

Week 9

Surface Structure and Catalysis

9.1 Surface Structure and Catalysis

5/23:

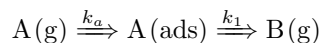
- Final exam:
 - Single sheet with problems on both sides and a blank piece of paper to write answers on.
 - Total time: 50 minutes.
 - We only need to look into the specific subchapters in the final exam outline.
 - The computation problem will be from either PSet 5 or 6.
 - 7 true/false problems on concepts from the chapters specified in the outline.
 - 2 true/false problems relative to plots that have been drawn in class or elsewhere.
 - Relatively easy compared to the midterm.
- Review of last lecture.
- The Langmuir adsorption isotherm implies rate laws for surface-catalyzed gas-phase reactions.



- The observed rate law is given by

$$\frac{d[\text{B}]}{dt} = k_{\text{obs}} P_{\text{A}}$$

- Assume that this reaction occurs by the following two-step mechanism.



- The rate law for this mechanism is

$$\frac{d[\text{B}]}{dt} = k_1 [\text{A(ads)}] = k_1 \sigma_{\text{A}}$$

where $\sigma_{\text{A}} = \sigma_0 \theta$.

- Derivation.

- We have that

$$\frac{1}{\theta} = 1 + \frac{1}{K_c [\text{A}]}$$

so

$$\frac{d[\text{B}]}{dt} = k_1 \frac{\sigma_0 K_c [\text{A}]}{1 + K_c [\text{A}]} = k_1 \frac{\sigma_0 b P_{\text{A}}}{1 + b P_{\text{A}}}$$

where we have defined $b = K_c / k_{\text{B}} T$.

- At low gas pressures, $bP_A \ll 1$. Here, the rate law becomes first order in reactant pressure.

$$\frac{d[B]}{dt} = k_1 \sigma_0 b P_A = k_{\text{obs}} P_A$$

- At high pressure, $bP_A \gg 1$. Here, the rate law becomes zero order in reactant pressure.

$$\frac{d[B]}{dt} = k_1 \sigma_0 = k_{\text{obs}}$$

- Most reactions are studied at low pressure and the observed rate constant is equal to the product $k_1 \sigma_0 b$.
- Relation to enzyme catalysis.
 - There, we formed an enzyme-substrate complex, which then decomposed.
 - Here, we form a substrate-adsorption complex that then decomposes.
 - In surface catalysis, we refer to our surface as the substrate. It's a lattice on which our reaction happens.
 - For enzyme catalysis, we learned that the rate has a linear dependence on substrate concentration for small [S] and no dependence for big [S].
 - Recall that the Michaelis-Menten mechanism is a reaction mechanism for enzyme catalysis.
 - It predicts our first \rightarrow zero order substrate concentration dependence change.
 - It also comes packaged with the Lineweaver-Burk plot.
- The surface structure is different from that of the bulk.
- Surface characterization tools.
 - Scanning electron microscopy (SEM).
 - A scanning electron microscope (SEM) is a type of electron microscope that produces images of a sample by scanning the surface with a focused beam of electrons. The electrons interact with atoms in the sample, producing various signals that contain information about the surface topography and composition of the sample.
 - There's also transmission, that detects electrons which pass through the surface.
 - Low-energy electron diffraction (LEED).
 - Electrons with kinetic energies in the range of 5000-10 000 kJ mol⁻¹ are commonly called low-energy electrons and penetrate the surface of a metal to only about 500 pm.
- The surfaces have many types of defects.

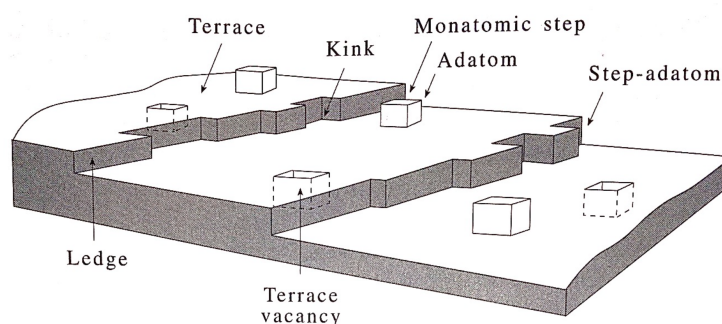
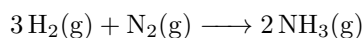
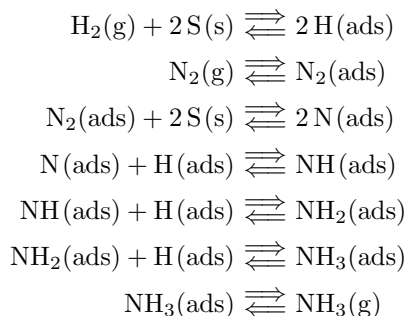


Figure 9.1: Surface features and defects.

- An illustration of some of the possible structural defects that occur on a surface. The surface is characterized by ledges, steps, and terraces.
- The steps can be one or many rows of atoms. The steps also need not be straight, which gives rise to kinks.
- Single atoms (or **adatoms**) may sit anywhere on a terrace.
- There can also be vacancies on the terrace, leaving small holes in the surface. These holes are indicated by dotted cubes.
- The defects are often some of the active sites.
 - The locations of the defects are locations where the surface energy is high. These high energy spots become sweet spots for reactions. Molecules will come in, bind to that high energy site, and use the energy to form a product.
- Doping.
 - *p*-type doping of semiconductors can introduce holes. *n*-type doping of semiconductors introduces electrons.
- Defect types.
 - We can have hole defects, line defects, and plane defects.
 - Some defects can be bad, degrading the whole material, but in catalysis, they're good.
- The reaction between H₂ and N₂ to produce NH₃ can be surface catalyzed.



- Mechanism.



- Splitting nitrogen is the hardest part.
 - The second step is physisorption.
 - The third step is dissociative chemisorption.
- The relative rates of ammonia synthesis for different transition metal catalysts can be plotted.
 - The shape of the plotted data is influenced by the opposing effects of the strength of the surface nitrogen bond and the activation energy of the dissociative chemisorption of N₂.
- Summary of what's essential in Chapter 31.
 - Miller indices and drawing the planes to which they correspond.
 - If we only need to draw one on the exam, skip the one through the origin and draw the next one.
 - The total scattering intensity (e.g., from the homework).
 - Isotherms.
 - We need to be clear about the information that the Langmuir plot can give us.
- Tian leaves the door open for us to reach out to him in the future.
- Also don't worry about the midterm too much; Tian will try to adjust in the best possible way.

9.2 Chapter 31: Solids and Surface Chemistry

From McQuarrie and Simon (1997).

- 5/24:
- McQuarrie and Simon (1997) covers the derivation of rate laws for surface-catalyzed reactions from class.
 - McQuarrie and Simon (1997) derives rate laws for bimolecular gas-phase reactions occurring via the **Langmuir-Hinshelwood mechanism** and **Eley-Rideal mechanism**.
 - McQuarrie and Simon (1997) covers surface structure, including SEM and LEED.
 - The activation barrier in nitrogen fixation is so high (owing to the BDE of N_2) that even though the reaction is exothermic, the reactant molecules can be stored together forever with no reaction ever taking place.
 - On an iron surface, however, the BDE of N_2 is approximately 10 kJ mol^{-1} .
 - **Volcano curve**: A plot with a linear ascent and descent.
 - An example is the plot of the relative rates of ammonia synthesis for different transition metal catalysts, which peaks in the middle.
 - The two forces at play in this particular plot are an increase in d electrons decreasing the strength of the metal-nitrogen bond in adsorbed NH_3 molecules, and an increase in d electrons increasing the N_2 BDE.
 - Surface orientation also affects reaction rate: A smooth 110 surface gives rise to a negligible yield of ammonia, while a rough 111 surface has the highest yield.
 - This particular result stems from changes in the BDE of N_2 across the types of surfaces.