Chemical Kinetics and Reaction Engineering

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Lectures notes for a graduate-level course.
Compiled on 2025-11-23.

This document was typeset using Typst (https://typst.app°).

Contents

1. Setting the Stage

1.1. Course Perspective

Before we set sail on our journey, it is probably wise to state upfront what this course does—and does not—entail. After all, it would be a bit difficult to appreciate the journey if you have no idea about the destination.

This course is specifically designed to provide a foundational understanding of how chemical reactions proceed and how to engineer them. Given the extremely diverse and increasingly interdisciplinary areas of research that the modern chemical engineer can pursue, this course focuses on topics that are likely to be of widespread relevance to researchers. This, primarily, translates to a significant focus on reaction kinetics.

As a field of study, reaction kinetics is fascinating from a metascience perspective. In my somewhat biased opinion, there is no field of study in the chemical sciences that is more prone to misconceptions and questionable assumptions. Part of the reason for this pedagogical challenge is that kinetics can be both a theoretically rigorous *and* a purely empirical science depending on how one approaches the topic (naturally, we will lean more towards the former in this course). After all, if the rate coefficient k should actually be $4k$, this is of no major concern if one treats kinetics as merely an exercise in statistical regression, but it can influence the meaning of the underlying kinetic parameters if treated from a theoretical basis.

Perhaps a more notable cause of pedagogical challenges in the reaction kinetics literature —including both textbook and research articles—is that the intersection of kinetics and thermo-dynamics can become fraught with logical inconsistencies. Frequently, derivations in reaction kinetics are carried out under assumptions of thermodynamic ideality. When these assumptions break down, it is tempting to re-introduce correction factors in a *post hoc* manner, but doing so often yields deceptively incorrect mathematical expressions. One of the most notable examples of this is the inclusion of activity coefficients in the derivation of transition state theory. The lack of attention dedicated to the proper accounting of standard-state properties further complicates matters as well.

This course seeks to present reaction kinetics with as theoretically sound of a basis as possible, emphasizing rigor and precision at each step of the journey. Additionally, most derivations are carried out in full without steps left as "an exercise for the reader," as this is often where errors are most likely to arise. Interactive plots are presented throughout the text to allow the reader to engage more directly with the underlying equations when doing so would yield unique insights.

Of course, given the nature of limited time, there must always be tradeoffs. In the design of this course, several topics of relevance to reactor engineering have been intentionally omitted or alluded to only in passing. Nonetheless, the hopes is that this course will ultimately provide unique insights into the fundamentals of chemical reactions and their kinetics in a way that is broadly applicable to the modern graduate student regardless of their chosen area of study. Rest assured—there is plenty to learn and much left to be discovered!

1.2. Why Reaction Engineering

Chemical reactions and the reactor vessels in which they occur have a profound impact on society and life as we know it. In this section, we will briefly highlight a few representative examples of chemical reactors that are relevant to our everyday lives, mainly to provide context for why it is worth pursuing the fundamentals of chemical reaction engineering in the first place.

1.2.1. The Sun

Before we discuss conventional chemical reactors designed by humans, it is worth taking a moment to appreciate that the fundamental principles of reaction engineering can be applied to an enormous range of systems that long predate an industrialized society. To demonstrate this point, consider the Sun. In many ways, the Sun can be thought of as a massive chemical reactor: it is a confined volume in which a chain reaction is continually taking place, providing the energy that sustains life on Earth via the conversion of hydrogen into helium. While these reactions are nuclear rather than chemical, the same fundamental principles of reactor analysis apply. The Sun is a reminder that the principles of reaction kinetics are not just relevant to industrial processes but to the very fabric of the universe itself. Of course, one could go even further to argue that the Big Bang itself is the largest reaction of all with our universe as the largest reactor, but that is a discussion best left for another time.

1.2.2. Cells and Enzymes

Fast-forward many millions of years after the formation of the Sun, and we arrive at the evolution of life on Earth. Cellular life itself is a testament to chemical reactors in action. Surely, you may recall that the mitochondria is the powerhouse of the cell, and these miniature reactors are carrying out complex reaction cascades via the citric acid cycle to support cellular respiration.

As chemical engineers, we can draw significant inspiration from nature's chemical reactors. For instance, consider methanotrophs: a family of bacteria that primarily metabolize methane as their main source of chemical energy. Methane itself is a greenhouse gas that, while in lower concentrations than carbon dioxide in the atmosphere, has an 80× higher global warming potential within the first 20 years of its release. Chemical engineers have been inspired by methanotrophs to research ways to directly convert methane—the primary component of natural gas—into cleaner and more valuable chemical feedstocks. Heterogeneous catalysts, for example, that mimic the structure of the active sites in methane monooxygenase enzymes found within methanotrophs have been shown to directly and selectively convert of methane into methanol. While carrying out this process efficiently and cost-effectively at industrial scales remains a "holy grail", it is worth keeping in mind that the core principles of reaction engineering spans many disciplines that can each benefit from the insights of one another.

1.2.3. Ammonia Synthesis

Continuing our highly abbreviated journey through time, we arrive at human civilization and, eventually, the dawn of the modern chemical industry as we know it today. In the early 1900s, one of society's most important chemical reactors was developed: the ammonia reactor. Powered by

the Haber–Bosch process devised by Fritz Haber and Carl Bosch, the modern ammonia reactor is the main industrial mechanism for producing the ammonia that is used in nitrogen fertilizers. The Haber–Bosch process itself constitutes the following net reaction:

$$N_2 + 3H_2 \rightleftharpoons 2NH_3. \tag{1}$$

Colloquially referred to as "converting air into bread", this process produces the ammonia that is central to nitrogen fertilizers, a process so important to society that it is believed to have been a critical factor in the global population boom during the 20th century.[1] In fact, it is estimated that up to half of the nitrogen atoms in the human body may have gone through the Haber–Bosch process. We will revisit the ammonia reactor and the Haber–Bosch process several times throughout this course, as it is an excellent example that ties together many of the fundamental concepts of chemical reaction engineering.

1.2.4. Making and Leveraging Liquid Hydrocarbons

Fast forwarding to the 1930s, the rise of the automobile and increased reliance on fossil fuels led to several advances in reactor technologies. One representative discovery was the catalytic cracker: a reactor that uses an aluminosilicate material known as Zeolite Y to catalyze the conversion of high-molecular weight, linear alkanes found in petroleum into smaller, more valuable hydrocarbons.[2] Another relevant process pioneered during this time period is the Fischer–Tropsch process, which converts carbon monoxide and hydrogen (known as synthesis gas or "syngas") into liquid hydrocarbons.[3] Historically, countries with substantial coal resources have benefitted the most from the Fischer–Tropsch process as a means of producing diesel fuels without relying on foreign imports of oil. The synthesis gas in this case is produced via coal gasification, wherein coal is reacted with oxygen, steam, or air at high temperatures.

1.2.5. Green Technologies

While much of the history of chemical engineering is intricately tied to the fossil fuel industry, its future is far more diverse in scope. Recently, there has been a significant push towards leveraging chemical reaction engineering principles to address the many clean energy and sustainability challenges facing our planet. Some areas of interest include the design of fuel cells that convert hydrogen and oxygen into electricity, porous materials that can capture and convert carbon dioxide, and cutting-edge technologies to "upcycle" plastic waste into valuable commodity chemicals. Even historical chemical processes continue to receive substantial research interest. For instance, due to the demanding operating conditions of the Haber–Bosch process, it is

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[1]For additional historical context about the Haber–Bosch process and the complicated history of Fritz Haber himself, watch "The Man Who Killed Millions and Saved Billions" by Veritasium: https://www.youtube.com/watch?v=IV3dnLzthDA°. The book titled *The Alchemy of Air: A Jewish Genius, a Doomed Tycoon, and the Scientific Discovery That Fed the World but Fueled the Rise of Hitler* by T. Hager may also be of interest.

[2]If you ever find yourself driving back to Princeton from New York City, take a look in the westward direction near the entrance of Interstate 95. You will likely be able to see the Phillips 66 Bayway Refinery, which has a fluid catalytic cracking unit (among other chemical reactors). Roughly one out of every 20 ships in New York Harbor are bound for this refinery, where crude oil is distilled, cracked, and purified.

[3]For a molecular-scale view of how the Fischer–Tropsch reaction works, watch the following animation from the Eindhoven University of Technology: https://www.youtube.com/watch?v=44OU4JxEK4k°.

estimated to contribute 1.4% of global carbon dioxide emissions. Identifying new catalysts and chemical processes for energy-intensive reactions of central importance to society remains a major way that engineers can leverage the principles of kinetics to foster a better future.

2. Reaction Rates and Rate Constants

2.1. Generic Expressions for Chemical Reactions

2.1.1. Stoichiometry for Individual Reactions

We start by considering a generic chemical reaction given by the following expression:

$$\alpha A + \beta B \longrightarrow \gamma C + \delta D, \tag{2}$$

where A and B are reactants, C and D are products, and α, β, γ, and δ are the corresponding stoichiometric numbers to ensure that mass is conserved. For now, we will assume that this reaction is an *elementary* reaction, meaning that it is a single, well-defined reaction step.
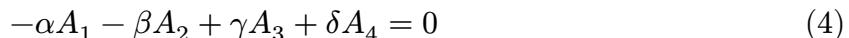
It is often useful to think about chemical reactions in a more mathematically oriented framework. For this, we will define A_j as the j-th species taking place in the reaction (starting from $j = 1$). We will also define ν_j as the stoichiometric coefficient of species A_j, wherein reactants have $\nu_j < 0$ and products have $\nu_j > 0$ by convention.

For our example reaction given by Equation 2, we would have

$$\begin{aligned} \boldsymbol{A} &= \begin{pmatrix} A_1 & A_2 & A_3 & A_4 \end{pmatrix} \\ \boldsymbol{\nu} &= \begin{pmatrix} -\alpha & -\beta & \gamma & \delta \end{pmatrix}, \end{aligned} \tag{3}$$

where A_1, A_2, A_3, and A_4 are synonymous with species A, B, C, and D, respectively.

From this convenient set of mathematical notation, we can rewrite our chemical reaction as

$$-\alpha A_1 - \beta A_2 + \gamma A_3 + \delta A_4 = 0 \tag{4}$$

or more generally as

$$\sum_j \nu_j A_j = 0, \tag{5}$$

the latter of which is true for any balanced chemical reaction.[4]

2.1.2. Stoichiometry for Multiple Reactions

Naturally, the next step is to consider multiple chemical reactions taking place. For instance, perhaps we instead have the following two elementary reactions:

$$\begin{aligned} \alpha A + \beta B &\rightarrow \gamma C \\ \gamma C &\rightarrow \delta D. \end{aligned} \tag{6}$$

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[4]This can be written in matrix form as $\boldsymbol{\nu} \cdot \boldsymbol{A}^{\mathrm{T}} = 0$, where the superscript "T" indicates that the row vector is transposed to form a column vector.

Here, we will use i to denote individual reactions in contrast with j for distinguishing species. In this case, we will define a two-dimensional stoichiometric matrix $\nu_{i,j}$, which simply means "the stoichiometric number for the j-th species in the i-th reaction." For our example, we have

$$
\boldsymbol{A} = \begin{pmatrix} A_1 & A_2 & A_3 & A_4 \end{pmatrix}
$$
$$
\boldsymbol{\nu} = \begin{pmatrix} -\alpha & -\beta & \gamma & 0 \\ 0 & 0 & -\gamma & \delta \end{pmatrix}.
$$
(7)

For our example reaction, we have

$$
-\alpha A_1 - \beta A_2 + \gamma A_3 = 0, \quad -\gamma A_3 + \delta A_4 = 0.
$$
(8)

In analogy with Equation 5, we can write a general expression for a balanced set of chemical equations in nearly the same way:

$$
\sum_j \nu_{i,j} A_j = 0,
$$
(9)

where the above expression is written for each reaction i.[5]

Throughout this course, we will mostly write out the systems of equations, avoiding the need for a linear algebra-based perspective. However, the matrix representations were nonetheless included in our prior discussion to emphasize a more mathematically compact way of thinking about expressing chemical reactions and to clarify the meaning of the subscripts we will use frequently throughout the course. The matrix forms are also convenient from a computational perspective, as they are a more efficient way to express the system of equations.

2.2. The Rate of Reaction

2.2.1. Defining the Rate

2.2.1.1. Rate of Change for a Species

With the generic reactions introduced in Section 2.1, we can ask the fundamental question: what is the rate of change of the j-th species in a given reaction, denoted r_j? Intuitively, one might say that r_j is simply the number of moles of A_j being generated per unit time. Most commonly, however, we will define r_j in an intensive manner such that it has the following units:

$$
r_j = \frac{\left[\text{moles of } A_j\right]}{[\text{time}] \cdot [\text{reaction space}]}.
$$
(10)

Here, the reaction space is typically a representative volume used to normalize the rate so that it is an intensive property. When the chemical reactor and its contents are spatially uniform, the reaction space can be the reactor volume itself; otherwise, it is limited to a differential, volumetric element in the reactor under consideration.

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[5]This can be written more compactly in matrix form as $\boldsymbol{\nu} \cdot \boldsymbol{A}^{\mathrm{T}} = \boldsymbol{0}$.

Written algebraically, the rate of generation for species A_j can be given as

$$r_j \equiv \frac{1}{V}\frac{\mathrm{d}n_j}{\mathrm{d}t}, \tag{11}$$

where V is the normalizing system volume, n_j is the number of moles of the j-th species, and t is time. In practice, other normalizations for r_j can be used in place of volume. For instance, in catalytic reactions, it is oftentimes more convenient to normalize the rate on the basis of the surface area or weight of the catalyst that is driving the reaction.

> **⚠ Caution**
>
> Note that the definition of r_j is not necessarily the rate of change in species concentration, as that equality can only be made if there is a constant and uniform volume. To demonstrate this point, let us define $[A_j]$ as the concentration of species A_j. We can rewrite $n_j = [A_j]V$ to arrive at
>
> $$r_j = \frac{1}{V}\frac{\mathrm{d}([A_j]V)}{\mathrm{d}t} = \frac{1}{V}\left(V\frac{\mathrm{d}[A_j]}{\mathrm{d}t} + [A_j]\frac{\mathrm{d}V}{\mathrm{d}t}\right). \tag{12}$$
>
> If—and only if—the reaction volume remains constant, we have
>
> $$r_j = \frac{1}{V}\left(V\frac{\mathrm{d}[A_j]}{\mathrm{d}t}\right) = \frac{\mathrm{d}[A_j]}{\mathrm{d}t}. \tag{13}$$

For a system of several reactions, we will likely be interested in the *net* rate of change in species A_j. This is nothing more than the sum of all the rates of change for species A_j across each reaction. Returning to the set of reactions given in Equation 6,

$$\alpha A + \beta B \rightarrow \gamma C$$
$$\gamma C \rightarrow \delta D, \tag{14}$$

we can define the individual rates of change for each species as

$$\begin{aligned}
r_A &= r_{1,A}\\
r_B &= r_{1,B}\\
r_C &= r_{1,C} + r_{2,C}\\
r_D &= r_{2,D}.
\end{aligned} \tag{15}$$

More generally, the rate of change of the j-th species can be expressed as

$$r_j = \sum_i r_{i,j}, \tag{16}$$

where the summation is taken over each reaction i in the reaction scheme.

2.2.1.2. Rate of a Reaction

2.2.1.2.1. In Relation to Rates of Change for Species

Continuing our terminology adventure, we can ask: what is the rate for the i-th reaction (instead of the j-th species)? We will define the rate of reaction, r_i, to be proportional to the rate of generation or consumption of each species based on the corresponding stoichiometric coefficients.

For instance, the rates of the two reactions in Equation 6,

$$\alpha A + \beta B \to \gamma C$$
$$\gamma C \to \delta D,$$

(17)

can be written out as

$$r_1 = -\frac{r_{1,A}}{\alpha} = -\frac{r_{1,B}}{\beta} = \frac{r_{1,C}}{\gamma}$$
$$r_2 = -\frac{r_{2,C}}{\gamma} = \frac{r_{2,D}}{\delta}.$$

(18)

In mathematical terms, we can state more generally that for the i-th reaction and j-th species that

$$r_i \equiv \frac{r_{i,j}}{\nu_{i,j}}.$$

(19)

Unlike the rate of change for a species, the rate of reaction is always a positive quantity, which is the motivation behind the sign conventions in the above expression.

With this formalism, we can rewrite the net rate of change for a given species across multiple reactions (originally presented in Equation 16) in terms of the individual reaction rates. For our example set of reactions, we would have

$$r_A = -\alpha r_1$$
$$r_B = -\beta r_1$$
$$r_C = \gamma r_1 - \gamma r_2$$
$$r_D = \delta r_2.$$

(20)

Take a moment to contrast the above expressions with Equation 15, which was written in terms of the rate of change for each species rather than the rates of reaction.

More generally, we can express the rate of change for a given species as simply the sum of each reaction rate scaled by the corresponding stoichiometric coefficients. In other words,

$$r_j = \sum_i \nu_{i,j} r_i,$$

(21)

where the summation is taken over each reaction i in the reaction scheme.[6]

2.2.1.2.2. In Relation to the Extent of Reaction

Thus far, we have defined the rate of a reaction as being some property that is defined by the rates of change of each species, normalized in an internally consistent manner that is not dependent on the choice of species. However, we can provide a slightly more proper definition if we introduce a new term: the extent of reaction. The extent of a reaction, ξ, is a measure of the reaction progress (typically in units of moles) based on the number of chemical transformations,[7] typically defined as

$$\mathrm{d}\xi \equiv \frac{\mathrm{d}n_j}{\nu_j}. \tag{22}$$

With this, we can define the rate of the i-th reaction as

$$r_i = \frac{1}{V}\frac{\mathrm{d}\xi_i}{\mathrm{d}t}. \tag{23}$$

We can confirm that our definitions are internally consistent via substitution:

$$r_i = \frac{1}{V}\frac{\frac{\mathrm{d}n_{i,j}}{\nu_{i,j}}}{\mathrm{d}t} \tag{24}$$

$$r_i = \frac{1}{\nu_{i,j}}\frac{1}{V}\frac{\mathrm{d}n_{i,j}}{\mathrm{d}t} \tag{25}$$

$$r_i = \frac{r_{i,j}}{\nu_{i,j}}, \tag{26}$$

which is identical to Equation 19.

At this point, it may feel like this is all just a dozen different ways to say very similar things. This would not be a false statement! It is important to be extremely precise when discussing reaction kinetics. A "rate" can mean many different things depending on the context.

2.2.2. The Rate Function

In general, we write the rate of reaction as being the product of temperature- and concentration-dependent terms,

$$r = f(\text{temperature}) \cdot f(\text{concentration}). \tag{27}$$

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[6]We can rewrite Equation 21 more generally in matrix form as $r^{\mathrm{T}}_{\text{species}} = \nu^{\mathrm{T}} \cdot r$, where r_{species} and r are the *net* production rates of each species and the *individual* reaction rates, respectively.

[7]For a reaction $2\mathrm{A} \longrightarrow \mathrm{B} + \mathrm{C}$ with an initial value of $N_{\mathrm{A}} = 2$ mol and final value of $N_{\mathrm{A}} = 0.5$ mol, we would have $\xi = -(0.5\ \text{mol} - 2\ \text{mol})/2 = 0.75$ mol. This value of ξ could then be used to find the relative change in B and C based on their stoichiometric coefficients.

For elementary reactions, we can generally describe this relationship via a power-law expression. By way of example, for the elementary reaction given by Equation 2, $\alpha A + \beta B \longrightarrow \gamma C + \delta D$, we can state

$$r \propto [A]^\alpha [B]^\beta. \tag{28}$$

Here, [A] and [B] refer to the molar concentrations of species A and B, respectively. Each exponent is referred to as a partial order, and the overall reaction order is the sum of the exponents. For $\alpha = \beta = 1$, the reaction would be said to be first-order in both [A] and [B], and it would be a second-order reaction.

As a matter of convention, we will define a temperature-dependent proportionality factor, k, such that we can rewrite Equation 28 as

$$r = k[A]^\alpha [B]^\beta. \tag{29}$$

To ensure that the rate has the units given by Equation 10, the units of k in Equation 29 must be $\mathrm{s}^{-1} \cdot \left(\mathrm{mol/m^3}\right)^{1-(\alpha+\beta)}$ when the rate is normalized on a per-unit volume basis. Typically, k is referred to as the rate constant or rate coefficient.[8] Regardless of the name, it is important to emphasize that the value of k is not a constant and can depend on several factors, most notably temperature. The key assumption here is that the effects of temperature and effects of composition are fully decoupled.

When the reactants are gases, it is common to report the quantity of these species in terms of partial pressures, such that Equation 29 is instead given by

$$r = k p_A^\alpha p_B^\beta, \tag{30}$$

where p_j is the partial pressure of the j-th species (i.e. the pressure of the j-th species if it were to occupy the entire volume alone). In the case of Equation 30, the units of k instead must be given by $\mathrm{s}^{-1} \cdot \left(\mathrm{mol/m^3}\right) \cdot \mathrm{bar}^{-(\alpha+\beta)}$.

For a set of several plausible reactions, we can fully generalize this approach by defining the rate of the i-th reaction as

$$r_i = k \prod_{j, \nu_{i,j} < 0} \left[A_j\right]^{|\nu_{i,j}|}, \tag{31}$$

where $\nu_{i,j} < 0$ is simply stating that the multiplication is being carried out for the reactants only. As previously alluded to, if we are dealing with gas-phase species, it may be more convenient to replace $\left[A_j\right]$ with p_j, but otherwise the expression remains the same.

Before continuing, it is important to reiterate that Equation 31 is only strictly valid for elementary reactions. If we have a non-elementary reaction, in many cases it is still possible to use an

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[8] While some in the community have pushed to refer to k as a rate coefficient rather than a rate constant, it begs the question—what about an equilibrium constant?

expression analogous to Equation 31, but there is no guarantee that the reaction orders for each species will be directly related to their stoichiometry. In fact, the reaction orders may be non-integer or even negative, ultimately depending on the kinetics of the constituent elementary reactions. There are also many instances, as we will show throughout this course, where a power-law expression is not suitable to describe a non-elementary reaction.

2.2.3. Reversible Reactions

Now, we will consider a slight variation on Equation 2 wherein the reaction is reversible:

$$\alpha A + \beta B \underset{k^-}{\overset{k^+}{\rightleftharpoons}} \gamma C + \delta D. \tag{32}$$

In principle, all reactions are reversible, although if one direction is orders of magnitude slower than the other, invoking irreversibility is often a logical assumption. We can write the rate expression for Equation 32 in essentially the same was as for Equation 2. To do so, we simply write the rate expression given by Equation 29 for each reaction—both forward and reverse:

$$r^+ = k^+ [A]^\alpha [B]^\beta \tag{33}$$

$$r^- = k^- [C]^\gamma [D]^\delta. \tag{34}$$

The *net* rate of reaction is given by the difference between Equation 33 and Equation 34:

$$r = r^+ - r^- = k^+ [A]^\alpha [B]^\beta - k^- [C]^\gamma [D]^\delta. \tag{35}$$

For a set of several plausible reversible reactions, we can fully generalize this approach by defining the net rate of reaction i as

$$r_i = r_i^+ - r_i^- = k_i^+ \prod_{j, \nu_{i,j}<0} [A_j]^{|\nu_{i,j}|} - k_i^- \prod_{j, \nu_{i,j}>0} [A_j]^{\nu_{i,j}}. \tag{36}$$

Of course, whether one chooses to consider a reversible reaction as a single composite reaction or as two separately enumerated reactions is entirely a matter of preference and convenience.

For reversible reactions, an additional property known as the reversibility, z_i, can be helpful to introduce. The reversibility of reaction i is nothing more than a ratio of the forward and reverse rates:

$$z_i \equiv \frac{r_i^-}{r_i^+}. \tag{37}$$

The reason that the reverse reaction rate is in the numerator is that a lower value of z_i would imply that the forward reaction rate is greater, which is internally consistent with the notion that it would also be less reversible. While we will not spend too much time focusing on reversibility just yet, it will return later on in the course when we cover de Donder relations.

2.3. Expressions for the Rate Constant

2.3.1. The Arrhenius Equation

The most common expression used to evaluate the rate constant is the Arrhenius equation:

$$k = A \exp\left(-\frac{E_\mathrm{a}}{RT}\right), \tag{38}$$

where A is the pre-exponential factor, E_a is the activation energy, R is the ideal gas constant, and T is the absolute temperature.[9] By linearizing the equation, one finds that[10]

$$\ln(k) = -\frac{E_\mathrm{a}}{R}\left(\frac{1}{T}\right) + \ln(A), \tag{39}$$

such that plotting $\ln(k)$ vs. $1/T$ should yield a straight line of slope $-E_\mathrm{a}/R$ and y-intercept of $\ln(A)$, as depicted in Figure 1.
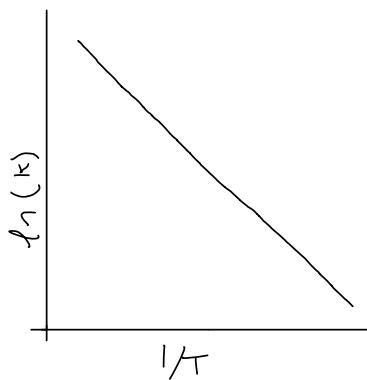
Figure 1: Linearized Arrhenius plot.

One can also use Equation 38 to find the ratio of two rate constants, k_1 and k_2, at different absolute temperatures, T_1 and T_2, via

$$\frac{k_2}{k_1} = \exp\left(-\frac{E_\mathrm{a}}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)\right). \tag{40}$$

In general, if one has a plot of $\ln(k)$ vs. $1/T$ though, it is better to rely on regression and/or interpolation rather than using Equation 40 since the former will more naturally account for statistical uncertainty in the underlying data.

Since one is rarely studying a single, isolated, elementary reaction, there is no inherent guarantee that the Arrhenius plot will be linear when plotted as $\ln(k)$ vs. $1/T$. A common example in heterogeneous catalysis is shown in Figure 2, where the increasing temperature can cause different kinetic processes to dominate, such as diffusion limitations, mass transfer limitations, or even the reaction proceeding homogeneously (e.g. in the gas phase). Different linear regimes

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[9]The units of A depend on the molecularity of the reaction to ensure that k itself has appropriate units.

[10]Strictly speaking, one must divide by the corresponding units before taking the logarithm, but we will omit this for brevity. Nonetheless, the units that were divided out should be mentioned on the axes of any real data.

in an Arrhenius plot can also indicate a change in the underlying mechanism with temperature. In fact, for a non-elementary reaction, there is no guarantee that the experimentally observed activation energy (i.e. the "apparent" activation energy) is positive.
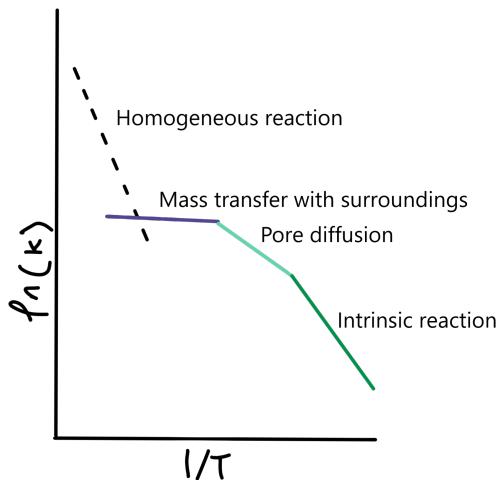
Figure 2: Different linear regimes in an Arrhenius plot for a surface-catalyzed reaction.

The astute observer might question what thermodynamic property E_a refers to in Equation 38. For now, we will simply state that the Arrhenius equation is an empirical relationship and so E_a is best thought of as simply a parameter describing the sensitivity of the rate constant, and thereby the rate, to changes in temperature.[11] We will revisit the Arrhenius equation from a more rigorous, thermodynamic perspective when we cover transition state theory.

2.3.2. Modifications to the Arrhenius Equation

While the original formulation of the Arrhenius equation remains widely used to this day, it has limitations. Most notably, Equation 38 assumes that the pre-exponential factor is a constant. In reality, the pre-exponential factor exhibits some degree of temperature-dependence. A modified form of the Arrhenius equation can be used to account for this fact:

$$k = A'T^n \exp\left(-\frac{E_a}{RT}\right), \tag{41}$$

where n is an additional fitting parameter known as the temperature exponent. As we will show when covering transition state theory, there is theoretical justification for having $n > 0$. The use of the modified Arrhenius equation in Equation 41 does limit the physical interpretability of the activation energy and pre-refactor terms in this way. Regardless, the effect of T^n is generally relatively small and is difficult to observe experimentally without highly precise measurements.

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[11]Speaking of empirical, the start date and temperature dependence of the Japanese cherry blossom blooming season is often modeled with the Arrhenius equation. This has been used to better understand the effects of climate change, as in P. Shi, et al., "Timing of Cherry Tree Blooming: Contrasting Effects of Rising Winter Low Temperatures and Early Spring Temperatures", *Agric. For. Meteorol.*, 240, 78–89 (2017). For other unusual examples, refer to K.J. Laidler, "Unconventional Applications of the Arrhenius Law", *J. Chem. Educ.*, 49, 343–344 (1972).

2.4. Thermodynamic Equilibrium

While this is a course on the kinetics of chemical reactions, we must also acknowledge the importance of thermodynamics, which dictates the equilibrium conditions of a reacting system. We will also see how the two concepts are intrinsically related.

2.4.1. Equilibrium Constants Based on Concentrations and Partial Pressures

When a reversible reaction reaches chemical equilibrium ("eq"), the net rate is precisely zero since the forward and reverse rates of reaction must be equal to one another. For the elementary reaction

$$\alpha A + \beta B \underset{k^-}{\overset{k^+}{\rightleftharpoons}} \gamma C + \delta D, \tag{42}$$

we have

$$0 = k^+ [A]_{eq}^\alpha [B]_{eq}^\beta - k^- [C]_{eq}^\gamma [D]_{eq}^\delta. \tag{43}$$

We can algebraically rearrange Equation 43 to yield

$$\frac{k^+}{k^-} = \frac{[C]_{eq}^\gamma [D]_{eq}^\delta}{[A]_{eq}^\alpha [B]_{eq}^\beta}. \tag{44}$$

The expression given by the right-hand side of Equation 44[12] leads to the definition of the concentration-based equilibrium constant, K_C, which can be expressed compactly as

$$K_C \equiv \prod_j \left[A_j \right]^{\nu_j} \tag{45}$$

and describes the ratio of the forward to reverse rate constants of a reversible reaction at equilibrium.[13] If one were to use partial pressures, p_j, instead of concentrations, one can define a pressure-based equilibrium constant, K_p, as[14]

$$K_p \equiv \prod_j p_j^{\nu_j}, \tag{46}$$

where—for ideal gases—we have $p_j = y_j p$ with y_j the mole fraction of species j and p the total pressure.

2.4.2. Thermodynamic Non-Idealities

The astute observer may notice a potential conundrum with Equation 45 and Equation 46: the resulting expressions may not be dimensionless (depending on the values for ν_j). You may recall

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[12]It is only true that $K_C = k^+/k^-$ for an elementary reaction and so we will not use that as a formal definition.

[13]Going forward, we will omit the "eq" subscript since it is implicit when dealing with an equilibrium constant. However, be careful to only using equilibrium values in this expression and not, for instance, initial values.

[14]For an ideal gas, one can also conveniently state $K_p = K_C (RT)^\delta$ where $\delta = \sum_j \nu_j$.

from thermodynamics that the standard Gibbs free energy of a reaction, $\Delta G°$, can be related to the equilibrium constant via $-RT \ln(K)$, where R is the ideal gas constant and T is the absolute temperature. Therefore, K must be dimensionless in order to properly take the natural logarithm. How can we rationalize this anomaly, and what kind of K is appropriate to use?

The answer comes down to activities. The activity of a species, a_j, is unitless and is the effective concentration (or pressure) of that species in a mixture. For instance, the activity expression generally used to describe solids and liquids is given by

$$a_j = \gamma_j \frac{[A_j]}{C°} \tag{47}$$

where γ_j is the dimensionless activity coefficient, and $C°$ is the standard-state concentration. The activity coefficient is simply whatever value is needed to account for non-idealities. Physically, $\gamma_j < 1$ if species attract one another, whereas $\gamma_j > 1$ if they repel one another. For an ideal mixture, γ_j is a value of 1. The value for $C°$ is typically taken as 1 mol/L for liquids but should always be mentioned when reporting data.

When describing the activities of gases, it is general convention to refer to the fugacity (the effective partial pressure) of a species, f_j, or a dimensionless fugacity coefficient φ_j as follows:

$$a_j = \frac{f_j}{p°} = \varphi_j y_j \frac{p}{p°}, \tag{48}$$

where $p°$ is the standard-state reference pressure typically taken as 1 bar but should always be mentioned when reporting data. For an ideal gas ($\varphi_j = 1$), we can state that $f_j = y_j p = p_j$, such that the fugacity is the same as the partial pressure. The concept of fugacity is simply a matter of terminology and bookkeeping, which will account for attractive intermolecular interactions that can occur at low temperatures or high pressures. From a pedagogical perspective, the main takeaway is that activities are the true property of interest for equilibrium calculations, rather than concentrations of partial pressures, in order for everything to be internally consistent.

> ⚠ **Caution**
>
> When we refer to a standard state, this is a choice that the practitioner makes. The standard state thermodynamic properties are independent of the pressure at which the reaction is actually carried out; rather, they are associated with a hypothetical process. In contrast, the standard state does *not* indicate a particular temperature, which must be specified separately and is typically the observed temperature.[15] As such, state thermodynamic properties taken from a database may need to be adjusted to the experimentally relevant temperature.

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[15]While similar in name, the standard state is not the same concept as the standard temperature and pressure (STP).

2.4.3. Equilibrium Constants Based on Activity

Equation 47 and Equation 48 allow us to rationalize the unit conundrum of Equation 45 and Equation 46: there is a "missing" standard state reference that will ensure the equilibrium constant is unitless, even in the case of an ideal mixture. To tie it all together, we can state

$$K_{\text{acid}} \equiv \prod_j a_j^{\nu_j}. \tag{49}$$

As such, we have

$$\Delta G^\circ = -RT \ln(K_{\text{acid}}), \tag{50}$$

where the equilibrium constant must formally be based on activities. Note that K_{acid} is specifically for the temperature that corresponds to ΔG°, which may differ from the temperature of the reaction under investigation. We will address the temperature-dependence of K_{acid} when we introduce the van 't Hoff equation shortly.

For the sake of convenience later on, we can also now interrelate K_{C} and K_{acid} by plugging in Equation 47 into Equation 49 and then invoking the definition of K_{C}:

$$K_{\text{acid}} = \prod_j \left(\gamma_j \frac{[A_j]}{C^\circ} \right)^{\nu_j} = \frac{K_{\text{C}}}{(C^\circ)^\delta} \prod_j \gamma_j^{\nu_j}, \tag{51}$$

where δ is the change in stoichiometric numbers given simply as $\delta \equiv \sum_j \nu_j$. If ideal conditions can be assumed, then $\gamma_j = 1$ and $K_{\text{acid}} = K_{\text{C}}/(C^\circ)^\delta$. In this form, we can see that the units are appropriately addressed even though concentrations are used directly. The same procedure can, of course, be done for partial pressures as well:

$$K_{\text{acid}} = \prod_j \left(\frac{f_j}{p^\circ} \right)^{\nu_j} = \prod_j \left(\varphi_j y_j \frac{p}{p^\circ} \right)^{\nu_j} = \frac{K_{\text{p}}}{(p^\circ)^\delta} \prod_j \varphi_j^{\nu_j}, \tag{52}$$

In most practical cases, the deviations from non-ideality can be assumed to be small, and we will oftentimes use concentrations or partial pressures in place of activities. However, for concentrated solutions and gases at low temperature or high pressures, the differences can become noticeable and should be considered.[16]

2.4.4. Thermodynamic Considerations in the Haber–Bosch Process

Most chemical reactions, especially in industrially relevant processes, are not carried out at thermodynamic equilibrium. However, understanding equilibrium behavior of a chemical reaction can be incredibly important for understanding the inherit limits of operation and what reaction conditions might (or might not) be most suitable.

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[16]To learn more about potential pitfalls when neglecting activity in equilibrium expressions, refer to C.G. McCarty, E. Vitz, "pH Paradoxes: Demonstrating That It Is Not True That pH ≡ -log[H+]", *J. Chem. Educ.*, 83, 752–757 (2006).

For this example, we will consider the ammonia synthesis reaction given by

$$N_2 + 3H_2 \rightleftharpoons 2NH_3. \tag{53}$$

It is known from experiments that at 298 K, $\Delta G^\circ = -32.8$ kJ/mol and $\Delta H^\circ = -91.8$ kJ/mol. The equilibrium constant for this reaction can be written as follows by invoking Equation 52 for this reaction:

$$K_a = \frac{\left(\frac{f_{NH_3}}{p^\circ}\right)^2}{\left(\frac{f_{N_2}}{p^\circ}\right)\left(\frac{f_{H_2}}{p^\circ}\right)^3} = \frac{f_{NH_3}^2}{\left(f_{N_2}\right)\left(f_{H_2}\right)^3}(p^\circ)^2. \tag{54}$$

If we rewrite the expression in terms of mole fractions,

$$K_a = \frac{\left(\varphi_{NH_3} y_{NH_3}\right)^2}{\left(\varphi_{N_2} y_{N_2}\right)\left(\varphi_{H_2} y_{H_2}\right)^3}\left(\frac{p^\circ}{p}\right)^2, \tag{55}$$

it becomes clear that increasing the total pressure will increase the equilibrium concentration of NH_3 in order for K_a to remain constant.

Given that $\Delta G^\circ \equiv \Delta H^\circ - T\Delta S^\circ$, we can state that

$$K_a = \exp\left(-\frac{\Delta G^\circ}{RT}\right) = \exp\left(-\frac{\Delta H^\circ}{RT}\right)\exp\left(\frac{\Delta S^\circ}{R}\right), \tag{56}$$

such that

$$\exp\left(-\frac{\Delta H^\circ}{RT}\right)\exp\left(\frac{\Delta S^\circ}{R}\right) = \frac{\left(\varphi_{NH_3} y_{NH_3}\right)^2}{\left(\varphi_{N_2} y_{N_2}\right)\left(\varphi_{H_2} y_{H_2}\right)^3}\left(\frac{p^\circ}{p}\right)^2. \tag{57}$$

From this expression, one can conclude that for an exothermic process (i.e. $\Delta H^\circ < 0$), the equilibrium mole fraction of NH_3 will increase with decreasing temperature.

The effects of both pressure and temperature can also be inferred from Le Chatelier's principle, which is simply a qualitative explanation of the above phenomenon. In the case of pressure, the reaction has a greater number of moles of reactants than products, so increasing pressure shifts the equilibrium to the right. In the case of temperature, the reaction is exothermic, so decreasing the temperature will shift the equilibrium to the right as well. The benefit of the approach we have outlined here is that you can define precisely how this equilibrium is shifted.

To summarize, increasing the total pressure and decreasing temperature both increase the equilibrium mole fraction of NH_3. However, this is clearly a problem when we think back to our kinetic perspective. We know from the Arrhenius equation that the rate constant increases exponentially with temperature, so low temperatures will generally yield slower reaction rates. This is especially relevant given that the extremely strong triple bond of N_2 must be broken

for ammonia to be successfully synthesized. As a result, we have an inherent tradeoff between thermodynamics and kinetics.

The way to address this challenge is through the use of a catalyst that increases the rate of reaction, such that *relatively* moderate temperatures can be used. Industrially, iron-based catalysts are often used for this process, and the operating temperature is generally kept around 400 °C. As for the pressures, they are kept relatively high at 100–200 bar to shift the equilibrium toward the production of ammonia. The discovery of a heterogeneous catalyst that can more efficiently synthesize ammonia at near-ambient temperatures and pressures is one of the holy grails of reaction engineering.

2.4.5. Demonstrating that the Equilibrium Constant is a State Function

In the previous example, you may have noticed that $N_2 + 3H_2 \rightleftharpoons 2NH_3$ is likely not an elementary reaction since it is virtually impossible for four species to react simultaneously. Here, we will demonstrate that the definition of K_a holds true regardless of whether the reaction is elementary or non-elementary.

The most straightforward way to convince yourself of this fact is that ΔG° is a state function, which in turn must mean that K_a is a state function as well. If we have a non-elementary reaction with ΔG°, the value for ΔG° will be the same as the sum of all the ΔG° values for the elementary steps. Put another way, ΔG° does not depend on whether a reaction is elementary or not. Since $K_a = \exp(-\Delta G^\circ/RT)$, the same holds true for K_a.

Consider a net reaction given by

$$A \underset{}{\overset{K_a}{\rightleftharpoons}} D, \quad \Delta G^\circ \tag{58}$$

which in reality is composed of several elementary steps:

$$\begin{aligned} A &\underset{}{\overset{K_{a,1}}{\rightleftharpoons}} B, \quad \Delta G_1^\circ \\ B &\underset{}{\overset{K_{a,2}}{\rightleftharpoons}} C, \quad \Delta G_2^\circ \\ C &\underset{}{\overset{K_{a,3}}{\rightleftharpoons}} D, \quad \Delta G_3^\circ. \end{aligned} \tag{59}$$

We know that $\Delta G^\circ = \Delta G_1^\circ + \Delta G_2^\circ + \Delta G_3^\circ$. This can be expressed equivalently as

$$\Delta G^\circ = -RT \ln\left(K_{a,1}\right) - RT \ln\left(K_{a,2}\right) - RT \ln\left(K_{a,3}\right) \tag{60}$$

or

$$\Delta G^\circ = -RT \ln\left(K_{a,1} K_{a,2} K_{a,3}\right). \tag{61}$$

Since $\Delta G^\circ = -RT \ln(K_a)$, this implies that $K_a = K_{a,1} K_{a,2} K_{a,3}$. By invoking the definition of the activity-based equilibrium constant, we arrive at

$$K_{a,1}K_{a,2}K_{a,3} = \frac{a_B}{a_A}\frac{a_C}{a_B}\frac{a_D}{a_C} = \frac{a_D}{a_A}, \tag{62}$$

such that

$$K_a = \frac{a_D}{a_A}, \tag{63}$$

just as we would expect. Extrapolating from this analysis, it can be readily shown that the definition of $K_a \equiv \prod_j a_j^{\nu_j}$ holds true regardless of whether the equilibrium reaction is elementary.

2.4.6. The van 't Hoff Equation

2.4.6.1. Temperature Dependence of the Equilibrium Constant

Here, we seek to describe the temperature dependence of the equilibrium constant. We start with the definition of Gibbs free energy given by

$$\Delta G° = \Delta H° - T\Delta S°, \tag{64}$$

where $\Delta G°$, $\Delta H°$, and $\Delta S°$ are the standard-state Gibbs free energy, enthalpy, and entropy changes of reaction, respectively.

As previously emphasized, the equilibrium constant-based definition of Gibbs free energy is

$$\Delta G° = -RT\ln(K_a). \tag{65}$$

Combining the two expressions, we have

$$\ln(K_a) = -\frac{\Delta H°}{RT} + \frac{\Delta S°}{R}. \tag{66}$$

If we can assume that $\Delta H°$ and $\Delta S°$ are both independent of temperature (an approximation that is typically reasonable when considering relatively small differences in T), one can state

$$\ln\left(\frac{K_{a,2}}{K_{a,1}}\right) = -\frac{\Delta H°}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right) \tag{67}$$

by subtracting Equation 66 at two distinct temperatures. The above relationship is particularly useful when taking an equilibrium constant from tabulated thermochemical data (typically at 273 K or 298.15 K) and determining the corresponding equilibrium constant at the temperature of interest.

2.4.6.2. Connecting van 't Hoff and Arrhenius

With our understanding of the role of thermodynamics, we can turn to how Arrhenius came about his famous equation through making an analogy to prior work by van 't Hoff. If we differentiate Equation 66 with respect to T and make the same assumption that $\Delta H°$ and $\Delta S°$ are again independent of temperature, we arrive at

$$\frac{\mathrm{d}\ln(K_{\mathrm{a}})}{\mathrm{d}T} = \frac{\Delta H^\circ}{RT^2}, \tag{68}$$

which is the formal definition of the van 't Hoff equation.

If we consider a reversible elementary reaction of the form A $\leftrightarrows$ B with no thermodynamic non-idealities such that $K_{\mathrm{a}} = K_{\mathrm{C}} = k^+/k^-$, then we can rewrite Equation 68 using as

$$\frac{\mathrm{d}\ln(k^+/k^-)}{\mathrm{d}T} = \frac{\Delta H^\circ}{RT^2} \tag{69}$$

and thereby

$$\frac{\mathrm{d}\ln(k^+)}{\mathrm{d}T} - \frac{\mathrm{d}\ln(k^-)}{\mathrm{d}T} = \frac{\Delta H^\circ}{RT^2}. \tag{70}$$

By invoking $\Delta H^\circ \approx E_{\mathrm{a,f}} - E_{\mathrm{a,r}}$, where $E_{\mathrm{a,f}}$ and $E_{\mathrm{a,r}}$ are the activation energies for the forward and reverse reactions, one can state that

$$\frac{\mathrm{d}\ln(k^+)}{\mathrm{d}T} - \frac{\mathrm{d}\ln(k^-)}{\mathrm{d}T} = \frac{E_{\mathrm{a,f}}}{RT^2} - \frac{E_{\mathrm{a,r}}}{RT^2}. \tag{71}$$

Largely by a matter of inspection, Arrhenius concluded that the following is likely to be true:

$$\frac{\mathrm{d}\ln(k^+)}{\mathrm{d}T} = \frac{E_{\mathrm{a,f}}}{RT^2}, \quad \frac{\mathrm{d}\ln(k^-)}{\mathrm{d}T} = \frac{E_{\mathrm{a,r}}}{RT^2}, \tag{72}$$

which, when integrated, is equivalent to the Arrhenius equation given by Equation 38. Clearly, this "derivation" lacks rigor, and we will later show that ΔH° is not generally synonymous with the difference in activation energies. For now, we will accept the applicability of the Arrhenius equation largely based on empirical evidence until we cover transition state theory.

2.5. Differential Kinetic Analysis

Consider a reaction of the form A + B $\longrightarrow$ C. In practice, we may not know *a priori* whether this reaction proceeds precisely as written (i.e. if it is elementary or not). We may, nonetheless, propose a rate law of the form

$$r = k[\mathrm{A}]^\alpha[\mathrm{B}]^\beta, \tag{73}$$

although there is no guarantee that α and β are the stoichiometric numbers.[17]

This is where the concept of "apparent" kinetics comes in. Strictly speaking, k, α, and β that are determined from experiments will be "apparent" rate parameters, meaning that they are based on empirical observations that may or may not be due to a combination of elementary

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[17] Additionally, there is no guarantee that the rate law model parameters will be a sufficient fit to the experimental data over a range of operating conditions.

steps. In contrast, we refer to the rate parameters of a true elementary step as the "intrinsic" rate parameters.

2.5.1. Apparent Activation Energy

The intrinsic activation energy differs from the apparent activation energy in that the latter may represent the kinetics of many constituent reactions. The linearized form of the Arrhenius equation is so widely used that the definition of the apparent activation energy is generally derived from this functional form by taking the partial derivative with respect to temperature:

$$\ln\left(k_{\text{app}}\right) = -\frac{E_{\text{app}}}{R}\left(\frac{1}{T}\right) + \ln\left(A_{\text{app}}\right) \tag{74}$$

$$\frac{\partial \ln\left(k_{\text{app}}\right)}{\partial T} = -\frac{E_{\text{app}}}{R}\frac{\partial\left(\frac{1}{T}\right)}{\partial T} \tag{75}$$

$$\frac{\partial \ln\left(k_{\text{app}}\right)}{\partial T} = \frac{E_{\text{app}}}{RT^2} \tag{76}$$

$$E_{\text{app}} \equiv RT^2\frac{\partial \ln\left(k_{\text{app}}\right)}{\partial T}. \tag{77}$$

Here, the "app" subscript is referring to an apparent (i.e. observed) rate constant determined from experiments, meaning that it may describe a net, non-elementary reaction consisting of several elementary steps. Strictly speaking, we have also implicitly assumed that A_{app} is not a function of temperature, which is a reasonable approximation over a relatively small temperature range.

While Equation 77 is the formal definition of the apparent activation energy,[18] we should not lose sight of the fact that we can still use a plot of $\ln\left(k_{\text{app}}\right)$ vs. $1/T$ to back out E_{app} over a particular range of temperatures. In fact, that is precisely what Equation 75 is stating: take the instantaneous slope at a particular value of T in a plot of $\ln\left(k_{\text{app}}\right)$ vs. $1/T$, and you will get a value of $-E_{\text{app}}/R$.

2.5.2. Apparent Reaction Orders

We can also define an apparent reaction order, $\alpha_{j,\text{app}}$, for each species in a similar manner. First, for a reaction $A + B \longrightarrow C$, we will postulate a power-law rate expression of the form

$$r = k_{\text{app}}[A]^\alpha[B]^\beta, \tag{78}$$

which can be rewritten as

$$\ln(r) = \ln\left(k_{\text{app}}\right) + \alpha \ln([A]) + \beta \ln([B]). \tag{79}$$

---

[18]Some references define the apparent activation energy as $E_{\text{app}} \equiv RT^2\frac{\partial \ln(r)}{\partial T}$. However, this is only strictly true if one is not varying the reactant concentrations. Similarly, one should exercise caution when interpreting rate law parameters from a plot of $\ln(r)$ vs. $1/T$ if the reactant concentrations may vary.

Provided we are not simultaneously modifying k_{app}, we can determine α by holding [B] fixed and finding the slope in a plot of $\ln(r)$ vs. $\ln([A])$.[19] Similarly, we can determine β by holding [A] fixed and finding the slope in a plot of $\ln(r)$ vs. $\ln([B])$. In differential form, this can be expressed as follows:

$$\alpha_{j,\text{app}} \equiv [A_j] \left(\frac{\partial \ln(r)}{\partial [A_j]} \right)_{[A_k], k \neq j}. \tag{80}$$

Given enough rate and concentration data, one can also carry out a multiple linear regression analysis to determine the apparent reaction orders if preferred.

It is worth noting, as we will demonstrate throughout this course, that apparent reaction orders of non-elementary reactions may be non-integer or even negative. Reaction orders will appear as zero if the concentration of a particular species does not notably influence the observed rate, as is commonly the case if that species is in great excess.[20]

2.5.3. Practical Measurements

A few questions may naturally arise when thinking about how one would measure the rate parameters in practice. Perhaps the most notable to ask is: how can one monitor the change in rate as a function of only *one* reactant's concentration? Arguably the most natural solution is to carry out the reaction such that all reactants except one are present in large excess, such that the reaction appears 0th order in every species except the one for which the reaction order is desired.

Beyond relying on reagents being in excess, one can carry out an *initial rate* experiment, where you measure r at extremely small values of t. Consider $[A]_0$ and $[B]_0$ as the initial concentration of reactants. For $t \approx 0$, the concentrations of the reactants remain largely unchanged from their initial values: $[A] \approx [A]_0$ and $[B] \approx [B]_0$. This allows you to measure changes in r with respect to isolated changes in either [A] or [B] by modifying the initial concentration of either species.

A very similar concept exists for surface-catalyzed reaction, in which the reaction is typically run in a differential reactor. A differential reactor has an extremely small amount of catalyst, such that the *conversion* of the starting reagents is extremely small. The conversion of a species, X_j, is defined as

$$X_j \equiv \frac{\text{moles of } A_j \text{ reacted}}{\text{moles of } A_j \text{ fed}}. \tag{81}$$

For a reaction taking place in a constant-volume reactor like a flask,

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[19]This assumes that β does not change with [A], which is a fairly reasonable assumption unless changes in [A] alter the mechanism.

[20]For additional discussion about apparent 0th order kinetics, refer to F.J. Arnáiz, "Mice in the Box for Zero-Order Kinetics", *J. Chem. Educ.*, 76, 10, 1458 (1999).

$$X_j = \frac{[A_j]_0 - [A_j]}{[A_j]_0} = 1 - \frac{[A_j]}{[A_j]_0}. \tag{82}$$

For a differential reactor where reagents are flowed through a bed of catalyst, it is oftentimes more natural to use molar flow rates in place of concentrations. The differential reactor is analogous to an initial rate experiment, as it allows the practitioner to measure r in a regime where the consumption of starting reagents is near-infinitesimal.

2.6. Integrated Rate Expressions
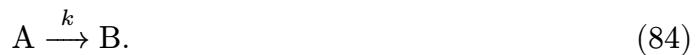
When studying a new reaction of interest, one is typically interested in how the species concentrations change as a function of time. In this subsection, we will derive analytical expressions to describe this phenomenon. Throughout this subsection, we will make an important assumption:

$$r_j \equiv \frac{1}{V}\left(\frac{\mathrm{d}n_j}{\mathrm{d}t}\right) = \frac{\mathrm{d}[A_j]}{\mathrm{d}t}. \tag{83}$$

This implies that we have kinetic data from a reaction taking place with a constant volume batch reactor or that we are focusing on a specific volume element within the reacting vessel.

2.6.1. Irreversible, First-Order Reaction

For simplicity, we will start by considering an irreversible, first-order, elementary reaction given by the expression

$$A \xrightarrow{k} B. \tag{84}$$

The rate law for this reaction can be given by

$$r_A = \frac{\mathrm{d}[A]}{\mathrm{d}t} = -k[A]. \tag{85}$$

Separating the variables and integrating this expression yields[21]

$$\int_{[A]_0}^{[A]} \frac{1}{[A]'}\,\mathrm{d}[A]' = -k\int_0^t \mathrm{d}t' \tag{86}$$

$$\ln\left(\frac{[A]}{[A]_0}\right) = -kt. \tag{87}$$

We can simplify Equation 87 to

$$[A] = [A]_0 e^{-kt}. \tag{88}$$

---

[21]The ' marks are included simply to indicate a variable of integration that differs from the integral bounds.

From Equation 88, a plot of $\ln([A])$ vs. t from the experimental data should be linear for a first-order, irreversible reaction.[22] As a sanity check, we can also see that when $t \to \infty$, $[A] \to 0$ as expected.

2.6.2. Irreversible Reactions of Arbitrary Order

We will now generalize the above approach by considering an irreversible, elementary reaction given by the expression

$$n\mathrm{A} \xrightarrow{k} m\mathrm{B}, \tag{89}$$

where n is an arbitrary stoichiometric number. The rate of change in $[A]$ can be given by

$$r_\mathrm{A} = \frac{\mathrm{d}[A]}{\mathrm{d}t} = -nk[A]^n. \tag{90}$$

> ⚠️ **Caution**
>
> Most sources write Equation 90 as $r_\mathrm{A} = -k[A]^n$ and continue the derivation as such. However, if we are specifically considering an elementary reaction where we have the convention that $r = r_j/\nu_j$, then including the stoichiometric coefficient as a multiplicative factor is important for internal consistency. To convince yourself of this, you already know that the rate law is $r = k[A]^n$ for this elementary reaction. Therefore, r_A must be $-nk[A]^n$ in order for $r = -r_\mathrm{A}/n$.

Separating the variables and integrating this expression yields

$$\int_{[A]_0}^{[A]} \frac{1}{[A]'^n}\,\mathrm{d}[A]' = -nk \int_0^t \mathrm{d}t' \tag{91}$$

$$\frac{[A]^{-n+1}}{-n+1} - \frac{[A]_0^{-n+1}}{-n+1} = -nkt \quad (n \neq 1). \tag{92}$$

We can simplify Equation 92 to

$$[A]^{-n+1} = [A]_0^{-n+1} - n(-n+1)kt \tag{93}$$

$$[A]^{-n+1} = [A]_0^{-n+1} + n(n-1)kt. \tag{94}$$

---

[22]If experimental data is collected and found to fit well to Equation 88, it would be consistent with a first-order, irreversible reaction but that does not guarantee that it is truly first order nor does it imply that the reaction is necessarily elementary. For instance, a true rate law of $r = k[A][B]$ might appear first order in $[A]$ if $[B]$ is in great excess, such that only changes in $[A]$ appreciably alter the rate. This would be more precisely referred to as pseudo-first order in $[A]$.

From Equation 94, a plot of $[A]^{-n+1}$ vs. t from the experimental data should be linear for a given stoichiometric coefficient n. The same procedure can be done for bimolecular reactions; the only difference is that the algebra is slightly more complicated.

It is always a good practice to do some sanity checks. For this analysis, let us take $n = 2$ just for demonstration purposes and see what happens when $t \to \infty$.

$$\frac{1}{[A]} = \frac{1}{[A]_0} + 2k \cdot \infty \tag{95}$$

$$[A] = \frac{1}{\frac{1}{[A]_0} + \infty} = 0. \tag{96}$$

This is just as we would expect since at infinite time, all the reactant should be consumed.

Now let us take $n = -2$ instead for demonstration purposes and see what happens when $t \to \infty$. This time, we have

$$[A]^3 = [A]_0^3 + 6k \cdot \infty \tag{97}$$

$$[A] = \left([A]_0^3 + 6k \cdot \infty\right)^{1/3} = \infty. \tag{98}$$

At first glance, this may seem unusual. We have $[A]$ increasing with t without bound despite being the reactant. The reason for this seemingly odd behavior is that we specifically derived the integrated rate law for an *elementary* reaction. If we have $n < 0$, then we must instead be describing the reverse reaction, such that $[A]$ increases with time from its starting value of $[A]_0$.

2.6.3. Coupled Reactions

Naturally, many reactions involve multiple mechanistic steps. For instance, consider the following consecutive reaction, which we will assume to consist of two distinct elementary steps:

$$A \xrightarrow{k_1} B \xrightarrow{k_2} C. \tag{99}$$

As usual, we will write out the rates of change for each species:

$$r_A = \frac{d[A]}{dt} = -k_1[A]$$

$$r_B = \frac{d[B]}{dt} = k_1[A] - k_2[B] \tag{100}$$

$$r_C = \frac{d[C]}{dt} = k_2[B].$$

To understand the behavior of this coupled reaction, our next step is to integrate with respect to time. We will consider the reaction starting at $t = 0$ with only the reagent (A) and no intermediates (B) or products (C). As before, we know that

$$[A] = [A]_0 e^{-k_1 t}. \tag{101}$$

Now we can substitute Equation 101 into the expression for r_B to arrive at

$$\frac{d[B]}{dt} = k_1 [A]_0 e^{-k_1 t} - k_2 [B]. \tag{102}$$

The integration here is a bit messy, but one can show with some effort that

$$[B] = [A]_0 \frac{k_1}{k_2 - k_1} \left(e^{-k_1 t} - e^{-k_2 t} \right). \tag{103}$$

From here, we could substitute Equation 103 into the expression for r_C and integrate to find an expression for $[C]$ with respect to time. That said, it is a fair bit simpler to just invoke the conservation of mass:

$$[C] = [A]_0 - [A] - [B], \tag{104}$$

where we have assumed $[B]_0 = [C]_0 = 0$.

📊 Interactive Plot

https://marimo.app/l/2emhpu°

2.7. Stochastic Reactions

Note: This topic was not covered in class and is solely for the interested reader.

2.7.1. The Gillepsie Algorithm

In the previous subsection, we took a deterministic approach to describing the behavior of reaction events. In the limit of small numbers of molecules, however, this approach begins to break down. In this subsection, we will briefly take a stochastic, atomistic approach to understanding chemical reactions. A stochastic approach is particularly common in biochemical simulations, such as reactions taking place within cellular environments where the number of reacting molecules is small.

For the sake of example, consider the serial reactions $A \longrightarrow B \longrightarrow C$, which can be written as two discrete steps:

$$\begin{aligned} A &\xrightarrow{k_1} B \\ B &\xrightarrow{k_2} C. \end{aligned} \tag{105}$$

Here, we are considering each reaction as a discrete event involving individual molecules and that these reactions are uncorrelated with one another. We define the propensity, a_j, of each reaction in an analogous way as we define the reaction rate:

$$a_1 = k_1 x_\text{A}, \quad a_2 = k_2 x_\text{B}, \tag{106}$$

where each x_j is the discrete number of j molecules in the reactor (rather than the continuous value of concentration). We will also consider the time t to be discretized, such that we are simulating reaction snapshots (or lack thereof) at each time step.

To carry out this stochastic simulation, we follow the algorithm of Gillepsie.[23] With this, the procedure looks like the following:

1. Initialize the time to $t = t_0$ ($t_0 = 0$ is the natural choice) and the number of molecules (also known as the state vector) to $\boldsymbol{x} = \boldsymbol{x}_0$.
2. Calculate each propensity a_i via Equation 106.
3. Calculate the sum of the propensities, $a_\text{tot} \equiv \sum_i a_i$.
4. Calculate the time step, τ, given by $\tau \equiv -\ln(R_1)/a_\text{tot}$, where R_1 is a (pseudo) random number between 0 and 1.
5. Update the time based on the value of τ.
6. Determine which reaction is likely to occur at this new time point by finding the smallest value of j that satisfies $\sum_{i=1}^{j} a_i > R_2 \cdot a_\text{tot}$ where R_2 is another (pseudo) random number.
7. We update the number of molecules to be $\boldsymbol{x}_1 = \boldsymbol{x}_0 + \Delta \boldsymbol{x}_j$.
8. Finally, we repeat steps 2–8 until t becomes sufficiently large that the reaction landscape has been fully characterized.

Since the end result is a single stochastic simulation, one might rerun the entire simulation to identify if the behavior changes. In the limit of small numbers of molecules, it is very possible for the stochastic simulation to converge to results that differ from the deterministic solution. In this scenario, it is critical to use the stochastic approach. In the limit of large numbers of molecules, one gets the same solution as typical power-law kinetics, which is a nice way to justify its validity.

2.7.2. An Example of the Gillepsie Algorithm

> **📊 Interactive Plot**
>
> https://marimo.app/l/blubdx°

Let us consider a specific example where we start with 100 molecules of A, 0 molecules of B, and 0 molecules of C and let them react via A $\longrightarrow$ B $\longrightarrow$ C. We will describe the Gillepsie algorithm by way of example, assuming here that $k_1 = 2$ and $k_2 = 1$:

1. Our state vector is given by $\boldsymbol{x} = [100, 0, 0]$, and we invoke $t_0 = 0$.
2. We calculate the propensities of each reaction as $a_1 = 2 \cdot 100 = 200$ and $a_2 = 1 \cdot 0 = 0$.
3. We calculate the sum of the propensities as $a_\text{tot} = 200 + 0 = 200$.

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[23]For further details, refer to D.T. Gillepsie, "Stochastic Simulation of Chemical Kinetics", *Annu. Rev. Phys. Chem.*, 58 (2007).

4. We pick a random number R_1 (let's say 0.73) and calculate the time step as $\tau = -\ln(0.73)/100 \approx 0.00157$.

5. We update the time as $t_1 = t_0 + \tau = 0.00157$.

6. We pick another random number R_2 (let's say 0.31) to determine which reaction is likely to occur by asking: is $a_1 > R_2 \cdot a_{\text{tot}}$? The answer is yes for our example because $200 > 0.31 \cdot 200$, so we take $j = 1$ and state that reaction 1 will occur at our new time point t_1.[24]

7. We update the number of molecules to be $x_1 = [100, 0, 0] + [-1, 1, 0] = [99, 1, 0]$.

8. We repeat steps 2–8 until t becomes sufficiently large that the reaction landscape has been fully characterized.

2.8. Delplots

Here, we will introduce the concept of a delplot, which can be used to discern qualitative, temporal behavior of reaction networks.[25]

2.8.1. The Rank of a Species

We must introduce a new concept: the "rank" of a species, which is the numerical order in which a species is formed. If a given species is produced first, it will have rank 1 and is called primary; if produced second, it will have rank 2 and is called secondary, and so on. Written out, for the reaction $\text{A} \longrightarrow \text{B} \longrightarrow \text{C} \longrightarrow \text{D}$, B is primary, C is secondary, and D is tertiary. This is distinct from the order of that species, which we will reserve for the exponential dependence of the rate on concentration. In a net reaction composed of many elementary reactions, it is also possible for a species to exhibit multiple ranks.

Plots of species concentrations as a function of time are very powerful ways to determine the rank of different product species. This becomes immediately apparent when considering the simple reaction

$$\text{A} \xrightarrow{k_1} \text{B} \xrightarrow{k_2} \text{C}. \tag{107}$$

A plot of the species concentrations as a function of time will indicate that B has a non-zero initial slope, whereas C has a zero initial slope since it cannot form until B is first produced (Figure 3).

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[24]You might notice that it will always be the case that $j = 1$ is selected by this algorithm in the first time step. This is to be expected because $\text{B} \longrightarrow \text{C}$ cannot occur unless $\text{A} \longrightarrow \text{B}$ happens first. When we update the simulation, this will no longer be the case, and the probability that reaction $j = 2$ will occur will increase as the population of B increases.

[25]N.A. Bhore, M.T. Klein, K.B. Bischoff, "The Delplot Technique: A New Method for Reaction Pathway Analysis", *Industrial and Engineering Chemistry Research*, 29, 313–316 (1990).
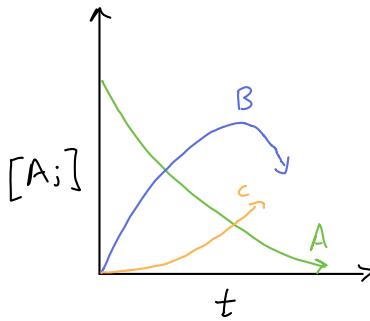
Figure 3: Concentration profile for the A $\longrightarrow$ B $\longrightarrow$ C reaction, highlighting the different y-intercept values.

In mathematical terms, we have

$$\frac{\mathrm{d}[A]}{\mathrm{d}t} = -k_1[A], \qquad \frac{\mathrm{d}[B]}{\mathrm{d}t} = k_1[A] - k_2[B], \qquad \frac{\mathrm{d}[C]}{\mathrm{d}t} = k_2[B]. \tag{108}$$

For $t \to 0$, we have $[A] \to [A]_0$, $[B] \to 0$, and $[C] \to 0$, such that

$$\left(\frac{\mathrm{d}[A]}{\mathrm{d}t}\right)_{t\to 0} = -k_1[A]_0, \qquad \left(\frac{\mathrm{d}[B]}{\mathrm{d}t}\right)_{t\to 0} = k_1[A]_0, \qquad \left(\frac{\mathrm{d}[C]}{\mathrm{d}t}\right)_{t\to 0} = 0. \tag{109}$$

This is in contrast with a parallel reaction scheme like

$$\begin{aligned} A &\xrightarrow{k_1} B \\ A &\xrightarrow{k_2} C, \end{aligned} \tag{110}$$

where both B and C would have a non-zero initial slope. Again, in mathematical form we can write

$$\frac{\mathrm{d}[A]}{\mathrm{d}t} = -k_1[A] - k_2[A], \qquad \frac{\mathrm{d}[B]}{\mathrm{d}t} = k_1[A], \qquad \frac{\mathrm{d}[C]}{\mathrm{d}t} = k_2[A]. \tag{111}$$

For $t \to 0$, we have

$$\left(\frac{\mathrm{d}[A]}{\mathrm{d}t}\right)_{t\to 0} = -(k_1 + k_2)[A]_0, \quad \left(\frac{\mathrm{d}[B]}{\mathrm{d}t}\right)_{t\to 0} = k_1[A]_0, \quad \left(\frac{\mathrm{d}[C]}{\mathrm{d}t}\right)_{t\to 0} = k_2[A]_0. \tag{112}$$

What we have concluded from this simple exercise is that the initial slope (i.e. the rate of change in species concentration extrapolated to $t = 0$) can provide information about the rank of the species. For this set of examples, we found that the product C was primary if it had a finite (i.e. not zero) initial slope. If one were to measure a zero initial slope for the rate of change of $[C]$, it can be concluded immediately that C did not come from A since primary products have a finite initial slope. As we will show, this kind of analysis can be made more general.

2.8.2. The First-Rank Delplot to Determine Primary Products

Consider a more complicated reaction network like

$$A \xrightarrow{k_1} B \xrightarrow{k_3} C$$
$$A \xrightarrow{k_2} D. \tag{113}$$

Assuming the reaction starts with only A, then it can be shown that the integrated rate laws are given by

$$[A] = [A]_0 e^{-(k_1+k_2)t}$$

$$[B] = \frac{k_1[A]_0}{k_3 - k_1 - k_2}\left(e^{-(k_1+k_2)t} - e^{-k_3t}\right)$$

$$[C] = \frac{k_1 k_3 [A]_0}{k_3 - k_1 - k_2}\left(\frac{1 - e^{-(k_1+k_2)t}}{k_1 + k_2} - \left(1 - \frac{e^{-k_3t}}{k_3}\right)\right) \tag{114}$$

$$[D] = \frac{k_2[A]_0}{k_1 + k_2}\left(1 - e^{-(k_1+k_2)t}\right)$$

in the case where $k_3 \neq k_1 + k_2$.

The approach we will take here is as follows. For each product P, we will make a plot of Y_P/X_A vs. X_A and extrapolate to $X_A \to 0$ (i.e. $t \to 0$). Here, X_A is the conversion of A as defined in Equation 82, and Y_P is the yield of product P from reactant A, which is given as

$$Y_P = \frac{[P] - [P]_0}{[A]_0}. \tag{115}$$

We will show that this approach can distinguish whether the product is primary or not based on whether the y-axis intercept has a finite value or not. Written mathematically, we seek to carry out the following analysis

$$\lim_{X_A \to 0}\left(\frac{Y_P}{X_A}\right) = \lim_{X_A \to 0}\left(\frac{[P]/[A]_0}{1 - [A]/[A]_0}\right) = \lim_{X_A \to 0}\left(\frac{[P]}{[A]_0 - [A]}\right), \tag{116}$$

where we have assumed that there is no starting product P.

Of course, for our toy example we already know that B and D are primary products, whereas C is not primary. There would be no need to carry out any sort of analysis in this case. However, we will use this reaction scheme for demonstration purposes to justify our approach, which can then be applied to experimental data for which we do not know the ranks *a priori*.

We now substitute Equation 114 into Equation 116 and will start with identifying the value for species B.

$$\lim_{t \to 0} \left(\frac{Y_\mathrm{B}}{X_\mathrm{A}} \right) = \lim_{t \to 0} \frac{\frac{k_1 [\mathrm{A}]_0}{k_3 - k_1 - k_2} \left(e^{-(k_1 + k_2)t} - e^{-k_3 t} \right)}{[\mathrm{A}]_0 - [\mathrm{A}]_0 e^{-(k_1 + k_2)t}}. \tag{117}$$

If we naively plugged in $t = 0$ exactly into the above expression, we would be left with $0/0$. Instead, we must take advantage of L'Hôpital's rule, wherein

$$\lim_{z \to z_0} \frac{f(z)}{g(z)} = \frac{f'(z_0)}{g'(z_0)}, \tag{118}$$

provided that f and g are both differentiable functions. Thankfully, the derivatives are fairly straightforward in this case due to the nature of exponentials. We will omit the algebra to simply state that the limit becomes

$$\lim_{t \to 0} \left(\frac{Y_\mathrm{B}}{X_\mathrm{A}} \right) = \frac{k_1}{k_1 + k_2}. \tag{119}$$

If one were to carry out the same analysis for C and D, we would also have

$$\lim_{t \to 0} \left(\frac{Y_\mathrm{C}}{X_\mathrm{A}} \right) = 0$$
$$\lim_{t \to 0} \left(\frac{Y_\mathrm{D}}{X_\mathrm{A}} \right) = \frac{k_2}{k_1 + k_2}. \tag{120}$$

Here, we have found that B and D have finite values for the intercept, whereas C has a zero value. We know from the reaction scheme that B and D are primary, whereas C is not primary. It turns out that this method of determining primary from non-primary products can be fully generalized and is independent of the functional form of the kinetic equations at each step.

This analysis is referred to as the first-rank delplot. If the y-axis intercept of the first-rank delplot is finite, the product is primary. If the y-axis intercept is zero, the product is not primary. In practice, one may not know the ranks in advance, such that creating a plot of $Y_\mathrm{P}/X_\mathrm{A}$ vs. X_A would be insightful for determining product ranks. A sketch of the first-rank delplots for the aforementioned reaction networks is shown in Figure 4.
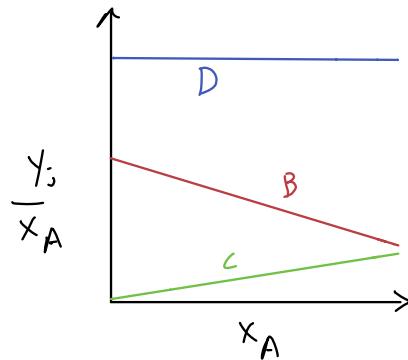
Figure 4: First-rank delplot for the reaction scheme A $\longrightarrow$ B $\longrightarrow$ C, A $\longrightarrow$ D. Note that the finite y-intercept values points to a primary product, whereas a zero y-intercept value points to a higher rank product.

2.8.3. Higher Rank Delplots for Non-Primary Products

While first-rank delplots can determine whether a product is primary or not primary, in general it cannot be used to identify the particular rank of any non-primary species. Higher rank delplots allow 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 and can be used to determine whether a product is secondary or not. 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 $X_A \to 0$ (i.e. no y-intercept), the product's rank is primary. The second-rank delplot for the aforementioned reaction scheme is shown in Figure 5.
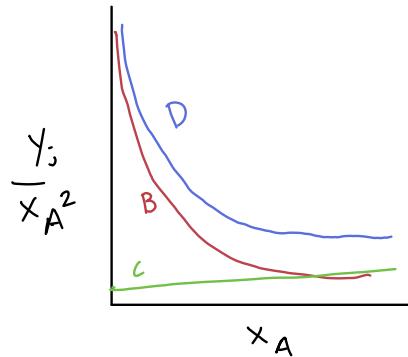
Figure 5: Second-rank delplot for the reaction scheme A $\longrightarrow$ B $\longrightarrow$ C, A $\longrightarrow$ D. Note that the finite y-intercept values points to a secondary product, whereas a diverging y-intercept value points to a lower rank product.

2.8.4. Generalized Delplot Approach

The delplot process is summarized in Table 1.[26] We will use the following notation when describing delplots: ^1P_A. Here, the top-left superscript is the rank m of the delplot (not the

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[26]While convenient, the delplot method has some subtle challenges when used in practice. M.T. Klein has several discussions of these limitations and ways to address them, such as in N.S. Abo-Ghander and M.T. Klein "Delplot-Compliant Data: Molecular Observables versus Reaction Intermediates", *Energy and Fuels*, 34, 15443–15447 (2020).

rank of the species), P represents the product species we are investigating, and the subscript A represents the species for which the conversion is being tracked. A delplot of rank m is simply a plot of Y_P/X_A^m vs. X_A.[27] Note that in practice, plots of S_P/X_A^{m-1} (where S_P is the selectivity towards P) vs. X_A are typically used since $S_P = Y_P/X_P$.

REACTION ORDER	Species rank $= 1$	Species rank > 1
$n = 1$	^1P_A = finite	^mP_A = finite if species rank $= m$ $^mP_A = 0$ if species rank $> m$ ^mP_A = diverges if species rank $< m$
$n > 1$	^1P_A = finite	$^mP_A = 0$ if species rank $\geq m$
$n < 1$	^1P_A = finite	^mP_A = diverges if species rank $= m$ $^mP_A = 0$ if species rank $> m$

Table 1: Summary of delplot intercepts for a product P based on the conversion of A. m is the rank of the delplot, and the reaction order refers to the reaction producing product P. For $n > 1$ and $n < 1$, this analysis is only strictly valid if the last step is the only one with $n \neq 1$.

To demonstrate how Table 1 can be used for higher-order reactions, second-rank and third-rank delplots are shown in Figure 6 and Figure 7, respectively, for the reaction scheme

$$A \longrightarrow B \longrightarrow C$$
$$A \longrightarrow D, \tag{121}$$

with the $B \longrightarrow C$ reaction being second order and all other reactions being first order. Since B and D are primary products from a first-order reaction, a second-rank delplot diverges for these species since the species rank (one) is less than the rank of the delplot (two), as is evident from the first row and third column of Table 1. Since C is a secondary product from a reaction order greater than one, a second-rank delplot has a zero y-intercept since the species rank (two) is equal to the rank of the delplot (two), as is evident from the second row and third column of Table 1. If the reaction producing C were first order, then the intercept would instead be finite.

As for the third-rank delplot, we again refer to Table 1 and find that B and D diverge since their rank (two) is less than the rank of the delplot (three). If the reaction producing C were first order, we would expect the intercept to diverge for this species too. However, this is not what we observe. Since the reaction producing C is greater than first order, C happens to have a finite intercept instead.

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[27]Delplots can be of limited use when m is large due to propagation of error associated with raising low-conversion limit data to a large power.
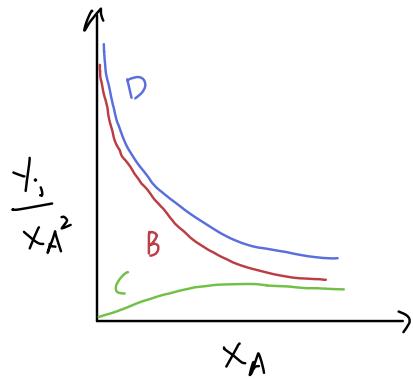
Figure 6: Second-rank delplot for the reaction scheme A $\longrightarrow$ B $\longrightarrow$ C, A $\longrightarrow$ D with B $\longrightarrow$ C being second order and all other reactions being first order. Note that the zero y-intercept value points to a secondary product for C since the reaction order producing it is >1, whereas a diverging y-intercept value points to a lower rank product for B and D since the reaction orders producing these species is 1.
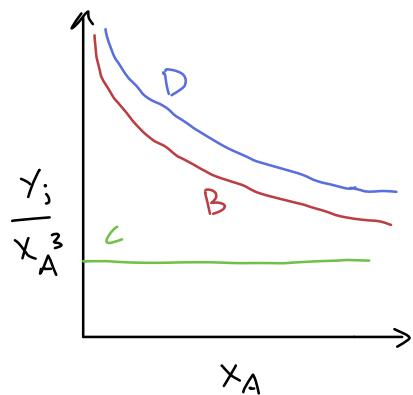
Figure 7: Third-rank delplot for the reaction scheme A $\longrightarrow$ B $\longrightarrow$ C, A $\longrightarrow$ D with B $\longrightarrow$ C being second order and all other reactions being first order. Note that the finite y-intercept values points to a lower rank product for C since the reaction order is >1, whereas a diverging y-intercept value points to a lower rank product for B and D since the reaction order is 1.

3. Analytical Rate Expressions for Reaction Mechanisms

3.1. Simplifying Rate Expressions

In Section 2.6, we demonstrated how to derive rate expressions via integration of differential equations. In practice, it is often difficult to arrive at a closed-form, analytical solution for reaction mechanisms of practical interest. Instead, one must either numerically integrate a system of differential equations or make simplifying approximations to derive an algebraic solution. In this section, we will focus on common ways to derive analytical rate expressions that can provide significant insight into a proposed reaction mechanism.

Throughout this section, we will also relax the assumption that we know in advance what the mechanism may be. In general, the procedure to determine a plausible mechanism is as follows:

1. Postulate elementary steps, specifically bond-making and bond-breaking events.
2. If possible, derive a closed-form solution to the rate law that describes the rate as a function of experimental observables. This may involve making several assumptions based on what is known about the reaction itself.
3. Test the rate law against any available data and repeat the process as-needed.

While this procedure may show that a proposed reaction mechanism is consistent with the experimental data, it is worth keeping in mind that this does not definitively prove that the individual elementary steps are complete and accurate.

3.1.1. The Pseudo-Steady State Hypothesis

3.1.1.1. Mathematical Argument

One of the most widely used assumptions in reaction network analysis is the pseudo-state state hypothesis (PSSH), which allows for the assumption that the net rate of change of a species, r_j, can be approximated as zero if A_j is extremely short-lived. This approximation is most commonly invoked for high-energy intermediates, such as radical species, and is valid after a (typically brief) induction period. It generally requires that the intrinsic rate of consumption of the intermediate is much greater than the rate(s) of production, such as species B in the elementary reaction sequence

$$A \xrightarrow{k_1} B \xrightarrow{k_2} C, \quad k_2 \gg k_1. \tag{122}$$

If we were to invoke PSSH, we would state $r_B \approx 0$. Note that it does *not* mean that we directly set [B] to zero or a constant value, which would have the potential to over-simplify the equations, as we will justify below.

To demonstrate the PSSH, we will revisit the solutions to the differential equations that were derived for the $A \longrightarrow B \longrightarrow C$ series reaction in Section 2.6.3:

$$[A] = [A]_0 e^{-k_1 t}. \tag{123}$$

$$[B] = [A]_0 \frac{k_1}{k_2 - k_1} \left(e^{-k_1 t} - e^{-k_2 t} \right). \tag{124}$$

$$[C] = [A]_0 - [A] - [B]. \tag{125}$$

If we invoke $k_2 \gg k_1$, we can approximate the above expressions as follows:[28]

$$[A] = [A]_0 e^{-k_1 t} \tag{126}$$

$$[B] = [A]_0 \frac{k_1}{k_2} e^{-k_1 t} = \frac{k_1}{k_2} [A] \tag{127}$$

$$[C] = [A]_0 \left(1 - e^{-k_1 t} \right). \tag{128}$$

Now, what would the expressions look like if we specifically invoked the PSSH condition of $r_B \approx 0$ from the very beginning? Given that we are dealing with elementary reactions, we can state

$$r_B = k_1 [A] - k_2 [B]. \tag{129}$$

and, therefore, by setting $r_B \approx 0$ we have

$$[B] = \frac{k_1}{k_2} [A]. \tag{130}$$

This is exactly the same expression as Equation 127, justifying our use of the PSSH in this scenario. Also note that [B] is not a constant value nor is it zero. While certainly small, [B] changes linearly with [A].

If we take the time derivatives of each species concentration, we can observe some other interesting behavior:

$$r_A = \frac{d[A]}{dt} = -[A]_0 k_1 e^{-k_1 t} \tag{131}$$

$$r_B = \frac{d[B]}{dt} = -[A]_0 \frac{k_1^2}{k_2} e^{-k_1 t} (\approx 0) \tag{132}$$

$$r_C = \frac{d[C]}{dt} = [A]_0 k_1 e^{-k_1 t}. \tag{133}$$

We can see from the above expressions that $r_A = -r_C$, which is another feature of PSSH when dealing with series reactions and is to be expected since r_B is negligible in comparison (i.e. A can be thought of as almost instantaneously being transformed into C given the short lifetime of B). Of course, this is merely an *approximation*, but it is a quite useful one.

---

[28]Note that, although $k_1/k_2 \ll 0$, we cannot directly set $[B] = 0$ because never producing B would mean that C would never be produced.

3.1.1.2. Demonstration

We will now demonstrate the utility of the PSSH in action. Consider the following reaction:[29]

$$2NO + O_2 \longrightarrow 2NO_2 \tag{134}$$
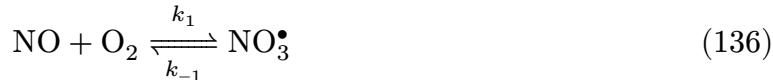
Based on the stoichiometry, one might propose an elementary rate law of the form

$$r \overset{?}{=} k[NO]^2[O_2]. \tag{135}$$

It is known from experiments that the reaction does appear to be second order in $[NO]$ and first order in $[O_2]$. However, termolecular reactions in the gas-phase are extremely rare, so one might conclude that it would be unlikely for the reaction to proceed as written despite the observed rate law. Unusually, r has also been observed to *decrease* with increasing temperature. These details allow us to definitively conclude that Equation 134 cannot actually be an elementary reaction. We will rationalize this so-called "anti-Arrhenius" behavior below.

First, we must propose a mechanism. Since it is not expected that you know the intricacies of atmospheric chemistry, we will simply take the following as provided to us:

$$NO + O_2 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} NO_3^\bullet \tag{136}$$

$$NO_3^\bullet + NO \overset{k_2}{\longrightarrow} 2NO_2. \tag{137}$$

Then, we write out the elementary rate law for r_{NO_2} based on Equation 137:

$$r_{NO_2} = 2k_2[NO_3^\bullet][NO]. \tag{138}$$

Note the factor of 2 in Equation 138, which is needed because two NO_2 molecules are produced for every reaction of $NO_3^\bullet$ and NO, as originally noted in Equation 19.

Since $NO_3^\bullet$ is a short-lived radical species, we can choose to invoke the PSSH to simplify matters. Namely, the PSSH lets us state that the $NO_3^\bullet$ will have a net rate of formation that is essentially zero:

$$r_{NO_3^\bullet} \approx 0 = k_1[NO][O_2] - k_{-1}[NO_3^\bullet] - k_2[NO_3^\bullet][NO]. \tag{139}$$

---

[29]Note that NO is a radical, and O_2 is a diradical, but we will omit the radical symbols for brevity and to avoid confusion. Both are not short-lived like $NO_3^\bullet$, which is the main distinction.

Ideally, we would like to substitute in for $NO_3^\bullet$ in Equation 138 since it is not easy to observe experimentally given its short lifetime. With this in mind, we will solve for $NO_3^\bullet$ in Equation 139 to get

$$[NO_3^\bullet] = \frac{k_1[NO][O_2]}{k_{-1} + k_2[NO]}. \tag{140}$$

Substituting in Equation 140 into Equation 138 yields

$$r_{NO_2} = \frac{2k_1 k_2[NO]^2[O_2]}{k_{-1} + k_2[NO]}. \tag{141}$$

From here, the rate of reaction, r, can be computed simply as $r_{NO_2}/2$ since $r = r_j/\nu_j$.

In principle, we can stop with the above expression. However, it would not clearly explain the observed rate behavior. If we invoke that $k_{-1} \gg k_2[NO]$,[30] the rate expression would simplify to

$$r_{NO_2} = \frac{2k_1 k_2}{k_{-1}}[NO]^2[O_2], \tag{142}$$

This leads us to the first important observation. While the simplified rate law above is second order in $[NO]$ and first order in $[O_2]$, which matches the stoichiometry of the net reaction $2NO + O_2 \longrightarrow 2NO_2$, the rate law is clearly not that of an elementary reaction. This example illustrates that even if the apparent orders of a reaction match those from the elementary rate law, it does not necessarily imply that a reaction is elementary.

The second important observation is that Equation 142 can be rewritten as

$$r_{NO_2} = \frac{2A_1 A_2}{A_{-1}} \exp\left(-\frac{E_{a,1} - E_{a,-1} + E_{a,2}}{RT}\right)[NO]^2[O_2]. \tag{143}$$

If we define

$$A_{app} \equiv \frac{A_1 A_2}{A_{-1}} \tag{144}$$

$$E_{a,app} \equiv E_{a,1} - E_{a,-1} + E_{a,2}, \tag{145}$$

where A_{app} and $E_{a,app}$ are an apparent pre-factor and activation barrier,[31] then

$$r_{NO_2} = 2A_{app} \exp\left(-\frac{E_{a,app}}{RT}\right)[NO]^2[O_2]. \tag{146}$$

---

[30]This would be the case if the reverse reaction rate for Step 1 is much faster than Step 2 since this would imply that $k_{-1}[NO_3^\bullet] \gg k_2[NO_3^\bullet][NO]$ and, therefore, $k_{-1} \gg k_2[NO]$.

[31]Note that applying the definition of the apparent activation energy (Equation 77) to $k_{app} \equiv k_1 k_2/k_{-1}$ would yield the same expression for $E_{a,app}$.

Depending on the relative magnitudes of the intrinsic activation energies, it is possible for $E_{\text{a,app}} < 0$. Indeed, this reaction is known from experiments to have an empirically measured kinetic barrier of -3.3 kJ/mol (albeit via a slightly more complex mechanism than the elementary steps proposed here).

3.1.2. Pressure-Dependent Rate Constants
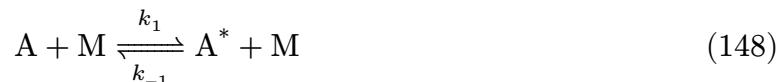
While pressure is not a component in the definition of the intrinsic rate constant, it turns out that some reactions do exhibit pressure-dependent apparent rate constants, which we will demonstrate below.

Consider the following isomerization reaction:

$$CH_3NC \longrightarrow CH_3CN. \tag{147}$$

If this reaction were elementary, first-order kinetics would be observed. However, experiments have shown that this is only true at high pressures. Herein, we will explain this anomaly by invoking the Lindemann mechanism.[32]

The Lindemann mechanism states that a unimolecular reaction $A \longrightarrow B$ can be described by the following steps:

$$A + M \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} A^* + M \tag{148}$$

$$A^* \xrightarrow{k_2} B, \tag{149}$$

where A is the reactant, A^* is the "activated" form of A, and M is a gas molecule that imparts sufficient energy into A to initiate the reaction.

The rate of production of B based on the above mechanism can be given by

$$r_B = k_2 [A^*]. \tag{150}$$

Since A^* is a high-energy species that can spontaneously decompose, we can safely invoke the PSSH like we have previously done for radical species. This allows us to state

$$r_{A^*} \approx 0 = k_1 [A][M] - k_{-1} [A^*][M] - k_2 [A^*]. \tag{151}$$

Solving for $[A^*]$ yields

$$[A^*] = \frac{k_1 [A][M]}{k_{-1}[M] + k_2}. \tag{152}$$

---

[32]The Lindemann mechanism is useful from a pedagogical standpoint, but, in reality, it is not quantitatively accurate. For a more accurate treatment, refer to the Rice–Ramsperger–Kassel–Marcus (RRKM) theory.

Combining Equation 148 and Equation 152 results in the following rate expression without any transient intermediates in it:

$$r_{\mathrm{B}} = \frac{k_1 k_2 [\mathrm{M}][\mathrm{A}]}{k_{-1}[\mathrm{M}] + k_2}. \tag{153}$$

Let's now consider the behavior in different pressure regimes. In the low pressure limit, $[\mathrm{M}]$ is small since there are few other particles for A to collide with. In such scenarios, it is reasonable to propose that we have $k_{-1}[\mathrm{M}] \ll k_2$, such that

$$r_{\mathrm{B}} \approx k_1 [\mathrm{A}][\mathrm{M}] \quad (\text{low } P). \tag{154}$$

In the high pressure limit, $[\mathrm{M}] \gg 0$ since there are many opportunities for collisions, resulting in $k_{-1}[\mathrm{M}] \gg k_2$, such that

$$r_{\mathrm{B}} \approx \frac{k_1 k_2}{k_{-1}}[\mathrm{A}] \quad (\text{high } P). \tag{155}$$

From this analysis, we can conclude that at low pressures, the rate expression would appear as second-order overall, whereas at high pressures, the rate expression would appear first-order overall.

3.1.3. Radical Chain Reactions

Consider the following gas-phase, photochemical reaction:

$$\mathrm{H_2 + Br_2 \longrightarrow 2\,HBr}. \tag{156}$$

If the reaction were elementary, the rate law would be $r = k[\mathrm{H_2}][\mathrm{Br_2}]$. However, this functional form is known to disagree with kinetic data, which points to a one-half order in $\mathrm{Br_2}$ at low conversions of the reagents. For this reason, one can immediately conclude that the reaction is not elementary and must, instead, be composed of several substituent elementary reactions with the formation of transient—but kinetically important—intermediates. A more representative rate law for Equation 156 can be found by postulating elementary steps, applying approximations as needed, and solving for a closed-form solution, which we will do below.

First, we must come up with plausible mechanistic steps. For pedagogical purposes, we will start by assuming that the following reaction mechanism is known and will back-justify why it makes sense:

$$\mathrm{Br_2} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} 2\mathrm{Br}^\bullet \tag{157}$$

$$\mathrm{Br}^\bullet + \mathrm{H_2} \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} \mathrm{HBr} + \mathrm{H}^\bullet \tag{158}$$

$$\mathrm{H}^\bullet + \mathrm{Br_2} \overset{k_3}{\longrightarrow} \mathrm{HBr} + \mathrm{Br}^\bullet. \tag{159}$$
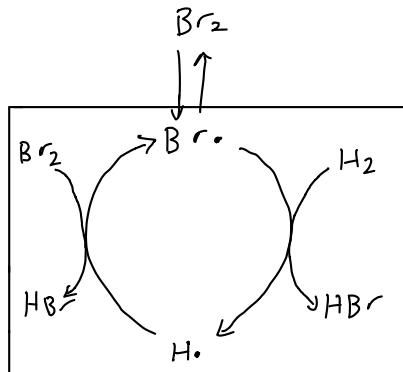
Figure 8: Reaction cycle for the radical chain reaction involving Br_2 and H_2.

The reaction scheme is depicted in Figure 8. This mechanism is known as a radical chain propagation mechanism, as radicals are perpetually consumed and produced over the course of the reaction. In the forward direction, Equation 157 is known as an initiation reaction since it generates radical species that will initiate the larger reaction cascade. In the reverse direction, Equation 157 is known as a termination reaction since it decreases the active pool of radicals. Equation 158 and Equation 159 are known as propagation reactions, as they produce at least as many radicals as are consumed and, thereby, they propagate the chain reaction. In this case, the propagation reactions are also the source of the observed product, HBr. Note how each elementary step in the mechanism consists of clearly defined collisions between molecules and at most two reacting species (ternary reactions are rare, albeit not impossible, in general).

With a greater understanding of the proposed mechanism, we will start by writing the elementary rate law for the production of HBr, the species produced in the net reaction:

$$r_{\mathrm{HBr}} = k_2[\mathrm{Br}^\bullet][\mathrm{H}_2] - k_{-2}[\mathrm{HBr}][\mathrm{H}^\bullet] + k_3[\mathrm{H}^\bullet][\mathrm{Br}_2]. \tag{160}$$

To simplify Equation 160, we will invoke the PSSH, approximating the rate of formation and consumption of both the $\mathrm{Br}^\bullet$ and $\mathrm{H}^\bullet$ radicals as zero given their transient nature:

$$r_{\mathrm{Br}^\bullet} \approx 0 = 2k_1[\mathrm{Br}_2] - 2k_{-1}[\mathrm{Br}^\bullet]^2 - k_2[\mathrm{Br}^\bullet][\mathrm{H}_2] + k_{-2}[\mathrm{HBr}][\mathrm{H}^\bullet] + k_3[\mathrm{H}^\bullet][\mathrm{Br}_2] \tag{161}$$

$$r_{\mathrm{H}^\bullet} \approx 0 = k_2[\mathrm{Br}^\bullet][\mathrm{H}_2] - k_{-2}[\mathrm{HBr}][\mathrm{H}^\bullet] - k_3[\mathrm{H}^\bullet][\mathrm{Br}_2]. \tag{162}$$

Ultimately, we want to be able to write r_{HBr} without any transient intermediates in it. We can start by noting that if we add together Equation 161 and Equation 162, then we get[33]

$$[\mathrm{Br}^\bullet] = \sqrt{\frac{k_1[\mathrm{Br}_2]}{k_{-1}}}. \tag{163}$$

---

[33]Naturally, we ignore the negative root, which would be unphysical.

With an expression for $[Br^\bullet]$, we can plug Equation 163 plug back into Equation 162 to yield

$$[H^\bullet] = \frac{k_2\sqrt{\frac{k_1[Br_2]}{k_{-1}}}[H_2]}{k_{-2}[HBr] + k_3[Br_2]}. \tag{165}$$

Plugging Equation 163 and Equation 165 into Equation 160 yields the desired rate expression, after slogging through some algebra:

$$r_{HBr} = 2k_2\sqrt{\frac{k_1}{k_{-1}}}[H_2]\sqrt{[Br_2]}\left(1 + \frac{k_{-2}[HBr]}{k_3[Br_2]}\right)^{-1}. \tag{166}$$

As was originally stated, it is known from experiments that the rate expression is one-half order in $[Br_2]$ at low conversions. A low conversion implies that there is negligible product, such that $[HBr] \approx 0$. With this observation, we can simplify Equation 166 to

$$r_{HBr} = 2k_2\sqrt{\frac{k_1}{k_{-1}}}[H_2]\sqrt{[Br_2]}. \tag{167}$$

With such expressions, one will typically combine rate constants for the sake of simplicity and to reduce the number of fitted parameters when validating a rate expression. Here, we can define

$$k_{app} \equiv k_2\sqrt{\frac{k_1}{k_{-1}}}, \tag{168}$$

such that

$$r_{HBr} = 2k_{app}[H_2]\sqrt{[Br_2]} \tag{169}$$

at low conversions. As expected, Equation 169 has an apparent one-half order in $[Br_2]$ in this regime and is consistent with observations from experiments. Of course, that does not necessarily

prove that the proposed mechanism is the true mechanism, but it does mean it is at the very least plausible.

3.1.4. Using Bond-Dissociation Enthalpies

When looking at the proposed mechanism in Section 3.1.3, one might ask why certain plausible reactions were omitted. For instance, it would be worth asking why we did not include the following reactions:

$$H_2 \longrightarrow 2H^\bullet, \qquad HBr \longrightarrow H^\bullet + Br^\bullet. \tag{170}$$

This can be explained from an analysis of the bond dissociation energies for each relevant species. A bond dissociation energy is, as the name suggests, the reaction energy required to dissociate a chemical bond. The room-temperature bond dissociation enthalpies, $\Delta H^\circ_{\mathrm{rxn}}$, for several gas-phase species relevant to the $H_2 + Br \longrightarrow 2\,HBr$ radical chain reaction can be found in Table 2.

Species	$\Delta H^\circ_{\mathrm{rxn}}$ (kJ/mol)
H_2	436
HBr	366
Br_2	194

Table 2: Standard-state bond dissociation enthalpies at 298 K.

As is evident from looking at a potential energy diagram (Figure 9), the definition of the transition state implies that the activation energy must be *at least* as large as the bond-dissociation energy, so bond-dissociation energies can be thought of as a lower-bound on the possible value for E_a. With this in mind, based on Table 2 we can reasonably conclude that the rate constants for $H_2 \longrightarrow 2H^\bullet$ and $HBr \longrightarrow H^\bullet + Br^\bullet$ would likely be small relative to the rate constants of the other steps, such that their rates of reaction can be neglected under most reasonable reaction conditions. It is for this reason that these steps are excluded in the provided mechanism.
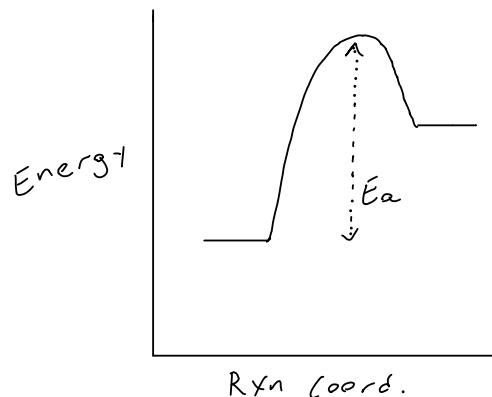
Figure 9: Sample potential energy diagram for an endothermic reaction.

Later in the course, we will describe a related rule-of-thumb known as the Brønsted–Evans–Polanyi (BEP) relationship,[34] which states that $E_a \propto \Delta H°$ for a given reaction family.[35] Namely, as we will later show,
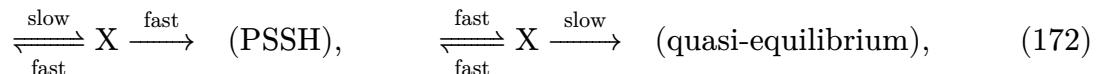
$$E_a = E_0 + \alpha \Delta H°, \tag{171}$$

where this relationship can be thought of as being largely empirical, and $0 \leq \alpha \leq 1$. Nonetheless, it implies that—for a given reaction family—the more endothermic (or less exothermic) the reaction enthalpy is, the higher the activation barrier tends to be for that process. The $\Delta H°$ values can be obtained from experiments or tabulated thermochemical data,[36] such as the CRC Handbook of Chemistry and Physics.

3.1.5. Quasi-Equilibrium Approximation

3.1.5.1. Description

Distinct from the PSSH, we can consider a scenario where one or more of the reversible reaction steps are effectively in equilibrium, which we will refer to as the quasi-equilibrium hypothesis. Note that we are referring to a *reaction* here rather than the lifetime of a *species*, the latter of which was the case when invoking PSSH. For the sake of clarity, the PSSH and quasi-equilibrium approximations generally differ in which steps are considered relatively fast. For example,

$$\underset{\text{fast}}{\overset{\text{slow}}{\rightleftharpoons}} X \overset{\text{fast}}{\longrightarrow} \quad \text{(PSSH)}, \qquad \underset{\text{fast}}{\overset{\text{fast}}{\rightleftharpoons}} X \overset{\text{slow}}{\longrightarrow} \quad \text{(quasi-equilibrium)}, \tag{172}$$

where, for the model reaction schemes, we have $k_1 \ll k_{-1}, k_2$ and $k_1, k_{-1} \gg k_2$ for PSSH and quasi-equilibrium, respectively.[37] PSSH would imply that $r_X \approx 0$, and the quasi-equilibrium approximation would imply that $r_1 = r_1^+ - r_1^- \approx 0$, where r_1 is the net rate of the fast equilibrium step. The way to rationalize the quasi-equilibrium approximation is that perturbing the system slightly (e.g. removing X) would cause a near-immediate return to its original state (e.g. by producing more X). In other words, the reaction is rapidly equilibrated.

3.1.5.2. Demonstration

Understanding the depletion of ozone, O_3, in the atmosphere is of critical importance for climate modeling. The main ozone-depleting reactions are cycles of the following form:

$$\begin{aligned} R + O_3 &\longrightarrow RO + O_2 \\ RO + O &\longrightarrow R + O_2, \end{aligned} \tag{173}$$

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[34] Also referred to as the Bell–Evans–Polanyi relationship depending on who you prefer to take the credit.
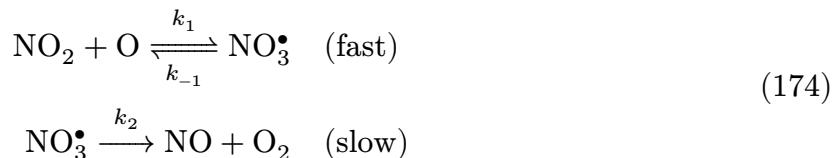
[35] It is a bit of a tautology in that a reaction family is one that follows the Brønsted–Evans–Polanyi relationship.

[36] Recall from thermodynamics that $\Delta H°$, which is the enthalpy change associated with the reaction, can be calculated from the tabulated standard-state enthalpy of formation, $\Delta_f H_j°$, for each species via $\Delta H° = \sum_j \nu_j \Delta_f H_j°$. Since $\Delta H°$ is a state function, if formation enthalpy data is not directly available, bond-dissociation enthalpies can also be used to compute $\Delta H°$ by constructing a net equation matching the reaction of interest.

[37] For additional details, refers to J.F. Perez-Benito, "Some Considerations on the Fundamentals of Chemical Kinetics: Steady State, Quasi-Equilibrium, and Transition State Theory", *J. Chem. Educ.*, 94, 1238–1246 (2017).

which yields the net reaction $O_3 + O \longrightarrow 2O_2$, where R = NO, OH, or Cl radicals. The NO and OH species are known decomposition products of the greenhouse gases N_2O and CH_4, respectively. While it is well-known that increased concentrations of greenhouse gases like N_2O and CH_4 lead to global warming of the troposphere by absorbing infrared radiation, these same gases also cause a decrease in the temperature of the stratosphere because they are also effective emitters of infrared radiation. Somewhat counterintuitively, this cooling of the stratosphere is problematic in that it is known to accelerate the rates of ozone depletion. The reason for this is that the second reaction in the above sequence is known to proceed with a negative apparent activation energy, as we will justify below.

Let us focus on the net reaction $NO_2 + O \rightleftharpoons NO + O_2$. Again, we will take it from the atmospheric science experts that a reasonable mechanism to propose can be given as follows:[38]

$$NO_2 + O \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} NO_3^\bullet \quad \text{(fast)}$$

$$NO_3^\bullet \overset{k_2}{\longrightarrow} NO + O_2 \quad \text{(slow)}$$
(174)

Here, when we say that the second step is "slow", we are specifically implying that $k_1, k_{-1} \gg k_2$.

Since the stoichiometric numbers of NO and O_2 are identical, the rate of product formation for either species is identical. We will call this r_P and note that

$$r_P = k_2[NO_3^\bullet].$$
(175)

Since we would not like to deal with a concentration of an intermediate in our rate expression, we will need to get rid of $[NO_3^\bullet]$. By acknowledging the fact that the first step (both forward and reverse) is much faster than the second step, we can assume that it is in quasi-equilibrium. This allows us to state that the forward and reverse rates for Step 1 are approximately the same:

$$k_1[NO_2][O] \approx k_{-1}[NO_3^\bullet]$$
(176)

or

$$[NO_3^\bullet] \approx K_1[NO_2][O],$$
(177)

where $K_1 \equiv k_1/k_{-1}$.[39] Substituting in $[NO_3^\bullet]$ into Equation 175 yields

$$r_P = k_2 K_1[NO_2][O].$$
(178)

Naturally, we can combine constants together via $k_{app} \equiv k_2 K_1$ if desired and arrive at

$$r_P = k_{app}[NO_2][O],$$
(179)

---

[38]Even though NO and O are radical and diradical species, respectively, we will omit the radical symbol since it is not the focus of our discussion.

[39]You could have arrived at Equation 177 by directly invoking the definition of the equilibrium constant as well.

with the rate law for the reaction, r, being identical. Before continuing, it must be re-emphasized that the result would be quite different if we instead invoked PSSH where we would instead be saying that $r_{\mathrm{NO_3^\bullet}} = 0$.

The question now is how the above expression can be used to rationalize the anti-Arrhenius behavior that is experimentally observed. From our definition of k_{app}, for this reaction we have

$$k_{\mathrm{app}} \equiv k_2 K_1 = A_2 \exp\left(-\frac{E_{\mathrm{a},2}}{RT}\right) \exp\left(-\frac{\Delta H_1^\circ}{RT}\right) \exp\left(\frac{\Delta S_1^\circ}{R}\right), \tag{180}$$

or more compactly

$$k_{\mathrm{app}} = A_2 \exp\left(\frac{\Delta S_1^\circ}{R}\right) \exp\left(-\frac{E_{\mathrm{a},2} + \Delta H_1^\circ}{RT}\right), \tag{181}$$

such that

$$A_{\mathrm{app}} \equiv A_2 \exp\left(\frac{\Delta S_1^\circ}{R}\right), \quad E_{\mathrm{app}} \equiv E_{\mathrm{a},2} + \Delta H_1^\circ. \tag{182}$$

It can be immediately seen that E_{app} can be negative if ΔH_1° is exothermic and has a magnitude greater than that of $E_{\mathrm{a},2}$, the latter of which must be positive since it is an intrinsic activation energy. In fact, this reaction is known to proceed with a negative apparent activation energy of -1.7 kJ/mol. A schematic of the energetic landscape is depicted below:
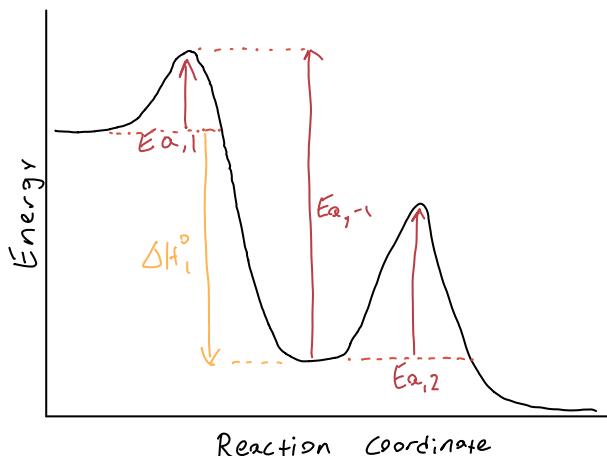
Figure 10: Energetic landscape for the proposed reaction scheme.

At this point, you may think that there is an inherent contradiction going on. If $E_{\mathrm{a},2}$ is less than $E_{\mathrm{a},-1}$, how is it possible for the second reaction to be slower than the forward and reverse directions of the first reaction? Certainly, if $\mathrm{NO_3^\bullet}$ is a short-lived radical, one might reasonably think that it should be consumed quickly. In reality, we must remember that the intrinsic rate constant for each reaction is a function of both the Arrhenius pre-factor and the activation energy. In other words, $k_{-1} \gg k_2$ is possible if $A_{-1} \gg A_2$, which is known to be the case here. This exercise demonstrates that the intrinsic activation energy is not always the full picture. Here, enthalpic

requirements are insufficient on their own to explain the anti-Arrhenius behavior, and there are entropic arguments that are just as critical.[40]
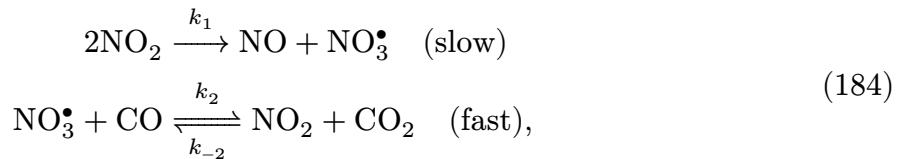
3.1.6. Rate-Determining Step

Here, we will take our assumptions to the logical extreme and consider what happens when one reaction step completely dominates the kinetics: a concept known as the rate-determining step.

Consider the following reaction:

$$NO_2 + CO \longrightarrow NO + CO_2. \tag{183}$$

From experiments, it is known that the rate appears to only be dependent on $[NO_2]$, for which it is second order in $[NO_2]$. Since this does not match the stoichiometry, we can immediately conclude that there must be elementary steps not shown. In fact, there are two:

$$
\begin{aligned}
2NO_2 &\xrightarrow{k_1} NO + NO_3^\bullet \quad \text{(slow)} \\
NO_3^\bullet + CO &\underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} NO_2 + CO_2 \quad \text{(fast)},
\end{aligned}
\tag{184}
$$

where we are now specifically stating that $r_1 \ll r_{-2}, r_2$.

For the reaction to be second-order in $[NO_2]$ and not depend on other species, it is evident that the first step must be substantially slower than the second step such that it dominates the kinetic expression. Indeed, that is the case: the bimolecular reaction of two NO_2 molecules is substantially slower than the reaction of $NO_3^\bullet$ and CO. The rate law in this case can be approximated as

$$r = k_1[NO_2]^2, \tag{185}$$

which is based solely on the rate-determining step (i.e. the first reaction). It does not contain any transient intermediates in it, so we can leave it as-is without further manipulation. Clearly, Equation 185 agrees with the experimental observation that the rate appears to be dependent on $[NO_2]^2$ but not on $[CO]$.

This example also highlights how the presence of a rate-determining step inherently implies that any other reversible steps are inherently in quasi-equilibrium. This is because quasi-equilibrium can generally be invoked when the forward and reverse rates are much faster than the surrounding steps in the proposed mechanism.

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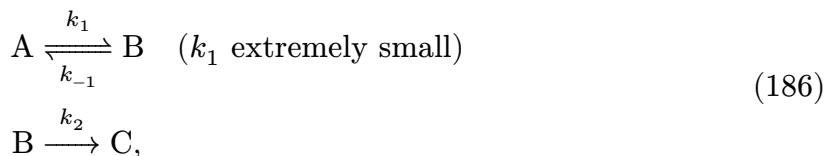
[40]For additional details, refer to L.E. Revell and B.E. Williamson, "Why Are Some Reactions Slower at Higher Temperatures?", *J. Chem. Educ.*, 90, 1024–1027 (2013).

> ⚠️ **Caution**
>
> While it is tempting to invoke a rate-determining step since it greatly simplifies the algebra, one should be cautious about doing so without being extremely precise about what is being invoked. Let's revisit a similar set of reactions:
>
> $$A \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} B \quad (k_1 \text{ extremely small})$$
>
> $$B \xrightarrow{k_2} C, \tag{186}$$
>
> where $k_1 \ll k_{-1}, k_2$. Here, we are considering a set of reactions where the forward rate constant of the first step is very small with respect to that of the reverse reaction and second step. Without invoking any assumptions about rate-determining steps yet, the rate of reaction can be derived in the usual way as
>
> $$r = \frac{k_1 k_2}{k_{-1} + k_2}[A]. \tag{187}$$
>
> If we were to invoke the rate-determining step concept, we might naively state
>
> $$r = k_1[A]. \tag{188}$$
>
> However, it is clear that this is not generally valid. If $k_{-1} \ll k_2$, then indeed we can state that Equation 187 can be correctly approximated by Equation 188. However, we have made no specific assumption in the problem statement about the value of k_{-1} with respect to k_2. If $k_{-1} \gg k_2$, then we have
>
> $$r = \frac{k_1 k_2}{k_{-1}}[A], \tag{189}$$
>
> which does not equal the rate-determining step solution. Furthermore, it would be difficult to justify calling $A \longrightarrow B$ the rate-determining step if k_1 has precisely the same weight as k_{-1} and k_2. This exercise is simply to demonstrate that a rate-determining step cannot necessarily be invoked from information about k for a particular step, particularly when reversible reactions are considered.[41]

3.2. Enzyme Kinetics

3.2.1. Michaelis–Menten Kinetics

The reactions described in this chapter are entirely general. In fact, the same governing principles can be used to understand biological reactions like those occurring in the presence of enzymes. Enzymes, like all catalysts, alter the reaction mechanism in such a way as to reduce the apparent

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[41]For additional details, refer to S. Kozuch, J.M.L. Martin, "The Rate-Determining Step is Dead. Long Live the Rate-Determining State!", *ChemPhysChem*, 12, 1413–1418 (2011).

activation energy, increasing the overall rate of reaction. In biological systems, this is achieved through the adsorption of a substrate (i.e. reactant), S, at a binding pocket of the enzyme to ultimately produce a given product P via the presence of one or more catalytic intermediates ES (e.g. an enzyme–substrate complex). If we define the free enzyme as E, we can write a simplified reaction mechanism as follows:

$$E + S \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} ES$$

$$ES \xrightarrow{k_2} E + P. \tag{190}$$

The goal is to find an expression for the rate of production of P. From the elementary reaction steps, we can state that[42]

$$r_P = k_2[ES]. \tag{191}$$

However, the concentration of ES is not a quantity than can be easily measured. As such, our next step is to find a way to rewrite the concentration of ES in terms of observables and constants.

Writing out the rate expression for ES, we get

$$r_{ES} \approx 0 = k_1[E][S] - k_{-1}[ES] - k_2[ES], \tag{192}$$

where we have set the expression equal to zero by invoking the pseudo-state state hypothesis given the transient nature of the ES intermediate.[43] Solving for the concentration of ES in Equation 192 yields

$$[ES] = \frac{k_1[E][S]}{k_{-1} + k_2}. \tag{193}$$

Knowing the concentration of free enzyme, [E], at a given point in time can be quite difficult. Fortunately, we can take advantage of the conservation of mass to simplify things a bit. Namely, we can state that the total concentration of enzyme, $[E]_0$, does not change over the course of the reaction such that

$$[E]_0 = [E] + [ES], \tag{194}$$

where we have implicitly assumed that we are starting the reaction from scratch, such that $[ES]_0 = 0$. By solving for the [E] in Equation 194 and substituting the resulting expression into Equation 193, we arrive at

$$[ES] = \frac{k_1([E]_0 - [ES])[S]}{k_{-1} + k_2} \tag{195}$$

---

[42]In the literature, you may see v used in place of r_P. The v is meant to symbolize reaction velocity.

[43]In reality, there is an induction period before pseudo-steady state is reached. If the enzyme concentration is much larger than that of the substrate, this induction period may be large. However, it is typically the case that there is much more substrate than enzyme.

$$[\text{ES}] + \frac{k_1[\text{ES}][\text{S}]}{k_{-1} + k_2} = \frac{k_1[\text{E}]_0[\text{S}]}{k_{-1} + k_2} \tag{196}$$

$$[\text{ES}] = \frac{\frac{k_1[\text{E}]_0[\text{S}]}{k_{-1}+k_2}}{1 + \frac{k_1[\text{S}]}{k_{-1}+k_2}} \tag{197}$$

$$[\text{ES}] = \frac{[\text{E}]_0[\text{S}]}{\frac{k_{-1}+k_2}{k_1} + [\text{S}]}. \tag{198}$$

Substituting Equation 198 into Equation 191 yields

$$r_\text{P} = \frac{k_2[\text{E}]_0[\text{S}]}{\frac{k_{-1}+k_2}{k_1} + [\text{S}]}. \tag{199}$$

We have now arrived at an analytical solution for the rate of generation of the product that is solely dependent on experimental observables and constants. In practice, Equation 199 is typically rewritten as

$$r_\text{P} = \frac{V_\text{max}[\text{S}]}{K_\text{M} + [\text{S}]}, \tag{200}$$

where

$$V_\text{max} \equiv k_2[\text{E}]_0 \tag{201}$$

and

$$K_\text{M} \equiv \frac{k_{-1} + k_2}{k_1}. \tag{202}$$

The expression given in Equation 200 is known as the Michaelis–Menten equation and is a simple model of enzyme reaction kinetics.

In the limit of $[\text{S}] \gg K_\text{M}$, the rate is pseudo zeroth-order in $[\text{S}]$, approaching a value of V_max, thereby giving it its name of the maximum rate. In the limit of $[\text{S}] \ll K_\text{M}$, the rate is pseudo first-order in $[\text{S}]$. K_M is known as the Michaelis constant and describes the concentration of S at which the reaction rate is half of V_max.

It is worth noting that S is the free substrate, whereas one often measures the total substrate in experiments. In practice, one can typically assume that the concentration of substrate is much greater than the total enzyme concentration, such that the total substrate can be used. This is known as the free ligand approximation. We have also assumed in this derivation that the production of P is irreversible. One can re-derive r_P with reversible product binding in precisely the same way; the math simply gets slightly messier.

3.2.2. Linearizing the Michaelis–Menten Equation

When analyzing experimental data, it is oftentimes useful to fit to a linear equation. This can be achieved quite readily be rearranging the Michaelis–Menten equation to

$$\frac{1}{r_{\text{P}}} = \frac{K_{\text{M}}}{V_{\text{max}}} \frac{1}{[\text{S}]} + \frac{1}{V_{\text{max}}}. \tag{203}$$

Here, the inverse of the reaction rate is plotted against the inverse concentration of the substrate, which in turn can be used to obtain K_{M} and V_{max} from the slope and y-intercept. Such a plot is known as a Lineweaver–Burk plot.

> **📊 Interactive Plot**
>
> <div align="center">https://marimo.app/l/pbceww°</div>

There is, however, a very important limitation in using Lineweaver–Burk plots. By relying on inverse rate on the y-axis and inverse concentration on the x-axis, the experimental data will not be distributed evenly across the range of values. This may result in poorly determined fit parameters V_{max} and K_{M}. There are many other ways to linearize the Michaelis–Menten equation, which have their own limitations. In modern times, it is generally recommended to do nonlinear regression on the Michaelis–Menten equation directly to avoid such complications.

> **📊 Interactive Plot**
>
> <div align="center">https://marimo.app/l/f43w0q°</div>

4. Rate Expressions for Heterogeneous Reactions

In Section 3, we were mainly focused on homogeneous reactions, with the brief exception of Michaelis–Menten kinetics. In practice, many reactions are carried out in the presence of a heterogeneous catalyst that accelerates the overall rate of reaction. In this section, we will shift our focus to surface catalysis, wherein a reactant in a continuum diffuses into a catalyst particle, adsorbs to the surface, reacts to form a new species, desorbs, diffuses out of the catalyst particle, and re-enters the continuum. We will focus on developing a basic kinetic model from elementary steps including adsorption, desorption, and surface reaction.

4.1. Adsorption Rate Laws

4.1.1. Physisorption and Chemisorption
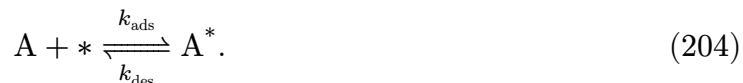
Adsorption of the substrate to the catalyst surface is the critical first step in a catalytic reaction. Before proceeding, we should clarify some terminology. Adsorption is the process by which a gas or solution phase molecule or atom binds to a surface. The adsorbate is the molecule or atom binding to the surface, and the adsorbent is the surface itself. Note that absorption is different than adsorption; absorption is the bulk uptake of a fluid without a corresponding phase change.

Molecule A can adsorb to a surface site $*$ via one of two main mechanisms: chemisorption or physisorption. Chemisorption involves the formation of a bond between the adsorbate and the surface and involves a change in the electronic structure of the adsorbate. In contrast, physisorption is largely due to electrostatic and van der Waals interactions without a significant change in the electronic structure of the adsorbate. Chemisorption is typically a much stronger interaction than physisorption but both are incredibly important. Additionally, it is possible for a molecule to dissociate upon adsorption to form two separate adsorbate. This does not need to be a diatomic molecule. For instance, CH_4 can dissociatively adsorb to form $CH_3^{\bullet}$ and $H^{\bullet}$. There is typically a notable activation barrier for the dissociative adsorption process.

The adsorption process can happen on a variety of different types of surfaces. For instance, one might consider the adsorption of a molecule to a metal surface like Pd or Rh. Alternatively, one might consider the adsorption of a molecule along the internal surface of a highly porous material like an aluminosilicate zeolite. Porous materials are particularly unique choices for adsorbents, as they can have incredibly high surface areas; for instance, nanoporous solids known as metal–organic frameworks can have surface areas up to 7000 m^2/g, such that one gram of material can have the surface area of a football field.

4.1.2. Molecular Adsorption

Since adsorption is a pre-requisite for heterogeneous reactions, we will focus on developing a kinetic description of the adsorption process. We will start with the simple case of one adsorbate that adsorbs in a non-dissociative (i.e. molecular) fashion to a surface site:

$$A + * \underset{k_{des}}{\overset{k_{ads}}{\rightleftarrows}} A^{*}. \tag{204}$$

For example, this could be $CO + * \rightleftharpoons CO^*$. The equation for the rate of adsorption and desorption can be written as

$$
\begin{aligned}
r_{\text{ads}} &= k_{\text{ads}} p_A [*] \\
r_{\text{des}} &= k_{\text{des}} [A^*].
\end{aligned}
\tag{205}
$$

From here, we are going to investigate equilibrium adsorption behavior to better understand this phenomena. In other words, we will consider the situation where the rates of the adsorption and desorption processes are equal (i.e. $r_{\text{ads}} = r_{\text{des}}$), such that

$$
K_{\text{ads}} = \frac{k_{\text{ads}}}{k_{\text{des}}} = \frac{[A^*]}{p_A [*]}.
\tag{206}
$$

We can see that the above expression is the same as the thermodynamic definition of the equilibrium constant we described in Section 2.4.1.

It is difficult to directly interpret Equation 206 given the fact that $[*]$ remains in the expression. Instead, we would prefer to rely on $[*]_0$, which is the number density of all adsorption sites (both vacant and occupied) rather than just the vacant sites. We prefer $[*]_0$ because $[*]$ will fluctuate over the course of the reaction and is not easily measurable.

We can write a site balance that states the number of sites does not change:

$$
[*]_0 \equiv [*] + \sum_j [A_j^*],
\tag{207}
$$

where the summation accounts for all possible adsorbate species at the surface sites.[44] In the case of Equation 204, the site balance becomes

$$
[*]_0 = [*] + [A^*].
\tag{208}
$$

Solving for $[*]$ in Equation 206 and substituting into Equation 208 yields

$$
\begin{aligned}
[*]_0 &= \frac{[A^*]}{K_{\text{ads}} p_A} + [A^*] \\
[*]_0 &= [A^*] \left(\frac{1}{K_{\text{ads}} p_A} + 1 \right).
\end{aligned}
\tag{209}
$$

Typically, a parameter θ_j is defined that describes the fractional surface coverage of species j, such that

$$
\theta_A \equiv \frac{[A^*]}{[*]_0} = \frac{1}{\frac{1}{K_{\text{ads}} p_A} + 1} = \frac{K_{\text{ads}} p_A}{1 + K_{\text{ads}} p_A}.
\tag{210}
$$

---

[44] This assumes that the concentration of surface sites remains constant over the course of the reaction, which is not always the case (e.g. if catalyst deactivation or coking occurs, such that the sites must be regenerated).

> **⚠ Caution**
>
> Be careful with units. If K_{ads} were to be given in units of cm^3/mol, then you would need to replace p_A with [A] for everything to be self-consistent. This can be done by invoking an equation of state (e.g. the ideal gas law, if applicable).

Equation 210 is referred to as a Langmuir adsorption isotherm, which describes the equilibrium adsorption behavior and is depicted in Figure 11. For $p_A K_{ads} \ll 1$ (i.e. at low partial pressure of A), $\theta_A \to K_{ads}p_A$. For $p_A K_{ads} \gg 1$ (i.e. at high partial pressure of A), $\theta_A \to 1$.
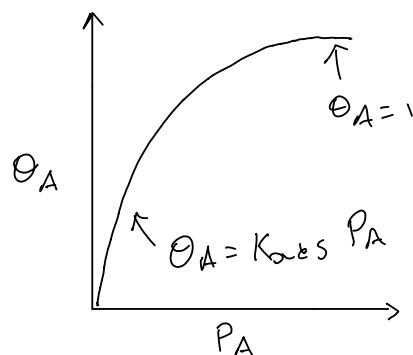
Figure 11: Langmuir adsorption isotherm.

It is important to note several implicit assumptions for classical Langmuir theory to hold. Generally speaking, a Langmuir adsorption isotherm does not account for multilayer coverages. As such, it is best suited for describing monolayer adsorption. Furthermore, it assumes that all the adsorption sites are energetically uniform, such that the probability of an adsorbate binding to a given adsorption site is identical across the catalyst surface.[45] It also assumes that there are no adsorbate–adsorbate interactions, which in reality can depend on the adsorbate and the interatomic distance between adsorption sites. All of these are fairly substantial approximations that can break down in real catalytic systems. Nonetheless, the Langmuir adsorption isotherm remains a valuable tool for understanding adsorption behavior.

It is useful to think about how θ_A might change with temperature and how it is related to thermodynamics. For this analysis, we note that K_{ads} is a function of temperature and that we can write

$$\theta_A = \frac{\exp\left(-\frac{\Delta H^\circ - T\Delta S^\circ}{RT}\right)p_A}{1 + \exp\left(-\frac{\Delta H^\circ - T\Delta S^\circ}{RT}\right)p_A}. \tag{211}$$

From this expression, it can be shown that increasing T will decrease θ_A.[46] This is easily explained in physical terms by the fact that the adsorbate has more kinetic energy and, therefore, is more

---

[45] Metal ions or clusters hosted on an amorphous support like silica is a clear example of a material where the active sites are energetically diverse.

[46] This inherently assumes that $\Delta S^\circ < 0$, which is typically the case for adsorption since the translational degrees of freedom are lost.

likely to be liberated from the surface. It can also be shown that decreasing $\Delta H°$ (i.e. making it more negative since adsorption is generally exothermic) will increase θ_A. Again, this can be easily explained by the fact that a more exothermic adsorption energy implies a stronger bond to the surface, making the species less likely to desorb.

> **📊 Interactive Plot**
>
> https://marimo.app/l/e0dix3°.

Before continuing, it should be noted that we can rewrite our rates of adsorption and desorption in terms of fractional coverage as follows:

$$r_{ads} = k_{ads}p_A[*] = k_{ads}p_A[*]_0\theta_* = k_{ads}p_A[*]_0(1-\theta_A)$$
$$r_{des} = k_{des}\left[A^*\right] = k_{des}[*]_0\theta_A,$$

$$(212)$$

where we took advantage of the fact that $\sum_j \theta_j = 1$, where j includes both the adsorbate species and the vacant sites. We can only use Equation 210 for the definition of θ_A, however, if the adsorption or desorption process is equilibrated.

4.1.3. Multi-Site Adsorption

It is natural to think about how one might modify the Langmuir equation for a scenario where there are two or more energetically distinct adsorption sites on the catalyst surface. The procedure is no different than before if we make a leap of faith and assume that the adsorption at each binding site is independent from one another, such that we can treat the adsorption as a sum of individual Langmuir models. In other words, we can write

$$\theta_A = \sum_s M_s \frac{K_{ads,s}p_A}{1 + K_{ads,s}p_A},$$

$$(213)$$

where $K_{ads,s}$ is now an "equilibrium constant" for the adsorption of species A at site s, and M_s is the maximum capacity of site s. Here, M_s and $K_{ads,s}$ are both fitting parameters determined from an experimentally measured adsorption isotherm. Generally, it is impossible to enumerate all possible surface sites, and even if one could, the number of fitting parameters would be huge. Instead, this model is typically used when it is clear there are (for instance) two major yet distinct adsorption sites that adsorbates can bind to.

4.1.4. Competitive Adsorption

Continuing our journey with the Langmuir adsorption model, we will now consider the scenario where we have multiple species competing for surface sites, such as

$$A + * \rightleftharpoons A^*$$
$$B + * \rightleftharpoons B^*.$$

$$(214)$$

For the sake of simplicity, we will invoke the same assumptions for the Langmuir adsorption isotherm as in Section 4.1.2 with the additional caveat that each site must only hold one molecule of A or B but not both simultaneously.

Under equilibrium conditions, we can state

$$K_{\text{ads,A}} = \frac{[\text{A}^*]}{p_\text{A}[*]} \tag{215}$$

$$K_{\text{ads,B}} = \frac{[\text{B}^*]}{p_\text{B}[*]}. \tag{216}$$

The site balance can be rewritten as

$$[*]_0 = [*] + [\text{A}^*] + [\text{B}^*]. \tag{217}$$

Once again, we seek to get rid of $[*]$. To do so, we start by solving for $[*]$ in Equation 215 and plugging this into Equation 217:

$$[*]_0 = \frac{[\text{A}^*]}{K_{\text{ads,A}}p_\text{A}} + [\text{A}^*] + [\text{B}^*]. \tag{218}$$

Since we will ultimately want an expression for θ_A that is independent of $[\text{B}^*]$, we will solve for $[\text{B}^*]$ in Equation 216 and plug this into Equation 218:

$$[*]_0 = \frac{[\text{A}^*]}{K_{\text{ads,A}}p_\text{A}} + [\text{A}^*] + K_{\text{ads,B}}p_\text{B}[*]. \tag{219}$$

It looks like we have $[*]$ in our expression again, so we substitute in $[*]$ from Equation 215 to get

$$[*]_0 = \frac{[\text{A}^*]}{K_{\text{ads,A}}p_\text{A}} + [\text{A}^*] + \frac{[\text{A}^*]K_{\text{ads,B}}p_\text{B}}{K_{\text{ads,A}}p_\text{A}}$$

$$[*]_0 = [\text{A}^*]\left(\frac{1}{K_{\text{ads,A}}p_\text{A}} + 1 + \frac{K_{\text{ads,B}}p_\text{B}}{K_{\text{ads,A}}p_\text{A}}\right). \tag{220}$$

Therefore,

$$\theta_\text{A} \equiv \frac{[\text{A}^*]}{[*]_0} = \frac{1}{\frac{1}{K_{\text{ads,A}}p_\text{A}} + 1 + \frac{K_{\text{ads,B}}p_\text{B}}{K_{\text{ads,A}}p_\text{A}}} = \frac{K_{\text{ads,A}}p_\text{A}}{1 + K_{\text{ads,A}}p_\text{A} + K_{\text{ads,B}}p_\text{B}}. \tag{221}$$

By analogy for species B, the following result can be found:

$$\theta_\text{B} = \frac{K_{\text{ads,B}}p_\text{B}}{1 + K_{\text{ads,A}}p_\text{A} + K_{\text{ads,B}}p_\text{B}}. \tag{222}$$

As you might be able to already tell, we can generalize the adsorption isotherm for arbitrary numbers of adsorbates as

$$\theta_A = \frac{K_{ads,A} p_A}{1 + \sum_j K_{ads,j} p_j}. \tag{223}$$
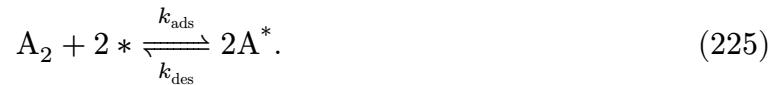
Finally, we can revisit our rates of adsorption and desorption to write them in terms of fractional coverages:

$$r_{ads,A} = k_{ads,A} p_A [*] = k_{ads,A} p_A [*]_0 \theta_* = k_{ads,A} p_A [*]_0 (1 - \theta_A - \theta_B)$$
$$r_{des,A} = k_{des,A} \left[A^* \right] = k_{des,A} [*]_0 \theta_A. \tag{224}$$

If the adsorption and desorption processes are equilibrated, then we can use Equation 223 to substitute in for θ_A and θ_B.

4.1.5. Dissociative Adsorption

Now, we will consider a dissociative adsorption process:[47]

$$A_2 + 2* \underset{k_{des}}{\overset{k_{ads}}{\rightleftharpoons}} 2A^*. \tag{225}$$

We will again invoke the typical assumptions of the Langmuir adsorption isotherm with the additional caveat that the individual A^* species adsorb onto separate surface sites.

However, there is an important subtlety that needs to be emphasized. For dissociative adsorption to occur, there must be a pair of adjacent sites for the adsorbate to dissociate onto. Put another way, it is not just *any* two surface sites. To make sure we do not make a logical error here, we will temporarily rewrite our equation as

$$A_2 + ** \underset{k_{des}}{\overset{k_{ads}}{\rightleftharpoons}} A**A, \tag{226}$$

where $**$ indicates a pair of adjacent, accessible surface sites, and $A**A$ is a pair of adjacent, occupied surface sites.

To write the elementary rate law for the forward and reverse reactions, we now need an expression for $[**]$ and $[A**A]$. We will start by introducing the answer and then justifying why it is the case. Namely, lattice statistics allows us to state:

$$[**] = \frac{z}{2} \frac{[*]^2}{[*]_0} \tag{227}$$

and

---

[47]Dissociative chemisorption is both an adsorption and surface reaction process. We include it in the adsorption section to compare and contrast expressions for the adsorption isotherm.

$$[A**A] = \frac{z}{2} \frac{\left[A^*\right]^2}{[*]_0}, \tag{228}$$

where z is the coordination number of the site, and a $1/2$ factor is introduced to avoid over-counting when dealing with identical pairs of species or sites.[48]
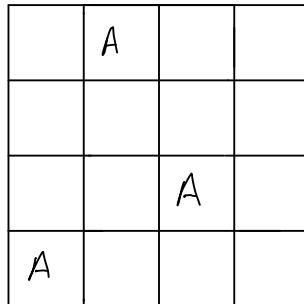
Figure 12: Schematic of adsorption on a square lattice with vacant sites and adsorbed A species. This cartoon example of a surface would have $z = 4$ for each site, assuming the surface repeats infinitely in x and y.

The way we can justify the above expressions is as follows. Consider the expression for $[* *]$. We want to find the number density of adjacent pairs of vacant sites. The probability of randomly picking a vacant site on the lattice is $[*]/[*]_0$, and we can start by considering all possible sites on the surface: $[*]_0 \cdot ([*]/[*]_0)$. Once we have picked a vacant site, we want to see if we can pick another one that is adjacent to our choice. For this, the probability of finding a vacant site is again $[*]/[*]_0$, but this time we are not considering all possible sites ($[*]_0$); rather, we are considering only the sites adjacent to the first pick (i.e. the number of coordinating sites), such that we have $z \cdot ([*]/[*]_0)$. For the likelihood of both events to occur, we multiply the two independent event likelihoods together to arrive at $[* *] = z \cdot ([*]^2/[*]_0)$. The final factor of $1/2$ comes in to prevent double-counting when dealing with indistinguishable pairs of sites or species on the surface. An analogous process can be carried out for $[A**A]$.

The equations for the rate of adsorption and desorption can now be written as

$$
\begin{aligned}
r_{\text{ads}} &= k_{\text{ads}} p_{A_2} [* *] = \frac{z k_{\text{ads}} p_{A_2} [*]^2}{2[*]_0} \\
r_{\text{des}} &= k_{\text{des}} [A**A] = \frac{z k_{\text{des}} \left[A^*\right]^2}{2[*]_0}.
\end{aligned}
\tag{229}
$$

In other words, there is an additional factor of $z/2[*]_0$ that needs to be included than if one were to write the elementary rate law solely based on Equation 225. Setting both expressions equal to one another to invoke equilibrium conditions yields

---

[48]Implicit in the lattice statistics-based expression is the so-called Hinshelwood assumption, wherein the adsorbates are considered to be randomly distributed on the surface without any degree of spatial correlation.

$$K_{\text{ads}} = \frac{\left[\text{A}^*\right]^2}{p_{\text{A}_2}[*]^2}. \tag{230}$$

Reassuringly, our expression for K_{ads} is the same expression we would expect based on the thermodynamic definition of the equilibrium constant.[49] From here onward, we will simply invoke the thermodynamic definition of the equilibrium constant when the quasi-equilibrium approximation is invoked.

> ⚠️ **Caution**
>
> If we had not accounted for the statistical siting, we would instead have $r_{\text{ads}} = k_{\text{ads}} p_{\text{A}_2}[*]^2$ and $r_{\text{des}} = k_{\text{des}} \left[\text{A}^*\right]^2$, which will overestimate the rates of adsorption and desorption and change the units on our rate constant. That said, there would be no change in our expression for K_{ads} regardless of whether we accounted for site-pair statistics or not.

The site balance is given by

$$[*]_0 = [*] + \left[\text{A}^*\right]. \tag{231}$$

Since we want to have an expression for θ_{A} that is independent of $[*]$, we can solve for $[*]$ in Equation 230 and plug it into Equation 231 to get

$$[*]_0 = \frac{\left[\text{A}^*\right]}{\sqrt{K_{\text{ads}} p_{\text{A}_2}}} + \left[\text{A}^*\right]$$

$$[*]_0 = \left[\text{A}^*\right]\left(\frac{1}{\sqrt{K_{\text{ads}} p_{\text{A}_2}}} + 1\right). \tag{232}$$

Therefore,

$$\theta_{\text{A}} = \frac{1}{\frac{1}{\sqrt{K_{\text{ads}} p_{\text{A}_2}}} + 1} \tag{233}$$

$$\theta_{\text{A}} = \frac{\sqrt{K_{\text{ads}} p_{\text{A}_2}}}{1 + \sqrt{K_{\text{ads}} p_{\text{A}_2}}}. \tag{234}$$

---

[49]For dissociative adsorption of the form $\text{AB} + 2* \rightleftharpoons \text{A}^* + \text{B}^*$, it may appear that the kinetic-based definition of K given by $r^+ = r^-$ would not be equal to the thermodynamic definition of $K = \left[\text{A}^*\right]\left[\text{B}^*\right]/p_{\text{AB}}[*]^2$ because the elementary reaction in the forward direction involves two seemingly indistinguishable surface sites ($z/2$), whereas the reverse has two distinguishable adsorbates (z), resulting in a stray factor of 2 in the numerator. While beyond the scope of this course, the forward rate expression should actually have a factor of z instead of $z/2$ for reasons outlined in the Supporting Information of N.K. Razdan, A. Bhan, "Kinetic Description of Site Ensembles on Catalytic Surfaces", *Proc. Natl. Acad. Sci. U.S.A.*, 118, e2019055118 (2021).

We can see that when $\sqrt{K_{\text{ads}}p_{A_2}} \ll 1$ (i.e. in the limit of low partial pressures of A_2), $\theta_A \to \sqrt{K_{\text{ads}}p_{A_2}}$, which is significantly different than the linear behavior observed for the non-dissociative Langmuir adsorption isotherm.

We can also revisit our rate expressions to write them in terms of surface coverages of observable species:

$$r_{\text{ads}} = \frac{zk_{\text{ads}}p_{A_2}[*]^2}{2[*]_0} = \frac{z}{2}k_{\text{ads}}p_{A_2}[*]_0\theta_*^2 = \frac{z}{2}k_{\text{ads}}p_{A_2}[*]_0(1-\theta_A)^2 = k'_{\text{ads}}p_{A_2}[*]_0(1-\theta_A)^2$$

$$r_{\text{des}} = \frac{zk_{\text{des}}\left[A^*\right]^2}{2[*]_0} = \frac{z}{2}k_{\text{des}}[*]_0\theta_A^2 = k'_{\text{des}}[*]_0\theta_A^2,$$

(235)

where k' indicates a rate constant that includes the $z/2$ numerical factor. If the adsorption and desorption processes are equilibrated, we can use Equation 234 to determine the value of θ_A.

4.1.6. Non-Langmuir Isotherms

4.1.6.1. Henry's Law

The simplest adsorption model is given by Henry's isotherm. Henry's isotherm states, in analogy with Henry's law, that

$$\theta_A = K_H p_A, \tag{236}$$

where K_H is Henry's adsorption constant and is generally a fitting parameter. Henry's isotherm states that there is a direct, linear relationship between coverage and partial pressure. This is clearly false for many adsorption processes but is valid when the partial pressure of the adsorbate is low, such that there are negligible interactions between adsorbed molecules and the adsorption sites are plentiful. We can see that Henry's isotherm is related to the Langmuir isotherm in the limit of small p_A:

$$\theta_A = \frac{K_{\text{ads}}p_A}{1 + K_{\text{ads}}p_A} \to K_{\text{ads}}p_A \quad (K_{\text{ads}}p_A \ll 1). \tag{237}$$

That said, it is also true that Henry's isotherm can be applicable at more appreciable partial pressures, provided the adsorption of the molecule is very weak. This is by no means an improvement on the Langmuir model but can make sense to use if the adsorption isotherm is in the linear regime.

4.1.6.2. Two-Parameter, Empirical Isotherm Models

We can also consider models that capture behavior the Langmuir model does not. As previously discussed, the Langmuir model of adsorption made some critical approximations. Perhaps the most notable is the assumption that the adsorption enthalpy of each site is constant (i.e. independent of coverage). There are many models that attempt to directly or indirectly capture this

behavior, some of which are outlined below:[50]

$$\theta_A = \alpha p_A^{1/\beta} \quad \text{(Freundlich isotherm)}$$

$$\theta_A = \frac{K_{\text{ads}}p_A}{\left(1 + (K_{\text{ads}}p_A)^\beta\right)^{1/\beta}} \quad \text{(Tóth isotherm)} \tag{238}$$

$$\theta_A = \frac{RT}{\alpha} \ln(\beta p_A) \quad \text{(Temkin isotherm)}.$$

There are many other functional forms that have been proposed and that can potentially be dreamed up. In all three cases presented here, there is additional flexibility compared to the (single-site) Langmuir adsorption isotherm, as there are two fitting parameters instead of one if the practitioner is attempting to fit an experimentally measured adsorption isotherm. Naturally, each of these models have their own limitations. Most notably, many alternate models have the unphysical scenario where θ_A can become greater than one for large p_A. Nonetheless, these models can capture adsorption on surface complexities better than the single-site Langmuir equation because of their additional flexibility, at the expense of reduced interpretability. Both the Freundlich and Tóth isotherms were proposed as ways to deal with surface heterogeneity. The Temkin isotherm was proposed as a way to indirectly deal with adsorbate–adsorbate interactions.

4.1.6.3. BET Theory for Multilayer Adsorption

Note: This topic was not covered in class and is solely for the interested reader.

The models we have discussed so far assume that there is only a monolayer of adsorbates along the surface. However, multiple layers of adsorbates that are stabilized by van der Waals interactions are oftentimes possible, particularly at low temperatures and high gas pressures. To address this limitation, we will introduce Brunauer–Emmett–Teller (BET) theory. In BET theory, we make the following assumptions:

1. Adsorption occurs on well-defined sites with one molecule adsorbing per surface site.
2. The molecule adsorbed at layer i can itself act as an adsorption site for a gas molecule to form at layer $i + 1$. There are no interactions between the gas molecules in a given layer.
3. The uppermost layer of adsorbates is in equilibrium with the gas phase.
4. The heat of adsorption for the first layer is the strongest and constant. The heat of adsorption for the remaining layers can be approximated as the heat of liquefaction.
5. At the saturation pressure, the number of layers approaches infinity, such that it becomes analogous to the surface being surrounded by a fluid phase.
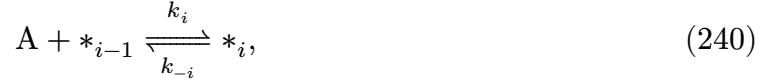
With these assumptions in place, we consider the adsorption of species A onto the surface of a material. The adsorption of species A onto the bare surface $*_0$ yields a new site $*_1$:

---

[50]For some cautionary comments about the Temkin isotherm, refer to K. Chu, "Revisiting the Temkin Isotherm: Dimensional Inconsistency and Approximate Forms", *Ind. Eng. Chem. Res.*, 60, 13140–13147 (2021).

$$A + *_0 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} *_1 . \tag{239}$$

Generalizing this process to multiple layers, we have

$$A + *_{i-1} \underset{k_{-i}}{\overset{k_i}{\rightleftharpoons}} *_i, \tag{240}$$

where k_i refers to the rate constant for formation of layer i (i.e. adsorption onto layer $i - 1$), and k_{-i} refers to desorption from layer i. With this numbering scheme, a perfect monolayer would mean that all adsorbates exist on layer $i = 1$, for instance.

We will refrain from providing a detailed derivation of the BET isotherm here, as it is mainly useful for determining the surface area of a material rather than kinetic data. Simply providing the big reveal, the BET isotherm for multi-layer physisorption can be shown to be

$$\theta = \frac{cx}{(1-x)(1+x(c-1))}, \quad \text{where } c \equiv \frac{K_1}{K_\ell} \text{ and } x \equiv \frac{P}{P_0}, \tag{241}$$

where K_ℓ is the equilibrium constant for adsorption and desorption off of a liquid surface of the molecular species, P is the pressure of the adsorbate, and P_0 is its vapor pressure. Generally, c is simply referred to as the BET c constant. The BET isotherm is most accurate when P/P_0 is between roughly 0.05 and 0.3. At low pressures, the heterogeneous nature of the surface sites can play a notable role. At high pressures, nanoscale and microscale irregularities in the surface itself can impact the results.

It is always worth testing out limiting behavior. In the case of low pressures, it is unlikely for there to be multilayer adsorption, so we should expect the BET isotherm to be analogous to the Langmuir isotherm in this limit. Indeed, plugging $x \ll 1$ we get

$$\theta \approx \frac{cx}{1+cx}, \tag{242}$$

which is the same functional form as the Langmuir isotherm of

$$\theta = \frac{K_{\text{ads}}P}{1+K_{\text{ads}}P} \tag{243}$$

and is fully equivalent if $c = K_{\text{ads}}P_0$.

As previously alluded to, the BET isotherm is typically used for surface area measurements. This is done by noting that

$$\theta = \frac{v}{v_{\text{m}}}, \tag{244}$$

where v is the volume of the gas adsorbed to the surface and v_m is the volume of gas that would be adsorbed if there were precisely a full monolayer of coverage. This allows us to rewrite Equation 241 slightly as

$$v = \frac{v_\text{m} c x}{(1-x)(1+x(c-1))}.$$

(245)

Generally, one will pick a sample to study and carry out an isotherm measurement with a given adsorbate molecule, which is most typically N_2. The value for x is the independent variable controlled by the experimentalist by changing the pressure of gas introduced to the system. In modifying x, the volume of adsorbed gas v is measured, from which both v_m and c can be obtained as fitting parameters for the particular temperature and adsorbate–adsorbent system.

With the value for v_m obtained from experiments, the specific surface area of the material (typically reported in m^2/g), S_BET, can be computed as
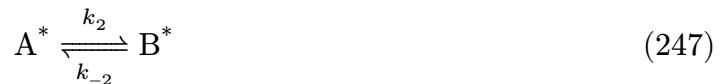
$$S_\text{BET} = \frac{v_\text{m} N_\text{A} \alpha}{V} \cdot \frac{1}{m_\text{adsorbent}},$$

(246)

where N_A is Avogadro's number, α is the adsorption cross section of the adsorbate (i.e. the area that a single adsorbate would cover when adsorbed), V is the molar volume of gas at the same conditions as v_m was obtained, and $m_\text{adsorbent}$ is the mass of the adsorbent. Typically, α and V are tabulated quantities, and $m_\text{adsorbent}$ is readily measurable.

4.2. Surface Reaction Rate Laws

4.2.1. Single-Site Mechanisms

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. One simple example of this kind of mechanism would be

$$\text{A}^* \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} \text{B}^*$$

(247)

for the transformation of species A to B on the catalyst surface. The net rate for the surface reaction ("SR") is as follows:

$$r_\text{SR} = k_2 \left[\text{A}^*\right] - k_{-2} \left[\text{B}^*\right].$$

(248)

At this point, it is worth clarifying some terminology you may see in the literature. Oftentimes, it can be more convenient to report or simulate data based on fractional coverages rather than concentrations. If we divide through the above expression by $[*]_0$ on both sides, we get

$$r'_\text{SR} \equiv \frac{r_\text{SR}}{[*]_0} = k_2 \theta_\text{A} - k_{-2} \theta_\text{B}.$$

(249)

Notice how the two rate expressions are analogous, with concentrations replaced by fractional coverages. Here, the rate has been normalized by the concentration of active sites and, therefore, has units of 1/time. When dealing with the rate of a net reaction, this site-normalized form of the rate is referred to as a turnover frequency (TOF). The TOF represents the number of reacting molecules per active site and unit time (assuming that all adsorption sites defined by $[*]_0$ are all the possible active sites) since it represents the number of times the catalytic active sites have "turned over" a reaction. Since TOFs are normalized by the concentration of active sites and most real catalysts have heterogeneity in the active species, the TOF is best thought of as an averaged property.[51]

4.2.2. Dual-Site Mechanisms

One can also consider a different type of surface reaction that consists of a reaction involving two surface sites.[52] For instance,

$$\mathrm{A}^* + \mathrm{B}^* \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} \mathrm{C}^* + \mathrm{D}^*. \tag{250}$$

It might be tempting to write that the net rate for the surface reaction is as follows:

$$r_{\mathrm{SR}} \overset{?}{=} k_2 \left[\mathrm{A}^*\right]\left[\mathrm{B}^*\right] - k_{-2}\left[\mathrm{C}^*\right]\left[\mathrm{D}^*\right]. \tag{251}$$

However, this is not the case. Species A^* cannot react with species B^* unless they are nearest neighbors. Therefore, we need to account for this in our rate expression, similar to how we needed to account for the probability of adjacent sites in our dissociative adsorption example from Section 4.1.5.

With this knowledge and in analogy with the statistical corrections introduced in Section 4.1.5, the rate expression can be given by

$$r_{\mathrm{SR}} = \frac{k_2 z \left[\mathrm{A}^*\right]\left[\mathrm{B}^*\right]}{[*]_0} - \frac{k_{-2} z \left[\mathrm{C}^*\right]\left[\mathrm{D}^*\right]}{[*]_0}, \tag{252}$$

where z is the coordination number of the adsorption site. Note that we use a multiplicative factor of $z/[*]_0$ instead of $z/2[*]_0$ because A^* and B^* are distinguishable. If the surface reaction takes place between two indistinguishable species, we would need to retain the 1/2 factor.

From here on out, we will lump the z (or $z/2$) factor, where applicable, into the rate constant for the sake of simplicity:

---

[51] For additional considerations when reporting and interpreting TOFs, refer to F. Schüth, M.D. Ward, J.M. Buriak, "Common Pitfalls of Catalysis Manuscripts Submitted to Chemistry of Materials", *Chem. Mater.*, 30, 3599–3600 (2018). More detailed discussion on this topic can be found in S. Kozuch, J.M.L. Martin, "Turning Over Definitions in Catalytic Cycles", *ACS Catal.*, 2, 2787–2794 (2012) and the corresponding response G. Lente, "Comment on 'Turning Over Definitions in Catalytic Cycles'", *ACS Catal.*, 3, 381–382 (2013).

[52] The surface reaction $\mathrm{A}^* + * \rightleftharpoons \mathrm{B}^* + *$ would be another type of dual-site mechanism with an analogous solution.

$$r_{\text{SR}} = \frac{k_2' \left[A^* \right] \left[B^* \right]}{[*]_0} - \frac{k_{-2}' \left[C^* \right] \left[D^* \right]}{[*]_0}. \tag{253}$$

If we wanted to write the above expression in terms of a site-normalized rate, we would instead have

$$r_{\text{SR}}' \equiv \frac{r_{\text{SR}}}{[*]_0} = k_2' \theta_A \theta_B - k_{-2}' \theta_C \theta_D. \tag{254}$$

Notice how the above expression is analogous to Equation 251 with concentrations replaced by fractional coverages. If we had not accounted for the $z/[*]_0$ factor, then this analogy would no longer hold.

4.2.3. 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 a Langmuir–Rideal mechanism. When the adsorbed molecule reacts with a molecule that is loosely physisorbed nearby, it is instead referred to as an Eley–Rideal reaction.

The general equation for such a process is

$$A^* + B \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} C^*. \tag{255}$$

The net rate for the surface reaction is as follows:

$$r_{\text{SR}} = k_2 \left[A^* \right] p_B - k_{-2} \left[C^* \right]. \tag{256}$$

This is largely analogous to the typical single and dual-site surface reactions, except that here we are considering the partial pressure of species B rather than the concentration of B^*. We also do not need to account for lattice statistics since there are no surface site pairs involved.
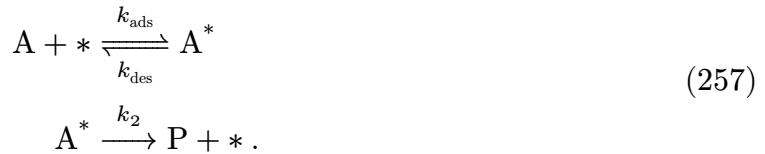
4.3. Catalytic Reaction Mechanisms

4.3.1. LHHW Kinetics: The Pedagogical Case

With our newfound knowledge of the individual steps that take place in a catalytic reaction, we can combine them to produce a kinetic model. When invoking Langmuirian adsorption behavior with the assumption that adsorbates are randomly distributed on the surface (known as the Hinshelwood assumption), the resulting kinetic models are known as Langmuir–Hinshelwood–Hougen–Watson (LHHW) models.

4.3.1.1. Rate Law Derivation

Consider the simple reaction scheme given by

$$A + * \underset{k_{\text{des}}}{\overset{k_{\text{ads}}}{\rightleftharpoons}} A^* \tag{257}$$

$$A^* \xrightarrow{k_2} P + *.$$

for the net reaction $A \longrightarrow P$.[53] The net reaction rate is given by $r = r_P$, and so we will focus on the rate of product production from here. The rate of product production is given by

$$r_P = k_2 \left[A^*\right]. \tag{258}$$

We ultimately want to write our rate without transient intermediates. If we are able to assume that the adsorption of A is quasi-equilibrated, then we have

$$K_{\text{ads}} = \frac{\left[A^*\right]}{p_A [*]} \tag{259}$$

$$\left[A^*\right] = K_{\text{ads}} p_A [*]. \tag{260}$$

The quasi-equilibrium approximation is fairly reasonable to invoke here because surface reactions are typically much slower than the adsorption or desorption steps, although there are certainly exceptions.

Additionally, we have the site balance of

$$[*]_0 = [*] + \left[A^*\right], \tag{261}$$

which if we solve for $[*]$ and plug the resulting expression into Equation 260 yields

$$\left[A^*\right] = K_{\text{ads}} p_A \left([*]_0 - \left[A^*\right]\right) \tag{262}$$

$$\left[A^*\right] + K_{\text{ads}} p_A \left[A^*\right] = K_{\text{ads}} p_A [*]_0 \tag{263}$$

$$\left[A^*\right] = \frac{K_{\text{ads}} p_A [*]_0}{1 + K_{\text{ads}} p_A}. \tag{264}$$

Plugging this into our original rate expression from Equation 258 results in

$$r_P = \frac{k_2 K_{\text{ads}} p_A [*]_0}{1 + K_{\text{ads}} p_A}. \tag{265}$$

Note that if we chose to write the above expression in terms of a turnover frequency, there would be no $[*]_0$ term remaining, which is a common feature of LHHW rate expressions.

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[53]It is typically the case that the reaction and desorption steps are separate elementary processes. However, we are considering them as one elementary process here for the sake of demonstration.

4.3.1.2. Alternate Approach

What if we were not convinced that we could invoke the quasi-equilibrium approximation on the reversible adsorption step? Here, we will show that the pseudo-steady state approach yields a very similar—and, in fact, more general—result.

We once again start with our rate of production:

$$r_{\text{P}} = k_2 \left[\text{A}^* \right]. \tag{266}$$

However, instead of invoking an equilibrium condition, we apply the pseudo-steady state approximation on the transient intermediate A^* as follows:

$$r_{\text{A}^*} \approx 0 = k_{\text{ads}} p_{\text{A}} [*] - k_{\text{des}} \left[\text{A}^* \right] - k_2 \left[\text{A}^* \right]. \tag{267}$$

We also have the same site balance of

$$[*]_0 = [*] + \left[\text{A}^* \right]. \tag{268}$$

Combining our site balance with Equation 267 will ultimately yield

$$\left[\text{A}^* \right] = \frac{K_{\text{ads}} p_{\text{A}} [*]_0}{1 + K_{\text{ads}} p_{\text{A}} + \frac{k_2}{k_{\text{des}}}}, \tag{269}$$

such that

$$r_{\text{P}} = \frac{k_2 K_{\text{ads}} p_{\text{A}} [*]_0}{1 + K_{\text{ads}} p_{\text{A}} + \frac{k_2}{k_{\text{des}}}}. \tag{270}$$

We can see that the pseudo-steady state solution is identical to the quasi-equilibrium solution when $k_2 / k_{\text{des}} \ll 1 + K_{\text{ads}} p_{\text{A}}$. This is expected to be the case for the quasi-equilibrium approach since k_{des} must be very high compared to k_2 for quasi-equilibrium to be invoked in the first place. The quasi-equilibrium approximation can be thought of as a more strict approximation than the pseudo-steady state hypothesis, as demonstrated by this example.

4.3.1.3. Limiting Cases

4.3.1.3.1. Strong Adsorption

Here, we will explore some limiting cases for r_{P} using the quasi-equilibrium form from Equation 265:

$$r_P = \frac{k_2 K_{ads} p_A [*]_0}{1 + K_{ads} p_A}. \tag{271}$$

If A adsorbs strongly to the surface (and/or we are in the high pressure limit of p_A), then we arrive at

$$r_P \approx k_2 [*]_0 \quad (K_{ads} p_A \gg 1). \tag{272}$$

In this scenario, the apparent reaction order of A is 0 because virtually all the sites are covered in A, such that slight variations in A do not have an appreciable influence on the overall rate. We know the apparent reaction order is 0 in A from the fact that there is no p_A term in the simplified rate law. We can also see this from the formal definition given in Equation 80:

$$\alpha_{A,app} = p_A \left(\frac{\partial \ln(r)}{\partial p_A} \right)_{p_i, i \neq j} = p_A \frac{\partial \ln(k_2 [*]_0)}{\partial p_A} = 0. \tag{273}$$

In this scenario, the apparent rate constant would simply be[54]

$$k_{app} = k_2. \tag{274}$$

By extension, the apparent activation energy is the activation energy associated with k_2, which we will denote $E_{a,2}$. This too can be derived from the formal definition given in Equation 77:

$$E_{app} = RT^2 \frac{\partial \ln(k_{app})}{\partial T} \tag{275}$$

$$E_{app} = RT^2 \frac{\partial \ln\left(A_2 e^{-\frac{E_{a,2}}{RT}}\right)}{\partial T} = RT^2 \frac{\partial \left(A_2 - \frac{E_{a,2}}{RT}\right)}{\partial T} = RT^2 \left(\frac{E_{a,2}}{RT^2} \right) = E_{a,2}. \tag{276}$$

4.3.1.3.2. Weak Adsorption

In the opposite extreme, if A adsorbs very weakly to the surface (and/or we are in the low p_A limit), then we arrive at

$$r_P \approx k_2 K_{ads} p_A [*]_0 \quad (K_{ads} p_A \ll 1). \tag{277}$$

Here, the apparent reaction order of A is 1. Additionally, the apparent rate constant would now be

$$k_{app} = k_2 K_{ads}. \tag{278}$$

We can rewrite the apparent rate constant as

$$k_{app} = A_2 \exp\left(-\frac{E_{a,2}}{RT}\right) \exp\left(-\frac{\Delta G^\circ_{ads}}{RT}\right) \tag{279}$$

---

[54]Since $[*]_0$ is typically constant, you could in principle lump this term into k_{app}. However, since we typically treat k as being independent of concentrations, it is left out here.

$$k_{\text{app}} = A_2 \exp\left(-\frac{E_{\text{a},2}}{RT}\right) \exp\left(-\frac{\Delta H^\circ_{\text{ads}}}{RT}\right) \exp\left(\frac{\Delta S^\circ_{\text{ads}}}{R}\right) \tag{280}$$

$$k_{\text{app}} = A_2 \exp\left(\frac{\Delta S^\circ_{\text{ads}}}{R}\right) \exp\left(-\frac{E_{\text{a},2} + \Delta H^\circ_{\text{ads}}}{RT}\right). \tag{281}$$

As such, we arrive at a functional form of

$$k_{\text{app}} = A_{\text{app}} \exp\left(-\frac{E_{\text{a,app}}}{RT}\right), \tag{282}$$

where

$$A_{\text{app}} = A_2 \exp\left(\frac{\Delta S^\circ_{\text{ads}}}{R}\right), \qquad E_{\text{a,app}} = E_{\text{a},2} + \Delta H^\circ_{\text{ads}}. \tag{283}$$

The same result can be found from the formal definition of the apparent activation energy like was done in Section 4.3.1.3.1. These apparent kinetic parameters are particularly useful for interpreting kinetic data obtained from experiments, where the net reaction is the main observable phenomena.

You may also notice something unusual with Equation 283. Since $\Delta H^\circ_{\text{ads}}$ is generally exothermic, depending on the value of $E_{\text{a},2}$, it is possible for $E_{\text{a,app}}$ to be negative. A negative apparent activation energy has been observed in several catalytic reactions, including the adsorption and cracking of *n*-alkanes in zeolites.[55]

4.3.2. Reaction Stoichiometric Numbers
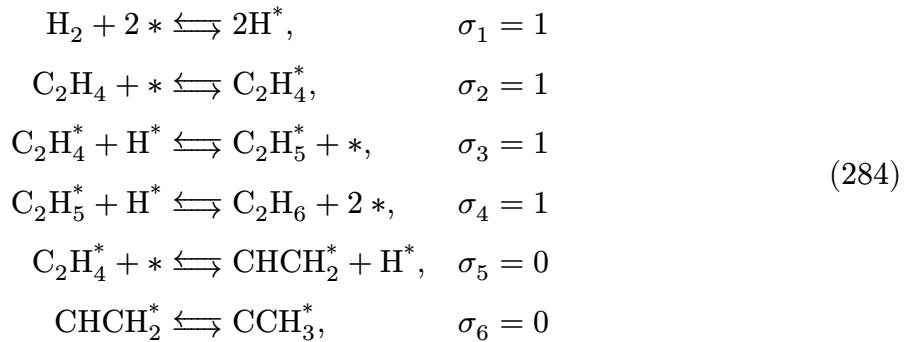
Before continuing on to more complex catalytic mechanisms, it is worth introducing a new bit of terminology. Typically, we propose a mechanism composed of many elementary steps that represent the atomistic details of the catalytic reaction as best as we can imagine. In this context, the concept of the reaction stoichiometric coefficient σ_i becomes important. Simply put, σ_i is the number of times that the i-th reaction needs to occur to yield the net reaction stoichiometry.

Consider the hydrogenation of ethylene given by the net reaction $H_2 + C_2H_4 \rightleftharpoons C_2H_6$. The following reaction mechanism is one that has been proposed in the literature:[56]

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[55]Refer to J. Wei, "Adsorption and Cracking of *n*-Alkanes over ZSM-5: Negative Activation Energy of Reaction", *Chem. Eng. Sci.*, 51, 2995–2999 (1996). Dr. James Wei, a chemical engineer, was the Dean of Engineering at Princeton University from 1991–2002.

[56]In reality, it is likely that $C_2H_6^*$ would be formed, and the desorption would be a separate step altogether. However, we have combined the steps here simply for the sake of simplicity.

$$H_2 + 2* \rightleftharpoons 2H^*, \qquad \sigma_1 = 1$$

$$C_2H_4 + * \rightleftharpoons C_2H_4^*, \qquad \sigma_2 = 1$$

$$C_2H_4^* + H^* \rightleftharpoons C_2H_5^* + *, \qquad \sigma_3 = 1$$

$$C_2H_5^* + H^* \rightleftharpoons C_2H_6 + 2*, \qquad \sigma_4 = 1 \qquad (284)$$

$$C_2H_4^* + * \rightleftharpoons CHCH_2^* + H^*, \quad \sigma_5 = 0$$

$$CHCH_2^* \rightleftharpoons CCH_3^*, \qquad \sigma_6 = 0$$

The reaction stoichiometric numbers, σ_i, describe the number of times that reaction step contributes to arrive at the net reaction. Some steps can have $\sigma_i = 0$ but still be important for the overall catalytic mechanism. For instance, even though reaction step 5 does not factor into the net reaction equation, it can still influence the kinetics by decreasing the population of $C_2H_4^*$ species and is potentially worth accounting for in a kinetic model.

If we assume that we have surpassed the induction period beyond which the pseudo-steady state hypothesis can be invoked on adsorbed intermediates, we can write

$$r_{H^*} \approx 0 = 2r_1 - r_3 - r_4 + r_5$$

$$r_{C_2H_4^*} \approx 0 = r_2 - r_3 - r_5$$

$$r_{C_2H_5^*} \approx 0 = r_3 - r_4 \qquad (285)$$

$$r_{CHCH_2^*} \approx 0 = r_5 - r_6$$

$$r_{CCH_3^*} \approx 0 = r_6,$$

where we are defining r_i to be the net rate for the i-th reaction step given by $r_i \equiv r_i^+ - r_i^-$.

From this system of equations, we can conveniently write

$$r_1 = r_2 = r_3 = r_4, \quad r_5 = 0, \quad r_6 = 0. \qquad (286)$$

This leads us to the following relationship:

$$r_i = \sigma_i r, \qquad (287)$$

where r is the net rate of the overall reaction. Put another way, in analogy with the definition of the rate of reaction based on the species-based stoichiometric numbers (Equation 19), we can state that for a catalytic cycle in pseudo-steady state that

$$r = \frac{r_i}{\sigma_i} \quad (\sigma_i \neq 0), \qquad (288)$$

where r is the net rate of the overall reaction cycle.
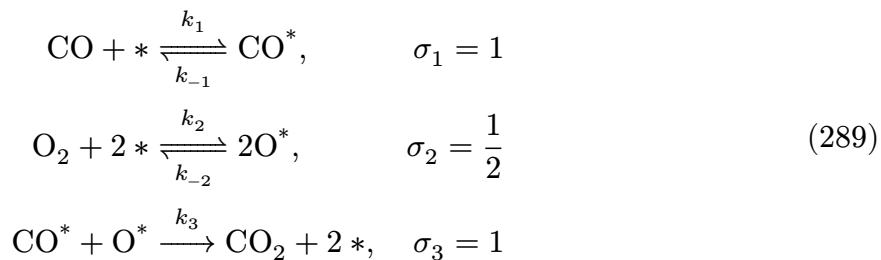
> **⚠ Caution**
>
> Equation 288 generally holds when describing a catalytic reaction when the system is considered to be at steady state (i.e. after some time period where further accumulation or depletion of adsorbates on the surface is negligible). This is often a fairly reasonable assumption to invoke. Note, however, that it only applies when the reaction proceeds through a single catalytic cycle. If there are multiple catalytic cycles, Equation 288 may not be valid.

4.3.3. LHHW Kinetics: Carbon Monoxide Oxidation

4.3.3.1. Rate Law Derivation

We will consider the reaction of CO and O_2 to produce CO_2, which takes place on a palladium surface via the net reaction $CO + \frac{1}{2}O_2 \longrightarrow CO_2$. This reaction is one of several that occur inside a catalytic converter.[57] Let us consider the following proposed reaction mechanism:

$$
\begin{aligned}
CO + * &\underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} CO^*, && \sigma_1 = 1 \\
O_2 + 2* &\underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} 2O^*, && \sigma_2 = \frac{1}{2} \\
CO^* + O^* &\overset{k_3}{\longrightarrow} CO_2 + 2*, && \sigma_3 = 1
\end{aligned}
\tag{289}
$$

We will assume that it is given that the bimolecular surface reaction of CO^* and O^* is rate-limiting. Our goal is to find a rate law for this reaction mechanism, which we might compare against experimental data to determine if the proposed mechanism is plausible or not.

Since the third reaction is said to be rate-limiting, we can state that $r = r_3$.[58] Based on our prior discussion of bimolecular surface reactions and the consideration of lattice statistics (refer to Section 4.2.2), we can write the rate of reaction as

$$
r = \frac{k_3' \left[CO^*\right]\left[O^*\right]}{[*]_0},
\tag{290}
$$

where we have defined $k_3' \equiv k_3 z$ as a matter of simplicity.[59]

---

[57] For an interesting video on catalytic converters, check out the following from Technology Connections: https://youtu.be/Aytf6ARcs8s°.

[58] If we had written the net reaction as $2\,CO + O_2 \longrightarrow 2CO_2$, then we would instead have $r = r_3/2$ since $\sigma_3 = 2$ in such a scenario. This is simply a matter of bookkeeping based on the precise definition of the "reaction" that is being considered for the reaction rate law.

[59] If you prefer to think about the rate of change of the product, note that $r = r_3 = r_{CO_2}$ since CO_2 is only produced in the third reaction. In other words, the rate of reaction is identical to the rate of CO_2 production here.

Since $[CO^*]$ and $[O^*]$ cannot be easily measured, we seek to replace these variables in Equation 290. By stating that the third reaction is rate-limiting, this implies that the other reversible adsorption steps are all quasi-equilibrated. Invoking the quasi-equilibrium condition yields

$$K_1 = \frac{[CO^*]}{p_{CO}[*]}, \qquad K_2 = \frac{[O^*]^2}{p_{O_2}[*]^2}. \tag{291}$$

Solving for the adsorbed species concentrations yields

$$[CO^*] = K_1 p_{CO}[*], \qquad [O^*] = [*]\sqrt{K_2 p_{O_2}}. \tag{292}$$

Now we write out the site balance:

$$[*]_0 = [*] + [CO^*] + [O^*]. \tag{293}$$

Plugging Equation 292 into Equation 293 yields

$$[*]_0 = [*] + K_1 p_{CO}[*] + [*]\sqrt{K_2 p_{O_2}}$$
$$[*] = \frac{[*]_0}{1 + K_1 p_{CO} + \sqrt{K_2 p_{O_2}}}. \tag{294}$$

Plugging Equation 294 into Equation 292 results in

$$[CO^*] = \frac{K_1 p_{CO}[*]_0}{1 + K_1 p_{CO} + \sqrt{K_2 p_{O_2}}}, \qquad [O^*] = \frac{[*]_0 \sqrt{K_2 p_{O_2}}}{1 + K_1 p_{CO} + \sqrt{K_2 p_{O_2}}}. \tag{295}$$

Finally, substituting Equation 295 into Equation 290 results in the desired rate expression based on experimental observables:

$$r = \frac{k_3' K_1 p_{CO}[*]_0 \sqrt{K_2 p_{O_2}}}{\left(1 + K_1 p_{CO} + \sqrt{K_2 p_{O_2}}\right)^2}. \tag{296}$$

Note that if we did not include the $z/[*]_0$ correction in Equation 290, the resulting rate expression at the end of the derivation would have a $[*]_0^2$ term instead of $[*]_0$ in the numerator. In general, the presence of higher-order $[*]_0$ terms is a sign that lattice statistics have been neglected.[60]

4.3.3.2. Limiting Cases

As a sanity check, we can see that if $p_{CO} \to \infty$ or $p_{O_2} \to \infty$, then $r_{CO_2} \to 0$, which makes sense since both species need to be present on the surface so they can react with one another.

---

[60]For an alternate opinion about the $[*]_0$ term in catalytic rate expressions, refer to D. Kiani, I.E. Wachs, "The Conundrum of Pair Sites in Langmuir–Hinshelwood Reaction Kinetics in Heterogeneous Catalysis", *ACS Catal.*, 14, 10260–10270 (2024). Note that the aforementioned paper is at odds with N.K. Razdan, A. Bhan, "Kinetic description of site ensembles on catalytic surfaces", *Proc. Natl. Acad. Sci. U.S.A.*, 118, e2019055118 (2021).

We can also consider what happens in other limiting cases. For instance, if CO binds very strongly such that K_1 is sufficiently large, we may arrive at the simplified equation

$$r = \frac{k_3'[*]_0\sqrt{K_2 p_{O_2}}}{K_1 p_{CO}} \quad \left(K_1 p_{CO} \gg 1 + \sqrt{K_2 p_{O_2}}\right), \tag{297}$$

where the apparent order of CO is –1, and the apparent order of O_2 is +1/2. The apparent order of –1 in CO makes sense because the surface is nearly covered by CO adsorbates, so increasing CO further will only reduce the overall rate.

Conversely, if O_2 binds very strongly such that K_2 is sufficiently large, we may arrive at the simplified equation

$$r \approx \frac{k_3' K_1 p_{CO}[*]_0}{\sqrt{K_2 p_{O_2}}} \quad \left(\sqrt{K_2 p_{O_2}} \gg 1 + K_1 p_{CO}\right), \tag{298}$$
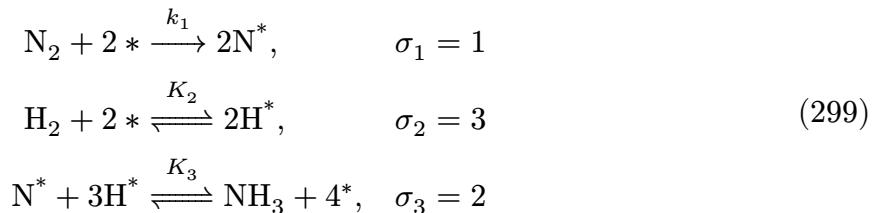
which has CO with an apparent order of +1 but O_2 with an apparent order of –1/2, indicating that O_2 is now inhibiting the overall rate, as would be expected. In each of these limiting cases, it is important to remember that these are not the rate laws themselves but rather what may be observed experimentally for a given set of conditions.

4.3.4. Most Abundant Reaction Intermediate

We will introduce one common approximation in analyzing the kinetics of catalytic mechanisms. When one adsorbate on the surface is present in great excess, it is referred to as the most abundant reaction intermediate (MARI). Invoking the MARI approximation can greatly simplify mechanistic analyses.

4.3.4.1. Ammonia Synthesis

Consider ammonia synthesis via the Haber–Bosch process, which occurs with the net reaction $N_2 + 3H_2 \longrightarrow 2NH_3$. We will consider the following proposed mechanism:

$$\begin{aligned} N_2 + 2* &\xrightarrow{k_1} 2N^*, & \sigma_1 &= 1 \\ H_2 + 2* &\xrightleftharpoons{K_2} 2H^*, & \sigma_2 &= 3 \\ N^* + 3H^* &\xrightleftharpoons{K_3} NH_3 + 4*, & \sigma_3 &= 2 \end{aligned} \tag{299}$$

As part of the problem setup, we will assume that it is known that the dissociative adsorption of N_2 is the rate-limiting step. This is a fairly reasonable approximation given the extremely strong triple bond of N_2, which is difficult to cleave. We will also take it as given that H^* is the MARI on the basis of experiments. Note that from the written expressions, it should be clear that the third reaction is not elementary given how many surface species are involved in the reaction. As we will show below, this is perfectly okay if we can invoke the MARI approximation.

The rate of reaction is based on the rate-limiting step (i.e. N_2 dissociation), such that $r = r_1$.[61] Therefore, we can write out the rate law as follows:

$$r = \frac{k_1' p_{N_2} [*]^2}{[*]_0}.$$

(300)

We wish to get rid of $[*]$ as usual, so we will write a site balance. Here, however, our site balance can be greatly simplified by invoking the MARI approximation:

$$[*]_0 = [H^*] + [*].$$

(301)

We have two species here that we wish to get rid of: $[H^*]$ and $[*]$. Since the first reaction is rate-limiting, this causes the other reactions to be in quasi-equilibrium. We proceed by invoking quasi-equilibrium on step 2 to arrive at

$$K_2 = \frac{[H^*]^2}{p_{H_2} [*]^2}.$$

(302)

Solving for $[H^*]$ yields

$$[H^*] = [*] \sqrt{K_2 p_{H_2}},$$

(303)

where we naturally only take the positive root solution. We can plug the above expression into our site balance to arrive at

$$[*] = \frac{[*]_0}{1 + \sqrt{K_2 p_{H_2}}}.$$

(304)

Plugging the above expression into our rate expression results in

$$r = \frac{k_1' p_{N_2} [*]_0}{\left(1 + \sqrt{K_2 p_{H_2}}\right)^2}.$$

(305)
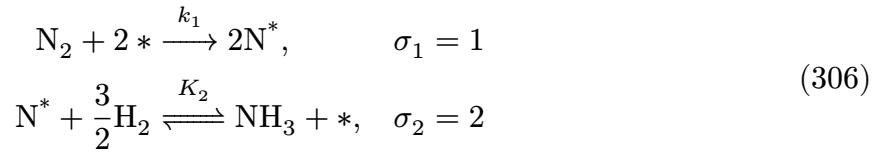
We can see that the rate expression can be written without any transient intermediates and without knowing any particular details about the non-elementary (i.e. third) step in the proposed mechanism since K_3 never appears in our rate. In essence, the MARI approximation allows us to greatly reduce the complexity of our mechanism.

4.3.4.2. Ammonia Synthesis Revisited

We will again consider the Haber–Bosch process with the net reaction $N_2 + 3H_2 \longrightarrow 2NH_3$. Here, however, we will consider a slightly modified set of reaction equations:

---

[61]The net rate of ammonia production would be given by $r = r_1 = r_3/2$ by invoking Equation 288. That said, there is not much you can do to find r_3 directly based on the information in the problem statement, especially since the reaction is non-elementary.

$$N_2 + 2* \xrightarrow{k_1} 2N^*, \qquad \sigma_1 = 1$$

$$N^* + \frac{3}{2}H_2 \xrightleftharpoons{K_2} NH_3 + *, \quad \sigma_2 = 2 \tag{306}$$

We will still invoke that the dissociative adsorption of N_2 is rate-limiting. However, now we will consider the case where N^* is the MARI, perhaps due to the use of a different catalyst than in the previous example. This example is notably different in that the rate-determining step is also the one involving the MARI. Clearly, the second equation cannot possibly be an elementary step, but as we will once again demonstrate, this is perfectly acceptable if we are able to invoke the MARI approximation.

The rate of reaction can be expressed based on the rate-determining step as $r = r_1$, such that

$$r = \frac{k_1' p_{N_2}[*]^2}{[*]_0}. \tag{307}$$

As usual, we want to get rid of $[*]$ from our rate expression. We will invoke quasi-equilibrium on the second step since it is, by definition, fast with respect to the rate-determining step. Even though we cannot write step 2 using an elementary rate expression, we can still express its equilibrium constant via

$$K_2 = \frac{p_{NH_3}[*]}{[N^*]p_{H_2}^{3/2}}, \tag{308}$$

as demonstrated in Section 2.4.5.

We also have our site balance, which can be written in simplified form due to the MARI approximation:

$$[*]_0 = [*] + [N^*]. \tag{309}$$

Note that we have excluded any other surface species even though there must be some amount of H^* on the surface in order to make NH_3.

Solving for $[N^*]$ in Equation 308 yields

$$[N^*] = \frac{p_{NH_3}[*]}{K_2 p_{H_2}^{3/2}}, \tag{310}$$

and plugging $[N^*]$ into the site balance results in

$$[*]_0 = [*] + \frac{p_{NH_3}[*]}{K_2 p_{H_2}^{3/2}} \tag{311}$$

$$[*] = \frac{[*]_0}{1 + \frac{p_{NH_3}}{K_2 p_{H_2}^{3/2}}}. \tag{312}$$
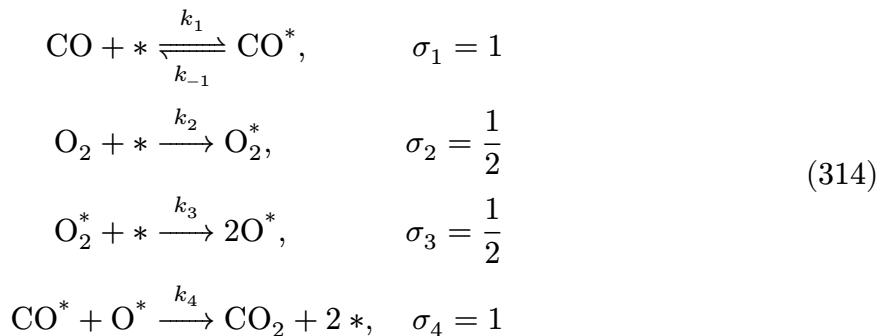
Finally, we can plug the above equation into our rate expression and simplify:

$$r = \frac{k_1' p_{N_2} [*]_0}{\left(1 + \frac{p_{NH_3}}{K_2 p_{H_2}^{3/2}}\right)^2}. \tag{313}$$

The main conclusion from this exercise is that we do not need any information about intermediate steps in the mechanism or the underlying details of the steps associated with K_2. When invoking the MARI, we were able to write the rate expression using an equilibrium expression and an elementary rate law.

4.3.4.3. CO Oxidation Revisited

In Section 4.3.3, we went over a representative LHHW kinetic model derivation for CO oxidation. We will now revisit the CO oxidation process given by $CO + \frac{1}{2}O_2 \longrightarrow CO_2$ via a slightly different proposed mechanism involving the irreversible adsorption of O_2 to a single surface site, after which it dissociates:

$$
\begin{aligned}
CO + * &\underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} CO^*, & \sigma_1 &= 1 \\[6pt]
O_2 + * &\overset{k_2}{\longrightarrow} O_2^*, & \sigma_2 &= \frac{1}{2} \\[6pt]
O_2^* + * &\overset{k_3}{\longrightarrow} 2O^*, & \sigma_3 &= \frac{1}{2} \\[6pt]
CO^* + O^* &\overset{k_4}{\longrightarrow} CO_2 + 2*, & \sigma_4 &= 1
\end{aligned}
\tag{314}
$$

As part of the problem setup, we will assume that CO^* is the MARI on the basis of experiments in contrast with how we approached the mechanism in Section 4.3.3. Furthermore, as part of the problem setup, the reversible adsorption of CO on the surface is assumed to be quasi-equilibrated. Note, however, that this does not tell us anything specifically about a single rate-determining step.

If we wish to derive the rate law, it may not be immediately clear how to proceed given the information in the problem setup. Nonetheless, by invoking Equation 288, life gets a bit easier. Given the reaction stoichiometric coefficients, we can state that

$$r = r_1 = 2r_2 = 2r_3 = r_4, \tag{315}$$

where $r_1 = r_1^+ - r_1^-$, and the other individual reaction rates are describing the rate of the corresponding irreversible reaction. This allows us to find any of the individual reaction rates in order to find the rate law since they are all interrelated.

While there are several ways to approach this problem, we will focus on the second reaction:

$$r = 2r_2 = 2k_2 p_{O_2}[*]. \tag{316}$$

We need to get rid of the $[*]$ term, and this will involve the use of a site balance, which is simplified in our case due to the MARI approximation in the problem setup:

$$[*]_0 = [*] + [CO^*]. \tag{317}$$

If we were to plug Equation 317 into Equation 316, we would still have a $[CO^*]$ term to get rid of. This implies that we will need some information about the adsorption of CO. By invoking the quasi-equilibrium approximation as stated in the problem setup, we have

$$K_1 = \frac{[CO^*]}{p_{CO}[*]}. \tag{318}$$

Solving or CO^* in the above expression and plugging it into the site balance yields

$$[*]_0 = [*] + K_1 p_{CO}[*], \tag{319}$$

which can be rewritten as

$$[*] = \frac{[*]_0}{1 + K_1 p_{CO}}. \tag{320}$$

Plugging Equation 320 into Equation 316 yields our rate expression:

$$r = \frac{2k_2 p_{O_2}[*]_0}{1 + K_1 p_{CO}}. \tag{321}$$

This exercise has demonstrated how a rate law can be determined for a surface-catalyzed reaction without needing to invoke the rate-determining step concept.

As a final note, we will make a brief comment about the apparent activation energy in the limit of $K_1 p_{CO} \gg 1$, which might be the case for a catalyst where CO binds to the surface very strongly and/or when the system is flooded with CO. In doing so, we have

$$r = \frac{2k_2 p_{O_2}[*]_0}{K_1 p_{CO}} \quad (K_1 p_{CO} \gg 1). \tag{322}$$

The apparent rate constant, from which the apparent activation energy can be derived, would be given by

$$k_{\text{app}} \equiv \frac{k_2}{K_1} = \frac{A_2 \exp\left(-\frac{E_{\text{a},2}}{RT}\right)}{\exp\left(-\frac{\Delta G_1^\circ}{RT}\right)} = A_2 \exp\left(-\frac{E_{\text{a},2} - \Delta G_1^\circ}{RT}\right)$$

$$k_{\text{app}} = A_2 \exp\left(\frac{\Delta S_1^\circ}{R}\right) \exp\left(-\frac{E_{\text{a},2} - \Delta H_1^\circ}{RT}\right), \tag{323}$$

such that
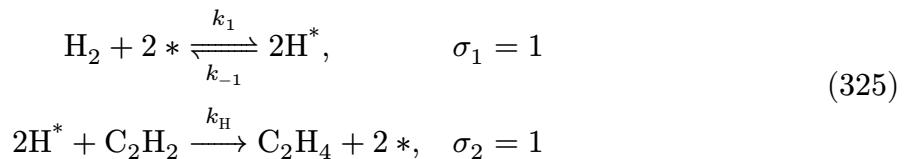
$$A_{\text{app}} = A_2 \exp\left(\frac{\Delta S_1^\circ}{R}\right), \qquad E_{\text{app}} = E_{\text{a},2} - \Delta H_1^\circ. \tag{324}$$

Since the activation energy for an adsorption process is almost always zero,[62] this implies that $E_{\text{app}} \approx -\Delta H_1^\circ$. In other words, the apparent activation energy for this reaction is approximately the negative value of the heat of adsorption of CO on the surface (when $K_1 p_{\text{CO}} \gg 1$).[63]

4.3.5. Non-LHHW Kinetics

4.3.5.1. Eley–Rideal Mechanism

Consider the net reaction $C_2H_2 + H_2 \longrightarrow C_2H_4$ with the following proposed mechanism:[64]

$$H_2 + 2* \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} 2H^*, \qquad \sigma_1 = 1$$

$$2H^* + C_2H_2 \overset{k_H}{\longrightarrow} C_2H_4 + 2*, \quad \sigma_2 = 1 \tag{325}$$

We will assume that the hydrogenation reaction is rate-limiting, such that the H_2 adsorption is quasi-equilibrated.

Here, we have a reaction between an adsorbed species and a loosely physisorbed species (i.e. an Eley–Rideal mechanism, as previously discussed in Section 4.2.3), which is slightly different than the typical LHHW kinetics since the reaction is not taking place solely on the surface.[65] The rate of product formation, which is identical to the rate of reaction here, is given by

$$r = \frac{k_H' \left[H^*\right]^2 p_{C_2H_2}}{[*]_0}. \tag{326}$$

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[62]For an exception, refer to K. Carsch et al., "Multi-Gas Adsorption with Single-Site Cooperativity in a Metal–Organic Framework", *Science* (in press).

[63]For example, refer to M. Boudart, "Heterogeneous Molecular Catalysis: Oxymoron or Reality?", *J. Mol. Catal. A: Chem.*, 120, 271 (1997). Boudart was a faculty member in the Department of Chemical Engineering at Princeton University from 1954–1961.

[64]The second step is an example of a termolecular reaction that is actually quite likely to occur. Since the adsorbates are anchored onto the surface, it is natural for C_2H_2 to be hydrogenated in this way if it is well-aligned with the two hydrogen adsorbates.

[65]For a critical discussion on the viability of Eley–Rideal mechanisms compared to Langmuir–Rideal mechanisms, refer to D. Kiani, I.E. Wachs, "Practical Considerations for Understanding Surface Reaction Mechanisms Involved in Heterogeneous Catalysis" *ACS Catal.*, 14, 16770–16784 (2024).

To get rid of the intermediate in our rate expression, we can invoke the quasi-equilibrium assumption on the first step to arrive at

$$K_1 = \frac{\left[H^*\right]^2}{p_{H_2}[*]^2} \tag{327}$$

$$\left[H^*\right] = [*]\sqrt{K_1 p_{H_2}}.$$

Plugging this into our expression for r yields

$$r = \frac{k_H' K_1 [*]^2 p_{H_2} p_{C_2H_2}}{[*]_0}. \tag{328}$$

Now we can write our site balance:

$$[*]_0 = [*] + \left[H^*\right] = [*] + [*]\sqrt{K_1 p_{H_2}} = [*]\left(1 + \sqrt{K_1 p_{H_2}}\right), \tag{329}$$

such that

$$[*] = \frac{[*]_0}{1 + \sqrt{K_1 p_{H_2}}}. \tag{330}$$

Substituting this into r yields

$$r = \frac{k_H' K_1 [*]_0 p_{H_2} p_{C_2H_2}}{\left(1 + \sqrt{K_1 p_{H_2}}\right)^2}. \tag{331}$$

This is essentially a simplified form of the analogous LHHW model.

4.3.5.2. Mars–van Krevelen Mechanism

In some cases, the catalytic adsorption sites can be part of the catalytic cycle itself, such as the formation of a high-energy defect site or vacancy in the lattice that is reversibly formed and consumed during the course of the reaction. This is known as a Mars–van Krevelen cycle. There are several references that can be read to learn more about the derivation of the rate in a Mars–van Krevelen mechanism. We refrain from doing so here simply as a matter of brevity and, in part, because it has been shown that the original derivation has numerous logical inconsistencies that are difficult to justify.[66]

4.3.5.3. Limitations of LHHW

Aside from variations on the typical surface reactions invoked in LHHW models, there are many inherent assumptions of LHHW kinetics that may be violated in reality. LHHW kinetic models inherit all the assumptions associated with the Langmuir model of adsorption, including energetically uniform adsorption sites and a lack of adsorbate–adsorbate interactions. If this

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[66]M.A. Vannice, "An analysis of the Mars–van Krevelen rate expression", *Catal. Today*, 123, 18–22 (2007).

approximation breaks down, additional complexity must be introduced. Additionally, through the Hinshelwood assumption, the adsorbates are assumed to be randomly distributed on the surface.

A clear demonstration of a failure mode with the LHHW model is related to a phenomenon described as "jamming." Consider the dissociative chemisorption reaction

$$H_2 + 2* \xrightarrow{k} 2H^*. \tag{332}$$

We know that the site-normalized rate for this process can be given by

$$r' = k' p_{H_2} \theta_*^2. \tag{333}$$

If we treat adsorption as occurring on a 2D lattice, it is possible to have a "jammed lattice" at sufficiently high values of θ_H like that shown in Figure 13. Here, there are still vacant sites available (i.e. $\theta_* > 0$). However, none of these vacant sites can lead to a further reaction because there is no space for two H atoms to adsorb at adjacent sites. In other words, r' should be zero in the jammed state, but this is inconsistent with Equation 333 for $\theta_* > 0$. Clearly, the Langmuir–Hinshelwood formalism cannot reproduce the jammed state where $\theta_* > 0$ but $\theta_{**} = 0$.
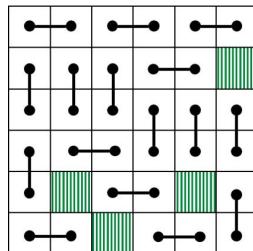
Figure 13: Depiction of a jammed lattice, where the vacant squares are free surface sites.

Of course, this does not necessarily mean a LHHW model cannot yield a sufficiently good fit to experimentally obtained kinetic data. Rather, it means that the interpretability may be limited. We refer the interested reader to external sources for further discussions about potential improvements to the LHHW formalism, particularly as it relates to dealing with site ensembles.[67]

[67] N.K. Razdan, A. Bhan, "Kinetic description of site ensembles on catalytic surfaces", *Proc. Natl. Acad. Sci. U.S.A.*, 118, e2019055118 (2021). Also refer to N.K. Razdan, A. Bhan, "Catalytic site ensembles: A context to reexamine the Langmuir–Hinshelwood kinetic description", *J. Catal.*, 404, 726–744 (2021).

5. Chemical Reactor Archetypes

Previously, we have discussed the kinetics of chemical reactions without discussing the details of the reactor used to run the reactions. Here, we provide a brief overview of different reactor technologies operating isothermally. Later in the course, we will revisit the reactor design equations to account for non-isothermal effects.

5.1. The Material Balance

In order to understand the behavior of chemical reactors, we must start with the key governing principle behind it all: the conservation of mass. Consider a chemical reaction taking place inside a reactor, and focus on a unit volume within the reactor itself. We can ask ourselves the question: what is the rate of change of species A_j within our control volume? Species A_j will enter the control volume, exit the control volume, and (potentially) be generated or consumed due to a chemical reaction. This is depicted in Figure 14.
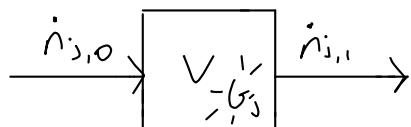
Figure 14: Schematic of a reactor volume, V, with an inlet molar flow given by $\dot{n}_{j,0}$, outlet molar flow given by $\dot{n}_{j,1}$ and rate of producing species A_j from chemical reactions given by G_j.

Written out, this can be described as follows:

$$\left(\text{rate of accumulation of } A_j\right) = \left(\text{rate of flow of } A_j \text{ in}\right) - \left(\text{rate of flow of } A_j \text{ out}\right) \\ + \left(\text{rate of generation of } A_j\right) \tag{334}$$

or mathematically as

$$\frac{\mathrm{d}n_j}{\mathrm{d}t} = \dot{n}_{j,0} - \dot{n}_{j,1} + G_j, \tag{335}$$

where $\mathrm{d}n_j / \mathrm{d}t$ is the rate of change of species A_j in the control volume (i.e. its rate of accumulation), $\dot{n}_{j,0}$ is the molar flow rate of species A_j into the volume, $\dot{n}_{j,1}$ is the molar flow rate of species A_j out of the volume at time t, and G_j is the rate of generation of species A_j from chemical reactions.

The generation term, G_j, is of particular importance given that it is the direct consequence of any chemical reactions taking place in the system. By definition, its value is positive if A is serving as a net product in the chemical reactions taking place, while its value is negative if A is serving as a net reactant being consumed. Typically, one measures the change in concentration of a species over time, which we have been denoting as r_j. We can express G_j more concretely as follows:

$$G_j = \int r_j \, \mathrm{d}V \tag{336}$$

where r_j is the rate of production of species A_j, such that it is positive if more A_j is being generated over the course of the reaction and negative if it is being consumed. If the reaction mixture is uniform over the volume, them $G_j = r_j V$ is a suitable approximation to make.

5.2. Batch Reactors

A batch reactor is a relatively simple reactor archetype that has no input or output when the chemical reaction is occurring, as shown in Figure 15. While simple, the batch reactor is the most common reactor archetype when studying the reaction kinetics of liquid-phase reactions.
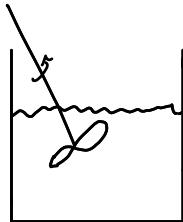
Figure 15: Schematic of a constant-volume batch reactor.

5.2.1. Concentration Basis

Without any inputs or outputs, the batch reactor has $\dot{n}_{j,0} = \dot{n}_{j,1} = 0$. As such, the mole balance is

$$\frac{\mathrm{d}n_j}{\mathrm{d}t} = \int r_j \, \mathrm{d}V. \tag{337}$$

If the reaction mixture is perfectly mixed (i.e. spatially uniform) so that r_j is independent of the volume element under consideration (a common assumption for the batch reactor), then we can consider V to be the entire reactor volume and state that

$$\frac{\mathrm{d}n_j}{\mathrm{d}t} = r_j V. \tag{338}$$

Solving for the rate of reaction of species A_j, we see that

$$r_j = \frac{1}{V} \frac{\mathrm{d}n_j}{\mathrm{d}t}. \tag{339}$$

If we assume that the batch reactor operates with a constant volume for the reaction mixture, as is oftentimes the case, we can write the rate directly in terms of concentration:

$$r_j = \frac{\mathrm{d}\left[A_j\right]}{\mathrm{d}t}. \tag{340}$$

We have arrived at the rate expression we have used countless times throughout this course.
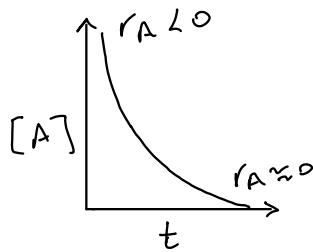
Figure 16: Concentration profile of reactant A as a function of time and its relation to r_A.

5.2.2. Conversion Basis

We may also wish to write the rate equation in terms of a fractional conversion. Recognizing that $X_j = 1 - n_j/n_{j,0}$ and therefore $n_j = n_{j,0}(1 - X_j)$, we can plug this into Equation 339 to get

$$r_j = \frac{n_{j,0}}{V}\frac{\mathrm{d}(1 - X_j)}{\mathrm{d}t} \tag{341}$$

$$r_j = -\frac{n_{j,0}}{V}\frac{\mathrm{d}X_j}{\mathrm{d}t}. \tag{342}$$
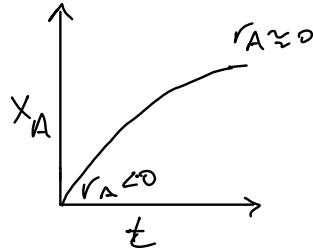
Figure 17: Conversion profile of reactant A as a function of time and its relation to r_A.

In general, one can substitute in the rate law for r_j and integrate in order to find the time to achieve a pre-specified concentration or conversion:

$$t = -n_{j,0}\int_0^{X_j}\frac{1}{r_j V}\,\mathrm{d}X_j'. \tag{343}$$

The analytical solution of this form is typically known as a design equation since it guides the design of how we wish to construct and operate our reactor.

5.3. Plug-Flow Reactors

A plug-flow reactor (PFR) is a tubular reactor that has a continuous, flowing stream containing the reaction mixture, as shown in Figure 18. The PFR is particularly common when measuring the kinetics of gas-phase reactions. Generally, solid-catalyzed vapor-phase reactions—as are common in the field of heterogeneous catalysis—are carried out with what is known as a packed-bed reactor (PBR), which in an idealized case can be modeled as a PFR.

Figure 18: Schematic of a plug-flow reactor.

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 A_j through a differential slice of the reactor volume, $\mathrm{d}V$. Assuming steady-state conditions (i.e. excluding start-up and shut-down periods), the differential mole balance can be written as

$$0 = \dot{n}_j|_V - \dot{n}_j|_{V+\delta V} + r_j \delta V \tag{344}$$

$$r_j = \frac{\dot{n}_j|_{V+\delta V} - \dot{n}_j|_V}{\delta V}. \tag{345}$$

Taking the limit as $\delta V \to 0$ (i.e. invoking the definition of the derivative) yields

$$r_j = \frac{\mathrm{d}\dot{n}_j}{\mathrm{d}V}. \tag{346}$$

Under the assumption of a constant volumetric flow rate, we can define a property known as the residence time, τ, as

$$\tau \equiv \frac{V}{\dot{v}} = \frac{A_c z}{\dot{v}} = \frac{z}{u}, \tag{347}$$

where $\dot{v}$ is the volumetric flow rate (i.e. m^3/s), A_c is the cross-sectional area of the reactor tube (i.e. m^2), z is the length of the reactor (i.e. m), and u is the linear velocity of the fluid (i.e. m/s). The value of τ has units of time and reflects the time a given packet of fluid spends inside the reactor. The residence time is the natural analogue to the clock time t used in the batch reactor derivation. We can plug the definition of τ into Equation 346 to arrive at

$$r_j = \frac{\mathrm{d}[A_j]}{\mathrm{d}\tau} = u\frac{\mathrm{d}[A_j]}{\mathrm{d}z}. \tag{348}$$

As is likely quite apparent, the design equation for a PFR is identical to that of a batch reactor where we have swapped out t for τ. For instance, if we revisit the derivation of the concentration profile for an irreversible, first-order reaction described in Section 2.6.1, we would now have $[A] = [A]_0 e^{-k\tau}$ instead of $[A] = [A]_0 e^{-kt}$.

Figure 19: Schematic of a packed-bed reactor. To ensure a consistent concentration profile in the axial dimension, the cylindrical tube needs to be filled with catalyst pellets.

If the reaction is carried out with a heterogeneous catalyst (as is the case with a PBR like that shown in Figure 19), then the catalyst mass W may be used in place of V to normalize the rate, such that Equation 346 becomes

$$r_j = \frac{d\dot{n}_j}{dW},\tag{349}$$

where r_j now has units of mol/(kg-catalyst $\cdot$ s). Similarly, τ will be more naturally described by $\tau \equiv W/\dot{m}$, where $\dot{m}$ is the mass flow rate.[68]

5.4. Continuous-Stirred Tank Reactors

The continuous-stirred tank reactor (CSTR) has an inlet and outlet flow of chemicals, as shown in Figure 20. CSTRs are typically assumed to be operated near steady state (such that the accumulation term is zero) and are assumed to be perfectly mixed.
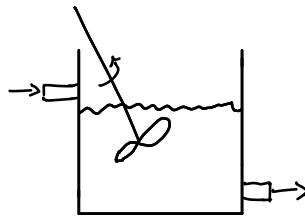
Figure 20: Schematic of a continuous-stirred tank reactor.

The mole balance for the CSTR can be written as

$$\frac{dn_j}{dt} = \dot{n}_{j,0} - \dot{n}_j + r_j V,\tag{350}$$

where $\dot{n}_{j,0}$ and $\dot{n}_j$ are the inlet and outlet molar flow rates of the j-th species, respectively. The above expression becomes the following after invoking steady-state conditions:

$$0 = \dot{n}_{j,0} - \dot{n}_j + r_j V.\tag{351}$$

Solving for the reaction rate yields

$$r_j = \frac{\dot{n}_j - \dot{n}_{j,0}}{V}.\tag{352}$$

With the above expression, we aim to write r_j in terms of species concentrations. To do so, note that for a given flow rate with a spatially uniform concentration across the reactor volume, we have

$$\dot{n}_j = [A_j]\dot{v},\tag{353}$$

where $\dot{v}$ is the volumetric flow rate. Plugging Equation 353 into Equation 352 results in

$$r_j = \frac{([A_j]\dot{v}) - ([A_j]\dot{v})_0}{V}.\tag{354}$$

---

[68]Note, however, that τ in this case technically has units of (kg-catalyst $\cdot$ s)/(kg-fluid). In order to make the units of Equation 348 work out, $[A_j]$ should have units of mol/kg-fluid, which can be related to the typical units of mol/volume through a factor of ρ.

At steady state, the volumetric flow rates in and out of the reactor are identical, such that

$$r_j = \frac{\dot{v}\left([A_j] - [A_j]_0\right)}{V}.$$ (355)

Like with the PFR, we often wish to think about the time that a given packet of fluid is within the reactor, which we will again refer to as τ as defined by $\tau \equiv V/\dot{v}$. In the context of a CSTR, we refer to τ as the space time (or average residence time) since a distribution of residence times are possible. With our definition of τ, we can write the rate expression as

$$r_j = \frac{[A_j] - [A_j]_0}{\tau}.$$ (356)

Unlike the batch reactor and PFR, the CSTR design equation contains no derivatives and is merely a simple algebraic equation.

5.4.1. Example

Consider the first-order, elementary reaction in a CSTR given by

$$\text{A} \longrightarrow \text{B}.$$ (357)

The fractional conversion of A is given by

$$X_A = 1 - \frac{[A]}{[A]_0}$$ (358)

$$[A] = [A]_0(1 - X_A).$$ (359)

Plugging this into Equation 356 yields

$$r_A = \frac{[A]_0(1 - X_A) - [A]_0}{\tau}$$ (360)

$$r_A = -\frac{[A]_0 X_A}{\tau}.$$ (361)

We know that the rate law can be written as

$$r_A = -k[A].$$ (362)

Plugging in the rate expression results in

$$-k[A] = -\frac{[A]_0 X_A}{\tau}$$ (363)

$$X_A = \frac{k\tau[A]}{[A]_0}.$$ (364)

Plugging in Equation 359 again yields

$$X_{\mathrm{A}} = \frac{k\tau[\mathrm{A}]_0(1 - X_{\mathrm{A}})}{[\mathrm{A}]_0} \tag{365}$$

$$X_{\mathrm{A}} = k\tau - k\tau X_{\mathrm{A}} \tag{366}$$

$$X_{\mathrm{A}} = \frac{k\tau}{1 + k\tau}. \tag{367}$$

For large values of $k\tau$, the conversion of A will approach 1 as expected.

5.5. Comparing Flow Reactors

We can also make a direct comparison between CSTRs and PFRs. The conversion-based design equation for the PFR is extremely similar to that of the CSTR:

$$r_j = -\dot{n}_{j,0}\frac{\mathrm{d}X_j}{\mathrm{d}V} \quad \text{(PFR)} \qquad r_j = -\dot{n}_{j,0}\frac{X_j}{V} \quad \text{(CSTR)}. \tag{368}$$

The above conversion-based design equations can be readily derived by using the definition of conversion, $X_j = 1 - \dot{n}_j/\dot{n}_{j,0}$, such that $\dot{n}_j = \dot{n}_{j,0}(1 - X_j)$ can be plugged into Equation 346 (PFR) and Equation 352 (CSTR).

We can also write the conversion-based design equations in terms of the necessary reactor volume to achieve a given conversion, which (when plotted) results in a Levenspiel plot:

$$V = \int_0^{X_j} -\frac{\dot{n}_{j,0}}{r_j}\,\mathrm{d}X_j' \quad \text{(PFR)} \qquad V = -\frac{\dot{n}_{j,0}}{r_j} \cdot X_j \quad \text{(CSTR)}. \tag{369}$$

For the PFR, the volume is simply the area under the curve in a Levenspiel plot of $-\dot{n}_{j,0}/r_j$ vs X_j. In contrast, for the CSTR, the volume is the area of a rectangle with height $-\dot{n}_{j,0}/r_j$ and width X_j in a Levenspiel plot. This is demonstrated in Figure 21. It is also apparent from Figure 21 that, for a given conversion, a CSTR has a larger required volume than the corresponding PFR.
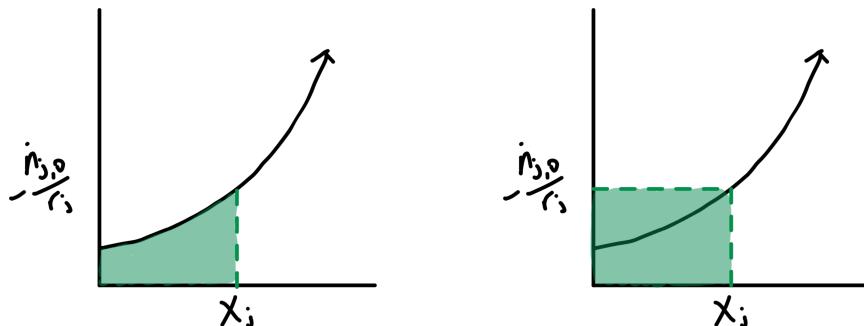
Figure 21: Levenspiel plots for a PFR (left) and CSTR (right) showing a graphical method to determine the required reactor volume for a given conversion (shaded region).

When considering several CSTRs in series, the total required volume can be reduced, as shown in Figure 22. From this comparison, it also becomes immediately clear that an infinite set of CSTRs in series would behave identically to a PFR.
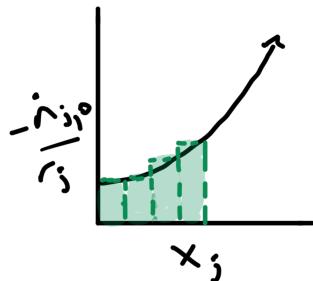
Figure 22: Levenspiel plot for a series of four CSTRs.

6. Nonisothermal Considerations

It might come as no surprise that many reactions are not operated isothermally. After all, most reactions involve an appreciable heat of reaction, and it may not always be possible or desirable to operate them with a constant heat exchange rate to maintain a given temperature.

This fact becomes critical to account for when realizing that the rate of reaction varies as a function of temperature. For instance, consider the constant-volume batch reactor design equation of

$$r_j(T) = \frac{\mathrm{d}[A_j]}{\mathrm{d}t} \quad \left(\text{with } \frac{\mathrm{d}T}{\mathrm{d}t} = 0\right), \tag{370}$$

where we are denoting $r_j(T)$ to make it clear that the rate is a function of temperature (e.g. via the Arrhenius equation). Normally, we would derive an expression for r_j and integrate to identify how the species concentration changes like in Section 2.6. Implicitly, this procedure was done under the assumption that we were operating at a given value of T. However, in a non-isothermal reactor, the value of T is not a constant value and will change with time. Therefore, under non-isothermal conditions we have

$$r_j(T) = \frac{\mathrm{d}[A_j]}{\mathrm{d}t} \quad \left(\text{with } \frac{\mathrm{d}T}{\mathrm{d}t} \neq 0\right). \tag{371}$$

Ultimately, this leads us to a coupled system of differential equations (i.e. both mass and energy balances) that must be solved simultaneously in order to understand how the reaction proceeds with time.

6.1. General Energy Balance

We will begin with the general energy balance

$$\frac{\mathrm{d}E}{\mathrm{d}t} = \dot{m}_0 \hat{E}_0 - \dot{m}_1 \hat{E}_1 + \dot{Q} + \dot{W}, \tag{372}$$

where E represents the total energy of the system, $\dot{m}$ is a mass flow rate, $\hat{E}$ is an energy per unit mass, $\dot{Q}$ is the rate of heat added to the system, and $\dot{W}$ is the rate of work done on the system. The subscripts 0 and 1 indicate the inlet and outlet streams, if applicable.

6.1.1. Work Terms

The work term is defined as

$$\dot{W} = \dot{W}_\mathrm{f} + \dot{W}_\mathrm{s} + \dot{W}_\mathrm{b}, \tag{373}$$

where the individual terms are for work done by flow streams moving through the reactor, shaft work being done by stirrers, compressors, and other equipment, and work done when moving the system boundary (if moved), respectively.

We define $\dot{W}_f$ as

$$\dot{W}_f = \dot{v}_0 P_0 - \dot{v}_1 P_1, \tag{374}$$

where $\dot{v}$ is the volumetric flow rate and P is the pressure of the stream. We can define $\dot{W}_b$ in differential form as

$$\dot{W}_b = -P\frac{dV}{dt}, \tag{375}$$

where P here is the pressure within the reactor.[69]

With this, we will rewrite $\dot{W}$ as

$$\dot{W} = \dot{v}_0 P_0 - \dot{v}_1 P_1 + \dot{W}_s - P\frac{dV}{dt}, \tag{376}$$

where we will also leave the shaft work as an abstract variable for now since it depends on what equipment is being used.[70] With a slightly more illustrative expression for $\dot{W}$, we can rewrite Equation 372 as

$$\frac{dE}{dt} = \dot{m}_0 \hat{E}_0 - \dot{m}_1 \hat{E}_1 + \dot{Q} + \dot{v}_0 P_0 - \dot{v}_1 P_1 + \dot{W}_s - P\frac{dV}{dt}. \tag{377}$$

6.1.2. Energy Terms

The total energy of the system is the sum of all internal, potential, and kinetic energies:

$$E \equiv U + KE + PE. \tag{378}$$

We can rewrite our energy balance derivative as

$$\frac{d(U + KE + PE)}{dt} = \dot{m}_0 \left(\hat{U}_0 + \widehat{KE}_0 + \widehat{PE}_0 \right) - \dot{m}_1 \left(\hat{U}_1 + \widehat{KE}_1 + \widehat{PE}_1 \right)$$
$$+ \dot{Q} + \dot{v}_0 P_0 - \dot{v}_1 P_1 + \dot{W}_s - P\frac{dV}{dt}. \tag{379}$$

We will now take advantage of the definition of enthalpy, $H \equiv U + PV$, to say that

$$\hat{H} = \hat{U} + \frac{P\dot{v}}{\dot{m}}. \tag{380}$$

Now we can state

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[69]Even though the volume may be changing, the pressure is assumed to be constant. To rationalize this, think about it as the volume of the system is changing in order to maintain the pressure at a constant value.

[70]Note that $\dot{v} = \dot{m}/\rho$, where ρ is the fluid density and $\dot{m}$ is the mass-flow rate. As such, you may see $\dot{m}/\rho$ used in place of $\dot{v}$ in the energy balance depending on the properties that are easiest to measure.

$$\frac{d(U + \mathrm{KE} + \mathrm{PE})}{dt} = \dot{m}_0 \left(\hat{H}_0 - \frac{P_0 \dot{v}_0}{\dot{m}_0} + \widehat{\mathrm{KE}}_0 + \widehat{\mathrm{PE}}_0 \right) - \dot{m}_1 \left(\hat{H}_1 - \frac{P_1 \dot{v}_1}{\dot{m}_1} + \widehat{\mathrm{KE}}_1 + \widehat{\mathrm{PE}}_1 \right)$$
$$+ \dot{Q} + \dot{v}_0 P_0 - \dot{v}_1 P_1 + \dot{W}_\mathrm{s} - P \frac{dV}{dt} \tag{381}$$

We can now simplify our expression to be

$$\frac{d(U + \mathrm{KE} + \mathrm{PE})}{dt} = \left[\dot{m}_0 \left(\hat{H}_0 + \widehat{\mathrm{KE}}_0 + \widehat{\mathrm{PE}}_0 \right) - \dot{v}_0 P_0 \right] - \left[\dot{m}_1 \left(\hat{H}_1 + \widehat{\mathrm{KE}}_1 + \widehat{\mathrm{PE}}_1 \right) - \dot{v}_1 P_1 \right]$$
$$+ \dot{Q} + \dot{v}_0 P_0 - \dot{v}_1 P_1 + \dot{W}_\mathrm{s} - P \frac{dV}{dt}, \tag{382}$$

such that it simplifies to the following:

$$\frac{d(U + \mathrm{KE} + \mathrm{PE})}{dt} = \dot{m}_0 \left(\hat{H}_0 + \widehat{\mathrm{KE}}_0 + \widehat{\mathrm{PE}}_0 \right) - \dot{m}_1 \left(\hat{H}_1 + \widehat{\mathrm{KE}}_1 + \widehat{\mathrm{PE}}_1 \right)$$
$$+ \dot{Q} + \dot{W}_\mathrm{s} - P \frac{dV}{dt}. \tag{383}$$

We will leave our general expression at this for now.

6.2. Batch Reactors

6.2.1. General Approach

The batch reactor has no flow streams, so our energy balance collapses down to

$$\frac{d(U + \mathrm{KE} + \mathrm{PE})}{dt} = \dot{Q} + \dot{W}_\mathrm{s} - P \frac{dV}{dt}. \tag{384}$$

From here, we will make some assumptions. The first assumption is that the shaft work is negligible (i.e. $\dot{W}_\mathrm{s} = 0$), which is generally true so long as the stirrers and other equipment are not drawing significant power. The second approximation we will make is that the kinetic energy of the fluid does not appreciably change (i.e. $d\mathrm{KE}/dt = 0$), which is particularly reasonable for a batch reactor but even for flow reactors since the flows themselves are usually not drastically changing speeds. The final approximation we will make is that the change in potential energy is negligible (i.e. $d\mathrm{PE}/dt = 0$), which is reasonable for a batch reactor but may not be reasonable for reactors in the presence of external fields (e.g. an electrochemical system).

With this, we have

$$\frac{dU}{dt} = \dot{Q} - P \frac{dV}{dt}. \tag{385}$$

Internal energy is a bit difficult to think about from an experimental perspective, so we will use enthalpy for the rest of our derivation, noting that the differential form is given by

$$dH \equiv dU + d(PV) = dU + P\,dV + V\,dP. \tag{386}$$

Substituting in for $\mathrm{d}U$ and plugging into Equation 385 results in

$$\frac{\mathrm{d}H - P\,\mathrm{d}V - V\,\mathrm{d}P}{\mathrm{d}t} = \dot{Q} - P\frac{\mathrm{d}V}{\mathrm{d}t} \tag{387}$$

$$\frac{\mathrm{d}H}{\mathrm{d}t} - V\frac{\mathrm{d}P}{\mathrm{d}t} = \dot{Q}. \tag{388}$$

For single-phase systems, we can write the total differential of the enthalpy as

$$\mathrm{d}H = \left(\frac{\partial H}{\partial T}\right)_{P,n_j}\mathrm{d}T + \left(\frac{\partial H}{\partial P}\right)_{T,n_j}\mathrm{d}P + \sum_j \left(\frac{\partial H}{\partial n_j}\right)_{T,p,n_{k\neq j}}\mathrm{d}n_j. \tag{389}$$

The left-most derivative is the definition of the constant-pressure heat capacity:

$$C_{\mathrm{P}} \equiv \left(\frac{\partial H}{\partial T}\right)_{P,n_j}. \tag{390}$$

Now for the second term. We will take advantage of a few thermodynamic relationships here without re-deriving them from scratch. Namely,

$$\left(\frac{\partial H}{\partial P}\right)_{T,n_j} = V - T\left(\frac{\partial V}{\partial T}\right)_{P,n_j} = V - T\alpha V = V(1 - \alpha T), \tag{391}$$

where α is the coefficient of thermal expansion defined as

$$\alpha \equiv \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_{P,n_j}. \tag{392}$$

Finally, the last term to deal with is quite simple. It is simply a restatement of the sum of partial molar enthalpies,[71] $\bar{H}_j$, where

$$\bar{H}_j \equiv \left(\frac{\partial H}{\partial n_j}\right)_{T,p,n_{k\neq j}}. \tag{393}$$

Now to put it all together:

$$\mathrm{d}H = m\hat{C}_{\mathrm{P}}\,\mathrm{d}T + V(1 - \alpha T)\,\mathrm{d}P + \sum_j \bar{H}_j\,\mathrm{d}n_j. \tag{394}$$

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[71]Note that a partial molar property is not the same as a molar property. The partial molar enthalpy describes the enthalpy change as a function of the moles of a specific species, whereas the molar enthalpy is an averaged change over all species in the system. This also implies that $\sum_j n_j \bar{H}_j = H$.

Here, we have chosen to use the specific heat capacity, $\hat{C}_{\mathrm{P}}$, in place of an extensive heat capacity since the former is a more natural property to measure. The mass can be determined quite easily from $m = \rho V$ as well, which is typically easier to measure.

Plugging the above expression into Equation 388 results in

$$\frac{m\hat{C}_{\mathrm{P}}\,\mathrm{d}T + V(1-\alpha T)\,\mathrm{d}P + \sum_j \bar{H}_j\,\mathrm{d}n_j}{\mathrm{d}t} - V\frac{\mathrm{d}P}{\mathrm{d}t} = \dot{Q}$$

$$m\hat{C}_{\mathrm{P}}\frac{\mathrm{d}T}{\mathrm{d}t} + V(1-\alpha T)\frac{\mathrm{d}P}{\mathrm{d}t} + \sum_j \bar{H}_j\frac{\mathrm{d}n_j}{\mathrm{d}t} - V\frac{\mathrm{d}P}{\mathrm{d}t} = \dot{Q}. \tag{395}$$

$$m\hat{C}_{\mathrm{P}}\frac{\mathrm{d}T}{\mathrm{d}t} - \alpha TV\frac{\mathrm{d}P}{\mathrm{d}t} = -\sum_j \bar{H}_j\frac{\mathrm{d}n_j}{\mathrm{d}t} + \dot{Q}.$$

It may seem like this is still a mess (and to some degree, it is), but we have made a lot of progress. Every algebraic term in this expression is something that can be experimentally measured or computed, although the trickiest term here is probably the summation term. We will take care of that now.

We know from the material balance on the batch reactor (Equation 339) that

$$\frac{\mathrm{d}n_j}{\mathrm{d}t} = r_j V. \tag{396}$$

For reasons that will become clearer shortly, we can use Equation 21 to restate the above expression as

$$\frac{\mathrm{d}n_j}{\mathrm{d}t} = V\sum_i \nu_{i,j} r_i, \tag{397}$$

where as usual i indicates the index of a reaction and j indicates the index of a species. Plugging this expression into our energy balance yields

$$m\hat{C}_{\mathrm{P}}\frac{\mathrm{d}T}{\mathrm{d}t} - \alpha TV\frac{\mathrm{d}P}{\mathrm{d}t} = -V\sum_j \bar{H}_j \sum_i \nu_{i,j} r_i + \dot{Q}. \tag{398}$$

We can re-group this a bit to help us out in visualizing a substitution that is about to come:

$$m\hat{C}_{\mathrm{P}}\frac{\mathrm{d}T}{\mathrm{d}t} - \alpha TV\frac{\mathrm{d}P}{\mathrm{d}t} = -V\sum_i \left(\sum_j \nu_{i,j}\bar{H}_j\right) r_i + \dot{Q}. \tag{399}$$

If we assume that the partial molar enthalpies are the same as pure component enthalpies, then we can take advantage of the following relationship that exists for a given reaction i and species j:

$$\sum_j \nu_{i,j}\bar{H}_j = \Delta H_{\mathrm{rxn},i}, \tag{400}$$

such that

$$m\hat{C}_{\text{P}}\frac{\mathrm{d}T}{\mathrm{d}t} - \alpha TV\frac{\mathrm{d}P}{\mathrm{d}t} = -V\sum_i \Delta H_{\text{rxn},i}r_i + \dot{Q}. \tag{401}$$

Should we wish to consider a net reaction rather than individual elementary reactions, the above expression can also be rewritten without the summation as

$$m\hat{C}_{\text{P}}\frac{\mathrm{d}T}{\mathrm{d}t} - \alpha TV\frac{\mathrm{d}P}{\mathrm{d}t} = -\Delta H_{\text{rxn}}rV + \dot{Q}. \tag{402}$$

There we have it—a compact expression for the energy balance in a single-phase batch reactor, which can be coupled with the material balance to better understand reaction progress.

6.2.2. Simplifying Cases

6.2.2.1. Summary

From here, there are many simplifications that can be made depending on the system under investigation:

$$m\hat{C}_{\text{P}}\frac{\mathrm{d}T}{\mathrm{d}t} = -V\sum_i \Delta H_{\text{rxn},i}r_i + \dot{Q} \quad \text{(constant } P \text{ or incompressible)} \tag{403}$$

$$m\hat{C}_{\text{V}}\frac{\mathrm{d}T}{\mathrm{d}t} = V\sum_i \left(-\Delta H_{\text{rxn},i} + \frac{\alpha}{\kappa}T\Delta V_{\text{rxn},i}\right)r_i + \dot{Q} \quad \text{(constant } V) \tag{404}$$

$$m\hat{C}_{\text{V}}\frac{\mathrm{d}T}{\mathrm{d}t} = V\sum_i \left(-\Delta H_{\text{rxn},i} + RT\sum_j \nu_{i,j}\right)r_i + \dot{Q} \quad \text{(constant } V, \text{ideal gas)} \tag{405}$$

The full details on how to derive the above expressions are provided below for clarity.

6.2.2.2. Constant Pressure or Incompressible Fluid

If the reactor operates under constant pressure, then we can say $\mathrm{d}P/\mathrm{d}t = 0$. If the reactor fluid is incompressible, then $\alpha = 0$. In both cases, we have

$$m\hat{C}_{\text{P}}\frac{\mathrm{d}T}{\mathrm{d}t} = -V\sum_i \Delta H_{\text{rxn},i}r_i + \dot{Q}. \tag{406}$$

This is a typical energy balance when dealing with liquid-phase reactions in a batch reactor.

6.2.2.3. Constant Volume

This derivation is not covered in class but is included here for the interested reader.

The constant pressure assumption is likely reasonable for most liquids but is going to be questionable for most gas-phase reactions. Here, we will derive an expression for a constant volume

reactor that may be a bit more suitable for gases. To start, we will return to our energy balance in Equation 401 from before we made any assumptions about constant pressure:

$$m\hat{C}_{\mathrm{P}}\frac{\mathrm{d}T}{\mathrm{d}t} - \alpha TV\frac{\mathrm{d}P}{\mathrm{d}t} = -V\sum_i \Delta H_{\mathrm{rxn},i} r_i + \dot{Q}. \tag{407}$$

Then we will write out the total derivative for pressure in terms of T, V, and n_j as

$$\mathrm{d}P = \left(\frac{\partial P}{\partial T}\right)_{V,n_j} \mathrm{d}T + \left(\frac{\partial P}{\partial V}\right)_{T,n_j} \mathrm{d}V + \sum_j \left(\frac{\partial P}{\partial n_j}\right)_{T,V,n_{k\neq j}} \mathrm{d}n_j. \tag{408}$$

For constant pressure, we have $\mathrm{d}V = 0$, such that

$$\mathrm{d}P = \left(\frac{\partial P}{\partial T}\right)_{V,n_j} \mathrm{d}T + \sum_j \left(\frac{\partial P}{\partial n_j}\right)_{T,V,n_{k\neq j}} \mathrm{d}n_j. \tag{409}$$

Plugging this into our energy balance yields

$$m\hat{C}_{\mathrm{P}}\frac{\mathrm{d}T}{\mathrm{d}t} - \alpha TV\frac{\left(\frac{\partial P}{\partial T}\right)_{V,n_j} \mathrm{d}T + \sum_j \left(\frac{\partial P}{\partial n_j}\right)_{T,V,n_{k\neq j}} \mathrm{d}n_j}{\mathrm{d}t} = -V\sum_i \Delta H_{\mathrm{rxn},i} r_i + \dot{Q} \tag{410}$$

$$\frac{\mathrm{d}T}{\mathrm{d}t}\left(m\hat{C}_{\mathrm{P}} - \alpha TV\left(\frac{\partial P}{\partial T}\right)_{V,n_j}\right) - \alpha TV\sum_j \left(\frac{\partial P}{\partial n_j}\right)_{T,V,n_{k\neq j}} \frac{\mathrm{d}n_j}{\mathrm{d}t} = -V\sum_i \Delta H_{\mathrm{rxn},i} r_i + \dot{Q}.$$

From here, we will take advantage of a known thermodynamic relationship:

$$m\hat{C}_{\mathrm{P}} = m\hat{C}_{\mathrm{V}} + \alpha TV\left(\frac{\partial P}{\partial T}\right)_{V,n_j}. \tag{411}$$

Plugging this into our expression, we have

$$m\hat{C}_{\mathrm{V}}\frac{\mathrm{d}T}{\mathrm{d}t} - \alpha TV\sum_j \left(\frac{\partial P}{\partial n_j}\right)_{T,V,n_{k\neq j}} \frac{\mathrm{d}n_j}{\mathrm{d}t} = -V\sum_i \Delta H_{\mathrm{rxn},i} \Delta r_i + \dot{Q}. \tag{412}$$

This is much simpler, but there is still more to be done here. We will take advantage of another thermodynamic relationship

$$\left(\frac{\partial P}{\partial n_j}\right)_{T,V,n_{k\neq j}} = \frac{\bar{V}_j}{V\kappa}, \tag{413}$$

where $\bar{V}_j$ is the partial molar volume of species j and κ is the isothermal compressibility defined as

$$\kappa \equiv -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_{T,n_j}. \tag{414}$$

Plugging this in, we get

$$m\hat{C}_{\mathrm{V}}\frac{\mathrm{d}T}{\mathrm{d}t} - \frac{\alpha}{\kappa}T\sum_j \bar{V}_j\frac{\mathrm{d}n_j}{\mathrm{d}t} = -V\sum_i \Delta H_{\mathrm{rxn},i}\Delta r_i + \dot{Q}. \tag{415}$$

Plugging in our expression for $\mathrm{d}n_j/\mathrm{d}t$ from the material balance in Equation 396 further simplifies things to

$$m\hat{C}_{\mathrm{V}}\frac{\mathrm{d}T}{\mathrm{d}t} - \frac{\alpha}{\kappa}TV\sum_j \bar{V}_j\sum_i \nu_{i,j}r_i = -V\sum_i \Delta H_{\mathrm{rxn},i}\Delta r_i + \dot{Q}, \tag{416}$$

which we again re-group as

$$m\hat{C}_{\mathrm{V}}\frac{\mathrm{d}T}{\mathrm{d}t} - \frac{\alpha}{\kappa}TV\sum_i \left(\sum_j \bar{V}_j\nu_{i,j}\right)r_i = -V\sum_i \Delta H_{\mathrm{rxn},i}\Delta r_i + \dot{Q}. \tag{417}$$

Like we did for the partial molar enthalpy in Equation 400, we will state

$$\sum_j \nu_{i,j}\bar{V}_j = \Delta V_{\mathrm{rxn},i}, \tag{418}$$

where $\Delta V_{\mathrm{rxn},i}$ is the change in volume over the course of reaction i. Therefore,

$$m\hat{C}_{\mathrm{V}}\frac{\mathrm{d}T}{\mathrm{d}t} - \frac{\alpha}{\kappa}TV\sum_i \Delta V_{\mathrm{rxn},i}r_i = -V\sum_i \Delta H_{\mathrm{rxn},i}r_i + \dot{Q}. \tag{419}$$

Combining the sums gets us our general but slightly more manageable expression for the energy balance of a constant-volume batch reactor,

$$m\hat{C}_{\mathrm{V}}\frac{\mathrm{d}T}{\mathrm{d}t} = V\sum_i \left(-\Delta H_{\mathrm{rxn},i} + \frac{\alpha}{\kappa}T\Delta V_{\mathrm{rxn},i}\right)r_i + \dot{Q}. \tag{420}$$

6.2.2.4. Ideal Gas at Constant Volume

This derivation is not covered in class but is included here for the interested reader.

If our reacting mixture is an ideal gas mixture, we can make some further simplifications by noting that

$$\kappa \equiv -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_{T,n_j} = -\frac{1}{V}\left(\frac{\partial\left(\frac{nRT}{P}\right)}{\partial P}\right)_{T,n_j} = \frac{1}{V}\frac{nRT}{P^2} = \frac{1}{V}\frac{PV}{P^2} = \frac{1}{P} \tag{421}$$

$$\alpha \equiv \left(\frac{1}{V}\right)\left(\frac{\partial V}{\partial T}\right)_{P,n_j} = \frac{1}{V}\left(\frac{\partial \left(\frac{nRT}{P}\right)}{\partial T}\right)_{P,n_j} = \frac{1}{V}\frac{nR}{P} = \frac{1}{V}\frac{PV}{PT} = \frac{1}{T}. \qquad (422)$$

Plugging these expressions into Equation 420 yields

$$m\hat{C}_V \frac{dT}{dt} = V\sum_i \left(-\Delta H_{\mathrm{rxn},i} + P\Delta V_{\mathrm{rxn},i}\right)r_i + \dot{Q}. \qquad (423)$$

Finally, we can note that

$$\Delta V_{\mathrm{rxn},i} = \frac{\Delta n_{\mathrm{rxn},i}RT}{P}, \qquad (424)$$

such that

$$m\hat{C}_V \frac{dT}{dt} = V\sum_i \left(-\Delta H_{\mathrm{rxn},i} + RT\sum_j \nu_{i,j}\right)r_i + \dot{Q}, \qquad (425)$$

where we took advantage of the fact that $\Delta n_{\mathrm{rxn},i} = \sum_j \nu_{i,j}$.

6.2.3. Example Application of the Energy Balance

6.2.3.1. Defining and Solving a System of ODEs

Since it may appear mostly as an abstract concept up until now, it is worth taking a step back to think about how we might apply the energy balance in practice.

Consider the gas-phase, elementary reaction of

$$\mathrm{A} \xrightarrow{k} 2\mathrm{B} \qquad (426)$$

that takes place in a well-mixed, adiabatic batch reactor at constant volume without the constraint of isothermal operation. For the sake of simplicity, we will consider the gases to behave ideally. Naturally, we might wish to understand how the temperature of the reactor changes as a function of time.

To answer this question, we start by writing the typical material balance for species A as

$$r_A = \frac{d[A]}{dt}. \qquad (427)$$

Since the reaction is elementary, we also know the rate expression can be given as:

$$r_A = -k[A], \qquad (428)$$

such that

$$\frac{d[A]}{dt} = -k[A]. \qquad (429)$$

Thus far, this is essentially the same procedure we have done many times before, such as in Section 2.6. However, we cannot proceed with the integration yet since $k(T)$ and $T(t)$ for non-isothermal operation.

We now move onto the simplified energy balance for an ideal gas at constant volume from Equation 405 to state

$$m\hat{C}_V \frac{\mathrm{d}T}{\mathrm{d}t} = (-\Delta H_{\mathrm{rxn}} + RT)rV, \tag{430}$$

where we note that $\sum_j \nu_j = 1$ for the given reaction and $\dot{Q} = 0$ for an adiabatic process. We know that

$$r = -r_A = k[A], \tag{431}$$

such that

$$m\hat{C}_V \frac{\mathrm{d}T}{\mathrm{d}t} = (-\Delta H_{\mathrm{rxn}} + RT)k[A]V. \tag{432}$$

This leaves us with a system of differential equations that must be solved simultaneously:

$$\frac{\mathrm{d}[A]}{\mathrm{d}t} = -k[A], \quad \frac{\mathrm{d}T}{\mathrm{d}t} = \frac{(-\Delta H_{\mathrm{rxn}} + RT)k[A]V}{m\hat{C}_V}. \tag{433}$$

To make matters even clearer, we can substitute in the Arrhenius equation for k to state

$$\frac{\mathrm{d}[A]}{\mathrm{d}t} = -A' \exp\left(-\frac{E_a}{RT}\right)[A], \quad \frac{\mathrm{d}T}{\mathrm{d}t} = \frac{(-\Delta H_{\mathrm{rxn}} + RT)A' \exp\left(-\frac{E_a}{RT}\right)[A]V}{m\hat{C}_V}, \tag{434}$$

where A' is the pre-exponential factor (to distinguish it from species A).

From this set of equations, we can see that both expressions depend on $[A]$ and T, both of which evolve with t. For the case where $\Delta H_{\mathrm{rxn}} < 0$, we see that $\mathrm{d}T/\mathrm{d}t > 0$, such that the temperature will increase continually until all of species A is consumed. Clearly, there needs to be some amount of temperature control in order for the reactor operation to be safe and industrially viable.

Generally, these systems of ordinary differential equations (ODEs) can only be solved numerically. The details of numerical methods are beyond the scope of this course, but it is still useful to have a high-level understanding of what is involved in setting up such equations.

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6.2.3.2. An Analytical Example

Consider the exothermic, elementary, liquid-phase reaction given by

$$A + B \xrightarrow{k} C, \tag{435}$$

which is carried out in a bach reactor. A cooling coil maintains the reactor temperature at a given value of T.

6.2.3.2.1. Maintaining Isothermal Operation

Here, we will ask the following question: how much heat needs to be removed by the cooling coil to maintain isothermal operation? To address this question, we start by assuming that the incompressible-fluid energy balance from Equation 403 is suitable:

$$m\hat{C}_P \frac{dT}{dt} = -\Delta H_{rxn} rV + \dot{Q}. \tag{436}$$

Since we are operating isothermally, $dT/dt = 0$, such that

$$\Delta H_{rxn} rV = \dot{Q}. \tag{437}$$

We know that $r = -r_A = -d[A]/dt$, such that

$$-\Delta H_{rxn} V \frac{d[A]}{dt} = \dot{Q}. \tag{438}$$

Integrating

$$\int_{[A]_0}^{[A]} -\Delta H_{rxn} V \, d[A]' = \int_0^t \dot{Q} \, dt'. \tag{439}$$

and simplifying

$$Q = -\Delta H_{rxn} V([A] - [A]_0). \tag{440}$$

The above expression makes intuitive sense. We know that $[A] < [A]_0$, such that $Q < 0$ if ΔH_{rxn} is exothermic. Additionally, the more exothermic the reaction is and the more A that gets converted, the more heat will need to be removed.

6.2.3.2.2. Adiabatic Temperature Rise

Now we will relax the assumption of isothermal operation and ask: if operated adiabatically, how would the temperature change over the course of the reaction? We return to the energy balance:

$$m\hat{C}_P \frac{dT}{dt} = -\Delta H_{rxn} rV + \dot{Q}. \tag{441}$$

Now, we set $\dot{Q} = 0$, such that

$$m\hat{C}_{\mathrm{P}}\frac{\mathrm{d}T}{\mathrm{d}t} = -\Delta H_{\mathrm{rxn}}rV. \tag{442}$$

We know that $r = -\,\mathrm{d}[\mathrm{A}]/\,\mathrm{d}t$, such that

$$m\hat{C}_{\mathrm{P}}\frac{\mathrm{d}T}{\mathrm{d}t} = \Delta H_{\mathrm{rxn}}\frac{\mathrm{d}[\mathrm{A}]}{\mathrm{d}t}V. \tag{443}$$

Now we can integrate to find an expression for the temperature change

$$\int_{T_1}^{T_2} \mathrm{d}T' = \int_{[\mathrm{A}]_0}^{[\mathrm{A}]} \frac{\Delta H_{\mathrm{rxn}}V}{m\hat{C}_{\mathrm{P}}}\,\mathrm{d}[\mathrm{A}]', \tag{444}$$

which simplifies to

$$\Delta T = \frac{\Delta H_{\mathrm{rxn}}V([\mathrm{A}] - [\mathrm{A}]_0)}{m\hat{C}_{\mathrm{P}}}. \tag{445}$$

This expression also makes intuitive sense. Since $[\mathrm{A}] < [\mathrm{A}]_0$, if ΔH_{rxn} is exothermic, then $\Delta T > 0$. Additionally, the more exothermic the reaction is and the more A that gets consumed, the larger the temperature rise will be.

6.3. Plug Flow Reactors

6.3.1. Energy Balance

For the sake of brevity, we will forego a detailed derivation of the PFR energy, especially since it is very similar to that of the batch reactor (as was observed for the material balance).[72] Instead, in analogy with the single-phase batch reactor energy balance given by Equation 402, we will simply state that single-phase PFR energy balance is

$$\rho\hat{C}_{\mathrm{P}}\frac{\mathrm{d}T}{\mathrm{d}\tau} + (1 - \alpha T)\frac{\mathrm{d}P}{\mathrm{d}\tau} = -\sum_i \Delta H_{\mathrm{rxn},i}r_i + \frac{\dot{Q}}{V}. \tag{446}$$

Assuming the cross-sectional area, A_{c}, of the PFR is constant, then we can equivalently write the derivatives in terms of z instead of τ via a simple change of variables (i.e. using the relationship of $\tau = z/u$ from Equation 347):

$$\rho u\hat{C}_{\mathrm{P}}\frac{\mathrm{d}T}{\mathrm{d}z} + u(1 - \alpha T)\frac{\mathrm{d}P}{\mathrm{d}z} = -\sum_i \Delta H_{\mathrm{rxn},i}r_i + \frac{\dot{Q}}{V}, \tag{447}$$

where u is the linear velocity of the fluid.

If the pressure drop along the reactor is negligible or the fluid is an ideal gas mixture (i.e. $\alpha T = 1$), then $\mathrm{d}P/\,\mathrm{d}\tau = \mathrm{d}P/\,\mathrm{d}z = 0$, simplifying the energy balance further:

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[72]For a thorough derivation of reactor energy balances, refer to Chapter 6 of *Chemical Reactor Analysis and Design Fundamentals* by J.B. Rawlings and J.G. Ekerdt.

$$\rho u \hat{C}_\mathrm{P} \frac{\mathrm{d}T}{\mathrm{d}z} = -\sum_i \Delta H_{\mathrm{rxn},i} r_i + \frac{\dot{Q}}{V} \quad \text{(negligible pressure drop or ideal gas)}. \quad (448)$$

Alternatively, if the fluid is incompressible (i.e. $\alpha = 0$) as is commonly assumed for liquid-phase reactions, then

$$\rho u \hat{C}_\mathrm{P} \frac{\mathrm{d}T}{\mathrm{d}z} + u \frac{\mathrm{d}P}{\mathrm{d}z} = -\sum_i \Delta H_{\mathrm{rxn},i} r_i + \frac{\dot{Q}}{V} \quad \text{(incompressible)}. \quad (449)$$

6.3.2. Hot Spots and Thermal Runaway

We will now revisit the example carried out with the batch reactor in Section 6.2.3 with a few modifications. Consider again the gas-phase, elementary reaction of

$$A \xrightarrow{k} 2B, \quad (450)$$

where A and B behave ideally. We now decide to consider a PFR with constant cross-sectional area (rather than a batch reactor with constant volume). Once again, we will not make any assumptions about isothermal operation. As was shown in the batch reactor example, the temperature will continually rise if $\Delta H_{\mathrm{rxn}} < 0$ and $\dot{Q} = 0$, so we will make one other modification: we will surround the PFR with a heat transfer fluid that allows for the possibility of heat transfer between the reacting fluid and its surroundings (i.e. $\dot{Q} \neq 0$). As a reminder, the goal will be to write a coupled set of mass and energy balances for the PFR.

Qualitatively similar to the batch reactor example, from the PFR material balance given by Equation 348 and the simplified ideal gas energy balance given by Equation 448, we can state

$$\frac{\mathrm{d}[A]}{\mathrm{d}\tau} = -k[A], \quad \rho \hat{C}_\mathrm{P} \frac{\mathrm{d}T}{\mathrm{d}\tau} = -\Delta H_{\mathrm{rxn}} k[A] + \frac{\dot{Q}}{V}. \quad (451)$$

The $\dot{Q}$ term is what can prevent a continual increase in temperature over the reactor length for an exothermic reaction, provided $\dot{Q} < 0$. The highest temperature position along the reactor length is termed the hot spot.

If ΔH_{rxn} is highly exothermic, the hot spot can spike to extremely high temperatures very quickly if one is not careful. The exothermic reaction causes an increase in temperature, which itself increases the rate of reaction. If the rate of heat loss to the surroundings via $\dot{Q}$ is not sufficiently large, then the reaction will go to completion extremely quickly, raising the temperature to dangerously high values. Clearly, robust temperature control is a necessity when dealing with non-isothermal reactors. This not a niche point—such considerations are just as relevant for even the simplest of reactions in the lab!

> **📊 Interactive Plot**
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6.4. Continuous-Stirred Tank Reactors

6.4.1. General Approach

To derive the expression for the CSTR energy balance, we start again from the general energy balance given by Equation 383, neglecting the kinetic and potential energy terms as well as the shaft work:

$$\frac{\mathrm{d}U}{\mathrm{d}t} = \dot{m}_0 \hat{H}_0 - \dot{m}\hat{H} + \dot{Q} - P\frac{\mathrm{d}V}{\mathrm{d}t}. \tag{452}$$

Here, we are omitting the "1" subscript because, for a well-mixed reactor, the outlet stream properties are assumed to be the same as the reactor contents. Using the definition of enthalpy from Equation 386, we can restate the above expression as

$$\frac{\mathrm{d}H}{\mathrm{d}t} - V\frac{\mathrm{d}P}{\mathrm{d}t} - P\frac{\mathrm{d}V}{\mathrm{d}t} = \dot{m}_0 \hat{H}_0 - \dot{m}\hat{H} + \dot{Q} - P\frac{\mathrm{d}V}{\mathrm{d}t}, \tag{453}$$

which simplifies to

$$\frac{\mathrm{d}H}{\mathrm{d}t} - V\frac{\mathrm{d}P}{\mathrm{d}t} = \dot{m}_0 \hat{H}_0 - \dot{m}\hat{H} + \dot{Q}. \tag{454}$$

6.4.2. Energy Balance

6.4.2.1. Summary

Once again, many simplifications can be made. The energy balance under steady-state conditions, constant $\hat{C}_\mathrm{P}$, constant P, and $\dot{v}_0 = \dot{v}_1$ is shown below:

$$0 = -\sum_i \Delta H_{\mathrm{rxn},i} r_i + \frac{\rho \hat{C}_\mathrm{P}(T_0 - T)}{\tau} + \frac{\dot{Q}}{V} \quad \text{(steady-state)} \tag{455}$$

We will not discuss the derivation in class for the sake of time, but the details have been reproduced below for clarity.

6.4.2.2. Derivation

This derivation is not covered in class but is included here for the interested reader.

Like the batch reactor example, we can consider a single-phase system where the enthalpy changes due to temperature, pressure, and the moles of species j. Plugging in the definition of $\mathrm{d}H$ from Equation 394 into the above expression yields

$$\frac{m\hat{C}_\mathrm{P}\,\mathrm{d}T + V(1 - \alpha T)\,\mathrm{d}P + \sum_j \bar{H}_j\,\mathrm{d}n_j}{\mathrm{d}t} - V\frac{\mathrm{d}P}{\mathrm{d}t} = \dot{m}_0 \hat{H}_0 - \dot{m}\hat{H} + \dot{Q}, \tag{456}$$

which simplifies to

$$m\hat{C}_{\mathrm{P}}\frac{\mathrm{d}T}{\mathrm{d}t} - \alpha TV\frac{\mathrm{d}P}{\mathrm{d}t} + \sum_j \bar{H}_j\frac{\mathrm{d}n_j}{\mathrm{d}t} = \dot{m}_0\hat{H}_0 - \dot{m}\hat{H} + \dot{Q}. \tag{457}$$

We know from the material balance on the CSTR (Equation 350) that

$$\frac{\mathrm{d}n_j}{\mathrm{d}t} = \dot{n}_{j,0} - \dot{n}_j + r_jV, \tag{458}$$

or equivalently by invoking Equation 21:

$$\frac{\mathrm{d}n_j}{\mathrm{d}t} = \dot{n}_{j,0} - \dot{n}_j + V\sum_i \nu_{i,j}r_i. \tag{459}$$

Plugging the CSTR material balance into Equation 457 and following the same approach taken in the batch reactor derivation from Section 6.2.1 results in

$$m\hat{C}_{\mathrm{P}}\frac{\mathrm{d}T}{\mathrm{d}t} - \alpha TV\frac{\mathrm{d}P}{\mathrm{d}t} = -V\sum_i \Delta H_{\mathrm{rxn},i}r_i + \sum_j \dot{n}_{j,0}\big(\bar{H}_{j,0} - \bar{H}_j\big) + \dot{Q}. \tag{460}$$

From here, we can start applying our typical approximations. For instance, we can invoke steady-state conditions to arrive at

$$0 = -V\sum_i \Delta H_{\mathrm{rxn},i}r_i + \sum_j \dot{n}_{j,0}\big(\bar{H}_{j,0} - \bar{H}_j\big) + \dot{Q}. \tag{461}$$

To make matters a bit simpler, we can represent the partial molar enthalpies in terms of partial molar heat capacities via[73]

$$\bar{H}_j - \bar{H}_{j,0} = \bar{C}_{\mathrm{P},j}(T - T_0), \tag{462}$$

such that

$$0 = -V\sum_i \Delta H_{\mathrm{rxn},i}r_i + \sum_j \dot{n}_{j,0}\bar{C}_{\mathrm{P},j}(T_0 - T) + \dot{Q}. \tag{463}$$

Leveraging the definition of a partial molar property, we can state

$$\sum_j \dot{n}_{j,0}\bar{C}_{\mathrm{P},j} = \dot{n}_0 c_{\mathrm{P}} = \dot{m}_0\hat{C}_{\mathrm{P}}, \tag{464}$$

such that we can rewrite the energy balance as

$$0 = -V\sum_i \Delta H_{\mathrm{rxn},i}r_i + \dot{m}_0\hat{C}_{\mathrm{P}}(T_0 - T) + \dot{Q}. \tag{465}$$

If we wish to express the above energy balance in terms of τ, we can divide through by V to arrive at

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[73]Naturally, this requires that the heat capacity does not change between the inlet and outlet.

$$0 = -\sum_i \Delta H_{\text{rxn},i} r_i + \frac{\dot{m}_0}{V} \hat{C}_{\text{P}} (T_0 - T) + \frac{\dot{Q}}{V}, \qquad (466)$$

which becomes

$$0 = -\sum_i \Delta H_{\text{rxn},i} r_i + \frac{\rho \hat{C}_{\text{P}} (T_0 - T)}{\tau} + \frac{\dot{Q}}{V} \qquad (467)$$

after invoking $\dot{m}_0 = \dot{v}_0 \rho_0$, $\tau \equiv V/\dot{v}$, and a constant volumetric flow rate.

6.4.3. Multiple Steady States

While Equation 455 look slightly simpler than the batch and PFR energy balances since it is a series of algebraic expressions rather than differential equations, there is still quite interesting behavior that can emerge. Namely, unlike other reactor archetypes, CSTRs are known to exhibit multiple physically plausible steady state solutions.

Consider a CSTR operated adiabatically and at steady-state conditions with the following single-phase, exothermic reaction:

$$A \xrightarrow{k} B. \qquad (468)$$

The energy balance can be concisely written using Equation 455 to state

$$0 = -\Delta H_{\text{rxn}} r + \frac{\rho \hat{C}_{\text{P}} (T_0 - T)}{\tau}. \qquad (469)$$

Similarly, we know from Equation 356 that the material balance for the CSTR can be written as

$$r_{\text{A}} = \frac{[\text{A}] - [\text{A}]_0}{\tau} \qquad (470)$$

for a constant volumetric flow rate. Substituting in our elementary rate law of $r = -r_{\text{A}} = k[\text{A}]$, we arrive at the following system of equations:

$$0 = -\Delta H_{\text{rxn}} k[\text{A}] + \frac{\rho \hat{C}_{\text{P}} (T_0 - T)}{\tau}, \quad 0 = (1 + k\tau)[\text{A}] - [\text{A}]_0. \qquad (471)$$

This system of non-linear equations is a bit deceptive. Depending on the initial guess one uses and the reaction conditions themselves, different solutions can potentially be found, each of which may be physically valid. In these scenarios, the CSTR exhibits multiple steady states, and small perturbations to the reaction conditions can trigger drastic changes in the reaction.

📊 **Interactive Plot**

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7. Transition State Theory

In the previous sections, we have made extensive use of the rate constant, k. Here, we seek to provide theoretical insights into what factors dictate the value of k while also providing an atomistic justification for the functional form of the Arrhenius equation.

7.1. Simple Kinetic Theories

Before discussing transition state theory, it is worthwhile to briefly introduce simpler kinetic models and their limitations.

7.1.1. Collision Theory

Perhaps the simplest model one can consider is collision theory. Consider the reaction of two species, such as $A + B \longrightarrow C$. Here, we will treat each species as a hard sphere, wherein a reaction only occurs if the center of the two spheres become closer than some distance σ_{AB}. The natural definition for σ_{AB} is

$$\sigma_{AB} = \frac{1}{2}(\sigma_A + \sigma_B), \tag{472}$$

where σ_A is the diameter of A, and σ_B is the diameter of B. As shown in Figure 23, it immediately becomes clear that the potential energy landscape for such an interaction does not match reality. Namely, the attractive region is completely ignored.
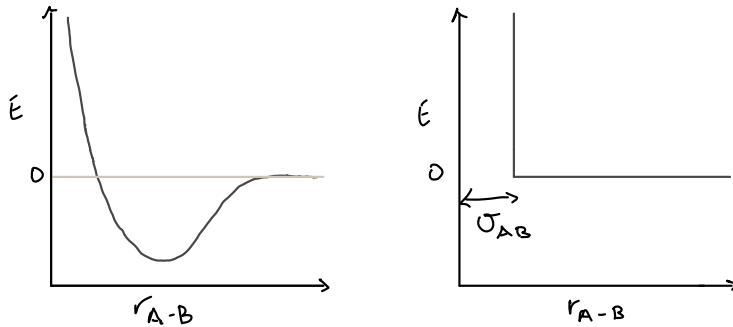
Figure 23: Comparison of a typical potential energy diagram for a reaction between A and B (left) and that of a hard-sphere model (right).

Assuming that A and B follow a Maxwell–Boltzmann distribution of speeds at a given temperature T,[74] the frequency of collisions that occur at a given temperature can be shown to be[75]

$$\bar{Z} = n_A n_B \sigma_{AB}^2 \left(\frac{8 \pi k_B T}{\mu_{AB}} \right)^{\frac{1}{2}}, \tag{473}$$

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[74]For additional details refer to "Chapter 2: The Mechanisms of Chemical Reactions in Homogeneous Phases" in J.B. Butt, *Reaction Kinetics and Reactor Design* (2nd ed.).

[75]For the collision of identical species, $\bar{Z}$ should include a 1/2 factor to prevent double counting.

where n_A and n_B are the number density of A and B (i.e. units of particle/m^3), and μ_{AB} is the so-called reduced mass of the AB system given as

$$\mu_{AB} \equiv \frac{m_A m_B}{m_A + m_B}, \tag{474}$$

where m_A and m_B represent the mass of species A and B, respectively.

The typical units of $\bar{Z}$ are collisions/cm^3-s (i.e. the number of collisions to occur in a given volume over a given time period). When scaled up from number of collisions to a mole of collisions via Avogadro's constant, $\bar{Z}$ can be naively thought of as a rate of reaction, as is clear from dimensional analysis alone. In doing so, one might say that

$$\bar{Z} = r = k n_A n_B \tag{475}$$

for an elementary, bimolecular reaction of A and B. By inspection of Equation 473, this would imply that

$$k = \sigma_{AB}^2 \left(\frac{8\pi k_B T}{\mu_{AB}} \right)^{\frac{1}{2}}. \tag{476}$$

While this is reasonably suitable in describing the direct collision of two species, it is not reflective of the kinetics of reactions because there is no exponential dependency on temperature that we know must exist from the Arrhenius equation.

The missing link is that molecules only react if they collide with sufficient energy. We, therefore, must define a threshold energy η^*, above which reactions can proceed. This allows us to refine our expression for k to instead be given as

$$k = \sigma_{AB}^2 \left(\frac{8\pi k_B T}{\mu_{AB}} \right)^{\frac{1}{2}} \exp \left(-\frac{\eta^*}{k_B T} \right). \tag{477}$$

Typically, a multiplicative factor of p is also included, which is known as the steric factor and is essentially a catch-all term for all additional factors that influence the collision–reaction probability beyond those associated with the energy.

With Equation 477, we have an exponential energy dependence, but we also see that there is a $\sqrt{T}$ term as well. The $\sqrt{T}$ dependence in what is—effectively—the pre-exponential factor provides some justification for Equation 41 where we wrote the modified form of the Arrhenius equation with a factor $A'T^n$ (here, $n = 0.5$). In general, while collision theory clearly has major limitations, it can be fairly reasonable in describing reactions with very low values of η^* like radical reactions.

7.2. Setting the Stage for Transition State Theory

7.2.1. Rate in Terms of an Equilibrium Constant

We seek to write an expression for the rate constant, k, in terms of quantities that can be readily computed from theory and/or experimentally measured. Transition state theory (TST) is what makes this possible. We will start by considering the following reaction:[76]

$$A + B \xrightarrow{k} P \tag{478}$$

In transition state theory, we assume that there is some transient complex (the transition state) that connects the reactants and products along the minimum energy pathway of the reaction coordinate. This means we can rewrite our reaction as[77]

$$A + B \overset{K_C^\ddagger}{\rightleftharpoons} AB^\ddagger \longrightarrow P. \tag{479}$$

The net rate of reaction can be represented as

$$r = k^\ddagger [AB]^\ddagger, \tag{480}$$

where $k^\ddagger$ is the rate constant for producing P from the activated complex and $[AB]^\ddagger$ is the concentration of the transition state species. In practice, we will denote $k^\ddagger$ as $\nu^\ddagger$ because it is a frequency (in units of time^{-1}) that arises from the vibrational mode along the reaction coordinate that connects the transition state to the product, such that

$$r = \nu^\ddagger [AB]^\ddagger. \tag{481}$$

The concentration of the transition state species, however, is not an observable quantity since the transition state itself is fleeting. To take care of this challenge, we assume that the transition state is in quasi-equilibrium with the reactants, such that we can return to the definition of the equilibrium constant:

$$K_C^\ddagger = \frac{[AB]^\ddagger}{[A][B]}. \tag{482}$$

Solving for $[AB]^\ddagger$, we can arrive at

$$r = \nu^\ddagger K_C^\ddagger [A][B]. \tag{483}$$

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[76]We have chosen a bimolecular reaction here simply for demonstration purposes, but the results that follow are not inherently restricted to a particular molecularity if proper care is taken.

[77]Here, we are tacitly assuming that there is no recrossing, such that we are considering a single isolated event such that P cannot convert back to the reagents. Naturally, it is possible in practice for a product to return to the transition state if enough energy is supplied, but we consider this as a separate event altogether. In practice, recrossing events will decrease k from transition state theory, and this is corrected in a *post hoc* manner via the transmission coefficient κ discussed shortly.

This should look strikingly familiar in an abstract kind of way. If we compare this to our typical rate expression for a elementary reaction, $r = k[\text{A}][\text{B}]$, it becomes self-evident that

$$k = \nu^{\ddagger} K_{\text{C}}^{\ddagger}. \tag{484}$$

The question now is where to go from here. We will later show that $\nu^{\ddagger} \approx k_{\text{B}}T/h$. Before then, however, we need to figure out what to do with $K_{\text{C}}^{\ddagger}$.

7.2.2. Rate in Terms of Molecular Partition Functions

The most pressing situation to address in our definition of k is $K_{\text{C}}^{\ddagger}$. Thankfully, with a healthy dose of statistical thermodynamics, this becomes relatively manageable. Although it will not be derived here, from statistical mechanics it is known that the equilibrium constant can be expressed in terms of molecular partition functions as follows:

$$K_{\text{a}}^{\ddagger} \equiv \frac{a^{\ddagger}}{a_{\text{A}} a_{\text{B}}} = \frac{Z^{\ddagger}}{Z_{\text{A}} Z_{\text{B}}} \quad \text{(unnormalized)}, \tag{485}$$

where Z_j is the (unitless) molecular partition function[78] for the j-th species. We will forego a formal derivation linking Z_j to the equilibrium constant. That said, we can think of it as being intuitively reasonable because the ratio of molecular partition functions describes the distribution of energetic states between the products and reactants, which dictates the direction for the equilibrium in a manner analogous to the change in Gibbs free energy.

In practice, the molecular partition functions are generally defined with respect to the lowest energy state for that molecule. If we adopt this convention, then $K_{\text{a}}^{\ddagger}$ becomes

$$K_{\text{a}}^{\ddagger} \equiv \frac{a^{\ddagger}}{a_{\text{A}} a_{\text{B}}} = \frac{Z^{\ddagger}}{Z_{\text{A}} Z_{\text{B}}} \exp\left(-\frac{\Delta E_0^{\ddagger}}{RT}\right), \tag{486}$$

as we will justify shortly. Here, $\Delta E_0^{\ddagger}$ is the energy difference between the transition state and reactants at 0 K (i.e. the sum of electronic energy and zero-point energy contributions). We will adopt this convention for the partition functions going forward.

Before proceeding, recall that we were dealing with concentrations and $K_{\text{C}}^{\ddagger}$ in Equation 484. As such, we will instead use

$$K_{\text{C}}^{\ddagger} = \frac{1}{N_{\text{A}}^{1-m}} \frac{Z'^{\ddagger}}{Z'_{\text{A}} Z'_{\text{B}}} \exp\left(-\frac{\Delta E_0^{\ddagger}}{RT}\right), \tag{487}$$

where Z'_j is the molecular partition function per unit volume for the j-th species. The need for Z'_j being in units of volume^{-1} is so that we arrive at the appropriate units for $K_{\text{C}}^{\ddagger}$. The factor

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[78]The molecular partition function is the sum over all energetic states in the system. In the canonical ensemble, it is given as $Z(N, V, T) \equiv \sum_i \exp(-E_i/k_{\text{B}}T)$ for all possible states i.

of $1/N_A^{1-m}$, where m is the molecularity (i.e. $m = 2$ for this example),[79] is included simply as a means of ensuring that $K_C^{\ddagger}$ is in molar units since the partition functions are defined on a per-molecule basis.

It may seem that we have not made much progress here because we do not yet know how to calculate Z'_j. Not to worry though, as that will be addressed below.

7.3. Contributions to the Partition Function

The total molecular partition function for a species can be broken down into the products of vibrational, rotational, translational, and electronic partition functions. Written mathematically,

$$Z' = \frac{z_{\text{trans}}}{V} z_{\text{rot}} z_{\text{vib}} z_{\text{el}}, \tag{488}$$

where the z values are all unitless. As we will show below, the natural place to introduce the units of inverse volume in Z' is with the translational partition function. These individual contributions can also be used to define the translational, rotational, vibrational, and electronic contributions to the thermodynamic state functions as well.

7.3.1. Translational Partition Function

We now must define each of the partition functions. The translational partition function derived from the particle-in-a-box model in quantum chemistry is typically approximated as

$$z_{\text{trans}} = V \left(\frac{2\pi m k_B T}{h^2} \right)^{\frac{3}{2}} = \frac{V}{\Lambda^3}, \quad \Lambda \equiv \frac{h}{\sqrt{2\pi m k_B T}}, \tag{489}$$

where V is a reference volume containing the molecule,[80] m is the mass of the molecule, h is Planck's constant (units of J-s), and Λ is the thermal de Broglie wavelength. As with all partition functions, z_{trans} is unitless. This, in turn, means that z_{trans}/V has units of inverse volume.

It is also worth noting that z_{trans} can be generalized to an arbitrary set of d integer dimensions (e.g. in the case of a system that does not have all three translational degrees of freedom). To do so, it is as simple as stating

$$z_{\text{trans}} = \left(\frac{L}{\Lambda} \right)^d, \tag{490}$$

where L is now a reference length associated with the degree of translational motion.[81]

---

[79]We could have equally used $\delta^{\ddagger}$ in place of $1 - m$, where where $\delta^{\dagger}$ is the change in stoichiometric numbers between the transition state and reactants. Since we are only focusing on a single transition state-producing event, we use for $1 - m$ simplicity.

[80]The presence of V is what ultimately dictates the need for choosing a "standard-state" for the sake of internal consistency. If one is considering a gas, it is typically more natural to replace V with pressure P, such as by invoking the ideal gas law of the form $V = k_B T/P$ and taking the pressure to be a standard-state value of 1 bar.

[81]If invoking reduced translational degrees of freedom, Equation 489 will need to be normalized by the appropriate dimensionality (e.g. a reference area A if $d = 2$ rather than V as with $d = 3$).

7.3.2. Rotational Partition Function

Moving onward, we will now investigate the rotational partition function. The rotational partition function is derived based on the rigid–rotor quantum-mechanical model and is different depending on the shape of the molecule. Generally, it can be approximated as follows:

$$
\begin{aligned}
z_{\text{rot}} &= 1 \quad \text{(monatomic)} \\
z_{\text{rot}} &= \frac{8\pi^2 I k_{\text{B}} T}{\sigma h^2} = \frac{T}{\sigma \Theta_{\text{rot}}}, \quad \Theta_{\text{rot}} \equiv \frac{h^2}{8\pi^2 I k_{\text{B}}} \quad \text{(linear)} \\
z_{\text{rot}} &= \frac{8\pi^2 \left(8\pi^3 I_1 I_2 I_3\right)^{\frac{1}{2}} (k_{\text{B}} T)^{\frac{3}{2}}}{\sigma h^3} = \frac{1}{\sigma} \left(\frac{\pi T^3}{\Theta_{1,\text{rot}} \Theta_{2,\text{rot}} \Theta_{3,\text{rot}}}\right)^{\frac{1}{2}} \quad \text{(nonlinear)},
\end{aligned}
\tag{491}
$$

where Θ_{rot} is the characteristic rotational temperature.[82] In these equations, σ represents the rotational symmetry number and is determined by the number of spatial orientations of the subject molecule that are identical. For instance, σ is a value of 2 for linear molecules with a center of symmetry (e.g. a homonuclear diatomic molecule) and 1 for linear molecules without a center of symmetry (e.g. a heteronuclear diatomic molecule).[83]

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

$$
I \equiv \sum_i m_i r_i^2,
\tag{492}
$$

where M_i is the mass of atom (not species) i and r_i is the distance of atom i to the axis of rotation.[84] For a diatomic molecule, the moment of inertia can be conveniently expressed as

$$
I = \frac{M_1 M_2}{M_1 + M_2} d^2 = \mu d^2, \quad \mu \equiv \frac{M_1 M_2}{M_1 + M_2},
\tag{493}
$$

where μ is called the reduced mass and d is the distance between the two atoms.

7.3.3. Vibrational Partition Function

The vibrational partition function is derived based on the harmonic-oscillator quantum-mechanical model and is given by

---

[82]Like with the translational partition function, the temperature dependence of the form $T^{d/2}$ provides a clue about the degrees of freedom. For instance, the $T^{3/2}$ dependence for a non-linear molecule indicates it has 3 degrees of rotational freedom, whereas the T^1 dependence for a linear molecule indicates it only has 2.

[83]The NIST Chemistry WebBook has a variety of physical properties, including rotational symmetry numbers of common molecules. The rotational properties (e.g. moments of inertia, rotational symmetry number) of common molecules can be found on the NIST Chemistry WebBook as well NIST's Computational Chemistry Comparison and Benchmark DataBase, among other resources.

[84]For a linear, symmetric molecule like CO_2 (i.e. O=C=O), the moment of inertia is $I = M_O d_{CO}^2 + M_O d_{CO}^2 = 2 M_O d_{CO}^2$, where M_O is the mass of the oxygen atom and d_{CO} is the C–O bond length. This is because the central atom is the location of the axis of rotation.

$$z_{\text{vib}} = \exp\left(-\frac{E_{\text{ZPVE}}}{k_{\text{B}}T}\right) \prod_{i=1}^{N} \frac{1}{1 - \exp\left(-\frac{h\nu_i}{k_{\text{B}}T}\right)} \quad \text{(unnormalized)}, \tag{494}$$

where

$$E_{\text{ZPVE}} \equiv \frac{1}{2} \sum_{i} h\nu_i. \tag{495}$$

Here, N is the number of vibrational modes, ν_i is the i-th vibrational frequency, and E_{ZPVE} is known as the zero-point vibrational energy.

However, as mentioned earlier, the convention is such that the molecular partition functions will be defined based on their lowest-energy states as the point of reference. As such, we will factor out the E_{ZPVE} term. The corresponding vibrational partition function is now

$$z_{\text{vib}} = \prod_{i=1}^{N} \frac{1}{1 - \exp\left(-\frac{h\nu_i}{k_{\text{B}}T}\right)} = \prod_{i=1}^{N} \frac{1}{1 - \exp\left(-\frac{\Theta_{i,\text{vib}}}{T}\right)}, \quad \Theta_{i,\text{vib}} \equiv \frac{h\nu_i}{k_{\text{B}}}, \tag{496}$$

where $\Theta_{i,\text{vib}}$ is known as the characteristic vibrational temperature. The vibrational frequencies of common molecules can be found on the NIST Chemistry WebBook as well NIST's Computational Chemistry Comparison and Benchmark DataBase, among other resources.

> 🧠 **Helpful Tip**
>
> The $\exp(-E_{\text{ZPVE}}/RT)$ term that we have factored out from z_{vib} does not disappear entirely. Instead, it ends up being included as part of the $\exp\left(-\Delta E_0^{\ddagger}/RT\right)$ term in our expression for $K_C^{\ddagger}$ given by Equation 487. Since $E_0 \equiv E_{\text{el}} + E_{\text{ZPVE}}$, the latter term comes from the modified vibrational partition function.

The number of vibrational modes for a molecule can be determined as follows:

$$\begin{aligned}
N &= 0 \quad \text{(monatomic)} \\
N &= 3N_0 - 5 \quad \text{(linear)} \\
N &= 3N_0 - 6 \quad \text{(nonlinear)}.
\end{aligned} \tag{497}$$

For transition states, one of the N vibrational modes is imaginary. As we will justify shortly when we define $\nu^{\ddagger}$, only the real vibrational modes will need to be included in calculating z_{vib}. Additionally, for a molecule adsorbed on a surface, the number of vibrational modes will be given by $N = 3N_0$ instead.[85]

---

[85]For an isolated molecule with N_0 atoms, there are three degrees of freedom per atom (one for each dimension) for a total of $3N_0$ degrees of freedom. However, three of these $3N_0$ degrees of freedom are associated with translational motion in x, y, and z. Two (linear) or three (non-linear) of these degrees of freedom are due to rotation. This is the cause of the $3N_0 - 5$ or $3N_0 - 6$ vibrational modes for a free molecule. If the molecule is

Finally, it should be noted that vibrational spectra are normally reported in units of wavenumbers (cm^{-1}), denoted $\tilde{\nu}$. To convert a wavenumber to a frequency, the following relationship can be used: $\nu_i = c\tilde{\nu}_i$, where c is the speed of light.

7.3.4. Electronic Partition Function

Finally, the electronic partition function is given by

$$z_{\text{el}} = \sum_i g_i \exp\left(-\frac{\varepsilon_i}{k_{\text{B}}T}\right), \tag{498}$$

where g_i is the degeneracy of electronic state i and ε_i is the electronic energy for electronic state i. As with the vibrational partition function, we will adopt the ground-state (i.e. $i = 0$) as the zero-energy reference point, such that all values of ε_i are taken with respect to ε_0. For the sake of simplicity, excited states (i.e. $i \geq 1$) are often assumed to have a negligible contribution to z_{el} due to their high energies with respect to the ground state.

By ignoring the contribution from excited states and setting $\varepsilon_0 = 0$ eV by convention, we can simply state

$$z_{\text{el}} = g_0. \tag{499}$$

The ground-state degeneracy, g_0, is analogous to the spin multiplicity, defined as the number of unpaired electrons plus one. For instance, $\text{CH}_3^\bullet$ has one unpaired electron and therefore has $g_0 = 2$ (i.e. the ground-state has a degeneracy of 2). Similarly, most non-radical species have $q_{\text{el}} \approx 1$. However, this is not universally true. For instance, the ground-state magnetic configuration of O_2 has two unpaired electrons, such that $g_0 = 3$ (i.e. the ground-state is a triplet).

> 🧠 **Helpful Tip**
>
> The $\exp(-\varepsilon_0/RT)$ term that we have factored out from z_{el} by setting $\varepsilon_0 = 0$ eV does not disappear entirely. Instead, it ends up being included as part of the $\exp\left(-\Delta E_0^\ddagger/RT\right)$ term in our expression for $K_{\text{C}}^\ddagger$ given by Equation 487. Since $E_0 \equiv E_{\text{el}} + E_{\text{ZPVE}}$, the former term comes from the modified electronic partition function (where $E_{\text{el}} = \varepsilon_0$).

7.4. Rates of Reaction from Partition Functions

7.4.1. The Idealized Case

With the partition function business out of the way, let's revisit our expression for the concentration-based rate constant:

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strongly adsorbed, the translational and rotational degrees of freedom are not present, and all $3N_0$ degrees of freedom are associated with vibrations.

$$K_C^{\ddagger} = \frac{1}{N_A^{1-m}} \frac{Z'^{\ddagger}}{Z_A' Z_B'} \exp\left(-\frac{\Delta E_0^{\ddagger}}{RT}\right). \tag{500}$$

We now know how to compute the partition functions, which is a relief. The main ingredients we need to either compute or measure are the geometries and vibrational modes of the system (and the spin multiplicity or excited states, if relevant).

Revisiting our rate expression from Equation 483, we have

$$r = \nu^{\ddagger} K_C^{\ddagger}[A][B]$$
$$r = \nu^{\ddagger} \frac{1}{N_A^{1-m}} \frac{Z'^{\ddagger}}{Z_A' Z_B'} \exp\left(-\frac{\Delta E_0^{\ddagger}}{RT}\right)[A][B]. \tag{501}$$

We are still left to figure out what do we do about $\nu^{\ddagger}$. The motion along the minimum energy pathway through the transition state is along a vibrational mode representing the bond-breaking or bond-making event. As alluded to previously, $\nu^{\ddagger}$ can be thought of as a vibrational frequency describing this event. We know from the definition of the vibrational partition function (Equation 496) that a single vibrational mode can be expressed as

$$z_{\text{vib, TS mode}} = \left(1 - \exp\left(-\frac{h\nu^{\ddagger}}{k_B T}\right)\right)^{-1} \approx \frac{k_B T}{h\nu^{\ddagger}}, \tag{502}$$

where the latter approximation is made because $h\nu^{\ddagger} \ll k_B T$ in most cases since $\nu^{\ddagger}$ is usually not particularly large.[86] With some rearrangement, we have

$$\nu^{\ddagger} = \frac{k_B T}{h} \frac{1}{z_{\text{vib, TS mode}}}. \tag{503}$$

This expression implies that we can state $\nu^{\ddagger} = k_B T/h$, provided that we remove this one vibrational mode associated with the transition state in the expression for $z_{\text{vib}}^{\ddagger}$. As for which mode to remove, it is the one and only imaginary mode associated with the transition state.

By plugging our result into Equation 501, we arrive at

$$r = \frac{k_B T}{h} K_C^{\ddagger}[A][B]$$
$$r = \frac{k_B T}{h} \frac{1}{N_A^{1-m}} \frac{Z'^{\ddagger}}{Z_A' Z_B'} \exp\left(-\frac{\Delta E_0^{\ddagger}}{RT}\right)[A][B]. \tag{504}$$

From the above expression, we can write $r = k[A][B]$ where

---

[86]We have implicitly taken advantage of the Taylor expansion $\exp(x) = 1 + x + x^2/2! + x^3/3! + \dots$ and dropped the second-order and higher terms.

$$k = \frac{k_\mathrm{B} T}{h} K_\mathrm{C}^{\ddagger} \tag{505}$$

or, equivalently, in terms of the partition functions,[87]

$$k \equiv A \exp\left(-\frac{\Delta E_0^{\ddagger}}{RT}\right), \quad A \equiv \frac{k_\mathrm{B} T}{h} \frac{1}{N_\mathrm{A}^{1-m}} \frac{Z'^{\ddagger}}{Z'_\mathrm{A} Z'_\mathrm{B}}. \tag{506}$$

Thinking back to the modified Arrhenius expressions with temperature-dependence terms on the prefactor as in Equation 41, we can see the T^n dependence of the prefactor has $n = 0$ for the empirical Arrhenius expression and $n = 1$ from transition state theory. In practice, however, the temperature effects of this T factor are often negligible when comparing k values at different temperatures, as the exponential term is the main dominating factor.

7.4.2. Example: Applying Transition State Theory

7.4.2.1. Overview

Let us consider the following gas-phase reaction:

$$\mathrm{F}^{\bullet} + \mathrm{H}_2 \longrightarrow \mathrm{HF} + \mathrm{H}^{\bullet}. \tag{507}$$

We wish to find the rate constant at 300 K by invoking transition state theory. Well, now what?

We start by invoking our transition state theory definition of k:

$$k = \frac{k_\mathrm{B} T}{h} \frac{1}{N_\mathrm{A}^{1-m}} \frac{Z'^{\ddagger}}{Z'_{\mathrm{F}^{\bullet}} Z'_{\mathrm{H}_2}} \exp\left(-\frac{\Delta E_0^{\ddagger}}{RT}\right). \tag{508}$$

We know that the molecularity of this reaction is two, so $m = 2$ here. We also know the temperature of interest, which is T = 300 K.

Next, we will tackle the partition functions, recognizing that

$$\frac{Z'^{\ddagger}}{Z'_{\mathrm{F}^{\bullet}} Z'_{\mathrm{H}_2}} = \frac{\left(z'_\mathrm{trans} z_\mathrm{rot} z_\mathrm{vib} z_\mathrm{el}\right)^{\ddagger}}{\left(z'_\mathrm{trans} z_\mathrm{rot} z_\mathrm{vib} z_\mathrm{el}\right)_{\mathrm{F}^{\bullet}} \left(z'_\mathrm{trans} z_\mathrm{rot} z_\mathrm{vib} z_\mathrm{el}\right)_{\mathrm{H}_2}}. \tag{509}$$

7.4.2.2. Translational Partition Function

We recall that the translational partition function (per unit volume) is given by

$$z'_\mathrm{trans} = \left(\frac{2\pi m k_\mathrm{B} T}{h^2}\right)^{\frac{3}{2}}. \tag{510}$$

We have everything we need to compute the translational partition functions, so we will do just that:

---

[87]Note that $\Delta E_0^{\ddagger}$ is not the same as E_a, although it is analogous. The $\Delta E_0^{\ddagger}$ term is at 0 K, whereas E_a includes thermal corrections.

$$\frac{(z'_{\text{trans}})^{\ddagger}}{(z'_{\text{trans}})_{\text{F}\bullet}(z'_{\text{trans}})_{\text{H}_2}} = \frac{\left(\frac{2\pi m_{\text{TS}} k_{\text{B}} T}{h^2}\right)^{\frac{3}{2}}}{\left(\frac{2\pi m_{\text{F}} k_{\text{B}} T}{h^2}\right)^{\frac{3}{2}} \left(\frac{2\pi m_{\text{H}_2} k_{\text{B}} T}{h^2}\right)^{\frac{3}{2}}}$$

$$= \frac{9.407 \times 10^{28} \frac{1}{\text{L}}}{\left(8.086 \times 10^{28} \frac{1}{\text{L}}\right)\left(2.795 \times 10^{27} \frac{1}{\text{L}}\right)} = 4.162 \times 10^{-28} \text{L},$$

where $m_{\text{TS}} = m_{\text{F}} + m_{\text{H}_2}$, which can be readily obtained from the periodic table. Note that the magnitudes of the translational partition functions are quite large. This is expected.

To summarize, the only non-tabulated information needed when calculating the translational partition function (on a per-volume basis) is:

1. The experimentally relevant (absolute) temperature, T.
2. The number of translational degrees of freedom for each species, d.

7.4.2.3. Rotational Partition Function

Now we shall move onto the rotational partition function. We recall that

$$z_{\text{rot}} = 1 \qquad \text{(monatomic)}$$

$$z_{\text{rot}} = \frac{8\pi^2 I k_{\text{B}} T}{\sigma h^2} \qquad \text{(linear)}.$$

The F atom is monatomic, so $(z_{\text{rot}})_{\text{F}\bullet} = 1$. That is easy enough.

By definition, H_2—like any diatomic species—is linear. The moment of inertia can then be given as

$$I_{\text{H}_2} = \frac{M_{\text{H}} M_{\text{H}}}{M_{\text{H}} + M_{\text{H}}} d_{\text{H--H}}^2 = 4.583 \times 10^{-48} \text{ kg m}^2, \tag{513}$$

where M_{H} is the mass of the hydrogen atom, and $d_{\text{H--H}}$ is the H—H bond distance in H_2, which is known to be 0.74 Å. We also know or can readily look up that

$$\sigma_{\text{H}_2} = 2. \tag{514}$$

The reason for this value is that H_2 has two indistinguishable orientations through symmetrical rotations: rotation by 0° (i.e. no rotation) and rotation by 180°. This gives us all the information we need to calculate $(z_{\text{rot}})_{\text{H}_2}$.

For the transition state, we first need to know if it is linear or non-linear. In practice, the easiest way to determine this is through a quantum-mechanical calculation (e.g. using density functional theory). Here, we will assume that theory suggests the transition state is linear. The geometry of the transition state from theory will also dictate σ, but in this case it is apparent without doing so that

$$\sigma_{\text{TS}} = 1 \tag{515}$$

given the asymmetric nature of an F—H—H transition state. The moment of inertia also depends on the transition state geometry but is a bit trickier to determine in this case since the center of mass is not in the midpoint of the structure. In any case, we will assume that quantum-chemical modeling suggests that the moment of inertia is

$$I_{\text{TS}} = 1.234 \times 10^{-46} \text{ kg m}^2. \tag{516}$$

With this, we can write

$$\frac{(z_{\text{rot}})^\ddagger}{(z_{\text{rot}})_{\text{F}\bullet}(z_{\text{rot}})_{\text{H}_2}} = \frac{\frac{8\pi^2 I_{\text{TS}} k_{\text{B}} T}{\sigma_{\text{TS}} h^2}}{(1)\left(\frac{8\pi^2 I_{\text{H}_2} k_{\text{B}} T}{\sigma_{\text{H}_2} h^2}\right)} = \frac{91.917}{(1)(1.707)} = 53.851 \tag{517}$$

To summarize, the non-tabulated information needed when calculating the rotational partition function is:

1. The experimentally relevant (absolute) temperature, T.
2. Whether each species (i.e. reactants, transition state) are monatomic, non-linear, or linear. This is usually self-evident from the molecules themselves, but density functional theory can always be used to determine the molecular geometry if there is uncertainty (e.g. as might be the case with the transition state).
3. The rotational symmetry number, σ, for each species. Again, this depends on the geometry.
4. The moment of inertia, I, for each species. This also depends on the geometry, although rotational spectroscopy can be used to discern this information for the reactants.

As can be seen above, the key information needed here is the geometry of the reactants and transition state. Since it is impossible to experimentally isolate a transition state, one must either make assumptions about the transition state geometry or rely on quantum-chemical calculations.

7.4.2.4. Vibrational Partition Function

Now we will tackle the vibrational partition function. We recall the functional form is as follows:

$$z_{\text{vib}} = \prod_{i=1}^{N} \frac{1}{1 - \exp\left(-\frac{h\nu_i}{k_{\text{B}} T}\right)}, \tag{518}$$

where the number of vibrational modes will vary depending on the geometry of the molecule.

F is monatomic, so there are no vibrational modes and

$$(z_{\text{vib}})_{\text{F}\bullet} = 1. \tag{519}$$

H_2 is linear and has two atoms, the number of vibrational modes is given by $3(2) - 5 = 1$. It is known from spectroscopy that the vibrational stretching frequency of H_2 is 4395 cm^{-1}. Plugging this in yields

$$(z_{\text{vib}})_{\text{H}_2} \approx 1 \tag{520}$$

since large vibrational modes do not substantially contribute to z_{vib}.

The transition state has three atoms and is assumed to be linear. Normally, there would be $3(3) - 5 = 4$ vibrational modes. However, because this is a transition state, one of those modes becomes associated with the motion along the reaction coordinate and so there are only three real vibrational modes. From quantum-mechanical calculations, we will say that these values are 4007 cm^{-1}, 398 cm^{-1}, and 398 cm^{-1}. This results in

$$(z_{\text{vib}})^{\ddagger} = 1.378 \tag{521}$$

With this information, we can write

$$\frac{(z_{\text{vib}})^{\ddagger}}{(z_{\text{vib}})_{\text{F}^{\bullet}}(z_{\text{vib}})_{\text{H}_2}} = \frac{1.378}{(1)(1)} = 1.378. \tag{522}$$

To summarize, the non-tabulated information needed when calculating the rotational partition function is:

1. The experimentally relevant (absolute) temperature, T.
2. The (real) vibrational modes for the reactants and transition state. For the reactants, this can be determined from spectroscopy (e.g. IR, Raman). However, this is not possible for the transition state. In practice, the vibrational modes are typically computed from quantum-chemical calculations.

7.4.2.5. Electronic Partition Function

For the electronic partition function, we recall that

$$z_{\text{el}} = g_0, \tag{523}$$

where we have chosen to neglect the contribution from the excited electronic states and have taken the ground-state energy as the zero-energy reference. Since H_2 has no unpaired electrons, we can state

$$(z_{\text{el}})_{\text{H}_2} = 1. \tag{524}$$

However, $\text{F}^{\bullet}$ has one unpaired electron and so

$$(z_{\text{el}})_{\text{F}^{\bullet}} = 2. \tag{525}$$

As for the transition state, whether it has radical character or not may be a little less clear. However, one useful rule of thumb is that (provided the total number of electrons remains the same) the total number of unpaired electrons cannot change from odd to even or vice versa.[88] In other words,

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[88]This is because an odd-numbered spin multiplicity can only occur when the total number of unpaired electrons is even and vice versa.

$$(z_{\text{el}})^\ddagger = 2. \tag{526}$$

Therefore,

$$\frac{(z_{\text{el}})^\ddagger}{(z_{\text{el}})_{\text{F}\bullet}(z_{\text{el}})_{\text{H}\bullet}} = \frac{2}{(2)(1)} = 1. \tag{527}$$

To summarize, the (non-tabulated) information needed is:

1. Whether the excited electronic states can be ignored (typically the case).
2. The spin multiplicity (i.e. number of unpaired electrons + 1) for each species. For the reactants, this can be determined from a magnetic susceptibility balance or from Mössbauer spectroscopy.

7.4.2.6. Putting It All Together

Now we will put all the pieces together:

$$k_{\text{TST}} = \frac{k_{\text{B}}T}{h} N_{\text{A}}\left(4.162 \times 10^{-28}\text{L}\right)(53.851)(1.378)(1) \exp\left(-\frac{\Delta E_0^\ddagger}{RT}\right). \tag{528}$$

This simplifies to

$$k_{\text{TST}} = \left(1.163 \times 10^{11} \text{ L/mol-s}\right) \exp\left(-\frac{\Delta E_0^\ddagger}{RT}\right). \tag{529}$$

We have the pre-exponential factor. Now we need the $\Delta E_0^\ddagger$ term. Strictly speaking, $\Delta E_0^\ddagger$ can only be computed from quantum-mechanical calculations. Here, we will take it as provided to us that $\Delta E_0^\ddagger$ = 6 kJ/mol. This gets us

$$k_{\text{TST}} = 1.05 \times 10^{10} \text{ L/mol-s}. \tag{530}$$

For comparison, the NIST Kinetics Database indicates that $k = 1.4 \times 10^{10}$ L/mol-s for this reaction (at 298 K, which is close enough to our 300 K scenario). Usually, transition state theory will over-estimate the actual value of k, although in this case it does not. The reason for k_{TST} being less than k here is likely just due to underlying errors in the quantum-chemical calculations.

7.5. Accounting for Thermodynamic Non-Idealities

7.5.1. Derivation in Terms of Activity Coefficients

In the derivations of the transition state theory rate constant thus far, we have implicitly neglected any thermodynamic non-idealities. Now it is time for us to revisit our expressions with a fresh mindset. Recall that we started off our transition state theory derivation with

$$r = \nu^\ddagger [\text{AB}]^\ddagger = \frac{k_{\text{B}}T}{h}[\text{AB}]^\ddagger, \tag{531}$$

as originally shown in Equation 481. Instead of substituting in for $K_c^{\ddagger}$ to get rid of the $[AB]^{\ddagger}$ intermediate, we will instead take advantage of the definition of $K_a^{\ddagger}$ given by Equation 51:

$$K_a^{\ddagger} = \left(\frac{1}{C^{\circ}}\right)^{1-m} \frac{\gamma^{\ddagger}[AB]^{\ddagger}}{\gamma_A[A]\gamma_B[B]}. \tag{532}$$

Solving for $[AB]^{\ddagger}$ yields

$$[AB]^{\ddagger} = (C^{\circ})^{1-m} K_a^{\ddagger} \frac{\gamma_A \gamma_B}{\gamma^{\ddagger}} [A][B]. \tag{533}$$

Plugging this into our rate expression now yields

$$
\begin{aligned}
r &= \frac{k_B T}{h} (C^{\circ})^{1-m} K_a^{\ddagger} \frac{\gamma_A \gamma_B}{\gamma^{\ddagger}} [A][B] \\
r &= \frac{k_B T}{h} (C^{\circ})^{1-m} \frac{Z^{\ddagger}}{Z_A Z_B} \exp\left(-\frac{\Delta E_0^{\ddagger}}{RT}\right) \frac{\gamma_A \gamma_B}{\gamma^{\ddagger}} [A][B].
\end{aligned}
\tag{534}
$$

Here, the definition of $K_a^{\ddagger}$ was substituted in from Equation 486. Note that the partition functions (i.e. Z) are their unitless values, not normalized by the reference volume (i.e. Z') since that was needed to reproduce the constants of $K_C^{\ddagger}$, whereas we are dealing with $K_a^{\ddagger}$. Equation 534 is the non-ideal analogy to Equation 504.

From the above expression, we can write $r = k_{\text{nonideal}}[A][B]$, where

$$k_{\text{nonideal}} = \frac{k_B T}{h} (C^{\circ})^{1-m} K_a^{\ddagger} \frac{\gamma_A \gamma_B}{\gamma^{\ddagger}} \tag{535}$$

or, equivalently, in terms of the partition functions,

$$
\begin{aligned}
k_{\text{nonideal}} &\equiv A_{\text{nonideal}} \exp\left(-\frac{\Delta E_0^{\ddagger}}{RT}\right) \\
A_{\text{nonideal}} &\equiv \frac{k_B T}{h} (C^{\circ})^{1-m} \frac{Z^{\ddagger}}{Z_A Z_B} \frac{\gamma_A \gamma_B}{\gamma^{\ddagger}}.
\end{aligned}
\tag{536}
$$

Comparing the non-ideal rate constant in Equation 536 with the idealized case in Equation 506, we see that the difference in the rate when accounting for thermodynamic non-idealities can be traced back to the ratio of activity coefficients via the following relationship:[89]

$$k_{\text{nonideal}} = k_{\text{ideal}} \frac{\gamma_A \gamma_B}{\gamma^{\ddagger}}. \tag{537}$$

---

[89]Note that $1/N_A^{1-m} \prod_{j,\nu_j<0} Z_j'^{|\nu_j|}$ in the definition of A_{ideal} is equivalent to $(C^{\circ})^{1-m} \prod_{j,\nu_j<0} Z_j^{|\nu_j|}$ in the definition of A_{nonideal} since $Z_j' \equiv Z_j/V$.

A natural question to ask at this point is what value this analysis can provide if it relies on $\gamma^{\ddagger}$, which cannot be readily determined from experiments. One answer is that it is possible—like with other aspects of the transition state theory representation of k—to determine $\gamma^{\ddagger}$ from theory. Perhaps more importantly, however, is that Equation 537 can be used in a qualitative way to rationalize the effects of non-idealities.

For instance, in the liquid-phase, if a solvent selectively stabilizes a given species, the activity coefficient for that species will likely be greater than 1.[90] Therefore, we can say that if we stabilize the reactants via solvation, then k_{nonideal} would increase. In contrast, if our reaction media selectively stabilizes the transition state, then k_{nonideal} will decrease. Similar arguments can be made about gas-phase reactions by considering the fugacity coefficient φ_j in place of the activity coefficient γ_j.

7.5.2. Replacing Concentrations with Activities

Naturally, another question one might ask is: can one simply replace concentrations by activities in a rate expression if we wish to account for thermodynamic non-idealities? Consider a rate law of the form

$$r = k[\text{A}][\text{B}]. \tag{538}$$

Using Equation 537, we can state

$$r_{\text{nonideal}} = k_{\text{nonideal}}[\text{A}][\text{B}] \tag{539}$$

$$r_{\text{nonideal}} = k_{\text{ideal}} \frac{\gamma_{\text{A}} \gamma_{\text{B}}}{\gamma^{\ddagger}} [\text{A}][\text{B}]. \tag{540}$$

By recognizing that $a_j \equiv \gamma_j \left[A_j \right] / C^{\circ}$, we can rewrite the above expression as

$$r_{\text{nonideal}} = k_{\text{ideal}} (C^{\circ})^m \frac{1}{\gamma^{\ddagger}} a_{\text{A}} a_{\text{B}}. \tag{541}$$

Therefore, while it is perfectly reasonable to use activities in a rate expression,[91] one must take care in doing so. Namely, the additional component that needs to be accounted for is the factor of $1/\gamma^{\ddagger}$ (in addition to ensuring the units work out via the appropriate factors of C°).

7.6. Degrees of Freedom in Transition State Theory

As was shown previously, the rate constant for a given elementary step is related to the ratio of partition functions for the transition state and the reactant(s):

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[90]From a qualitative standpoint, this is because the effective concentration (i.e. activity) of the solute will necessarily be higher since it will be less accessible given that it is highly solvated.

[91]This is in contrast with statements made in G. Lente, "Facts and Alternative Facts in Chemical Kinetics: Remarks About the Kinetic Use of Activities, Termolecular Processes, and Linearization Techniques", *Curr. Opin. Chem. Eng.*, 21, 76–83 (2018).

$$k \propto \frac{Z'^{\ddagger}}{Z'_{\mathrm{A}} Z'_{\mathrm{B}}}. \tag{542}$$

If one considers a free molecule (e.g. in the gas phase), it has three translational degrees of freedom, three rotational degrees of freedom (if nonlinear) or two rotational degrees of freedom (if linear), and several vibrational degrees of freedom depending on the number of atoms, N_0. We will represent this as follows, where the exponents in quotes are simply how many degrees of freedom there are.[92]

$$Z' = z'^{(3)}_{\mathrm{trans}} z^{(m)}_{\mathrm{rot}} z^{(N)}_{\mathrm{vib}} z_{\mathrm{el}}, \tag{543}$$

where

$$
\begin{aligned}
m &= 0, \quad N = 0 \quad \text{(monatomic)} \\
m &= 2, \quad N = 3N_0 - 5 \quad \text{(linear)} \\
m &= 3, \quad N = 3N_0 - 6 \quad \text{(non-linear)}.
\end{aligned}
\tag{544}
$$

For a transition state, one vibrational degree of freedom is lost and becomes an imaginary mode, such that

$$Z'^{\ddagger} = z'^{\ddagger(3)}_{\mathrm{trans}} z^{\ddagger(m)}_{\mathrm{rot}} z^{\ddagger(N-1)}_{\mathrm{vib}} z^{\ddagger}_{\mathrm{el}}. \tag{545}$$

With this in mind, we can often make order-of-magnitude arguments and simplifications to approximate a rate constant.
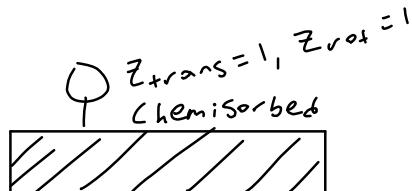

Figure 24: Schematic of a chemisorbed molecule on a surface. If the adsorbate is strongly bound, it will have no translational or rotational degrees of freedom.

When a molecule adsorbs onto a surface, some degrees of freedom are lost. If the adsorbate is chemisorbed onto the surface (Figure 24), then the adsorbate molecule will likely have no translational or rotational degrees of freedom remaining, depending on how strongly it is adsorbed. The vibrational degrees of freedom are still present, although the vibrational modes are likely to differ substantially from the gas phase, and there are now $3N_0$ vibrational modes instead of $3N_0 - 5$ or $3N_0 - 6$. As for the surface itself, it is immobile, so it does not have any translational or rotational degrees of freedom. While the surface does have vibrational degrees of freedom, if there is relatively little coupling between the vibrational modes of the adsorbate and surface,

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[92]We have tacitly assumed that the excited states are energetically negligible, such that $z_{\mathrm{el}} = g_0$ and therefore z_{el} has only one degree of freedom.

then the vibrational modes of the surface atoms may remain unchanged such that they can be neglected.[93]

If the adsorbate is somewhat weakly bound, then the remaining degrees of freedom are likely to be somewhere between that used for a free gas and that of a chemisorbed species. More complicated expressions are available to model these intermediate behaviors, such as the hindered translator–hindered rotor model.[94] Additional consideration can be found in the literature related to molecules that adsorb within porous materials, where spatial confinement may restrict some degrees of freedom.[95]

7.7. A Thermodynamic Perspective to Transition State Theory

Previously, we derived an expression for k based on a statistical mechanics approach (i.e. using partition functions). We will show in this subsection that an analogous expression can be derived from simple thermodynamic arguments, albeit without the atomistic details.

7.7.1. The Eyring Equation

Here, we will derive the Eyring equation,[96] which takes an analogous functional form as the transition state theory formalism for the rate constant but does not rely on statistical mechanics.

We start by recalling that

$$\Delta G^{\circ\ddagger} = -RT\ln\left(K_{\mathrm{a}}^{\ddagger}\right), \tag{546}$$

such that

$$K_{\mathrm{a}}^{\ddagger} = \exp\left(-\frac{\Delta G^{\circ\ddagger}}{RT}\right). \tag{547}$$

Plugging $K_{\mathrm{a}}^{\ddagger}$ into our expression for k_{nonideal} in Equation 535 (which we will simply refer to as k here) yields

$$k = \frac{k_{\mathrm{B}}T}{h}(C^{\circ})^{1-m}\exp\left(-\frac{\Delta G^{\circ\ddagger}}{RT}\right)\frac{\gamma_{\mathrm{A}}\gamma_{\mathrm{B}}}{\gamma^{\ddagger}}. \tag{548}$$

In the thermodynamically ideal case (i.e. $\gamma_{\mathrm{A}} = \gamma_{\mathrm{B}} = \gamma^{\ddagger} = 1$), this expression is known as the Eyring equation. By convention, C° is typically taken as P/RT at 1 bar for gases or as 1 M for liquids.

Naturally, when taking advantage of the thermodynamic relationship

---

[93]The accuracy of this approximation is quite variable but is generally reasonable when there is a large mass difference between the adsorbate and surface atoms and relatively weak adsorption.

[94]L.H. Sprowl, C.T. Campbell, L. Árnadóttir, "Hindered Translator and Hindered Rotor Models for Adsorbates: Partition Functions and Entropies," *J. Phys. Chem. C*, 120, 9719–9731 (2016).

[95]P.J. Dauenhauer, O.A. Abdelrahman, "A Universal Descriptor for the Entropy of Adsorbed Molecules in Confined Spaces", *ACS Catal.*, 4, 1235–1243 (2018).

[96]Fun fact: Henry Eyring was a faculty member at Princeton from 1931–1946.

$$\Delta G^\circ = \Delta H^\circ - T \Delta S^\circ, \tag{549}$$

we can rewrite the above expression as

$$k = \frac{k_\mathrm{B} T}{h} C^{\circ 1-m} \exp\left(\frac{\Delta S^{\circ \ddagger}}{R}\right) \exp\left(-\frac{\Delta H^{\circ \ddagger}}{RT}\right) \frac{\gamma_\mathrm{A} \gamma_\mathrm{B}}{\gamma^\ddagger} \tag{550}$$

or in Arrhenius form as

$$k \equiv A \exp\left(-\frac{\Delta H^{\circ \ddagger}}{RT}\right), \quad A \equiv \frac{k_\mathrm{B} T}{h} C^{\circ 1-m} \exp\left(\frac{\Delta S^{\circ \ddagger}}{R}\right) \frac{\gamma_\mathrm{A} \gamma_\mathrm{B}}{\gamma^\ddagger}. \tag{551}$$

With this, we can write our usual rate equation of the form $r = k[\mathrm{A}][\mathrm{B}]$ in terms of enthalpies and entropies of activation.[97]

An Arrhenius-type plot can also be made of $\ln(k/T)$ vs. $1/T$ to back out $\Delta H^{\circ \ddagger}$ from the slope and $\Delta S^{\circ \ddagger}$ from the y-intercept. In the ideal case where the activity coefficients can be neglected, we have

$$\ln\left(\frac{k}{T}\right) = -\frac{\Delta H^{\circ \ddagger}}{R} \cdot \frac{1}{T} + \left[\ln\left(\frac{k_\mathrm{B}}{h} C^{\circ 1-m}\right) + \frac{\Delta S^{\circ \ddagger}}{R}\right]. \tag{552}$$

The linearized expression is only useful if one can assume that $\Delta H^{\circ \ddagger}$ and $\Delta S^{\circ \ddagger}$ are reasonably independent of temperature.

7.7.2. The Transmission Coefficient

In practice, a multiplicative correction factor κ, known as the transmission coefficient, is often included in the expression for k. For instance, it can be used to correct the Eyring equation representation of the rate constant via

$$k = \kappa \frac{k_\mathrm{B} T}{h} C^{\circ 1-m} \exp\left(-\frac{\Delta G^{\circ \ddagger}}{RT}\right) \tag{553}$$

in the thermodynamically ideal case. The value for κ is between 0 and 1, in which case it represents the probability that the vibrational motion given by $\nu^\ddagger$ pushes the transition state forward towards the products as opposed to backwards towards the reactants.[98] In other words, the rate constant (and rate) from transition state theory is generally an upper-estimate if all variables in the uncorrected rate expression were computed with perfect accuracy. Unless otherwise stated, we will assume that $\kappa = 1$.

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[97]There is sometimes a linear correlation between $\Delta H^{\circ \ddagger}$ and $\Delta S^{\circ \ddagger}$ but not necessarily for the reasons one might anticipate. Refer to G.C. McBane, "Chemistry from Telephone Numbers: The False Isokinetic Relationship", *J. Chem. Educ.*, 75, 919–922 (1998).

[98]In contrast with J.F. Perez-Benito, "Some Considerations on the Fundamentals of Chemical Kinetics: Steady State, Quasi-Equilibrium, and Transition State Theory", *J. Chem. Educ.*, 94, 1238–1246 (2017), k cannot be proportional to $\kappa(1-\kappa)$ otherwise $r \to 0$ as $\kappa \to 1$ and there becomes an unphysical maximum in the rate at $\kappa = 1/2$.

7.7.3. Relationship Between Activation Enthalpy and Activation Energy

We can also ask how the apparent activation energy commonly reported in experiments from an Arrhenius plot is related to $\Delta H^{\circ\ddagger}$. First, we recall the definition of the apparent activation energy from Equation 77:

$$E_{\mathrm{a}} = RT^2 \frac{\partial \ln(k)}{\partial T}. \tag{554}$$

Plugging in k from the Eyring equation into the above expression yields

$$E_{\mathrm{a}} = RT^2 \frac{\partial \ln\left(\frac{k_{\mathrm{B}}T}{h} C^{\circ 1-m} \exp\left(\frac{\Delta S^{\circ\ddagger}}{R} \right) \exp\left(-\frac{\Delta H^{\circ\ddagger}}{RT} \right) \right)}{\partial T} \tag{555}$$

$$E_{\mathrm{a}} = RT^2 \left(\frac{\partial \ln\left(\frac{k_{\mathrm{B}}}{h} \right)}{\partial T} + \frac{\partial \ln(T)}{\partial T} + \frac{\partial \ln\left(C^{\circ 1-m} \right)}{\partial T} + \frac{\partial \left(\frac{\Delta S^{\circ\ddagger}}{R} \right)}{\partial T} - \frac{\partial \left(\frac{\Delta H^{\circ\ddagger}}{RT} \right)}{\partial T} \right) \tag{556}$$

$$E_{\mathrm{a}} = RT^2 \left(0 + \frac{1}{T} + \frac{\partial \ln\left(C^{\circ 1-m} \right)}{\partial T} + 0 + \frac{\Delta H^{\circ\ddagger}}{RT^2} \right) \tag{557}$$

$$E_{\mathrm{a}} = \Delta H^{\circ\ddagger} + RT + RT^2 \left(\frac{\partial \ln\left(C^{\circ 1-m} \right)}{\partial T} \right). \tag{558}$$

At this point, we pause. What we do from here depends on what system we are studying. If we are studying a solid or a liquid, we might reasonably state that C° is independent of temperature. In this case, we end up with

$$E_{\mathrm{a}} = \Delta H^{\circ\ddagger} + RT \quad \text{(solids, liquids)}. \tag{559}$$

However, if we are studying a gas, it is more natural to use a standard-state pressure P°. Assuming the ideal gas law holds, we instead have

$$E_{\mathrm{a}} = \Delta H^{\circ\ddagger} + RT + RT^2 \left(\frac{\partial \ln\left(\left(\frac{P^\circ}{RT} \right)^{1-m} \right)}{\partial T} \right) \tag{560}$$

$$E_{\mathrm{a}} = \Delta H^{\circ\ddagger} + RT + RT^2 \left(\frac{m-1}{T} \right) \tag{561}$$

$$E_{\mathrm{a}} = \Delta H^{\circ\ddagger} + mRT \quad \text{(ideal gas)}. \tag{562}$$

In both cases, the derivation has implicitly assumed that $\Delta H^{\circ\ddagger}$ and $\Delta S^{\circ\ddagger}$ are independent of temperature, which is only true if we are considering relatively small temperature differences.

Clearly, Equation 562 indicates there are several possible meanings for a "kinetic barrier." Therefore, one should take care in clarifying which property is being reported.[99]

7.8. de Donder Relations

7.8.1. Reaction Affinity and Reversibility

In the formulation of transition state theory, we derived the forward directional rate from reactant(s) to product(s) via the intermediate formation of an activated complex. It is worth thinking about how we can now leverage this information to describe reversible reactions.[100] One of the most fundamental properties of a reversible elementary reaction is its reversibility, first introduced in Equation 37 and repeated here as $z_i \equiv r_i^-/r_i^+$.

To make things a bit simpler to follow for those who do not enjoy gratuitous product notation as much as me, we will invoke an arbitrary reaction: $A + B \rightleftharpoons P$. Assuming we are dealing with directional rates in an elementary reaction, we know that

$$z_i = \frac{r_i^-}{r_i^+} = \frac{k_i^-[\text{P}]}{k_i^+[\text{A}][\text{B}]}. \tag{563}$$

Our end-goal here will be to show that

$$z_i = \exp\left(\frac{\Delta G_i}{RT}\right), \tag{564}$$

which will lead to a new concept known as the reaction affinity. We will start by finding an expression for the rate constants, after which we will revisit the concentration terms.

From the Eyring equation, we know that

$$k_i^+ = \frac{k_\text{B}T}{h}(C^\circ)^{-1}\exp\left(-\frac{G^{\circ\ddagger} - G_\text{A}^\circ - G_\text{B}^\circ}{RT}\right)\frac{\gamma_\text{A}\gamma_\text{B}}{\gamma^\ddagger}$$

$$k_i^- = \frac{k_\text{B}T}{h}\exp\left(-\frac{G^{\circ\ddagger} - G_\text{P}^\circ}{RT}\right)\frac{\gamma_\text{P}}{\gamma^\ddagger}. \tag{565}$$

Therefore,

$$\frac{k_i^-}{k_i^+} = C^\circ \exp\left(\frac{G_\text{P}^\circ - G_\text{A}^\circ - G_\text{B}^\circ}{RT}\right)\frac{\gamma_\text{P}}{\gamma_\text{A}\gamma_\text{B}}$$

$$\frac{k_i^-}{k_i^+} = C^\circ \exp\left(\frac{\Delta G_i^\circ}{RT}\right)\frac{\gamma_\text{P}}{\gamma_\text{A}\gamma_\text{B}}. \tag{566}$$

---

[99] For a discussion on the relationship between the apparent activation energy and enthalpy in multi-step reactions with multiple transition states, refer to Z. Mao, C.T. Campbell, "Apparent Activation Energies in Complex Reaction Mechanisms: A Simple Relationship via Degrees of Rate Control", *ACS Catal.*, 9, 9465–9473 (2019).

[100] For a thorough review on this topic, refer to N.K. Razdan, T.C. Lin, A. Bhan, "Concepts Relevant for the Kinetic Analysis of Reversible Reaction Systems", *Chem. Rev.*, 123, 2950–3006 (2023).

That takes care of part of our expression for the reversibility given by Equation 563. For the ratio of concentrations, we know that this looks like an equilibrium constant. Technically, we have made no assumptions about being at equilibrium here. As such, we will invoke the concept of the reaction quotient:

$$Q_{\mathrm{a}} \equiv \prod_j a_j^{\nu_j} \quad \text{(out-of-equilibrium)}. \tag{567}$$

The relationship between the reaction quotient and Gibbs free energy is given by

$$\Delta G_i = RT \ln\left(\frac{Q_{\mathrm{a}}}{K_{\mathrm{a}}}\right) \tag{568}$$

$$\Delta G_i = \Delta G_i^{\circ} + RT \ln(Q_{\mathrm{a}}). \tag{569}$$

$$\Delta G_i = \Delta G_i^{\circ} + RT \ln\left(\prod_j a_j^{\nu_{i,j}}\right). \tag{570}$$

Here, ΔG_i is at the reaction conditions (i.e. not necessarily standard state). Note that at equilibrium (and at standard state conditions), $Q_{\mathrm{a}} = K_{\mathrm{a}}$ and therefore $\Delta G_i = 0$.

We can convert between activities and concentrations to arrive at the following expression for our toy reaction:

$$\Delta G_i = \Delta G_i^{\circ} + RT \ln\left(\frac{\gamma_{\mathrm{P}} \frac{[\mathrm{P}]}{C^{\circ}}}{\gamma_{\mathrm{A}} \frac{[\mathrm{A}]}{C^{\circ}} \gamma_{\mathrm{B}} \frac{[\mathrm{B}]}{C^{\circ}}}\right)$$

$$\frac{[\mathrm{P}]}{[\mathrm{A}][\mathrm{B}]} = \frac{1}{C^{\circ}} \frac{\gamma_{\mathrm{A}} \gamma_{\mathrm{B}}}{\gamma_{\mathrm{P}}} \exp\left(\frac{\Delta G_i - \Delta G_i^{\circ}}{RT}\right). \tag{571}$$

Now we can plug both Equation 566 and Equation 571 into Equation 563, which thankfully simplifies very cleanly to

$$z_i = \frac{r_i^-}{r_i^+} = \exp\left(\frac{\Delta G_i^{\circ}}{RT}\right) \exp\left(\frac{\Delta G_i - \Delta G_i^{\circ}}{RT}\right) = \exp\left(\frac{\Delta G_i}{RT}\right). \tag{572}$$

By convention, we will define

$$\mathcal{A}_i \equiv -\Delta G_i, \tag{573}$$

where $\mathcal{A}_i$ is known as the reaction affinity of the i-th reaction step. With this, we have

$$z_i = \frac{r_i^-}{r_i^+} = \exp\left(-\frac{\mathcal{A}_i}{RT}\right). \tag{574}$$

The same result will hold regardless of the molecularity of the elementary reaction or if we neglected thermodynamic non-idealities. Equation 574 is known as the de Donder relation, which is a thermodynamic relationship between the forward and reverse rates of reaction.

> ⚠️ **Caution**
>
> There is a clear parallel between the de Donder relation and the equilibrium constant:
>
> $$z_i = \frac{r_i^-}{r_i^+} = \exp\left(-\frac{\mathcal{A}_i}{RT}\right), \quad K_{\mathrm{a}} = \frac{k_i^+}{k_i^-} = \exp\left(-\frac{\Delta G^\circ}{RT}\right). \tag{575}$$
>
> That said, it must be stressed once more that the de Donder relation is computed using the reaction conditions and does not involve a standard state. The de Donder relationship also describes a ratio of rates, not rate constants.

We can see that $z_i < 1$ (i.e. the reaction proceeds in the forward direction) only if $\mathcal{A}_i > 0$ and vice versa. Another way to frame this is by stating

$$\mathcal{A}_i r_i \geq 0 \tag{576}$$

for a reaction to proceed as-written, which is known as de Donder's inequality. Here, r_i is the net reaction rate of step i. Another way to describe de Donder's inequality is that for an elementary reaction to proceed in the forward direction, both r_i and $\mathcal{A}_i$ must be positive; similarly, if the elementary reaction is to proceed in the reverse direction, both r_i and $\mathcal{A}_i$ must be negative. For full clarity, there is no direct relationship between $\mathcal{A}_i^\circ$ and the viability of the net reaction proceeding in a given direction—it only depends on $\mathcal{A}_i$ at the reaction conditions.

The de Donder relationship can also be used to describe the net rate of reaction:

$$r_i \equiv r_i^+ - r_i^- = r^+ - r^+ \exp\left(-\frac{\mathcal{A}_i}{RT}\right) = r^+\left(1 - \exp\left(-\frac{\mathcal{A}_i}{RT}\right)\right). \tag{577}$$

When written in this manner, it is clear that the net rate of reaction can be expressed as a combination of kinetic and thermodynamic terms.

7.8.2. Ruling Out Reaction Mechanisms

We can use the de Donder relations as a way to immediately rule out physically impossible reaction mechanisms.[101] For instance, consider the cyclic reaction scheme in Figure 25.

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[101] For additional details, refer to W.L. Holstein and M. Boudart, "Application of the De Donder Relation to the Mechanism of Catalytic Reactions", *J. Phys. Chem. B*, 101, 9991–9994 (1997).
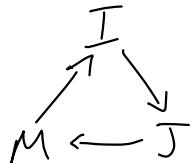
Figure 25: A closed reaction cycle that is not viable. Each arrow represents the net direction each reaction is presumed to occur.

Like with any set of state functions in a closed cycle, we know that

$$\sum_i \mathcal{A}_i = 0, \tag{578}$$

such that
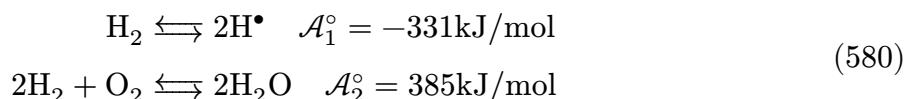
$$\mathcal{A}_1 + \mathcal{A}_2 + \mathcal{A}_3 = 0. \tag{579}$$

However, it is impossible for this statement to be true unless $\mathcal{A}_i = 0$ for each step, which would imply no reaction progress. At least one of the reaction steps must have $\mathcal{A}_i < 0$ in order for $\sum_i \mathcal{A}_i = 0$, which violates de Donder's inequality and implies that such a reaction scheme is not viable as written. Put another way, via de Donder's inequality, we know that one of the reaction steps must actually proceed in the reverse direction, breaking the cyclic nature of the proposed mechanism.

7.8.3. Thermodynamics vs. Kinetic Coupling

7.8.3.1. Thermodynamic Coupling

We can also leverage de Donder relations in non-cyclic reactions. Consider the following proposed reaction sequence:

$$\begin{aligned}
\mathrm{H_2} &\rightleftharpoons 2\mathrm{H}^\bullet \quad \mathcal{A}_1^\circ = -331\mathrm{kJ/mol} \\
2\mathrm{H_2} + \mathrm{O_2} &\rightleftharpoons 2\mathrm{H_2O} \quad \mathcal{A}_2^\circ = 385\mathrm{kJ/mol}
\end{aligned} \tag{580}$$

for the following overall reaction:

$$3\mathrm{H_2} + \mathrm{O_2} \rightleftharpoons 2\mathrm{H_2O} + 2\mathrm{H}^\bullet. \tag{581}$$

For now, we will consider the reaction taking place at standard state conditions such that $\mathcal{A}_i = \mathcal{A}_i^\circ$.

When looking at the individual steps, we see that the first step has $\mathcal{A}_i < 0$, and de Donder's inequality must hold for every individual step in the proposed mechanism. This is true even if there is "thermodynamic coupling," wherein we combine thermodynamically favorable and unfavorable steps to have an overall positive affinity.

The overall reaction affinity for any reaction can be given by

$$\mathcal{A} \equiv \sum_i \sigma_i \mathcal{A}_i, \tag{582}$$

such that for the reaction of interest here we have $\mathcal{A} = 54$ kJ/mol since $\sigma_1 = \sigma_2 = 1$. However, as previously stated, having $\mathcal{A} > 0$ is a necessary but not sufficient condition.

7.8.3.2. Kinetic Coupling

Now, we will revisit the mechanism in Section 7.8.3.1 but relax the assumption that we are operating at standard state conditions. In this scenario, $\mathcal{A}_i \neq \mathcal{A}_i^\circ$, and even though $\mathcal{A}_1^\circ < 0$, this does not necessarily mean the step is impossible since the de Donder relations apply to $\mathcal{A}_i$ and not $\mathcal{A}_i^\circ$. We will show that a concept known as kinetic coupling can enable the reaction to proceed as-written.

We know from the definition of Gibbs free energy, and thereby reaction affinity, that

$$\mathcal{A}_i = \mathcal{A}_i^\circ - RT \ln \left(\prod_j a_j^{\nu_{i,j}} \right), \quad \mathcal{A}_i^\circ = RT \ln(K_{\mathrm{a}}), \tag{583}$$

such that

$$\mathcal{A}_i = RT \ln \left(\frac{K_{\mathrm{a}}}{\prod_j a_j^{\nu_{i,j}}} \right) = RT \ln \left(\frac{\left(\prod_j a_j^{\nu_{i,j}} \right)_{\mathrm{eq}}}{\prod_j a_j^{\nu_{i,j}}} \right). \tag{584}$$

Therefore, the viability of the reaction mechanism at a given set of reaction conditions is dependent on how much the species activities (or concentrations, in the ideal case) differ from those at equilibrium.

For instance, consider the moment the reaction is started. H_2 will only just have started to dissociate, such that $a_{\mathrm{H}\bullet} \approx 0$. Therefore, the reaction affinity for this step immediately after the reaction begins can be given as

$$\mathcal{A}_1 = \lim_{a_{\mathrm{H}\bullet} \to 0} RT \ln \left(\frac{\left(a_{\mathrm{H}\bullet}^2 / a_{\mathrm{H}_2} \right)_{\mathrm{eq}}}{a_{\mathrm{H}\bullet}^2 / a_{\mathrm{H}_2}} \right) = +\infty, \tag{585}$$

such that $\mathcal{A}_1 > 0$ even though $\mathcal{A}_1^\circ < 0$. This makes sense because the only direction the reaction can initially proceed is in the forward direction. When the extent of reaction is non-negligible (e.g. at steady state), however, the highly negative value of $\mathcal{A}_1^\circ$ suggests the step would be unlikely to proceed in the forward direction as-written.

Ultimately, this brings us to the idea of kinetic coupling wherein a thermodynamically unfavorable (i.e. $\mathcal{A}_i^\circ < 0$) step can be overcome by having the concentration of a reactant kept high or a product concentration kept low with respect to its standard state, equilibrium value via coupling with another step in the mechanism.

For $H_2 \rightleftharpoons 2H^\bullet$ to proceed in the forward direction at steady state, there would need to be a separate, favorable reaction that it could kinetically couple to—namely one that would rapidly and continually consume $H^\bullet$, such as some radical scavenger.

7.9. Degree of Rate Control

7.9.1. The Degree of Rate Control of an Elementary Step

In Section 3.1.6, we introduced the concept of a rate-determining step that can greatly simplify a proposed mechanism. The rate-determining step also indicates, albeit indirectly, where improvements can be made to tune the overall rate of reaction most effectively. While a valuable principle, in most cases, it is not possible to identify a single rate-determining step. In these scenarios, we can rely on a concept known as the degree of rate control to guide our reaction engineering efforts.[102]

The degree of rate control, $X_{\mathrm{RC},i}$ for elementary step i is defined as

$$X_{\mathrm{RC},i} \equiv \frac{k_i}{r}\left(\frac{\partial r}{\partial k_i}\right)_{k_{j\neq i}, K_i} = \left(\frac{\partial \ln(r)}{\partial \ln(k_i)}\right)_{k_{j\neq i}, K_i}. \tag{586}$$

Here, the partial derivative is taken such that the forward and reverse rate constants, k_j, for all steps other than i are constant. Additionally, the equilibrium constant, K_i, for step i is held fixed. While not explicitly written, it is also tacitly assumed that the reaction conditions themselves are constant (e.g. T, species concentrations) since we are focusing on the impact that an infinitesimal change on only the rate constant has on the rate. The reason that there is a factor of k_i/r proceeding the partial derivative in Equation 586 is to ensure that the expression is normalized such that it describes the relative change in the net rate scaled by the given k_i.

By definition, if $X_{\mathrm{RC},i}$ is positive, then it implies that increasing the rate constant k_i will increase the reaction rate and *vice versa*. In this case, step i is said to be a rate-limiting (rather than determining) step. Similarly, if $X_{\mathrm{RC},i}$ is negative, it implies that increasing the rate constant k_i will decrease the reaction rate and *vice versa*. In this case, step i is said to be a rate-inhibiting step.

Since the degree of rate control is most often applied to understand how perturbations on a free energy diagram influence reactivity, it is natural to replace k_i in Equation 586 with free energy. From the Eyring equation, we know that

$$k_i = C^{\circ^{1-m}} \frac{k_\mathrm{B} T}{h} \exp\left(-\frac{\Delta G_i^{\circ\ddagger}}{RT}\right) \tag{587}$$

$$\ln(k_i) = \ln\left(C^{\circ^{1-m}} \frac{k_\mathrm{B} T}{h}\right) - \frac{\Delta G_i^{\circ\ddagger}}{RT}. \tag{588}$$

---

[102]For further details, refer to C.T. Campbell, The Degree of Rate Control: A Powerful Tool for Catalysis Research, *ACS Catalysis*, 4, 2770–2779 (2017). https://doi.org/10.1021/acscatal.7b00115°.

Taking the derivative of both sides under the assumption that we are considering a given value of T yields

$$\partial \ln(k_i) = -\partial \left(\frac{\Delta G_i^{\circ \ddagger}}{RT} \right) \tag{589}$$

since the derivative of a constant is always zero. Therefore, we can write that the degree of rate control is also equal to

$$X_{\mathrm{RC},i} = \left(\frac{\partial \ln(r)}{\partial \left(-\frac{\Delta G_i^{\circ \ddagger}}{RT} \right)} \right)_{k_{j \neq i}, K_i} = \left(\frac{\partial \ln(r)}{\partial \left(-\frac{G_{\mathrm{TS},i}^{\circ}}{RT} \right)} \right)_{G_{j \neq i}^{\circ \ddagger}, G_m^{\circ}}, \tag{590}$$

where the partial derivative in the latter expression is taken such that the Gibbs free energy of the transition states for all steps other than i are constant and the Gibbs free energy of all intermediates m are constant.

7.9.2. The Thermodynamic Degree of Rate Control for an Intermediate

Admittedly, thinking about modifying the free energy of a transition state is a bit awkward. It is far more intuitive to think about how one might change the free energy of an intermediate along the reaction pathway. Thankfully, it is straightforward to extend the degree of rate control concept to intermediates as well, in which case it is often referred to as the thermodynamic degree of rate control. The thermodynamic degree of rate control for intermediate n is given as

$$X_{\mathrm{TRC},n} \equiv \frac{1}{r} \left(\frac{\partial r}{\partial \left(-\frac{G_n^{\circ}}{RT} \right)} \right)_{G_{m \neq n}^{\circ}, G_i^{\circ \ddagger}} = \left(\frac{\partial \ln(r)}{\partial \left(-\frac{G_n^{\circ}}{RT} \right)} \right)_{G_{m \neq n}^{\circ}, G_i^{\circ \ddagger}}. \tag{591}$$

Here, we are taking the derivative with the Gibbs free energy of all reactants, products, and intermediates other than n as constant as well as the free energy of all transition states as fixed. The difference between $X_{\mathrm{RC},i}$ and $X_{\mathrm{TRC},n}$ is graphically depicted in Figure 26.
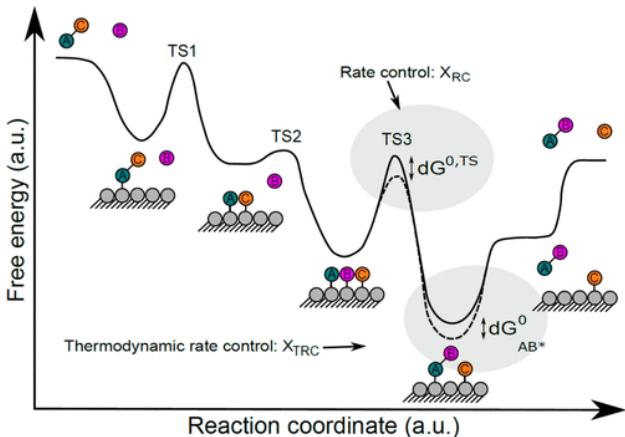
Figure 26: "Schematic standard-state free-energy surface for the reaction AC(g) + B(g) → AB(g) + C(g), showing the degree of rate control based on a transition state free energy change and intermediate free energy change. Source: C. Campbell, *ACS Catal.*, 4, 2770–2779 (2017).

7.9.3. The Generalized Degree of Rate Control

Given the similarity between $X_{\mathrm{RC},i}$ and $X_{\mathrm{TRC},n}$, a generalized degree of rate control for species i can be written as

$$\mathrm{DRC}_i = \frac{1}{r}\left(\frac{\partial r}{\partial\left(-\frac{G_i^\circ}{RT}\right)}\right)_{G_{j\neq i}^\circ} = -\left(\frac{\partial \ln(r)}{\partial\left(\frac{G_i^\circ}{RT}\right)}\right)_{G_{j\neq i}^\circ},\tag{592}$$

where the partial derivative is now taken such that the free energy of all species other than i (including reactants, products, intermediates, transition states) is held fixed. In general,

$$\sum_{\mathrm{steps}} X_{\mathrm{RC},i} = \sum_{\mathrm{TSs}} \mathrm{DRC}_i = 1.\tag{593}$$
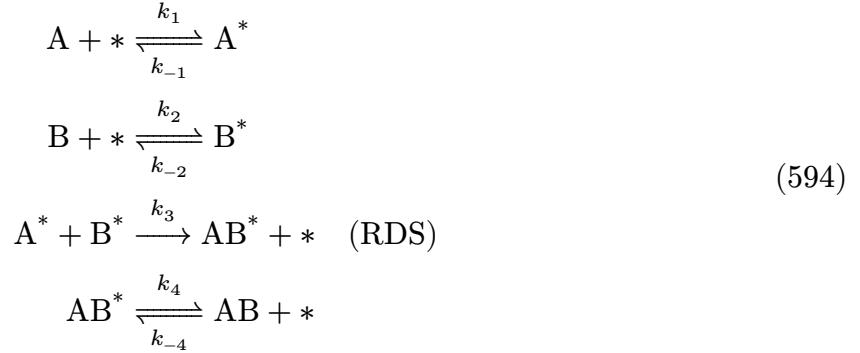
This implies that for a catalytic mechanism with a single rate-determining step i, the value of $X_{\mathrm{RC},i}$ is equal to 1, whereas it is 0 for the remaining steps since they do not contribute to the overall rate to a first approximation.

Ultimately, this brings us back to the concept of a rate-determining step. Some argue that there is no such thing as a rate-determining step.[103] Instead, what we have are rate-determining states, which are the states (including both minima and transition states) along the reaction coordinate that exhibit the largest degree of rate control.

7.9.4. Applying the Degree of Rate Control to a Model Reaction

While the value of the degree of rate control is in being able to analyze complex reaction networks, we will demonstrate its use on a toy reaction scheme simply for demonstration purposes. Consider the following reaction:

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[103]S. Kozuch, J.M.L. Martin, The Rate-Determining Step is Dead. Long Live the Rate-Determining State! *ChemPhysChem*, 12, 1413–1418 (2011). https://doi.org/10.1002/cphc.201100137°.

$$\text{A} + * \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \text{A}^*$$

$$\text{B} + * \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} \text{B}^*$$

$$\text{A}^* + \text{B}^* \overset{k_3}{\longrightarrow} \text{AB}^* + * \quad \text{(RDS)}$$

$$\text{AB}^* \underset{k_{-4}}{\overset{k_4}{\rightleftharpoons}} \text{AB} + * \tag{594}$$

for the surface-catalyzed reaction $\text{A} + \text{B} \longrightarrow \text{AB}$ where the third reaction is the rate-determining step, thereby making the other steps in quasi-equilibrium. For the sake of demonstration, assume that the rate law can be approximated by

$$r = k_3 \frac{K_2}{K_1} \frac{p_\text{B}}{p_\text{A}}. \tag{595}$$

We can write the rate law in terms of standard-state Gibbs free energies using the Eyring equation for k_3 and the definition of the equilibrium constant for K_1 and K_2:

$$r = \left[\frac{k_\text{B}T}{h} \frac{1}{C^\circ} \exp\left(-\frac{\Delta G_3^{\circ\ddagger}}{RT} \right) \right] \left[\frac{C^\circ \exp\left(-\frac{\Delta G_2^\circ}{RT} \right)}{C^\circ \exp\left(-\frac{\Delta G_1^\circ}{RT} \right)} \right] \frac{p_\text{B}}{p_\text{A}} \tag{596}$$

$$r = \frac{k_\text{B}T}{h} \frac{p_\text{B}}{p_\text{A}} \frac{1}{C^\circ} \exp\left(\frac{-\Delta G_3^{\circ\ddagger} - \Delta G_2^\circ + \Delta G_1^\circ}{RT} \right). \tag{597}$$

Note that the numerator inside the exponential is equivalent to

$$-\Delta G_3^{\circ\ddagger} - \Delta G_2^\circ + \Delta G_1^\circ =$$
$$-\left(G_3^{\circ\ddagger} - G_{\text{A}^*}^\circ - G_{\text{B}^*}^\circ \right) - \left(G_{\text{B}^*}^\circ - G_\text{B}^\circ - G_*^\circ \right) + \left(G_{\text{A}^*}^\circ - G_\text{A}^\circ - G_*^\circ \right), \tag{598}$$

such that

$$r = \frac{k_\text{B}T}{h} \frac{p_\text{B}}{p_\text{A}} \frac{1}{C^\circ} \exp\left(\frac{-G_3^{\circ\ddagger} + 2G_{\text{A}^*}^\circ + G_\text{B}^\circ - G_\text{A}^\circ}{RT} \right) \tag{599}$$

$$r = \frac{k_\text{B}T}{h} \frac{p_\text{B}}{p_\text{A}} \frac{1}{C^\circ} \exp\left(\frac{-G_3^{\circ\ddagger} + 2G_{\text{A}^*}^\circ}{RT} \right), \tag{600}$$

where the reactants (A and B) are taken as the zero-energy references and can therefore be removed. Now we can calculate the generalized degree of rate control using Equation 592 to arrive at

$$\text{DRC}_{\text{TS}_3} = 1, \quad \text{DRC}_{\text{A}^*} = -2. \tag{601}$$

The degree of rate control for the rate-determining state (i.e. the transition state associated with the rate-determining step) is 1, which is a general feature of rate-determining steps.

From this analysis, we can gain insights into how to improve the reaction via catalyst design. In general, we wish to stabilize transition states with large, positive degrees of rate control since it is these species that have the most outsized impact on the rate. However, we need to do so without significantly stabilizing intermediates with large, negative degrees of rate control since this would counteract the improvements to the rate.

8. Energy and Reactivity Trends

In this section, we will cover energy and reactivity trends. We have already introduced some of these trends, most notably the Brønsted–Evans–Polanyi (BEP) relationship. Now, we can provide more context for such equations.

8.1. Linear Free Energy Relationships

8.1.1. Brønsted Relationship

One of the earliest forms of linear free energy relationships (LFERs) has to do with acid–base chemistry. Consider the following acid-catalyzed reaction:

$$\text{AH} \underset{}{\overset{K_{\text{acid}}}{\rightleftharpoons}} \text{H}^+ + \text{A}^-$$
$$\text{R} \overset{k}{\longrightarrow} \text{P}, \tag{602}$$

where the acid AH is acting as a catalyst to enable the conversion of R to P. In other words, $\text{R} \longrightarrow \text{P}$ is the net reaction but is not elementary since it involves a more complex mechanism with the acid. Here, K_{acid} is an acid dissociation equilibrium constant given by

$$K_{\text{acid}} = \frac{[\text{H}^+][\text{A}^-]}{[\text{AH}]}. \tag{603}$$

It has been shown that there exists an empirical relationship wherein the stronger the acid is (i.e. the larger K_{acid} is), the faster the conversion of R to P is (i.e. the larger k is). This relationship is typically expressed as

$$\log(k) = \alpha \log(K_{\text{acid}}) + c, \tag{604}$$

where $\alpha > 0$ and c is a constant.[104] A similar relationship is found for base-catalyzed reactions, except that the slope (i.e. α) has the opposite sign.

Equation 605 is known as the Brønsted relationship and was one of the first reported linear free energy relationships. If a new acid is investigated and it yields significant deviations from the Brønsted relationship for a given acid-catalyzed reaction, then it is likely that the reaction proceeds via a different mechanism.

Since $\log(k) \propto E_\text{a}$ via the Arrhenius equation and $\log(K_{\text{acid}}) \propto \Delta G^\circ$, in invoking the above relationship, one is implying that there exists a linear relationship between the activation energy for the reaction and the free energy of acid dissociation:

$$E_\text{a} = a\Delta G^\circ_{\text{acid}} + b, \tag{605}$$

where E_a is the (apparent) barrier associated with $\text{R} \longrightarrow \text{P}$, and $\Delta G^\circ_{\text{acid}}$ is the standard-state Gibbs free energy associated with $\text{HA} \rightleftharpoons \text{H}^+ + \text{A}^-$. Here, a and b are empirical constants, and

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[104]The reason for invoking the log transformations here is that $\text{p}K_{\text{acid}} = -\log(K_{\text{acid}})$, and $\text{p}K_{\text{acid}}$ values are widely tabulated for acids.

$a > 0$. The more exergonic the acid dissociation process is, the lower the activation energy is for the acid-catalyzed reaction $R \longrightarrow P$.

8.1.2. The Evans–Polanyi Model

We will now seek to provide one explanation for why such linear (free) energy relationships can exist by invoking what is known as the Evans–Polanyi model. Consider the reaction

$$AB + C \longrightarrow A + BC. \tag{606}$$

The potential energy diagram for this reaction is shown in Figure 27. As the reaction coordinate progresses, r_{AB} increases, and r_{BC} decreases until it reaches the equilibrium bond length of r_{BC}.
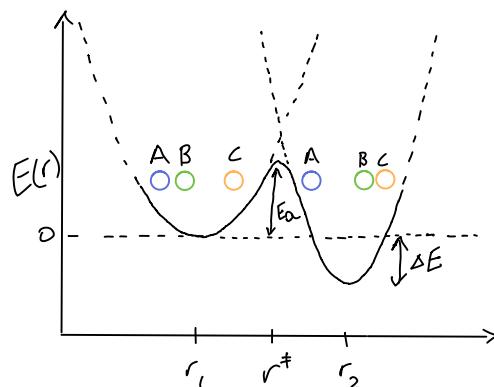

Figure 27: Schematic of the reaction coordinate for $AB + C \longrightarrow A + BC$.

The Evans–Polanyi model approximates the energy landscape by a series of two straight lines that intersect at the transition state, as shown in Figure 28.
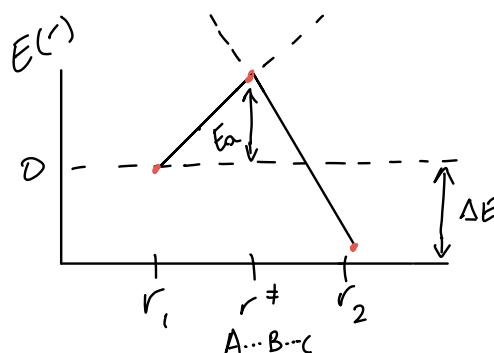

Figure 28: Schematic of the reaction coordinate for $AB + C \longrightarrow A + BC$.

The equation of the first line from reactants to the transition state is given by

$$E_{AB}(r) = m_1(r - r_1), \tag{607}$$

where E_{AB} is the energy of A—B, m_1 is the slope of the aforementioned line, and r_1 is the equilibrium bond length of A—B. Here, r is once again the position along the reaction coordinate (i.e. a variable). By definition, $m_1 > 0$. Note that the zero-energy reference is taken as the

reactants by convention, so the y-intercept is 0. For this demonstration, we will use the above expression for the line to note that at $E_{\mathrm{AB}}(r^{\ddagger})$, we are at the transition state, such that

$$E_{\mathrm{a}} = m_1(r^{\ddagger} - r_1). \tag{608}$$

In analogy with the first line, the equation of the second line is given by

$$E_{\mathrm{BC}}(r) = m_2(r - r^{\ddagger}) + E_{\mathrm{a}}, \tag{609}$$

where E_{a} is as the energy of the transition state with respect to the reactants. Here, by definition, $m_2 < 0$. For this demonstration, we will use the above expression for the line to note that at $E_{\mathrm{BC}}(r_2)$, we are at the value of ΔE, such that

$$\Delta E = m_2(r_2 - r^{\ddagger}) + E_{\mathrm{a}}. \tag{610}$$

By solving for $r^{\ddagger}$ in Equation 608 and plugging this into the above expression, we arrive at

$$\Delta E = m_2\left(r_2 - \left(\frac{E_{\mathrm{a}}}{m_1} + r_1\right)\right) + E_{\mathrm{a}}. \tag{611}$$

After some rearrangement, we have

$$E_{\mathrm{a}} = \frac{m_1}{m_1 - m_2}(\Delta E - m_2(r_2 - r_1)). \tag{612}$$

We can define

$$a \equiv \frac{m_1}{m_1 - m_2}, \quad b \equiv -am_2(r_2 - r_1) \tag{613}$$

to arrive at

$$E_{\mathrm{a}} = a\Delta E + b. \tag{614}$$

For clarity, a must be positive because $m_1 > 0$ and $m_2 < 0$. In turn, b must also be positive.

We have now arrived at an expression relating the activation energy (a kinetic parameter) to the reaction energy (a thermodynamic parameter) via a linear relationship involving two constants. If ΔE is made more exothermic (e.g. by increasing the stability of the product), it will result in a corresponding decrease in E_{a}.

When $a \to 1$, the change in E_{a} is highly sensitive to changes in ΔE. Any stabilization of the product will cause a correlated change in the energy of the transition state and, thereby, the activation energy. When $a \to 0$, the change in E_{a} is barely sensitive to changes in ΔE. Any stabilization of the product will have minimal impact on the energy of the transition state and, thereby, the activation energy.

Returning back to the Brønsted relationship and similar linear free energy relationships, recall that we had a correlation between E_{a} and ΔG°. In general, trends in ΔH° tend to closely

match trends in ΔE. Provided that the entropy of activation is similar across the reactions being considered, then $\Delta G°$ will match trends in ΔE as well, such that it does not the scaling is largely independent of the choice of thermodynamic state function.

8.1.3. Revisiting the Brønsted–Evans–Polanyi Relationship

We can see that Equation 614 looks very similar to the Brønsted–Evans–Polanyi (BEP) empirical relationship we have invoked throughout the course, given by $E_a = \alpha \Delta H° + E_0$. In this case, the BEP relationship uses $\Delta H°$ trends in place of ΔE, as the former is experimentally measurable, and trends for $\Delta H°$ are largely the same as trends for ΔE. Once again, if the product is stabilized relative to the reactant (i.e. $\Delta H°$ is made more exothermic), then E_a tends to be reduced.

To be clear, the BEP relationship is not identical to the Evans–Polanyi model, but it takes a similar functional form. Like with a, the value of α takes on values of $0 \leq \alpha \leq 1$ and describes the position of the transition state along the reaction coordinate. With the BEP relationship, a value of $\alpha \to 0$ refers to an early transition state (i.e. one that is closer to the side of the reactants), whereas $\alpha \to 1$ refers to a late transition state (i.e. one that is closer to the side of the products).

The value of α is a constant for a given reaction family and is not a parameter that should be thought as tunable. Instead, α simply describes the sensitivity of the activation energy to changes in $\Delta H°$. In the case of the BEP relationship, $\alpha \to 0$ yields a situation in which changes to $\Delta H°$ barely change E_a. In contrast, if $\alpha \to 1$, then changes to $\Delta H°$ will significantly change E_a.

Intuition behind the BEP relationship can best be gained by interpreting it within the context of Hammond's postulate, which states that highly exothermic reactions tend to have early transition states, whereas highly endothermic reactions tend to have late transition states (Figure 29). The lower the energy of the transition state with respect to the reactants, the closer to the reactants the transition state will be and, therefore, changes to the product stability will not play a major role (and vice versa).
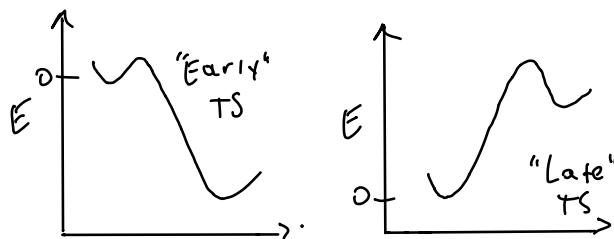

Figure 29: Demonstration of the Hammond postulate, which correlates the relative energy of the transition state to whether the geometry is reactant- or product-like.

8.1.4. Hammett and Taft Parameters

8.1.4.1. Hammett Parameters

Chemists have a whole suite of correlations between rate constants and various empirical parameters. Perhaps the most famous such relationship is the Hammett relationship. The Hammett

relationship compares the reactivity of different organic molecules that have varying functional (R) groups (Figure 30).
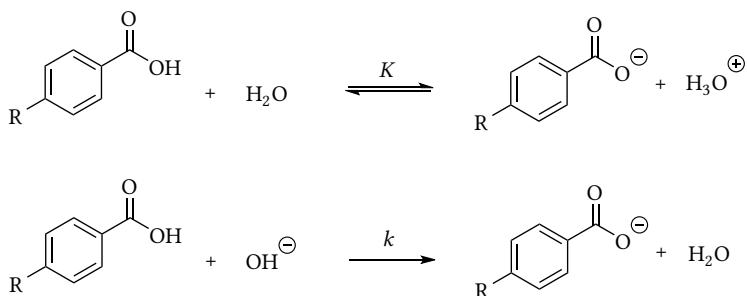

Figure 30: For a series of molecules with different R groups, the Hammett relationship links the acid-dissociation equilibrium constant to the rate constant.

Specifically, the Hammett relationship describes a linear–logarithmic relationship between the rate constant of a given reaction and its equilibrium constant for acid-dissociation:

$$\log(k_R) = \rho \log(K_R) + c, \tag{615}$$

where ρ and c are fitting parameters, and the subscript "R" stands for the R group. Since $\log(k) \propto E_a$ and $\log(K) \propto \Delta G^\circ$, the Hammett relationship is a linear-free energy relationship.

In practice, one typically wishes to compare the rate across various R groups with respect to the unsubstituted form of the molecule (i.e. R = H). In this case, one can also write

$$\log(k_H) = \rho \log(K_H) + c, \tag{616}$$

such that

$$\log(k_R) - \log(k_H) = \rho \log(K_R) - \rho \log(K_H), \tag{617}$$

which can be written more compactly as follows:

$$\log\left(\frac{k_R}{k_H}\right) = \rho\sigma_R, \quad \sigma_R \equiv \log\left(\frac{K_R}{K_H}\right). \tag{618}$$

The above expression is the typical form of the Hammett relationship.

Here, σ_R is known as the Hammett parameter. Hammett parameters are widely tabulated for different functional groups (typically for both the meta- and para- positions, where applicable) and are based on the acid-dissociation equilibrium constants of the substituted and unsubstituted forms of a molecule, which can be readily measured. The Hammett parameters are dependent solely on the different functional group and not the reaction conditions. In contrast, ρ depends on the reaction environment and conditions.[105]

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[105]For a table of commonly used Hammett parameters, refer to C. Hansch, A. Leo, A. Taft, "A Survey of Hammett Substituent Constants and Resonance and Field Parameters", *Chem. Rev.*, 91, 165–195 (1991). Note that σ_m and σ_p refer to *meta* and *para* substituents, respectively.

In practice, if you were studying the reactivity of several organic molecules, you would look up the σ_R values of the differing functional groups, measure k for each reaction, and make a plot of $\log(k_R/k_H)$ vs. σ_R (while forcing the y-intercept to be 0) to find ρ. For new molecules you have not tested yet, you would be able to determine the rate constant via the linear correlation you developed.

When comparing different possible substituents, if a given R group has a higher σ_R value, this means that its acid-dissociation reaction is shifted more towards the products (i.e. the molecule is more acidic). This is typically due to some combination of inductive and/or resonance effects that helps stabilize the negative charge of the conjugate base.

If $\sigma_R > 0$, such a substituent is considered to be an electron-withdrawing group because it will stabilize the product anion by withdrawing electron density (i.e. negative charge) away from the reactive site (compared to the unsubstituted analogue). If $\sigma_R < 0$, such a substituent is considered to be an electron-donating group since the electron density is increased near the reactive site.
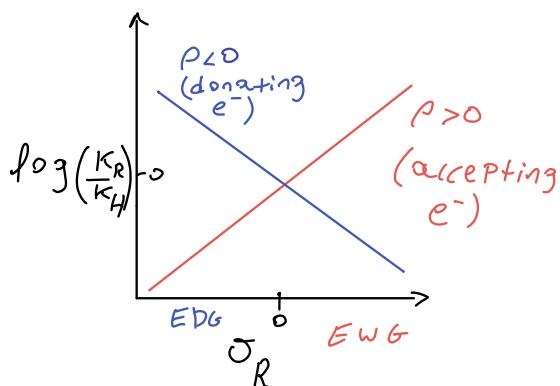

Figure 31: Two representative Hammett plots highlighting the meaning of positive and negative ρ values as well as the range of electron-donating groups (EDGs) and electron-withdrawing groups (EWGs).

As for ρ, it describes the sensitivity of the rate constant to the electron-donating or electron-withdrawing character of the substituent. For a positive ρ, the reaction is assisted by electron-withdrawing groups ($\sigma_R > 0$). The molecule is accepting electron density from the other reagent during the course of the reaction, and the electron-withdrawing group helps stabilize this buildup of electron density at the active center. For a negative ρ, the reaction is assisted by electron-donating groups ($\sigma_R < 0$). The molecule is donating electron density to the other reagent during the course of the reaction, and the electron-donating group helps stabilize this transfer of negative charge. These effects are summarized in Figure 31.

8.1.4.2. Taft Parameters

There are many variations on the Hammett parameter idea to account for different effects. One notable model is the Taft equation, which seeks to more directly capture steric effects that are largely neglected by the Hammett parameter. The Taft equation is given by

$$\log\left(\frac{k_R}{k_{CH_3}}\right) = \rho^* \sigma_R^* + E_{s,R}, \tag{619}$$

where ρ^* is a sensitivity factor analogous to the Hammett parameter ρ. Instead of the Hammett parameter σ_R, two Taft parameters σ_R^* and $E_{s,R}$ are both tabulated for a given substituent. The σ_R^* term captures inductive (i.e. electron-donating or electron-withdrawing) effects like with the Hammett relationship, whereas the $E_{s,R}$ parameter captures sterics. The behavior of ρ^* with respect to electron-donating and electron-withdrawing groups is analogous to that of the Hammett relationship. Unlike the Hammett relationship, the Taft relationship has k_R normalized with respect to a CH_3 substituent.

8.2. Scaling Relationships in Catalysis

Refer to PowerPoint slides for the following topics:
- Physisorption trends
- Chemisorption scaling relationships
- Transition state scaling relationships
- Universal BEP relationships
- Sabatier principle
- Volcano plots
- Breaking linear scaling relationships

9. Concluding Comment

Congratulations! You have come far and learned much. For future research directions in reaction engineering, we refer the reader to external references.[106]

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[106]P. Bollini et al., "Vision 2050: Reaction Engineering Roadmap", *ACS Engineering Au*, 6, 364–390 (2023).