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# CHEMICAL ENGINEERING KINETICS

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Based on CHEM\_ENG 408 at Northwestern University



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# 1 BRIEF REVIEW OF REACTOR ARCHETYPES

## 1.1 THE MASS BALANCE

The key equation governing processes on the reactor level is the mass balance. In order to inherently account for the proper stoichiometry, this is most typically written as a mole balance. The general mole balance for a species  $i$  is given as

$$F_{i0} - F_i + G_i = \frac{dN_i}{dt}$$

where  $F_{i0}$  is the input molar flow rate,  $F_i$  is the output molar flow rate,  $G_i$  is the generation term, and the differential term is the accumulation.

If the system variables are uniform throughout the system volume, then

$$G_i = r_i V$$

where  $r_i$  is the reaction rate of species  $i$  and  $V$  is the system volume. More generally speaking, if  $r_i$  changes with position in the system volume, then

$$G_i = \int r_i dV$$

such that the mole balance can be written as

$$F_{i0} - F_i + \int r_i dV = \frac{dN_i}{dt}$$

Two other useful expressions that should be kept in mind are as follows. For a uniform concentration of  $i$  across the system volume

$$N_i = C_i V$$

Additionally, for a given flow rate

$$F_i = C_i \dot{v}$$

where  $\dot{v}$  is volumetric flow rate.

## 1.2 BATCH REACTOR

A batch reactor is a constant volume reactor has no input or output when the chemical reaction is occurring. The batch reactor is often a good reactor archetype for slow reactions. With this information, it is clear that the batch reactor has  $F_{i0} = F_i = 0$ . As such, the mole balance is

$$\frac{dN_i}{dt} = \int r_i dV$$

If the reaction mixture is perfectly mixed (i.e. spatially uniform) so that  $r_i$  is independent of position (a common assumption for the batch reactor), then we can state

$$\frac{dN_i}{dt} = r_i V$$

Solving for the rate of reaction of species  $i$ , we see that

$$r_i = \frac{1}{V} \frac{dN_i}{dt} = \frac{dC_i}{dt}$$

where  $C_i$  is the concentration of species  $i$  and the expression  $N_i = C_i V$  was utilized.

Occasionally, batch reactors can be operated at a constant pressure but with a system volume that changes as a function of time. In this special case,

$$r_i = \frac{1}{V(t)} \frac{dN_i}{dt} = \frac{1}{V(t)} \frac{d}{dt}(C_i V(t)) = \frac{dC_i}{dt} + \frac{C_i}{V(t)} \frac{dV}{dt}$$

### 1.3 CONTINUOUS-STIRRED TANK REACTOR

The continuous-stirred tank reactor (CSTR) has an inlet and outlet flow of chemicals. CSTRs are operated at steady state (such that the accumulation term is zero) and are assumed to be perfectly mixed. As such, the mole balance for the CSTR can be written as

$$F_{i0} - F_i + r_i V = 0$$

Solving for the reaction rate yields

$$r_i = -\frac{F_{i0} - F_i}{V}$$

Utilizing the relationship of  $F_i = C_i \dot{v}$ , we can then say

$$r_i = -\frac{C_{i0} \dot{v}_0 - C_i \dot{v}}{V}$$

Since the system is at steady state, we know that  $\dot{v}_0 = \dot{v}$  such that the expression becomes

$$r_i = -\frac{\dot{v}(C_{i0} - C_i)}{V}$$

Noting that the residence time is defined as

$$\tau \equiv \frac{V}{\dot{v}}$$

we can simplify the rate expression as

$$r_i = -\frac{C_{i0} - C_i}{\tau}$$

### 1.4 PLUG-FLOW REACTOR

The plug-flow reactor (PFR) is a tubular reactor operated at steady state and has axial gradients but no radial gradients. These types of reactors are useful for fast reactions that could not be as easily observed in a batch environment. Since the concentration varies continuously down the reactor tube, so does the reaction rate (except for zeroth order reactions).

For a PFR, the design equation can be solved by differentiating the mole balance with respect to volume, but an easier way is to perform a mole balance on species  $i$  in a differential segment of the reactor volume,  $\Delta V$ . This differential balance can be written as

$$F_i(V) - F_i(V + \Delta V) + r_i \Delta V = 0$$

since the system is in steady state. Solving for the rate, dividing by  $\Delta V$ , and letting it approach zero (while applying the definition of the derivative) yields

$$r_i = \frac{dF_i}{dV}$$

Once again substituting in for  $\tau \equiv V/\dot{v}$  and  $F_i = C_i\dot{v}$  (assuming steady state conditions such that  $\dot{v}$  is constant) yields

$$r_i = \frac{dC_i}{d\tau}$$

Note that the design equation can be written in terms of the length of the reactor,  $z$ , and the cross-sectional area,  $A_c$ , if  $V \equiv A_c z$ . Occasionally, with PFRs, the superficial velocity will be referred to, which is simply  $u \equiv \dot{v}/A_c$ .

## 2 POWER LAW BASICS

### 2.1 ARRHENIUS EQUATION

The main assumption behind the Arrhenius expression is that  $r_i = f(T) \cdot f(C_i)$ . This is an approximation, but it works quite well. The rate coefficient is the term that is a function of temperature but may also depend on things like catalyst or solvent. Empirically, the Arrhenius expression states that

$$k = k_0 e^{-\frac{E}{RT}}$$

where  $k$  is the rate coefficient,  $k_0$  is the pre-exponential factor,  $E$  is the activation energy,  $T$  is the temperature, and  $R$  is the ideal gas constant. By linearizing the equation, one finds that

$$\ln(k) = -\frac{E}{R} \left( \frac{1}{T} \right) + \ln(A)$$

such that plotting  $\ln(k)$  vs.  $1/T$  should yield a straight line of slope  $-E/R$  and y-intercept of  $\ln(A)$ .

To find the ratio of two rate coefficients and two temperatures,

$$\frac{k_2}{k_1} = \exp \left( -\frac{E}{R} \left( \frac{1}{T_2} - \frac{1}{T_1} \right) \right)$$

To provide context, the Arrhenius expression is based on the Van't Hoff expression, which states that

$$\frac{d \ln k}{dT} = \frac{\Delta H_{\text{rxn}}}{RT^2}$$

If we state that  $k$  is the rate coefficient, replace  $\Delta H_{\text{rxn}}$  with  $E$  for the activation energy, assume that  $E \neq f(T)$  and  $k_0 \neq f(T)$ , and integrate then we will arrive at the Arrhenius equation. This is shown a little more rigorously below.

Assume that we have a unimolecular reaction, such as the isomerization reaction  $A \leftrightarrow R$  with forward reaction rate  $k_f$ , reverse reaction rate  $k_r$ , and equilibrium constant  $K_c \equiv k_f/k_r$ . The Van't Hoff equation can be written as

$$\frac{d \ln K_c}{dT} = \frac{\Delta H_{\text{rxn}}}{RT^2}$$

which can also be expressed as

$$\frac{d \ln \left( \frac{k_f}{k_r} \right)}{dT} = \frac{\Delta H_{\text{rxn}}}{RT^2}$$

and thereby

$$\frac{d(\ln k_f)}{dT} - \frac{d(\ln k_r)}{dT} = \frac{\Delta H_{\text{rxn}}}{RT^2}$$

Arbitrarily, we set  $\Delta H_{\text{rxn}} = \Delta H_f - \Delta H_r$  such that the expression becomes

$$\frac{d(\ln k_f)}{dT} - \frac{d(\ln k_r)}{dT} = \frac{\Delta H_f}{RT^2} - \frac{\Delta H_r}{RT^2}$$

Separating the forward and reverse components and integrating will yield the Arrhenius expression in the forward and reverse directions, respectively.

## 2.2 MASS-ACTION KINETICS

### 2.2.1 OVERVIEW

We assume that rates can be described by

$$\text{Rate} = f(T) \cdot g(C_i)$$

where  $f(T)$  is the rate constant from Arrhenius' law and  $g(C_i)$  is the rate law. Empirically, we say that

$$g(C_i) = C_A^\alpha C_B^\beta C_C^\gamma \dots$$

which is typical rate law kinetics. In this expression, if  $\alpha, \beta, \gamma, \dots$  are the stoichiometric coefficients of a reaction, it *may* be (but is not necessarily) an elementary step. Typically, we find that for elementary steps  $\sum \alpha\beta\gamma \dots < 3$ .

### 2.2.2 FIRST ORDER KINETICS

We will start by considering the elementary reaction



The rate law can be given by

$$-\frac{dC_A}{dt} = kC_A$$

Integrating this expression yields

$$-\int_{C_{A0}}^{C_A} \frac{1}{C_A} dC_A = k \int_0^t dt$$

which becomes

$$-\ln\left(\frac{C_A}{C_{A0}}\right) = kt$$

and thereby

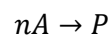
$$C_A = C_{A0}e^{-kt}$$

and a plot of  $\ln(C_A)$  vs.  $t$  should be linear for first order kinetics. The half-life can be given by

$$t_{\frac{1}{2}} = \frac{\ln(2)}{k}$$

### 2.2.3 N-TH ORDER KINETICS

The above process can be done for any integer  $n$ . We will consider the general reaction



The rate law can be given by



$$-\frac{dC_A}{dt} = kC_A^n$$

Integrating this expression yields

$$-\int_{C_{A0}}^{C_A} \frac{1}{C_A^n} dC_A = k \int_0^t dt$$

which becomes

$$\frac{C_A^{-n+1}}{-n+1} - \frac{C_{A0}^{-n+1}}{-n+1} = kt$$

For  $n \neq 1$ , we can state that

$$\frac{1}{C_A^{n-1}} = \frac{1}{C_{A0}^{n-1}} + (n-1)kt$$

and a plot of  $1/C_A^{n-1}$  vs.  $t$  should be linear. The half-life can be given by the general formula

$$t_{\frac{1}{2}} = \frac{2^{n-1} - 1}{(n-1)kC_{A0}^{n-1}}$$

The units of the rate constant for an  $n$ th order reaction are given by  $k [=] \text{concentration}^{1-n} \text{ s}^{-1}$ .

#### 2.2.4 REVERSIBLE REACTIONS

We will consider the reaction



The rate law can be given by

$$-\frac{dC_A}{dt} = k_f C_A - k_r C_P$$

where  $k_f$  and  $k_r$  represent the rate constants of the forward and reverse reactions, respectively. For the case of no initial concentration of  $P$ , one can state that

$$C_{A0} - C_A = C_P$$

Therefore

$$-\frac{dC_A}{dt} = k_f C_A - k_r (C_{A0} - C_A)$$

This can be rearranged to

$$-\frac{dC_A}{dt} = (k_f + k_r) \left( C_A - \frac{k_r}{k_f + k_r} C_{A0} \right)$$

To simplify the algebra, we define a quantity  $k_{eq}$  such that

$$k_{eq} \equiv \frac{k_f}{k_r} = \frac{C_{P,eq}}{C_{A,eq}} = \frac{C_{A0} - C_{A,eq}}{C_{A,eq}}$$

This implies that

$$C_{A,eq} = \frac{k_r}{k_f + k_r} C_{A0}$$

Therefore,

$$-\frac{dC_A}{dt} = (k_f + k_r)(C_A - C_{A,eq})$$

which can be integrated to

$$-\int_{C_{A0}}^{C_A} \frac{dC_A}{C_A - C_{A,eq}} = (k_f + k_r) \int_0^t dt$$

which is equal to

$$\ln\left(\frac{C_{A0} - C_{A,eq}}{C_A - C_{A,eq}}\right) = (k_f + k_r)t$$

## 2.3 DETERMINING THE RATE LAW AND RATE CONSTANTS

### 2.3.1 DIFFERENTIAL METHOD

The differential method says that we should propose a rate law of the type

$$-\frac{dC_A}{dt} = kC_A^\alpha$$

We then can rewrite this as

$$\ln\left(-\frac{dC_A}{dt}\right) = \ln k + \alpha \ln C_A$$

which can be used to fit a function to find the slope and order  $\alpha$ . It is also possible to plot  $\ln\left(-\frac{dC_A}{dt}\right)_{t=0}$  vs.  $\ln(C_{A,0})$  for many initial concentrations to back out the rate constant and order. Of course, any conclusion from either method depends on the fit and is only as good as the data. Oftentimes, we are only given the concentration as a function of time, not the rate of the reaction. There are three main ways to get the rate from the dataset.

The first method is the graphical method, wherein a smooth curve is drawn through the experimental data points on a  $C_A$  vs.  $t$  graph. At each time instant of interest, tangents are drawn to this curve, the slope of the tangent line is the derivative value at that time instant and is therefore the rate.

The second method is the polynomial method, wherein a polynomial of suitable order is fit to the data. The derivative can then be evaluated by differentiating the polynomial expression (typically, the simplest monotonic function is the best choice).

The third method is the finite difference method, wherein we can approximate the derivative via a numerical finite difference equation. This, however, requires a sufficient data size to do accurately.

### 2.3.2 INTEGRAL METHOD

The integral method simply involves deriving the rate laws for a hypothetical reaction order and seeing if the data fits the linearized equations. This is essentially just a guess and check method.

### 2.3.3 REGRESSION METHOD

If we assume a rate law to the  $n$ th power, we can use the general integrated rate law of

$$\frac{1}{C_A^{n-1}} = \frac{1}{C_{A0}^{n-1}} + (n-1)kt$$

to solve for  $n$ . This can be done through a non-linear least-squares analysis (a typical curve fitting toolbox would suffice).

### 2.3.4 WORKING WITH PSEUDO ORDERS

Sometimes it's easier to assume an order and use pseudo rate constants. For instance, if we assume a rate law of the form

$$\text{rate} = k_{\text{rxn}} C_A^n$$

then we can arbitrarily assume pseudo first order to make it

$$\text{rate} = k_{1\text{st}} C_A$$

where

$$k_{1\text{st}} \equiv k_{\text{rxn}} C_A^{n-1}$$

We can linearize this to get

$$\ln(k_{1\text{st}}) = \ln(k_{\text{rxn}}) + (n-1) \ln(C_A)$$

so that the slope of a  $\ln(k_{1\text{st}})$  vs.  $\ln(C_A)$  curve would be equal to  $n-1$ .

### 3 WORKING WITH MULTIPLE ELEMENTARY STEPS

#### 3.1 GENERAL APPROACH

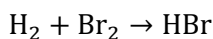
When dealing with a reaction that has multiple elementary steps, the following procedure should be used in general:

- 1) Postulate elementary steps (in particular, bond making and bond breaking events)
- 2) Postulate a mechanism (determining fast vs. slow reactions as well as reversible vs. equilibrium reactions)
- 3) Derive a closed-form rate law that describes the rate as a function of observables
- 4) Test the rate law against available data and refine as necessary

#### 3.2 SYNTHESIS OF HBr

##### 3.2.1 ELEMENTARY STEPS

Consider the reaction



We will see that the rate expression for this reaction is not as simple as one would initially anticipate. For HBr, we can write the following possible elementary steps:

Initiation – these are reactions that turn the reactants into radical species

1.  $\text{Br}_2 \rightarrow \text{Br}\cdot + \text{Br}\cdot$  (denoted  $k_1$ )
2.  $\text{H}_2 \rightarrow \text{H}\cdot + \text{H}\cdot$  (denoted  $k_4$ )

Degenerate reactions – these reactions produce the same products as reactants and are important if isotopically labeled for determining kinetically relevant steps

1.  $\text{Br}\cdot + \text{Br}_2 \rightarrow \text{Br}_2 + \text{Br}\cdot$
2.  $\text{H}\cdot + \text{H}_2 \rightarrow \text{H}_2 + \text{H}\cdot$

Propagation – these are reactions that produce at least as many radicals as are consumed to propagate the chain reaction

1.  $\text{Br}\cdot + \text{H}_2 \rightarrow \text{HBr} + \text{H}\cdot$  (denoted  $k_2$ )
2.  $\text{H}\cdot + \text{Br}_2 \rightarrow \text{HBr} + \text{Br}\cdot$  (denoted  $k_3$ )
3.  $\text{HBr} + \text{H}\cdot \rightarrow \text{Br}\cdot + \text{H}_2$  (denoted  $k_{-2}$ )
4.  $\text{HBr} + \text{Br}\cdot \rightarrow \text{H}\cdot + \text{Br}_2$  (denote  $k_{-3}$ )

Termination – these are reactions that convert radical species into stable species

1.  $\text{Br}\cdot + \text{H}\cdot \rightarrow \text{HBr}$  (denoted  $k_5$ )
2.  $\text{H}\cdot + \text{H}\cdot \rightarrow \text{H}_2$  (denoted  $k_{-4}$ )
3.  $\text{Br}\cdot + \text{Br}\cdot \rightarrow \text{Br}_2$  (denoted  $k_{-1}$ )

##### 3.2.2 RATE EXPRESSIONS

With the reactions listed, we now write out the mass action kinetics.

The overall balance for  $\text{Br}_2$  is

$$r_{\text{Br}_2} = \frac{d[\text{Br}_2]}{dt} = -k_1[\text{Br}_2] + \frac{1}{2}k_{-1}[\text{Br}\cdot]^2 - k_3[\text{H}\cdot][\text{Br}_2] + k_3[\text{HBr}][\text{Br}\cdot]$$

The overall balance for HBr is

$$r_{\text{HBr}} = \frac{d[\text{HBr}]}{dt} = k_2[\text{Br}\cdot][\text{H}_2] + k_3[\text{H}\cdot][\text{Br}_2] - k_{-2}[\text{HBr}][\text{H}\cdot] - k_{-3}[\text{HBr}][\text{Br}\cdot] + k_5[\text{Br}\cdot][\text{H}\cdot]$$

The overall balance for Br· is

$$r_{\text{Br}\cdot} = \frac{d[\text{Br}\cdot]}{dt} = 2k_1[\text{Br}_2] - k_2[\text{Br}\cdot][\text{H}_2] + k_3[\text{H}\cdot][\text{Br}_2] + k_{-2}[\text{HBr}][\text{H}\cdot] - k_{-3}[\text{HBr}][\text{Br}\cdot] - k_5[\text{Br}\cdot][\text{H}\cdot] - 2k_{-1}[\text{Br}\cdot]^2$$

And we can do an analogous thing for the other species, but you get the idea.

### 3.2.3 THE PSEUDO-STEADY STATE HYPOTHESIS

Once the rate expressions are written, they can either be solved simultaneously without any simplification using a standard computational ODE-solving package, or algebraic simplifications can be made to make the expression more manageable. The most common assumption to make is the pseudo-steady-state hypothesis (PSSH), which states that the rate of appearance of a given species is essentially 0. This is most commonly applied to intermediate radical species, in this case Br· and H·. It is also important to check that for all chain reactions, the rate of initiation should equal the rate of termination if PSSH is applied.

### 3.2.4 BOND DISSOCIATION ENERGIES

Another simplification that can be made is neglecting small terms. To make this decision, it is easiest to look at bond dissociation energies (BDE) to predict the size of rate constants and relative concentrations. In this reaction, the BDE for H<sub>2</sub> is 104.2 kcal/mol, the BDE for HBr is 87.5 kcal/mol, and the BDE for Br<sub>2</sub> is 46 kcal/mol. We then note that the BDE is proportional to the activation energy via the Evans-Polanyi relationship. The Evans-Polanyi relationship states that

$$E_a = E_0 + \alpha\Delta H_{\text{rxn}}$$

where  $E_0$  is a constant for a given family of reactions and  $\alpha$  is the position of the transition state along the reaction coordinate (from 0 to 1).

Therefore, based on the BDEs listed, we can assume that  $k_1 \gg k_4$  due to the low BDE of Br<sub>2</sub> compared to H<sub>2</sub>. This BDE analysis means that  $[\text{Br}\cdot] \gg [\text{H}\cdot]$ . As such, we will remove the  $k_4$  term. We also note that since there is so little  $[\text{H}\cdot]$  in the system,  $r_{-4} \approx 0$ . We will also consider reaction 3 only in the forward direction because of the relatively high BDE of HBr. Applying the PSSH and including these assumptions results in the following solution

$$r = \frac{k[\text{H}_2][\text{Br}_2]^{\frac{1}{2}}}{k' + \frac{[\text{HBr}]}{[\text{Br}_2]}}$$

At low conversion (i.e.  $[\text{HBr}] \approx 0$ ), we see that the equation becomes first order in H<sub>2</sub> and half order in Br<sub>2</sub>. Looking at limiting cases like this is helpful in accurately describing the kinetics.

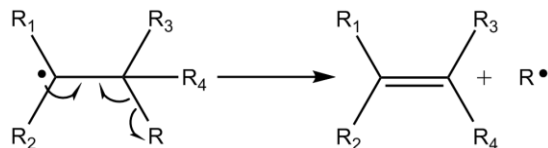
## 3.3 COMPLEX REACTIONS: CRACKING

### 3.3.1 TERMINOLOGY

Before getting into the mechanism for ethane cracking, it is important to go over some terminology used in this field of research. The two most common propagation steps in hydrocarbon pyrolysis and cracking are hydrogen abstraction and  $\beta$ -scission.

Hydrogen abstraction takes the general form of  $X\cdot + H-Y \rightarrow X-H + Y\cdot$ . The radical that is produced from a hydrogen abstraction process is called a  $\mu$  species. It is literally the abstraction of a hydrogen from an otherwise stable substrate.

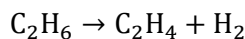
$\beta$ -scission takes the following general form:



The radical that is produced from a  $\beta$ -scission reaction is called a  $\beta$  species.

### 3.3.2 MECHANISM AND MASS-ACTION KINETICS

In this example, we will consider ethane cracking:



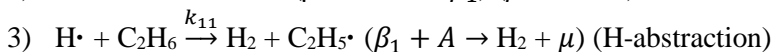
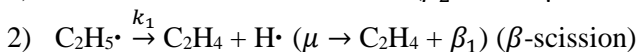
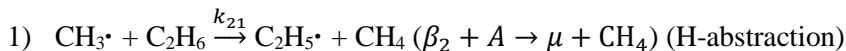
Writing out the possible elementary steps:

Initiation – in cracking, initiation occurs with a single molecule breaking down into two identical free radicals

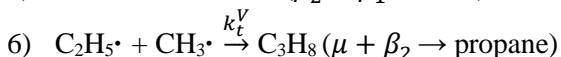
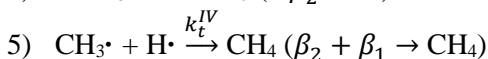
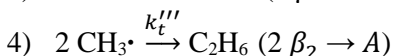
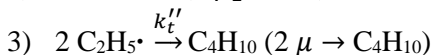
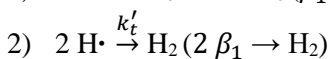
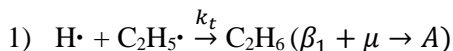


(note that  $CH_3CH_3 \rightarrow C_2H_5\cdot + H\cdot$  has a significantly higher BDE)

Propagation – The two main reactions are H-abstraction and  $\beta$ -scission



Termination



A couple of things should be noted before continuing. Of course, other reactions can be written but they are not especially likely to occur. Also, it should be noted that the methyl C-H bond is one of the strongest aliphatic C-H bonds and therefore  $CH_4$  does not tend to form  $CH_3\cdot$  radicals very frequently. Finally, the propagation steps are conventionally written in the spontaneous (i.e. exothermic) direction in the literature.

Writing out the mass-action expressions:

$$r_A = \frac{dA}{dt} = -\alpha A - k_{21}\beta_2 A - k_{11}\beta_1 A + k_t\beta_1\mu + \frac{1}{2}k_t'''\beta_2^2 + \dots$$

$$r_{\beta_1} = \frac{d\beta_1}{dt} = k_1\mu - k_{11}\beta_1 A - k_t\beta_1\mu - 2k_t'\beta_1^2 - k_t^{IV}\beta_1\beta_2 + \dots$$

$$r_{\beta_2} = \frac{d\beta_2}{dt} = 2\alpha A - k_{21}\beta_2 A - 2k_t'''\beta_2^2 - k_t^{IV}\beta_1\beta_2 + \dots$$

$$r_\mu = \frac{d\mu}{dt} = k_{21}A\beta_2 - k_1\mu + k_{11}\beta_1 A - k_t\beta_1\mu - k_t^V\mu - 2k_t''\mu^2 + \dots$$

### 3.3.3 SIMPLIFICATIONS BASED ON CONCENTRATIONS

These expressions can be simplified by employing the PSSH on the radical species  $\beta_1$ ,  $\beta_2$ , and  $\mu$ . We can also trim the expressions based on low rate coefficients and/or concentrations. The only low rate coefficient is in the initiation step, but you cannot delete the initiation term since then the reaction will never occur. However, we will remove any reactions of  $\beta_2$  with another radical based on experimental data that shows that no significant amounts of  $\text{CH}_4$ , butane, propane, or other larger hydrocarbons are observed because  $\text{CH}_4$  is so stable that it is unlikely it will dissociate.

### 3.3.4 SIMPLIFICATIONS BASED ON STATISTICAL TERMINATION

Additional simplifications can be made based on the assumption of statistical termination. Take the  $\beta_1$  and  $\mu$  radicals as an example. A table can be made as follows showing the rate coefficients for each possible combination:

	$\beta_1$	$\mu$
$\beta_1$	$k_t'$	$k_t$
$\mu$	$k_t$	$k_t''$

If we assume statistical termination, then the  $k_t$  reaction should occur twice as likely as the  $k_t'$  and  $k_t''$  reaction. As such, if we let  $\omega$  be the rate constant for termination, we can state that

$$\omega = k_t' = k_t'' = \frac{1}{2}k_t$$

### 3.3.5 SIMPLIFICATIONS BASED ON THE LONG-CHAIN APPROXIMATION

The long-chain approximation can be made when the rate of propagation is significantly faster than the rate of initiation and/or termination.

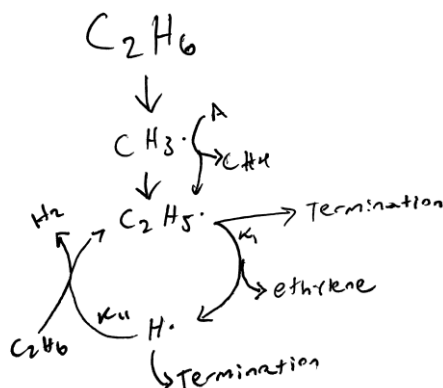
### 3.3.6 ETHANE CRACKING RATE LAW

Combining all of the previous assumptions allows us to arrive at the rate law for ethane cracking:

$$r_A = \frac{k_{11} \left(\frac{\alpha A}{\omega}\right)^{\frac{1}{2}} A}{1 + \frac{k_{11} A}{k_1}}$$

This rate law shows that at low partial pressure of  $A$ , the reaction is 3/2 order in  $A$  whereas at high partial pressure of  $A$  the reaction is 1/2 order in  $A$ .

In order to better understand what is going on in this mechanism, a diagram can be drawn like the one below. We see that there is a radical ratcheting cycle between the ethyl radical and hydrogen radical. This controls most of the kinetics of the process (hence the presence of  $k_1$  and  $k_{11}$ ).



### 3.3.7 DETERMINING OBSERVED ACTIVATION ENERGIES

At low partial pressure of  $A$ , we have

$$r_A = \frac{k_{11} \alpha^2 A^2}{\omega^2}$$

To calculate the overall or observed activation energy, we can rewrite the expression as

$$r_A \sim \frac{(A_{11} \exp(-\frac{E_{11}}{RT})) (A_\alpha \exp(-\frac{E_\alpha}{RT}))^{\frac{1}{2}}}{(A_\omega \exp(-\frac{E_\omega}{RT}))^{\frac{1}{2}}}$$

This shows us that the observed activation energy for this reaction is

$$E_{obs} = E_{11} + \frac{1}{2}E_\alpha - \frac{1}{2}E_\omega$$

This approach can be used anytime rate coefficients are multiplied and/or divided together. If rate coefficients are added or subtracted, the only way to find an observed activation energy is to break it into different regimes where the addition/subtraction disappears.

### 3.3.8 GENERAL OVERVIEW OF SIMPLIFICATION PROCESS

1. Postulate steps
2. Write out mass-action kinetics
3. Apply PSSH on intermediate radicals
  - a. This, in turn, sets the rate of initiation equal to the rate of termination
4. Use BDEs and/or experimental data about which species are not observed to further reduce the mechanism
5. If applicable, apply the long-chain approximation such that the rate of propagation is much greater than the rate of initiation and termination
6. The goal is to write the rate in change of reactant (or product) as a function of only experimentally observable (i.e. stable) species and the corresponding rate coefficients



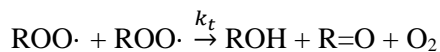
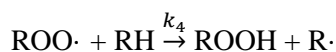
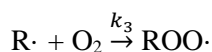
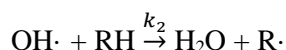
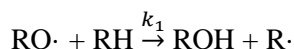
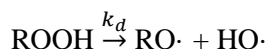
### 3.3.9 COMPLEX REACTIONS: ADDITIVES

Reactions can be controlled not only by changing pressure and temperature but also by introducing additives. These may include things such as initiators for polymerization, reactive species for the stable operation of combustion engines, anti-oxidants (to prevent oxidation), vitamins (i.e. radical cofactors), and so on. In these cases, the ratio that the rate has change is called the enhancement factor. A value greater than 1 means the reaction is enhanced whereas a value less than 1 means the reaction is impeded.

One common class of additives is radical initiators. These are species that can produce radical species under mild conditions and therefore promote radical reactions. They generally possess weak bonds (i.e. bonds with a small BDE). Organic peroxides (e.g. benzoyl peroxide) are therefore oftentimes used as radical initiators since the BDE of the O-O bond in the peroxides is very weak, and the resulting oxyl radicals are unstable and preferentially abstract hydrogen.

### 3.4 COMPLEX REACTIONS: RADICAL CHAIN AUTOXIDATION

Assume we have the following autoxidation mechanism:



Mass action kinetics and PSSH

$$\frac{d[\text{RH}]}{dt} = -k_1[\text{RO}\cdot][\text{RH}] - k_2[\text{OH}\cdot][\text{RH}] + k_4[\text{ROO}\cdot][\text{RH}]$$

$$\frac{d[\text{RO}\cdot]}{dt} = 0 = -k_1[\text{RO}\cdot][\text{RH}] + k_d[\text{ROOH}]$$

$$\frac{d[\text{OH}\cdot]}{dt} = 0 = -k_2[\text{OH}\cdot][\text{RH}] + k_d[\text{ROOH}]$$

$$\frac{d[\text{R}\cdot]}{dt} = 0 = k_1[\text{RO}\cdot][\text{RH}] + k_2[\text{OH}\cdot][\text{RH}] - k_3[\text{R}\cdot][\text{O}_2] + k_4[\text{ROO}\cdot][\text{RH}]$$

$$\frac{d[\text{ROO}\cdot]}{dt} = 0 = k_3[\text{R}\cdot][\text{O}_2] - k_4[\text{ROO}\cdot][\text{RH}] - 2k_t[\text{ROO}\cdot]^2$$

Add together  $d[\text{R}\cdot]/dt$  and  $d[\text{ROO}\cdot]/dt$  to get

$$0 = k_1[\text{RO}\cdot][\text{RH}] + k_2[\text{OH}\cdot][\text{RH}] - 2k_t[\text{ROO}\cdot]^2$$

We note that from  $d[\text{RO}\cdot]/dt$

$$k_1[\text{RO}\cdot][\text{RH}] = k_d[\text{ROOH}]$$

We note that from  $d[\text{OH}\cdot]/dt$

$$k_2[\text{OH}\cdot][\text{RH}] = k_d[\text{ROOH}]$$

so

$$0 = 2k_d[\text{ROOH}] - 2k_t[\text{ROO}\cdot]^2$$

This shows that the rate of initiation equals the rate of termination, as it should from the PSSH. We can then use this to rewrite the rate in change of RH as

$$\frac{d[\text{RH}]}{dt} = 2k_d[\text{ROOH}] + k_4[\text{RH}] \left( \frac{k_d}{k_t} [\text{ROOH}] \right)^{\frac{1}{2}}$$

We can combine rate coefficients to rewrite this as

$$\frac{d[\text{RH}]}{dt} = 2k_d[\text{ROOH}] + k'[\text{RH}][\text{ROOH}]^{\frac{1}{2}}$$

If we know in advance that we can apply the long-chain approximation, then the left-hand term becomes negligible. To make an educated decision, we should look at BDEs. They are as follows:

$$\text{ROO-H, } 366 \text{ kJ/mol} \mid \text{RO-H, } 441 \text{ kJ/mol} \mid \text{HO-H, } 497 \text{ kJ/mol} \mid \text{R-H, } 416 \text{ kJ/mol}$$

We can now calculate the  $\Delta H_{\text{rxn},4}$  associated with reaction 4.

$$\Delta H_{\text{rxn},4} = \text{BDE}_{\text{bonds broken}} - \text{BDE}_{\text{bonds formed}} = \text{BDE}_{\text{RH}} - \text{BDE}_{\text{ROOH}} \approx 50 \text{ kJ/mol}$$

From this, we can see that  $k_4$  is likely a small quantity, and so the long-chain approximation probably isn't best to use here.

If we want to find the selectivity of ROH versus R=O, we note that ROH is produced in both reaction 1 and the termination step while R=O only is produced in the termination step. The selectivity is then

$$\frac{\frac{d[\text{ROH}]}{dt}}{\frac{d[\text{R}=\text{O}]}{dt}} = \frac{\text{step 1} + \text{step t}}{\text{step t}} = \frac{k_1[\text{RO}\cdot][\text{RH}] + k_t[\text{ROO}\cdot]^2}{k_t[\text{ROO}\cdot]^2} = \frac{k_d[\text{ROOH}]}{k_t[\text{ROO}\cdot]^2} + 1 = 2$$

## 4 CONSEQUENCES OF CHEMICAL EQUILIBRIA

### 4.1 RELATIONSHIPS BETWEEN THERMODYNAMICS AND EQUILIBRIUM

#### 4.1.1 TEMPERATURE-DEPENDENCE OF THERMODYNAMIC QUANTITIES

In this section, we will make great use of  $\Delta G_{\text{rxn}}^\circ$  and  $\Delta H_{\text{rxn}}^\circ$ . The superscript  $\circ$  indicates a standard reference state, most typically 1 bar when dealing with gases. The standard state does not refer to a temperature, although most tabulated values are at 298.15 K. Since both Gibbs free energy and enthalpy are functions of temperature, this can complicate equilibrium calculations because tabulated quantities are most often reported at temperatures other than the reaction conditions (and oftentimes the temperature of the system changes throughout the course of a given reaction).

To find the  $\Delta H_{\text{rxn}}^\circ$  at a particular temperature  $T$ , one can use the following relationship:

$$\Delta H_{\text{rxn}}^\circ(T) = \Delta H_{\text{rxn},T_{\text{ref}}}^\circ + \int_{T_{\text{ref}}}^T \Delta C_p^\circ(T) dT$$

The  $\Delta H_{\text{rxn},T_{\text{ref}}}^\circ$  term refers to the standard enthalpy of reaction at a tabulated reference temperature. This is typically known from the heats of formation of each species at the same reference temperature ( $\Delta H_{f_i,T_{\text{ref}}}^\circ$ ). The relationship is

$$\Delta H_{\text{rxn},T_{\text{ref}}}^\circ = \sum_i \nu_i \Delta H_{f_i,T_{\text{ref}}}^\circ$$

For species in the most stable state (e.g. monatomic carbon or diatomic oxygen), the enthalpies of formation are assigned to be zero by convention.

The  $\Delta C_p^\circ$  term is change heat capacity term weighted by stoichiometric ratios and is also a function of temperature. This is

$$\Delta C_p^\circ(T) = \sum_i \nu_i C_{p,i}^\circ$$

The value of the heat capacity for a given species ( $C_{p,i}^\circ$ ) can be found in reference tables as well. It is often reported as a power series of temperature with empirically derived coefficients.

An analogous expression can be written for the standard Gibbs free energy change of reaction at a reference temperature:

$$\Delta G_{\text{rxn},T_{\text{ref}}}^\circ = \sum_i \nu_i \Delta G_{f_i,T_{\text{ref}}}^\circ$$

### 4.2 THE EQUILIBRIUM CONSTANT

#### 4.2.1 ACTIVITY EQUILIBRIUM CONSTANT

The equilibrium constant, using activities, is defined as

$$K_a = \prod_i a_i^{\nu_i}$$

where  $a_i$  is the activity of a given species.

The activity equilibrium constant can be related to  $\Delta G$  by

$$K_a = e^{-\frac{\Delta G_{\text{rxn}}^\circ}{RT}}$$

However, it is critical to note that since  $\Delta G_{\text{rxn}}^\circ$  is typically found from  $\Delta G_{f,i}^\circ$  at a reference temperature,  $T_{\text{ref}}$ , then the resulting  $K_a$  is only valid at  $T_{\text{ref}}$ :

$$K_{a,T_{\text{ref}}} = e^{-\frac{\Delta G_{\text{rxn},T_{\text{ref}}}^\circ}{RT_{\text{ref}}}}$$

In order to determine the  $K_a$  at a temperature other than the reference temperature, one must use the following relationship

$$\ln\left(\frac{K_{a,T_2}}{K_{a,T_1}}\right) = \int_{T_1}^{T_2} \frac{\Delta H_{\text{rxn}}^\circ(T)}{RT^2} dT$$

where  $T_1$  typically is  $T_{\text{ref}}$ . Since  $\Delta H_{\text{rxn}}^\circ$  is a function of temperature, this must usually be accounted for using the aforementioned temperature-dependence relationships. However, if this temperature effect can be ignored, then the equation simplifies to

$$\ln\left(\frac{K_{a,T_2}}{K_{a,T_1}}\right) = -\frac{\Delta H_{\text{rxn}}^\circ}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

#### 4.2.2 ACTIVITIES FOR GASES

The most general way to compute the activity of an arbitrary mixture of gases is by using fugacities:

$$a_i = \frac{f_i}{P_{\text{ref}}} = \gamma_i \frac{P_i}{P_{\text{ref}}} = \varphi_i y_i \frac{P}{P_{\text{ref}}}$$

where  $\varphi_i$  is the dimensionless fugacity coefficient and  $\gamma_i$  is the activity coefficient. For ideal species,  $\varphi_i = \gamma_i = 1$ . Therefore, for a gas mix at low enough pressure that the system can be assumed to be ideal, we can simplify this expression by saying

$$a_i = y_i \frac{P}{P_{\text{ref}}}$$

where  $P$  is the total pressure of the system.<sup>1</sup> This then means that

$$K_a = \left(\frac{P}{P_{\text{ref}}}\right)^\delta \prod_i y_i^{v_i}$$

where  $\delta$  is the change in (stoichiometric) moles.

#### 4.2.3 ACTIVITIES FOR LIQUIDS

Activities for liquids can be written as

$$a_i = \gamma_i x_i$$

<sup>1</sup> Since partial pressure is just  $P_i = P y_i$ , we can optionally rewrite activity as  $a_i = P_i/P_{\text{ref}}$

where  $\gamma_i$  is specifically the Raoult's law activity coefficient and indicates ideal behavior according to Raoult's law. As  $x_i \rightarrow 1$ , the value of the activity coefficient also approaches 1. As  $x_i \rightarrow 0$ , the activity coefficient approaches an infinitely dilute case denoted  $\gamma_i^\infty$  and can be found by dividing the Henry's law constant by the saturation vapor pressure. The value of  $\gamma_i^\infty$  is large for poorly soluble, low volatility species. If  $\gamma_{\text{product}}^\infty > \gamma_{\text{reactants}}^\infty$  then there is an equilibrium shift toward products.

Dilute solutions typically follow Henry's law instead of Raoult's law, and it is more conventional to use concentration. As such,

$$a_i = \gamma_i \frac{C_i}{C_{\text{ref}}}$$

where  $C_i$  refers to the concentration of a species  $i$ ,  $C_{\text{ref}}$  is typically 1 M. For an ideal liquid mixture, the activity coefficient approaches 1 and

$$a_i = \frac{C_i}{C_{\text{ref}}}$$

Therefore, for ideal solutions

$$K_a = \left(\frac{1}{C_{\text{ref}}}\right)^\delta \prod_i C_i^{\nu_i}$$

#### 4.2.4 RELATIONSHIP BETWEEN VARIOUS EQUILIBRIUM CONSTANTS

Oftentimes, equilibrium constants in terms of pressure, concentration, and mole fraction are used. These are as follows, respectively:

$$K_p = \prod_i P_i^{\nu_i}$$

$$K_c = \prod_i C_i^{\nu_i}$$

$$K_y = \prod_i y_i^{\nu_i}$$

For an ideal gas, the following relationships hold:

$$K_a = \left(\frac{1}{P_{\text{ref}}}\right)^\delta K_p = \left(\frac{P}{P_{\text{ref}}}\right)^\delta K_y$$

$$K_p = K_c (RT)^\delta$$

For an ideal liquid mixture, we have that

$$K_a = \left(\frac{1}{C_{\text{ref}}}\right)^\delta K_c$$

We therefore see that for ideal solutions,  $K_a \approx K_p \approx K_c$  (taking into account reference terms to take care of units).

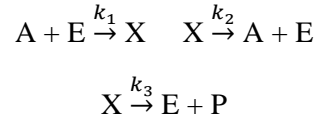
## 4.3 ENZYME KINETICS

### 4.3.1 DERIVATION OF THE MICHAELIS-MENTEN EQUATION

Catalysts are defined as agents that decrease the activation energy of a reaction without being consumed. Therefore, at a given temperature, the reaction rate increases in the presence of a catalyst.

We will use the following nomenclature when discussing both physical and biological catalysts: E (free catalyst), A (reactant), P (product), and all other species (e.g. X, Y) are catalytic intermediates (e.g. an enzyme-substrate complex).

Let us consider the reaction mechanism  $A + E \leftrightarrow X \rightarrow P + E$ , which I will enumerate as follows



The goal is to find the rate of appearance of P in terms of observable quantities and constants. If we apply PSSH to our intermediate X, we get

$$\frac{dX}{dt} = 0 = k_1[A][E] - k_2[X] - k_3[X]$$

Applying a mass (i.e. site) balance to the catalyst yields

$$E_T = [E] + [X]$$

where  $E_T$  is the total amount of catalyst. It is ideal to write  $[X]$  in terms of  $E_T$  instead of  $[E]$  because  $E_T$  is a constant with time. Therefore,

$$[X] = \frac{k_1[A]E_T}{k_1[A] + k_2 + k_3}$$

We can write the rate in change of product as

$$\frac{d[P]}{dt} = k_3[X] = \frac{k_1k_3[A]E_T}{k_1[A] + k_2 + k_3}$$

Dividing by  $k_1$  yields

$$\frac{d[P]}{dt} = \frac{k_3[A]E_T}{[A] + \frac{k_2 + k_3}{k_1}}$$

We say that  $V_{\max} \equiv k_3E_T$  and  $K_M \equiv (k_2 + k_3)/k_1$  to get the typical form of the Michaelis-Menten equation

$$\frac{d[P]}{dt} = \frac{V_{\max}[A]}{[A] + K_M}$$

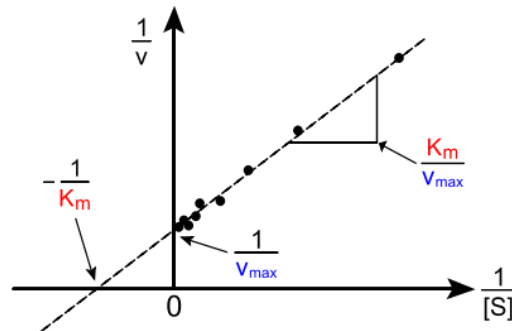
The value of  $K_M$  is the concentration of A at which the rate is half of its maximum. The value of  $V_{\max}$  is the maximum rate at  $[A] \gg K_M$ . From this equation, it is clear that at  $[A] \ll K_M$ , the rate appears to be first order in A. At  $[A] \gg K_M$ , the rate is pseudo zeroth order in A (and therefore independent of A). At all  $[A]$ , the rate is proportional to the total enzyme concentration.

### 4.3.2 PLOTTING MICHAELIS-MENTEN DATA

Oftentimes, a linearized plot is desired. This can be done using a Lineweaver-Burk plot, where the inverse of the rate is plotted against the inverse concentration of the substrate. This is merely a linearization of the Michaelis-Menten equation to

$$\frac{1}{r_P} = \frac{K_M}{V_{\max}} \frac{1}{[A]} + \frac{1}{V_{\max}}$$

This then leads to the following linearized for (here, the substrate is denoted S)

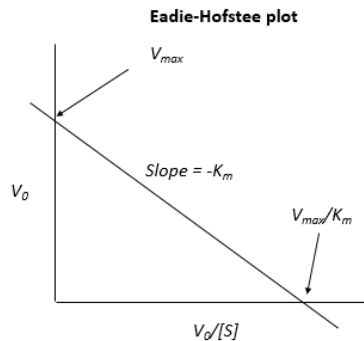


The Eadie-Hofstee plot is another way to linearize the Michaelis-Menten equation, which uses the following equation

$$r_P = -K_M \frac{r_P}{[A]} + V_{\max}$$

and has a plot with characteristics shown below

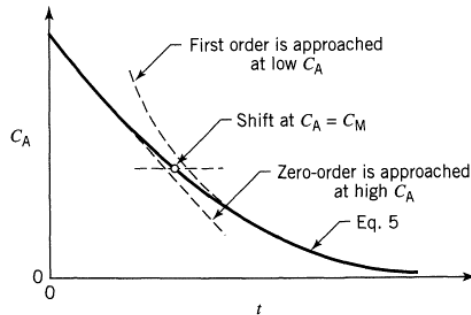
Since the Lineweaver-Burke plot uses inverse values, it unevenly weights data points in concentration and reaction rate whereas Eadie-Hofstee plots do not. However, the Eadie-Hofstee plot's abscissa and ordinate are dependent on the reaction rate, and therefore any experimental error will be present in both axes. Any uncertainty also propagates unevenly and becomes larger over the abscissa, giving weight to smaller values of  $r_P/[A]$ .



In a batch reactor, one often wants to plot  $[A]$  as a function of time. To obtain this, the Michaelis-Menten equation must be integrated. Doing so yields

$$K_M \ln \left( \frac{C_{A0}}{C_A} \right) + (C_{A0} - C_A) = k_3 E_T t$$

Plotting concentration as a function of time yields a function that clearly changes slope as it switches from first order to zeroth order regimes

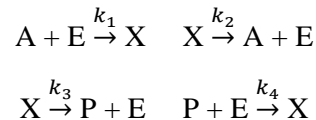


The equation can also be linearized in the following form

$$\frac{C_{A0} - C_A}{\ln\left(\frac{C_{A0}}{C_A}\right)} = V_{\max} \left( \frac{t}{\ln\left(\frac{C_{A0}}{C_A}\right)} \right) - K_M$$

#### 4.3.3 REVERSIBLE PRODUCT BINDING

Instead of irreversible product binding, we will now consider reversible product binding given by  $A + E \leftrightarrow X \leftrightarrow P + E$ , which I will enumerate as follows



Applying PSSH on species X yields

$$0 = (k_1[A] + k_4[P])[E] - (k_2 + k_3)[X] = 0$$

The site balance can be given by

$$E_T = [X] + [E]$$

Substituting in for [E] allows us to write the following (I will drop the brackets for brevity now)

$$X = \frac{(k_1A + k_4P)E_T}{k_1A + k_4P + k_2 + k_3}$$

We can write the mass-action equation for the product as

$$\frac{dP}{dt} = k_3X - k_4PE$$

Substituting in for [X] and making use of stoichiometry (i.e.  $P = A_0 - A$ ) yields

$$\frac{dP}{dt} = E_T \left( \frac{(k_1 + k_3 + k_2k_4)A - k_2k_4A_0}{(k_1 + k_4)A + k_2 + k_3 + k_4A_0} \right)$$

In the case of no reversible binding, at  $t \rightarrow \infty$  we will have  $[A] \rightarrow 0$ . However, for reversible binding, at  $t \rightarrow \infty$  we will have  $[A]$  approach some constant non-zero equilibrium value.



#### 4.3.4 COMPETITIVE INHIBITION

Competitive inhibition occurs when there are two competing substrates for the same enzyme. This can be generally given by the following two equations:  $A + E \leftrightarrow X \rightarrow P + E$  and  $B + E \leftrightarrow Y$ . I will enumerate these reactions as the same as before but now with a  $k_4$  and  $k_5$  for the new set of reactions.

The site balance in this case is now given by

$$E_T = E + X + Y$$

The resulting rate equation can be found to be

$$\frac{dP}{dt} = \frac{k_3 E_T A}{K_M(1 + NB_0) + A}$$

where

$$K_M \equiv \frac{k_2 + k_3}{k_1}$$

and

$$N \equiv \frac{k_4}{k_5}$$

#### 4.3.5 NON-COMPETITIVE INHIBITION

Non-competitive inhibition occurs when a substrate, B, can bind to a remote site on an enzyme that prevents A from binding or leaving the site that converts A to P. This is given by the following series of three reactions:  $A + E \leftrightarrow X \rightarrow P + E$  and  $B + E \leftrightarrow Y$  and  $B + X \leftrightarrow Z$ . As can be seen from this set of equations, B can bind to either the free enzyme or the bound enzyme, both of which prevent the formation of P. We will enumerate these reactions the same as before but with  $k_6$  and  $k_7$  for the new set of reactions.

The site balance can be written as

$$E_T = E + X + Y + Z$$

The rate expression then becomes

$$\frac{dP}{dt} = \frac{k_3 E_T A}{K_M + A + NB_0 K_M + LAB_0} = \frac{\left(\frac{k_3}{1 + LB_0}\right) E_T A}{K_M \left(\frac{1 + NB_0}{1 + LB_0}\right) + A}$$

where the new constant  $L$  is given by

$$L \equiv \frac{k_6}{k_7}$$

## 5 REACTION NETWORKS

### 5.1 INTRODUCTION TO REACTION NETWORKS

Previously, we have discussed rate laws for a single reaction of the type  $A \rightarrow B$ . However, oftentimes we have to deal with a complex reaction network, where there are many products produced from a reactant (or multiple reactants), but little information is known *a priori* about how the products are actually produced. Specifically, the reaction topology is often desired. In this section, we will refer to the “rank” of a species as the numerical order in which a product appears. If it comes first, it will have rank 1 and be called primary; if second, it will have rank 2 and be called secondary, and so on. This is distinct from the order of that species, which we will reserve for the value of  $n$  in  $\text{rate} = kC_A^n$  (i.e. the dependence of rate on concentration).

We will define yield of a species  $i$  (compared to a reactant  $A$ ) as

$$Y_i \equiv \frac{N_i - N_{i0}}{N_{A0}}$$

We will define the conversion of a reactant  $A$  as

$$X_A \equiv 1 - \frac{N_A}{N_{A0}}$$

We will define selectivity of a species  $i$  (compared to a reactant  $A$ ) as

$$S_i \equiv \frac{Y_i}{X_A} = \frac{N_i - N_{i0}}{N_{A0} - N_A}$$

The differential selectivity will therefore be defined as

$$S_{di} \equiv \frac{\partial Y_i}{\partial X_A}$$

### 5.2 DELPLOTS

To determine the rank of a reaction product, the method of delplots can be used. The first-rank delplot is used to distinguish primary products from non-primary products. Higher rank delplots allow for the discernment of products that are secondary, tertiary, and so on. The following notation will be used to describe delplots:  ${}^1P_A$ . Here, the left-hand superscript is a number representing the rank of the delplot (in this case 1), P represents a product P, and the subscript A means that it is based on the conversion of species A.

The first-rank delplot is a plot of selectivity versus conversion. In other words, it is a plot of  $Y_P/X_A$  vs.  $X_A$ . For each product P, the delplot is extrapolated to  $X_A \rightarrow 0$  (i.e. when  $t \rightarrow 0$  or  $\tau \rightarrow 0$ ). This y-intercept, denoted as  ${}^1P_A$ , can be evaluated as

$${}^1P_A = \lim_{\tau \rightarrow 0} \frac{P/A_0}{(A_0 - A)/A_0} = \lim_{\tau \rightarrow 0} \frac{P}{A_0 - A}$$

This can be evaluated algebraically from given expressions of the concentrations of each product as a function of time or numerically from the actual plots of selectivity versus conversion.

If a finite  $y$ -intercept is found in the first-rank delplot, then the product is primary because the initial rate of formation of a primary product is always finite. If the  $y$ -intercept is zero, then the product is non-primary (i.e. the rank is greater than 1) because the initial rate of a non-primary product is always zero (i.e. it lags).

Higher rank delplots allows for the sorting of products of rank greater than 1. The second-rank delplot consists of a plot of  $Y_P/X_A^2$  vs.  $X_A$ . The  $y$ -intercept of the second-rank delplot for a product P is

$${}^2P_A = \lim_{\tau \rightarrow 0} \frac{P/A_0}{\left(\frac{A_0 - A}{A_0}\right)^2} = \lim_{\tau \rightarrow 0} \frac{A_0 P}{(A_0 - A)^2}$$

If a finite intercept is found, the product is secondary. If a zero intercept is found, the product's rank is greater than secondary. If a divergence is found as  $\tau \rightarrow 0$  (i.e. no  $y$ -intercept), the product's rank is primary.

This can be summarized generally. The delplot of rank  $m$  is a plot of  $Y_P/(X_A)^m$  vs.  $X_A$ . The  $y$ -intercept can be found via

$${}^mP_A = \lim_{\tau \rightarrow 0} \frac{P/A_0}{\left(\frac{A_0 - A}{A_0}\right)^m}$$

The following general procedure can then be employed, which has been extended to include orders other than first order. In the table,  $r$  is the rank of the species and  $m$  is the rank of the plot. Note that it is often too difficult to notice changes from 0 intercepts to finite intercepts for  $n > 1$  when the rank is high. If you encounter a species that has a 0 intercept no matter the rank of the Delplot, it is likely either  $n = 1$  and a really high rank species (perhaps it is produced from intermediate species you are not aware of) or  $n > 1$  and some rank at the end of the chain. The specific order can often be determined by looking at concentration versus time plots. In general, delplots are limited at ranks greater than about 2 or 3 due to the large propagation of error that occurs.

Order	Rank = 1	Rank > 1
$n = 1$	${}^1P_A = \text{finite (otherwise 0)}$	${}^mP_A = 0$ for $r > m$ ${}^mP_A = \text{finite}$ for $r = m$ ${}^mP_A = \text{diverges}$ for $r < m$
$n < 1$	${}^1P_A = \text{finite (otherwise 0)}$	${}^mP_A = 0$ for $r > m$ ${}^mP_A = \text{diverges}$ for $r = m$
$n > 1$	${}^1P_A = \text{finite (otherwise 0)}$	${}^mP_A = 0$ for $r \geq m$ ${}^mP_A = \text{finite}$ for $r < m$

## 6 KINETIC THEORY

### 6.1 COLLISION THEORY

#### 6.1.1 DISTRIBUTION LAWS

Collision theory can be used to estimate kinetic parameters from first-principles. It assumes that the molecules are hard spheres and react by collision with one another. It also assumes that the attractive forces between the species are negligible.

Although it will not be derived here, it can be found that the probability distribution for a given speed,  $c$ , is given by

$$P(c) dc = \frac{4c^2}{\alpha^3 \sqrt{\pi}} \exp\left(-\frac{c^2}{\alpha^2}\right) dc$$

where  $\alpha$  is the most probable speed can be found via

$$\alpha = \sqrt{\frac{2k_B T}{m}}$$

The distribution of kinetic energy can be derived from this expression and can be given by

$$P(E) dE = \frac{4}{\alpha^3} \sqrt{\frac{2E}{\pi m^3}} \exp\left(-\frac{2E}{m\alpha^2}\right) dE$$

#### 6.1.2 COLLISION FREQUENCIES

With the hard-sphere assumption and the distribution laws established, we can write an expression for the number of collisions experienced per molecule per second. First, let us define the reaction cross section as

$$\sigma_{AB} = \frac{1}{2}(\sigma_A + \sigma_B)$$

The reaction cross section  $\sigma_{AB}$  represents the distance between the centers of species  $A$  and  $B$  below which collisions can occur. If we consider the trajectory of a single molecule  $A$  through a stationary matrix of  $B$  moving at a fixed speed, then the collision frequency is then given by

$$Z_{AB} = \pi \sigma_{AB}^2 c_A n_B$$

where  $c_A$  is the speed of species  $A$  and  $n_B$  is the number density of  $B$ . The average speed from the Maxwell distribution can be given as

$$c_{\text{avg}} = \sqrt{\frac{8k_B T}{\pi \mu_{AB}}}$$

where  $\mu_{AB}$  is the reduced mass of  $AB$ , given by

$$\mu_{AB} \equiv \frac{m_A m_B}{m_A + m_B}$$

For the case of identical molecules, the reduced mass simplifies to half the mass of the molecule. This relative speed is useful because now we can write the collision frequency of  $A$  moving through a matrix of  $B$  molecules when  $A$  has a Maxwell distribution of speeds

$$Z_{AB} = \pi \sigma_{AB}^2 n_B \sqrt{\frac{8k_B T}{\pi \mu_{AB}}}$$

If both molecules  $A$  and  $B$  have Maxwellian distributions, then

$$Z_{AB} = \pi \sigma_{AB}^2 n_A n_B \sqrt{\frac{8k_B T}{\pi \mu_{AB}}}$$

If there is only one molecular species  $A$  then the collision frequency is given by

$$Z_{AA} = 4\pi \sigma_{AA}^2 n_A^2 \sqrt{\frac{k_B T}{\pi m_A}}$$

### 6.1.3 RATE CONSTANTS

Naively, one could say that since  $Z$  is a collision frequency, then it is a rate and then  $Z_{AB} = r_A = -kn_A n_B$  for a bimolecular reaction of  $A$  and  $B$ . This would imply that  $k = \pi \sigma_{AB}^2 \sqrt{\frac{8k_B T}{\pi \mu_{AB}}}$ . While this is reasonable for the pure collision of two species, it not reflective of the kinetics of *reactions* because there is no exponential dependence on temperature. The missing link here is that molecules only react if they collide with sufficient energy transfer. We therefore must define a threshold energy,  $\eta^*$ , above which reactions can occur. We then find that the reactive collision number is

$$Z = p \pi \sigma_{AB}^2 \sqrt{\frac{8k_B T}{\pi \mu_{AB}}} \exp\left(-\frac{\eta^*}{k_B T}\right) n_A n_B$$

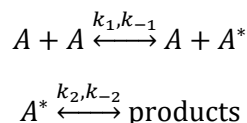
Here,  $p$  is a steric factor which is effectively a correction factor (unless otherwise defined, it can be taken as a value of 1). For  $r_A = -kn_A n_B$ , we then have that

$$k = p \pi \sigma_{AB}^2 \sqrt{\frac{8k_B T}{\pi \mu_{AB}}} \exp\left(-\frac{\eta^*}{k_B T}\right)$$

From the above expression, we see that there is an exponential temperature dependence as would be expected from Arrhenius' law, but there is also a  $\sqrt{T}$  dependence in what would be analogous to the pre-exponential factor, which is otherwise assumed to be independent of temperature in the Arrhenius equation. The collision theory equation is fairly accurate for low values of  $\eta^*$ , such as very exothermic elementary steps like radical recombination.

## 6.2 LINDEMANN THEORY

The prior equation for  $k$  from collision theory is not suitable for unimolecular reactions because it assumes that bonds are formed from the collision of two molecules and does not capture decomposition that isn't from this relative kinetic energy of translational motion. We will present here a simplified version of Lindemann theory in which collisions are instantaneous. Let us assume a reaction mechanism of



If we apply PSSH on the activated intermediate, we get

$$\frac{dC_{A^*}}{dt} = 0 = k_1 C_A^2 - k_{-1} C_A C_{A^*} - k_2 C_{A^*}$$

Solving for  $C_{A^*}$  yields

$$C_{A^*} = \frac{k_1 C_A^2}{k_2 + k_{-1} C_A}$$

The rate of product formation is then given by

$$r = k_2 C_{A^*} = \frac{k_1 k_2 C_A^2}{k_2 + k_{-1} C_A}$$

At high pressures (i.e. high concentrations), we get

$$r \approx \frac{k_1 k_2}{k_{-1}} C_A = k_\infty C_A$$

where  $k_\infty$  is the observable rate constant. At low pressures (i.e. low concentrations) we get

$$r \approx k_1 C_A^2$$

We know that collision theory works very well for radical decomposition, so we can assume that  $k_{-1}$  can be estimated well from collision theory and is therefore

$$k_{-1} = \pi \sigma_{AA}^2 n_A^2 \sqrt{\frac{8k_B T}{\pi \mu_{AB}}}$$

where the exponential energy term can be ignored because  $\eta^* \approx 0$  for this reaction. The probability distribution function of energies in this system can also be found to be

$$f(E^*) = \frac{\exp\left(-\frac{E^*}{k_B T}\right) \left(\frac{E^*}{k_B T}\right)^{n-1}}{(n-1)!}$$

where  $n$  is the number of degrees of vibrational freedom. For a nonlinear polyatomic molecule, it is given by  $n = 3N - 6$  and a linear molecule it is given by  $n = 3N - 5$  where  $N$  is the number of atoms in the molecule. We can say that the equilibrium constant for the first reaction is given by

$$K_1 = \frac{k_1}{k_{-1}} = \frac{C_{A^*}}{C_A}$$

The term  $C_{A^*}/C_A$  is essentially the fraction of the total number of molecules with energy greater than  $E^*$ , so

$$\frac{k_1}{k_{-1}} = f(E^*)$$

We then have that

$$k_1 = \pi \sigma_{AA}^2 n_A^2 \sqrt{\frac{8k_B T}{\pi \mu_{AB}}} \frac{\exp\left(-\frac{E^*}{k_B T}\right) \left(\frac{E^*}{k_B T}\right)^{n-1}}{(n-1)!}$$

If we look back at the rate constant for the high concentration case,

$$k_\infty = \frac{k_1 k_2}{k_{-1}} = k_2 f(E)$$

If we want to know what the observable rate constant is, we need to find  $k_2$ . The value of  $k_2$  is the probability that the product decays and is given by

$$k_2 = \bar{v} \left(1 - \frac{E^*}{nk_B T}\right)^{1-n}$$

After some math that is omitted here for brevity, we can arrive at the following expression for the observable rate constant in the limit of high  $E^*$ ,

$$k_\infty = \bar{v} \exp\left(-\frac{E^*}{k_B T}\right)$$

which has the familiar form of the Arrhenius expression ( $\bar{v}$  is an intrinsic frequency factor and thus has the units of the pre-exponential factor in the Arrhenius equation). We then see that Lindemann theory succeeds where collision theory fails – in the high  $E^*$  limit.

## 6.3 TRANSITION STATE THEORY

### 6.3.1 PARTITION FUNCTIONS

Transition state theory (TST) treats the activated intermediate as a real species which means that we can use thermodynamics to estimate its properties. Let us consider the follow equilibrium of the transition state complex



We then have that

$$K_C^\ddagger = \frac{[ABC^\ddagger]}{[AB][C]}$$

This can be determined from statistical mechanics via the following expression<sup>2</sup>

$$K_C^\ddagger = \frac{N_A^{n-1} Q^\ddagger}{Q_{AB} Q_C} \exp\left(-\frac{\Delta U^\ddagger}{RT}\right)$$

where  $n$  is the molecularity. The  $\Delta U^\ddagger$  can only be obtained from calculations (typically the difference of zero-point energies of reactants and the transition state), the value of  $n$  is the molecularity of the reaction,

---

<sup>2</sup> More generally, for the reaction  $aA + bB \leftrightarrow cC + dD$ , we have that  $K_C = N_A^{n-1} \exp\left(-\frac{\Delta U^\ddagger}{RT}\right) \prod_i Q_i^{v_i}$ .

and  $N_A$  is Avogadro's number (to convert the units properly to a mole basis). The  $Q$  values here represent partition functions with units of inverse volume and are the products of vibrational, rotational, translational, and electronic partition functions. Written mathematically,

$$Q = Q_t Q_r Q_v^N Q_e$$

where  $N$  is the number of vibrational modes. The value of  $N$  is  $3N_0 - 5$  for linear molecules and  $3N_0 - 6$  for nonlinear polyatomic molecules where  $N_0$  is the number of atoms. However, a key point must be addressed for transition states. The power of  $N$  *must be decreased by one* for transition states because there is one less degree of freedom due to the pseudo-bond formed. For this,

$$Q^\ddagger = Q_t Q_r Q_v^{N-1} Q_e$$

We now must define each of the partition functions. The translational partition function is defined as

$$Q_t \equiv \left( \frac{2\pi m k_B T}{h^2} \right)^{\frac{3}{2}}$$

and has units of inverse volume. It typically has a value of about  $10^{24} \text{ cm}^{-3}$ . Importantly, if we can constrain the system to be in a 2D space instead of 3D space, the exponent drops by a factor of 1/2.

The rotational partition function is different depending on the shape of the molecule. For a linear molecule,

$$Q_r = \frac{8\pi^2 I k_B T}{\sigma h^2}$$

and for a nonlinear molecule

$$Q_r = \frac{8\pi^2 (8\pi^3 I_1 I_2 I_3)^{\frac{1}{2}} (k_B T)^{\frac{3}{2}}}{h^3 \sigma}$$

In these equations,  $\sigma$  represents the symmetry number and is determined by the number of spatial orientations of the subject molecule that are identical. For easy reference, it is a value of 2 for linear molecules with a center of symmetry and 1 for linear molecules without a center of symmetry. The quantity  $I$  is the moment of inertia, and for the nonlinear case they are the three principal moments. The moment of inertia is defined as

$$I = \sum_i m_i r_i^2$$

where  $r$  is the distance to the axis of rotation. For a diatomic molecule, the moment of inertia is  $I = \mu R^2$  where  $\mu$  is the reduced mass and  $R$  is the distance between the two atoms. For a linear, symmetric molecule like  $\text{CO}_2$ , the moment of inertia is  $I = 2m_{\text{O}} r_{\text{CO}}^2$ , where  $m_{\text{O}}$  is the mass of the oxygen atom and  $r_{\text{CO}}$  is the C-O bond length. For a triatomic linear molecule, such as a D-D-H transition state, the moment of inertia would approximately be  $I = m_{\text{D}} r_{\text{DD}}^2 + m_{\text{H}} r_{\text{HD}}^2$  (this assumes the center of the molecule is the center of mass, which is a reasonable approximation). The value of  $Q_r$  is unitless and approximately  $10^2 - 10^4$  for linear molecules and  $10^3 - 10^6$  for nonlinear molecules.

The vibrational partition function is given by



$$Q_v = \prod_i^n \left( 1 - \exp\left(-\frac{h\nu_i}{k_B T}\right) \right)^{-1}$$

where  $n$  is the degrees of vibrational freedom and  $\nu_i$  is the vibrational frequency from IR or Raman spectroscopy. The value of  $Q_v$  is unitless and approximately 1 to 10. Note that spectra normally yield wavenumbers with units of inverse length. To convert a wavenumber  $\tilde{\nu}$  to frequency, use  $\nu_i = c\tilde{\nu}_i$ .

Finally, the electronic partition function is given by

$$Q_e = \sum_i g_i \exp\left(-\frac{E_i}{k_B T}\right)$$

where  $g_i$  is the degeneracy and  $E_i$  is the electronic energy above the ground state.

If it is impossible or too inconvenient to calculate the partition functions directly, one can still make order of magnitude arguments. Generally, we can say that

$$Q_i \approx f_t^3 f_r^a f_v^N f_e$$

where  $a = 2$  and  $N = 3N_0 - 5$  for a linear molecule and  $a = 3$  and  $N = 3N_0 - 6$  for a polyatomic nonlinear molecule. For the transition state,

$$Q^\ddagger \approx f_t^3 f_r^a f_v^{N-1} f_e$$

We then can plug in  $f_t^3 \approx 10^{24} \text{ cm}^{-3}$ ,  $f_r^2 \approx 10^2 - 10^4$  (linear) or  $f_r^3 \approx 10^3 - 10^6$  (nonlinear),  $f_v \approx 1 - 3$ , and  $f_e \approx 1$ .

When using TST, oftentimes a number of approximations are made to make the math easier. Generally speaking,  $Q_e$  is neglected unless dealing with transition metals in their excited states, radicals, or certain species like oxygen, which is triplet in the ground state. Also, for species with large vibrational frequencies,  $Q_v \approx 1$ . Another important thing to realize is that  $Q_r = 1$  if the species is monatomic.

### 6.3.2 COMPUTING RATES OF REACTION

Keeping with the prior example, the rate of reaction is simply

$$r = v_\ddagger [ABC^\ddagger]$$

where  $v_\ddagger$  is the frequency of passage over the energy barrier and  $[ABC^\ddagger]$  is the concentration of the transition state. Substituting in for  $C_\ddagger$  using the previously defined  $K_C^\ddagger$  yields

$$r = v_\ddagger K_C^\ddagger [AB][C]$$

We can define the frequency  $v_\ddagger$  as the thermal energy provided such that

$$v_\ddagger = \frac{RT}{N_A h} = \frac{k_B T}{h}$$

so that we can say

$$r = \frac{k_B T}{h} K_C^\ddagger [AB][C]$$

Plugging in for  $K_c^\ddagger$  yields

$$r = \frac{k_B T N_A^{n-1} Q^\ddagger}{h Q_{AB} Q_C} \exp\left(-\frac{\Delta U^\ddagger}{RT}\right) [AB][C]$$

We should note that this takes the form of an Arrhenius-like expression. We can say that the pre-exponential factor is

$$k_0 = \frac{k_B T N_A^{n-1} Q^\ddagger}{h Q_{AB} Q_C}$$

such that

$$k = k_0 \exp\left(-\frac{\Delta U^\ddagger}{RT}\right)$$

and then we get a functional form of

$$r = k[AB][C]$$

like we would expect. For reference, a loose TST – something like bond dissociation – has  $k_0 \approx 10^{16} \text{ s}^{-1}$  and a tight TST – something like associative bonding – has  $k_0 \approx 10^9 \text{ M}^{-1} \text{ s}^{-1}$ .

We have therefore seen that for the general equation  $k = k_0 T^m \exp\left(-\frac{E_a}{RT}\right)$ ,  $m = 0$  for Arrhenius (which is empirical and works over small  $T$  ranges),  $m = 1/2$  for collision theory (which works best for small  $E_a$ ), and  $m = 1$  for large transition state theory (which works best for large  $E_a$ ).

### 6.3.3 THERMODYNAMIC ANALYSIS

Recall that

$$\Delta G^\ddagger = -RT \ln(K_a^\ddagger)$$

We can then of course use the fact that

$$\Delta G^\ddagger = \Delta H^\ddagger - T\Delta S^\ddagger$$

to say

$$K_a^\ddagger = \exp\left(\frac{\Delta S^\ddagger}{R}\right) \exp\left(-\frac{\Delta H^\ddagger}{RT}\right)$$

We can then write the rate expression as

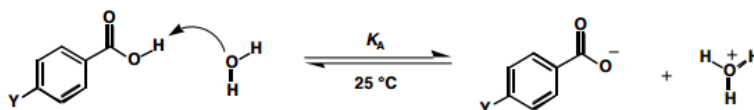
$$r = \frac{\frac{k_B T}{h} \exp\left(\frac{\Delta S^\ddagger}{R}\right) \exp\left(-\frac{\Delta H^\ddagger}{RT}\right)}{C^\circ{}^{n-1}} [AB][C]$$

where  $C^\circ$  is a reference concentration (usually given by  $P/RT$  at 1 bar and  $T$  for gases or as the molal concentration of pure components for liquids) and  $n$  is the molecularity.

### 6.3.4 HAMMETT EQUATION

Recall that we have the Evans-Polanyi relationship of  $E = E_0 + \alpha\Delta H_{\text{rxn}}$  for a family of reactions. We note that, from TST, a family of reactions is similar if it has a similar  $\Delta S^\ddagger$ . Oftentimes, other quantities aside from the Evans-Polanyi relationships are used, especially when dealing with organic molecules. They use thermochemical or structural properties.

One of the most common set of parameters are the Hammett constants. Consider the reaction of aromatic species with various substituent groups, denote  $x$ . An example is shown below (the group is indicated by a  $Y$  though)



The Hammett equation relates the substituted group  $x$  with the rate of reaction and takes into account the effect of inductive and resonance effects. It can be given by

$$\log\left(\frac{k_x}{k_H}\right) = \gamma_H \sigma_x$$

where  $\sigma_x \equiv \log\left(\frac{K_x}{K_H}\right)$  and is a tabulated quantity<sup>3</sup>. The lower case  $k$  values refer to reaction rate constants, and the capital  $K$  values refer to equilibrium (acid) dissociation constants. For the Hammett equation, a substituted group of  $x = H$  (i.e. the group is a hydrogen atom) is often used as a reference.

Higher values of  $\sigma_x$  indicate that the equilibrium constant is increased for a chemical group  $x$  with respect to the hydrogen reference, meaning that the reaction is shifted more in the forward direction (specifically, via a stabilization of negative charge via resonance and inductive effects). Therefore, the acidity of the reactant molecule increases when  $\sigma_x > 0$ . Such a substituent is considered to be an electron-withdrawing group because it will stabilize the product anion by withdrawing negative charge away from the reaction site. Conversely, molecules with  $\sigma_x < 0$  indicate an electron-donating group where the acid dissociation is disfavored since the electron density is increased near the reaction site.

There are also trends that can be seen with the  $\gamma_H$  values, which are easier to see when you make the equation  $k_x = k_H 10^{\gamma_H \sigma_x}$ . For  $\gamma_H > 1$ , the reaction is more sensitive to substituents than the reference molecule, and negative charge is built up in the transition state of the reaction. The reaction is assisted by electron-withdrawing groups. For  $\gamma_H = 0$ , there is no sensitivity to substituents, and no charge is built or lost. For  $\gamma_H < 0$ , the reaction builds up positive charge in the transition state of the reaction. The reaction is assisted by electron-donating groups.

It should also be noted that  $\sigma_x$  values are approximately additive, so if an aromatic ring has 2 Cl groups, then the  $\sigma_x$  value can be approximated as  $2\sigma_{\text{Cl}}$ .

There are alternate forms of the Hammett parameter that are parameterized for the reactions that require positive and negative charge stabilization, given by  $\sigma^+$  and  $\sigma^-$ , respectively. For pure inductive effects,  $\sigma'$  can be used.

<sup>3</sup> Some references use  $\log_{10}$  whereas others use  $\ln$ .

### 6.3.5 TAFT EQUATION

The Taft equation is another linear free energy relationship and was developed as a modification to the Hammett relationship. The Taft equation describes the effect of sterics and induction. The general equation is

$$\log\left(\frac{k_x}{k_{\text{CH}_3}}\right) = \gamma^* \sigma^* + E_s$$

where  $\sigma^*$  is a purely inductive effect and  $E_s$  is a purely steric effect. In the limit of steric effects being negligible, it simplifies to the same functional form as the Hammett equation. The trends in  $\gamma^*$  are then the same as the trends for  $\gamma_H$ .

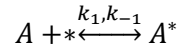
## 7 SURFACE CATALYSIS

### 7.1 ADSORPTION RATE LAWS

#### 7.1.1 MOLECULAR ADSORPTION

We will now consider surface catalysis, wherein a reactant in a continuum diffuses into a catalyst particle, binds to the surface, reacts to form a new species, desorbs, diffuses out of the catalyst particle, and enters the continuum. As can be seen from this outline, heterogeneous catalysis incorporates adsorption, transport phenomena, reactions, and bulk reactor models. We will focus on developing a basic kinetic model first from elementary steps including adsorption, desorption, and surface reaction.

Consider the first step: adsorption. We will use an asterisk to denote a surface site. As such, the adsorption step can be given by



For example, this could be  $\text{CO} + \text{S}^* \leftrightarrow \text{CO}^*$  (note that when dealing with gases, such as CO, it is standard to use a partial pressure instead of concentration). This specific type of adsorption is referred to molecular (or non-dissociative) adsorption. The equation for the net rate of adsorption can then be written as

$$r_{\text{ad}} = k_1 C_A C_* - k_{-1} C_{A^*} = k_1 \left( C_A C_* - \frac{C_{A^*}}{K_A} \right)$$

where  $K_A \equiv k_1/k_{-1}$  and is referred to as the adsorption equilibrium constant. The adsorption rate constant  $k_1$  is relatively independent of temperature whereas the desorption constant  $k_{-1}$  increases exponentially with increasing temperature, such that the equilibrium adsorption constant  $K_A$  decreases exponentially with increasing temperature. A site balance can generally be written as

$$C_T = C_* + \sum_i C_{i^*}$$

where the summation term accounts for any other adsorbed species to the surface sites. In this example,

$$C_T = C_* + C_{A^*}$$

We know that at equilibrium, the net rate of adsorption should be zero. Employing this condition yields

$$C_{A^*} = K_A C_A C_*$$

Substituting in for  $C_*$  from the site balance yields

$$C_{A^*} = K_A C_A (C_T - C_{A^*})$$

which can be rearranged to

$$C_{A^*} = \frac{K_A C_A C_T}{1 + K_A C_A}$$

This equation is specifically called the Langmuir isotherm. This equation can be linearized to the following form for data-fitting purposes, as shown below

$$\frac{C_A}{C_{A^*}} = \frac{1}{K_A C_T} + \frac{C_A}{C_T}$$

Typically, the parameter  $\theta$  is defined as the number of moles of species adsorbed divided by the number of moles in the monolayer. This would be

$$\theta = \frac{C_{A^*}}{C_T} = \frac{K_A C_A}{1 + K_A C_A}$$

The linearized form is

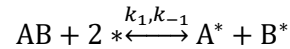
$$\frac{1}{\theta} = \frac{1}{K_A C_A} + 1$$

Oftentimes,  $\theta$  is defined as the volume adsorbed divided by the volume adsorbed at saturation:  $V/V_M$ . In this definition, the above expression simply becomes

$$\frac{1}{V} = \left(\frac{1}{C_A}\right) \left(\frac{1}{K_A V_M}\right) + \frac{1}{V_M}$$

### 7.1.2 DISSOCIATIVE ADSORPTION

It is possible to have types of adsorption that differ from the previous scenario. For instance, consider a molecule AB. It can either adsorb molecularly, as described before, or it can dissociate and have A bound to one surface site and B bound to a different surface site. This is described below



This could be  $CO + 2 * \leftrightarrow C^* + O^*$ , for instance. In this case, the adsorption rate can be written as

$$r_{ad} = k_1 C_{AB} C_*^2 - k_{-1} C_{A^*} C_{B^*} = k_1 \left( C_{AB} C_*^2 - \frac{C_{A^*} C_{B^*}}{K_A} \right)$$

where  $K_A \equiv k_1/k_{-1}$  once again. For dissociative adsorption, both  $k_1$  and  $k_{-1}$  increase exponentially with temperature, unlike the case with molecular adsorption. We can then employ equilibrium conditions such that

$$C_{A^*} C_{B^*} = K_A C_{AB} C_*^2$$

The site balance is now

$$C_T = C_* + C_{A^*} + C_{B^*}$$

Substituting in for  $C_*$  into our rate equation at equilibrium yields

$$C_{A^*} C_{B^*} = K_A C_{AB} (C_T - C_{A^*} - C_{B^*})^2$$

For the case of  $C_{A^*} = C_{B^*}$  (which would be anticipated), we can arrive at

$$C_{A^*} = C_{B^*} = \frac{(K_A C_{AB})^{\frac{1}{2}} C_T}{1 + 2(K_A C_{AB})^{\frac{1}{2}}}$$

We now have a Langmuir isotherm for this system. Using the  $\theta$  nomenclature, this is the same as

$$\theta = \frac{(K_A C_{AB})^{\frac{1}{2}}}{1 + 2(K_A C_{AB})^{\frac{1}{2}}}$$

The equation can be linearized by

$$\frac{\sqrt{C_{AB}}}{C_{A^*}} = \frac{1}{C_T \sqrt{K_A}} + \frac{2\sqrt{C_{AB}}}{C_T}$$

which equivalently is the following when  $C_T$  is multiplied through and  $\sqrt{C_{AB}}$  is divided through

$$\frac{1}{\theta} = \frac{1}{\sqrt{K_A C_{AB}}} + 2$$

It can be easily shown that the dissociative adsorption process of  $A_2 + 2 * \leftrightarrow 2A^*$  is identical to the case before but the denominator in the expression for  $C_{A^*}$  is  $1 + (K_A C_{A_2})^{\frac{1}{2}}$  where the factor of 2 disappears because the site balance is just  $C_T = C_* + C_{A^*}$ . Therefore, in this case

$$C_{A^*} = \frac{(K_A C_{A_2})^{\frac{1}{2}} C_T}{1 + (K_A C_{A_2})^{\frac{1}{2}}}$$

We can define the  $\theta$  parameter then such that

$$\theta = \frac{(K_A C_{A_2})^{\frac{1}{2}}}{1 + (K_A C_{A_2})^{\frac{1}{2}}}$$

which can be linearized to

$$\frac{1}{\theta} = \frac{1}{\sqrt{K_A C_{A_2}}} + 1$$

Oftentimes, a plot of  $1/\theta$  vs.  $1/\sqrt{C_{A_2}}$  will have deviations at high and low coverages (and by extension high and low partial pressures) due to adsorbate-adsorbate interactions and site heterogeneity.

### 7.1.3 COMPETITIVE ADSORPTION

It is possible to have two species (A and B) competing for surface sites. The site balance would then be written as

$$C_T = C_* + C_{A^*} + C_{B^*}$$

We start at

$$C_{A^*} = K_A C_A C_*$$

Plugging in the new site balance yields

$$C_{A^*} = K_A C_A (C_T - C_{A^*} - C_{B^*})$$

We know that

$$C_{B^*} = K_B C_B C_*$$

So

$$C_{A^*} = K_A C_A (C_T - C_{A^*} - K_B C_B C_{A^*})$$

which can be rearranged to

$$C_{A^*} = \frac{K_A C_A C_T}{1 + K_A C_A + K_B C_B}$$

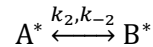
An analogous procedure for B would yield

$$C_{B^*} = \frac{K_B C_B C_T}{1 + K_A C_A + K_B C_B}$$

## 7.2 SURFACE REACTION RATE LAWS

### 7.2.1 SINGLE SITE

After a reactant has been adsorbed, it can then react. A single site mechanism is one in which the site where the reactant is adsorbed is the only one involved in the reaction. Written out, this would be



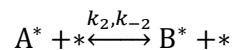
for the transformation of species A to B on the catalyst surface. The rate law for this is given by

$$r_{SR} = k_2 \left( C_{A^*} - \frac{C_{B^*}}{K_{SR}} \right)$$

where  $K_{SR} \equiv k_2/k_{-2}$ .

### 7.2.2 DUAL SITE

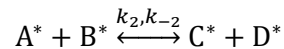
A dual-site mechanism is one in which a reactant adsorbed to a site reacts with a separate site. One way this can be written is by the following equation:



The rate law for this is given by

$$r_{SR} = k_2 \left( C_{A^*} C_* - \frac{C_{B^*} C_*}{K_{SR}} \right)$$

A dual site reaction may also consist of a reaction between two adsorbed species, given by



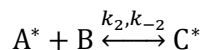
The rate law for this is given by

$$r_{SR} = k_1 \left( C_{A^*} C_{B^*} - \frac{C_{C^*} C_{D^*}}{K_{SR}} \right)$$



### 7.2.3 REACTION WITH UNBOUND SPECIES

A reaction can also occur between an adsorbed molecule and a molecule in the continuum (when the adsorbed molecule reacts with a molecule in the gas phase, this is typically referred to as an Eley-Rideal mechanism). The general equation is

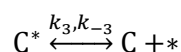


The corresponding rate equation is

$$r_{\text{SR}} = k_2 \left( C_{A^*} C_B - \frac{C_{C^*}}{K_{\text{SR}}} \right)$$

### 7.3 DESORPTION RATE LAWS

The process of desorption is given by



The rate of desorption can be given by

$$r_{\text{Des}} = k_3 \left( C_{C^*} - \frac{C_C C_*}{K_{\text{Des}}} \right)$$

where  $K_{\text{Des}} \equiv k_3/k_{-3}$ . We can easily see that the desorption equilibrium constant is simply the inverse of the adsorption equilibrium constant. As such, we can arrive at

$$r_{\text{Des}} = k_3 (C_{C^*} - K_{\text{Ad}} C_C C_*)$$

or

$$r_{\text{Des}} = k_{-3} \left( \frac{C_{C^*}}{K_{\text{Ad}}} - C_C C_* \right)$$

if we divide through by the adsorption equilibrium constant.

### 7.4 DETERMINING THE REACTION MECHANISM AND RATE-LIMITING STEP

The following procedure can generally be employed when trying to determine the reaction mechanism for a given reaction in terms of measurable:

1. Propose a mechanism consisting of an adsorption step, surface reaction step, and desorption step
2. Assume a rate-limiting step. The first guess should generally be the surface reaction step.
3. Write out the elementary rate law for the rate-limiting step
4. There will be immeasurable species in Step 3 that you will want removed. Write out the elementary rate laws for the relevant reactions and apply equilibrium as needed to solve for the concentrations of adsorbed species ( $C_{i^*}$ ). If the reactions are not reversible, then instead say that the net rate of generation of  $C_{i^*}$  is zero and apply PSSH.
5. Write out the site balance and solve for the concentration of vacant sites (plugging in quantities from Step 4). You don't want the concentrations of empty sites in the overall rate expression, so this will help get rid of them.
6. Derive the rate law by combining Steps 2-5.
7. Compare the results with experimental data. If the data does not agree, choose a different rate-limiting step and/or propose a different mechanism.

## 7.5 NONIDEALITIES

### 7.5.1 NONIDEAL SURFACES

Real surfaces are not perfect and have defects/deformations that cause  $\Delta H_{\text{ads}}$  to not be constant over the entire surface. We know that the equilibrium constant is

$$K_{\text{eq}} = \exp\left(-\frac{\Delta G_{\text{ads}}}{RT}\right) = \exp\left(\frac{\Delta S_{\text{ads}}}{R} - \frac{\Delta H_{\text{ads}}}{RT}\right)$$

From thermodynamics and the above expression, we then see that  $\Delta H_{\text{ads}} < 0$  is favorable and  $\Delta S_{\text{ads}} > 0$  is favorable. In reality,  $\Delta H_{\text{ads}}$  is a function of  $\theta$ . The Langmuir models, derived in the following subsections, assume  $\Delta H_{\text{ads}}$  is a constant and is only good for isolated sites.

Additional models have been developed. The Temkin model states that

$$\Delta H_{\text{ads}}(\theta) = \Delta H_{\text{ads}}^0(1 - \alpha\theta)$$

where  $\Delta H_{\text{ads}}^0$  is the heat of adsorption at zero surface coverage and  $\alpha$  is a fitting parameter. This expression is an empirical relationship that simply makes  $\Delta H_{\text{ads}}$  linearly decrease with increasing  $\theta$ . For molecular adsorption, the Temkin isotherm is

$$\theta \approx \frac{RT}{\Delta H_{\text{ads}}^0 \alpha} \ln(K_A C_A)$$

The Freundlich model states that

$$\Delta H_{\text{ads}}(\theta) = -\Delta H_{\text{ads}}^0 \ln(\theta)$$

This model completely breaks down as  $\theta \rightarrow 0$ . It can be shown via the Clausius-Clapeyron equation that the Freundlich isotherm for molecular adsorption takes the form of

$$\theta = \alpha C_A^m$$

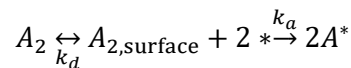
where  $\alpha$  and  $m$  fitting parameters. The value of  $m$  is directly related to the intensity of adsorption. The value of  $\alpha$  is an indicator of the adsorption capacity.

### 7.5.2 STICKING PROBABILITY

The sticking probability is defined

$$S(\theta) = \frac{\# \text{ molecules that stick}}{\# \text{ molecules hitting surface}}$$

This is often reported as  $S(\theta)/S(0)$  in the literature. Ideally,  $S(\theta)$  linearly decreases with increasing  $\theta$  since the loss of available sites makes it less likely that a molecule will stick when it hits the surface. However, in reality it can take on other shapes. For instance, let us consider



This is showing that a diatomic gas  $A_2$  comes in contact with the surface but does not always bind it. We can apply PSSH to the  $A_{2,\text{surface}}$  intermediate such that

$$\frac{d[A_{2,\text{surface}}]}{dt} = \phi F_A - k_d[A_{2,\text{surface}}] - k_a[A_{2,\text{surface}}](1 - \theta)^2 \approx 0$$

Here,  $\phi$  is the trapping ratio,  $F_A$  is the flux of  $A$ , and  $\theta$  is the fractional coverage. Note that the  $(1 - \theta)^2$  term comes in because that is effectively  $C_*^2/C_T^2$ . We know that the sticking coefficient is

$$S(\theta) = \frac{k_a[A_{2,\text{surface}}](1 - \theta)^2}{F_A}$$

since this represents the number of molecules that stick to the surface divided by the number of molecules that hit. Plugging in the PSSH equation solved for  $F_A$  into the above definition of the sticking coefficient yields

$$S(\theta) = \frac{k_a[A_{2,\text{surface}}](1 - \theta)^2\phi}{k_d[A_{2,\text{surface}}] + k_a[A_{2,\text{surface}}](1 - \theta)^2} = \frac{k_a(1 - \theta)^2\phi}{k_d + k_a(1 - \theta)^2}$$

At zero coverage,

$$S(0) = \frac{k_a\phi}{k_d + k_a}$$

so that

$$\frac{S(\theta)}{S(0)} = \frac{(k_d + k_a)(1 - \theta)^2}{k_d + k_a(1 - \theta)^2}$$

If we define  $K \equiv k_a/k_d$  then we arrive at

$$\frac{S(\theta)}{S(0)} = \frac{(1 + K)(1 - \theta)^2}{1 + K(1 - \theta)^2}$$

Recall from the molecular adsorption section that  $K$  decreases exponentially with increasing temperature. As such, at the low temperature limit and low values of  $\theta$ , we find that  $S(\theta)/S(0) \approx 1$ . At the high temperature limit, we find that  $S(\theta)/S(0) \approx (1 - \theta)^2$ .

## 8 REACTIONS IN HETEROGENEOUS SYSTEMS

### 8.1 DEFINITIONS

#### 8.1.1 DIFFUSIVITY

In kinetic processes that occur with heterogeneous catalysts, the reactant must diffuse through the porous catalyst in order to react. Therefore, there are oftentimes diffusion limitations that must be considered. We will first define a few relevant terms when dealing with transport in porous media.

The void fraction and tortuosity of a porous particle are defined as

$$\varepsilon \equiv \text{void fraction} = \frac{\text{volume of void space}}{\text{total volume (voids + solids)}}$$

$$\tau \equiv \text{tortuosity} = \frac{\text{actual distance between two points}}{\text{shortest distance between two points}}$$

There is also the molecular diffusivity, often denote  $D_m$ , which is a strong function of the particle diameter. The effective diffusivity (for a species  $A$ ) is defined as

$$D_{EA} = \frac{\varepsilon D_{m,A}}{\tau}$$

#### 8.1.2 THIELE MODULUS

The Thiele modulus for reaction order  $n$  in a spherical geometry is defined as<sup>4</sup>

$$\phi_n^2 = \frac{R^2 k_n C_{A,s}^{n-1}}{D_{EA}} \sim \frac{\text{surface reaction}}{\text{diffusivity}}$$

When the Thiele modulus is small, the kinetics are reaction limited whereas when it is large, the reaction is diffusion limited. Note that when  $n = 1$ , there is no dependence on  $C_{A,s}$ . The general definition of the Thiele modulus for an arbitrary geometry is given by

$$\phi_n^2 = W^2 \left( \frac{n+1}{2} \cdot \frac{k_n C_{A,s}^{n-1}}{D_{EA}} \right)$$

where  $W$  is an arbitrary volume/surface area expression for the particular shape. It should be noted that this definition of  $\phi_n^2$  is different by a numerical factor. Generally, just use the first definition for spheres and the second one for more complicated geometries. Everything is an order of magnitude argument anyway.

#### 8.1.3 EFFECTIVENESS FACTOR

The effectiveness factor is defined as

$$\eta = \frac{\text{observed reaction rate}}{\text{reaction rate if all } C_A = C_{A,s}}$$

<sup>4</sup> Note that the definition of the Thiele modulus oftentimes has the  $k_n$  term replaced with a  $k_n \rho_B S_A$  term. In this,  $\rho_B$  is the bulk density and  $S_A$  is the surface area divided by the mass of the catalyst. This is because oftentimes rates are reported in moles/(cm<sup>2</sup> s) and therefore  $k_n$  has different units than usual. If one is dealing with a rate that has moles/(cm<sup>3</sup> s) or equivalent dimensions, then simply omit the  $S_A \rho_B$  unit correction term in the definition. If one is dealing with a rate that has units of 1/s then keep the  $\rho_B$  term but omit the  $S_A$  term.

In the limit of  $\eta \rightarrow 1$  ( $\phi_n \rightarrow 0$ ), there are no diffusion limits. In the limits of  $\eta \rightarrow 0$  (for  $\phi_n \rightarrow \infty$ ), there are significant diffusion limits. For a first-order reaction in a sphere,

$$\eta = \frac{3(\phi_1 \coth(\phi_1) - 1)}{\frac{R^2 k_1 \rho_B S_A}{D_{EA}}} = \frac{3}{\phi_n^2} (\phi_n \coth(\phi_n) - 1)$$

It turns out the right-hand form of this expression is true for other orders in spherical catalysts as well since the reaction order only changes the power of  $n - 1$  in the Thiele modulus.

For a flat plate,

$$\eta = \frac{\tanh(\phi)}{\phi}$$

The observed rate is

$$-r_{A,\text{obs}} = -\eta r_{A,s} = \eta k_0 e^{-\frac{E_a}{RT}} C_{A,s}^n = \eta k_n C_{A,s}^n$$

where  $k_n$  is the intrinsic rate constant. Also note that  $\eta k_n = k_{\text{obs}}$ .

## 8.2 LIMITING CASES

### 8.2.1 NO DIFFUSION LIMITATIONS

There are negligible diffusion limitations when  $\eta$  is close to 1 and when  $\phi$  is close to zero. When the Thiele modulus is small,

$$\phi \rightarrow 0, \quad \eta \rightarrow 1$$

For small  $\phi$ , the observed reaction rate is the surface rate (no diffusion limits), so

$$\phi = \text{small}, \quad \eta \rightarrow 1, \quad r_{A,\text{obs}} = r_{A,s}, \quad k_n = -\frac{r_{\text{obs}}}{C_{A,s}^n}$$

This can happen at small particle radius, small rate constants, high effective diffusivity, and/or low temperatures. Therefore, when running at these conditions, one is measuring the real (i.e. intrinsic rate constant).

### 8.2.2 DIFFUSION LIMITATIONS

There are diffusion limitations when  $\eta$  is less than 1 and when  $\phi$  is greater than zero. It is always true that for large Thiele modulus,

$$\phi \rightarrow \infty, \quad \eta \propto \frac{1}{\phi}$$

The above expression becomes an equality of  $\eta \rightarrow 3/\phi$  for a sphere and  $\eta \rightarrow 1/\phi$  for a plate. Then,

$$\frac{\eta_1}{\eta_2} = \frac{\phi_{n,2}}{\phi_{n,1}}$$

For large  $\phi$ , we know that for a sphere is the following

$$\phi = \text{large}, \quad -r_{A,\text{obs}} = \eta k_n C_{A,s}^n = \frac{3}{\phi_n} k_n C_{A,s}^n = \frac{3}{R} \sqrt{D_{EA}} \sqrt{k_n} C_{A,s}$$

Recall that  $k_n$  is an intrinsic rate constant and can be expressed as  $\sqrt{k_n} = \sqrt{k_{n,0}} \exp\left(-\frac{E_a}{2RT}\right)$  where  $k_{n,0}$  is the pre-exponential factor. This therefore says that for large  $\phi$  (diffusion limitations), we have

$$\phi = \text{large}, \quad E_{A,\text{obs}} = \frac{E_A}{2}$$

If one includes the temperature dependence of  $D_{EA}$ , it can be shown that

$$E_{A,\text{obs}} = \frac{E_A + E_{\text{diffusion}}}{2}$$

The apparent order can be expressed as the following (for  $n \neq 1$ )

$$n_{\text{app}} = n + \frac{n-1}{2} \frac{d \ln \eta}{d \ln \phi_n}$$

such that the observed order is between the true order and 1.

One can find the diffusivity in the diffusion limiting regime by backing out  $\eta$  from

$$r_{A,\text{obs}} = \eta k_n C_{A,S}^n$$

then using this value of  $\eta$  to back out  $D_{EA}$  from

$$\eta = \frac{3}{\phi} = 3 \left( R \sqrt{\frac{k_n C_{A,S}^{n-1}}{D_{EA}}} \right)^{-1}$$

### 8.3 DETERMINING IF DIFFUSION LIMITATIONS ARE DOMINANT

#### 8.3.1 CHANGING PARTICLE SIZE

It is generally true that the ratio of any two rates is

$$\frac{r_{A,\text{obs},1}}{r_{A,\text{obs},2}} = \frac{\eta_1}{\eta_2}$$

provided  $k_n$  and  $C_{A,S}$  is the same between the two rates (e.g. if you change the catalyst size). If all the parameters are the same except catalyst size, one can also state that

$$\frac{\phi_1}{\phi_2} = \frac{R_1}{R_2}$$

For the case of diffusion limitations, since  $\eta \propto 1/\phi$ , one can state that

$$\frac{\eta_1}{\eta_2} = \frac{\phi_{n,2}}{\phi_{n,1}}$$

Therefore, when in a diffusion limiting regime,

$$\frac{r_{A,\text{obs},1}}{r_{A,\text{obs},2}} = \frac{R_2}{R_1}$$

The above expression can be tested to see if one is operating in the diffusion-limiting regime. Conversely, there are no diffusion limitations if changing the radius has no impact on the observed rate.

### 8.3.2 WEISZ-PRATER CRITERION

Start with the definition of the Thiele modulus rearranged slightly as

$$k_n = \frac{\phi_n^2}{R^2 C_{A,S}^{n-1}} D_{EA}$$

Substituting this into the rate expression yields

$$r_{A,\text{obs}} = \eta \frac{\phi_n^2}{R^2} D_{EA} C_{A,S}$$

This can be rearranged to

$$\eta \phi_n^2 = \frac{r_{A,\text{obs}} R^2}{D_{EA} C_{A,S}}$$

For  $\phi \ll 1$ ,  $\eta = 1$  there is no pore diffusion limitations and so we expect  $\eta \phi_n^2 \ll 1$ . For  $\phi \gg 1$ ,  $\eta \propto 1/\phi_n$  there is strong pore diffusion limitations and  $\eta \phi_n^2 \gg 1$ . Note that for first order, the above expression simplifies to

$$\eta \phi_1^2 = \frac{k_{\text{obs}} R^2}{D_{EA}}$$

Oftentimes, the above expression is written with a  $W^2$  instead of  $R^2$  such that for a sphere  $W^2 = (R/3)^2$ . This causes a difference of a factor of 9 but should not change the overall trend.

## 8.4 EXTERNAL MASS TRANSFER

### 8.4.1 MASS TRANSFER COEFFICIENT

In this section, we will consider the case where  $C_{A,\text{bulk}} \neq C_{A,\text{surf}}$ . In reality, there is a boundary layer between the bulk and the pellet surface where the concentration varies. The mass flux at the surface of the catalyst can be given by

$$\text{mass flux} = k_g (C_{A,b} - C_{A,s})$$

where  $k_g$  is the mass transfer coefficient. Of course, the rate of reaction at the catalyst surface is given by  $r_A = k C_{A,s}^n$ . Let us assume, for example,  $n = 2$ . We can then equate these two expressions, solve for  $C_{A,s}$ , and plug back into  $r_A$  to arrive at

$$r_A = k_g \left( \left( 1 + \frac{k_g}{2k C_{A,b}} \right) - \sqrt{\left( 1 + \frac{k_g}{2k C_{A,b}} \right) - 1} \right) C_{A,b}$$

This is clearly neither 1<sup>st</sup> nor 2<sup>nd</sup> order but some intermediate. In the limit of  $k \gg k_g$ , we arrive at

$$r_A = k_g C_{A,s}$$

which is 1<sup>st</sup> order and limited due to mass transfer. Contrastingly, in the limit of  $k_g \gg k$ , we arrive at

$$r_A = k C_{A,s}^2$$

which is what we'd expect – 2<sup>nd</sup> order and a rate limited by reaction.

### 8.4.2 MASS TRANSFER IN REACTOR ENGINEERING

In reactors, one typically does not measure the rate directly. Instead, inputs and outputs are measured. For example, the differential conversion is usually found, which is defined as

$$X_A = \frac{F_{A0} - F_A}{F_{A0}}$$

The rate is then found from

$$r_A = -\frac{X_A F_{A0}}{W}$$

where  $W$  is the catalyst weight. Oftentimes, it is best to keep  $X_A < 10\%$  since the kinetics can't be read easily if it is higher.

### 8.4.3 NONISOTHERMAL THEORY

A number of catalytic reactions are accompanied by thermal effects from the heat of reaction, so it is important to consider a combined mass and energy balance approach. The result of such an approach yields

$$T_s - T_{s,s} = \frac{D_{eA}(-\Delta H)}{\lambda_e} (C_{A,s} - C_A)$$

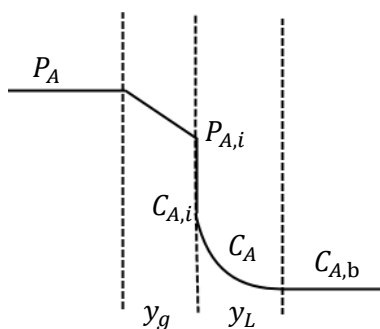
where  $T_s$  is the temperature on the outer surface of the particle,  $T_{s,s}$  is the surface of a pore in the particle, and  $\lambda_e$  is the effective thermal conductivity in the pore. The large possible temperature difference is when  $C_A \rightarrow 0$ . In this case we can say that

$$\frac{(\Delta T_s)}{T_{s,s}} = \frac{D_{eA}(-\Delta H)C_{A,s}}{\lambda_e T_{s,s}} \equiv \beta$$

where  $\beta$  is the reaction heat parameter.

### 8.4.4 THIN-FILM DIFFUSION REACTION

We now want to know how a reaction can speed up the mass transfer, which is incorporated in an enhancement factor,  $F$ . Consider the following concentration profile for diffusion and reaction into a thin film from the bulk. The leftmost side represents the bulk gas phase whereas the rightmost side represents the bulk liquid phase. The length  $y_g$  is the gas film length, and  $y_L$  is the film length. In the film, Henry's Law applies, and  $P_{A,i} = HC_{A,i}$ .



We will define the following gas film and liquid film mass transfer coefficients



$$k_g = \frac{D_{A,g}}{y_g}, \quad k_L = \frac{D_{A,L}}{y_L}$$

For a pseudo first order, irreversible reaction,

$$C_A = \frac{C_{A,i} \sinh\left(\gamma \left(1 - \frac{y}{y_L}\right)\right) + C_{A,b} \sinh\left(\gamma \frac{y}{y_L}\right)}{\sinh(\gamma)}$$

where  $\gamma$  is the Hatta parameter defined as

$$\gamma \equiv y_L \sqrt{\frac{k}{D_{A,L}}} = \frac{\sqrt{k D_{A,L}}}{k_L}$$

The flux at the interface can be given by

$$N_{A,i} = \frac{\gamma}{\tanh(\gamma)} \left(1 - \frac{C_{A,b}}{C_{A,i}} \frac{1}{\cosh(\gamma)}\right) k_L C_{A,i}$$

The effectiveness factor is

$$\eta_L = \frac{N_{A,i} A_v}{k C_{A,i}}$$

where  $N_{A,i}$  is the flux at the interface,  $A_v$  is the surface area per volume, and  $k C_{A,i}$  is the reaction rate at the interface. If we define the Sherwood number as

$$\text{Sh} = \frac{k_L}{A_v D_A}$$

It can be shown that the effectiveness factor is

$$\eta_L = \frac{1}{\text{Sh} \gamma \tanh(\gamma)} \left(1 - \frac{C_{A,b}}{C_{A,i}} \frac{1}{\cosh(\gamma)}\right)$$

For very fast reactions ( $\gamma > 5$  or so and  $C_{A,b} \rightarrow 0$ ), we get

$$\eta_L = \frac{1}{\gamma \text{Sh}} = A_v \sqrt{\frac{D_A}{k}}$$

We can also define the enhancement factor as

$$F = \frac{N_{A,\text{obs}}}{k_L (C_{A,i} - C_{A,b})} = \frac{\gamma}{\tanh(\gamma)} \left(1 - \frac{C_{A,b}}{C_{A,i}} \frac{1}{\cosh(\gamma)}\right)$$

For very fast reactions,

$$F = \frac{\gamma}{\tanh(\gamma)} \approx \gamma$$