Kinetics of Surface Catalysed Reactions

A wide variety of rate laws and reaction mechanisms can apply to surface catalysed reactions. A few of these are considered below.

UNIMOLECULAR DECOMPOSITION

Examples of unimolecular decomposition reactions include:

1. Decomposition of NH_3 to N_2 and H_2 on metal surfaces
2. Decomposition of phosphine on glass
3. Decomposition of formic acid on glass, Pt, Ag, Au, or TiO_2 (in this case there are two competing reactions: $HCOOH \rightarrow CO + H_2O$ and $HCOOH \rightarrow CO_2 + H_2$)

Unimolecular surface reactions can often be described by the mechanism

$$A_{(g)} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} A_{(ads)} \xrightarrow{k_2} \text{Products}$$

The rate of product formation is $k_2\theta_A$ (where θ_A is the surface coverage of A), and provided $k_2 << k_{-1}$ (i.e. the rate of reaction of adsorbed A molecules is much greater than the rate of desorption of unreacted A), the Langmuir adsorption isotherm can be used to determine θ_A, giving

$$\text{rate} = k_2\theta_A = \frac{k_2K_AP_A}{1+K_AP_A} \qquad (1)$$

This type of reaction shows two limiting rate laws, corresponding to the two extreme behaviours of the Langmuir isotherm:

a) At low pressure ($P_A \rightarrow 0$), θ_A is very small and proportional to the pressure. The rate becomes first order in A(g).

$$\text{rate (low P)} = k_2K_AP_A \qquad (2)$$

b) At high pressures θ_A is approximately equal to unity, and the reaction is zeroth order

$$\text{rate (high P)} = k_2 \qquad (3)$$

Inhibition

A complication in surface reactions arises when a substance other than the reactant is adsorbed on the surface. This reduces the effective surface area, and therefore the rate. If the fraction of the surface covered by the reactant (A) is θ_A, and that covered by the inhibitor is θ_I, we have

$$\theta_A = \frac{K_AP_A}{1+K_AP_A+K_IP_I} \qquad (4)$$

[Exercise: Derive the above equation by setting up Langmuir equations for θ_A and θ_I (i.e. $k_AP_AN(1-\theta_I-\theta_A) = k'_A\theta_A$; $k_IP_IN(1-\theta_I-\theta_A) = k'_I\theta_I$, where k and k' are adsorption and desorption rates and N is the number of available surface sites) and solving for θ_A]

The reaction rate, $k_2\theta_A$, is therefore

$$\text{rate} = \frac{k_2K_AP_A}{1+K_AP_A+K_IP_I} \tag{5}$$

If the pressure of the reactant is low compared to that of the inhibitor, so that the available surface is only sparsely covered by the reactant, then $K_AP_A \ll 1+K_IP_I$, and

$$\text{rate} = \frac{k_2K_AP_A}{1+K_IP_I} \tag{6}$$

If, in addition, the inhibitor is very strongly adsorbed, then $K_IP_I \gg 1$, and

$$\text{rate} = \frac{k_2K_AP_A}{K_IP_I} \tag{7}$$

The reaction rate is then first order in reactant and inversely proportional to the inhibitor pressure. Special cases of this arise when the inhibitor is a product of the reaction.

Activation energies

The rate constant k_2 obeys the Arrhenius law, while the temperature dependence of the equilibrium constant follows the Van't Hoff relationship. We have

$$\frac{d\ln k_2}{dT} = \frac{E}{RT^2} \qquad \text{and} \qquad \frac{d\ln K}{dT} = -\frac{\Delta H_{ads}}{RT^2} \tag{8a,b}$$

If the pressure is low, we know from (2) that the rate is $k_{eff}P_A$, where $k_{eff} = k_2K_A$. Combining this with the above expressions gives

$$\frac{d\ln(\text{rate})}{dT} = \frac{d\ln k_{eff}}{dT} = \frac{d\ln k_2}{dT} + \frac{d\ln K_A}{dT} = \frac{E-\Delta H_{ads}}{RT_2} \tag{9}$$

i.e. the apparent activation energy is $E_a=E-\Delta H_{ads}$, the true activation energy E reduced by the heat of adsorption ΔH_{ads} of the reactant. At high pressure equation (3) applies and the apparent activation energy is equal to the true activation energy, as shown below.

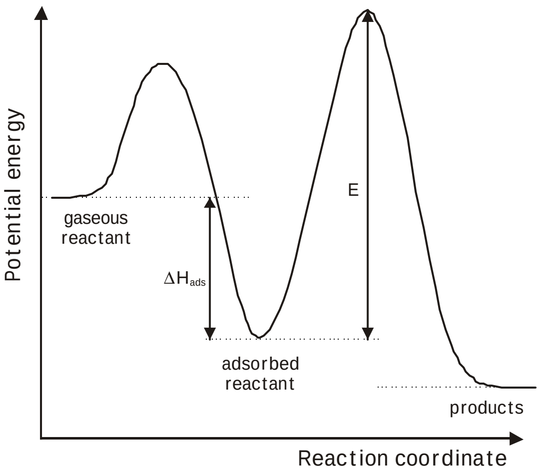


Figure: At low pressure most of the molecules are not adsorbed and only have to acquire energy $E-\Delta H_{ads}$ to cross the activation barrier. At high pressure most molecules are adsorbed to the surface and have to acquire energy E to cross the barrier.

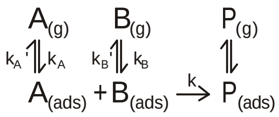
When a reaction is inhibited, the activation energy is modified due to the adsorption energy of the inhibitor. This is due to the fact that a molecule of inhibitor must be desorbed before a reactant molecule can adsorb to the surface. Equations can be derived in an analagous way to those above.

BIMOLECULAR REACTIONS

Bimolecular reactions involving surfaces fall into several different categories, depending on whether one or both molecules are adsorbed on the surface. Expressions for rates of inhibited reactions can be readily derived in a similar way to those for unimolecular reactions above. We will consider three types of bimolecular surface reactions:

a) Reaction between two adsorbed molecules (Langmuir-Hinshelwood mechanism)

If molecules A and B compete for the same surface sites, then the reaction can be represented as shown below.



If the rate of reaction between A and B on the surface is much slower than attainment of the adsorption-desorption equilibrium, then assuming Langmuir behaviour gives

$$k_A(1-\theta_A-\theta_B)P_A = k_A'\theta_A \tag{10a}$$

$$k_B(1-\theta_A-\theta_B)P_B = k_B'\theta_B \tag{10b}$$

Solving for θ_A and θ_B, and setting the reaction rate equal to $k\theta_A\theta_B$ gives

$$\text{rate} = \frac{kK_AK_BP_AP_B}{(1+K_AP_A+K_BP_B)^2} \tag{11}$$

Various approximations can now be made, depending on the relative magnitudes of the two equilibrium constants. If one species, say A, is only weakly adsorbed, so that $K_A \ll K_B$, then for roughly equal pressures of the two species, $P_A \approx P_B$, the above expression becomes

$$\text{rate} = \frac{kK_AK_BP_AP_B}{(1+K_BP_B)^2} \tag{12}$$

which reduces at high pressure to

$$\text{rate} = \frac{kK_AP_A}{K_BP_B} \tag{13}$$

High pressures of B inhibit the reaction by saturating the surface. At low pressures, when $K_BP_B \ll 1$, we obtain

$$\text{rate} = kK_AK_BP_AP_B \tag{14}$$

and the rate is directly proportional to P_B. A maximum occurs in the rate at some point in between the high and low pressure cases as the pressure of B is increased. This maximum rate may be determined by differentiating (11) with respect to B.

b) Reaction between a gas molecule and an adsorbed molecule (Langmuir-Rideal or Eley-Rideal mechanism)

The mechanism is as shown below

$$\begin{array}{l} A_{(g)} \\ {\scriptstyle k_A'}\upharpoonleft\!\downharpoonright{\scriptstyle k_A} \\ A_{(ads)} + B_{(g)} \xrightarrow{k} P \end{array}$$

Note that we cannot assume that no B adsorbs to the surface. B will still compete with A for surface sites, and this must be accounted for in the expression for the rate by the now familiar K_BP_B term in the denominator. The rate is given by

$$\text{rate} = k\theta_AP_B = \frac{kK_AP_AP_B}{1+K_AP_A+K_BP_B}$$

The Eley-Rideal mechanism does not lead to a maximum in the rate as PA and/or PB are changed, a property which can be used to distinguish this mechanism from the Langmuir-Hinshelwood mechanism. Surface combinations of atoms and free radicals generally occur by Eley-Rideal mechanisms.

c) Adsorption of two gases without mutual displacement

A third possibility is that reaction occurs between two molecules which adsorb on different types of surface sites. In this case they do not displace each other from the surface (i.e. A and B do not compete for surface sites). At equilibrium, we have

$$\frac{\theta_A}{1-\theta_A} = K_AP_A \quad \text{and} \quad \frac{\theta_B}{1-\theta_B} = K_BP_B$$

The reaction rate is then

$$\text{rate} = k\theta_A\theta_B = \frac{kK_AP_AK_BP_B}{(1+K_AP_A)(1+K_BP_B)}$$

The dependence of rate on PA and PB in this case is very different from that of the previous two mechanisms, and this type of mechanism can be readily distinguished by measuring rates over a wide range of pressures. Examples of processes in which this mechanism is favoured include reaction between hydrogen and nitrous oxide on gold and reaction between hydrogen and CO_2 on tungsten.

Examples

1. *Oxidation of CO*

O_2 undergoes dissociative adsorption on a Pt(III) surface, while CO is strongly chemisorbed. If O_2 is adsorbed first, its surface distribution is quite open. Subsequent adsorption of CO is therefore possible, and reaction could occur via either a Langmuir-Hinshelwood or an Eley-Rideal mechanism.

Langmuir-Hinshelwood:

$O_{2(g)} \rightarrow 2O_{(ads)}$
$CO_{(g)} \rightarrow CO_{(ads)}$
$O_{(ads)} + CO_{(ads)} \rightarrow CO_{2(ads)}$
$CO_{2(ads)} \rightarrow CO_{2(g)}$

Eley-Rideal:

$O_{2(g)} \rightarrow 2O_{(ads)}$
$O_{(ads)} + CO_{(g)} \rightarrow CO_{2(g)}$

Since CO is strongly adsorbed, a Langmuir-Hinshelwood mechanism would seem more likely, and this is confirmed by experiment. Molecular beam studies have shown that there is a ~1ms time lag between CO arriving at the surface and CO_2 leaving the surface, at a temperature of 440 K. CO_2 only adsorbs weakly to the surface, and so the long time lag can only be explained if the reaction occurs via a strongly adsorbed CO species.

2. *Synthesis of ammonia*

In the Haber-Bosch process, ammonia is formed from reaction between N_2 and H_2 using an Fe_3O_4 catalyst. Both H_2 and N_2 undergo dissociative adsorption onto the surface of the catalyst, N_2 much more slowly than H_2. For a long time it was not known whether adsorbed H atoms reacted with atomic or molecular N_2 adsorbed on the surface. The problem was resolved by an Auger spectroscopy study, which showed that the number density of adsorbed atomic nitrogen falls rapidly at higher pressures of H_2, indicating that adsorbed N is involved in the reaction and that dissociative adsorption of N_2 is the rate determining step. The overall reaction mechanism and a potential energy diagram for the process are shown below.

$H_{2(g)} \rightarrow 2H_{(ads)}$
$N_{2(g)} \rightarrow N_{2(ads)}$
$N_{2(ads)} \rightarrow 2N_{(ads)}$
$N_{(ads)} + H_{(ads)} \rightarrow NH_{(ads)}$
$NH_{(ads)} + H_{(ads)} \rightarrow NH_{2(ads)}$
$NH_{2(ads)} + H_{(ads)} \rightarrow NH_{3(ads)}$
$NH_{3(ads)} \rightarrow NH_{3(g)}$