{21} - \gamma_{32}$$

$$\Rightarrow \boxed{\cos\theta_c = \frac{W_{ad}}{\gamma_{21}} - 1}$$

wetting: $0^\circ < \theta_c < 90^\circ \Leftrightarrow 1 < \frac{W_{ad}}{\gamma_{21}} < 2$

non-wetting: $90^\circ < \theta_c < 180^\circ \Leftrightarrow 0 < \frac{W_{ad}}{\gamma_{21}} < 1$

Simple Mixtures

E.g. binary mixture of water (H_2O) and ethanol (CH_3CH_2OH)

$$X_E = \frac{n_E}{n_E+n_W} \qquad X_W = \frac{n_W}{n_E+n_W}$$

Volume: $V(n_1, n_2)$

$$V(\alpha n_1, \alpha n_2) = \alpha V(n_1, n_2)$$

$$V(n_1, n_2) = n_1 \underbrace{\left.\frac{\partial V}{\partial n_1}\right|_{n_2}}_{=V_1} + n_2 \underbrace{\left.\frac{\partial V}{\partial n_2}\right|_{n_1}}_{=V_2}$$

partial molar volumes

Molecular Mass:

$M_W = 18\ \mathrm{g/mol}$ $\qquad M_E = 46\ \mathrm{g/mol}$

$\Rightarrow$ molar Volume $V^0 := \frac{M}{\rho_0}$

molar mass of mixture

$$M = X_W M_W + X_E M_E$$

molar volume of ideal mixture

$$V^{id} = X_W V_W^0 + X_E V_E^0$$

Partial molar Gibbs energies

$$\boxed{\mu_J = \frac{\partial G}{\partial n_J}\Big|_{p,T,n'}}$$ chemical potential

$\Rightarrow \quad G = n_W \mu_W + n_E \mu_E$

fundamental equation of chemical thermodynamics:

$$dG = Vdp - SdT + \mu_A dn_A + \mu_B dn_B + \dots$$

⇒ Work of mixing at constant pressure ($dp = 0$) and constant temperature ($dT = 0$)

$$dw_{add} = \mu_A dn_A + \mu_B dn_B$$

e.g. work done in an electrochemical cell!

better definition of chemical potential

$$dU = -pdV \overset{-Vdp}{\vee} + SdT \overset{+TdS}{\vee} + dG$$

$$= -pdV + TdS + \mu_A dn_A + \mu_B dn_B + \dots$$

$dV = 0 \quad dS = 0$

$$dU = \mu_A dn_A + \mu_B dn_B + \dots$$

$$\boxed{\mu_J = \frac{dU}{dn_J}\Big|_{S,V,n'}}$$

Gibbs – Duhem equation :

binary system

$$dG = \mu_A \, dn_A + n_A \, dn_B + n_A \, d\mu_A + n_B \, d\mu_B$$

on the other hand fundamental equation of chemical thermodynamics

$$dG = \mu_A \, dn_A + \mu_B \, dn_B$$

$$\Rightarrow \quad n_A \, d\mu_A + n_B \, d\mu_B = 0 \qquad d\mu_B = -\frac{n_A}{n_B} \, d\mu_A$$

in general:

$$\boxed{\sum_j n_j \, d\mu_j = 0}$$

Thermodynamic of Mixing

Gibbs energy of mixing:

~~perfect~~

2 ideal gases, n_A, n_B, at temperature T and pressure p

$$\mu = \mu^0 + RT \ln \frac{p}{p^0}$$

$$G_{initial} = n_A \left(\mu_A^0 + RT \ln \frac{p}{p^0} \right) + n_B \left(\mu_B^0 + RT \ln \frac{p}{p^0} \right)$$

$$G_{final} = n_A \left(\mu_A^0 + RT \ln \frac{p_A}{p^0} \right) + n_B \left(\mu_B^0 + RT \ln \frac{p_B}{p^0} \right)$$

$p = p_A + p_B$ partial pressure

$$\Rightarrow \boxed{\Delta_{mix} G = n_A RT \ln \frac{p_A}{p} + n_B RT \ln \frac{p_B}{p}}$$

$$= nRT \left(x_A \ln x_A + x_B \ln x_B \right)$$

④

entropy of mixing:

$$\Delta_{mix} S = - \left.\frac{\partial \Delta_{mix} G}{\partial T}\right|_{p, n_A, n_B}$$

$$= - nR \left(x_A \ln x_A + x_B \ln x_B \right)$$