3.3 Two dimensional equation of state and isotherms

We consider two phases $\alpha$ and $\beta$ in equilibrium with a surface $S$ dividing them.

For the whole system \( G = G^\alpha + G^\beta + G^s \)

For the bulk phases ($\alpha$ or $\beta$) \( G = E + PV - TS \)  
\( \uparrow \) Internal energy

For the interface \( G = E^s + \gamma A - TS^s \)  
\( \uparrow \) surface tension  
(volume replaced by area)

\[
\text{work} = F \, dx = \gamma l \, dx = \gamma \, dA
\]
\[
\gamma = \frac{F}{l} = - \frac{\text{force}}{\text{distance}} ; \text{ but } P = \frac{\text{force}}{\text{area}}
\]
\[ G = \sum_{\alpha\beta s} (E + PV - TS) + \gamma A \]
\[ dG = \sum_{\alpha\beta s} (dE + PdV + VdP - TdS - SdT) + A d\gamma + \gamma dA \]

a reversible process,

\[ dE = \delta q - \delta w + d\Sigma \mu_i n_i = \sum_{\alpha\beta s} dE \]
\[ = \sum_{\alpha\beta s} \{ TdS - (PdV + \delta W_{\text{non-PV}}) + \Sigma_i \mu_i dn_i + \Sigma_i n_i d\mu_i \} \]

substitute into \( dG \)

\[ dG = \sum_{\alpha\beta s} (VdP - SdT + \Sigma_i \mu_i dn_i + \Sigma_i n_i d\mu_i - \delta W_{\text{non-PV}}) + A d\gamma + \gamma dA \]

and \( \sum_{\alpha\beta s} \delta W_{\text{non-PV}} = \gamma dA \)

\[ \therefore dG = \sum_{\alpha\beta s} (VdP - SdT + \Sigma_i \mu_i dn_i + \Sigma_i n_i d\mu_i) + A d\gamma \quad \text{---------(1)} \]

\[ dG = VdP - SdT + \Sigma_i \mu_i dn_i \quad \text{---------(2)} \quad \text{always true for a system} \]
(1) − (2) gives \[ \Sigma_{\alpha\beta s} (\Sigma_i n_i \, d\mu_i) + A \, d\gamma = 0 \]

\[ \Sigma_i n_i^\alpha d\mu_i + \Sigma_i n_i^\beta d\mu_i + \Sigma_i n_i^s d\mu_i + A \, d\gamma = 0 \]

For bulk phases at constant T and P,

\[ \Sigma_i n_i \, d\mu_i = 0 \quad \text{Gibbs-Duhem equation} \]

\[ \therefore \Sigma_i n_i^s d\mu_i + A \, d\gamma = 0 \quad \text{Gibbs adsorption equation in the interface} \]

For two-component systems \( (1: \text{solvent}, 2: \text{solute}) \)

\[ n_1^s d\mu_1 + n_2^s d\mu_2 + A d\gamma = 0 \quad \rightarrow \, d\gamma = - \frac{n_1^s}{A} \, d\mu_1 - \frac{n_2^s}{A} \, d\mu_2 \]

\[ \Gamma_i = - \frac{n_i^s}{A} \quad \text{surface excess of component } i \]

\[ \therefore -d\gamma = \Gamma_1 d\mu_1 + \Gamma_2 d\mu_2 \]
Keep in mind, there is a transition zone between two phases (i.e. no precise dividing plane)

(transition zone is very small)

Try to define a dividing surface, in order to give the concept of a surface excess.

For a general property \( P \), varying in the zone of \( \tau \), the dividing surface is determined, such that overestimated \( P_\alpha = \) underestimated \( P_\beta \).

In the case of adsorption, usually we choose \( P = n_1 \) (solvent) to define dividing surface, such that

\[
\Gamma_1 = \frac{n_1^s}{\Lambda} = \text{surface excess of solvent} = 0
\]

(no solvent adsorbed at the interface)
if \( n_2^\beta > n_2^\alpha \), this means that the real situation has an excess in reference to \( X_0 \) plane.

\[-d\gamma = \Gamma_2 \, d\mu_2 = \Gamma_2^1 \, d\mu_2\]

\[\mu_2 = \mu_2^0 + RT \ln a_2\]

\[\therefore \, d\mu_2 = RT \frac{d a_2}{a_2} = RT \frac{dC}{C}\]

(a dilute solution)

\[\Gamma_2^1 = -\frac{C}{RT} \left( \frac{d\gamma}{dC} \right)^T = -\frac{1}{RT} \left( \frac{d\gamma}{d\ln C} \right)^T = -\frac{1}{2.303} \frac{1}{RT} \left( \frac{d\gamma}{d\log C} \right)^T\]

(at constant temperature)

Gibbs equation
For interface between an aqueous solution and air

\[ \gamma \]
\[ \gamma_0 \]

1. \[ \Gamma_2 > 0 \]
2. \[ \Gamma_2 < 0 \]

Break; threshold for micelles formation

Curves 1,3: positive adsorption at the interface \( \because \) slope < 0 \( \rightarrow \) \( \Gamma_2 > 0 \)

Curve 2: negative surface excess

Examples:

Curve 1. solute = unionized organic compounds
   high conc. at the interface

Curve 2. solute = inorganic electrolytes or highly hydrated organics
   low conc. at the interface

Curve 3. solute = amphipathic species

Micelles form at high concentration
Gibbs can not be used.
as \( C \to 0 \),

straight line relationship (curve 1 as an example)

\[
\gamma = \gamma_0 - mC \\
\pi = \gamma_0 - \gamma = \text{two dimensional pressure} \\
\pi = mC
\]

\[
\Gamma_2^1 = -\frac{c}{RT} \left( \frac{d\gamma}{dc} \right) T = -\frac{c}{RT} (-m) = \frac{mc}{RT} = \frac{\pi}{RT}
\]

\[
(\gamma = \gamma_0 - mC \to \left( \frac{d\gamma}{dC} \right) T = -m )
\]

\[
\frac{n_s^2}{A} = \frac{\pi}{RT} \quad \pi A = n_s^2 R T
\]

Two-dimensional (2-D) ideal gas law; for low conc.

Note: \( PV = nRT \) 3-D (for low pressures)
Example 3.2'

The slope of the 25°C line in Fig. on the low concentration side of the break is about -16.7 mN m\(^{-1}\). Calculate the surface excess and the area per molecule for the range of concentrations shown.

Plot of \(\gamma\) versus \(\log_{10} C\) for the dodecyl ether of hexaethylene oxide at (1) 15°C (2) 25°C (3) 35°C

Solution
Go back to gas adsorption:

\[-d\gamma = \Gamma_2 \, d\mu_2\]

\[\mu_2 = \mu_2^0 + RT \ln f \, P \quad (f: \text{activity coefficient})\]

Assume idea gas \((f = 1)\), \(\mu_2 = \mu_2^0 + RT \ln P\)

\[d\mu_2 = RT \, d \ln P\]

\[-d\gamma = RT \, \Gamma_2 \, d \ln P \quad \Gamma_2 = \text{amount adsorbed}\]

\[= RT \, \frac{n}{A} \, d \ln P = \frac{RT}{A_{sp}} \, \frac{n}{W} \, d \ln P\]

At constant temperature, \(\frac{n}{W}\) is a function of \(P\).

\[-\int_{\gamma_0}^{\gamma} d\gamma = \frac{RT}{A_{sp}} \int_{0}^{P} \frac{n}{W} d\ln P \quad \text{B.C.} \quad \frac{n}{W} \to 0 \quad \text{as} \quad P \to 0\]
and \( \gamma = \gamma_0 \) as \( P \to 0 \)

\[
\gamma_0 - \gamma = \pi = \frac{RT}{A_{sp}} \int_0^P \frac{n}{W} d\ln P
\]

\( \therefore \) if \( \frac{n}{W} = f(p) \) is known, then 2-D pressure can be expressed as a function of coverage (or 3-D pressure)

Suppose \( \frac{n}{W} = m \times P \) \( \therefore \) \textit{Henry’s law limit} \( \) (at very low pressures)

linear relation; an isotherm

\[
\pi = \frac{RT}{A_{sp}} \int_0^P mP \frac{dP}{P} = \frac{RT}{A_{sp}} mP = \frac{N_A kT n}{A_{sp} W}
\]

\( \therefore \) \( \sigma = \frac{A_{sp} W}{n N_A} \) = the area share for one molecular

\( \therefore \) \( \pi \sigma = kT \) \( \therefore \) 2-D equation of state

\( P v = kT \) \( \therefore \) 3-D equation of state

(the volume share for a molecule)
◆ From isotherm to obtain equation of state by Gibbs’ equation

◆ When adsorption is described by the Henry’s limit, the adsorbed state behaves like a two-dimensional ideal gas.

\[ \theta = m'P \quad \ldots \ldots \text{Henry’s limit (another form)} \]

\[ \frac{N_A n_\sigma}{A_{sp} W} \]

The compliance of the adsorbed layer with this ideality is difficult.

1. A homogenous surface required
   (adsorbate-adsorbent interaction should be homogeneous)

2. No molecular interaction occurs
   (adsorbate-adsorbate interaction has to be minimized)

Based on point 2, one can have another equation of state with an excluded area correction.
\[ \pi(\sigma - \sigma^0) = kT \quad \sigma^0: \text{molecular cross-sectional area} \]

Let us now consider the kind of isotherm associated with the modified equation of state.

\[ d\pi = -kT(\sigma - \sigma^0)^2 \, d\sigma \quad \text{and} \quad \pi = \gamma_0 - \gamma \]

\[ d\pi = -d\gamma = \frac{RT}{\Lambda_{sp}W} \, d\ln P = \frac{kT}{\sigma} \, d\ln P \]

(eq. of state) \quad (Gibbs eq.)

\[ \frac{\sigma d\sigma}{(\sigma - \sigma^0)^2} = d\ln P \quad \text{Let} \quad \frac{\sigma}{\sigma^0} = x \]

then \[ -\frac{xdx}{(x-1)^2} = d\ln P \quad , \quad \frac{\sigma^0}{\sigma} = \theta = \frac{1}{x} \quad (\theta: \text{surface coverage}) \]

\[-\ln(x-1) + \frac{1}{x-1} = \ln P + C \quad \text{an isotherm} \]
\[ \therefore \ln \left( \frac{\theta}{1-\theta} \right) + \left( \frac{\theta}{1-\theta} \right) = \ln P + C \]

Henry’s limit must apply, i.e. \( P \to 0, \theta \to 0 \)

\( \theta = m'P \) as the boundary condition for \( P \to 0 \)

\[ \ln \theta + \theta = \ln P + C \quad C = \ln m' \]

\[ \therefore \ln \left( \frac{\theta}{1-\theta} \right) + \left( \frac{\theta}{1-\theta} \right) = \ln P + \ln m' \]

or \( m'P = \left( \frac{\theta}{1-\theta} \right) \exp \left( \frac{\theta}{1-\theta} \right) \) ... Volmer equation

when \( \theta \) is in the limit of small values (still above the Henry’s limit).

\[ m'P = \frac{\theta}{1-\theta} \]

\[ \theta = \frac{m'p}{1 + m'p} \] ........ Langmuir equation
Summary

1. It’s possible to correlate an adsorption isotherm and a 2-D equation of state by working from either direction.

\[ \frac{n}{W} = mP \quad \text{Gibbs. eq} \quad \pi \sigma = kT \]

\[ \pi (\sigma - \sigma^0) = kT \quad \text{Volmer equation (isotherm)} \]

(Equation of state)

2. It’s difficult to conclude from an experimental isotherm what the 2-D surface phases are like. (The gross feature of more complex isotherms are also given by simpler isotherms)

\[ \theta \]

\[ P \]

can be applied simultaneously to Volmer equation and Langmuir equation, but cannot say which one is correct.
3. **2-D equation** of state are a useful source of isotherm. predict the temperature dependence
3.4. Other isotherms from surface equation of state

A. if a isotherm \( \frac{n}{W} = m'P \) ............. Henry’s law

or \( \theta = m'P \)

excluding molecular area and leading to two dimensional eq. of state \( \pi \sigma = kT \)

B. assume eq. of state, considering the molecular area

\( \pi(\sigma - \sigma^0) = kT \)

\( m'P = \left( \frac{\theta}{1-\theta} \right) \exp\left( \frac{\theta}{1-\theta} \right) \) … Volmer equation

C. van der Walls analog:

\( (\pi + \frac{a}{\sigma^2})(\sigma - b) = kT \)................................. (1)

Attraction between adsorbates
interaction between molecular $\propto (\text{conc.})^2 = \left(\frac{n}{V}\right)^2 = \left(\frac{1}{V}n\right)^2$

interaction between molecular $\propto \left(\frac{1}{\sigma}\right)^2$

Gibbs. eq $m'P = \frac{\theta}{1-\theta}\exp\left(\frac{\theta}{1-\theta} - \frac{2a\theta}{bkT}\right)$ ...........(2)

Hill- deBoer equation

when $a=0$, (2) become identical to the Volmer equation.

the specific feature of (1) is that there exists a critical temperature, such that:

$T > T_c$, one $\pi$ vs. one $\theta$

$T < T_c$, one $\pi$ vs. three $\theta$
Note: 3D van der Waals equation

\[ P \quad 1 \quad P \text{ with } 3 \quad V \]

- 3-D van der Waals two phases are present.

- 3-D van der Waals equation shows that the three-root region is identified with a region of two-phases equilibrium.

- There are evidences for this type of phases equilibrium in the 2-D system.

- This figure indicates that there are three phases on the surface:
  - Kr in 2-D surface, \( T_c = 86K \)
  - 3-D system, \( T_c = 210K \)
  - Ar in 2-D surface, \( T_c = 65K \)
  - 3-D system, \( T_c = 151K \)

Kr adsorption on graphite.
◆ At θ between 0.65–0.8, a second phase-equilibrium region appears. Beyond this region, the adsorbate become incompressible.

For 3D system, an equation of state for the solid-phase \( P = -mv + b \)

For 2D, \( \pi = -m\sigma + b \) (or \( \sigma = -\frac{1}{m}\pi + \frac{b}{m} \))

◆ \( \pi = -m\sigma + b \) (an equation of state for solid state

\[ d\pi = -m\ d\sigma = -d\gamma = \frac{RT}{A_{sp}} \frac{n}{W} \ d\ln P = \frac{kT}{\sigma} \ d\ln P \]  \( \sigma = \frac{A_{sp} W}{nN_A} \)

\[ -\frac{m\sigma d\sigma}{RT} = d\ln P \]

integration: \(-\frac{m\sigma^2}{2kT} = \ln P + C \)

\[ \ln P = -\frac{m}{2kT} A_{sp}^2 \left( \frac{n}{W} \right)^{-2} + C \]  an isotherm for solid phase

(Harkins–Jura isotherm; based on the linear equation: \( \pi = -m\sigma + b \))

ps: \( \frac{m}{2kT} \) is a constant, depending on the adsorbate properties

Plot of \( \ln P \) vs. \( \left( \frac{n}{W} \right)^{-2} \), you can obtain slope \( \propto A_{sp}^2 \)
◆ solids for which $A_{SP}$ is known may be used to calibrate the proportionality constant for a particular adsorbate.

Problems with the H-J model

![Graph showing mismatch between H-J and observation](image)

◆ the H-J model characterizes the surface as $\theta \rightarrow 1$

◆ This equation dose fit a fairly wide range of experiment data and gives reasonable values of $A_{SP}$, despite the occurrence of multilayer adsorption (especially for type II isotherms).

◆ An H-J program is generally present in modern adsorption apparatus.