3.3 Two dimensional equation of state and isotherms

α

S ========= Interface(吸附在表面上）

β
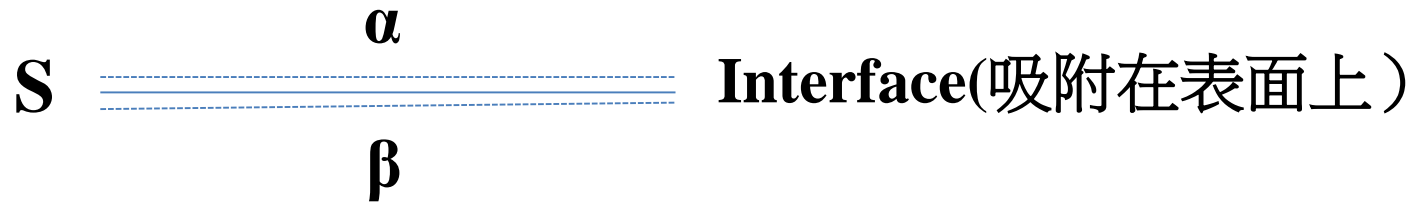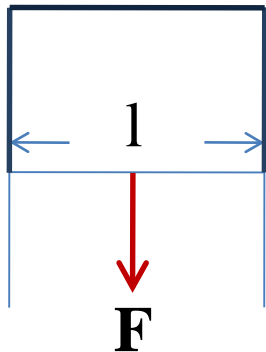
We consider two phases α and β in equilibrium with a surface S dividing them.

For the whole system $\quad G = G^\alpha + G^\beta + G^s$

For the bulk phases (α or β) $\quad G = E + PV - TS$

$\uparrow$ Internal energy

For the interface $\quad G = E^S + \gamma A - TS^S$

$\uparrow$ surface tension
(volume replaced by area)

surface tension

1

F

work = F dx = γldx = γ dA

$\gamma = \dfrac{F}{1} = - \dfrac{\text{force}}{\text{distance}}$; but P = $\dfrac{\text{force}}{\text{area}}$

$$G = \Sigma_{\alpha\beta s} (E + PV - TS) + \gamma A$$

$$dG = \Sigma_{\alpha\beta s} (dE + PdV + VdP - TdS - SdT) + Ad\gamma + \gamma dA$$

a reversible process,

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

substitute into dG

$$dG = \Sigma_{\alpha\beta s} (VdP - SdT + \Sigma_i \mu_i dn_i + \Sigma_i n_i d\mu_i - \delta W_{non-PV}) + A d\gamma + \gamma dA$$
and $\Sigma_{\alpha\beta s} \delta W_{non-PV} = \gamma dA$

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

$$dG = VdP - SdT + \Sigma_i \mu_i dn_i \text{ ....(2)} \quad \textbf{always true for a system}$$

(1) – (2) gives $\qquad \Sigma_{\alpha\beta s} (\Sigma_i n_i d\mu_i) + A d\gamma = 0$

$\Sigma_i n_i{}^{\alpha} d\mu_i + \Sigma_i n_i{}^{\beta} d\mu_i + \Sigma_i n_i{}^{s} d\mu_i + A d\gamma = 0$

For bulk phases at constant T and P,

$\Sigma_i n_i d\mu_i = 0$ $\qquad$ **Gibbs-Duhem equation**

$\therefore$ $\Sigma_i n_i{}^{s} d\mu_i + A d\gamma = 0$ $\quad$ **Gibbs adsorption equation in the interface**

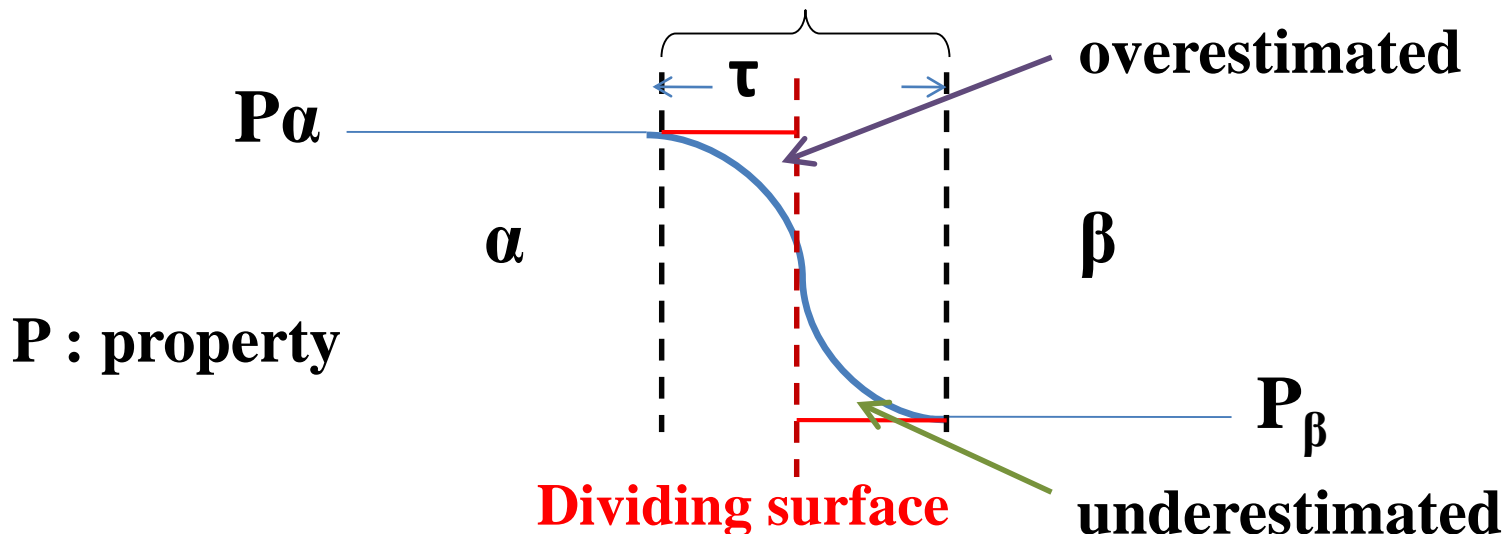**For two-component systems** $\qquad$ **(1: solvent, 2: solute)**

$n_1{}^{s} d\mu_1 + n_2{}^{s} d\mu_2 + A d\gamma = 0 \qquad \rightarrow d\gamma = - \dfrac{n_1^{s}}{A} d\mu_1 - \dfrac{n_2^{s}}{A} d\mu_2$

$\Gamma_i = - \dfrac{n_i^{s}}{A}$ $\quad$ **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)

$P\alpha$

τ

overestimated

α

β

P : property

P_β

Dividing surface

underestimated

◆ **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 τ, the dividing surface is determined, such that overestimated P_α = underestimated P_β.**

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

$$\Gamma_1 = \frac{n_1^s}{A} = \text{surface excess of solvent} = 0$$

(no solvent adsorbed at the interface)

small X_0

n_2^α

n_2^β
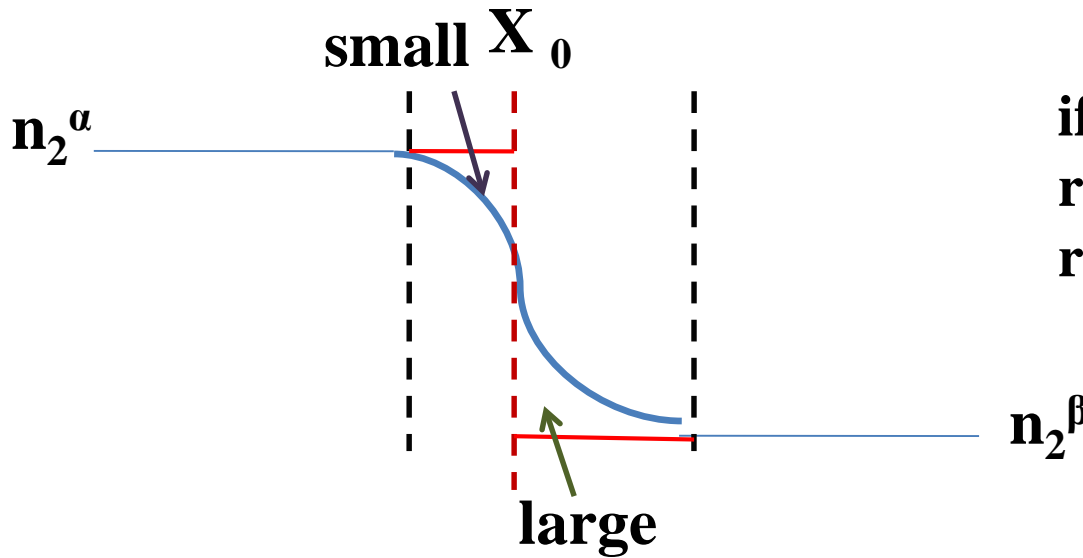
if $n_2^\beta > n_2^\alpha$, this means that the real situation has an excess in reference to X_o plane

large

on the basis of $\Gamma_1 = 0$, for dividing surface

$$-d\,\gamma = \Gamma_2\,d\,\mu_2 = \Gamma_2^1\,d\mu_2$$

$$\mu_2 = \mu_2^0 + RT\,\ln a_2$$

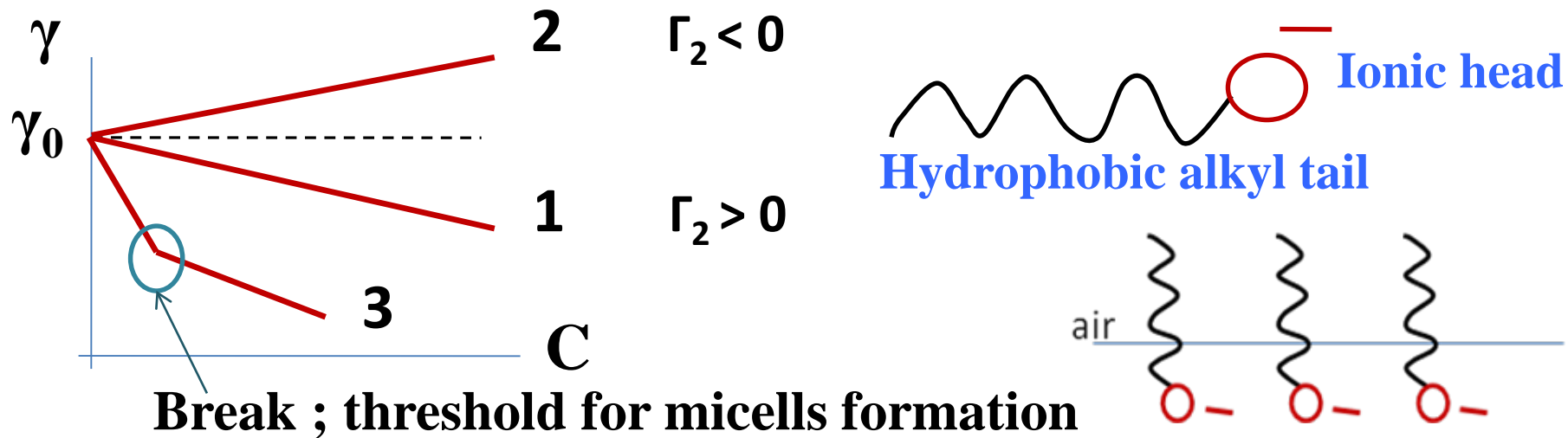$$\therefore\ d\mu_2 = RT\,\frac{d\,a_2}{a_2} = RT\,\frac{d\,C}{C}$$

(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

γ

γ_0

2 $\Gamma_2 < 0$

1 $\Gamma_2 > 0$

3

C

Ionic head

Hydrophobic alkyl tail

air

Break ; threshold for micells formation

Curves 1,3: positive adsorption at the interface $\because$ slope $< 0 \rightarrow \Gamma_2 > 0$
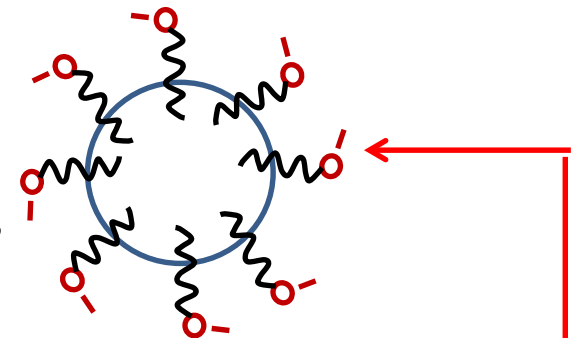
Curve 2 : negative surface excess

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

Micelles form at high concentration Gibbs can not be used.

Curve 3. solute = amphipathic species

as C→0,
straight line relationship (curve 1 as an example)

$\gamma = \gamma_0 - mC$

$\pi = \gamma_0 - \gamma \ = $ **two dimensional pressure** $\left[\dfrac{force}{length} \right]$

$\pi = m\ C$

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

$$(\gamma = \gamma_0 - mC \rightarrow \ \left(\frac{d\gamma}{dC}\right)T = -m\ )$$

$$\frac{n_2^s}{A} = \frac{\pi}{RT} \qquad \pi A = n_2^s RT$$

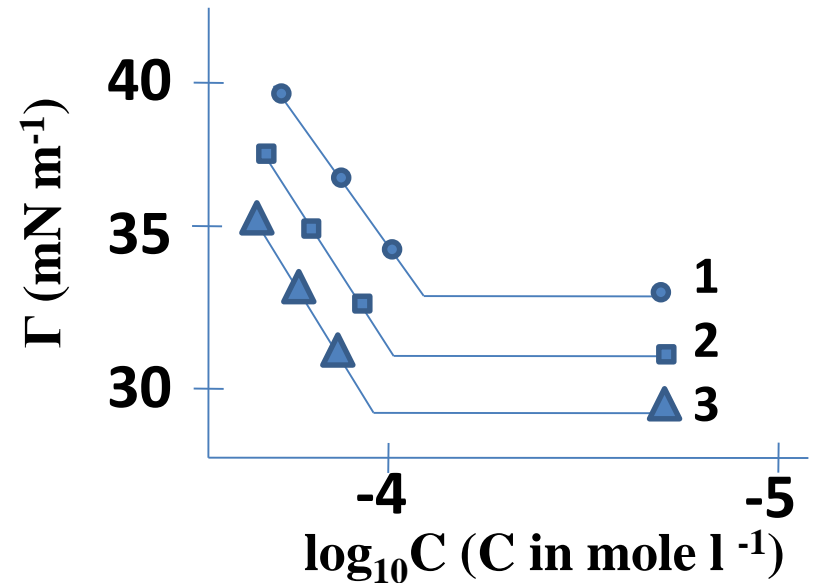**Two-dimensional (2-D) ideal gas law; for low conc.**

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 γ 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:

$$-d\gamma = \Gamma_2 \, d\mu_2$$

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

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, $\dfrac{n}{W}$ **is a function of P.**

$$-\int_{\gamma_0}^{\gamma} d\gamma = \frac{RT}{A_{sp}} \int_0^P \frac{n}{W} d\ln P \quad \text{B.C.} \quad \frac{n}{W} \rightarrow 0 \, , \text{ as } P \rightarrow 0$$

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 $\left(\dfrac{n}{W}\right) = m \times P$ ………. **Hennry's law limit**

(at very low pressures)

linear relation; an isotherm

$$\pi = \frac{RT}{A_{sp}} \int_0^p mp \frac{dP}{P} = \frac{RT}{A_{sp}} mp = \frac{N_A kTn}{A_{sp} w}$$

$\therefore \sigma = \dfrac{A_{sp} w}{n N_A} = $ **the area share for one molecular**

$\therefore \pi \sigma = kT$ … 2-D equation of state

$Pv = kT$ ... 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.**

$$\theta = m'P \quad \ldots\ldots \quad \textcolor{red}{\textbf{Henry's limit (another form)}}$$

$$\frac{N_A n \sigma}{A_{sp} W}$$

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.

$\pi(\sigma-\sigma^0)= k\,T$ $\qquad \sigma^0$: molecular cross-sectional area

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

$d\pi = -kT(\sigma-\sigma^0)^{-2}\,d\sigma$ and $\pi = \gamma_0-\gamma$

$$d\pi = -d\gamma = \frac{RT}{A_{sp}}\frac{n}{W}\,d\ln P = \frac{kT}{\sigma}\,d\ln P$$

(eq. of state) (Gibbs eq.)

$$-\frac{\sigma d\sigma}{(\sigma-\sigma^0)^2} = d\ln P \qquad \text{Let } \frac{\sigma}{\sigma^0} = x$$

then $\qquad -\dfrac{x\,dx}{(x-1)^2} = d\ln P$, $\qquad \dfrac{\sigma^0}{\sigma} = \theta = \dfrac{1}{x}$ (θ: surface coverage)

$-\ln(x-1) + \dfrac{1}{x-1} = \ln P + C$ $\qquad$ 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. $P \rightarrow 0$, $\theta \rightarrow 0$

$\theta = m'P$ as the boundary condition for $P \rightarrow 0$

$\ln\theta + \theta = \ln P + C$ 　　　 $C = \ln m'$

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

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

when θ is in the limit of small values (still above the Henry's limit).

$$m'P = \frac{\theta}{1-\theta}$$

$$\theta = \frac{m'p}{1+m'p} \quad \text{........ Langmuir equation}$$
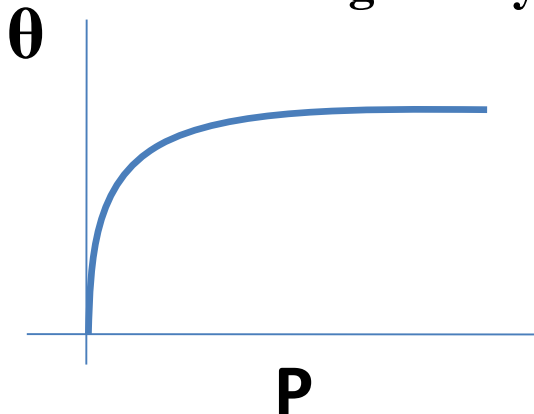
Summary

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

$$\frac{n}{W} = mP \quad \xrightarrow{\text{Gibbs. eq}} \quad \pi \, \sigma = k \, T$$

$$\pi \, (\sigma - \sigma^0) = kT \quad \longrightarrow \quad \text{Volmer equation (isotherm)}$$

(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)

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 $\dfrac{n}{W} = m'P$ .... Henry's law

or $\theta = m'P$

excluding molecular area and leading to two dimensional
eq. of state $\pi\,\sigma = k\,T$

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

$\pi(\sigma\text{-}\sigma^0) = k\,T$

$m'P = \left(\dfrac{\theta}{1-\theta}\right) \exp\left(\dfrac{\theta}{1-\theta}\right)$ ... **Volmer equation**

C. van der Walls analog:

$\left(\pi + \dfrac{a}{\sigma^2}\right)(\sigma - b) = k\,T$ .... (1)

Attraction between adsorbates

σ^0

(3-D system)

interaction between molecular $\propto$ **(conc.)²** $= \left(\dfrac{n}{V}\right)^2 = \left(\dfrac{1}{V/n}\right)^2$

(2-D system)

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

Gibbs. eq $\longrightarrow$ $\mathbf{m'P} = \dfrac{\theta}{1-\theta}\exp\left(\dfrac{\theta}{1-\theta} - \dfrac{2a\theta}{bkT}\right)$ ....(2)
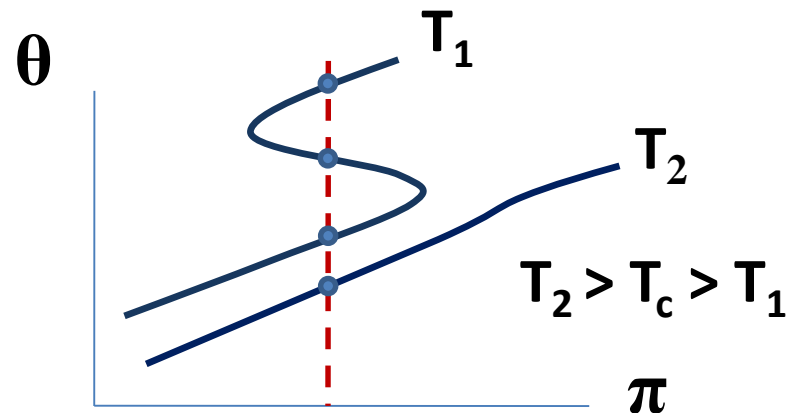
$\boxed{\textcolor{red}{\textbf{Hill- deBoer equation}}}$

when a=0, (2) become identical to the Volmer equation.
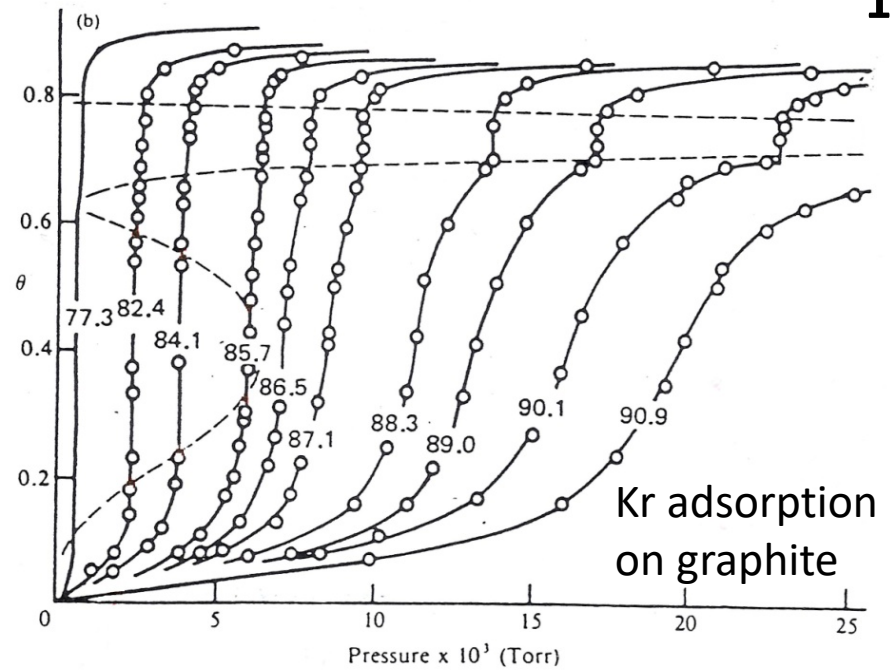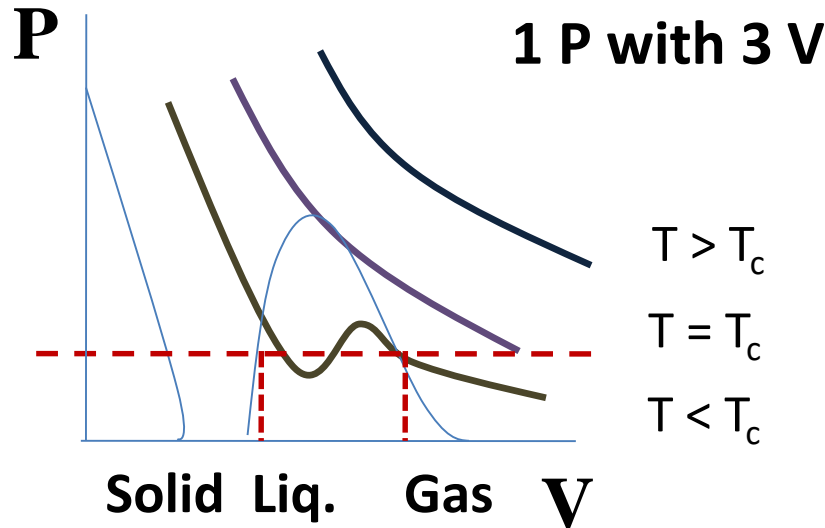
the specific feature of (1) is that there exists a critical temperature, such that :

$T > T_c$, one π vs. one θ

$T < T_c$, one π vs. three θ

$T_2 > T_c > T_1$

Note: 3D van der Waals equation

P

1 P with 3 V

$T > T_c$

$T = T_c$

$T < T_c$

Solid Liq.   Gas **V**

Kr adsorption on graphite

◆ **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-Dsystem, $T_c = 151K$

◆ **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, π = -mσ+b (or σ = -$\dfrac{1}{m}\pi + \dfrac{b}{m}$)

◆ **π = -m σ + b (an equation of state for solid state**

$$d\pi = \text{-m } d\sigma = \text{-}d\gamma = \frac{RT}{A_{sp}}\frac{n}{W}d\,\ln P = \frac{kT}{\sigma}d\,\ln P \qquad (\sigma = \frac{A_{sp}W}{nN_A})$$

$$-\frac{m\sigma d\sigma}{RT} = d\,\ln P$$

integration: $-\dfrac{m\sigma^2}{2kT} = \ln P + C$

$\ln P = - \dfrac{m}{2kT} A_{sp}^2 (\dfrac{n}{W})^{-2} + C$ **an isotherm for solid phase**
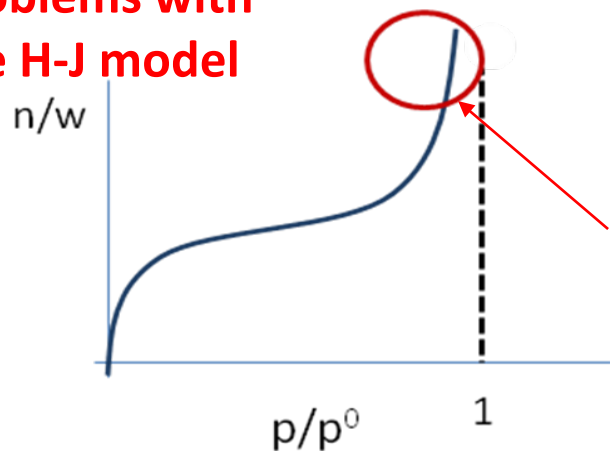
(Harkins–Jura isotherm; based on the linear equation: π = -m σ + b)

ps: $\dfrac{m}{2kT}$ **is a constant, depending on the adsorbate properties**

Plot of ln P vs. ($\dfrac{n}{W}$)$^{-2}$, 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

mismatch between H-J and observation

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

◆ **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.**