Lecture Note #5 (Spring, 2019)

Thermodynamics & Kinetics of Adsorption & Desorption

Reading: Kolasinski, ch.4

Thermodynamics of ad/desorption

Binding energies and activation barriers



Figure 4.1 One-dimensional potential energy curves for molecular adsorption: (a) nonactivated adsorption; (b) activated adsorption. $E_{ads'}$, $E_{des'}$, adsorption activation energy and desorption activation energy, respectively; $q_{ads'}$, heat released by adsorption; $z_{ea'}$, adsorbate-surface bond length.



Figure 4.2 Activated dissociative adsorption. $E_{ads'}$, $E_{des'}$, adsorption activation energy and desorption activation energy, respectively; $q_{ads'}$, heat released by adsorption; $z_{eq'}$, adsorbate-surface bond length.

Thermodynamic quantities

- Adsorption, especially chemisorption \to surface free energy $\downarrow \to$ surface tension, $\gamma \downarrow$
- Chemisorption \rightarrow usually exothermic process $\rightarrow \Delta S < 0$ (gas in 2D), $\Delta G < 0$ (constant T & P, free energy \downarrow , spontaneous) $\rightarrow \Delta G = \Delta H T\Delta S \rightarrow \Delta H < 0$ (exothermic)
- Temperature $\downarrow \rightarrow Adsorption \uparrow$
- exception: dissociate adsorbates & high translational mobility on the surface (ΔS > 0). Repulsion between adsorbates by coverage↑ → less exothermic

e.g., H₂ on glass: endothermic, H₂(g) \rightarrow 2H (glass), Δ S > 0 $\rightarrow \Delta$ H > 0

Table 4.1Definition of symbols

Nada	Number of adsorbates (molecules or atoms, as appropriate)
No	Number of surface sites or atoms (as defined by context)
Nove	Number of atoms/molecules exposed to (incident upon) the surface
A	Surface area (m^2 or, more commonly, cm^2)
σ	Areal density of adsorbates (adsorbates cm ⁻²), $\sigma = N_{ads}/A_s$
σ	Areal density of sites or surface atoms (cm^{-2})
σ	Areal density of empty sites (cm^{-2})
σ.	Areal density that completes a monolayer (cm^{-2})
θ	Coverage, fractional number of adsorbates (monolayers, ML), also sometimes called fractional coverage, $\theta \equiv \sigma/\sigma_0$
$\theta_{\rm sat}$	Saturation coverage, $\theta_{sat} \equiv \sigma_{sat}/\sigma_0$, where σ_0 is the number of surface atoms
δ	Relative coverage defined with respect to saturation, $\delta \equiv \sigma / \sigma_{sat} \equiv \theta / \theta_{sat}$
ε	Exposure, amount of gas incident on the surface, units of cm^{-2} or Langmuir
ε (M-A)	Binding energy of the M-A bond
Q _{ads}	Heat released when a single particle adsorbs (positive for exothermic)
L	Langmuir, unit of exposure, $1 L = 1 \times 10^{-6}$ torr $\times 1 s$
S	Sticking coefficient, $s = \sigma/\varepsilon$
	Integral sticking coefficient: total coverage divided by exposure, meaningful only if s is
	constant or as $\theta \rightarrow 0$ ML
	Instantaneous or differential sticking coefficient at coverage $\theta s(\theta) = dN_{ads}/dN_{exp} = d\sigma/d\varepsilon$, evaluated at a specific value of θ
<i>s</i> ₀	Initial sticking coefficient, sticking coefficient as $\theta \rightarrow 0$ ML

Heat of adsorption

Isosteric enthalpy(heat) of adsorption

- dG = Vdp SdT, and d(Δ G) = Δ Vdp Δ S dT for any change
- At equilibrium, $\Delta V dp \Delta S dT = 0$.
- $\Delta V = V_{ad} V_g \sim nRT/p$
- $(\partial p / \partial T)_{\theta} = \Delta \tilde{S} / \Delta V = (\Delta H / T) / (nRT/p) = p \Delta H / nRT^2$ at constant θ .
- d lnp = ($\Delta H_{ad}/R$) d(1/T) \rightarrow The slope of (ln p) (1/T) plot gives $\Delta H_{ad}/R$
- In genera, ΔH_{ad} is coverage-dependent because of
 - 1) Heterogeneity of the adsorption sites
 - 2) Lateral interaction between adjacent adsorbates
- cf. isoteric: constant adsorption isoteric enthalpy: standard enthalpy of adsorption at fixed coverage



Figure 4.3 Three different behaviours of the heat of adsorption, q_{ads} , as a function of coverage, θ . Case (1): the surface is composed of one and only one type of non-interacting site. Case (2): q_{ads} decreases linearly with θ . Case 3: the surface is composed of two types of sites with different binding energies that fill sequentially. As shown in §4.3, case 3 can also arise from strong lateral interactions.

Isosteric enthalpy(heat) of adsorption



CO on charcoal ΔH_m = -7.52 kJ/mol



- a) Physisorbed N_2 on rutile TiO₂ at 85 K
- b) Chemisorbed H on W
- c) Physisorbed Kr on graphized carbon black

Kinetics of adsorption

Langmuir model assumes that

- Uniform adsorption site
- Adsorption energy independent of θ
- No surface diffusion
- Monolayer coverage

A(g)+ * \rightarrow A(ad) : non-dissociative

 k_a : adsorption rate const, k_d : desorption rate const

$$d\theta/dt = k_a p(1 - \theta)$$
 : $k_a = Z_w s_0/p$
 $s_0 =$ initial sticking probability
(1 - θ): vacant site
p: partial pressure of A
 $s(\theta) = s_0 (1 - \theta)$

 $\theta(t) = 1 - \exp(-k_a t)$

 $A_2 + * → 2A(ad) : dissociative adsorption$ $• dθ/dt = k_a p(1- θ)^2 : k_a = 2 Z_w s_0/p$ $s(θ) = s_0 (1- θ)^2$ $θ(t) = k_a t / (1+ k_a t)$





Figure 4.6 Langmuir models (molecular and dissociative) of the sticking coefficient, s, as a function o coverage, θ .



Dissociaitive adsorption: surface coverage depends more weakly on pressure than for nondissociative adsorption

Figure 4.7 Langmuir models (molecular and dissociative) of coverage, σ , as a function of exposure, ε .

Dissociative Langmuir adsorption with lateral interaction



Figure 4.8 The effect of lateral interactions on the dissociative sticking coefficient as a function of interaction strength, ω , and coverage θ at a fixed surface temperature $T_s = 77$ K.

Precursor-mediated adsorption

- Marked deviation from Langmuir adsorption Langmuir adsorption; $s = s_0 (1 - \theta)^2$
- Coverage-insensitive s.
- Decrease in s with increasing Ts: re-evaporation of the precursor state.





 $N_2(g) \leftrightarrow N_2(ad) \rightarrow 2 \; N(ad)$

- Trapping in the physisorption well
- Precursor hopping on the surface to find an empty site → increase in s
- Re-evaporation of the precursor due to a finite surface lifetime τ ; $\tau = \tau_0 \exp(-E_d/RT)$

 $N_2(g) \rightarrow 2 N_{ad}$ 0.1 N₂/ W(100) 5= 300 K S 0.600000000 N₂/ W(100) S T_s= 300 K[°] 433 664 773 Surface coverage θ



Figure 4.9 Sticking of Cs on W. Replotted from the data of J. B. Taylor, I. Langmuir, Phys. Rev., 44 (1933) 423.



Figure 4.10 The Kisliuk model of precursor mediated adsorption. Incident molecules trap into intrinsic or extrinsic precursors. Thereafter, sticking becomes a competitive process between desorption out of the precursor and transfer into the stable chemisorbed state. α is the probability to enter into the precursor state.



Figure 4.11 The change of sticking coefficient, s, with coverage for precursor mediated adsorption is characterized by the parameter K. For K = 0, the sticking coefficient is constant, whereas for K = 1 it drops linearly with coverage as in Langmuirian adsorption. Large values of K decrease s relative to Langmuirian adsorption.

Adsorption isotherms from kinetics

Adsorption-desorption equilibrium A(g) + * \leftrightarrow A(ad)

- $d\theta/dt = k_a p(1 \theta) k_a \theta$
- •The desorption rate constant $k_d = k_d^0 \exp(-E_d/RT)$
- At equilibrium, $d\theta/dt = 0$, $\theta = K(T) p/[1+K(T) p]$ where $K = k_a / k_d$: equilibrium constant
- As $p \rightarrow \infty$, $\theta \rightarrow 1$
- θ -P plot at constant T is called Langmuir isotherm
- $\bullet T{\downarrow} \to adsorption{\uparrow}$
- As seen in the Fig., the coverage θ depends more sensitively on T than on p

cf. adsorption isotherm: coverage change by pressure at a temperature

NH₃/ charcoal



Measurement of adsorption isotherm

Volumetric measurement

 $\theta = K(T)p / [1+K(T) p]$ $\theta = V/V_m$ measured as a volume change, where V is the volume of gas adsorbed and V_m is the saturation volume (corresponding to complete coverage).

V/ $V_m = Kp /(1+Kp)$, P/V = (1+Kp)/K $V_m = p/V_m + 1/KV_m$

p/V vs. p plot gives a straight line. Slope = $1/V_m$ and intercept = $1/KV_m$







Figure 4.12 The six types of physisorption isotherms in which coverage (either relative coverage θ or absolute coverage σ) is plotted against pressure, p, of a gaseous adsorbing species (or concentration, c, of a species dissolved in a liquid solution). The coverage is often expressed as specific coverage, that is, coverage per unit mass of the substrate.

Langmuir adsorption isotherm



Figure 4.4 Langmuir isotherms exhibit a dependence on the temperature and binding energy. (a) Constant heat of adsorption for various temperatures T. (b) Constant temperature for various adsorption energies ε .

Classifications of adsorption isotherms

Brunner clasification

Type I: Langmuir adsorption

Type II: monolayer + multilayer

Type III: multilayer adsorption

Type IV: Type II

Type V: Type III on a porous adsorbent

- Finite pore volume limits the max. V_{ads} .
- Type II & IV: $\Delta H_{des} >> \Delta H_{vap}$
- Type III & V: $\Delta H_{des} \sim \Delta H_{vap}$



 p_0 = saturation vapor pressure

Examples of adsorption isotherms



CO/Pd(111)

Ar, NH3 /carbon black

Kr /carbon black

* carbon black graphitized at 3000 K

Multilayer physisorption

BET isotherm: Brunnauer, Emmett, Teller

- Langmuir adsorption extended to allow multilayer adsorption
- Equilibrium maintained between the adjacent layers
- ΔH^{o}_{des} for the first layer and ΔH^{o}_{vap} for the multilayers
- used for surface area measurements.

 $\begin{array}{ll} \mathsf{M}(g) + & \stackrel{*}{\longrightarrow} & \bigoplus \mathsf{M}_1(\mathrm{ad}) \\ \mathsf{M}(g) + \mathsf{M}_1(\mathrm{ad}) & \leftrightarrow \mathsf{M}_2(\mathrm{ad}) \\ & & \\ & & \\ \mathsf{M}(g) + \mathsf{M}_{\mathsf{n}\text{-}1}(\mathrm{ad}) \leftrightarrow \mathsf{M}_\mathsf{n}(\mathrm{ad}) \end{array}$







BET equation

- Extension of Langmuir equation beyond the 1st layer.
- Equilibrium between adjacent layers
- The rate of coverage change for each layer is zero.
- The 1st layer may be chemisorption, but the 2nd layer and beyond are always physisorption → Therefore, different k_a and k_d values may be involved.
- At equilibrium

$$d\theta_0/dt = -k_a p \theta_0 + k_d \theta_1 = 0$$

$$d\theta_1/dt = k_a p \theta_0 - k_d \theta_1 - k'_a p \theta_1 + k'_d \theta_2 = 0$$

$$d\theta_2/dt = k'_a p \theta_1 - k'_d \theta_2 - k'_a p \theta_2 + k'_d \theta_3 = 0$$

$$d\theta_{n-1}/dt = k'_a p \ \theta_{n-2} - k'_d \ \theta_{n-1} - k'_a \ p\theta_{n-1} + k'_d \ \theta_n = 0$$

- $k_a = Z_w s_0$, $k_d = v \exp(-\Delta H_{des}/RT)$ for the 1st layer • $k'_a = Z_w s'_0$, $k'_d = v' \exp(-\Delta H_{eva}/RT)$ for the 2nd layer and beyond.
- For miultilayer adsorption $s_0 \sim s'_0$ and $v \sim v'$. Then, $k_a \sim k'_a$.
- But E_{des} can be much larger than E'_{des} , hence k_d much smaller than k'_d .

 $d\theta_1/dt = 1 - 2 - 3 + 4$



• Let
$$k_a/k_d = K$$
, $k'_a/k'_d = K'$, and
 $c = K / K' = (k_a/k_d) / (k'_a/k'_d) \sim k'_d/k_d = \exp(\Delta H_{des} - \Delta H_{vap}) / RT$

$$\theta_{1} = (k_{a}/k_{d}) p \theta_{0} = \mathbf{K}p\theta_{0} = c\mathbf{K}'p\theta_{0}$$

$$\theta_{2} = [(k_{d} + k_{a}'p) \theta_{1} - k_{a}p \theta_{0}] /k'_{d} = (1/c + K'p) \theta_{1} - K'p \theta_{0} = c(K'p)^{2} \theta_{0}$$

$$\theta_{3} = [(k'_{d} + k'_{a}p) \theta_{2} - k'_{a}p \theta_{1}] /k'_{d} = (1 + K'p) \theta_{2} - K'p \theta_{1} = c(K'p)^{3} \theta_{0}$$

 $\theta_{n} = (1 + K'p) \ \theta_{n-1} - K'p \ \theta_{n-2} = c(K'p)^{n-1} \ \theta_{0} + (K'p)_{n}\theta_{0} - c(K'p)^{n-1} \ \theta_{0} = c(K'p)^{n} \ \theta_{0}$

$$\begin{array}{l} (1) \ \theta_0 + \theta_1 + \dots + \theta_n \ (n \to \infty) = 1 \\ \to \ \theta_0 + c K'p \ [1 + Kp + (K'p)^{2} + (K'p)^3 + \dots] \ \theta_0 = 1 \to \ \theta_0 \ [1 + c K'p \ /(1 - K'p)] = 1 \\ \to \ \theta_0 = 1/[1 + c K'p \ /(1 - K'p)] = (1 - K'p) \ / \ [1 + (c - 1)K'p] \\ (2) \ V/V_m = \ \theta_1 + 2 \ \theta_2 \ \dots + n \ \theta_n \ = c[\ K'p + 2(K'p)^2 + 3(K'p)^3 + \dots] \ \theta_0 \\ = (1 - K'p) \ c K'p \ / \ [1 + (c - 1)K'p] \ (1 - K'p)^2 \\ cf: \ 1 + x + x^2 + \dots = d(\ x + x^2 + x^3 \dots)/dx = d[x/(1 - x)]/dx = 1/(1 - x)^2 \end{array}$$

When p = p₀ (saturation vapor pressure), adsorption and desorption can take place at all sites. Therefore, k'_ap₀ (θ₀ + θ₁+ ... + θ_n) = k'_d (θ₀ + θ₁+ ... + θ_n) → k'_ap₀ = k'_d → K' = 1/p₀ and K' p = p/p₀ (3)

•
$$V/V_m = (1 - K'p) cK'p / [1+(c-1)K'p] (1-K'p)^2$$
 from (2) and (3)
= $c (p/p_0) / [1+(c-1)p/p_0]] (1-p/p_0) = V/V_m = cp p_0 / [p_0+(c-1)p] (p_0-p)$

• Rearranging, $[p_0+(c-1)p]/c p_0 V_m = p/V(p_0-p) \rightarrow p/V(p_0-p) = 1/cV_m + [(c-1)/cV_m] (p/p_0); y = a + bx type$

BET equation

 $p/V(p_0-p)$ vs. p/p_0 plot gives a straight line as shown in the Figure (next page)

$$\frac{p}{V(p_0 - p)} = \frac{1}{V_m c} + \frac{(c - 1)}{V_m c} \frac{p}{p_0}$$

Intercept = 1/cV_m

$$V_m = \frac{1}{\text{slope + intercept}}$$

V_m = monolayer capacity
c = exp (Δ H_{des} - Δ H_{vap})/RT

For a porous solid $V = \frac{V_{\rm m}cx}{(1-x)} \cdot \frac{1 - (n+1)x^n + nx^{n+1}}{1 + (c-1)x - cx^{n+1}}$

, where n is related to the pore size and $x = p/p_0$









Capillary Condensation

Porosity may result from

- 1) Gas evolution during the formation of the solid.
- 2) Fibrous structure.
- 3) Compaction of particulate solid.

Representative example: Zeolites

- Natural or synthetic materials
- SiO₄ and AlO₄ tetrahedra are linked by sharing O atoms
- 3D structure containing regular channels and cavties of sizes similar to those of small and medium –sized molecules.

Classification of pores

- Micropore s: width < 2nm
- Mesopores: width = 2nm ~ 50 nm
- Maropores: width > 50 nm



Hysteresis loop

Figure 5.7 Zeolite structure. (a) 6-ring containing two aluminium and four silicon tetrahedral centres. (b) Zeolite A structure. Each of the eight sodalite units depicted contains 24 aluminium or silicon tetrahedral centres arranged to give six 4-rings plus eight 6-rings

(a)

Pore size distribution: Mercury intrusion porosimetry

Rate of desorption

- Reverse process of adsorption
- Thermal desorption by phonon anihilation
- Temperature programmed desorption (TPD) information available: surface coverage, desorption kinetics, adsorption energy,

Desorption rate

 $d\theta/dt = k_d \theta^n$ $n = 0 : 0^{\text{th}}\text{-order desorption}$ $n = 1 : 1^{\text{th}}\text{-order desorption} : M(ad) \rightarrow M(g)$ $n = 2 : 2^{\text{th}}\text{-order desorption} : 2 A(ad) \rightarrow A_2(g)$

 $k_d = k_d^0 \exp(-E_{des}/RT)$ T = T₀ (1+ β t), where the heating rate β = 0.1~ 10 K/s



surface

Temperature programmed desorption (TPD)

A. 0th –order desorption

- $d\theta/dt = k_d = k_d^0 \exp(-E_{des}/RT)$
- For a multilayer $\theta = 1$.
- Exponential rate increase with T \rightarrow obtain E_{des}







1st –order desorption

- The peak temperature is coverage-independent
- Asymmetric peak shape

 $E_{\text{des}} = RT_{\text{p}} \left[\ln \left(\frac{AT_{\text{p}}}{\beta} \right) - 3.46 \right]$ ~ 31 kT_p Ex: T_p= 300 \rightarrow E_{des} = 0.81 eV.



2nd –order desorption

- Peak shift to a lower T with increasing coverage
- Almost-symmetric peak

