Introduction to microkinetic modeling

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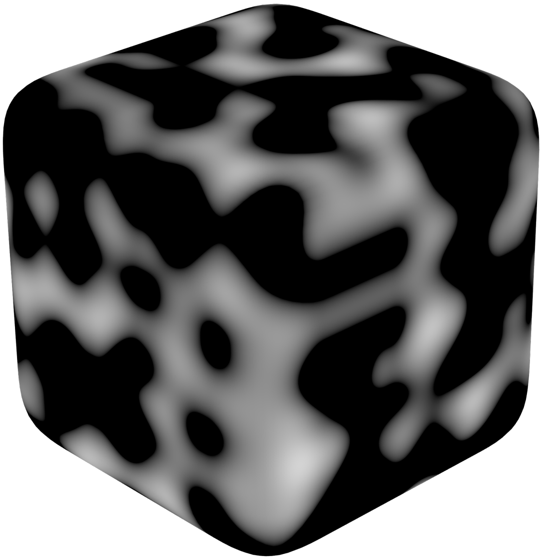
INTRODUCTION TO MICROKINETIC MODELING



by

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Preface

This book started out as two separate documents. One was a set of exercises for the Advanced Thermodynamics and Catalysis course and the other was a method and theory section at that time envisioned for my PhD thesis. Only a very small part of the material in this book eventually made it into the thesis, as the whole would be much too elaborate!

Since I started out in 2010 as a teaching assistant for the Advanced Thermodynamics and Catalysis course, I have been collecting useful questions to prepare the students for the final examination. And as is well known, if you give students questions, they demand answers in the form of detailed solutions. I believe in learning by example, so I was more than happy to write these solutions down on paper and I have spent many evenings behind my laptop typing the solutions in $\LaTeX$.

At the end of 2015, I was appointed as an assistant professor (tenure track). I was asked to take over the Advanced Thermodynamics and Catalysis course from Prof. Emiel Hensen, which I happily accepted. I changed the learning goals a bit to adopt my current research into the educational track. As a result, I had to come up with new lecture materials and I decided to bundle everything I made so far: the questions and solutions, the (envisioned) theory and method section for my thesis and the notes I made when I followed the kinetics course when I was a student. The result was a monster! My writing style had obviously changed significantly over the years and there was no clear story. Thus I spent the following two years rewriting the text.

In 2016, a draft version only containing a set of useful exercises and solutions were given to the students to practice. In 2017, the first version of the book was ready and about one hundred copies were printed and given to the second year Bachelor students as lesson material. I found out that students are really marvelous proofreaders. They will point out every little mistake, whether it is a spelling mistake or a miscalculation. In these two years, I received about 500 corrections. The current version is yet another iteration further down the road and my intention is to continuously update and improve the material in this book.

Within this book, I will elaborate on the connection between the smallest quantum scale and the larger macroscopic scale, providing a theoretical framework on which many kinetic studies in heterogeneous catalysis are based. I will focus on the underlying quantum chemical mechanism leading to the observed overall rate laws in chemistry and process engineering.

This book is organized in several chapters. I will start by introducing general kinetics and the equations governing the rate of change in chemical composition. Next, a statistical approach is formulated to deduce macroscopic observables from the constituting quantum chemical properties by means of averaging over many states. Energy, temperature and pressure are defined as our important parameters and we show how these concepts are connected with observables such as chemical composition in equilibrium as well as the chemical kinetics leading to these equilibria. Finally, we explain how the above-mentioned concepts can be used within the framework of microkinetic modeling in a predictive and illustrative manner to gain insights in how real-life catalytic processes work.

All chapters have exercises to help you practice with the lesson material. Solutions are provided in the appendix as well as more challenging exercises at the same difficulty as what can be expected on the final exam.

Since I am not a native English speaker, there is always the chance that I have used some odd grammatical structures or made (despite the careful proofreading of many students and myself) spelling errors. Feedback is thus always very welcome and I invite you to deliver it by e-mail to i.a.w.filot@tue.nl. Any useful comment will result in your name being mentioned in the acknowledgment section (of course, with your permission).

I sincerely hope this book is useful to you and provides you with a more in-depth understanding of the beautiful field of (micro-)kinetics!

Ivo Filot Eindhoven, 30th March 2018

Preface to version 1.5

With version 1.5, we have modified the book quite a bit. First of all, we got a lot of constructive feedback on the lay-out of the book. It was hard to see where a question or exercise would start or end. Evidently, the solutions to the exercises suffered from the same problem. We have changed the lay-out in such a way that the exercises and questions are clearly highlighted in the book, which hopefully makes it easier to find what you are looking for. While we were at it, we also added tabs on the sides of each page so you can efficiently find the chapter you are looking for.

Note that I have been saying *we*, instead of *I*. In the past three months, I have been receiving a lot of help from Tom van den Berg, who has been working on Chapter 5 of the book. In Chapter 5, a hands-on tutorial to use MKMCXX will be given. This was previously the purpose of Chapter 4, yet it felt short in the sense that it did not provide sufficient explanation in how to set-up such simulations from scratch. As such, Chapter 4 has been adapted to explain the algorithm behind microkinetic simulations using a series of simple Python scripts and Chapter 5 now deals to performing simulations using MKMCXX. Tom has also made a series of exercises to help the student practice using MKMCXX. We hope that these are beneficial to your understanding of the topic.

Finally, a lot of spelling, grammar, and other kinds of errors have been resolved on the basis of the feedback of a lot of people. As is traditional, the list of students can be found on the acknowledgment page. Enjoy the revision of the book and please keep sending in any questions and comments you might have!

Ivo Filot Geldrop, 24th December 2018

Acknowledgements

This book was not possible without the help of some very talented people. First of all, I need to mention Prof. Emiel Hensen and Prof. Hans Niemantsverdriet. These two excellent teachers gave the Catalysis and Kinetics course (*Reactiekinetiek en Katalyse*) when I was a young Bachelor student. I fondly remember the enthusiasm of Prof. Hensen and the very pedagogically correct learning style of Prof. Niemantsverdriet. During my PhD studies, I helped out as a teaching assistant for the kinetics course. In this period, I wrote many of the solutions to the questions which are embedded in this reader. These solutions were used and corrected by Remco Lancee, Alessandro Coumans and Lennart van Haandel. Often, Lennart offered alternative solution strategies to the questions, which I found very helpful.

When I became the teacher for the kinetics course, I was lucky to have very dedicated teaching assistants on my side as well. I wish to thank Bart Zijlstra, Robin Broos, Evert van Noort and Jasper Bouwman for helping out with the supervised self-study lessons. Michel van Etten not only helped out, but was also willing to host a couple of lectures when I was unavailable, which is highly appreciated. I also should mention that Tobias Kimpel was always available to step in when we needed an extra hand.

Last but not least, I wish to mention all of the students and colleagues who helped me in any way with improving this reader, whether it was by mentioning errors, offering suggestions or pointing out difficult parts:

- **Class of 2014/2015**: Marle Vleugels, Lisa Struik, Martin van Son.
- **Class of 2015/2016**: Jasper Bouwman, Camiel Steffanie, Remco Fijneman.
- **Class of 2016/2017**: Steven Kuijpers, Teun Nevels.
- **Class of 2017/2018**: Luuk Kempen, Stefan Zondag.
- **Class of 2018/2019**: Vera Crommentuijn, Jeroen Vennix, Cynthia Struijk, Stacey Fun, Lisa Cattenstart, Frank van Hertrooij, Nico van Rijswijk, Danny van den Eertwegh, Job Nijhuis.
- **Colleagues**: Kevin van Eeten, Jan Wiesfeld.

Do you miss your name in the list, but did you provide me with some feedback? Please let me know!

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CHAPTER 1

KINETICS

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1.1 Introduction

Kinetics is part of the science of motion. It deals with the rate of chemical reactions and treats chemistry from a dynamic viewpoint. The counterpart of kinetics is thermodynamics, which deals with the static point of view on chemistry. Thermodynamics is interested in the initial and final states of a system. Within kinetics, the mechanism whereby the system is converted from one state to another and the time wherein this process occurs is described. Thermodynamics deals with equilibria, whereas in kinetics equilibrium is a special situation wherein the forward and backward rates are equal to each other. As such, kinetics can be seen as a more fundamental science than thermodynamics. Unfortunately, the complexities that occur within the kinetic treatment of chemistry are such that it is difficult to always apply it with large accuracy and sometimes we find that for a more accurate treatment of certain properties, thermodynamics gives the more accurate answer.

Underlying both kinetics and thermodynamics are more fundamental theories such as statistical mechanics and quantum chemistry. The quantum description of matter is only valid at the smallest length and time scales and the description of large ensembles of particles over extended periods of time require a statistical description. Hence, kinetics and thermodynamics are the result of the merge between statistical mechanics and quantum chemistry.

In this chapter, we will start with a detailed description on kinetics with a strong focus on the description of dynamic processes within heterogeneous catalysis. This chapter serves as an overview and sets the stage for the contents of Chapter 2, where we zoom in on a fundamental aspect within kinetics which is the elementary reaction step. In Chapter 1, the elementary reaction step is considered as the fundamental building block within a kinetic mechanism, and in Chapter 2, we elaborate on the quantum chemical and statistical foundations of the elementary reaction step.

At the end of this Chapter, you should have a conceptual understanding of what chemokinetic networks are and how we can describe these in terms of elementary reaction steps. You are able to construct overall rate expressions for typical chemical processes and derive such expressions on the basis of a reaction mechanism. Finally, you will be able to express the dependence of these rate expressions on important boundary conditions such as temperature and pressure.

1.2 The rates of reactions

Consider a chemical reaction between molecules A and B that give products C and D according to the following reaction equation

$$\nu_a A + \nu_b B \underset{k^-}{\overset{k^+}{\rightleftharpoons}} \nu_c C + \nu_d D. \tag{1.1}$$

Herein, ν_x is the stoichiometric coefficient of component X and $k^{+/-}$ are the forward and backward rate constants. The rate of a chemical reaction can hence be defined as either the rate of disappearance of the reactants or the rate of formation of the products in the following fashion:

$$r = -\frac{1}{\nu_a}\frac{\mathrm{d}[A]}{\mathrm{d}t} = -\frac{1}{\nu_b}\frac{\mathrm{d}[B]}{\mathrm{d}t} = \frac{1}{\nu_c}\frac{\mathrm{d}[C]}{\mathrm{d}t} = \frac{1}{\nu_d}\frac{\mathrm{d}[D]}{\mathrm{d}t} \tag{1.2}$$

where $[X]$ is the concentration of component X and r is the reaction rate. Expression 1.2 should only be used for so-called elementary reaction steps. A detailed discussion on what exactly entails an elementary reaction step is given further on in this book[I], but for the time being it is sufficient to know that an elementary reaction step is a chemical reaction in which one or more chemical species react directly to form products in a single reaction step and with a single transition state.

An alternative way to define such an elementary reaction step is given by

$$R_j : \left\{ \sum_i \nu_i X_i \right\}. \tag{1.3}$$

[I] A detailed description of an elementary reaction step is provided in section 2.9.

When ν_i is negative, compound X_i is a reactant. On the other hand, when ν_i is positive, compound X_i is a product of the reaction. Using the same notation, equation 1.1 is given by

$$R_1 : \left\{ \sum_i \nu_i X_i \right\} = \{ -\nu_a A - \nu_b B + \nu_c C + \nu_d D \} . \tag{1.4}$$

The general rate expression for an elementary reaction step is then defined as

$$r_j = \frac{1}{\nu_i} \frac{\mathrm{d}[X_i]}{\mathrm{d}t}, \text{ for } i = 1, 2, \ldots, n \tag{1.5}$$

Note that the above considers the rate of a single chemical reaction. Often, we simply wish to know the rate of chemical change of a particular compound. From the general definition, the rate of change of a single compound in a single elementary reaction step is then given by

$$r_x = \frac{\mathrm{d}[X]}{\mathrm{d}t} = \nu_x \left(k^+ \prod_{\nu_i < 0} [X_i]^{\nu_i} - k^- \prod_{\nu_i > 0} [X_i]^{\nu_i} \right) . \tag{1.6}$$

For example, the rate of change of compound A in equation 1.1 would be

$$r_A = -\frac{\mathrm{d}[A]}{\mathrm{d}t} = \nu_A \left(k^+ [A]^{\nu_A} [B]^{\nu_B} - k^- [C]^{\nu_C} [D]^{\nu_D} \right) . \tag{1.7}$$

And in a similar fashion, for product C we would obtain the following rate expression

$$r_C = \frac{\mathrm{d}[C]}{\mathrm{d}t} = \nu_C \left(k^+ [A]^{\nu_A} [B]^{\nu_B} - k^- [C]^{\nu_C} [D]^{\nu_D} \right) . \tag{1.8}$$

Clearly, the part between the parentheses of equations 1.7 and 1.8 stays the same for each compound in the reaction. Hence, we can define the reaction rate of a compound within an elementary reaction step as follows

$$r_x = \nu_x r_j . \tag{1.9}$$

This equation should not come as a surprise as it is basically a rewritten version of equation 1.5. Furthermore, from the above equations, it should be apparent that r_j can be written as

$$r_j = \left(k^+ \prod_{\nu_i < 0} [X_i]^{\nu_i} - k^- \prod_{\nu_i > 0} [X_i]^{\nu_i} \right) . \tag{1.10}$$

Thus, we have formally defined how to construct the reaction rate expression of a single elementary reaction step and of a compound inside such a step given the stoichiometric coefficients and concentration of the compounds and the reaction rate constant of the elementary reaction step. The thing that remains is a motivation why we use an expression such as 1.10 to calculate the rate of chemical change.

A chemical reaction between compounds A and B can only occur when A and B meet each other in a chemical mixture. If we consider a tiny volume inside the mixture, the probability that compound A is inside that volume is directly proportional to the number density of A inside that volume. This number density is typically expressed as a concentration. In line with this reasoning, the probability of A **and** B being in the same volume is proportional to the product of the concentration of A and B. Hence, we see in formula 1.10 the product of the concentrations of all compounds on either side of the elementary reaction step.

This leaves us with a motivation for the reaction rate constant k. Whether or not a reaction event occurs does not only depend on whether A and B find each other in a chemical mixture. It is for instance also affected by the particular orientation of A and B with respect to each other or the (kinetic) energy of the compounds. Hence, the term k reflects the chance that a meeting of A and B results in a chemical reaction event.

For now, we simply use k as some given constant, but later in this book, we will provide a detailed discussion how the value of k can be calculated on the basis of statistical thermodynamics and quantum chemistry.[2]

1.2.1 Time-evaluation of a single elementary reaction step

Equation 1.6 is an ordinary differential equation which can be integrated over time to obtain an expression for the concentration of [X] as a function of time. For simple ordinary differential equations, analytical solutions can be constructed. Here, we show an example on the procedure. For more complex chemical systems, we have to resort to numerical approximations using a procedure known as microkinetic modeling. This is the topic of chapter 4 of this book.

For now, assume we have the following simple unimolecular elementary reaction step, given by

$$A \underset{k^-}{\overset{k^+}{\rightleftharpoons}} B. \tag{1.11}$$

Let us further assume that $k^+ >> k^-$. In other words, the reaction from A to B is considered to be irreversible[3] In that scenario, we can rewrite the above equation to

$$A \rightarrow B. \tag{1.12}$$

This gives us the following differential equations[4] for compounds A and B

$$r_A = \frac{\mathrm{d}[A]}{\mathrm{d}t} = -k[A] \tag{1.13}$$

$$r_B = \frac{\mathrm{d}[B]}{\mathrm{d}t} = k[A] \tag{1.14}$$

To solve this system of ordinary differential equations, we need to have two initial values for [A] and [B] at time $t = 0$. For simplicity, let us assume that $[A]_{t=0} = 1$ and $[B]_{t=0} = 0$.

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[2] See section 2.8 on 59 and further.

[3] This is termed the irreversibility assumption and is denoted by a single arrow within the reaction equation. In some situations, the reversibility of a reaction is taken into account but described by separate forward and backward reactions. In the text we will make clear which of the above options is used.

[4] Note that we have replaced k^+ by k for simplicity.

Thus we obtain the following expression for A

$$\frac{\mathrm{d}[A]}{\mathrm{d}t} = -k[A] \tag{1.15}$$

$$\frac{\mathrm{d}[A]}{[A]} = -k \ \mathrm{d}t \tag{1.16}$$

$$\int_{[A]_0}^{[A]_t} \frac{\mathrm{d}[A]}{[A]} = -k \int_0^t dt \tag{1.17}$$

$$\ln[A]_t - \ln[A]_0 = -kt \tag{1.18}$$

$$\ln\left(\frac{[A]_t}{[A]_0}\right) = -kt \tag{1.19}$$

$$[A]_t = [A]_0 \exp\left(-kt\right) \tag{1.20}$$

$$[A]_t = \exp\left(-kt\right) \tag{1.21}$$

and similarly, the following expression for B

$$\frac{\mathrm{d}[B]}{\mathrm{d}t} = k[A] \tag{1.22}$$

$$\frac{\mathrm{d}[B]}{\mathrm{d}t} = k \exp\left(-kt\right) \tag{1.23}$$

$$\mathrm{d}[B] = k \exp\left(-kt\right) \mathrm{d}t \tag{1.24}$$

$$\int_{[B]_0}^{[B]_t} \mathrm{d}[B] = k \int_0^t \exp\left(-kt\right) \mathrm{d}t \tag{1.25}$$

$$[B]_t - [B]_0 = k\left(-\frac{\exp\left(-kt\right)}{k} + \frac{\exp\left(0\right)}{k}\right) \tag{1.26}$$

$$[B]_t = 1 - \exp\left(-kt\right). \tag{1.27}$$

1.2.2 Sequential elementary reaction steps

The product of one elementary reaction step can be the reactant of another elementary reaction step. From this, we can easily envision series of connected elementary reaction steps. For example, consider the overall transformation from some particular reactant R to product P.

$$\mathrm{R} \rightarrow \mathrm{P} \tag{1.28}$$

that proceeds via the following elementary reaction steps

$$\mathrm{R} \leftrightarrows \mathrm{A} \tag{1.29}$$

$$\mathrm{A} \leftrightarrows \mathrm{B} \tag{1.30}$$

$$\mathrm{B} \leftrightarrows \mathrm{C} \tag{1.31}$$

$$\mathrm{C} \leftrightarrows \mathrm{P}. \tag{1.32}$$

Note that all elementary reaction steps considered here are unimolecular. If we assume that these reactions mainly operate in the forward direction (i.e. $k_f >> k_b$), then we can analytically derive the expression for the following overall reaction rate.

For each compound in our system, we can construct a differential equation from the rate expressions. That is,

$$\frac{\mathrm{d[R]}}{\mathrm{d}t} = -k'[\mathrm{R}] \tag{1.33}$$

$$\frac{\mathrm{d[A]}}{\mathrm{d}t} = k'[\mathrm{R}] - k'[\mathrm{A}] \tag{1.34}$$

$$\frac{\mathrm{d[B]}}{\mathrm{d}t} = k'[\mathrm{A}] - k'[\mathrm{B}] \tag{1.35}$$

$$\frac{\mathrm{d[C]}}{\mathrm{d}t} = k'[\mathrm{B}] - k'[\mathrm{C}] \tag{1.36}$$

$$\frac{\mathrm{d[P]}}{\mathrm{d}t} = k'[\mathrm{C}] \tag{1.37}$$

$$\tag{1.38}$$

In a similar fashion as the previous section, we obtain a set of ordinary differential equations, which is also called a *system* of ordinary differential equations. This system is somewhat more complex than the previous system, but it can still be integrated analytically. For simplicity, let us assume that the initial values are as follows: $[\mathrm{R}](t = 0) = 1$ and all other concentrations at $t = 0$ are zero.

Let us introduce some additional terminology. The set of all possible concentrations c_i is termed the **phase space** of the system. Here, this space is defined by

$$c_i \in [0, 1] \tag{1.39}$$

and

$$\sum_i c_i = 1 \tag{1.40}$$

Integration in time of the differential equations is then called **propagation in phase space**. The trajectory is the path in phase space corresponding to this time-integration.

The derivation of the analytical expression goes beyond the scope of this book, but the interested reader may consult any engineering mathematics book.[5] The methodology that we have used to obtain the solution was by using the so-called Laplace transformation.[1] The result is:

$$[\mathrm{R}] = \exp\left(-k't\right) \tag{1.41}$$

$$[\mathrm{A}] = k't \cdot \exp\left(-k't\right) \tag{1.42}$$

$$[\mathrm{B}] = \frac{1}{2}(k't)^2 \cdot \exp\left(-k't\right) \tag{1.43}$$

$$[\mathrm{C}] = \frac{1}{6}(k't)^3 \cdot \exp\left(-k't\right) \tag{1.44}$$

$$[\mathrm{P}] = 1 - \exp\left(-k't\right)\left(1 + k't + \frac{1}{2}(k't)^2 + \frac{1}{6}(k't)^3\right) \tag{1.45}$$

The concentration as a function of time is depicted in Figure 1.1. In this graph, $k' = 1$ s^{-1}. From this Figure, it can be seen that the concentration of B increases at a slower rate than the concentration of A and that the concentration of C increases at a slower rate than the concentration of B. This is of course logical. Each subsequent species in the kinetic network has to overcome an additional barrier that slows the rate of formation. Despite these barriers,

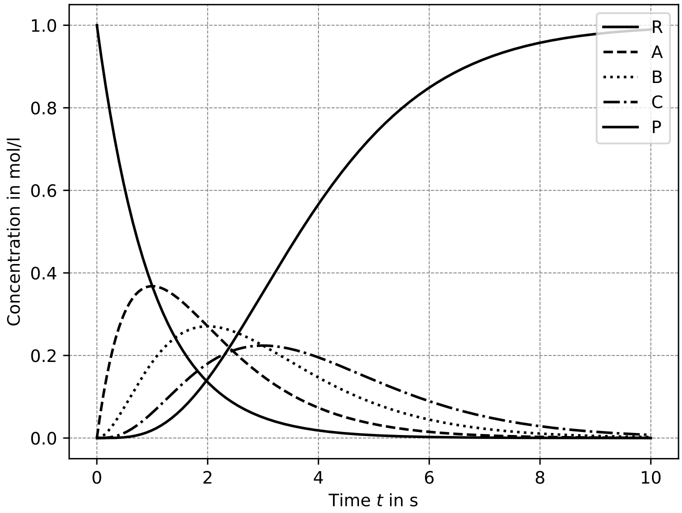

Figure 1.1: *Concentration as a function of time. At* $t = 0$*,* $R_{t=0} = 1$*. The system converges to the final result where* $P = 1$ *at* $t \to \infty$*.*

the final product P is still formed, because the reactions were considered irreversible. The driving force in this system is thus the strong negative enthalpy of the reaction.

Conclusively, we have seen how to construct a system of ordinary differential equations from a set of sequential elementary reaction steps. By setting appropriate initial conditions, we were able to integrate this system over time.

The above example also illustrates another important concept. In equation 1.6, we formulated the rate of change for a single molecule in a single elementary reaction step. Here, we have shown the situation wherein compound X takes part in multiple elementary reaction steps. In such scenarios, the rate of change of compounds X is simply the sum of all the rates of change of all elementary reaction steps wherein compound X takes part:

$$\frac{\mathrm{d[X]}}{\mathrm{d}t} = \sum_i \nu_{x,i} r_i, \tag{1.46}$$

where $\nu_{X,i}$ is the stoichiometric coefficient of compounds X in elementary reaction step i and r_i is the reaction rate of elementary reaction step i. Note that if compound X is not involved in reaction step i, $\nu_{X,i}$ is equal to zero and hence r_i does not contribute to the rate of change of compound X.

Combining the above equation with equation 1.10 leads to the general expression for the rate of change of compound X in a chemokinetic network:

$$\frac{\mathrm{d[X]}}{\mathrm{d}t} = \sum_j \left(\nu_{x,j} \left(k^+ \prod_{\nu_i < 0} [X_i]^{\nu_i} - k^- \prod_{\nu_i > 0} [X_i]^{\nu_i} \right) \right). \tag{1.47}$$

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[5] A good source is *Advanced Engineering Mathematics* from Erwin Kreyszig.

The steady state approximation

The procedure shown in the previous section is a powerful approach to understand the time-dependent behavior of a chemical network. The major drawback of this approach is that when the system of ordinary differential equations cannot be solved analytically, we have to resort to numerical approximations. Although the system used in the previous session could be solved analytically, this tends to be more of an exception than a rule. Here, we wish to introduce a powerful assumption, known as the **steady state assumption**, that helps us to obtain analytical expressions for systems of ordinary differential equations. In turn, these analytical expressions help us to evaluate the complex kinetic behavior.

Let us consider the following overall reaction[6], which relates to the decomposition of ozone.

$$2O_3 \rightarrow 3O_2 \tag{1.48}$$

The above overall reaction is a chemokinetic network which can be represented by two elementary reaction steps as shown below.

$$O_3 \xrightarrow{k_1} O_2 + O \tag{1.49}$$

$$O + O_3 \xrightarrow{k_2} 2O_2 \tag{1.50}$$

Let us for simplicity assume that both these reactions are irreversible, i.e. they only proceed in the forward direction. The three differential equations that describe the rate of change of all compounds in the network are given by

$$\frac{d[O_3]}{dt} = -k_1[O_3] - k_2[O][O_3] \tag{1.51}$$

$$\frac{d[O]}{dt} = k_1[O_3] - k_2[O][O_3] \tag{1.52}$$

$$\frac{d[O_2]}{dt} = k_1[O_3] + 2k_2[O][O_3] \tag{1.53}$$

We can solve the above system of ordinary differential equations numerically by providing initial value conditions, but an alternative method to gain insight in the network is to construct an overall rate expression. To obtain a simple analytical expression for the rate of production of oxygen from ozone, we apply an assumption. The assumption we are going to apply is the **steady state approximation**. This approximation assumes that the rate of change of one particular compound is equal to zero. The motivation for this assumption is that the particular compound for which the approximation is applied is much more reactive than the other compounds in the network in such a way that its change in concentration over time is zero. It makes sense to apply this assumption to O as an oxygen radical is known to be very reactive. This leads to the following expression

$$\frac{d[O]}{dt} = k_1[O_3] - k_2[O][O_3] = 0 \tag{1.54}$$

Solving the above equation for [O] gives

$$[O] = \frac{k_1}{k_2} \tag{1.55}$$

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[6] An overall reaction is a general kinetic expression that conveys the reactivity of one or more elementary reaction steps and reflects the stoichiometry of the overall process.

Inserting this result back into equation 1.53 results in

$$\frac{d[O_2]}{dt} = 3k_1[O_3]. \tag{1.56}$$

The above expression emphasizes another important point. We mentioned that equation 1.48 was an **overall reaction**. Had we treated it as an elementary reaction step, then we could readily derive the following differential equation for the rate of change in O_2:

$$\frac{d[O_2]}{dt} = 3k[O_3]^2. \tag{1.57}$$

Clearly, equations 1.56 and 1.57 are inherently different and lead to significantly different kinetics. This simple example illustrates a very important concept in kinetics. An **overall reaction** only expresses the stoichiometry (i.e. the mole balance) between the reactants and the products of a chemical process, but it cannot tell us *a priori* anything about the rate of change at which the process takes place (i.e. the kinetics). In contrast, the set of elementary reaction steps that constitute the process does not only allow us to investigate the kinetics of a reaction, but it is also a detailed representation of the **reaction mechanism**.

1.3 Chain reactions

A chain reaction is a sequence of elementary reaction steps wherein a reactive product, for instance a radical, causes additional elementary reaction steps to take place. An illustrative example is the reaction between hydrogen and chlorine to form hydrochloric acid

$$H_2 + Cl_2 \rightarrow 2HCl \tag{1.58}$$

which proceeds by the following set of elementary reaction steps:

$$Cl_2 \xrightarrow{k_1} 2Cl\cdot \tag{1.59}$$

$$Cl\cdot + H_2 \xrightarrow{k_2} HCl + H\cdot \tag{1.60}$$

$$H\cdot + Cl_2 \xrightarrow{k_3} HCl + Cl\cdot \tag{1.61}$$

$$2Cl\cdot \xrightarrow{k_4} Cl_2 \tag{1.62}$$

Note that for this particular set, the reactions only occur in the forward direction. This is either because the backward reaction is negligible compared to the forward one (which is the case for the second and third reaction), or because we explicitly model the forward and backward reaction as separate reactions (which is the case for the first and fourth reaction). In chain reactions, we can differentiate between initiation, propagation and termination steps. The first step, the formation of two chlorine radicals, is the initiation step. The second and third elementary reaction steps are the propagation steps. The fourth step is the reverse of the first step and is the termination step.

From the above four elementary reaction steps, we are able to derive an analytical expression for the rate of formation of hydrochloric acid by application of the previously proposed steady state approximation. The reasoning stays the same: on the time scales where the reaction takes place, we consider the concentration of the highly reactive compounds (i.e. the radicals) to be constant in time, hence we assume

$$\frac{\mathrm{d}[\mathrm{Cl}\cdot]}{\mathrm{d}t} = 0 \tag{1.63}$$

$$\frac{\mathrm{d}[\mathrm{H}\cdot]}{\mathrm{d}t} = 0. \tag{1.64}$$

Given the above four elementary reaction steps, we obtain the following five differential equations (i.e. one for each compound in the system of elementary reaction steps)

$$\frac{\mathrm{d}[\mathrm{Cl}_2]}{\mathrm{d}t} = -k_1[\mathrm{Cl}_2] - k_3[\mathrm{H}\cdot][\mathrm{Cl}_2] + k_4[\mathrm{Cl}\cdot]^2 \tag{1.65}$$

$$\frac{\mathrm{d}[\mathrm{H}_2]}{\mathrm{d}t} = -k_2[\mathrm{Cl}\cdot][\mathrm{H}_2] \tag{1.66}$$

$$\frac{\mathrm{d}[\mathrm{HCl}]}{\mathrm{d}t} = k_2[\mathrm{Cl}\cdot][\mathrm{H}_2] + k_3[\mathrm{H}\cdot][\mathrm{Cl}_2] \tag{1.67}$$

$$\frac{\mathrm{d}[\mathrm{Cl}\cdot]}{\mathrm{d}t} = 2k_1[\mathrm{Cl}_2] - k_2[\mathrm{Cl}\cdot][\mathrm{H}_2] + k_3[\mathrm{H}\cdot][\mathrm{Cl}_2] - 2k_4[\mathrm{Cl}\cdot]^2 = 0 \tag{1.68}$$

$$\frac{\mathrm{d}[\mathrm{H}\cdot]}{\mathrm{d}t} = k_2[\mathrm{Cl}\cdot][\mathrm{H}_2] - k_3[\mathrm{H}\cdot][\mathrm{Cl}_2] = 0. \tag{1.69}$$

To find a rate expression for the change in concentration of HCl, we need to obtain an equation for the concentration of the radicals (which is constant over time) and plug these into the rate expression for HCl. The trick to solve this problem, is to realize that given the steady-state approximation, we are allowed to add and/or subtract equations 1.68 and 1.69 from any of the above expressions since equations 1.68 and 1.69 equate to zero.

Summing 1.68 and 1.69 provides us with an expression for $[\mathrm{Cl}\cdot]$:

$$[\mathrm{Cl}\cdot] = \sqrt{\frac{k_1}{k_4}[\mathrm{Cl}_2]} \tag{1.70}$$

Plugging equation 1.70 back into equation 1.68 provides us (after some algebra) the following expression for $\mathrm{H}\cdot$

$$[\mathrm{H}\cdot] = \frac{k_2\sqrt{\frac{k_1}{k_4}}[\mathrm{H}_2]}{k_3\sqrt{[\mathrm{Cl}_2]}} \tag{1.71}$$

Finally, inserting the result of equations 1.70 and 1.71 into equation 1.67 gives us the following expression for the rate of change in HCl:

$$\frac{\mathrm{d}[\mathrm{HCl}]}{\mathrm{d}t} = 2k_2\sqrt{\frac{k_1}{k_4}}[\mathrm{H}_2][\mathrm{Cl}_2]^{\frac{1}{2}} \tag{1.72}$$

If 1.58 would have been an elementary reaction step, the rate expression would be

$$\frac{\mathrm{d}[\mathrm{HCl}]}{\mathrm{d}t} = 2k[\mathrm{H}_2][\mathrm{Cl}_2]. \tag{1.73}$$

Hence, we encounter again a situation where the rate expression derived from the set of elementary reaction steps is significantly different from the simple rate expression *assuming* that the overall reaction is an elementary reaction step.

1.4 Catalytic reactions

A catalyst is a compound which is added to the reaction mixture that accelerates the reaction without itself being consumed in the process. In turn, a reaction that uses a catalyst is termed a catalytic reaction. The key concept of catalysis is thus that the reactants associate with the catalytic material, undergo a chemical transformation and finally dissociate from the catalyst. There are different kinds of catalysts, but in this reader, we will focus on heterogeneous catalysts and the corresponding gas-solid kinetics.

A heterogeneous catalyst can be envisioned as a relatively large extended surface. This surface is composed of active sites, which are local positions on which a molecule can adsorb, react and desorb. The total number of active sites is considered constant and equal to N. Furthermore, we assume for the time being that all sites are equivalent and each site can only be occupied by a single species or be vacant. If an adsorbate X is adsorbed on a catalytic site, this is denoted by X*. The fractional coverage of sites covered by X is in turn denoted by θ_X.

In summary, our model assumes the following about active sites:

- The total number of sites is constant.
- All sites are equivalent.
- A single site can only adsorb a single molecule or atom.

From here on, we can define elementary reaction steps which deal with a catalytic surface. Let us consider the adsorption of reactant R on a catalytic site denoted by *

$$\mathrm{R} + * \underset{k_1^-}{\overset{k_1^+}{\rightleftharpoons}} \mathrm{R}* \tag{1.74}$$

and the reaction in which R* can be converted to product P, which immediately desorbs from the catalytic surface

$$\mathrm{R}* \xrightarrow{k_2^+} \mathrm{P} + *. \tag{1.75}$$

In order to derive kinetic equations for this system, we have to consider the dimensionality of the reaction rates. For some compounds, the rate of change will be expressed in the three-dimensional space of the gases. For the species which are associated with the catalyst, their rate of change pertains to the two-dimensional space of the catalyst surface. Thus, we have to define the following macroscopic equation for our rates

$$-V\frac{\mathrm{d}[R]}{\mathrm{d}t} = Nk_1^+\left(1-\theta_R\right)[R] - Nk_1^-\theta_R, \tag{1.76}$$

where V is the volume of the gases, N is the total number of catalytic sites in the volume V, θ_R is the fractional coverage of sites covered by R and $\left(1-\theta_R\right)$ the number of empty sites. The latter can also be denoted by θ_*.

For the rate of change for adsorbed R, we obtain the following expression

$$\frac{\mathrm{d}\theta_R}{\mathrm{d}t} = k_1^+\left(1-\theta_R\right)[R] - \left(k_1^- + k_2^+\right)\theta_R \tag{1.77}$$

and for the rate of change of product P

$$V\frac{\mathrm{d}[P]}{\mathrm{d}t} = Nk_2^+\theta_R \tag{1.78}$$

To obtain a kinetic expression for the rate of production of P, we can again make use of the steady state approximation. Here, we apply the approximation for the fractional coverage of R on the surface θ_R:

$$\frac{\mathrm{d}\theta_R}{\mathrm{d}t} = k_1^+ \left(1 - \theta_R\right) [R] - \left(k_1^- + k_2^+\right) \theta_R = 0 \tag{1.79}$$

From this, we can directly establish a relation for θ_R as a function of the concentrations of R:

$$\theta_R = \frac{\frac{k_1^+ [R]}{k_1^- + k_2^+}}{1 + \frac{k_1^+ [R]}{k_1^- + k_2^+}}. \tag{1.80}$$

Finally, plugging this result back into equation 1.78 gives

$$V \frac{\mathrm{d}[P]}{\mathrm{d}t} = N k_2^+ \frac{\frac{k_1^+ [R]}{k_1^- + k_2^+}}{1 + \frac{k_1^+ [R]}{k_1^- + k_2^+}}. \tag{1.81}$$

In conclusion, we have seen how to model a reaction that uses a catalytic surface. The novelty here was that we had to introduce additional terms into the kinetic equations to deal with the dimensionality of the space wherein the species reside (i.e. three-dimensional for the gas-phase species and two-dimensional for the adsorbates).

1.4.1 Langmuir adsorption isotherms

The adsorption of compounds on a catalytic surface is a pivotal step in any catalytic cycle, as without adsorption, no use is made of the catalytic material. The relationship between the surface coverage of a particular species and its corresponding gas-phase pressure at constant temperature is known as a *Langmuir adsorption isotherm*. This isotherm is named after Irving Langmuir, who studied the deterioration of tungsten filaments in incandescent light bulbs. For this purpose, he constructed a detailed theoretical framework which he later used to build a kinetic description of catalytic reactions. For his accomplishment in the field of catalysis, he was awarded with the Nobel Prize in Chemistry in 1932.

Using the theoretical framework as devised by Irving Langmuir, we are here going to explain different types of adsorption. The different types of adsorption are named after the nature of adsorption, which are

- **Direct or associative adsorption**: A gas-phase species adsorbs directly on the surface and retains its internal chemical bonding. A key example is the adsorption of N_2 or CO.
- **Dissociative adsorption**: A gas-phase species adsorbs on the surface and simultaneously dissociates. The adsorption of H_2 on many transition metals directly leads to the dissociation of the H_2 molecule by which the adsorbed state are two separate hydrogen atoms bonded to the surface.
- **Competitive adsorption**: Basically a form of adsorption wherein multiple species compete for the same type of active site. A typical example is the competitive adsorption of CO and H_2.[7]

In the next subsections, we will derive the Langmuir isotherm for these three types of adsorption.

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[7] There is also a form of competition wherein adsorbates on adjacent active sites tend to repel (or attract) each other. Such kind of lateral interactions are **not** meant here.

Direct adsorption

In the direct adsorption mechanism, a gas-phase species A adsorbs on the surface wherein its molecular form stays intact. The corresponding elementary reaction step is

$$\mathrm{A} + * \underset{k^-}{\overset{k^+}{\rightleftharpoons}} \mathrm{A}* \, . \tag{1.82}$$

This gives the following differential equation[8] for the rate of change in the surface coverage of A:

$$\frac{\mathrm{d}\theta_A}{\mathrm{d}t} = p_A k^+ \theta_* - k^- \theta_A . \tag{1.83}$$

If we assume that the catalytic surface is composed of only one type of site, than we can formulate the following mass balance for the fractional coverages

$$\theta_A + \theta_* = 1. \tag{1.84}$$

Applying equation 1.84 to equation 1.83 results in

$$\frac{\mathrm{d}\theta_A}{\mathrm{d}t} = p_A k^+ \left(1 - \theta_A\right) - k^- \theta_A . \tag{1.85}$$

Applying the steady state approximation to the above expression gives us an expression for the fractional coverage as a function of the gas-phase pressure

$$\theta_A = \frac{\frac{k^+}{k^-} p_A}{1 + \frac{k^+}{k^-} p_A} = \frac{K p_A}{1 + K p_A} \tag{1.86}$$

This functional form is termed a Langmuir adsorption isotherm. Note that in the above expression, we have used the equilibrium constant K, which is the ratio of the forward reaction rate constant and the backward reaction rate constant as given by

$$K = \frac{k^+}{k^-} . \tag{1.87}$$

In Figure 1.2, several Langmuir adsorption isotherms are plotted using equation 1.86 with different values for the equilibrium constant K. From this Figure, we can see that with increasing value for the equilibrium constant, the surface coverage is higher at a given pressure.

---

[8] Instead of the concentration of A in the gas phase as shown in the previous example, we here use the pressure as for gas-solid interactions, the latter is used more often. Both approaches are of course equally valid, as the collision chance scales linearly with both concentrations as well as pressure.

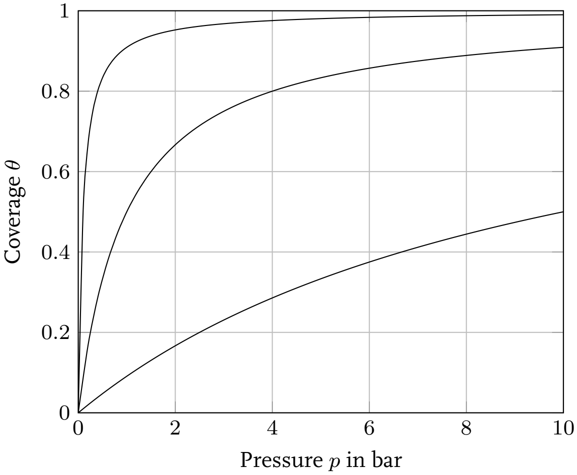

Figure 1.2: *Langmuir adsorption isotherms. The top line corresponds to an equilibrium constant of K=10 bar^{-1}, the middle one has an equilibrium constant of 1 bar^{-1} and the bottom line has an equilibrium constant of 0.1 bar^{-1}.*

Dissociative adsorption

The adsorption of certain di- or polyatomic molecules results in the immediate dissociation of these molecules upon adsorption on a catalytic surface. A typical example is the adsorption of H_2, which for a broad range of transition metals gives dissociative adsorption.

The elementary reaction step for the dissociative adsorption of species A_2 on a catalytic surface is given by

$$\mathrm{A_2} + 2* \underset{k^-}{\overset{k^+}{\rightleftharpoons}} 2\mathrm{A}* \tag{1.88}$$

and the corresponding differential equation is

$$\frac{\mathrm{d}\theta_A}{\mathrm{d}t} = p_A k^+ \left(1-\theta_A\right)^2 - k^- \theta_A^2. \tag{1.89}$$

Note that we have the same molar balance as shown in the previous section by which we can replace θ_* with $1-\theta_A$.

Applying the steady state approximation to this differential equation and solving for θ_A gives the following Langmuir adsorption isotherm

$$\theta_A = \frac{\sqrt{K p_{\mathrm{A_2}}}}{1+\sqrt{K p_{\mathrm{A_2}}}}. \tag{1.90}$$

In Figure 1.3, a comparison is shown between associative and dissociative adsorption.

Competitive adsorption

An interesting case occurs when two species compete for the same active sites. Consider the situation where compounds A and B both adsorb associatively on the same catalytic surface as given by the following two elementary reaction steps

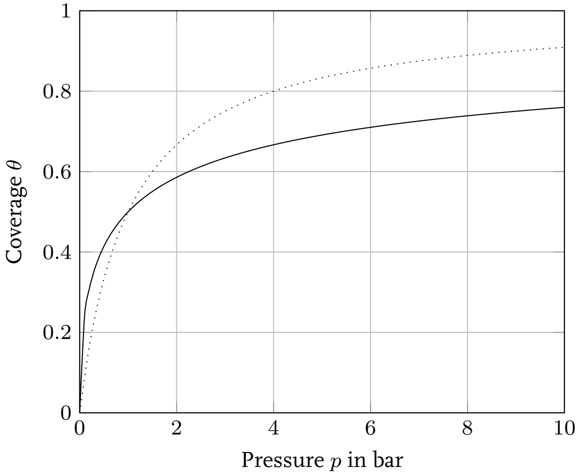

Figure 1.3: *Langmuir adsorption isotherms of associative versus dissociative adsorption. The dotted line corresponds to associative adsorption whereas the solid line represents dissociative adsorption. The equilibrium constant K is the same for both isotherms.*

$$A + * \underset{k_A^-}{\overset{k_A^+}{\rightleftharpoons}} A* \tag{1.91}$$

$$B + * \underset{k_B^-}{\overset{k_B^+}{\rightleftharpoons}} B* \,. \tag{1.92}$$

Applying the steady state approximation to both θ_A and θ_B gives the following expressions

$$\theta_A = K_A p_A \theta_* \tag{1.93}$$

$$\theta_B = K_B p_B \theta_* \tag{1.94}$$

To solve for θ_*, we introduce a site balance which for this situation is given by

$$\theta_A + \theta_B + \theta_* = 1. \tag{1.95}$$

Plugging equations 1.93 and 1.94 into equation 1.95 gives

$$K_A p_A \theta_* + K_B p_B \theta_* + \theta_* = 1 \tag{1.96}$$

Collecting all terms in θ_* gives

$$\left(K_A p_A + K_B p_B + 1\right) \theta_* = 1 \tag{1.97}$$

from which we can readily derive

$$\theta_* = \frac{1}{1 + K_A p_A + K_B p_B}. \tag{1.98}$$

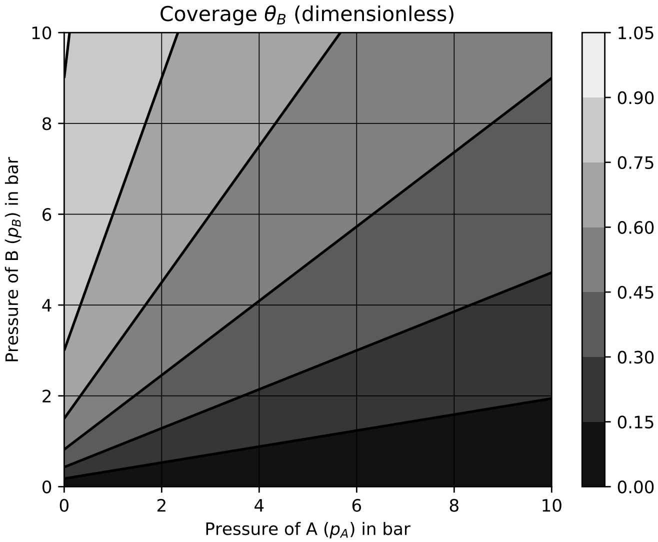

Figure 1.4: *Langmuir adsorption isotherms of competitive adsorption of A and B.*

Plugging this expression back into 1.93 and 1.94 gives

$$\theta_A = \frac{K_A p_A}{1 + K_A p_A + K_B p_B} \tag{1.99}$$

$$\theta_B = \frac{K_B p_B}{1 + K_A p_A + K_B p_B}. \tag{1.100}$$

The above two equations are the two Langmuir adsorption isotherms for competitive adsorption.

In Figure 1.4, a contour plot is given for competitive adsorption. The equilibrium constants K_A and K_B are both set to 1 bar^{-1}. The competition between the two adsorbates is clearly seen from the result that the coverage of B decreases with increasing pressure of A. Furthermore, because the equilibrium constants for both adsorption isotherms are equal to each other, the surface coverage of both components at elevated pressures equals $\theta_A = \theta_B = \frac{1}{2}$.

1.5 Reaction mechanisms in catalysis

Quite often, one is interested in the net production of a particular compound in a chemical reaction. In process engineering, it is common to consider part of the chemical process as a black box and model the system (or chemical reactor) purely on the basis of the long-living and stable compounds within the system. In other words, one neglects the intermediates or radicals as these are very short-lived and would be difficult to measure experimentally.

Given these limitations, macroscopic reaction rates are employed to express the production rates in terms of the concentration of the reactants. These production rates (or for that matter reaction rates) are often so-called power laws and are based on the overall reaction. An example of such an overall reaction is the oxidation of carbon monoxide over a car-exhaust clean-up catalyst as given by the following overall reaction equation:

$$CO + \frac{1}{2}O_2 \longrightarrow CO_2. \tag{1.101}$$

A simple approach for expressing overall reaction rates is to set up a rate based on a power law where the exponents in these power laws are set equal to the stoichiometric coefficients in the reaction equation. For example,

$$r = k[CO][O_2]^{\frac{1}{2}}. \tag{1.102}$$

However, many experiments showed that such an approach was too naive. It is rarely the case that the stoichiometric coefficient of the reactants are equal to the exponents in these power laws. The underlying reason for this is that such power laws do not properly describe the kinetics of the reaction. In order to have a proper description, we need to describe the kinetics of the elementary reaction steps constituting the overall reaction.

For example, the catalytic oxidation of CO can be decomposed in the following elementary reaction steps:[9]

$$CO + * \leftrightarrows CO* \tag{1.103}$$
$$O_2 + 2* \leftrightarrows 2O* \tag{1.104}$$
$$CO * + O* \leftrightarrows CO_2* \tag{1.105}$$
$$CO_2 + * \leftrightarrows CO_2* \tag{1.106}$$

Describing the kinetics of these four elementary reaction steps can give an overall rate expression for this reaction. Constructing a set of elementary reaction steps constituting the overall reaction is typically based on a mixture of chemical intuition, logics and carefully conducted experiments. For heterogeneous catalytic reactions, a good approach to construct a set of elementary reaction steps is to decompose the reactants on the catalytic surface to their constituting elements and subsequently (re-)assemble these elements into their final product.

To exemplify, let us consider ammonia synthesis. Herein, nitrogen and hydrogen gas is converted to ammonia over a catalytic surface. The first step is decomposing the nitrogen and hydrogen molecules to nitrogen and hydrogen atoms. In other words, the nitrogen and hydrogen molecules are dissociated over the catalytic surface. The corresponding elementary reaction steps are:

$$N_2 + 2* \leftrightarrows 2\,N* \tag{1.107}$$
$$H_2 + 2* \leftrightarrows 2\,H* \tag{1.108}$$

You might argue that nitrogen does not adsorb dissociatively[10] and that the nitrogen dissociation actually proceeds in two elementary reaction steps:

$$N_2 + * \leftrightarrows N_2* \tag{1.109}$$
$$N_2 * + * \leftrightarrows 2\,N* \tag{1.110}$$

In principle, both paths are valid. In order to resolve whether this happens in one or two steps is by using the definition of an elementary reaction step. An elementary reaction step

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[9] Note that in equation 1.105 a vacant site is formed after recombination of adsorbed CO and O.

[10] In fact, I gave this as an example for associative adsorption previously. Moreover, it is known that the N_2 bond is very strong, hence making such a pathway unlikely.

has a single transition state. As it turns out, for some metals, nitrogen adsorption immediately results in dissociation via a single transition state, while for other metals, nitrogen first molecularly adsorbs and then dissociates.

After adsorption and dissociation, ammonia is made by subsequent hydrogenation of the nitrogen atom on the surface. Each of these hydrogenation steps are elementary reaction steps as the formation of a single N-H bond occurs via a single transition state.

$$N * + H* \leftrightarrows NH * + * \tag{1.111}$$
$$NH * + H* \leftrightarrows NH_2 * + * \tag{1.112}$$
$$NH_2 * + H* \leftrightarrows NH_3 * + * \tag{1.113}$$

Finally, after the ammonia has been formed on the surface, it needs to desorb. This occurs in a single elementary reaction step. For some reactions, the final hydrogenation step immediately leads to desorption (such as is the case for methane). In that case, both hydrogenation and desorption occur in the same elementary reaction step, because it happens via a single transition state.

$$NH_3* \leftrightarrows NH_3 + * \tag{1.114}$$

We started this chapter by mentioning that the construction of power laws is a poor approach. You might argue against this, as in principle, you can still construct a single power law expression by *fitting* the exponents in the power law to a number of experiments. Such an approach however would not reveal much of the underlying process. Consider now what kind of advantages one would gain by loosing the black-box assumption and developing a complete (micro)kinetic model. One would have a better description of the short-lived intermediates or radicals. The effect of temperature and pressure could be studied in much greater detail. One could identify the elementary reaction step that limits the overall reaction and look for new catalytic materials that lower the reaction barrier of this elementary reaction step.

1.5.1 Potential energy diagram

If the set of elementary reaction steps that describe the mechanism is relatively simple, it is possible to construct a potential energy diagram (sometimes also termed a reaction energy diagram) from this set. The potential energy diagram describes the change in energy between the different thermodynamic states in the reaction and also shows the barrier of each elementary reaction step.

The potential energy diagram of a single elementary reaction step is given in Figure 1.5. In this Figure, the initial, transition and final state of the reaction are shown. The difference in energy between the initial and transition state corresponds to the activation energy. This is the barrier in terms of energy that has to be crossed in order for this reaction to proceed. The difference between the initial and final state corresponds to the reaction energy and is the amount of heat released by the elementary reaction step.

If you would approach this reaction from the right hand side, i.e. from the final state towards the initial state, then you would still need to cross the barrier imposed by the transition state. This barrier for the backward reaction is simply named the activation energy in the backward direction and is defined as the difference between the transition state and the final state. Conclusively, all elementary reaction steps can proceed in both the forward and the backward direction and regardless of the direction, you will encounter a barrier. The principle behind this is termed **microscopic reversibility**.

The potential energy diagram for CO oxidation is shown in Figure 1.6. In this diagram, on the left hand side, CO and $\frac{1}{2}O_2$ in the gas phase are given. First, CO and O adsorb on

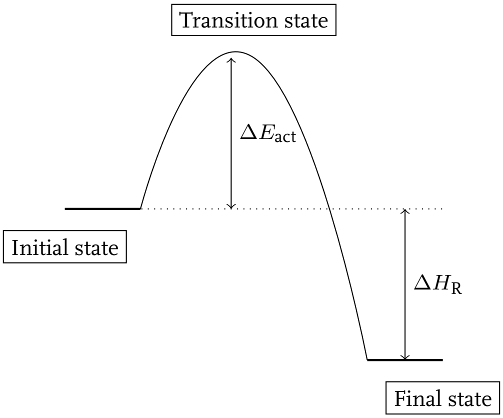

Figure 1.5: *Potential energy diagram of a single elementary reaction step*

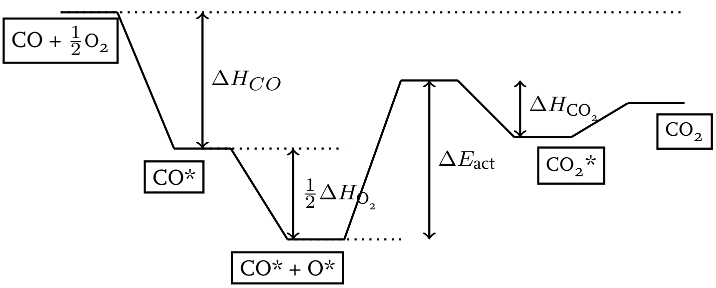

Figure 1.6: *Conceptual potential energy diagram for the CO oxidation reaction. ΔH_X corresponds to the adsorption energy of compound X. ΔE_{act} is the activation energy for the recombination reaction between adsorbed CO and O.*

the surface. Recall that O_2 adsorbs dissociatively and only a single oxygen is required for the CO oxidation, hence we only need to adsorb a single O atom. CO* can react with O* to form CO_2* on the surface, which in turn can leave the surface. Note that adsorption reactions are exothermic as new chemical bonds with the catalytic surface are formed. Similarly, dissociation steps are endothermic as chemical bonds with the catalytic surface are broken.

The potential energy diagram is a powerful concept to study the energetics of a reaction mechanism. Despite this, it only conveys the relative energy levels of the thermodynamic states and has therefore limited information about the kinetics of the reaction. To study the kinetics, one has to construct an expression for the overall reaction rate in terms of the set of elementary reaction steps, which will be the topic of the next section.

1.5.2 Rate-determining step and overall reaction rate

Given that we have a full understanding of the set of all elementary reaction steps of a catalytic reaction, how can we then construct an analytic expression for the overall reaction rate? The key assumption to use is to consider that one of the elementary reaction steps, typically a step over the catalytic surface, is the rate-determining step. In other words, the rate of the overall reaction equals the rate of the slowest elementary reaction step.

Let us consider again the example of CO oxidation towards CO_2, which occurs via the following four elementary reaction steps

$$CO + * \leftrightarrows CO* \tag{1.115}$$

$$O_2 + 2* \leftrightarrows 2O* \tag{1.116}$$

$$CO * + O* \leftrightarrows CO_2 * + * \tag{1.117}$$

$$CO_2 + * \leftrightarrows CO_2* \tag{1.118}$$

We wish to develop an analytical expression for the rate of production for CO_2 for this system. From the set of elementary reaction steps as defined above we are of course able to construct a set of ordinary differential equations and solve this set numerically given appropriate boundary conditions. However, if we wish to pursue an analytical expression, we are going to make a series of assumptions:

- We assume that the surface oxidation step ($CO * + O* \leftrightarrows CO_2 * + *$) is the rate-determining step. Thus, the overall reaction rate equals the rate of this elementary reaction step.
- We assume that all steps other than the rate-determining step are in quasi-equilibrium. This means that on the time scales by which the overall reaction occurs, all steps other than the rate-determining step have already reached a pseudo- or quasi-equilibrium. In other words, their rate of change is zero.
- We assume that CO and CO_2 adsorb associatively whereas O_2 adsorbs dissociatively. We have previously seen how to construct Langmuir adsorption isotherms for such a situation. Note that we had to assume a quasi-equilibrium in order to establish these Langmuir adsorption isotherms. In this situation, we have competitive adsorption of three components, but we will shortly see that it is not more complicated than competitive adsorption for two components.
- Finally, we employ a mean-field approximation. In this assumption, we neglect the local topology of the catalyst surface and assume that every compound on the catalytic surface can interact with every other compound on the catalytic surface. This concept is further illustrated in Figure 1.7. In this Figure, we note that all adsorbates (denoted by squares and circles) are randomly placed on the catalytic surface. In reality, an adsorbate sitting at the left bottom corner of the catalytic surface will never react with an adsorbate at the right top of the catalytic surface, however, within the mean-field approximation, we assume that everything is continuously randomly distributed and such interactions do occur. In other words, we neglect the local topology and thus we can describe the rate of reaction using simply the surface fractions of the adsorbed species.

Using the above assumptions, i.e. the quasi-equilibrium approximation, the rate-determining step approximation and the mean-field approximation, we obtain the following three equations for the surface coverage of CO, O_2 and CO_2:

$$\theta_{CO} = \frac{K_{CO}p_{CO}}{1 + K_{CO}p_{CO} + \sqrt{K_{O_2}p_{O_2}} + K_{CO_2}p_{CO_2}} \tag{1.119}$$

$$\theta_{O} = \frac{\sqrt{K_{O_2}p_{O_2}}}{1 + K_{CO}p_{CO} + \sqrt{K_{O_2}p_{O_2}} + K_{CO_2}p_{CO_2}} \tag{1.120}$$

$$\theta_{CO_2} = \frac{K_{CO_2}p_{CO_2}}{1 + K_{CO}p_{CO} + \sqrt{K_{O_2}p_{O_2}} + K_{CO_2}p_{CO_2}} \tag{1.121}$$

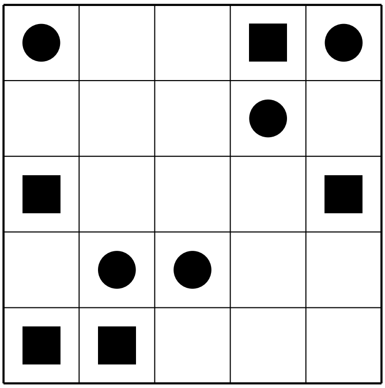

Figure 1.7: *Schematic depiction of the mean-field approximation. In the mean-field approximation, there is no interaction between the adsorbed species and all species are distributed randomly over the surface.*

The overall rate is equal to the rate of the rate-determining step, hence

$$r_{CO_2} = k_3^+ \theta_{CO}\theta_O - k_3^- \theta_{CO_2}\theta_* \tag{1.122}$$

$$= \frac{k_3^+ K_{CO}p_{CO}\sqrt{K_{O_2}p_{O_2}} - k_3^- K_{CO_2}p_{CO_2}}{\left(1 + K_{CO}p_{CO} + \sqrt{K_{O_2}p_{O_2}} + K_{CO_2}p_{CO_2}\right)^2} \tag{1.123}$$

This equation can be further simplified when we assume that the rate determining step is irreversible. In such circumstances, the forward rate is much larger than the backward rate and hence the equation simplifies to

$$r_{CO_2} = \frac{k_3^+ K_{CO}p_{CO}\sqrt{K_{O_2}p_{O_2}}}{\left(1 + K_{CO}p_{CO} + \sqrt{K_{O_2}p_{O_2}} + K_{CO_2}p_{CO_2}\right)^2}. \tag{1.124}$$

With the *irreversible step approximation* set, the reverse reaction is not occurring, but any product formed can still readsorb on the surface. Thus, we see a term in the denominator corresponding to adsorbed CO_2. On top of the irreversible step approximation we are allowed to make an even more stringent assumption termed the *zero-conversion approximation*. As the name implies, within this assumption no products are being formed and hence all components that are formed after the rate-determining step can be ignored and will thus not occur on the catalytic surface. The reaction rate then further simplifies to

$$r_{CO_2} = \frac{k_3^+ K_{CO}p_{CO}\sqrt{K_{O_2}p_{O_2}}}{\left(1 + K_{CO}p_{CO} + \sqrt{K_{O_2}p_{O_2}}\right)^2}. \tag{1.125}$$

Note that despite that the zero-conversion approximation and the irreversible step approximation are different approximations, under the zero-conversion limit the same kind of effects are present as under the irreversible step approximation. Whereas the zero-conversion limit does not state that the rate-determining step cannot proceed in the reverse direction, due to the fact that no product has been formed (i.e. we are working at zero conversion), there is no product present for the reverse reaction to occur. Admittedly, the difference is subtle, yet the reader is advised to use the approximations with caution and not to treat them as synonymous.

With these additional approximations installed, we can even further simplify this equation by making another assumption. Often, catalytic reactions have a surface compound which adsorbs much stronger than the other adsorbates. Thus, we expect to find that the surface is mainly covered with that compound and some free sites. For example, let us assume that CO binds much stronger that the other compounds. In that case,

$$K_{\text{CO}} p_{\text{CO}} \gg \sqrt{K_{\text{O}_2} p_{\text{O}_2}}, K_{\text{CO}_2} p_{\text{CO}_2} \tag{1.126}$$

and the above equation then simplifies to

$$r_{\text{CO}_2} = \frac{k_3^+ K_{\text{CO}} p_{\text{CO}} \sqrt{K_{\text{O}_2} p_{\text{O}_2}}}{(1 + K_{\text{CO}} p_{\text{CO}})^2}. \tag{1.127}$$

In this situation, we say that CO is the MARI, which stands for the *Most Abundant Reaction Intermediate*. The final assumption we can make is to consider that we are working at very low temperature by which the surface coverage of CO is not merely the most abundant intermediate among the reaction intermediates, the coverage of CO is also greater than the amount of available empty sites. In that case, the reaction rate simplifies to

$$r_{\text{CO}_2} = \frac{k_3^+ \sqrt{K_{\text{O}_2} p_{\text{O}_2}}}{K_{\text{CO}} p_{\text{CO}}}. \tag{1.128}$$

At this point, we have found the equation under the condition that the whole surface is covered with CO and thus that CO is poisoning the catalytic reaction. It should be noted that this assumption is rarely valid, except at very low temperature, i.e. well below typical operating conditions.

1.5.3 Reaction orders

The overall reaction rate depends on the pressures of the reactants and this dependency is reflected by the reaction order. The reaction order is basically a number which defines the scaling behavior of the reaction, i.e. if for instance the reaction order is 2, the rate of the reaction will quadruple if the pressure is doubled.

The reaction order can be calculated using the following formula

$$n_{\text{X}} = p_{\text{X}} \frac{\partial \ln r}{\partial p_{\text{X}}}. \tag{1.129}$$

To exemplify this, let us calculate the reaction order in CO for the CO oxidation reaction. We assume that the quasi-equilibrium assumptions holds and furthermore we consider CO to be the MARI.

$$
\begin{aligned}
n_{\mathrm{CO}} &= p_{\mathrm{CO}} \frac{\partial \ln r}{\partial p_{\mathrm{CO}}} \qquad (1.130)\\
&= p_{\mathrm{CO}} \frac{\partial \ln \dfrac{k_3^{+} K_{\mathrm{CO}} p_{\mathrm{CO}} \sqrt{K_{\mathrm{O_2}} p_{\mathrm{O_2}}}}{(1+K_{\mathrm{CO}} p_{\mathrm{CO}})^2}}{\partial p_{\mathrm{CO}}} \qquad (1.131)\\
&= p_{\mathrm{CO}} \frac{\partial}{\partial p_{\mathrm{CO}}} \left(\ln k_3^{+} + \ln K_{\mathrm{CO}} + \ln p_{\mathrm{CO}} + \frac{1}{2} \ln K_{\mathrm{O_2}} + \frac{1}{2} \ln p_{\mathrm{O_2}} - 2 \ln (1 + K_{\mathrm{CO}} p_{\mathrm{CO}}) \right) \qquad (1.132)\\
&= p_{\mathrm{CO}} \frac{\partial}{\partial p_{\mathrm{CO}}} \left(\ln p_{\mathrm{CO}} - 2 \ln (1 + K_{\mathrm{CO}} p_{\mathrm{CO}}) \right) \qquad (1.133)\\
&= 1 - 2 p_{\mathrm{CO}} \frac{\partial \ln (1 + K_{\mathrm{CO}} p_{\mathrm{CO}})}{\partial p_{\mathrm{CO}}} \qquad (1.134)\\
&= 1 - 2 \frac{p_{\mathrm{CO}}}{(1 + K_{\mathrm{CO}} p_{\mathrm{CO}})} \frac{\partial (1 + K_{\mathrm{CO}} p_{\mathrm{CO}})}{\partial p_{\mathrm{CO}}} \qquad (1.135)\\
&= 1 - 2 \frac{K_{\mathrm{CO}} p_{\mathrm{CO}}}{(1 + K_{\mathrm{CO}} p_{\mathrm{CO}})} \qquad (1.136)\\
&= 1 - 2 \theta_{\mathrm{CO}} \qquad (1.137)\\
& \qquad (1.138)
\end{aligned}
$$

The above result can be interpreted as follows. At very low surface coverage of CO, the reaction order in CO is equal to 1. This means that when we double the CO pressure, we expect that the reaction rate will double as well. Alternatively, at very high surface coverage of CO, the reaction order will be -1. In this case, doubling the CO pressure will result in a reduction of the reaction rate by a factor 2. The latter condition is the poisoning regime. Here, the CO surface coverage is so high that there are no available free sites for O_2 to adsorb and hence the reaction rate decreases with increasing CO pressure.

If CO is not the MARI, we have the following equation for the reaction rate.

$$
r_{\mathrm{CO_2}} = \frac{k_3^{+} K_{\mathrm{CO}} p_{\mathrm{CO}} \sqrt{K_{\mathrm{O_2}} p_{\mathrm{O_2}}}}{\left(1 + K_{\mathrm{CO}} p_{\mathrm{CO}} + \sqrt{K_{\mathrm{O_2}} p_{\mathrm{O_2}}} + K_{\mathrm{CO_2}} p_{\mathrm{CO_2}} \right)^2} \tag{1.139}
$$

In a similar fashion as shown above, we can calculate the reaction orders to be

$$
\begin{aligned}
n_{\mathrm{CO}} &= 1 - 2\theta_{\mathrm{CO}} \qquad (1.140)\\
n_{\mathrm{O_2}} &= \frac{1}{2} - \theta_{\mathrm{O}} \qquad (1.141)\\
n_{\mathrm{CO_2}} &= -\theta_{\mathrm{CO_2}} \qquad (1.142)
\end{aligned}
$$

The reaction rate as a function of coverage is shown in Figure 1.8 and the corresponding reaction order is given in Figure 1.9. From these Figures, we can see that the reaction order in O_2 is constant as a function of temperature, whereas the reaction order in CO changes from -1 to +1. In Figure 1.10, the surface coverages for CO*, O* and * are given. Using this Figure, we can rationalize the results obtained for the reaction orders. At low temperature, the surface is mainly covered with CO, hence the reaction order in CO is negative. With increasing temperature, the surface coverage of CO decreases and the amount of available sites increases. As a consequence, the reaction order in CO increases from -1 to +1. Because the surface coverage of O is very low in the temperature range under consideration, its corresponding reaction order is constant and amounts to $n_{\mathrm{O}} = \frac{1}{2}$ for the whole range.

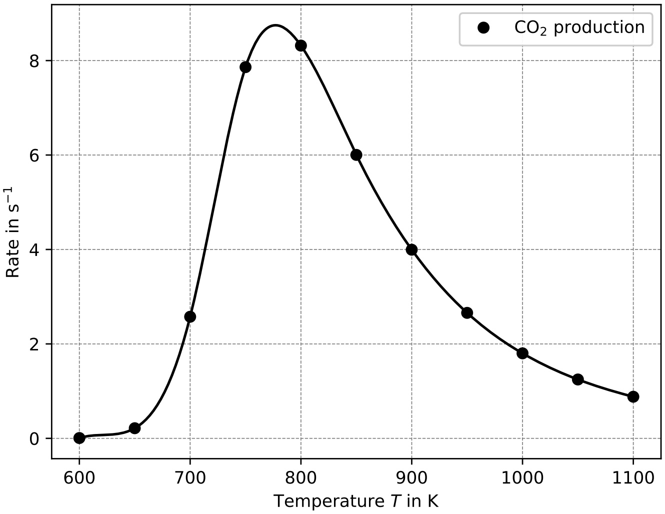

Figure 1.8: *Rate of* CO_2 *formation as a function of temperature*

1.5.4 Apparent activation energy

To express the dependence of the overall rate on the temperature, typically the concept of the apparent activation energy is employed. The higher the energy of the apparent activation energy, the higher the energy barrier that the overall reaction has to cross. The expression for the apparent activation energy is as follows

$$\Delta E_{\text{act}}^{\text{app}} = RT^2 \frac{\partial \ln r}{\partial T}, \tag{1.143}$$

where R is the gas constant and T is the temperature. Applying the above equation to the (simplified) reaction rate for CO_2 formation as given in equation 1.127

$$\begin{aligned}
\Delta E_{\text{act}}^{\text{app}} =& RT^2 \frac{\partial \ln \left(\frac{k_3^+ K_{\text{CO}} p_{\text{CO}} \sqrt{K_{\text{O}_2} p_{\text{O}_2}}}{(1+K_{\text{CO}} p_{\text{CO}})^2} \right)}{\partial T} && (1.144) \\
=& RT^2 \frac{\partial}{\partial T} \left(\ln k_3^+ + \ln K_{\text{CO}} + \ln p_{\text{CO}} + \frac{1}{2} \ln K_{\text{O}_2} + \frac{1}{2} \ln p_{\text{O}_2} - 2 \ln (1 + K_{\text{CO}} p_{\text{CO}}) \right) && (1.145) \\
=& RT^2 \frac{\partial}{\partial T} \left(\ln k_3^+ + \ln K_{\text{CO}} + \frac{1}{2} \ln K_{\text{O}_2} - 2 \ln (1 + K_{\text{CO}} p_{\text{CO}}) \right) && (1.146)
\end{aligned}$$

Let us take one step back from the above equation and study the results obtained so far before we continue deriving the final result. In the last step, we note that we have four terms that we have to differentiate. One term corresponds to the derivative towards T of the natural logarithm of the reaction rate constant, two similar terms but then for the equilibrium constant and a final term that corresponds to the part of the denominator of the overall reaction equation. To solve the last term, we need to apply the chain rule. Let us first solve

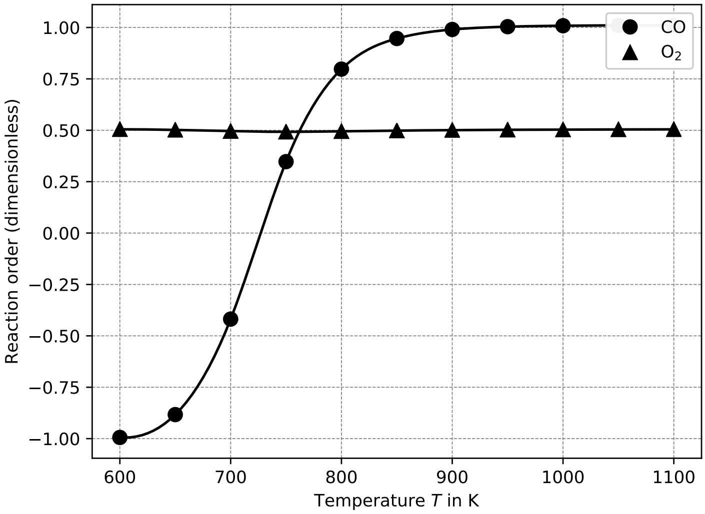

Figure 1.9: *Reaction order in* CO *and* O_2 *as a function of temperature*

the first three terms for which we need to know how k and K depend on the temperature. From thermodynamics (we will discuss this in more detail in Chapter 2), these terms depend on temperature in the following fashion:

$$k = \nu \exp\left(\frac{-\Delta E_{\text{act}}}{RT}\right), \tag{1.147}$$

where ν is the pre-exponential factor and ΔE_{act} is the reaction barrier for the corresponding elementary reaction step. Plugging the above in our expression and solving for the first term gives

$$\frac{\partial}{\partial T} \ln\left(\nu \exp\left(\frac{-\Delta E_{\text{act}}}{RT}\right)\right) = \frac{\partial}{\partial T}\left(\ln(\nu) + \frac{-\Delta E_{\text{act}}}{RT}\right) \tag{1.148}$$

$$= \frac{\Delta E_{\text{act}}}{RT^2}. \tag{1.149}$$

Similarly, the temperature dependence of the equilibrium constant is reflected by the following equation

$$K = \exp\left(\frac{-\Delta G_{\text{R}}}{RT}\right) = \exp\left(\frac{-\Delta H_{\text{R}} + T\Delta S_{\text{R}}}{RT}\right) = \exp\left(\frac{-\Delta H_{\text{R}}}{RT}\right)\exp\left(\frac{\Delta S_{\text{R}}}{R}\right), \tag{1.150}$$

where ΔG_{R} is the Gibbs Free energy, ΔH_{R} is the reaction enthalpy and ΔS_{R} is the reaction entropy. Thus, we can now solve for the second and third term in equation 1.146

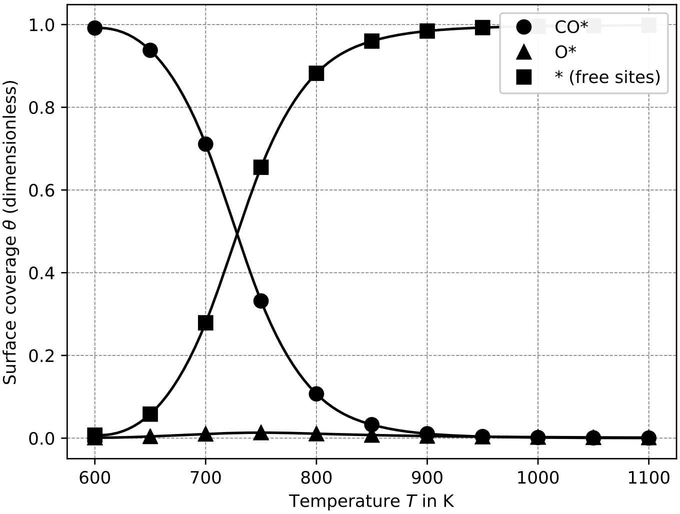

Figure 1.10: *Surface coverage in* CO *and* O_2 *as a function of temperature*

$$
\begin{aligned}
&\frac{\partial}{\partial T}\ln\left(\exp\left(\frac{-\Delta H_\mathrm{R}}{RT}\right)\exp\left(\frac{\Delta S_\mathrm{R}}{R}\right)\right) && \text{(1.151)}\\
=&\frac{\partial}{\partial T}\left[\ln\left(\exp\left(\frac{-\Delta H_\mathrm{R}}{RT}\right)\right)+\ln\left(\exp\left(\frac{\Delta S_\mathrm{R}}{R}\right)\right)\right] && \text{(1.152)}\\
=&\frac{\partial}{\partial T}\left(\frac{-\Delta H_\mathrm{R}}{RT}+\frac{\Delta S_\mathrm{R}}{R}\right) && \text{(1.153)}\\
=&\frac{\Delta H_\mathrm{R}}{RT^2} && \text{(1.154)}
\end{aligned}
$$

Finally, we have to solve for the fourth term in equation 1.146 which can be done by using the chain rule and applying the result of equation 1.154.

$$
\begin{aligned}
\frac{\partial}{\partial T}\left(2\ln\left(1+K_\mathrm{CO}p_\mathrm{CO}\right)\right)=&2\,\frac{\partial}{\partial T}\left(\ln\left(1+K_\mathrm{CO}p_\mathrm{CO}\right)\right) && \text{(1.155)}\\
=&2\,\frac{\partial\ln\alpha}{\partial\alpha}\frac{\partial\alpha}{\partial T}\text{ with }\alpha=1+K_\mathrm{CO}p_\mathrm{CO} && \text{(1.156)}\\
=&2\,\frac{1}{\alpha}\frac{\partial\alpha}{\partial T}\text{ with }\alpha=1+K_\mathrm{CO}p_\mathrm{CO} && \text{(1.157)}\\
=&2\,\frac{p_\mathrm{CO}}{1+K_\mathrm{CO}p_\mathrm{CO}}\frac{\partial K_\mathrm{CO}}{\partial T} && \text{(1.158)}\\
=&2\,\frac{p_\mathrm{CO}}{1+K_\mathrm{CO}p_\mathrm{CO}}\frac{\partial\exp\left(\frac{-\Delta H_\mathrm{R}}{RT}\right)\exp\left(\frac{\Delta S_\mathrm{R}}{R}\right)}{\partial T} && \text{(1.159)}\\
=&2\,\frac{p_\mathrm{CO}K_\mathrm{CO}}{1+K_\mathrm{CO}p_\mathrm{CO}}\frac{\Delta H_\mathrm{CO}}{RT^2} && \text{(1.160)}
\end{aligned}
$$

Note that the term $\frac{p_{\text{CO}} K_{\text{CO}}}{1+K_{\text{CO}} p_{\text{CO}}}$ corresponds to the Langmuir adsorption isotherm for CO under the conditions that CO is the MARI, hence, we can further reduce the above equation to

$$\frac{\partial}{\partial T}\left(2\ln\left(1+K_{\text{CO}}p_{\text{CO}}\right)\right) = 2\,\theta_{\text{CO}}\frac{\Delta H_{\text{CO}}}{RT^2} \tag{1.161}$$

Combining all four terms provides us with the following equation for the apparent activation energy

$$\begin{aligned}\Delta E_{\text{act}}^{\text{app}} =& RT^2\frac{\partial}{\partial T}\left(\ln k_3^{+} + \ln K_{\text{CO}} + \frac{1}{2}\ln K_{\text{O}_2} - 2\ln\left(1+K_{\text{CO}}p_{\text{CO}}\right)\right) && (1.162)\\ =&\Delta E_{\text{act}} + \Delta H_{CO} + \frac{1}{2}\Delta H_{\text{O}_2} - 2\Delta H_{CO}\theta_{CO} && (1.163)\\ =&\Delta E_{\text{act}} + \Delta H_{CO}\left(1-2\theta_{CO}\right) + \frac{1}{2}\Delta H_{\text{O}_2} && (1.164)\end{aligned}$$

We can interpret this equation on the basis of Figure 1.6. The overall activation energy of the kinetic network depends on the barrier of the rate-determining step. The barrier is decreased by the half of the adsorption heat of O_2 as oxygen adsorption is exothermic (i.e. ΔH for adsorption is always negative) and releases heat. The barrier is further decreased by the adsorption heat of CO, however, with increasing amount of CO on the surface, the reduction of the barrier by CO adsorption decreases to the point that at coverages larger than 0.5, the reaction barrier is *increased* by the heat of adsorption of CO.

1.6 Questions and Exercises

The answers to the questions and exercises are given at the end of this book in Appendix C (page 135).

1.6.1 Exercises

The exercises are marked by a number of gears to indicate their difficulty levels.

Exercise 1.1 ⚙

The decomposition of acetaldehyde

$$CH_3CHO \rightarrow CH_4 + CO \tag{1.165}$$

proceeds in the gas phase via methyl radicals according to

$$\begin{aligned}
&1.\ CH_3CHO \rightarrow CH_3{}^* + CHO^* \\
&2.\ CH_3{}^* + CH_3CHO \rightarrow CH_4 + CH_3CO^* \\
&3.\ CH_3CO^* \rightarrow CH_3{}^* + CO \\
&4.\ 2CH_3{}^* \rightarrow C_2H_6
\end{aligned} \tag{1.166}$$

Assume that all reactions are irreversible. Derive the rate expressions for the formation of CH_4 and C_2H_6 by using the steady-state approximation.

■

Exercise 1.2 ⚙

N_2O_5 is an unstable compound formed in the atmosphere upon interaction of NO_2 with oxygen. Its decomposition

$$2N_2O_5 \rightarrow 4NO_2 + O_2 \tag{1.167}$$

proceeds according to the following rate equation

$$r = \frac{d[O_2]}{dt} = k[N_2O_5] \tag{1.168}$$

Show that the following set of elementary reaction steps leads to this rate equation and provide an explicit expression for the overall rate constant k. Identify all reaction intermediates and apply the steady state approximation on these intermediates.

$$\begin{aligned}
&1.\ N_2O_5 \leftrightarrows NO_2 + NO_3 \\
&2.\ NO_2 + NO_3 \rightarrow NO + NO_2 + O_2 \\
&3.\ NO + NO_3 \rightarrow 2NO_2
\end{aligned} \tag{1.169}$$

Think deeper...

- Explain why the reaction order with respect to N_2O_5 is unity and not 2 as suggested by the overall rate equation.
- Derive a rate equation for the formation of NO_2 and relate it to the rate equation for O_2 formation.

■

Exercise 1.3

Derive the rate expression for N_2O for the reaction

$$2NO + H_2 \rightarrow N_2O + H_2O \tag{1.170}$$

using the steady-state expression. The mechanism constitutes the following elementary reaction steps

$$1.\ 2NO \leftrightarrows N_2O_2$$
$$2.\ N_2O_2 + H_2 \rightarrow N_2O + H_2O$$

■

Exercise 1.4

The exposure of sunlight to a mixture of methane and bromine gas results in a violent reaction releasing bromomethane and hydrogen bromide. This reaction proceeds according to the following mechanism:

$$1.\ Br_2 \rightarrow 2Br^*$$
$$2.\ CH_4 + Br^* \rightarrow CH_3{}^* + HBr$$
$$3.\ CH_3{}^* + Br_2 \rightarrow CH_3Br + Br^*$$
$$4.\ 2Br^* \rightarrow Br_2$$

- Identify the type of elementary reaction step in the above chain reaction. Distinguish between initiation, propagation and termination reactions.
- Derive a rate expression for the formation of CH_3Br. Clearly explain the assumptions you have used in the derivation.

■

Exercise 1.5

Derive the Langmuir adsorption isotherms for the following situations

(a) Molecular adsorption of CO.

(b) Dissociative adsorption of CO.

(c) Competitive adsorption of molecularly adsorbed CO and dissociatively adsorbed H_2. Assume there occurs no reaction between CO and H_2.

(d) Consider the mechanism of methanol formation through consecutive hydrogenation of CO. The rate-determining step is the first hydrogenation of CO with one H atom. This step is irreversible. All other steps are fast, except for the desorption of methanol which is considered to be in equilibrium with the gas phase. CO and H_2 adsorption are also quasi-equilibrated.

- Write down the mechanism.
- Reason why you only need to take the surface coverages of CO, H and CH_3COH into account.
- Derive an expression for the reaction rate.
- Give the limits (the domain) of the reaction orders for H_2, CO and methanol.

■

Exercise 1.6

Recent work has shown that the rate of catalytic synthesis of methanol from CO_2 and H_2 scales first-order with the partial pressure of CO_2 and $\frac{3}{2}$ order with the partial pressure of H_2.

The overall reaction equation is

$$CO_2 + 3H_2 \rightarrow CH_3OH + H_2O \tag{1.171}$$

The mechanism is thought to proceed in the following manner

$$
\begin{aligned}
1.\ & H_2 + 2* \leftrightarrows 2H^* \\
2.\ & CO_2 + * \leftrightarrows CO_2^* \\
3.\ & CO_2^* + H^* \leftrightarrows HCOO^* + * \\
4.\ & HCOO^* + H^* \leftrightarrows H_2COO^* + * \\
5.\ & H_2COO^* + H^* \leftrightarrows H_3CO^* + O^* \\
6.\ & H_3CO^* + H^* \leftrightarrows H_3COH^* + * \\
7.\ & H_3COH + * \leftrightarrows H_3COH^*
\end{aligned}
$$

a) Complete the mechanism by adding three elementary reaction steps which remove O^* as H_2O involving equilibrium between water in the gas phase and the adsorbed state.

b) Determine which step is most likely the rate determining step considering the reaction orders as obtained from the experimental results.

c) Derive the corresponding rate equation for methanol formation, assuming that the rate-determining step is irreversible (proceeds only in the forward direction) and all other steps are in quasi-equilibrium. Furthermore, assume that the surface is nearly empty. Show that $n_{H_2} = \frac{3}{2}$.

Think deeper...

At which molar fraction of H_2 is the reaction rate at its optimum?

■

Exercise 1.7

During the course lectures, CO oxidation was studied as a typical example of surface catalysis. It relates to the clean-up of exhaust gases from the combustion of transport fuels. The rate equation has been derived assuming that the surface reaction is the rate determining step. Furthermore assume that the rate-determining step is irreversible. Consider the following mechanism:

$$\begin{aligned} 1.\ CO + * &\leftrightarrows CO^* \\ 2.\ O_2 + 2^* &\rightarrow 2O^* \\ 3.\ CO^* + O^* &\rightarrow CO_2 + 2^* \end{aligned} \tag{1.172}$$

a) Which assumptions do you propose to compute the surface coverage of O atoms? Recall that we are considering in this question car-exhaust clean-up in the three-way automotive catalyst. Should the surface oxygen coverage be high or low in this process and why?

b) Derive the overall rate equation for the above mechanism.

■

Exercise 1.8

Consider the steam reforming of methane, which is a large-scale industrial process for the production of synthesis gas:

$$CH_4 + H_2O \rightarrow CO + 3H_2 \tag{1.173}$$

For a Ni catalyst supported on alumina, we find that the reaction orders are the following

- $n_{CH_4} > 0$
- $n_{H_2O} < 0$
- $n_{H_2} > 0$

a) What is synthesis gas and name at least two chemical processes that use synthesis gas as its feedstock.

b) In case we wish to produce H_2, for instance in ammonia production, what other important chemical reaction can be utilized to increase the amount of H_2 that can be produced from methane?

c) Why is steam reforming carried out under moderate pressure and high temperature?

d) Propose a mechanism involving recombination of adsorbed C* and adsorbed O* to form adsorbed CO* as the rate-determining step. Derive a reaction rate equation assuming that O* is the MARI. Assume that the adsorption of CH_4 is dissociative, whereas the adsorption of H_2O is molecular.

e) Are the experimental orders for Ni consistent with this model?

f) Derive another rate equation assuming that methane dissociation is rate-determining and assume again that O* is the MARI. What are the reaction orders in this case?

Exercise 1.9

The catalytic hydrogenolysis of ethane into methane is composed of the following elementary reaction steps

1. $C_2H_6 + 2* \leftrightarrows C_2H_5* + H*$
2. $C_2H_5* + H* \rightarrow 2CH_3*$
3. $CH_3* + H* \leftrightarrows CH_4 + 2*$
4. $H_2 + 2* \leftrightarrows 2H*$

Assume that step (2) is rate determining and that all other elementary reaction steps are in quasi-equilibrium.

a) If a small amount of D_2 is added to the reactants, $C_2H_{6-n}D_n$ is observed in the gas phase. Explain this phenomenon.

b) Deduce the rate equation for step (2).

c) Derive the expressions for the surface coverages of ethyl, methyl and hydrogen.

d) Give the full rate equation including the terms relevant when the reaction approaches equilibrium. In other words, assume that the rate-determining step is reversible.

e) Give the simplified rate equation in the case that H* is the MARI and very low conversion of ethane.

Think deeper...

Derive an expression for the apparent activation energy for the latter case.

Exercise 1.10

Consider the reaction between NO and CO in the presence of O_2 on a Rh catalyst. NO and CO adsorb molecularly. The surface NO dissociation step is much slower than all other elementary reaction steps. The rate of CO* + O* is comparable to the rate of dissociative O_2 adsorption. The other steps are quasi-equilibrated.

1. $NO + * \leftrightarrows NO*$
2. $CO + * \leftrightarrows CO*$
3. $O_2 + 2* \rightarrow 2O*$
4. $N_2 + 2* \leftrightarrows 2N*$
5. $NO* + * \rightarrow N* + O*$
6. $CO* + O* \rightarrow CO_2 + 2*$

Derive the rate equation for N_2 and CO_2 formation. Use the steady-state approximation on O* to derive this expression.

Think deeper...

In which technological application are these reactions important?

■

Exercise 1.11

Ethylene oxide is an important feedstock in the production of ethylene glycol. Ethylene oxide is made by partial oxidation of ethylene (C_2H_4) over a Ag catalyst. In this process, ethylene adsorbs molecularly whereas oxygen adsorbs dissociatively. The transition state for the formation of ethylene oxide has such a high barrier that this elementary reaction step is considered to be rate-determining. Assume that ethylene oxide immediately and irreversibly desorbs from the catalytic surface after formation. Further assume that all other elementary reaction steps are in quasi-equilibrium.

a) Provide an expression for the surface coverage of ethylene as a function of the partial pressure of ethylene and oxygen.

b) Derive an expression for the rate of formation of ethylene oxide as a function of the partial pressures of ethylene, ethylene oxide and oxygen.

c) At low temperature, it is found that oxygen is strongly adsorbed. Derive a simplified expression for this situation. What are the reaction orders in ethylene and oxygen?

d) Describe the surface composition for the situation described in item (c).

e) Derive an expression for the apparent activation energy for the situation described in item (c).

■

Exercise 1.12

Consider the catalytic oxidation of sulfur dioxide with molecular oxygen to sulfur trioxide. The overall reaction equation is

$$SO_2 + \frac{1}{2}O_2 \rightarrow SO_3 \tag{1.174}$$

The catalytic reaction proceeds over a catalytic surface containing only one type of surface sites. SO_2 adsorbs molecularly, whereas O_2 adsorbs dissociatively. SO_3 is formed on the catalytic surface by bond formation between adsorbed SO_2 and O. Adsorbed SO_3 is in quasi-equilibrium with SO_3 in the gas phase.

a) Give the elementary reaction steps of this proceses.

b) Assume that the surface reaction between SO_2 and O is the rate-determining step and is irreversible. Derive an expression for the rate of formation of SO_3.

c) Give the limits of the reaction orders in SO_2, SO_3 and O_2.

Assume from here on that O_2 is strongly adsorbed whereas SO_2 and SO_3 are only weakly adsorbed.

d) Provide an expression for the rate of formation of SO_3 and derive the reaction orders in terms of the surface composition (fractional occupancies).

e) Derive an expression for the apparent activation energy in terms of the surface composition (fractional occupancies).

Using a different catalyst, the following rate expression was found

$$r = k\left(\frac{K_{SO_2}p_{SO_2}}{1+K_{SO_2}p_{SO_2}+K_{SO_3}p_{SO_3}}\right)\left(\frac{K_{O_2}^{1/2}p_{O_2}^{1/2}}{1+K_{O_2}^{1/2}p_{O_2}^{1/2}}\right) \tag{1.175}$$

f) Provide a reasoning why the above rate expression differs from the previously described catalyst. What is the essential difference?

Exercise 1.13

Platinum is an efficient catalyst for oxidative dehydrogenation of ethanol towards acetaldehyde. The oxidizing agent is molecular oxygen. Mechanistic studies have shown that ethanol adsorbs molecularly, whereas oxygen adsorbs dissociatively. The rate-limiting step is the dehydrogenation of adsorbed ethanol to acetaldehyde coinciding with the release of a water molecule.

$$C_2H_5OH^* + O^* \rightarrow C_2H_4O + H_2O + 2^* \tag{1.176}$$

a) Derive an expression for the surface coverage of ethanol and oxygen in terms of their corresponding partial pressures.

b) Derive an expression for the rate of formation of acetaldehyde as a function of the partial pressures of ethanol, oxygen, acetaldehyde, and water.

Assume that at very low temperature, ethanol adsorbs strongly.

c) Provide an expression for the rate of formation considering the above assumption. What are the reaction orders in ethanol and in oxygen?

d) Derive an expression for the apparent activation energy and explain this result in terms of the surface composition and the reaction profile.

Assume the temperature is increased.

e) Describe the surface composition in this scenario.

Exercise 1.14

The synthesis of water from H_2 and O_2 over a Pt surface proceeds via the following elementary reaction steps:

$$\begin{aligned} 1.\ & H_2 + 2* \leftrightarrows 2H^* \\ 2.\ & O_2 + 2* \leftrightarrows 2O^* \\ 3.\ & O^* + H^* \leftrightarrows OH^* + * \\ 4.\ & OH^* + H^* \leftrightarrows H_2O^* + * \\ 5.\ & H_2O + * \leftrightarrows H_2O^* \end{aligned}$$

a) Assume that step (3) is the rate-determining step and provide a rate expression for this step containing both the forward as well as the backward rate.

b) Show that the rate expression can also be expressed as the equation shown below. Provide an equality for the constant $K_{\text{equilibrium}}$ in terms of the equilibrium constants of the individual elementary reaction steps.

$$r = k_3^+ \sqrt{K_1 K_2 p_{H_2} p_{O_2}} \left(1 - \frac{p_{H_2O}}{K_{\text{equilibrium}} p_{H_2} \sqrt{p_{O_2}}}\right) \theta_*^2 \tag{1.177}$$

c) Assume that oxygen is the MARI. Provide an expression for θ_* using this assumption.

d) Provide an expression for the reaction orders in hydrogen, oxygen and water under the assumption that O is the MARI and that the reaction is far from equilibrium.

e) Assume that the surface is nearly empty. Calculate the optimal gas phase composition (the ratio between hydrogen and oxygen) to find the best rate. Again assume that the reaction is operated far from equilibrium.

Think deeper...

Derive for case (e) an expression for the apparent activation energy and explain your results in terms of the surface processes and surface composition.

Exercise 1.15

Consider the reaction between NO and CO over a Pt surface. NO and CO adsorb molecularly. The surface NO dissociation step is considered to be much slower than all other elementary reaction steps in the system. As such, assume that NO dissociation is the rate-limiting step and that all other steps are in quasi-equilibrium. Note that step (5) is reversible and as such the reverse reaction needs to be taken into account as well.

$$\begin{aligned} &1.\ NO + * \leftrightarrows NO^* \\ &2.\ CO + * \leftrightarrows CO^* \\ &3.\ N_2 + * \leftrightarrows N_2^* \\ &4.\ N_2^* + * \leftrightarrows 2N^* \\ &5.\ NO^* + * \leftrightarrows N^* + O^* \\ &6.\ CO^* + O^* \leftrightarrows CO_2^* + * \\ &7.\ CO_2 + * \leftrightarrows CO_2^* \end{aligned} \tag{1.178}$$

a) Derive the rate equation for N_2 formation. Take the reversibility of the reaction into account and use an overall equilibrium constant K_{eq} in the term corresponding to the reverse reaction.

Assume that O* is the MARI

b) Derive a simplified rate equation for this case and give expressions for the reaction orders in NO, CO, N_2 and CO_2. Explain these dependencies in terms of the surface coverages.

The apparent activation energy is determined under the condition that the surface is nearly empty.

c) Derive an expression for the apparent activation energy in terms of the activation energy of the rate-determining step and the enthalpy changes of the other steps.

Think deeper...

What is the expression for the apparent activation energy for case (b)?

■

Exercise 1.16

The synthesis of hydrogen peroxide from hydrogen and oxygen over a metal surface proceeds via the following elementary reaction steps:

$$\begin{aligned} &1.\ H_2 + 2* \leftrightarrows 2H^* \\ &2.\ O_2 + * \leftrightarrows O_2^* \\ &3.\ O_2^* + H^* \leftrightarrows OOH^* + * \\ &4.\ OOH^* + H^* \leftrightarrows H_2O_2^* + * \\ &5.\ H_2O_2 + * \leftrightarrows H_2O_2^* \end{aligned}$$

a) Derive an expression for the rate of H_2O_2 formation assuming that step (3) is the slowest step. Take the reverse reaction explicitly into account (i.e. do **not** assume zero-conversion or an irreversible step approximation).

b) Assume now that the surface is nearly completely occupied with O_2 and that the reaction is conducted at very low conversion; simplify the above expression and determine the reaction orders with respect to H_2, O_2 and H_2O_2.

c) Derive an expression for the apparent activation energy under these conditions.

d) Derive also an expression for the apparent activation energy in the high-temperature limit when the surface is nearly empty.

■

Exercise 1.17

Methanol synthesis can proceed in the direct pathway by fourfold hydrogenation of CO to methanol. For this process, a catalyst is used which contains **two** types of active sites indicated by θ and τ. The active sites have a specific surface topology by which carbonaceous compounds, i.e. CH_xO, can only adsorb on site θ, but H can adsorb on both these sites. An asterisk (*) is used to indicate adsorbed compounds on site θ, whereas a pound sign (#) is used to indicate adsorbed compounds on site τ.

Assume the following:

- Methanol is formed by threefold hydrogenation of C to CH_3O and finally hydrogenating the O moiety to form methanol.
- The rate-determining step in this reaction is the hydrogenation of CHO to form CH_2O.
- The rate-determining step is irreversible and the system is assumed to operate in the zero conversion limit.
- Hydrogen adsorbs dissociatively at both the θ as well as the τ site. These sites are oriented in such a fashion that a single hydrogen molecule **cannot** adsorb on both these sites simultaneously.
- There is **no** migration of H between the θ and τ sites.
- All elementary reaction steps on the surface, i.e. between CH_xO^* and H#, proceed between the two different active sites.
- Although H* will not directly react with any CH_xO^* species, the adsorption of H* does result in an inhibiting term which needs to be modeled adequately.

a) Construct the set of elementary reaction steps that define this chemo-kinetic network. Use an asterisk (*) to indicate θ sites and a pound sign (#) to denote τ sites.

b) Derive the Langmuir adsorption isotherm for dissociative adsorption of hydrogen on the τ sites.

c) Derive an expression for the overall reaction rate as a function of the partial pressures of the reactants, the reaction rate constant of the rate-determining step and the equilibrium constants of the relevant elementary reaction steps. Identify the inhibiting term corresponding to adsorption of H on a θ site.

d) Derive the reaction order in H_2 and in CO.

e) Derive the apparent activation energy as a function of the relevant partial surface coverages.

■

CHAPTER 2

TRANSITION STATE THEORY

Contents

2.1 Introduction

Fundamental to the construction of microkinetic models lies transition state theory, which describes the reaction rates of elementary reaction steps. To get a sound understanding of this theory, first a short introduction into statistical thermodynamics is given. Next, the concept of partition functions is explained and the relevant partition functions for molecules (i.e. translational, rotational and vibrational) are derived.

Transition state theory was derived by Henry Eyring in 1935, building upon the earlier works of Max Trautz and William Lewis based on the kinetic theory of gases, known as collision theory. Since collision theory serves as a pedagogical introduction to the topic of transition state theory, we will also briefly discuss it in this chapter.

At the end of this Chapter, you are able to identify the degrees of freedom of molecules in order to calculate their partition functions. From there on, you are able to construct rate expressions from first-principles employing transition state theory. From here on, you can use this methodology to obtain quantitative rate constants necessary for the construction of microkinetic models.

2.2 Statistical method

On the basis of quantum chemistry, it is well known that by means of the Schrödinger equation the microscopic laws of a particle or a system with a number of particles ($N \approx 100$) can be defined. The question now arises what the observable properties are of a system containing an extremely large number of such particles. That is, we want to discuss the relationship between these microscopic dynamics and the observed properties of a large system.

The task of solving the Schrödinger equation for a many-body system (say $N = 10^{23}$ particles) is daunting to say the least and far from feasible for modern day computers. However, although one might think that the complexity and perhaps the obscurity would increase by increasing the number of particles, the opposite is true. It is already known from thermodynamics that a large system can be modeled by only a handful of parameters and we can consider macroscopic systems to be quite orderly.

We shall assume that the distinctive regularities are a consequence of the statistical laws governing the behavior of systems consisting of very many particles. Therefore we will avoid direct evaluation of the precise N-particle dynamics and assume that probability statistics provide the correct description of what we see during a macroscopic measurement.

We assume that we could observe a many-body system in a particular microscopic state. Such a characterization would require a huge amount of variables. So we will assume that that our system is quantal and obeys the Schrödinger equation:

$$i\hbar \frac{\partial}{\partial t} |\psi\rangle = \mathcal{H} |\psi\rangle \tag{2.1}$$

To specify the state $|\psi\rangle$ the system is in, we would require a number of variables of the Nth order, where N is the number of particles in the system. To exemplify, if we would consider the stationary states

$$\mathcal{H} |\psi_\nu\rangle = E_\nu |\psi_\nu\rangle \tag{2.2}$$

then the index ν would represent the collection of quantum numbers specifying the state $|\psi_\nu\rangle$. The space spanned by all the state vectors $|\psi\rangle$ is termed the **Hilbert space**. The equivalent term for classical systems is a **Phase space**.

Time evolution in the above-mentioned Hilbert space is governed by time-integration of the time-dependent Schrödinger equation. The path through the Hilbert space that encompasses the set of microstates is termed the **trajectory**. If we fix the total energy E, the total number of particles N and the total volume V of the system, then the trajectory will move on a ”surface” of state space, although the dimensionality of this space is still enormously high.

The basic concept within statistical mechanics is the following: If we wait long enough, the system will eventually flow through all the microscopic states consistent with the constraints we have imposed to control the system. If this is the case, then any observable property G asserted from measurements is given by

$$G_{\text{obs}} = \frac{1}{N} \sum_{a=1}^{N} G_a \tag{2.3}$$

where G_a is the ath measurement whose time duration is so short that it can be considered that the system is only in one microscopic state. If this is the case, then we can write G_{obs} as

$$G_{\text{obs}} = \sum_{\nu} \left[\frac{1}{N} n_\nu \right] G_\nu \tag{2.4}$$

where n_ν is the number of times the state ν is observed in N observations and G_ν is the expectation value for G when the system is in state ν. After a considerable amount of time, when all possible states have been visited, we can define the probability or fraction of time spent in ν and rewrite equation 2.3 as

$$G_{\text{obs}} = \sum_{\nu} P_\nu G_\nu, \tag{2.5}$$

where P_ν is the probability of finding the system in state ν.

From this we can formulate the following. If the system is of considerable size (i.e. $N \approx 10^{23}$) and we perform measurements long enough, then the time average (eq. 2.3) equals the ensemble average (eq. 2.5). Dynamical systems that obey this equivalence are said to be **ergodic**. Although it is difficult to establish whether a system is ergodic, it is thought that this property holds for many-body systems encountered in Nature.

This leads to the following postulate:

Postulate 1. *The (long) time average of a mechanical variable M in the thermodynamic system of interest is equal to the ensemble average M, in the limit as $N \to \infty$, provided that the system of the ensemble replicates the thermodynamic state and environment of the actual system of interest.[2, 3, 4]*

2.3 Maxwell-Boltzmann distribution law

As was pointed out in the previous section, during a measurement of a microscopic system, a time average would give the same result as an ensemble average. To quantify this idea, we need to define our ensemble as well as the probability or distribution of the various microscopic states leading to a second postulate:

Postulate 2. *In an ensemble ($N \to \infty$) representative of an isolated thermodynamic system, the particles in the ensemble are distributed uniformly, that is, with equal probability or frequency, over the possible quantum states consistent with the specified values of N, V and E.[2, 3, 4]*

With the above assumptions, the number of possible states or probability Ω_D for a given E and V is

$$\Omega_D = N! \prod_i \frac{(g_i)^{n_i}}{n_i!}, \tag{2.6}$$

where N is the total number of particles, the product loops over all possible states i, g_i is the degeneracy of state i and n_i is the number of molecules (or particles) put in state i (occupancy number). Moreover, the total energy of such a system would be the sum of the energies of the individual molecules:

$$E = \sum_i n_i \epsilon_i \tag{2.7}$$

where i loops over each of the molecules, ϵ_i is the energy per molecule and n_i is the number of molecules i.

Before we continue deriving the Maxwell-Boltzmann distribution, let us first explore the concept of thermodynamic probabilities. Consider a system consisting of three micro states (A, B, C) of the same energy (i.e. threefold degenerate). What are the probabilities of having three particles (1, 2 and 3) distributed equally over all three states over having all particles in a single micro state? The total number of probabilities can be easily calculated using equation 2.6 which yields

$$\Omega_D = 3! \frac{3^3}{3!} = 27. \tag{2.8}$$

To determine how many configurations there are for having all three particles in different micro states, consider the following rules for Maxwell-Boltzmann statistics.

- You can put zero or more particles in any given micro state.
- All particles can be distinguished from each other

There are six different configurations wherein each micro state has a single particle

1. $A_1 B_2 C_3$
2. $A_1 B_3 C_2$
3. $A_2 B_1 C_3$
4. $A_2 B_3 C_1$
5. $A_3 B_1 C_2$
6. $A_3 B_2 C_1$

On the other hand, there are only three different configurations wherein a single micro state has all three particles

1. $A_{1,2,3} B C$
2. $A B_{1,2,3} C$
3. $A B C_{1,2,3}$

This simple example shows that we expect that a configuration wherein the particles are spread out over the different micro states is more likely (i.e. it has more probabilities) than a configuration wherein all three particles are in a single micro state. Let us now use this concept to derive a general expression for very large systems.

If all states associated with a certain E and V value are equally probable, then the most probable state is the one where Ω_D has the largest value. Thus, it is required to find the values for $n_1, n_2, \cdots, n_i$ which make Ω_D (from eq. 2.6) a maximum. Therefore, we try to obtain the values for n_i which gives

$$\frac{\partial \Omega_D}{\partial n_i} = 0, \tag{2.9}$$

for all n_i under the restriction that the values for n_i adhere to equations 2.10 and 2.11.

$$n_1 + n_2 + \ldots \equiv \sum_i n_i = N \tag{2.10}$$

$$n_1\epsilon_1 + n_2\epsilon_2 + \ldots \equiv \sum_i n_i\epsilon_i = E \tag{2.11}$$

where N are the number of particles and E the energy of the system as assumed by properties of the system mentioned at the beginning of this section.

By changing the values of $n_1, n_2, \cdots n_i$ with a small amount ∂n_i, the value Ω_D is changed by the small amount $\partial \Omega_D$:

$$\partial \Omega_D = \left(\frac{\partial \Omega_D}{\partial n_1}\right)\partial n_1 + \left(\frac{\partial \Omega_D}{\partial n_2}\right)\partial n_2 + \cdots + \left(\frac{\partial \Omega_D}{\partial n_i}\right)\partial n_i \tag{2.12}$$

According to equation 2.10, the above gives

$$\partial n_1 + \partial n_2 + \cdots + \partial n_i + \cdots = 0 \tag{2.13}$$

and similarly equation 2.11 yields

$$\epsilon_1 \partial n_1 + \epsilon_2 \partial n_2 + \cdots + \epsilon_1 \partial n_i + \cdots = 0. \tag{2.14}$$

Maximizing Ω_D subject to these restrictive conditions can be done by means of Lagrange's method[1] of undetermined multipliers. We therefore introduce two new variables β and γ by which we obtain

$$\partial \Omega_D = \left(\frac{\partial \Omega_D}{\partial n_1} - \gamma - \beta\epsilon_1\right)\partial n_1 + \left(\frac{\partial \Omega_D}{\partial n_2} - \gamma - \beta\epsilon_2\right)\partial n_2 \tag{2.15}$$

$$+ \cdots + \left(\frac{\partial \Omega_D}{\partial n_i} - \gamma - \beta\epsilon_i\right)\partial n_i. \tag{2.16}$$

When Ω_D has a maximum value, i.e.

$$\partial \Omega_D = 0, \tag{2.17}$$

the values of n_i must therefore be such that the right-hand side of equation 2.15 vanishes. Suppose that we choose arbitrary values for $\partial n_3, \partial n_4, \cdots, \partial n_i, \cdots$, then $\partial n_1, \partial n_2$ should be chosen in such a way that equations 2.13 and 2.14 hold. Since equation 2.15 holds for any γ and β, let us choose values for γ and β such that:

---

[1] See Appendix B.5 on 131.

$$\frac{\partial \Omega_D}{\partial n_1} - \gamma - \beta \epsilon_1 = 0 \tag{2.18}$$

$$\frac{\partial \Omega_D}{\partial n_2} - \gamma - \beta \epsilon_2 = 0 \tag{2.19}$$

The only way to ensure that the right-hand side of equation 2.15 is zero for any small values of $\partial n_3, \partial n_4, \cdots, \partial n_i, \cdots$ is to equate all values between the brackets to zero, which generalizes to

$$\frac{\partial \Omega_D}{\partial n_i} - \gamma - \beta \epsilon_i = 0 \ (i = 1, 2, 3, \cdots). \tag{2.20}$$

By not minimizing Ω_D but $\ln \Omega_D$ instead, we obtain

$$\frac{\partial \ln(\Omega_D)}{\partial n_i} - \gamma - \beta \epsilon_i = 0 \tag{2.21}$$

By applying Stirling's approximation (see appendix B.1) to equation 2.6 we obtain the following equation

$$\ln \Omega_D = N \ln N - N + \sum_i (n_i \ln g_i) - \sum_i (n_i \ln n_i - n_i) \tag{2.22}$$

and taking the first derivative of the above yields

$$\frac{\partial \ln \Omega_D}{\partial n_i} = \ln g_i - \ln n_i. \tag{2.23}$$

By combining expression 2.21 and 2.23 this yields

$$\ln g_i - \ln n_i - \gamma - \beta \epsilon_i = 0 \tag{2.24}$$

and with some rearranging, this gives

$$\ln n_i = \ln g_i - \gamma - \beta \epsilon_i. \tag{2.25}$$

Finally taking the exponent on both sides, we obtain

$$\overline{n_i} = g_i e^{-\gamma} e^{-\beta \epsilon_i}. \tag{2.26}$$

Note that the above equation is the **Maxwell-Boltzmann distribution law**, which gives the values for each $\overline{n_i}$ for the most probable distribution of molecules among the energy levels. We will be using this result in the next section to define the entropy of a system and the concept of partition functions.

On the basis of equation 2.13, the sum of the most probable distribution of molecules should be equal to unity, thus giving:

$$\sum_i \overline{n_i} = N, \tag{2.27}$$

where $\overline{n_i}$ is the number of particles in state i for the most probable distribution Ω_D. Furthermore,

$$\begin{aligned} N &= g_1 e^{-\gamma} e^{-\beta\epsilon_1} + g_2 e^{-\gamma} e^{-\beta\epsilon_2} + \cdots + g_i e^{-\gamma} e^{-\beta\epsilon_i} + \cdots \\ &= e^{-\gamma}\left(g_1 e^{-\beta\epsilon_1} + g_2 e^{-\beta\epsilon_2} + \cdots + g_i e^{-\beta\epsilon_i} + \cdots\right) \\ &= e^{-\gamma} \sum_i g_i e^{-\beta\epsilon_i} \end{aligned} \tag{2.28}$$

Hence,

$$e^{-\gamma} = \frac{N}{\sum_i g_i e^{-\beta\epsilon_i}} = \frac{N}{f}, \tag{2.29}$$

where

$$f = \sum_i g_i e^{-\beta\epsilon_i}. \tag{2.30}$$

The sum f is coined by Planck as the *Zustandssumme*, but is also called the **molecular partition function** or sum-over-states. The term partition function becomes obvious when one wants to evaluate the most probable number of molecules in two different levels, for example:

$$\boxed{\frac{\overline{n_i}}{\overline{n_j}} = \frac{g_i e^{-\beta\epsilon_i}}{g_j e^{-\beta\epsilon_j}}} \tag{2.31}$$

In other words, for a given assembly of particles, the partition function shows how the molecules are allocated among the different energy levels or equivalently, how the total energy is partitioned among the molecules.

The only remaining matter is to define β. From thermodynamic considerations it is obvious that there is some relation between the value β and the temperature T. In order to give a clear relation between T and β, the *absolute thermodynamic temperature* [4, 5] needs to be defined according to:

$$\mathrm{d}Q = T\,\mathrm{d}S \tag{2.32}$$

wherein dS is the increase in entropy of a system when it adsorbs reversibly an amount of heat dQ at the temperature T. By defining the above, from experimental observations, the relation between β and T is given by

$$\beta = \frac{1}{k_b T} \tag{2.33}$$

where k_b is the Boltzmann constant. Thus, the partition function becomes

$$f = \sum_i g_i \exp\left(\frac{-\epsilon_i}{k_b T}\right). \tag{2.34}$$

2.4 Partition functions of subsystems

Sometimes it makes sense to calculate the overall partition function of a system by considering the individual partition functions of its subsystems. If a system can be divided into N subsystems with negligible interaction, then the overall partition function is given by

$$Z = \prod_i f_i. \tag{2.35}$$

For example, the total partition function for an ensemble of N distinguishable particles which all have the same partition function, the overall partition functions can be calculated from the product of the partition function of its subsystem. If the partition function of each of these subsystems is the same, the overall partition function is given by

$$Z = f^N. \tag{2.36}$$

If the subsystems are identical particles[2], which are impossible to distinguish from each other, the partition function is calculated by

$$Z = \prod_i \frac{f_i^{N_i}}{N_i!}, \tag{2.37}$$

which reduces to

$$Z = \frac{f^N}{N!}, \tag{2.38}$$

when the individual partition functions for the particles are the same.

2.5 Thermodynamic variables

The usefulness of the partition function becomes clear when we wish to calculate any thermodynamic properties. Such properties are the ensemble averages as given by

$$\langle V \rangle = \sum_i V_i p_i, \tag{2.39}$$

where V_i is the thermodynamic value V for micro state i and p_i is the probability of micro state i. For the total energy E for a system, this becomes

$$\begin{aligned}
\langle E \rangle &= \sum_i \epsilon_i p_i && (2.40)\\
&= \frac{\sum_i \epsilon_i \exp\left(\frac{-\epsilon_i}{k_b T}\right)}{\sum_i \exp\left(\frac{-\epsilon_i}{k_b T}\right)} && (2.41)\\
&= \frac{\sum_i \epsilon_i \exp\left(\frac{-\epsilon_i}{k_b T}\right)}{f} && (2.42)\\
&= k_b T^2 \frac{\partial \ln f}{\partial T}. && (2.43)
\end{aligned}$$

---

[2] We mean with identical here in the quantum mechanical sense.

Other useful relationships between the partition function and thermodynamic variables are for the entropy

$$S = k_b \ln \Omega_D \tag{2.44}$$

$$= \frac{\partial}{\partial T}\left(k_b T \ln f\right), \tag{2.45}$$

the pressure p

$$p = k_b T \left(\frac{\partial \ln f}{\partial V}\right), \tag{2.46}$$

and the chemical potential μ

$$\mu = -k_b T \left(\frac{\partial \ln f}{\partial N}\right). \tag{2.47}$$

The equilibrium constant K for a reaction $A + B \leftrightharpoons C + D$ can be defined as

$$K = \frac{f_C f_D}{f_A f_B} = \exp\left(\frac{-\Delta G_R}{k_b T}\right). \tag{2.48}$$

Here we introduce a simple example to illustrate the above. Consider two systems (A and B) which each have two states separated by an energy ϵ and where the ground state energy of A lies ϵ lower in energy than system B. The partition function for system A is then given by

$$f_A = \sum_i g_i \exp\left(-\frac{\epsilon_i}{k_b T}\right) \tag{2.49}$$

$$= 1 + \exp(-\frac{\epsilon}{k_b T}) \tag{2.50}$$

and for system B by

$$f_B = \sum_i g_i \exp\left(-\frac{\epsilon_i}{k_b T}\right) \tag{2.51}$$

$$= \exp(-\frac{\epsilon}{k_b T}) + \exp(-\frac{2\epsilon}{k_b T}). \tag{2.52}$$

In Figure 2.1, the partition function of A and B as well as the occupancy (n) of energy states A_0 and A_1 are shown as function of temperature. At very low temperature (please note the logarithmic plot), only the ground state of A is occupied as this is the lowest state. With increasing temperature, the first excited state of A becomes increasingly occupied. At very high temperature, system A is half the time in the ground state and half the time in the first excited state. From the ergodicity principle, this is the same as saying that if we would construct a large ensemble of particles of A, half of these particles would be in the ground state and half in the first excited state at any point in time. These occupancies are reflected by the partition function of A. As at low temperature only the ground state of A is occupied, the partition functions equals unity as this is the only state that A can reside in. With increasing temperature, the first excited state of A becomes accessible and hence the partition function increases towards a value of 2 with increasing temperature.

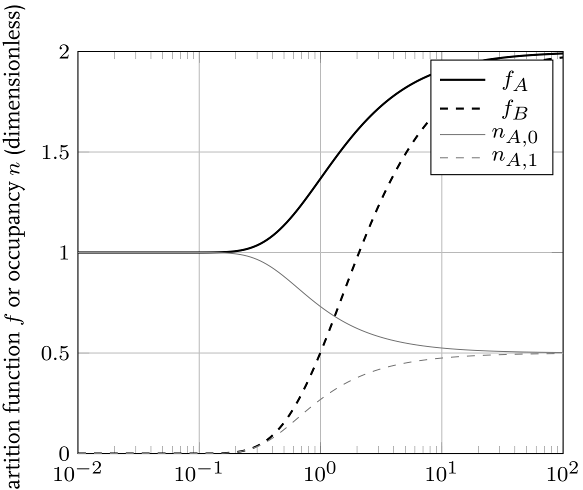

Figure 2.1: *Partition function f for system A and B and occupancies of the energy states of A as function of temperature.*

For system B, a similar reasoning is valid. Since the ground state of B lies higher than the ground state of A, at very low temperature it is unoccupied. Hence, the partition function of B is around zero at very low temperature as there are no states the system can occupy and hence there are no configurations possible. With increasing temperature, both the ground state as well as the first excited state increase in occupancy and the total partition function for B increases towards 2.

We can define an equilibrium between A and B with a corresponding equilibrium constant

$$K = \frac{f_B}{f_A} = \frac{\exp(-\frac{\epsilon}{k_bT}) + \exp(-\frac{2\epsilon}{k_bT})}{1 + \exp(-\frac{\epsilon}{k_bT})}. \tag{2.53}$$

The value for the equilibrium constant K as function of temperature is depicted in Figure 2.2. Herein, we can see that at very low temperature the value for K is almost 0 as at this temperature only states of A are occupied. At the very high temperature limit, all states of A and B are equally occupied. This is reflected by K, which has a value of unity.

We could for example also calculate the average energy, which for system A would be

$$E_A = k_bT^2 \left(\frac{\partial \ln f}{\partial T}\right) \tag{2.54}$$

$$= \frac{\exp(-\frac{\epsilon}{k_bT}) \cdot \epsilon}{1 + \exp(-\frac{\epsilon}{k_bT})} \tag{2.55}$$

and for system B

$$E_B = k_bT^2 \left(\frac{\partial \ln f}{\partial T}\right) \tag{2.56}$$

$$= \frac{\exp(-\frac{\epsilon}{k_bT}) \cdot \epsilon + \exp(-\frac{2\epsilon}{k_bT}) \cdot 2\epsilon}{\exp(-\frac{\epsilon}{k_bT}) + \exp(-\frac{2\epsilon}{k_bT})}. \tag{2.57}$$

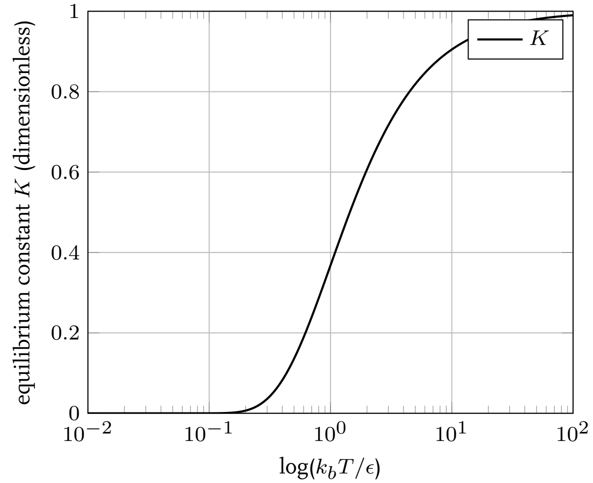

Figure 2.2: *Equilibrium between A and B as function of temperature.*

Careful examination of the above two formula shows that the average energy is simply the occupation fraction of a particular state multiplied by the energy of that state. This is of course exactly what you would expect for the average energy. At the lowest temperature, the average energy of a molecule corresponds to the energy of the ground state and with increasing temperature, the average energy increases as well as more states at higher energy are occupied.

From the above, it should be clear that once the partition function of a system has been defined, we are able to calculate many meaningful thermodynamic properties. In the next section, we will look into more detail what constitutes the partition function for molecules and which corresponding energy terms are relevant.

2.6 Partition functions for molecules

In section 2.3 we derived the formula (eq. 2.34 for the partition function for a Maxwell-Boltzmann distribution. To evaluate the partition function for a molecule, we need to investigate the possible energy levels inside a molecule. The total molecular energy ϵ is composed of a series of energy terms

$$\epsilon = \epsilon_{\text{trans}} + \epsilon_{\text{vib}} + \epsilon_{\text{rot}} + \epsilon_{\text{el}} + \epsilon_{\text{nuc}}, \tag{2.58}$$

where ϵ_{trans}, ϵ_{vib}, ϵ_{rot}, ϵ_{el}, and ϵ_{nuc} are the translational, vibrational, rotational, electronic and nuclear energies, respectively. All these energies are evaluated with respect to the lowest state allowed, thus we can refer to the energy ϵ as the **zero-point energy** or residual energy. This definition has particular consequences for the evaluation of the vibrational energies, which we will see shortly.

Furthermore, each of these energies can be coupled to a partition function, thus we obtain translational, vibrational, rotational... partition functions, by means of the following equation

$$f_k = \sum_i \exp\left(\frac{-\epsilon_i^k}{k_bT}\right), \tag{2.59}$$

where k can be any of the above mentioned types (translational, vibrational...).

Remember that a partition function represents the number of configurations possible at a particular energy. From this definition, it should be apparent that the total molecular partition function is simply the product of the individual partition functions[3] as given by

$$f_{\text{total}} = \prod_i f_i. \tag{2.60}$$

Simply speaking; if a molecular has x configurations given a translation energy ϵ_{trans} and y configurations for a vibrational energy ϵ_{vib}, the total number of configurations are $z = x \cdot y$ as the translational and vibrational configurations of the molecule are independent of each other.

The number of configurations for each type of partition function critically depend on the temperature as is evident from equation 2.31. As such, the number of configurations for each energy term differs significantly. The energy of the excited nuclear states is extremely large as compared to the ground state and for almost all terrestrial purposes (relatively low T), only the ground state of the nuclear energy is occupied. Therefore, within this work, we assume that the influence of the nuclear partition function is negligible and that the term cancels out.

For the electronic excited states we will provide a similar reasoning. On average, the electronic states are separated by about 2eV (equivalent to a wave number of 15000 cm^{-1}). Therefore, for low T, only the ground state is occupied and the electronic partition function is equal to the ground state electronic energy.

That leaves us to derive the partition functions for translation, rotation and vibration, which will be covered in the upcoming subsections.[4]

2.6.1 Translations

The translational kinetic energy of a molecule confined to a rectangular box of dimensions a x b x c depends on three quantum numbers, p, r, s as given by the following equation:

$$\epsilon_{p,r,s} = \frac{h^2}{8m}\left(\frac{p^2}{a^2} + \frac{r^2}{b^2} + \frac{s^2}{c^2}\right) \tag{2.61}$$

where h is Planck's constant and m is the mass of the particle and the labels p, r, s are particular translational quantum states such that

$$f_{\text{trans}} = f_x f_y f_z = \sum_p e^{-\epsilon_x(p)/k_b T} \sum_r e^{-\epsilon_y(r)/k_b T} \sum_s e^{-\epsilon_z(s)/k_b T} \tag{2.62}$$

Combining the two equations 2.61 and 2.62 yields

$$f_{\text{trans}} = \sum_{p=1} e^{-Ap^2} \sum_{r=1} e^{-Br^2} \sum_{s=1} e^{-Cs^2} \tag{2.63}$$

where A, B, C are

---

[3] Similar to how we evaluate the overall partition function given a set of partition functions for its subsystems as shown in section 2.4.

[4] To get a feeling of the values and meaning of the translational, rotational and vibrational partition functions, have a look at exercise 2.4 on page 68.

$$A = \frac{h^2}{8ma^2 k_b T} \tag{2.64}$$

$$B = \frac{h^2}{8mb^2 k_b T} \tag{2.65}$$

$$C = \frac{h^2}{8mc^2 k_b T} \tag{2.66}$$

Now assuming that the quantum states are a continuum and we take into account all the quantum states (up to infinity), than we can approximate the sum over states by an integral as

$$f_{\text{trans}} = \int_0^\infty e^{-Ap^2}\,\mathrm{d}p \int_0^\infty e^{-Br^2}\,\mathrm{d}r \int_0^\infty e^{-Cs^2}\,\mathrm{d}s. \tag{2.67}$$

By applying the standard integral

$$I = \int_0^\infty e^{-cz^2}\,\mathrm{d}z = \frac{1}{2}\left(\frac{\pi}{c}\right)^{\frac{1}{2}} \tag{2.68}$$

the expression for the translational partition function becomes

$$f_{\text{trans}} = \frac{(2\pi m k_b T)^{\frac{3}{2}}\,abc}{h^3} = \frac{(2\pi m k_b T)^{\frac{3}{2}}\,V}{h^3}. \tag{2.69}$$

Note that the above formula covers the full three-dimensional partition functions, however, in further chapters it is convenient to use the translational partition function for a single dimension. In that case, the equation reduces to:

$$\boxed{f_{\text{trans}} = \frac{L\sqrt{2\pi m k_b T}}{h}} \tag{2.70}$$

2.6.2 Vibrations

To obtain a value for the vibrational partition function, we will first elaborate how the vibrational partition function is obtained for a diatomic molecule and continue to extent this result to polyatomic molecules. Let the equilibrium internuclear distance be r_0. Then according to Hooke's law, perturbation in this internuclear distance r gives result to an increase of the potential energy of the molecule by:

$$V = \frac{1}{2}k\,(r - r_0)^2 \tag{2.71}$$

where k is the force constant.

The variation of r with time is in classical mechanics the simple harmonic motion, for which the frequency ω is given by

$$\omega = \frac{1}{2\pi}\sqrt{\frac{k}{\mu}} \tag{2.72}$$

where μ is the reduced mass of the molecule

$$\mu = \frac{m_A m_B}{m_A + m_B} \tag{2.73}$$

and m_A, m_B are the masses of the two nuclei.

The permitted vibrational energy levels are found according to quantum mechanics to be

$$\epsilon_{\text{vib}} = \left(\nu + \frac{1}{2}\right) h\omega \tag{2.74}$$

where ν is the vibrational quantum number which can have any non-negative integer value.

As explained in the beginning of this section, the vibrational energy is evaluated with respect to the lowest accessible vibrational state, thus losing the term $\frac{1}{2}$ in the value for the vibrational energy ϵ_{vib}. Therefore, we can write the vibrational energies as

$$\epsilon_{\text{vib}} = \nu h\omega \tag{2.75}$$

hence the partition function for a diatomic molecule is

$$f_{\text{vib}} = \sum_{\nu=0}^{\infty} e^{-\nu h\omega/k_b T} \tag{2.76}$$

To evaluate this summation, the right hand side of the above equation is written as

$$e^{-\nu h\omega/k_b T} = x^{\nu} \tag{2.77}$$

and equation 2.76 can be written as

$$f_{\text{vib}} = \sum_{\nu=0}^{\infty} x^{\nu} = 1 + x + x^2 + x^3 + x^4 + \cdots \tag{2.78}$$

This type of an infinite series is known as the geometric series (see section B.4 in the Appendix), which converges to

$$f_{\text{vib}} = \frac{1}{1 - e^{-h\omega/k_b T}} \tag{2.79}$$

The quantity $h\omega/k_b$ has the dimensions of temperature and is often denoted as the characteristic temperature for vibration and written as Θ, so that we can rewrite the previous equation as

$$f_{\text{vib}} = \frac{1}{1 - e^{-\Theta/T}} \tag{2.80}$$

The question that now arises is how to define equation 2.80 for a polyatomic molecule. For any given (non-linear) polyatomic molecule with a fixed centre of mass, $3\mathcal{N} - 6$ independent coordinates can be given for the relative position of each atom with respect to one another, where $\mathcal{N}$ is the number of atoms within the molecule.

The positions of the nuclei are defined by a set of coordinates q_i, by means of a change of basis, these variables q_i can be transformed (or rearranged) in such a way that the potential energy of a molecular configuration, relative to that of the equilibrium configuration, can be expressed as:

$$V = V_1 + V_2 + V_3 + \cdots + V_{3\mathcal{N}-6} = \sum_{i=1}^{3\mathcal{N}-6} V_i \tag{2.81}$$

where

$$V_l = \frac{1}{2} k_l \left(q_l - q_l^0 \right)^2 \tag{2.82}$$

where k_l is the force constant and q_l^0 the equilibrium value of q_l. [5]

Coordinates chosen in such a way that equations 2.81 and 2.82 are valid are termed **normal coordinates**. The associated frequencies of these normal coordinates are similar to those of the diatomic molecule as given by equation 2.75 and are termed the **normal modes**.

Considering that we are dealing with $3\mathcal{N} - 6$ normal modes for a given polyatomic molecule, we can rewrite equation 2.80 for the full vibrational partition function as:

$$f_{\text{vib}} = \prod_{i}^{3N-6} \frac{1}{1 - e^{-\Theta_i/T}} \tag{2.83}$$

However, it is more convenient to use the vibrational partition function per normal mode, which is given by:

$$\boxed{f_{\text{vib}} = \frac{1}{1 - e^{-h\omega/k_b T}}} \tag{2.84}$$

To conclude this subsection, a small note is in order here. In the beginning of this section we mentioned that we wrote, by definition, the partition functions with respect to the lowest accessible state allowed. This means, that we write the vibrational partition functions with respect to the zero point energy. The true vibrational partition function however, has this zero point energy term in the numerator and looks like:

$$f_{\text{vib}} = \frac{e^{-h\omega/2k_b T}}{1 - e^{-h\omega/k_b T}} \tag{2.85}$$

Remember

Whether or not the vibrational partition functions are defined with respect to the zero point energy or to the true electronic ground state, has an important consequence for the definition of the activation energy in transition state theory.

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[5] For a linear polyatomic molecule, the number of independent coordinates is given by $3\mathcal{N} - 5$, leading to only $3\mathcal{N} - 5$ vibrational degrees of freedom. This is explained in more detail in section 2.9 on 65.

2.6.3 Rotations

Finally, we have to define the rotational partition function. The rotational energy for a diatomic molecule is given by

$$\epsilon_{\text{rot}(J)} = \frac{J(J+1)h^2}{8\pi^2 I} \tag{2.86}$$

where J is any non-negative integer and I is the moment of inertia about an axis perpendicular to the molecular axis passing through the centre of mass of the molecule. As the energy level $\epsilon_{\text{rot}(J)}$ is degenerate with degeneracy $g_{\text{rot}} = 2J + 1$, the rotational partition function is

$$f_{\text{rot}} = \sum_{J=0}^{\infty} (2J+1) e^{-J(J+1)h^2/8\pi^2 I k_b T} \tag{2.87}$$

Similar as for the translational partition function, we replace the sum over states by an integral, thus obtaining

$$f_{\text{rot}} = \int_0^{\infty} (2J+1) e^{-J(J+1)h^2/8\pi^2 I k_b T} \, \mathrm{d}J \tag{2.88}$$

yielding

$$\boxed{f_{\text{rot}} = \frac{8\pi^2 I k_b T}{h^2}} \tag{2.89}$$

The above result is for a **diatomic molecule**. Furthermore note that this partition function contains both degrees of freedom (i.e. in two dimensions).

Just like we have seen for the vibrational frequencies, a part of the above formula has the dimension of temperature and we can define the characteristic temperature for rotation represented by Θ_{rot} as

$$\Theta_{\text{rot}} = \frac{h^2}{8\pi^2 I k_b} \tag{2.90}$$

which turns equation 2.89 into

$$f_{\text{rot}} = \frac{T}{\Theta_{\text{rot}}} \tag{2.91}$$

Note that the above derivation accounts for diatomic molecules. For polyatomic molecules, without further derivation, the rotational partition function is given by

$$f_{\text{rot}} = \left(\frac{k_b T}{hc} \right)^{3/2} \sqrt{\frac{\pi}{I_A I_B I_C}}, \tag{2.92}$$

where I_A, I_B, I_C, are the moments of inertia around the three orthogonal rotation axes A, B and C.[6]

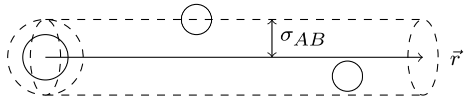

Figure 2.3: *Schematic depiction of the cylinder space swept out by molecule A. All molecules whose center are within the volume as defined by the cylinder will undergo a collision.*

2.7 Collision theory

Before we discuss transition state theory and derive the corresponding rate equation within this theory, we will first treat collision theory which is a somewhat simpler theory enabling us to calculate reaction rates, yet conveys a lot of important principles behind transition state theory.

Consider a mixture composed of molecules which are able to react with each other. Let us furthermore assume that these molecules can be represented as rigid spheres with diameters σ_A and σ_B for two types of molecules A and B with n_A and n_B the corresponding number of molecules per cubic meter. We can then define a bimolecular collision as the situation where there is contact of the surfaces of the two spheres.

We wish to calculate the number of collisions per second for one molecule of A. For a mixture of A and B, we can consider that one molecule of A will be moving in an arbitrary direction $\vec{r}$ with a mean velocity relative to a molecule of type B. A collision between A and B will occur in the situation wherein the center of molecule B is at a position within a distance $\sigma_{AB} = \left(\sigma_A + \sigma_B\right)/2$ of the line of flight of the center of molecule A during the passage of A. This is schematically depicted in Figure 2.3.

The total number of collisions of molecule A with those of type B per second can then be estimated from the volume swept out by a sphere of radius σ_{AB} multiplied by the number of molecules of type B per cubic meter, n_B. The required volume is

$$V = \pi\sigma_{AB}^2\overline{r} \tag{2.93}$$

and the collision number

$$n_{\text{col}} = \pi\sigma_{AB}^2\overline{r}n_B \tag{2.94}$$

2.7.1 Maxwell-Boltzmann velocity distribution

The appropriate mean relative velocity $\vec{r}$ can be calculated from the distribution of the velocities of molecules A and B. For this, we need to know the distribution of velocities of A and B, which can be obtained as special cases of the Boltzmann distribution of energy as given in equation 2.31. According to the latter, the probability that a molecule is in a level of energy ϵ_i and statistical weight g_i is proportional to $g_i \exp\left(\epsilon_i/k_BT\right)$. The probability may be represented by $\mathrm{d}n/n_0$, where $\mathrm{d}n$ is the number of molecules with energy ϵ_i and n_0 is the total number of molecules in the mixture.

Velocity has three components, i.e. in the $\dot{x}$, $\dot{y}$ and $\dot{z}$ direction. The translational energy in each of the directions is given by

$$\epsilon_i = \frac{1}{2}m\dot{x}^2, \tag{2.95}$$

where m is the mass of a molecule and $\dot{x}$ is the first derivative towards time of the position in the x direction. The statistical weight is the volume in phase space in units of h^f for f

degrees of freedom, which is given by

$$g_i = \frac{m\,\mathrm{d}\dot{x}\,\mathrm{d}x}{h}. \tag{2.96}$$

Therefore, the fractional number of molecules with x component of velocity between $\dot{x}$ and $\dot{x} + \mathrm{d}\dot{x}$ and x coordinate between x and $x + \mathrm{d}x$ is given by

$$\frac{\mathrm{d}n}{\mathrm{d}n_0} = A\frac{m\,\mathrm{d}\dot{x}\,\mathrm{d}x}{h}\exp\left(\frac{-m\dot{x}^2}{2k_BT}\right), \tag{2.97}$$

where A is a proportionality constant to ensure that the total fraction of molecules is unity (i.e. a molecule has to have a specific velocity). A can thus be determined by integrating with respect to $\dot{x}$ and x over their complete ranges from $-\infty$ to ∞ and 0 to a, respectively, where a is the length of the corresponding edge of the container in phase space, which is here assumed to be rectangular. Thus, we can find A by solving the following integral

$$\int \frac{\mathrm{d}n}{\mathrm{d}n_0} = 1 = \frac{Aam}{h}\int_{-\infty}^{\infty}\exp\left(\frac{-m\dot{x}^2}{2k_BT}\right) = \frac{Aam}{h}\sqrt{\frac{2\pi k_BT}{m}} \tag{2.98}$$

and thus

$$A = \frac{h}{a}\left(2\pi m k_BT\right)^{-1/2} \tag{2.99}$$

by which the final result is

$$\frac{\mathrm{d}n}{\mathrm{d}n_0} = \left(\frac{m}{2\pi k_BT}\right)^{1/2}\exp\left(\frac{-m\dot{x}^2}{2k_BT}\right)\mathrm{d}\dot{x}. \tag{2.100}$$

In three directions, the result is simply

$$\frac{\mathrm{d}n}{\mathrm{d}n_0} = \left(\frac{m}{2\pi k_BT}\right)^{3/2}\exp\left(\frac{-mv^2}{2k_BT}\right)\mathrm{d}\dot{x}\,\mathrm{d}\dot{y}\,\mathrm{d}\dot{z}, \tag{2.101}$$

where

$$v = |\vec{r}| = \sqrt{\dot{x}^2 + \dot{y}^2 + \dot{z}^2}. \tag{2.102}$$

Equation 2.101 can be rewritten for the case that we are not interested in which particular direction the molecules are moving, but only in their absolute velocity. The ”volume” element $\mathrm{d}\dot{x}\,\mathrm{d}\dot{y}\,\mathrm{d}\dot{z}$ then becomes $v^2 \sin\vartheta\,\mathrm{d}v\,\mathrm{d}\vartheta\,\mathrm{d}\varphi$. Integrating over the angles gives

$$\int_0^{\pi}\int_0^{2\pi}\sin\vartheta\,\mathrm{d}\vartheta\,\mathrm{d}\varphi = 4\pi \tag{2.103}$$

and applying this result to equation 2.101 gives

$$\frac{\mathrm{d}n}{\mathrm{d}n_0} = 4\pi\left(\frac{m}{2\pi k_BT}\right)^{3/2} v^2\exp\left(\frac{-mv^2}{2k_BT}\right)\mathrm{d}c. \tag{2.104}$$

Equation 2.104 is the common form of the Maxwell-Boltzmann velocity distribution law. The average velocity $\overline{v}$ is obtained by multiplying equation 2.104 by v and integrating from 0 to ∞ which gives

$$\overline{v} = \left(\frac{8k_BT}{\pi m}\right)^{1/2}. \tag{2.105}$$

If we want to know the mean *relative* velocity between two distributions, we have to multiply the two distribution equations 2.101 for each of the two distributions and change the velocity coordinates to relative velocity coordinates by the following substitution

$$r^2 = (\dot{x}_A - \dot{x}_B)^2 + (\dot{y}_A - \dot{y}_B)^2 + (\dot{z}_A - \dot{z}_B)^2. \tag{2.106}$$

Integrating this expression over all directions and velocities and multiplying by r gives the following mean relative velocity

$$\overline{r} = \left(\frac{8k_BT}{\pi \mu}\right)^{1/2}, \tag{2.107}$$

where m in equation 2.105 is replaced by the reduced mass μ which is given by

$$\mu = \frac{m_A m_B}{m_A + m_B}. \tag{2.108}$$

Note that in the special case that $m_A = m_B = m$,

$$\mu = \frac{m}{2} \tag{2.109}$$

and

$$\overline{r} = \sqrt{2}\overline{v} \tag{2.110}$$

Finally, we can plug equation 2.107 into equation 2.94 to obtain

$$n_{\text{col}} = \left(\frac{8k_BT}{\mu}\right)^{1/2} \sigma_{AB}^2 n_B. \tag{2.111}$$

From this, we can easily calculate the number of collisions per unit volume per molecule of type A with molecule B

$$Z_{AB} = \left(\frac{8\pi k_BT}{\mu}\right)^{1/2} \sigma_{AB}^2 n_A n_B. \tag{2.112}$$

In the case that molecule A and B are *like* molecules, the above equation simplifies to

$$Z = 2\left(\frac{\pi k_BT}{m}\right)^{1/2} \sigma^2 n^2. \tag{2.113}$$

2.7.2 Collision effectiveness

Not all collisions will result in a reaction and there are a number of important factors that determine the effectiveness of a collision. The most important one we will consider here is that the molecules that collide should have a minimum energy to overcome the underlying reaction barrier. This minimum energy corresponds to a minimum velocity and hence we can calculate using the Maxwell-Boltzmann velocity distribution an effectiveness factor q between 0 and 1 such that

$$r = qZ, \tag{2.114}$$

where r is the rate of the elementary reaction step and Z is the collision density. If we consider an energy ΔE_{act} corresponding to the minimum energy of activation by which a reaction will occur, we can calculate the value q as follows

$$q = \frac{\int_{v_{\text{min}}}^{\infty} 4\pi \left(\frac{\mu}{2\pi k_B T}\right)^{3/2} v^3 \exp\left(\frac{-\mu v^2}{2k_B T}\right) \mathrm{d}v}{\int_0^{\infty} 4\pi \left(\frac{\mu}{2\pi k_B T}\right)^{3/2} v^2 \exp\left(\frac{-\mu v^2}{2k_B T}\right) \mathrm{d}v} = \exp\left(\frac{-\Delta E_{\text{act}}}{k_B T}\right) \tag{2.115}$$

by which the final expression becomes

$$r_{\text{col}} = \left(\frac{8\pi k_B T}{\mu}\right)^{1/2} \sigma_{AB}^2 n_A n_B \exp\left(\frac{-\Delta E_{\text{act}}}{k_B T}\right) \tag{2.116}$$

for *unlike* molecules
and

$$r_{\text{col}} = 2\left(\frac{\pi k_B T}{m}\right)^{1/2} \sigma^2 n^2 \exp\left(\frac{-\Delta E_{\text{act}}}{k_B T}\right) \tag{2.117}$$

for *like* molecules.

2.7.3 Unimolecular reactions

There is a special case which deserves a bit of additional attention. Let us consider a unimolecular reaction. You might argue that such a reaction does not require molecules to meet rendering the concept of collisions as not very useful. For example, in an isomerization reaction, the molecule itself transforms to another configuration which in principle does not require a collision.

According to the hypothesis of Lindemann and Christiansen, all molecules acquire and lose energy by collisions with surrounding molecules. If we assume this hypothesis to be true, then we can construct the following set of elementary reaction steps for the reaction of A to P activated by a collision of another molecule M:

$$A + M \underset{k_1^-}{\overset{k_1^+}{\rightleftharpoons}} A* + M \tag{2.118}$$

$$A* \xrightarrow{k_2^+} P \tag{2.119}$$

Note that in the above equation, the asterisk designates an activated complex rather than an adsorbed species. Application of the steady state approximation to the reaction intermediate A* yields

$$\frac{\mathrm{d}[A*]}{dt} = k_1^+[A][M] - k_2^+[A*] - k_1^-[A*][M] = 0 \tag{2.120}$$

$$[A*] = \frac{k_1^+[A][M]}{k_2^+ + k_1^-[M]} \tag{2.121}$$

and hence the rate of reaction becomes

$$\frac{\mathrm{d}[P]}{dt} = \frac{k_1^+ k_2^+[A][M]}{k_2^+ + k_1^-[M]}. \tag{2.122}$$

For a mixture only containing A, [M] is [A]. In other words, the reaction of A to P is activated by a collision with another molecule of A and hence

$$\frac{\mathrm{d}[P]}{dt} = \frac{k_1^+ k_2^+[A]^2}{k_2^+ + k_1^-[A]}. \tag{2.123}$$

For sufficiently high pressures of A, this reaction will be first order. However, in the low pressure regime the above equation can be approximated by

$$\frac{\mathrm{d}[P]}{dt} = \frac{k_1^+ k_2^+[A]^2}{k_2^+ + k_1^-[A]} \approx k_1^+[A]^2. \tag{2.124}$$

The above dependency of the rate on the pressure can be verified by experimental means and it was found that the equation holds for several isomerization and decomposition reactions. Interestingly, this implies that unimolecular reactions in fact do not exist at all, because collisions with surrounding molecules are needed to bring the reacting molecule to a sufficiently high energetic state that it is capable of crossing the reaction barrier of the elementary reaction step.

2.8 Transition state theory

Within this section, we will derive the formula for the chemical rate using transition state theory. In principle, many similar derivations exist.[4, 7, 8] Here, we will employ a derivation wherein we assume that the reaction coordinate can be modeled as a translation.[6]

To derive a general formula for the reaction rate constant, let us introduce a simple model system. In Figure 2.4, the potential energy surface of the three-body complex H-H-H for the reaction $H_2 + H \rightarrow H + H_2$ is shown.[9]

Within this Figure, the two dark regions (denoted by A and B) designate the stable states, being the complex H_B-H_C with the atomic hydrogen H_A far away and the situation where $H_A - H_B$ are bonded and H_C as atomic hydrogen. One can construct a path between these two states (regions) as denoted by the dotted white line. This path that connects the two stable states wherein all the points on the path are higher in energy than the two stable states represents the reaction coordinate. At the center of this line lies a meta-stable state which is termed the transition state (denoted in the Figure as TS). The transition state is characterized as being a maximum in energy along the trajectory of the reaction coordinate and a minimum in all other directions (i.e. in any direction perpendicular to the reaction

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[6] There is a somewhat simpler derivation, but we leave this as an exercise to you. See exercise 2.12 for an alternative derivation of the Eyring equation on page 70

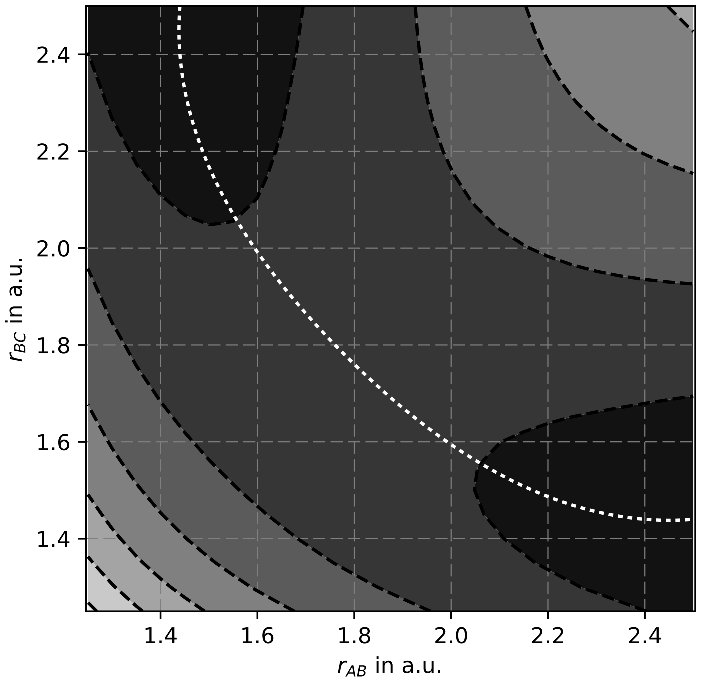

Figure 2.4: *Potential energy surface of the one-dimensional tri-atomic hydrogen system.* r_{AB} *and* r_{BC} *are the distances between* H_A *and* H_B *and between* H_B *and* H_C*, respectively. The white dotted line indicates the reaction coordinate of the elementary reaction step wherein a hydrogen atom is transferred between the two other hydrogen atoms.*

coordinate). In mathematical terms, such a point on the potential energy surface, which has different curvatures in different directions, is known as a *saddle point*.

An illustrative video showing the curvature of the PES of H_3 can be found on Youtube using this link:
▶ `https://www.youtube.com/watch?v=5y0DQhu1-CY`

We want to derive a rate constant which is defined as the speed at which species residing in state A go to state B. Using a statistical assumption, it is obvious that such a rate is proportional to the number of molecules residing in state A.

$$\text{rate} = k[A] \tag{2.125}$$

where k is termed the reaction rate constant and has the appropriate dimensions given the elementary reaction step.[7] In the derivation, we are going to use the following assumptions:

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[7] This definition for the dimensionality of the rate constant is actually a source of confusion. We will elaborate on the topic in section 2.10 on page 65.

1. The transition state and initial state are in thermal equilibrium in such a way that we can define an equilibrium constant K to describe the ratio of the species between the two states.

2. The transition state has a particular "width" in the direction of the reaction coordinate and species have a particular velocity at which they can cross this width.

3. Species that have passed the transition state from the initial state will immediately move towards the final state.

Given these three assumptions, an elementary reaction step can be envisioned as the following reaction sequence

$$R_{\text{IS}} \leftrightharpoons R_{\text{TS}} \rightarrow_{\text{irrev}} P \tag{2.126}$$

for which we can construct the following expression for the reaction rate constant k:

$$k = \nu K, \tag{2.127}$$

where ν is a crossing frequency (in s^{-1}) at which species at the transition state migrate to the final state.[8]

One could object to the above assumption as although the above is true for a system in equilibrium, we are looking for reaction rates, which are also valid out of equilibrium. How can we be sure that the equation 2.127 also holds when we study the transient behavior? From experiment though, it is found that rate constants do not change when the system approaches equilibrium[7], therefore, we believe that equation 2.127 holds, irrespective of whether our system is in equilibrium or not.

Going back to our model system, for the elementary reaction step $H_2 + H \to H + H_2$, the equilibrium constant K can be defined as

$$K = \frac{f_{\text{TS}}}{f_{\text{IS}}} = \frac{f'_{\text{TS}}}{f'_{\text{IS}}} \exp\left(\frac{-\Delta\epsilon_0}{k_B T}\right). \tag{2.128}$$

Within this equation, $\Delta\epsilon_0$ is the zero-point energy corrected energetic difference between the stable state A and the transition state. f_{IS} and f_{TS} are the total molecular partition functions of the complex (see equation 2.60) in the initial and transition state, respectively. The prime indicates that we have extracted the electronic partition function including the zero-point energy correction from the total molecular partition function and used the Boltzmann equation to construct the term $\exp\left(-\frac{\Delta\epsilon_0}{k_b T}\right)$.

For the derivation of ν we wish to evaluate some characteristic time τ for the system to pass through the transition state (and then set ν as the reciprocal value of the average τ). Given a width δ of the transition state and an average velocity v of the species, the time τ is given by

$$\tau = \frac{\delta}{v}. \tag{2.129}$$

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[8] It is unfortunate that the variable ν is also used for the stoichiometric coefficient, but we hope that from the context it is always clear what ν represents.

Thus, the reaction rate constant equation so far yields

$$k = \frac{v}{\delta}\frac{f'_{\mathrm{TS}}}{f'_{\mathrm{IS}}}\exp\left(\frac{-\Delta\epsilon_0}{k_B T}\right). \tag{2.130}$$

Next, we extract the partition function corresponding to the reaction coordinate from the total molecular partition function of the transition state. We have assumed that the partition function corresponding to the direction of the reaction coordinate is a translational partition function. By combination of equation 2.70 and the previous equation we obtain

$$k = \frac{v}{\delta}\frac{\delta\sqrt{2\pi m k_b T}}{h}\frac{f'_{\mathrm{TS}}}{f'_{\mathrm{IS}}}\exp\left(\frac{-\Delta\epsilon_0}{k_B T}\right). \tag{2.131}$$

The average velocity v **in one dimension** can be obtained in a similar fashion as shown for the Maxwell-Boltzmann velocity distribution in section 2.7.1:

$$\begin{aligned} v &= \frac{\int_0^\infty \exp\left(\frac{-mx^2}{2k_b T}\right)\dot{x}\mathrm{d}x}{\int_0^\infty \exp\left(\frac{-mx^2}{2k_b T}\right)\mathrm{d}x} && (2.132)\\ &= \sqrt{\frac{2k_b T}{\pi m}}. && (2.133) \end{aligned}$$

Plugging this equation into equation 2.131, and noting the introduction of the "2" in the denominator of the first term as only half of the crossings are from the IS to the FS, yields

$$k = \frac{\sqrt{\frac{2k_b T}{\pi m}}}{2\delta}\frac{\delta\sqrt{2\pi m k_b T}}{h}\frac{f''_{\mathrm{TS}}}{f'_{\mathrm{IS}}}\exp\left(\frac{-\Delta\epsilon_0}{k_B T}\right). \tag{2.134}$$

Note that a second prime is introduced for the total motional partition function for the transition state to indicate that we have extracted one translational partition function. The above equation can be rewritten to

$$\boxed{k = \frac{k_B T}{h}\frac{f^{\ddagger}_{\mathrm{TS}}}{f_{\mathrm{IS}}}\exp\left(\frac{-\Delta\epsilon_0}{k_B T}\right).} \tag{2.135}$$

Herein, we have dropped the primes and introduced a ‡ to indicate that one partition function is extracted from the total motional partition function for the transition state.

Equation 2.135 is known as the *Eyring equation* or *transition state theory equation*.

2.8.1 Comparison between Transition State Theory and Collision theory

The fundamental difference between transition state theory and collision theory is that the latter considers molecules to be rigid spheres and hence only the translational motion of these rigid spheres is considered. Hence, the degrees of freedom due to rotation and vibration are not considered in collision theory. Nevertheless, for a diatomic molecule with an internuclear distance of σ_{AB} without any vibrational degrees of freedom, transition state theory should give the same result as collision theory. If m_A and m_B are the masses of the two reactant molecules, the moment of inertia I is

$$I = \sigma_{AB} \frac{m_A m_B}{m_A + m_B} \tag{2.136}$$

and thus k can be written using expression 2.135 as

$$\begin{aligned}
k &= \frac{k_B T}{h} \frac{f_{\text{TS}}^{\ddagger}}{f_{\text{IS}}} \exp\left(\frac{-\Delta\epsilon_0}{k_B T}\right). && (2.137)\\
&= \frac{k_B T}{h} \frac{f_{\text{trans}}^{(3)} f_{\text{rot}}^{(2)}}{f_{\text{trans}}^{(3)} f_{\text{trans}}^{(3)}} \exp\left(\frac{\Delta E_{\text{act}}}{k_B T}\right) && (2.138)\\
&= \frac{k_B T}{h} \frac{\frac{(2\pi(m_A+m_B)k_B T)^{3/2}}{h^3} \frac{8\pi^2 \sigma_{AB}^2 \frac{m_A m_B}{m_A+m_B} k_B T}{h^2}}{\frac{(2\pi m_A k_B T)^{3/2}}{h^3} \frac{(2\pi m_B k_B T)^{3/2}}{h^3}} \exp\left(\frac{\Delta E_{\text{act}}}{k_B T}\right) && (2.139)\\
&= \left(8\pi k_B T \frac{m_A m_B}{m_A + m_B}\right)^{1/2} \sigma_{AB}^2 \exp\left(\frac{\Delta E_{\text{act}}}{k_B T}\right). && (2.140)
\end{aligned}$$

The above formula is equal to equation 2.116 when multiplied by the number density of A and B $n_A \cdot n_B$, showing that both theories provide the same rate expression.

2.8.2 Fundamental objection against collision theory

Despite the fact that collision theory and transition state theory give the same results when the underlying assumption of collision theory is applied to the choice of the partition functions within transition state theory, collision theory is in conflict with thermodynamics because it neglects vibrational and rotational degrees of freedom. This becomes immediately apparent if we derive the equilibrium constant from collision theory

$$\begin{aligned}
K &= \frac{k^+}{k^-} && (2.141)\\
&= \frac{\left(\frac{8\pi k_B T}{\mu_{AB}}\right)^{1/2} \sigma_{AB}^2 \exp\left(\frac{-\Delta E_{\text{act,f}}}{k_B T}\right)}{\left(\frac{8\pi k_B T}{\mu_{CD}}\right)^{1/2} \sigma_{CD}^2 \exp\left(\frac{-\Delta E_{\text{act,b}}}{k_B T}\right)} && (2.142)\\
&= \frac{\sigma_{AB}^2}{\sigma_{CD}^2} \sqrt{\frac{\mu_{CD}}{\mu_{AB}}} \exp\left(\frac{-\Delta H}{k_B T}\right). && (2.143)
\end{aligned}$$

The above formula correctly describes the relation between K and the enthalpy of the reaction, yet such an expression is only valid at 0K or in the case when there is no entropy change. In principle, this discrepancy could be resolved by introduction of a steric factor P in collision theory, however such an introduction would result in a loss of the fundamental understanding.

2.9 The potential energy surface

Although covered very briefly in the previous section (see Figure 2.4), we wish to extend our discussion on the concept of the potential energy surface of a molecule and its degrees of freedom. Given the geometry of the molecule, an energy corresponding to that that specific configuration can be defined or calculated. To uniquely define such a geometry, $n = 3N - 6$

coordinates for non-linear molecules and $n = 3N - 5$ for linear molecules need to be defined. These numbers correspond to the degrees of freedom that the molecule has. You might expect that each molecule has $3N$ degrees of freedom, as each atom can be positioned independently along each of the three Cartesian axes. The reduction comes from the fact that by a change of basis, three such coordinates pertain to the central position of the molecule (its translation with respect to an origin) and another three relate to the rotation of the molecule. A linear molecule only has two unique rotational axes, as it is impossible to define a rotational axis along the direction of the linearity of the molecule, hence for linear molecules the configurational degrees of freedom equal $3N - 5$. Thus, the energy of a (here, non-linear) molecule is a function of its coordinates as given by

$$E = f\left(x_0, x_1, \cdots, x_{3N-6}\right) = f\left(\vec{x}\right). \tag{2.144}$$

And the above function defines the potential energy surface in multidimensional space. The function f that calculates the energy is thus a map from high-dimensional space to a scalar value (i.e. the energy) as give by

$$f : \mathbb{R}^{3N-6} \rightarrow \mathbb{R}. \tag{2.145}$$

Functions that depend on a single variable are easily plotted in a graph. Two-dimensional functions can be plotted using a contour plot or a heat map. For three-dimensional functions you could create an isosurface plot, but for any higher-dimensional function you need to reduce the dimensionality in order to make a plot. Hence, potential energy surfaces can rarely be depicted in a graph. The reason we are able to construct a contour plot as seen in Figure 2.4 is because the one-dimensional H_3 system only has 2 degrees of freedom.

A molecule is considered to be stable when the Cartesian coordinates of its atoms are in such a geometry that the molecule resides in a local minimum on this potential energy surface. Such states are often coined initial and final states with regard to elementary reaction steps. A transition state is defined as being a maximum in one direction, i.e. the direction of the reaction coordinate, while being a minimum in all other directions on this potential energy surface. Here, we will address how we can analyze in which particular state (e.g. initial, transition or final state) a molecule is and what the relation of this state is with regard to its partition functions.

Mathematically, initial and final states as well as transition states are extrema on the potential energy surface. Extrema are points where the gradient equals zero:

$$\nabla E = \nabla f\left(x_0, x_1, \cdots, x_{3N-6}\right) = \vec{0} \tag{2.146}$$

To identify the type of the extreme, either a local minimum or a saddle point, we need to probe the second derivatives by constructing a Hessian matrix for which each element in the matrix is given by

$$H_{i,j} = \frac{\partial^2 E}{\partial x_i \partial x_j} = \frac{\partial^2 f\left(x_0, x_1, \cdots, x_{3N-6}\right)}{\partial x_i \partial x_j}. \tag{2.147}$$

Diagonalization of this Hessian matrix (see page 133) yields a series of eigenvalues and eigenvectors which are the force constants and the directions for the normal vibrations, respectively. If all of these force constants are positive, this means that all vibrations are real (see eq. 2.72) and the molecule is considered to be in a local minimum. To look at this from another perspective, in principle the force constants tell us to what extend the energy of a system increases as a result of a perturbation in one of the directions of the normal vibrations. If all these constants are positive, this means that by perturbing the molecule in **any** direction, its energy will increase. This is another way of saying that the molecule is in a local minimum. In line with the above reasoning, a transition state is characterized as being a maximum in energy in the direction of the reaction coordinate, therefore, a transition state should have one and only one negative force constant. This negative force constant then results in an imaginary frequency.

This now brings us to the relation of the potential energy surface of a molecule with respect to its partition functions. The partition functions of a molecule represent the motional degrees of freedom of that molecule. We can imagine that these motional degrees of freedom tell us something about the ways the molecule can be represented, or in other words, give us a number of the different configurations a molecule can have. Therefore, it is obvious to see that motional degrees of freedom add to the entropy of the species. Every molecule has $3N$ partition functions. If the molecule is in the gas phase and is linear, it has $3N - 5$ vibrational degrees of freedom. When the molecule is not linear (and in the gas phase), it has $3N - 6$ vibrational degrees of freedom. Linear molecules have one vibrational degree of freedom more than non-linear molecules in exchange of having one rotational degree of freedom less. Both linear as well as non-linear molecules have three translational degrees of freedom.

In contrast, molecules which are in the transition state have exchanged one of their degrees of freedom into an imaginary frequency. This imaginary frequency is represented in the Eyring formula (eq. 2.135) by the term $\frac{k_b T}{h}$. To derive a formula for the macroscopic rate for any elementary reaction step, one needs to identify the different degrees of freedom for initial, transition and final state in order to establish the required partition functions as well as the difference in energies between the states on the potential energy surface (i.e. the reaction and activation electronic energies). For the most basic types of reactions (adsorption, desorption and surface reaction), this procedure is discussed in the next chapter.

2.10 Dimensionality of equilibrium constants and reaction rate constants

From section 2.5 it should be clear that the equilibrium constant K is dimensionless. This is in contrast to many textbooks and articles wherein a unit is reported for the equilibrium constant, where it seems that the unit actually depends on the particular reaction. For example, one could define an equilibrium constant K for the gas phase reaction $A + B \rightarrow C$ as

$$K = \frac{p_C}{p_A p_B}, \tag{2.148}$$

which should clearly have the dimensionality of inverse pressure (e.g. bar^{-1}). The difference lies in whether K is a so-called standard equilibrium constant or not. The key word is standard. A standard equilibrium constant, often denoted with a superscript "0", refers to an equilibrium constant given a particular standard (e.g. at $T = 293.15$K and $p = 1$ atm). The standard equilibrium constant is defined as

$$K^0 = \exp\left(\frac{-\Delta G_r^0}{k_b T}\right) = \prod_i a_i^{\nu_i}, \tag{2.149}$$

where a_i refers to the activity of species i. For ideal gases, the activity is given by

$$a_i = \gamma_i \frac{p_i}{p^0}, \tag{2.150}$$

where p^0 is the standard pressure and γ_i is the activity coefficient. As these activities are (made) dimensionless, so is the equilibrium constant.

Similar to the equilibrium constant, we can also define reaction rate constants in the forward and backward direction for the gas phase reaction $A + B \rightarrow C$. The forward and backward rates are defined by

$$r^+ = k^+ p_A p_B \tag{2.151}$$

and

$$r^- = k^- p_C. \tag{2.152}$$

To construct any meaningful mass balance, r^+ and r^- should have the same units. This can only be achieved if the unit of k^+ and k^- differs. But if that is the case, than the equilibrium constant K is no longer dimensionless, since

$$K = \frac{k^+}{k^-}. \tag{2.153}$$

Again, the solution lies in the definitions. For reaction rates, we typically use pressures and concentrations, but in principle we should use activities and the forward and backward rates should be

$$r^+ = k^+ a_A a_B \tag{2.154}$$

and

$$r^- = k^- a_C. \tag{2.155}$$

However, as activities are assumed to scale linearly with concentrations and pressures and since the same standard is applied to all species, we often loose the strict definition for the sake of convenience. Thus, on the basis of the Eyring equation (equation 2.135), the reaction rate constants should have the unity of s^{-1}.

2.11 Questions and Exercises

The answers to the questions and exercises are given at the end of this book in Appendix C (page 135).

2.11.1 Questions

a) What type(s) of partition functions are relevant to chemistry? How do these types differ? To what kind of configurational freedoms do they relate?

b) What are the units of a partition function?

2.11.2 Exercises

The exercises are marked by a number of gears to indicate their difficulty levels.

✎ **Exercise 2.1** ⚙⚙

Consider the equilibrium for the dissociation of A in B and C according to

$$A \leftrightarrows B + C \tag{2.156}$$

A has four energy levels. One ground state, two degenerate excited states ΔE above its ground state and a second excited state $2\Delta E$ above the ground state. B has two energy levels of which the lowest energy level is ΔE above the ground state of A and another energy level that lies $2\Delta E$ above the ground state of A. The ground state of C lies at the same level as the ground state of B. Furthermore, there are two degenerate excited states that lie $2\Delta E$ above the ground state of C.

a) Provide the equilibrium condition for this system.

b) Express the equilibrium constant K in terms of the partition functions of A, B, and C.

c) What are the limiting values of K at zero and at infinite temperature?

■

✎ **Exercise 2.2** ⚙⚙

A molecule A has two energy states separated by ΔE.

a) Derive an expression for the partition function of A and calculate the value of the partition function at 0 K and infinitely high temperature.

b) Suppose that A is in equilibrium with its isomer B which has the following energy levels with respect to the ground state of isomer A: $\Delta E/2, 3\Delta E/4$ and ΔE. Derive an expression for the equilibrium constant K and compute the limiting values of K at low and high temperature.

■

✎ **Exercise 2.3** ⚙⚙⚙

Two isomers A and B are in equilibrium and possess the following spectroscopically determined energy levels

$$\epsilon_i^A = i\Delta E \tag{2.157}$$

$$\epsilon_i^B = \left(\frac{i}{2} + 1\right)\Delta E \tag{2.158}$$

with $i = 0, 1, 2, 3, ...$

Provide an expression for the equilibrium constant for the isomerization between A and B as a function of temperature and provide values for this constant at $T = 0.1\Delta E/k_b$, $T = 2\Delta E/k_b$, and $T = 10\Delta E/k_b$ and at infinitely high temperature. You will get an infinite geometric series for which an exact solution is known. If you forgot about geometric series, have a look at Appendix B.4 on page 131.

Exercise 2.4

a) Calculate the translational partition function of a N_2 molecule at 298 K in a container sized such that it contains one mole of ideal gas.

b) How does q_{trans} change with temperature, pressure and volume?

c) The wave number for the stretching frequency of N_2 is 2330 cm^{-1}. Calculate the vibrational partition function corresponding to this vibrational mode and with respect to the vibrational ground state.

d) Calculate the rotational partition function of N_2 at 298 K. The moment of inertia is $1.407 \cdot 10^{-46}$ kg $\cdot$ m^2 and the symmetry number of N_2 is 2.

e) Calculate the total partition function of N_2.

Exercise 2.5

a) Calculate the average velocity of an N_2 molecule at room temperature ($T = 298$K). Make use of the Maxwell-Boltzmann velocity distribution as given in equation 2.104 on 56. Feel free to directly use equation B.6 on page 130 to solve the integral.

b) At which temperature is the average velocity of N_2 equal to that of He at $T = 298$K?

c) Calculate the average translational energy of 1 mol of N_2 at 100, 298 and 1000 K. Feel free to directly use equation B.5 on page 130 to solve the integral.

Exercise 2.6

Given a mixture of N_2 and H_2 in a 1:3 ratio at 1 bar and $T = 298$K.

a) Calculate the number of molecules N_2 and H_2 in 1 m^3 of this mixture.

b) The collision diameter of H_2 is 0.271 nm and the collision diameter of N_2 is 0.373 nm. How many collisions are there per second between the H_2 molecules?

c) How many collisions are there between the N_2 molecules?

d) How many collisions are there between N_2 and H_2 molecules?

e) What is the total number of collisions in 1 m^3 of this mixture?

■

Exercise 2.7

Consider the gas phase isomerization of cyclopropane to propylene. Experimentally, it is found that the rate expression is given by the equation below

$$r = 2 \cdot 10^{15} \exp\left(\frac{-274000 \text{ J/mol}}{RT}\right) p_{\text{cyclopropane}} \tag{2.159}$$

a) Give values for the Arrhenius pre-exponential factor and the activation energy in kJ/mol.

b) Draw an energy diagram for this reaction from transition-state theory.

c) Why does the rate of this reaction decrease when the pressure is lowered?

■

Exercise 2.8

a) Provide the general equation for the reaction of a molecule R via the transition state $R\#$ to a product P according to transition state theory. Indicate in detail in which direction the reaction steps are allowed to proceed and provide a rate expression in terms of the relevant reaction constant and equilibrium constant. Draw an energy diagram which clearly shows the energy levels of R, $R\#$ and P, as well as the barrier energy ΔE.

b) Give the general expression for the reaction rate according to transition state theory in terms of the partition functions (no explicit expressions are required here) and ΔE.

c) What is the essential difference between transition state theory and collision theory?

■

Exercise 2.9

Consider the direct dissociative adsorption of methane on a Ru surface to give adsorbed CH_3 and H.

a) Give the main assumptions of transition state theory and draw the corresponding reaction energy diagram for this adsorption reaction.

b) Give the general expression for the rate constant based on transition state theory.

c) Qualitatively discuss the different factors in this equation, paying specific attention to the relevant partition functions and the activation energy.

d) The entropy of methane in the gas phase is about 130 J/mol/K. Estimate the pre-exponential factor for the dissociative adsorption of methane at 800 K.

e) Assuming that the activation energy is 50 kJ/mol, estimate the rate constant for dissociative adsorption at 800 K.

■

Exercise 2.10

a) Derive an expression for the rate of O_2 dissociation into two oxygen fragments in the gas phase according to transition state theory. Provide explicit expression for all relevant partition functions. Clearly convey what assumptions you use and relate the partition functions to the motional degrees of freedom of the system in the initial and transition state.

b) Rewrite your expression in the form of the Arrhenius equation and give the activation energy and the pre-exponential factor according to the Arrhenius equation.

■

Exercise 2.11

a) Assume Hooke's law to be valid and use a harmonic approximation of the potential energy surface. Calculate the force constant in the direction of the reaction coordinate and the force constant ($k = \frac{\partial^2 V}{\partial x^2}$) in the direction perpendicular to the reaction coordinate. Use a numerical approximation to calculate these force constants. Obtain the required values for your approximation from the contour lines in Figure 2.4. Do not worry if you cannot calculate it exactly, we are interested in rough values. In fact, if you are not able to even calculate a rough value, give at least the sign of the force constant (i.e. positive or negative).

b) Calculate the frequencies by $\omega = \sqrt{\frac{k}{m}}$. Use the rest mass of a H atom as the value for the mass m. What property does the frequency in the direction of the reaction coordinate have?

c) Based on your frequency analysis for a two-dimensional potential energy surface, propose a definition for a transition state on a multi-dimensional potential energy surface. *Hint: What are the properties of a stable point on a potential energy surface to be a transition state?*

■

Exercise 2.12

a) How does the vibrational frequency of a chemical bond relate to the strength of that chemical bond?

b) Would the frequency corresponding to a vibration in the direction of the reaction coordinate in the transition state be strong or weak? Relate your answer to the strength of a (to be formed / broken) bond in the transition state.

c) Assume that $k = \nu K$, where k is the rate constant according to transition state theory, ν is the frequency factor relating to crossing the transition state and K is the equilibrium constant between the initial state and the transition state. We are going to derive the frequency factor ν using a different assumption.

Assume that ν corresponds to the vibrational frequency in the direction of the reaction coordinate (note that the frequency factor ν and the vibrational frequency ω have the same dimensions!). Write down the expression for K in terms of the partition functions and separate the partition functions corresponding to motions that are perpendicular to the reaction coordinate from the single partition function corresponding to a motion in the direction of the reaction coordinate. Assume that the motion in the direction of the reaction coordinate is a loose vibration. Show that the answer is:

$$K = \frac{1}{1 - \exp\left(-\frac{h\omega}{k_b T}\right)} \cdot \frac{\prod_i f_i}{\prod_j f_j} \exp\left(-\frac{E_a}{k_b T}\right) \tag{2.160}$$

where f_i are the partition functions in the transition state and f_j are the partition functions in the initial state.

d) Assume that the frequency in the direction of the reaction coordinate is weak and that $\frac{h\omega}{k_b T} \ll 1$. Use a Taylor series (see Appendix section B.3) that is terminated after the linear term in x to rewrite the expression for the partition function of the loose vibration. Show that the answer is:

$$\frac{k_b T}{h\omega} \tag{2.161}$$

e) Plug the results you have obtained for K in the expression for k and assume that $\omega = \nu$. Show that you get the correct expression for the rate constant in transition state theory. Explain the difference between this derivation of the rate constant in transition state theory and the derivation earlier in the chapter. What is the similarity between a loose vibration and a translation?

■

2.12 Challenges

Challenges are relatively difficult topics aimed towards a more fundamental understanding of the theory. We suggest to tackle these challenges within a group. It is advisable to make use of a laptop as typically the use of Spreadsheet software such as Excel or a programming environment such as Python is recommended.

Challenge 2.1 | Maxwell-Boltzmann distribution

In this challenge, we are going to explore the Maxwell-Boltzmann distribution in greater detail by considering a relatively simple example. Consider an ensemble of **5 particles** among which you can distribute **6 units of energy**. There are a number of ways that 6 units of energy can be distributed over these 5 particles, which we are going to explore in this challenge. One way to distribute 6 units of energy among 5 particles is by placing all 6 energy units into a single particle and leaving the other four particles in the ground state. This can be done for each of the 5 particles, hence there are 5 ways of doing this.

To make this exercise a bit more tangible, we will differentiate between macrostates and microstates. We define a macrostate by only stating the number of particles in each energy level. Placing all 6 energy units into a single particle and leaving the other four in the ground state is in this terminology termed as a macrostate. Exactly which particle is excited and which are left in the ground state is in turn termed as a microstate. One way to look at this differentiation is by considering whether or not we treat the particles as distinguishable.[9] If the particle are indistinguishable, then we could only differentiate between the macrostates, but once we consider particles to be distinguishable, we can differentiate between many more states. Those additional states are termed microstates and each microstate can be categorized as a representation of a particular macrostate.

The description above is schematically represented in Figure 2.5. In this Figure, three macrostates and their corresponding number of microstates are given.

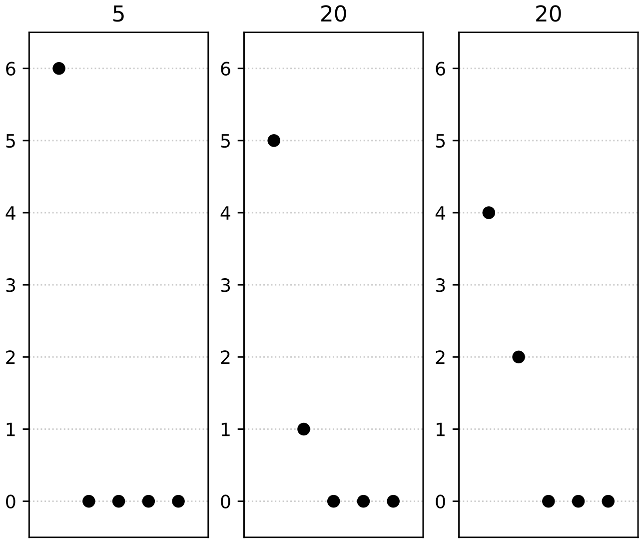

Figure 2.5: *Schematic depiction of the first three macrostates for distributing 6 units of energy over 5 particles. Above each subfigure is the number of microstates for that particular macrostate given.*

Within a Maxwell-Boltzmann distribution, all particles are distinguishable from each other. Hence, for the first macrostate as shown in Figure 2.5, there are 5 microstates. For the second and third macrostate, there are 20 microstates.

a) Show that the number of microstates for each macrostate is given by

$$\Omega_i = \frac{N!}{\prod_i n_i!}, \tag{2.162}$$

---

[9] Recall that within a Maxwell-Boltzmann distribution, particles are considered to be distinguishable.

where N is the total number of particles and n_i is the number of particles in energy level i. You only need to show that this formula is correct for the first three macrostates. You are not expected to derive this formula (although of course extra credits if you are able to do so).

b) Find the other macrostates (there are 10 in total) and show that the total number of microstates of all macrostates amounts to 210. You can identify the remaining macrostates by using the same schemes as shown in Figure 2.5, but another way of classifying them is by making ”sumrows”. A sumrow is constructed using a set of numbers which are added together to create the sum. In our case, the sum is always equals 6 and you can only use in total 5 digits. To exemplify this, the macrostates as shown in Figure 2.5 are the following sumrows:

(a) 6+0+0+0+0
(b) 5+1+0+0+0
(c) 4+2+0+0+0

Choose the method of your preference and show all 10 macrostates and calculate their corresponding number of microstates.

c) Show that the total number of microstates for distributing q levels of energy over N particles is given by

$$\Omega(N, q) = \binom{q + N - 1}{q} = \frac{(q + N - 1)!}{q!\,(N - 1)!}. \tag{2.163}$$

Again, you only have to show that equation 2.163 is valid for this example.

d) Calculate the average number of particles in each energy level using the following formula

$$n_j = \sum_i \frac{\Omega_i}{\Omega} n_{i,j}, \tag{2.164}$$

where Ω_i is the number of microstates in macrostate i, Ω is the total number of microstates and $n_{i,j}$ is the number of particles in energy level j in macrostate i. Plot this average number as a function of energy level i and determine the parameters A and c by fitting the following distribution function

$$n_i = A \cdot \exp\left(-c \cdot \epsilon_i\right). \tag{2.165}$$

Compare your distribution function with the Maxwell-Boltzmann distribution function. How well does the distribution function you constructed deviate from the exact Maxwell-Boltzmann distribution function? For example, you can calculate the R^2 of your fit, but a visual inspection is sufficient. Why does your distribution deviate from the exact result?

e) Use the equation you have obtained to calculate the temperature of this ensemble given that the energy levels are separated by 10 kJ/mol.

■

CHAPTER 3

ELEMENTARY REACTION STEPS

Contents

3.1 Introduction

In the previous chapter, we covered on the theory behind elementary reaction rates and the rate laws describing these. Moreover, we derived on the basis of statistical thermodynamics the general expression for an elementary reaction step:

$$\boxed{k = \frac{k_B T}{h} \frac{f_{\mathrm{TS}}^{\ddagger}}{f_{\mathrm{IS}}} \exp\left(\frac{-\Delta\epsilon_0}{k_B T}\right).} \tag{3.1}$$

To calculate the reaction rate constant, we need to plug in the partition functions corresponding to the degrees of freedom of the initial and transition state. For convenience, we repeat the formulas for the rotational, vibrational and translational partition functions in Table 3.1.

In this chapter we will extend on this theory and apply it to specific examples such as adsorption, desorption and surface reactions.

Table 3.1: *Formulas for the translational, vibrational and rotational partition functions. Note that the vibrational partition function is given with respect to the zero-point energy.*

Partition function	**Formula**
Translational (1D)	$\frac{L\sqrt{2\pi m k_b T}}{h}$
Vibrational	$\frac{1}{1-e^{-\Theta_i/T}}$
Rotational (diatomic)	$\frac{8\pi^2 I k_b T}{h^2}$
Rotational (polyatomic)	$\left(\frac{k_b T}{hc}\right)^{3/2} \sqrt{\frac{\pi}{I_A I_B I_C}}$

3.2 Adsorption

When a molecule absorbs from the gas phase to a (catalytic) surface, it undergoes a appreciable change in entropy, which is represented in formula 3.1 by the partition functions. In the gas phase, any non-linear molecule possesses three translational degrees of freedom as well as three rotational degrees of freedom. All other degrees of freedom correspond to internal vibrations. However, when the molecule absorbs, it loses several degrees of motional freedom. In general, upon (chemical) adsorption, the molecule no longer has any translational or rotational degrees of freedom and only vibrational degrees of freedom.

In the transition state, between the gaseous and absorbed state, the molecule has some number of motional degrees of freedom left, and with respect to transition state theory, the change in the degrees of freedom between initial and transition state can be correlated to the reaction rate. To exemplify this with respect to equation 3.1, we will denote the number of degrees of freedom of any specific type (either rotational, translational or vibrational) by a number written between round braces in superscript:

$$k = \frac{k_b T}{h} \frac{f_{\text{trans}}^{\ddagger(2)} f_{\text{rot}}^{\ddagger(3)} f_{\text{vib}}^{\ddagger(3N-6)}}{f_{\text{trans}}^{(3)} f_{\text{rot}}^{(3)} f_{\text{vib}}^{(3N-6)}} \tag{3.2}$$

The above formula represents non-activated adsorption, i.e. its activation energy $\epsilon_0 = 0$. Note that therefore the exponential term of equation 3.1 has dropped out as the exponent of zero gives unity. Furthermore, within this equation, it can be seen that the transition state (the nominator) has two degrees of translational freedom, three rotational degrees of freedom and otherwise $3N - 5$ vibrational degrees of freedom. As discussed in the previous section, one of the partition functions corresponding to an imaginary frequency in the direction of the reaction coordinate has been dropped out, resulting in a total number of partition functions of $3N - 1$ for the transition state.

In contrast, the initial state (the denominator) represent the molecule in the gas phase, which contains three rotational and three translational degrees of freedom as denoted by the number between round braces. Furthermore, all other $3N - 6$ degrees of freedom are vibrational. In other words, the molecule loses one translational degree of freedom from migrating from the gas phase to the surface.

From the above assumptions, we can derive a general rate of adsorption, which is known in Literature as Hertz-Knudsen adsorption. If we substitute the terms for the partition functions by their respective formulas, as given in Table 3.1 and furthermore assume that (1) the vibrational partition functions can be neglected as they approximate unity under typical reaction conditions and (2) there is no appreciable change in the rotational partition functions upon adsorption, we obtain the following formula:

$$k_{\text{ads}} = \frac{k_b T}{h} \frac{L^2 \left(2\pi m k_b T\right) h^3}{L^3 \left(2\pi m k_b T\right)^{\frac{3}{2}} h^2} \tag{3.3}$$

Rearrangements and cancellation of terms yields:

$$k_{\text{ads}} = \frac{k_b T}{L\sqrt{2\pi m k_b T}} \tag{3.4}$$

Finally, assuming the ideal gas law

$$P = \frac{k_b T}{V} \tag{3.5}$$

and noting that

$$A = \frac{V}{L} \tag{3.6}$$

$$\boxed{k_{\text{ads}} = \frac{PA}{\sqrt{2\pi m k_b T}}} \tag{3.7}$$

In the above equation, P denotes the partial pressure of the molecule in the gas phase and A denotes the area of the surface site on which the molecule absorbs.

Recall that the equation is valid only when the underlying assumptions are valid:

1. The transition state is a loose transition state in which the molecule still has several translational degrees and rotational degrees of freedom left
2. The molecule loses only one translational degree of freedom between initial and transition state
3. The ideal gas law is assumed to be valid
4. The rotational degrees of freedom do not change appreciable upon adsorption
5. The vibrational degrees of freedom can be neglected as they approximate unity upon this temperature

Although quite some assumptions are used (on top of the assumptions already made in the derivation of transition state theory!), nevertheless, from lots of experimental results it was found that the above equation holds. However, it can be the case that the kind of adsorption you are studying might very well go through an activated state or has a greater loss in degrees of freedom between initial and final. If that is the case, than you will have to re-derive equation 3.1 using the right partition functions and energies corresponding to your particular problem.

3.3 Desorption

Desorption is the opposite of adsorption: a bound compound leaves the catalytic surface and goes to the gas phase. In the previous section we considered that in the transition state, the compound had three rotational degrees of freedom, two translational degrees of freedom and $3N - 6$ vibrational degrees of freedom. Furthermore, we assume that in the initial state (the fully absorbed state), the compound only contains vibrational degrees of freedom. This gives us the following expression for the reaction rate:

$$k = \frac{k_b T}{h} \frac{f_{\text{trans}}^{\ddagger(2)} f_{\text{rot}}^{\ddagger(3)} f_{\text{vib}}^{\ddagger(3N-6)}}{f_{\text{vib}}^{(3N)}} \exp\left(\frac{-E_{\text{des}}}{k_b T}\right) \tag{3.8}$$

We can work this out by plugging in the formulas for the partition functions and assuming that the vibrational partition functions approximate unity.

$$k = \frac{k_b T}{h} \frac{A\left(2\pi m k_b T\right)}{h^2} \frac{8\pi^2 I k_b T}{\sigma h^2} \exp\left(\frac{-E_{\text{des}}}{k_b T}\right) \tag{3.9}$$

After reduction of the above equation by noting that we can express the term $\frac{h^2}{8\pi^2 I k_b}$ as a temperature, known as the characteristic temperature for rotation. After plugging this value in and combining similar terms, this yields:

$$\boxed{k = \frac{k_b T^3}{h^3} \frac{A\left(2\pi m k_b\right)}{\sigma \theta_{\text{rot}}} \exp\left(\frac{-E_{\text{des}}}{k_b T}\right)} \tag{3.10}$$

Note that in the above derivation, we have introduced the symmetry number σ, which represents the number of indistinguishable orientations of the particular molecule as a result of rotation. [10] For diatomic molecules, it is easily seen that the symmetry value is either two (when the atoms are identical) or one (when the atoms are different). However, if we are dealing with a rotational partition function of a polyatomic molecule, the symmetry factor can be larger than two.

The symmetry number for a particular compound can be easily derived from group theory. Once the point group of the complex is known, the symmetry number equals the sum of the different rotational symmetry operators.[11] To exemplify this: Ammonia belongs to the C_{3v} point group, which has one E and two C_3 symmetry operations. As such, the symmetry number for ammonia is 3. Likewise, benzene belongs to the D_{6h} symmetry group, which has one E, two C_6, two C_3 and seven C_2 rotational axes. This yields a symmetry number of 12 for benzene.

3.4 Surface reactions

Complexes absorbed on a catalytic surface typically only have vibrational degrees of freedom, as such, for reactions on a surface the pre-exponential factor is mainly governed by the $\frac{k_b T}{h}$ term in eq. 3.1. This term is roughly in the order of 10^{13}.

Surface reactions are activated, i.e. they proceed through an transition state. The difference between initial and final state is known as the activation energy or reaction barrier. With reference to the partition functions as given in Table 3.1 on page 76, the reaction barrier is equal to the difference in the electronic energy **corrected for the zero point energy**.

$$\Delta E_a = \Delta\epsilon_{\text{elec}} + \Delta\epsilon_{\text{zpe}} \tag{3.11}$$

Although for many reactions the zero point energy corrections tend to be in the order of 1-5 kJ/mol in comparison to electronic energies of roughly 30-100 kJ/mol and therefore negligible, they become especially important when dealing with (de-)hydrogenation reactions and can no longer be neglected.

If we can neglect the contribution of the vibrational partition function, the equation for a surface reaction becomes

$$\boxed{k = \frac{k_b T}{h} \exp\left(\frac{-E_{\text{a}}}{k_b T}\right)} \tag{3.12}$$

3.5 Hindered rotors

In the previous chapter we stated that normally complexes absorbed on a surface only have vibrational degrees of freedom. This is not always true. A well-known circumstance when we can no longer model the motional degrees of freedom for strongly absorbed complexes as vibrations is when they contain one or more rigid rotors. One can imagine a rigid rotor as a non-free rotation, such as is the case for a methyl (CH_3) or ammonia (NH_3) absorbed on the surface. Another example is when the molecule contains free methyl groups, which have no interaction with other complexes or with the catalytic surface.

Although it is not possible to give a (general) closed-form expression of the partition function, it is relatively easy to calculate the partition function either using a classical or a quantum mechanical approximation.[12] The latter is beyond the scope of this book, but we wish to give a couple of examples using the classical approximation.

Assume we have a NH_3 group absorbed on a catalytic surface in such a way that the rotation is parallel to the surface, then we can imagine that this rotation is hindered. The complex has a higher energy when the hydrogen atoms lie above the bonds between the metal atoms as when the hydrogen atoms lie in between the bonds. Furthermore, the energetic barrier for rotation is very low.

We will describe such a system using a Lagrangian:

$$L = T - V \tag{3.13}$$

note that we assume that $V \approx 0$ and that we can express T as the kinetic energy for rotation

$$T = \frac{1}{2} I\omega^2 = \frac{1}{2}\sum_i m_i R_i^2 \dot{\varphi}^2 \tag{3.14}$$

where I is the rotational moment of inertia and φ the angular velocity.

The partition function for this Lagrangian system is given by

$$f = \frac{1}{h}\int_0^{2\pi} \mathrm{d}\varphi \int_{-\infty}^{\infty} \mathrm{d}\gamma \exp\left(\frac{-E(\gamma)}{k_b T}\right) \tag{3.15}$$

where φ is the angle (and therefore represents position) and γ is the momentum. Note that E depends on the momentum, but not on the position of the atoms in the system.

We can derive an expression for γ by noting that

$$\gamma = \frac{\partial L}{\partial \dot{\varphi}} = I\varphi \tag{3.16}$$

Plugging the expression for γ into the expression for the kinetic energy gives

$$E = \frac{\gamma^2}{2I} \tag{3.17}$$

Using the expression for $E(\gamma)$, we can calculate the partition functions by means of equation 3.15, obtaining:

$$\boxed{f_{\text{hind. rot}} = \frac{2\pi}{h}\sqrt{2\pi I k_b T}} \tag{3.18}$$

In the beginning of this subsection, we considered the ammonia molecule as a hindered rotor. The rotational moment of inertia of this molecule is equal to

$$I_{\text{NH}_3} = 3 m_H R^2 \tag{3.19}$$

where m_H is the mass of a hydrogen atom and R the length of a N-H bond. Plugging this expression into equation 3.18 gives

$$f_{\text{hind. rot}} = \frac{(2\pi)^{\frac{3}{2}} R}{h}\sqrt{3 k_b m_H T} \tag{3.20}$$

3.6 Final remarks

The previous sections showed explicit formulas for adsorption, desorption and surface reactions. In principle, you can use these formulas to study describe the majority of the systems out there.

However, we are sometimes interested in that particularly peculiar system, wherein none of the above expressions are valid. In such a case, one has to start re-deriving the expression for the reaction rate by first inventorying the applicable partition function, plugging these into the general rate expression and finally deriving the reaction rate.

In the end, this chapter has shown you how to set up reaction rates. In the upcoming chapter we will show that the sum of all these elementary reaction steps is the basis of a microkinetic model which can be used to study the behavior of a chemical system.

3.7 Questions and Exercises

The answers to the questions and exercises are given at the end of this book in Appendix C (page 135).

3.7.1 Questions

1. What is the difference between a rotational degree of freedom and a hindered rotor? What are the similarities?
2. The zero point energy originates from the occupancy of the ground state of a vibration. When is this zero point energy correction more significant, for atoms with a low mass or with a high mass? Explain your reasoning.

3.7.2 Exercises

The exercises are marked by a number of gears to indicate their difficulty levels.

Exercise 3.1 ⚙

a) Calculate the rate constant for CO dissociation in the forward and the backward direction using appropriate assumptions regarding the nature of the partition functions. Take a forward barrier of ΔE_f = 80 kJ/mol and a backward barrier of ΔE_b = 120 kJ/mol. Use a temperature of 500K.

b) Calculate the rate constant for CO desorption. Use equation 3.10. For the surface area of the adsorption site, assume that CO is adsorbed on a threefold site of an FCC Rh lattice. The Rh-Rh distance is 2.71 Å. Use a *rotational* temperature (θ) of 2.8K, a desorption energy of 120 kJ/mol and a temperature of 500K.

c) Calculate the rate constant for CO adsorption. Assume that the partial pressure of CO is 20 bar. Use the same surface area as you used for the calculation of the desorption rate constant.

d) Why is the rate constant for desorption higher than for adsorption?

■

Exercise 3.2 ⚙

a) Calculate the forward rate constant of CH_2 hydrogenation to CH_3. Assume that CH_3 has one hindered rotor in the transition state and that all other configurational degrees of freedom are vibrational. Use an activation energy of 50 kJ/mol. Use a C-H bond length of 1.2 Å and a temperature of 500K.

b) Calculate the apparent activation energy of this elementary reaction step using the following expression: $E_a = RT^2 \frac{\partial \ln k}{\partial T}$. By what amount is the apparent activation energy higher than the electronic activation energy?

■

CHAPTER 4

MICROKINETIC MODELING

Contents

4.1 Introduction

In chapter 2, we explained how a system containing different chemical compounds can be described by only a very small number of macroscopic parameters, such as temperature, pressure and concentration. At the end of that chapter, we introduced transition state theory by which we are able to derive the Eyring equation which expresses the rate of interchange between the chemical compounds once the activation energy and the partition functions are known. In chapter 3, we provided a couple of examples of the rate of change for particular types of elementary reaction steps.

Within this chapter, we will show how to connect multiple elementary reaction steps together to set up a microkinetic model from scratch. We show how to construct the fundamental set of ordinary differential equations describing the system and how this set can be time-integrated using the appropriate boundary conditions and initial values. Finally, we show what observables one can derive from a microkinetic model and to which experimental data these observables can be related.

4.2 Microkinetic modeling of a simple catalytic reaction

Within this section, we will show how to set up a microkinetic model by providing a simple example of a catalytic reaction. For the moment, we will stick to unimolecular elementary reaction steps to keep things simple. More elaborate chemical systems will be shown further on in this chapter. The best way to understand how microkinetic simulations work is by constructing a microkinetic simulation by yourself. For this purpose, we have constructed a small set of Python scripts by which we will slowly introduce the methodology to you. These Python scripts are by no means the most efficient way to construct or perform a microkinetic simulation, but it serves as a handy tool to learn the principles behind such simulations.[1] The reader is encouraged to download the Python scripts and use these while reading this chapter. Look out for the QR codes with the download links in this chapter. We recommend running the scripts in a Python IDE such as Spyder.[2]

The steps we need to take to construct a microkinetic model are as follows:

1. Construct the set of elementary reaction steps.
2. Derive rate expressions for each of the elementary reaction steps.
3. Convert the set of rate expressions to a set of ordinary differential equations.
4. Define boundary conditions for the system (e.g. partial pressures), the initial values (e.g. initial surface concentrations) and any model parameters (e.g. temperature).
5. Solve the system of ordinary differential equations.
6. Interpret the results (using our chemical intuition).

4.2.1 Unimolecular catalytic reaction

A unimolecular reaction on a catalytic surface is given by the kinetic network below. In this network, A adsorbs on the catalytic surface, is then converted to B and finally B desorbs from the surface.

$$\mathrm{A} \longrightarrow \mathrm{A}* \longrightarrow \mathrm{B}* \longrightarrow \mathrm{B}. \tag{4.1}$$

The overall reaction for this chemokinetic network is

$$\mathrm{A} \longrightarrow \mathrm{B}, \tag{4.2}$$

which is composed of the following three elementary reaction steps

$$\mathrm{A} + * \leftrightarrows \mathrm{A}* \tag{4.3}$$

$$\mathrm{B} + * \leftrightarrows \mathrm{B}* \tag{4.4}$$

$$\mathrm{A}* \leftrightarrows \mathrm{B}*\,. \tag{4.5}$$

The above system has two adsorption-desorption steps and one surface step. We will express the rates for adsorption-desorption steps by using Hertz-Knudsen kinetics (see equations 3.7 and 3.10 on pages 77 and 78, respectively). Furthermore, we will use the assumptions as discussed in section 3.4 on page 78 for the surface reactions. The parameters for the adsorption and desorption steps are given in Tables 4.1 and 4.2, respectively.

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[1] In the next Chapter, the program MKMCXX will be introduced. This program is highly optimized to perform microkinetic simulations.

[2] More information about Spyder is found in this link: `https://www.spyder-ide.org/`

Table 4.1: *Kinetic parameters for the adsorption and desorption steps of A and B in the unimolecular reaction.*

Compound	A [m^2]	m (a.u.)	σ [-]	θ_{rot} [K]	E_{des} [kJ/mol]
A	$1 \cdot 10^{-20}$	1	1	1	120
B	$1 \cdot 10^{-20}$	1	1	1	220

Table 4.2: *Kinetic parameters for the conversion of A to B over the catalytic surface in the unimolecular reaction.*

Reaction	ν_f [s^{-1}]	ν_b [s^{-1}]	E_a^f [kJ/mol]	E_a^b [kJ/mol]
$\text{A*} \longrightarrow \text{B*}$	10^{13}	10^{13}	50	150

Note from these two Tables that adsorbed B is significantly more stable than adsorbed A (120 versus 220 kJ/mol, respectively). Furthermore, the reaction on the surface from A to B has a relatively low activation barrier (50 kJ/mol), while the barrier for the reverse reaction is quite high (150 kJ/mol). On the basis of the fundamental equations and the data in Tables 4.1 and 4.2, we can construct the following three Python functions to calculate the reaction rate constants for adsorption, desorption and the surface reaction as shown in Listing 4.1.

The Python code to time-integrate the unimolecular reaction at a specific temperature can be found using the following link: `https://www.mkmcxx.nl/downloads/input/solve_mkm_ode_unimol.py`

The function `calc_k_arr` as shown in Listing 4.1 calculates the Arrhenius-type rate constant as given by equation 3.12 on page 79. The functions `calc_kads` and `calc_kdes` calculate the reaction rates for adsorption and desorption, respectively. These functions are based on equations 3.7 and 3.10 on pages 77 and 78, respectively. The input parameters and the units of the variables are explained in the comment section of the corresponding functions.

In order to set up a microkinetic model using the above-mentioned kinetic parameters, we have to specify initial values, boundary conditions and model parameters. These are as follows

- **Initial values**: The initial values are the initial surface concentrations at time $t = 0$. For our system, we will consider the initial surface concentrations of compound A and B at $t = 0$ to be $\theta_A = \theta_B = 0$. The fraction of empty surface sites will be set to $\theta_* = 1$.

- **Boundary conditions**: The partial pressure of A is set to $p_A = 1$ atm and the partial pressure of B is set to $p_B = 0$ atm. In other words, we operate the reaction at zero conversion. This choice deserves some additional explanation. Within our microkinetic simulation, we wish to study the behavior of our catalyst. We wish to compare our theoretical model with a so-called initial rate experiment, where the production rate is measured close around $X = 0$.[3] In this situation, the reactants have only barely settled on the catalytic surface and only the adsorbed species are in a steady state. To ensure zero conversion, we keep the partial pressures in the gas phase fixed. Nevertheless, if one is interested in the solution at any non-zero conversion, it is easy to modify these settings by simply changing the gas phase pressures.

- **Model parameters**: As all rate expressions explicitly depend on the temperature, we also have to set the temperature as a model parameter. Typically, this is the only

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[3] This is often termed as that one operates the reaction at **differential conditions**.

Listing 4.1: *Python functions to calculate the reaction rate constants.*

```python
def calc_k_arr(T, nu, Eact):
    """
    Calculate reaction rate constant for a surface reaction

    T       - Temperature in K
    nu      - Pre-exponential factor in s^-1
    Eact    - Activation energy in J/mol
    """
    R = 8.3144598 # gas constant
    return nu * np.exp(-Eact / (R * T))

def calc_kads(T, P, A, m):
    """
    Reaction rate constant for adsorption

    T           - Temperature in K
    P           - Pressure in Pa
    A           - Surface area in m^2
    m           - Mass of reactant in kg
    """
    kb = 1.38064852E-23 # boltzmann constant
    return P*A / np.sqrt(2 * np.pi * m * kb * T)

def calc_kdes(T, A, m, sigma, theta_rot, Edes):
    """
    Reaction rate constant for desorption

    T           - Temperature in K
    A           - Surface area in m^2
    m           - Mass of reactant in kg
    sigma       - Symmetry number
    theta_rot   - Rotational temperature in K
    Edes        - Desorption energy in J/mol
    """
    kb = 1.38064852e-23 # boltzmann constant
    h = 6.62607004e-34  # planck constant
    R = 8.3144598       # gas constant
    return kb * T**3 / h**3 * A * (2 * np.pi * m * kb) / \
        (sigma * theta_rot) * np.exp(-Edes / (R*T))
```

mandatory model parameter, although one could imagine that for more complex types of simulations other model parameters are required. For example, if one models an electrochemical reaction, one could consider the pH of the solution or the potential as model parameters.

Using the initial values, boundary conditions and model parameters, the system of ordinary differential equations is completely defined and can be time-integrated. In contrast with the types of equations we saw in Chapter 1, this set of equations can no longer be solved analytically[4] and we have to use a numerical method to integrate this system over time. This can be done using an ordinary differential equation solver (in short: ODE solver). In this chapter, we will be using the SciPy library that readily provides an ODE solver.[5]

The set of ordinary differential equations for this system to solve is given in equations 4.6 - 4.8. Please note that in these equations k_b refers to the reaction rate constant in the backward direction and not to the Boltzmann constant.

$$\frac{\partial \theta_{\mathrm{A}}}{\partial t} = k_{\mathrm{ads,A}} \cdot p_{\mathrm{A}} \cdot \theta_{*} - k_{\mathrm{des,A}} \cdot \theta_{\mathrm{A}} - k_f \cdot \theta_{\mathrm{A}} + k_b \cdot \theta_{\mathrm{B}} \tag{4.6}$$

$$\frac{\partial \theta_{\mathrm{B}}}{\partial t} = k_{\mathrm{ads,B}} \cdot p_{\mathrm{B}} \cdot \theta_{*} - k_{\mathrm{des,B}} \cdot \theta_{\mathrm{B}} + k_f \cdot \theta_{\mathrm{A}} - k_b \cdot \theta_{\mathrm{B}} \tag{4.7}$$

$$\frac{\partial \theta_{*}}{\partial t} = -k_{\mathrm{ads,A}} \cdot p_{\mathrm{A}} \cdot \theta_{*} + k_{\mathrm{des,A}} \cdot \theta_{\mathrm{A}} - k_{\mathrm{ads,B}} \cdot p_{\mathrm{B}} \cdot \theta_{*} + k_{\mathrm{des,B}} \cdot \theta_{\mathrm{B}} \tag{4.8}$$

Using this set of ordinary differential equations and the proper boundary conditions, we can readily construct our Python code to time-integrate our chemokinetic system. The code is provided in Listing 4.2. By plotting the return variables of `solve_odes(T)` we can obtain a graph. This is done in the `main()` function of the script as can be seen in Listing 4.3.

Listing 4.3: *Python functions to perform the time-integration of the set of ordinary differential equation.*

```python
def main():
    plt.figure()
    x,y = solve_odes(1200)
    labels = ['A','B','*']
    for i in range(0, len(labels)):
        plt.semilogx(x, y[:,i], label=labels[i])
    plt.legend()
    plt.show()
```

The ODE solver is constructed using a generic interface as explained in detail on its webpage.[6] First, we need to construct a function that takes as input the two parameters t (time) and y (surface concentrations). Optionally, a list of parameters can be provided. Here, we provide as additional parameters the boundary conditions, which are the partial pressures and the model parameters, which is the temperature. In `dydt(T, y, params)`, the first derivative of the surface concentrations is calculated and returned as a vector. The time-integration is performed in the function `solve_odes(T)`. Herein, an integration object is constructed and the function `dydt(T, y, params)` is passed as input. We use the `vode` keyword, which stands for *Real-valued Variable-coefficient Ordinary Differential Equation*. We set the absolute and relative tolerances (`atol` and `rtol`) to 10^{-8}. The maximum number of steps between two output time steps of the integrator object is set to 1000, although the default value for this variable would probably suffice. An important thing to remember about chemokinetic systems is that their underlying set of ordinary differential equations

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[4] Recall that for constructing an analytical expression, we require a series of assumptions.

[5] `https://docs.scipy.org/doc/scipy/reference/generated/scipy.integrate.ode.html`

[6] `https://docs.scipy.org/doc/scipy/reference/generated/scipy.integrate.ode.html`

Listing 4.2: *Python functions to perform the time-integration of the set of ordinary differential equation.*

```python
def solve_odes(T):
    # initial conditions
    y0 = [0,0,1]
    t0 = 0
    t1 = 1e-6   # total integration time
    T = 1200    # temperature in K
    pa = 1e5    # pressure of A in Pa
    pb = 0      # pressure of B in Pa

    # construct ODE solver
    r = ode(dydt).set_integrator('vode', method='bdf',
           atol=1e-8, rtol=1e-8, nsteps=1000, with\_jacobian=True)
    r.set_initial_value(y0, t0).set_f_params([T, pa, pb])

    # integrate on a logaritmic scale
    xx = np.linspace(-12.0, np.log10(t1), int((np.log10(t1) + 12.0) * 10))
    yy = []
    tt = []
    for x in xx:
        tnew = 10.0**x
        tt.append(tnew)
        yy.append(r.integrate(tnew))

    return tt, np.matrix(yy)

def dydt(t, y, params):
    """
    Set of ordinary differential equations
    """
    T =  params[0]
    pa = params[1]
    pb = params[2]

    dydt = np.zeros(3)

    ma = 1.66054e-27
    mb = 1.66054e-27

    k_ads_a = calc_kads(T, pa, 1e-20, ma)
    k_des_a = calc_kdes(T, 1e-20, ma, 1, 1, 120e3)

    k_ads_b = calc_kads(T, pb, 1e-20, mb)
    k_des_b = calc_kdes(T, 1e-20, mb, 1, 1, 220e3)

    kf = calc_k_arr(T, 1e13, 50e3)
    kb = calc_k_arr(T, 1e13, 150e3)

    dydt[0] = k_ads_a * y[2] - k_des_a * y[0] - kf * y[0] + kb * y[1]
    dydt[1] = k_ads_b * y[2] - k_des_b * y[1] + kf * y[0] - kb * y[1]
    dydt[2] = -k_ads_a * y[2] + k_des_a * y[0] - k_ads_b * y[2] + k_des_b * y[1]

    return dydt
```

is a so-called stiff system. Stiff systems require special integration methods, such as `bdf` which stands for *Backward Differentation Formulas*. The `bdf` is one of the best methods to solve such systems. The other important thing to take care of is to either explicitly specify to calculate the Jacobian using finite differences (`with_jacobian=true`) or to construct a Jacobian function yourself. Here, we have opted for using the finite difference method, as it is much easier to use. An explicit function to calculate the Jacobian is however computationally much faster and is the recommended procedure.[7]

We have chosen to perform our integration on a logarithmic scale. The main advantage of this procedure is that we get a fixed number of data points for every time scale, beginning at the smallest time scales (i.e. corresponding to the fastest reactions) and ending at the longest time-scales (i.e. the slowest reactions). The results would be exactly the same if a linear time scale is chosen, it is just a preference we like to employ.

Before we start performing the simulations and interpreting its output, we would like to repeat some nomenclature here. All possible sets of concentrations applicable to our system is termed the *phase space*. To exemplify this statement with respect to our system, the complete phase space is defined by:

$$\theta_A, \theta_B, \theta_* \in [0, 1] \tag{4.9}$$

under the constraint (remember that there is conservation of mass)

$$\theta_A + \theta_B + \theta_* = 1 \tag{4.10}$$

Furthermore, if our system has no peculiarities such as strong non-linear behavior or bifurcations (if you have never heard of these terms before, just ignore them), then our system will most likely converge to a steady state solution, which is defined as:

$$\frac{\partial \theta_i}{\partial t} = 0 \tag{4.11}$$

for all i, where i is each compound in the system.

Let us apply this newly learned nomenclature to our system which models a unimolecular reaction. In Figures 4.1a-4.1d, the transient behavior of our system (i.e., the *state* of our system as a function of time) has been studied at four different temperatures. In Figures 4.1a-4.1c, a similar final result is obtained, which is the catalytic surface fully covered with B. Note that in Figure 4.1a, the surface concentrations no longer changes at $t \geq 10$. Therefore, we can say that at $t \geq 10$ the system is at its steady-state solution.

From the other Figures (4.1b-4.1d), we can see that the steady state solution is reached at different time t given a different temperature. At higher temperatures, the steady state solution is obtained in a shorter amount of time. This can easily be explained due to the fact that all elementary reaction rates increase exponentially with increasing temperature. Therefore, our system converges to the steady-state solution faster at elevated temperatures.

One might wonder then as to why the system in 4.1d (i.e., at a significantly high temperature, does not converge to a similar-steady solution as the other Figures. In 4.1d, it is found that the steady state solution has a nearly empty catalytic surface. This has to do with the temperature dependence of the pre-exponential factors for adsorption and desorption. From equations 3.7 and 3.10 on pages 77 and 78, respectively, it can be seen that the rate for adsorption drops with $\sqrt{T}$, while the rate for desorption **increases** by T^3. As the latter becomes dominant at high temperature, at highly elevated temperatures the desorption term dominates resulting in a nearly empty surface.

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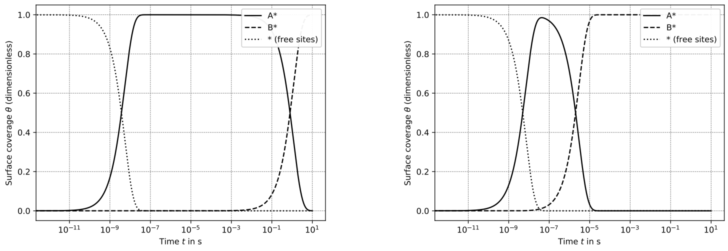
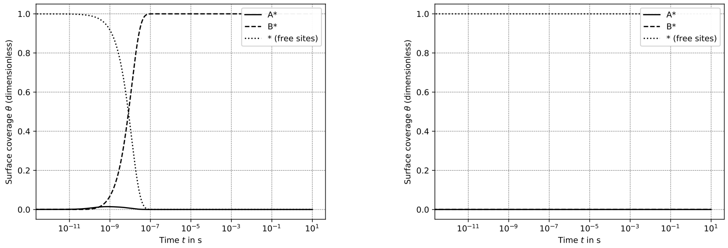
[7] Consult the web page of SciPy for more information how this is done.



(a) $T = 200K$. **(b)** $T = 350K$.



(c) $T = 800K$. **(d)** $T = 1500K$.

Figure 4.1: *Surface coverage as a function of time for the unimolecular catalytic surface reaction.*

In Figure 4.2, the consumption of A and the production of B are shown. Due to the strong difference in adsorption and desorption rates at different temperatures, a phenomenon similar to the is seen. The reasoning goes as follows: at very low temperature, all compounds adsorb easily on the surface, but due to the low temperature, there is not enough energy to overcome the reaction barrier and no products are formed. At too high temperature, the desorption rate is several orders of magnitude higher than the adsorption rate and almost no reagents are found on the surface. The kinetic energy of the gaseous species is too high, thus the molecules just ricochet off the surface. Due to the existence of these two competing effects, i.e. rate of dissociation versus surface coverage, the production of compound B with respect to temperature shows an optimum (at $T \approx 1175K$).

Finally, the uptake of compound A equals the production of compound B, as to be expected on the basis of the stoichiometry of the reaction and the inherent mass conservation of the method.

To summarize, we have shown that the overall (catalytic) unimolecular reaction is in fact a composition of three elementary reaction steps. By means of transition state theory, we are able to derive rate equations for these elementary reaction steps. The implementation of these rate equations reveal interesting transient phenomena and enable us to study the kinetic system as function of temperature. Despite that the unimolecular catalytic reaction is very illustrative, it lacks the details of a more realistic overall reaction. As such, we are going to describe a catalytic bimolecular reaction.

4.2.2 Bimolecular catalytic reaction

A typical bimolecular reaction in catalysis is the oxidation of CO to CO_2. This particular system is relevant to car-exhaust gas clean-up. The overall reaction is

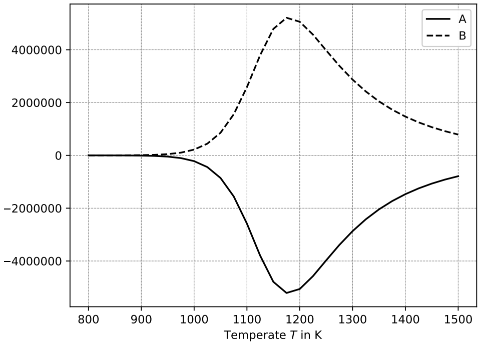


Figure 4.2: *Production rates of compounds A and B as a function of temperature.*

$$2\mathrm{CO} + \mathrm{O}_2 \rightarrow 2\mathrm{CO}_2 \tag{4.12}$$

and constitutes the following elementary reaction steps

$$\mathrm{CO} + * \leftrightarrows \mathrm{CO}* \tag{4.13}$$
$$\mathrm{O}_2 + 2* \leftrightarrows 2\mathrm{O}* \tag{4.14}$$
$$\mathrm{CO} * + \mathrm{O}* \leftrightarrows \mathrm{CO}_2 * + * \tag{4.15}$$
$$\mathrm{CO}_2 + * \leftrightarrows \mathrm{CO}_2* \tag{4.16}$$

These elementary reaction steps lead to the following set of ordinary differential equations

$$\frac{\partial \theta_{\mathrm{CO}}}{\partial t} = k_{1,\mathrm{ads}}\theta_* - k_{1,\mathrm{des}}\theta_{\mathrm{CO}} - k_{3,f}\theta_{\mathrm{CO}}\theta_{\mathrm{O}} + k_{3,b}\theta_{\mathrm{CO}_2}\theta_* \tag{4.17}$$
$$\frac{\partial \theta_{\mathrm{O}}}{\partial t} = 2k_{2,\mathrm{ads}}\theta_*^2 - 2k_{2,\mathrm{des}}\theta_{\mathrm{O}}^2 - k_{3,f}\theta_{\mathrm{CO}}\theta_{\mathrm{O}} + k_{3,b}\theta_{\mathrm{CO}_2}\theta_* \tag{4.18}$$
$$\frac{\partial \theta_{\mathrm{CO}_2}}{\partial t} = k_{4,\mathrm{ads}}\theta_* - k_{4,\mathrm{des}}\theta_{\mathrm{CO}_2} + k_{3,f}\theta_{\mathrm{CO}}\theta_{\mathrm{O}} - k_{3,b}\theta_{\mathrm{CO}_2}\theta_* \tag{4.19}$$
$$\begin{aligned}\frac{\partial \theta_*}{\partial t} &= -k_{1,\mathrm{ads}}\theta_* + k_{1,\mathrm{des}}\theta_{\mathrm{CO}} - 2k_{2,\mathrm{ads}}\theta_*^2 + 2k_{2,\mathrm{des}}\theta_{\mathrm{O}}^2 \\ &+ k_{3,f}\theta_{\mathrm{CO}}\theta_{\mathrm{O}} - k_{3,b}\theta_{\mathrm{CO}_2}\theta_* - k_{4,\mathrm{ads}}\theta_* + k_{4,\mathrm{des}}\theta_{\mathrm{CO}_2}\end{aligned} \tag{4.20}$$

This reaction is bimolecular in the sense that adsorbed CO needs to recombine with adsorbed O in order to form CO_2. The numerical values for the relevant rate expressions are given in tables 4.3 and 4.4.

The Python code to simulate CO oxidation as a function of temperature can be found using this link: `https://www.mkmcxx.nl/downloads/input/solve_mkm_ode_bimol.py`

Combining the data in Tables 4.3 and 4.4 and the set of ordinary differential equations leads to the Python code as shown in Listing 4.4. Note that we have introduced two auxiliary

Listing 4.4: *Python functions to construct the first derivative towards time of the surface concentrations. Note that we have introduced a set of auxiliary variables (i.e. r1f - r4b) to capture similar terms for the reaction rates.*

```python
def dydt(t, y, params):
    """
    Set of ordinary differential equations
    """
    T =  params[0]
    pa = params[1]
    pb = params[2]
    pc = params[3]

    dydt = np.zeros(4)

    ma = 28 * 1.66054e-27
    mb = 32 * 1.66054e-27
    mc = 80 * 1.66054e-27

    # calculate all reaction rate constants
    k_ads_1 = calc_kads(T, pa, 1e-20, ma)
    k_des_1 = calc_kdes(T, 1e-20, ma, 1, 2.8, 80e3)
    k_ads_2 = calc_kads(T, pb, 1e-20, mb)
    k_des_2 = calc_kdes(T, 1e-20, mb, 2, 2.08, 40e3)
    kf = calc_k_arr(T, 1e13, 120e3)
    kb = calc_k_arr(T, 1e13,  80e3)
    k_ads_4 = calc_kads(T, pc, 1e-20, mc)
    k_des_4 = calc_kdes(T, 1e-20, mc, 1, 0.561, 10e3)

    # collect similar terms in new variables
    r1f = k_ads_1 * y[3]
    r1b = k_des_1 * y[0]
    r2f = k_ads_2 * y[3]
    r2b = k_des_2 * y[1]**2
    r3f = kf * y[0] * y[1]
    r3b = kb * y[2] * y[3]
    r4f = k_ads_4 * y[3]
    r4b = k_des_4 * y[2]

    dydt[0] = r1f - r1b - r3f + r3b
    dydt[1] = 2.0 * r2f - 2.0 * r2b - r3f + r3b
    dydt[2] = r3f - r3b + r4f - r4b
    dydt[3] = -r1f + r1b - 2.0 * r2f + 2.0 * r2b + r3f - r3b - r4f + r4b

    return dydt
```

Table 4.3: *Parameters for the adsorption and desorption steps in CO oxidation. Note that the values used here are not necessarily representative for the actual process.*

Compound	A [m^2]	m (a.u.)	σ [-]	θ_{rot} [K]	E_{ads} [kJ/mol]
CO	$1 \cdot 10^{-20}$	28	1	2.8	80
O_2	$1 \cdot 10^{-20}$	32	2	2.08	40
CO_2	$1 \cdot 10^{-20}$	80	1	0.561	10

Table 4.4: *Parameters for the surface reaction of CO oxidation. Note that the values used here are not necessarily representative for the actual process.*

Reaction	ν_f[s^{-1}]	ν_b[s^{-1}]	E_a^f[kJ/mol]	E_a^b[kJ/mol]
$CO^* + O^* \longrightarrow CO_2{}^* + {}^*$	10^{13}	10^{13}	120	180

variables for each elementary reaction step to efficiently collect terms and calculate the first derivatives with respect to time.

For the boundary conditions, we have used the stoichiometric ratio of 1:2 for the partial pressure of O_2 and CO and set the total pressure to 20 atm.

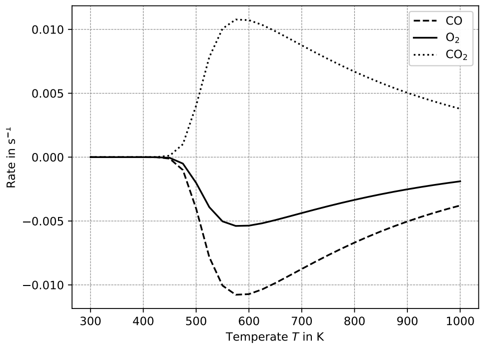


Figure 4.3: *Production rate of* CO_2 *and consumption rates of* CO *and* O_2 *as a function of temperature.*

The result for this simulation is given in Figure 4.3. From this Figure, we can see that the uptake of CO is the same as the production of CO_2, whereas the uptake of O_2 is half the uptake of CO. This shows that this reaction proceeds according to the stoichiometry, as was to be expected. Again, we note that there is an optimum in the production as a function of temperature. Similarly to the unimolecular reaction, this relates to the Sabatier's principle. If the temperature is too low, no coupling between CO and O will occur, if the temperature is too high, CO and O_2 will no longer adsorb on the surface in order to react.

In Figure 4.4, the surface coverage as a function of temperature is shown. Here we can see that at low temperature, the surface is mainly covered by CO. This is evident from the relatively strong adsorption energy of CO (80 kJ/mol). With increasing temperature, the surface coverage of CO decreases, whereas the number of free sites increases. This confirms our earlier reasoning regarding the optimal temperature for the reaction. If the temperature is too low, no reaction can occur between CO and O. In fact, the temperature is so low that CO poisons the surface (due to its high adsorption energy) by which the surface coverage of O is too low for an appreciable rate of coupling between CO and O to occur. With increasing temperature, the CO coverage decreases and consequently, the rate increases. At elevated

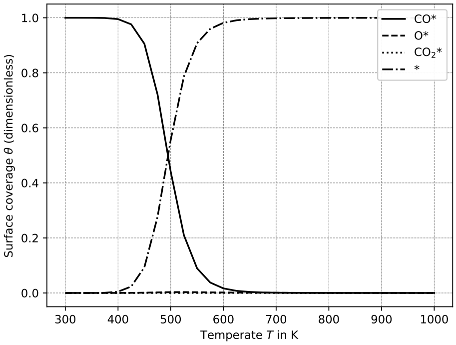


Figure 4.4: *Surface coverage as a function of temperature.*

temperatures, the CO coverage decreases even more and the surface becomes empty. At that point, the overall rate decreases again.

4.3 Reaction orders

In the previous section we mentioned that at low temperature, CO poisons the surface. Here, we will show another technique that confirms this fact. If CO indeed poisons the surface at low temperature, then we expect that the partial pressure of CO negatively influences the rate. A systematic way of investigating the influence of the reactants and the products on the reaction is by looking at the reaction order in these components. The reaction order is defined as follows (see also section 1.5.3 on page 22):

$$n_i = p_i \frac{\partial \ln r^+}{\partial p_i}, \tag{4.21}$$

where n_i is the reaction order in component i, r^+ is the rate in the forward direction (i.e. the rate corresponding to an initial rate experiment) and p_i the partial pressure of component i. The reaction orders are calculated using a linear fitting procedure. A short code snippet how this is done is shown in Listing 4.5. At the end of this chapter, we will also show that for some systems, an analytical expression can be derived.

The Python code to calculate the reaction order in CO at a specific temperature for the CO oxidation reaction can be found using this link: `https://www.mkmcxx.nl/downloads/input/solve_mkm_ode_calc_order.py`

In Listing 4.5, the numerical procedure to calculate the reaction order is shown. To calculate the derivative of the logarithm of the rate towards the partial pressure of CO, we calculate the rate at five different partial pressures of CO. These five partial pressures are generated by multiplying the coefficients 0.95, 0.98, 1.0, 1.02 and 1.05 with the partial pressure at the working we are interested in (in our example, this is 13.33 bar). The derivative is then calculated by performing a linear fit using the `polyfit` function. The order is finally calculated by multiplying the slope (as found in the linear fit) by the partial pressure. At $T = 800$ K, this gives a reaction order of about unity.

Listing 4.5: *Python functions to calculate the reaction order of CO at temperature T.*

```python
def main():
    """
    Calculate the reaction order in CO
    """
    T = 800 # temperature in K
    p,r = calc_order(T)
    m,b = np.polyfit(p, r, 1)
    plt.plot(p, r, 'o', label='Data points')
    plt.plot(p, m*p+b, '--', label='Linear fit')
    plt.legend()
    plt.xlabel('Pressure in Pa')
    plt.ylabel('log(rate)')
    plt.title('Reaction order CO = %f' % (m*p[2]))
    plt.show()

def calc_order(T):
    """
    Calculate reaction order at temperature T
    """
    pt = 20
    pa = 2.0/3.0 * pt * 1e5      # pressure of CO in Pa
    pb = 1.0/3.0 * pt * 1e5      # pressure of O2 in Pa
    pc = 0
    mc = 80 * 1.66054e-27

    # set series of factors to expend pressure in
    diffs = [0.95, 0.98, 1.0, 1.02, 1.05]
    rates = []
    for diff in diffs:
        x, y = solve_odes(T, pa * diff, pb, pc)
        r_co2 = calc_kdes(T, 1e-20, mc, 1, 0.561, 10e3) * y[-1,2]
        rates.append(r_co2)

    return np.multiply(diffs, pa), np.log(rates)
```

The reaction orders of CO and O_2 as function of temperature is found in Figure 4.5. From this Figure, we can see that at low temperature, the reaction order in CO is strongly negative. A value of -1 indicates that if we would double the partial pressure of CO, than the rate would decrease by a factor 2. With increasing temperature, we see that the reaction order in CO increases. This can be related to the surface coverage of CO. At sufficient temperature, CO no longer poisons the surface and a consequence, the reaction order increases to 0. Further increasing the temperature leads to a nearly empty surface. Such a surface is lacking in CO and increasing the partial pressure of CO would benefit the reaction rate. Thus, a positive reaction order is seen. In contrast, the reaction order in O_2 is nearly independent of temperature and has a constant value of 0.5. The value of 0.5 originates from the fact that O_2 dissociatively adsorbs on the surface. For the reaction to occur, only half a molecule of O_2 is needed. Thus doubling the partial pressure of O_2 only results in an increase of the overall reaction rate by a factor of $\sqrt{2}$.

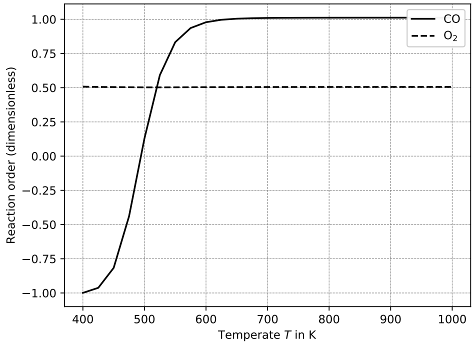


Figure 4.5: *Reaction orders in CO and* O_2 *as a function of temperature.*

Another way of looking at these reaction orders is from the perspective of a power law. Assume that we can model our reaction by the following expression

$$r = c p_{\mathrm{CO}}^{\nu_{\mathrm{CO}}} p_{\mathrm{O}_2}^{\nu_{\mathrm{O}_2}}, \tag{4.22}$$

then the reaction orders in CO and O_2 would match the exponents ν_i in this expression. Performing a series of experiments wherein the partial pressures of CO and O_2 followed by a fitting procedure would then provide the values for the variables in this equation. Important to realize is that the above expression is limited to a fairly small region in temperature as is evident from Figure 4.5. A significant variation of the temperature leads to a completely different value for the reaction order. Another way of looking at this is by saying that this approach is only valid locally. In contrast, constructing a microkinetic model provides the possibility of modeling a reaction over a very broad range of temperatures and pressures and is in a way a more global approach.

4.4 Apparent activation energy

Besides analyzing the dependence of the partial pressures of the reactants on the overall reaction rate by means of calculating the reaction orders, one can also investigate the influence of temperature on the activity by probing the apparent activation energy. The apparent activation energy is given by the following equation (see also section 1.5.4 on page 24):

$$\Delta E^{\text{app}}_{\text{act}} = RT^2 \frac{\partial \ln r^+}{\partial T}. \tag{4.23}$$

The procedure is very similar as to the one showed earlier for the calculation of the reaction orders. A linear fit is performed on the basis of equation 4.23 as shown in Listing 4.6. The only differences are that the coefficient interval is much smaller as the rate depends much stronger on the temperature as compared to the pressure and that we multiply the first derivative towards temperature by RT^2 to obtain an answer in units of energy.

Listing 4.6: *Python functions to calculate the apparent activation energy at temperature T.*

```python
def main():
    """
    Calculate the apparent activation energy
    """
    T = 500         # temperature in K
    R = 8.3144598   # gas constant

    p,r = calc_eapp(T)
    m,b = np.polyfit(p, r, 1)
    plt.plot(p, r, 'o', label='Data points')
    plt.plot(p, m*p+b, '--', label='Linear fit')
    plt.legend()
    plt.title('Eapp = %f kJ/mol' % (R*T**2*m/1e3))
    plt.xlabel('Temperature in K')
    plt.ylabel('log(rate)')
    plt.show()

def calc_eapp(T):
    """
    Calculate the apparent activation energy at temperature T
    """
    pt = 20
    pa = 2.0/3.0 * pt * 1e5      # pressure of CO in Pa
    pb = 1.0/3.0 * pt * 1e5      # pressure of O2 in Pa
    pc = 0
    mc = 80 * 1.66054e-27

    # set series of factors to expend pressure in
    diffs = [0.998, 0.999, 1.0, 1.001, 1.002]
    rates = []
    for diff in diffs:
        x, y = solve_odes(T * diff, pa, pb, pc)
        r_co2 = calc_kdes(T * diff, 1e-20, mc, 1, 0.561, 10e3) * y[-1,2]
        rates.append(r_co2)

    return np.multiply(diffs, T), np.log(rates)
```

The Python code to calculate the apparent activation energy at a specific temperature for the CO oxidation reaction can be found using this link: `https://www.mkmcxx.nl/downloads/input/solve_mkm_ode_calc_eact.py`

This derivative probes the effect on the overall rate as a result of a change in temperature. A positive value of the apparent activation energy indicates that the overall reaction rate increases when the temperature in increased. In contrast, a negative energy indicates that the overall reaction rate would be decreased as a result of a decrease in temperature. Consequently, if the apparent activation energy is zero, this means that the reaction is at an optimum with respect to temperature.

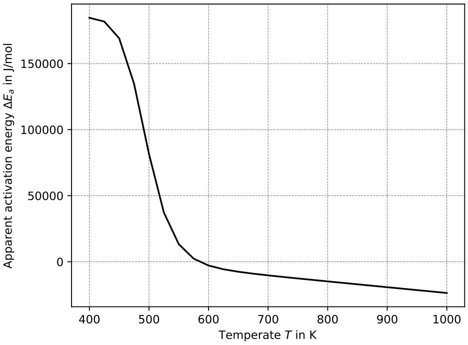


Figure 4.6: *Apparent activation energy as a function of temperature.*

In Figure 4.6, the apparent activation energy as a function of temperature is shown. From this Figure, it can be seen that at low temperature, the apparent activation energy is positive, whereas at high temperature, it is negative. This result can be directly interpreted in terms of the Sabatier's principle. At low temperature, the surface is partially blocked by CO (see Figure 4.4) and increasing the temperature results in more available sites by which the overall reaction rate can increase. In contrast, at high temperature the apparent activation energy is found to be negative. Here, lowering the temperature would result in more gaseous species to fixate on the surface. Thus, lowering the temperature would result in an increase of the overall reaction rate. Finally, around T=575K, the apparent activation energy is zero. Looking at Figure 4.3, we see that at this particular temperature, the overall reaction rate is at an optimum. This was to be expected, as finding the extremum of a function can be done by equating the first derivative of a function to zero.

Interestingly, a lot of chemical processes are run under certain conditions where the apparent activation energy is positive. Given the above explanation, one could reason that increasing the temperature would result in a higher activity and wonder why this is not done. The argument for not increasing the temperature is that the apparent activation energy only gives us an indication whether the overall reaction rate would increase or decrease with respect to temperature. It does not convey anything about the selectivity of the reaction. Typically, increasing the temperature of the reaction results in the production of unfavorable side products that eventually have to be removed from the production stream. As such, overall activity is rarely the most important criterion in deciding at which temperature the reaction should be operated.

The above discussion already shows that the rate r in equation 4.23 is not in a sense unique and has to be chosen with care. Rates are calculated with respect to a so-called key component. Here, we have always chosen the key component to be one of the reactants. This is of course a sensible choice, but if you are looking at a reaction wherein multiple products can be produced, it might be more sensible to pick one of these products that is of interest. Thus, the apparent activation energy is not some universal value for an overall reaction, but depends on the specific key component that has been chosen. As such, in the literature, the formula that is used to fit the apparent activation energy to the experiment is shown to make the matter clear. Often, the fitting of the apparent activation energy is combined with the fitting of the reaction orders and a formula such as the following is used:

$$r_j = \nu \exp\left(\frac{\Delta E_{\text{act}}^{\text{app}}}{RT}\right)\prod_i p_i^{\nu_i}, \tag{4.24}$$

where r_i is the rate of production or consumption of key component j, p_i is the partial pressure of reactant i, ν_i is the stoechiometric coefficient of reactant i, $E_{\text{act}}^{\text{app}}$ is the apparent activation energy and ν is a pre-exponential factor.

In the results as shown in Figure 4.6, we have chosen CO to be the key component. It should be clear though that, due to the stoichiometry, if we had chosen any other key component for our analysis, we would have obtained exactly the same result.

4.5 Degree of rate control

From the previous two sections, we have shown how to calculate the reaction orders and the apparent activation energy. Another step further is to investigate the effect of the reaction barrier of each of the elementary reaction steps on the overall reaction rate. To do this, we use the method of as introduced by Campbell and coworkers. Herein, a degree of rate control coefficient of a single elementary reaction step is defined as

$$\chi_i = \left(\frac{\partial \ln r}{\partial \ln k_i}\right)_{k_j \neq k_i, K_i}, \tag{4.25}$$

where χ_i is the degree of rate control coefficient, r the overall reaction rate, k_i the reaction rate constant for elementary reaction step i and K_i the equilibrium constant of elementary reaction step i as defined by

$$K_i = \frac{k_i^+}{k_i^-}. \tag{4.26}$$

Loosely speaking, the effect of lowering or increasing the reaction barrier of an elementary reaction step on the overall reaction rate is probed. Importantly, only the barrier is varied. All equilibrium constants including the reaction Gibbs free energy is kept constant. Schematically, this is depicted in Figure 4.7.

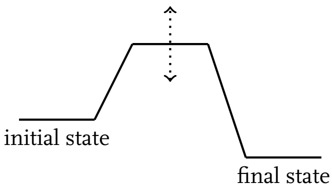


Figure 4.7: *Schematic representation of varying the reaction barrier of an elementary reaction step while keeping the Gibbs free energy of the reaction constant.*

A positive value of χ_i indicates that the elementary reaction step is rate-controlling. In other words, decreasing the reaction barrier for this elementary reaction step results in an increase of the overall reaction rate. In contrast, a negative value of χ_i means that the elementary reaction step is rate-inhibiting. Lowering the apparent activation energy then results in a decrease of the overall reaction rate. Finally, the sum of all DRC coefficients of all elementary reaction steps should be unity[8] as given by

$$\sum_i \chi_i = 1. \tag{4.27}$$

The DRC analysis for CO oxidation is given in Figure 4.8. From this Figure, we can see that independent of temperature, CO+O recombination on the catalytic surface is the rate-limiting step. This was to be expected as adsorption-desorption steps are rarely rate-limiting and this is the only elementary reaction step that occurs on the surface.

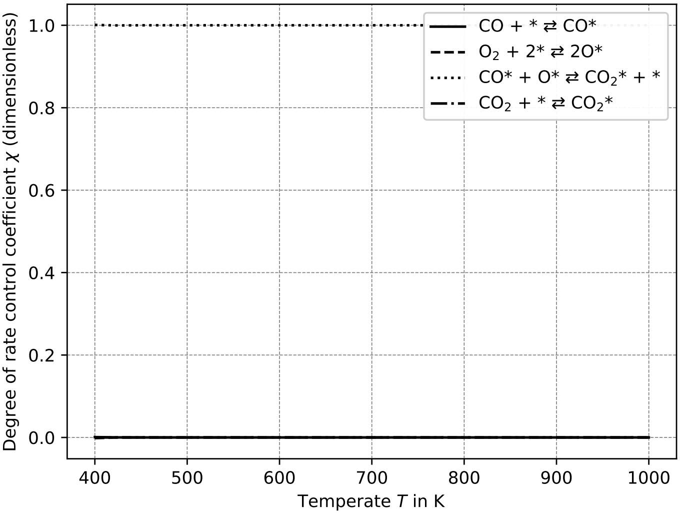


Figure 4.8: *Degree of rate control coefficient as function of temperature.*

Nevertheless, this result is very important as will become clearer in the next section. In the case that the DRC analysis shows that only one elementary reaction step has a DRC coefficient $\chi = 1$ and that all other elementary reaction steps have $\chi = 0$, then this means that this elementary reaction step is **rate-determining**. In other words, the overall reaction rate r only depends on the rate of this elementary reaction step. All other elementary reaction steps prior to the rate-determining elementary reaction step are then at pseudo-equilibrium. We will use this valuable approximation to create an analytic model of our kinetic system.

Finally, we should make an important note here. In the calculation of the degree of rate control, we have used the overall reaction rate r. In principle, one can also use the rate for any kind of particular reactant or product. The rate for this compound does not necessarily have to be the same as the overall reaction rate, though for reactions where there is only a single product, this is the case. But consider the situation wherein one reactant can form two different product. In that case, the degree of rate control of one particular product will not be the same as the degree of rate control of the reactant. It is up to the researcher to decide which rate is important and relevant in your analysis and it might be that several degree of rate control simulations have to be performed in order to fully convey the sensitivity on the elementary reaction steps of the reaction mechanism.

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[8] The proof for this equality is given in section B.8 of the Appendix.

4.6 Degree of selectivity control

Besides the degree of rate control, it can also be of interest what the influence of a particular elementary reaction step is on the selectivity rather than the activity of a reaction. In this evaluation, one solves the following differential

$$\epsilon_{i,c} = \left(\frac{\partial \eta_c}{\partial \ln k_i} \right)_{k_j \neq k_i, K_i}, \tag{4.28}$$

where $\epsilon_{i,c}$ is the degree of selectivity coefficient of compound c due to a change in elementary reaction step i and η_c is the selectivity of compound c.

Once the degree of rate control coefficients are known, it is fairly straightforward to calculate the $\epsilon_{i,c}$ coefficients as can be seen from the following derivation:

$$\begin{aligned}
\epsilon_{i,c} &= \left(\frac{\partial \eta_c}{\partial \ln k_i} \right)_{k_j \neq k_i, K_i} && (4.29)\\
&= \eta_c \left(\frac{\partial \ln \eta_c}{\partial \ln k_i} \right)_{k_j \neq k_i, K_i} && (4.30)\\
&= \eta_c \left(\frac{\partial \ln r_c / r_r}{\partial \ln k_i} \right)_{k_j \neq k_i, K_i} && (4.31)\\
&= \eta_c \left(\left(\frac{\partial \ln r_c}{\partial \ln k_i} \right)_{k_j \neq k_i, K_i} - \left(\frac{\partial \ln r_r}{\partial \ln k_i} \right)_{k_j \neq k_i, K_i} \right) && (4.32)\\
&= \eta_c \left(\chi_{c,i} - \chi_{r,i} \right) && (4.33)
\end{aligned}$$

In other words, the degree of selectivity control is the degree of rate control using the rate of the compound you are interested in minus the degree of rate control using the rate of the overall reaction (i.e. of a specific reactant), multiplied by the selectivity of the compound wherein you are interested. A positive degree of selectivity coefficient indicates that the selectivity of this compound will increase when the barrier of the corresponding elementary reaction step is lowered and a negative value indicates that the selectivity decreases if the barrier is lowered.

From the sum-rule for the degree of rate control coefficients, another sum rule can be constructed. It is fairly straightforward to see that

$$\sum_{i,c} \epsilon_{i,c} = 0. \tag{4.34}$$

4.7 Comparison with Langmuir-Hinshelwood kinetics

In the previous section we have seen that some kinetic networks have only a single elementary reaction step that is rate-controlling. In other words, that elementary reaction step is automatically the rate-*determining* elementary reaction step. Such a system has the requirements by which the Langmuir-Hinshelwood-Hougen-Watson approximation applies. Here, we will demonstrate this by solving the system for CO oxidation in an analytic fashion.

If $\mathrm{CO}* + \mathrm{O}* \rightarrow \mathrm{CO_2}* + *$ is the rate-determining step and we operate at zero conversion, then we can assume that all other steps that precede this step are at pseudo-equilibrium. Thus,

$$CO + * \leftrightarrows CO* \tag{4.35}$$

$$O_2 + 2* \leftrightarrows 2O* \tag{4.36}$$

and consequently

$$K_{CO} = \frac{\theta_{CO}}{p_{CO}\theta_*} \tag{4.37}$$

$$K_{O_2} = \frac{\theta_O^2}{p_{O_2}\theta_*^2}, \tag{4.38}$$

where K_i is the equilibrium constant for adsorption of compound i, θ_i is the surface coverage of compound i and θ_* is the fraction of free sites on the surface.

By introducing a mass balance, [9]

$$\theta_{CO} + \theta_O + \theta_* = 1, \tag{4.39}$$

we can calculate the fraction of free sites as a function of the equilibrium constants and the partial pressures.

$$1 = \theta_{CO} + \theta_O + \theta_* \tag{4.40}$$

$$= K_{CO}p_{CO}\theta_* + \sqrt{K_{O_2}p_{O_2}}\theta_* + \theta_* \tag{4.41}$$

$$= \left(1 + K_{CO}p_{CO} + \sqrt{K_{O_2}p_{O_2}}\right)\theta_* \tag{4.42}$$

$$\theta_* = \frac{1}{1 + K_{CO}p_{CO} + \sqrt{K_{O_2}p_{O_2}}} \tag{4.43}$$

We can use this result to explicitly calculate the coverages for θ_{CO} and θ_{O_2},

$$\theta_{CO} = \frac{K_{CO}p_{CO}}{1 + K_{CO}p_{CO} + \sqrt{K_{O_2}p_{O_2}}} \tag{4.44}$$

$$\theta_O = \frac{\sqrt{K_{O_2}p_{O_2}}}{1 + K_{CO}p_{CO} + \sqrt{K_{O_2}p_{O_2}}}. \tag{4.45}$$

At zero coverage, the overall rate is given by the *forward* rate of the rate-determining elementary reaction step as

$$r = k_{rds}\theta_{CO}\theta_{O_2} \tag{4.46}$$

$$= \frac{k_{rds}K_{CO}p_{CO}\sqrt{K_{O_2}p_{O_2}}}{\left(1 + K_{CO}p_{CO} + \sqrt{K_{O_2}p_{O_2}}\right)^2}. \tag{4.47}$$

---

[9] Note that we have neglected to take the surface coverage of CO_2. The motivation for this assumption is that we operate at zero conversion. This means that the partial pressure of CO_2 is zero so that any CO_2 that is formed on the surface, immediately desorbs to the gas phase.

At this point, we have an analytic expression for the overall rate. From this expression, we can derive analytic expressions for the reaction orders and the apparent activation energy.

$$n_{\mathrm{CO}} = p_{\mathrm{CO}} \frac{\partial \ln r}{\partial p_{\mathrm{CO}}} \tag{4.48}$$

$$= p_{\mathrm{CO}} \frac{\partial \ln \left(\frac{k_{\mathrm{rds}} K_{\mathrm{CO}} p_{\mathrm{CO}} \sqrt{K_{\mathrm{O_2}} p_{\mathrm{O_2}}}}{\left(1 + K_{\mathrm{CO}} p_{\mathrm{CO}} + \sqrt{K_{\mathrm{O_2}} p_{\mathrm{O_2}}}\right)^2} \right)}{\partial p_{\mathrm{CO}}} \tag{4.49}$$

$$= D_1 + \frac{1}{2} D_2 - 2 D_3, \tag{4.50}$$

where

$$D_1 = p_{\mathrm{CO}} \frac{\partial \ln \left(k_{\mathrm{rds}} K_{\mathrm{CO}} p_{\mathrm{CO}}\right)}{\partial p_{\mathrm{CO}}} \tag{4.51}$$

$$D_2 = p_{\mathrm{CO}} \frac{\partial \ln \left(K_{\mathrm{O_2}} p_{\mathrm{O_2}}\right)}{\partial p_{\mathrm{CO}}} \tag{4.52}$$

$$D_3 = p_{\mathrm{CO}} \frac{\partial \ln \left(1 + K_{\mathrm{CO}} p_{\mathrm{CO}} + \sqrt{K_{\mathrm{O_2}} p_{\mathrm{O_2}}}\right)}{\partial p_{\mathrm{CO}}}. \tag{4.53}$$

The terms D_i can be readily solved, which give

$$D_1 = 1 \tag{4.54}$$

$$D_2 = 0 \tag{4.55}$$

$$D_3 = \frac{K_{\mathrm{CO}} p_{\mathrm{CO}}}{1 + K_{\mathrm{CO}} p_{\mathrm{CO}} + \sqrt{K_{\mathrm{O_2}} p_{\mathrm{O_2}}}} \tag{4.56}$$

and combining these three terms results in

$$n_{\mathrm{CO}} = 1 - 2\theta_{\mathrm{CO}}. \tag{4.57}$$

In a similar fashion, we obtain

$$n_{\mathrm{O_2}} = \frac{1}{2} - \theta_{\mathrm{O}}. \tag{4.58}$$

These results are completely in line with the numerical results as shown in Figure 4.5, though here we have gained the insight that the reaction order can be directly related to the surface coverages. At a high surface coverage of CO, we see that the second term in the equation becomes 1, which gives a reaction order of $n_{\mathrm{CO}} = 1 - 2 \cdot 1 = -1$. With decreasing surface coverage, the reaction order increases and finally at low surface coverage of CO, the reaction order becomes 1.

For $n_{\mathrm{O_2}}$, we can see from Figure 4.4 that the surface coverage of O* is negligible at all temperatures ($\theta_O \approx 0$). From our analytical derivation we can see that the reaction order in O_2 should then be $n_{\mathrm{O_2}} = \frac{1}{2} - 1 \cdot 0 = \frac{1}{2}$. This confirms our results as seen in Figure 4.5 where indeed a reaction order of $\frac{1}{2}$ is seen for O_2.

The apparent activation energy can also be readily derived.

$$\Delta E_{\text{act}}^{\text{app}} = RT^2 \frac{\partial \ln r}{\partial T} \tag{4.59}$$

$$= RT^2 \frac{\partial \ln \left(\frac{k_{\text{rds}} K_{\text{CO}} p_{\text{CO}} \sqrt{K_{\text{O}_2} p_{\text{O}_2}}}{\left(1+K_{\text{CO}} p_{\text{CO}}+\sqrt{K_{\text{O}_2} p_{\text{O}_2}}\right)^2} \right)}{\partial T} \tag{4.60}$$

$$= D_1 + D_2 + \frac{1}{2} D_3 + 2 D_4 \tag{4.61}$$

where

$$D_1 = RT^2 \frac{\ln k_{\text{rds}}}{\partial T} \tag{4.62}$$

$$D_2 = RT^2 \frac{\ln K_{\text{CO}}}{\partial T} \tag{4.63}$$

$$D_3 = RT^2 \frac{\ln K_{\text{O}}}{\partial T} \tag{4.64}$$

$$D_4 = RT^2 \frac{\partial \ln \left(1 + K_{\text{CO}} p_{\text{CO}} + \sqrt{K_{\text{O}_2} p_{\text{O}_2}}\right)}{\partial T}. \tag{4.65}$$

which resolve to

$$D_1 = \Delta E_{\text{rds}} \tag{4.66}$$

$$D_2 = \Delta H_{\text{CO}} \tag{4.67}$$

$$D_3 = \Delta H_{\text{O}} \tag{4.68}$$

$$D_4 = \Delta H_{\text{CO}} \frac{K_{\text{CO}} p_{\text{CO}}}{1 + K_{\text{CO}} p_{\text{CO}} + \sqrt{K_{\text{O}_2} p_{\text{O}_2}}} + \frac{1}{2} \Delta H_{\text{O}_2} \frac{\sqrt{K_{\text{O}_2} p_{\text{O}_2}}}{1 + K_{\text{CO}} p_{\text{CO}} + \sqrt{K_{\text{O}_2} p_{\text{O}_2}}}. \tag{4.69}$$

Combining these terms gives

$$\Delta E_{\text{act}}^{\text{app}} = \Delta E_{\text{rds}} + \Delta H_{\text{CO}} \left(1 - 2\theta_{CO}\right) + \Delta H_{\text{O}_2} \left(\frac{1}{2} - \theta_{\text{O}}\right). \tag{4.70}$$

Note that in the above expression, the part between the round brackets are equal to the reaction orders:

$$\Delta E_{\text{act}}^{\text{app}} = \Delta E_{\text{rds}} + \Delta H_{\text{CO}} \left(n_{\text{CO}}\right) + \Delta H_{\text{O}_2} \left(n_{\text{O}_2}\right). \tag{4.71}$$

In other words, there is a clear relation between the apparent activation energy and the reaction order. As these reaction orders in turn depend on the surface coverages, the apparent activation energy also strongly depends on these surface coverages.

Again, the analytic expression provides us with a valuable insight what terms contribute to the apparent activation energy. Importantly, the dominant term of in the apparent activation energy is the barrier of the rate-determining step. All other terms relate to the energetics of all elementary reaction steps that precede the rate-determining step. Here, the adsorption of CO and O_2 are the two elementary reaction steps that precede the recombination of surface CO with O. Thus, the energetics of these steps (ΔH_i) are seen in the expression of the apparent activation energy.

The apparent activation energy in our example for CO dissociation can be interpreted as follows. For the overall reaction to proceed, the system should have enough energy (temperature) to overcome the barrier of the rate-determining step. When the surface is completely covered with CO, there are no free sites for O_2 to adsorb on. As such, first a CO needs to be desorbed before O_2 can adsorb. This desorption costs energy and therefore the apparent activation energy increases. Once CO is desorbed, oxygen can adsorb. As the adsorption process is exothermic, some energy is released which decreases the apparent activation energy. Let us assume that the surface coverage of CO is unity (completely covered), then the apparent activation energy becomes

$$\Delta E_{\text{act}}^{\text{app}} = \Delta E_{\text{rds}} + \Delta H_{\text{CO}}\left(n_{\text{CO}}\right) + \Delta H_{\text{O}_2}\left(n_{\text{O}_2}\right) \tag{4.72}$$

$$= 120\text{kJ/mol} + 80\text{kJ/mol} - 0.5 \cdot 40\text{kJ/mol} \tag{4.73}$$

$$= 180\text{kJ/mol} \tag{4.74}$$

From Figure 4.6 we can see that around 400K, the apparent activation energy indeed has a value of around 180 kJ/mol. Furthermore, from Figure 4.4 we see that this situation corresponds to a surface nearly fully covered with CO. Indeed, from the coverages as obtained from Figure 4.4 and using the formula for the apparent activation energy, Figure 4.6 can be completely reproduced.

4.8 Questions and Exercises

The answers to the questions and exercises are given at the end of this book in Appendix C (page 135).

4.8.1 Questions

1. What is the motivation for constructing a rate expression using a power law? Why are we allowed to use the stoichiometric coefficient of the reactant as the exponent in these power laws for elementary reaction steps, but not (necessarily) for overall reactions?

2. Propose a series of elementary reaction steps which constitute the methanation reaction ($CO + 3H_2 \rightarrow CH_4 + H_2O$).

3. Why does methane immediately desorb after hydrogenation of CH_3*, but ammonia does not after hydrogenation of NH_2*?

4. For an overall elementary reaction steps with a clear stoichiometry and only one type of product (i.e. having no side products), why does it not matter which key component is used in the analysis of the reaction order or the apparent activation energy? *Hint: Why does the stoichiometric coefficient drop out?*

5. Why is the surface coverage of O so low in the example of CO oxidation? (see Figure 4.4)

4.8.2 Exercises

The exercises are marked by a number of gears to indicate their difficulty levels.

✎ **Exercise 4.1** ⚙⚙

a) Calculate the degree of rate control parameters for all elementary reaction steps in the CO oxidation reaction from the analytical expression as given in equation 4.47.

b) Derive the reaction order for O_2 in the CO oxidation reaction and show that your result matches that of equation 4.58. *Hint: You need to use the chain-rule.*

■

✎ **Exercise 4.2** ⚙⚙

a) Show that equation 4.34 holds using the proof for the sum rule of the degree of rate control coefficients (eq. 4.27).

■

CHAPTER

5

PERFORMING MICROKINETICS WITH MKMCXX

This chapter is based on joint work with Tom van den Berg.

Contents

5.1 Introduction

In the previous chapter we explained how to set up a simple microkinetic model for a unimolecular and a bimolecular catalytic reaction. The reader was introduced to the stepwise approach to construct such a model. We were able to calculate the reaction rate by time-integration of the ordinary differential equations (ODE) underlying the kinetic system. Moreover, it was explained how one could numerically calculate the reaction order and the apparent activation energy for the reaction. Finally, the methodology behind the degree of rate control analysis and the degree of selectivity control analysis was explained.

In this chapter we will expand on the previous chapter by providing a hands-on tutorial how to perform microkinetics simulations using the MKMCXX tool. We will discuss the results of typical simulations and explain how to interpret these results. The whole procedure is explained using a couple of simple examples. The reader is invited to download the MKMCXX software and work alongside the book.

5.2 Installation

The program MKMCXX is a microkinetic modeling software suite for educational and research purposes. The program can be found on its website `http://www.mkmcxx.nl` and is free to use. The program is originally written for the Linux operating system but has since been ported to Windows. This chapter will focus on the use of MKMCXX in Windows as we anticipate that most readers of this book will be using Windows. It is advised to always use the latest stable version for Windows.

Download the zip package from the website and extract MKMCXX. The extracted folder will contain two directories. The subfolder `bin` consists of the executable of MKMCXX together with the necessary supporting files (i.e. the .dll files). The MKMCXX executable requires a set of command-line arguments in order to perform a simulation, hence you cannot start a simulation by simply opening the program by double-clicking on it. The second subfolder `place_different_runs_here` is used for the simulations. The example folder contains an input file (typically `input.mkm`) and a run file (`run.bat`). The run file is used to start the MKMCXX simulation using the input file in that specific folder. Alternatively, you can use the Command Prompt of Windows to start the simulation. A short tutorial how to install the program and how to use the Command Prompt of Windows to start a calculation is given in the YouTube video as found below.

Watch the short installation tutorial on YouTube using this link:
`https://www.youtube.com/watch?v=_edo3JvA0AA`

Important

We advise to create a new folder for every simulation to keep everything tidy and organized. Do not forget to add the input and run files into each folder.

5.3 The basic input

The input file of MKMCXX is structured into sections. The start of each section is indicated using the syntax as found in Table 5.1.

The input file consists of four mandatory sections[I] which are used to define the microkinetic model. These four sections are

1. `&compounds`: A list of all compounds in the system, for both gases as well as surface intermediates, and their corresponding initial concentration.

[I] MKMCXX offers several non-mandatory sections. These instructions can be found in Appendix F on 211.

Table 5.1: *Symbols recognized by MKMCXX to define of separate certain areas of the input.mkm file.*

Symbol	Function
&	The symbol & followed by a keyword will define a new section in the input file.
#	Placing # in the text will convert the text to comments. MKMCXX will not use comments when executed therefore this give the user the option to leave remarks in the input file.
;	Most sections in MKMCXX consist of several columns. These columns are separated by ;.

2. `&reactions`: All elementary reaction steps and their relevant kinetic parameters (e.g. activation barriers and pre-exponential factors).

3. `&settings`: Specifies the type of the simulation, the pressure and what kind of post-analytics need to be performed.

4. `&run`: A list of temperatures and total simulation times.

Here, we will explain how to construct a basic input file to perform an MKMCXX simulation utilizing a simple example question. The different sections of the input file and the interpretation of the results will be explained. It is strongly recommended to follow along with this example as this gives a much better understanding of the input file and MKMCXX.

Example question

Consider the catalytic oxidation of carbon monoxide to carbon dioxide. Assume that O_2 adsorbs dissociatively, whereas CO adsorbs molecularly. The overall reaction is given by

$$2\,CO + O_2 \longrightarrow 2\,CO_2. \tag{5.1}$$

Use the kinetic data as provided in Tables 5.2 and 5.3.

1. Calculate the steady-state production for catalytic CO oxidation. What is the optimal operating temperature for the oxidation with respect to the production of CO_2 between the temperatures 400-1400 K? Take steps of 20 K at a time and simulate for 1000 seconds. Assume ideal stoichiometry and a total pressure of 20 bar.

2. What are the reaction orders of CO and O_2 and what is the effect of partial pressure of the compounds on the reaction rate?

3. The apparent activation energy is a measure for the influence of temperature on the reaction rate. What is the apparent activation energy for the reaction at 700 K. At what temperature is the apparent activation energy 0?

4. Determine the rate controlling step. Does the rate controlling step vary with the temperature?

A demonstration video on how to set-up a MKMCXX input file can be found on YouTube using the link below. Please note that the chemo-kinetic network in this video is different from the one used in the example.
▶ `https://www.youtube.com/watch?v=TQ1EychXXc8`.

Table 5.2: *Parameters for the adsorption and desorption steps in CO oxidation.*

Compound	A [m^2]	m (a.u.)	σ [-]	θ_{rot} [K]	E_{ads} [kJ/mol]
CO	$1 \cdot 10^{-20}$	28	1	2.8	80
O_2	$1 \cdot 10^{-20}$	32	2	2.08	40
CO_2	$1 \cdot 10^{-20}$	80	1	0.561	10

2

To set up the microkinetic model for catalytic CO oxidation we will partially use the steps as previously shown in Chapter 4 on page 84.

1. Construct the set of elementary reaction steps that describes the reaction mechanism.
2. Define boundary conditions, initial values and data parameters for the system (e.g. temperature, pressure, concentrations).
3. Construct the input file for MKMCXX.
4. Interpret the results of the simulation using our chemical intuition.

We start with constructing the elementary reaction steps for CO oxidation. The overall reaction of CO oxidation (Equation 5.1) constitutes the following four elementary reaction steps:

$$\mathrm{CO} + * \leftrightarrows \mathrm{CO}* \tag{5.2}$$
$$\mathrm{O_2} + 2* \leftrightarrows 2\,\mathrm{O}* \tag{5.3}$$
$$\mathrm{CO} * + \mathrm{O}* \leftrightarrows \mathrm{CO_2} * + * \tag{5.4}$$
$$\mathrm{CO_2} + * \leftrightarrows \mathrm{CO_2}* \tag{5.5}$$

Next, we define the boundary conditions of the microkinetic model. From the description in the example question, we can obtain the following boundary conditions:

1. The pressure is 20 bar with a stoichiometric ratio of 1:2 for the partial pressures of CO and O_2, respectively.
2. The temperatures of the reaction are between 400 and 1400 K and modeled every 20 K.
3. The kinetic data for the rate expressions are given in Tables 5.2 and 5.3.

Table 5.3: *Parameters for the surface reaction of CO oxidation.*

Reaction	$\nu_f[\mathrm{s}^{-1}]$	$\nu_b[\mathrm{s}^{-1}]$	E_a^f[kJ/mol]	E_a^b[kJ/mol]
$\mathrm{CO}^* + \mathrm{O}^* \longrightarrow \mathrm{CO_2}^* + *$	10^{13}	10^{13}	120	180

5.3.1 Compounds

We start constructing the input file for the calculation by defining all compounds in our system. In MKMCXX a compound is defined by three arguments, separated by semicolons. These three arguments are:

1. The name of the compound, which can in principle be anything but it is advised to use the molecule structure for clarity. Please avoid special characters such as '#' as they have a different meaning in the input file.
2. Indicate whether the compound is a gas phase species or a surface intermediate. A value of 0 designates a gas phase species and a value of 1 a surface intermediate. From here on, we will use the term `isSite` to refer to this value.
3. The initial partial pressure as **fraction** of the total pressure. The latter is specified in the `&settings` section.

The list of compounds has to contain every compound in the system. That is, the input file must contain a complete list of reactants, products, catalyst sites and adsorbed intermediates of the reaction. In the next section, we will refer to these compounds when defining the elementary reaction steps. Neglecting to specify a compound will result in an error message of the program.

Let us start by first defining all gas phase compounds. In Listing 5.1, a snippet of the input file corresponding to the gas phase compounds can be found. We start by opening the `&compounds` section. The compounds are specified using three semicolon separated columns, wherein the first column sets the name of compounds, the second column whether the compound is a surface intermediate and the final column the starting concentration.

Listing 5.1: *Gaseous compounds*

```
#The line below tells MKMCXX to start indexing the compounds.
&compounds

#Name;  isSite; Concentration
CO;     0;      1.0
O2;     0;      2.0
CO2;    0;      0.0
```

Note that the gaseous compounds are not adsorbed onto the catalyst surface, thus `isSite` is set to 0. The concentration is partial pressure of each compounds with respect to the total pressure defined in the `&settings` section. Since the mixture of gaseous compounds is stoichiometric, the partial pressure of O_2 is twice as high as the partial pressure of CO.

Listing 5.2: *Adsorbed compounds*

```
#Adsorbed compounds
#Name;  isSite; Concentration
CO*;    1;      0.0
O*;     1;      0.0
CO2*;   1;      0.0
```

The input settings for the surface intermediates (adsorbed compounds) are provided in Listing 5.2. To clearly list the adsorbed compounds, it is advised to append a symbol to the compound names. Here, we have used a "*". Note that O_2 adsorbs dissociatively onto the catalyst surface, hence we only have O* and not O_2*.

Next to adsorbed species on the catalytic surface, an empty catalytic site is also a surface intermediate. The empty catalytic site is shown in Listing 5.3 and is named '*'. At the start of the reaction, we assume that the catalytic surface is empty (this is a common assumption in microkinetics) and hence we set the starting concentration to 1.0.

Listing 5.3: *Catalyst compounds*

```
#Catalyst
#Name;  isSite; Concentration
*;      1;      1.0
```

5.3.2 Reactions

The `&reactions` session specifies all elementary reaction steps in the system. The section is opened using the `&reactions` keyword. MKMCXX differentiates between two types of elementary reaction steps: Arrhenius-type (see Equation 3.12 on page 79) and Hertz-Knudsen type (see Equation 3.7 on page 77 and Equation 3.10 on page 78). The former is used for surface reaction, whereas the latter is used for adsorption/desorption reactions. Arrhenius-type reactions require 6 arguments and Hertz-Knudsen reactions require 8 arguments. For the adsorption and desorption the Hertz-Knudsen equations are a better approximation compared to the Arrhenius equations as they more adequately describe the entropy changes upon adsorption/desorption. The arguments for the Hertz-Knudsen equations are as follows:

1. Specify which set of equations need to be used by MKMCXX. The Hertz-Knudsen equations are specified by `HK` and the Arrhenius equations are specified by `AR`.
2. The adsorption or desorption reaction. The compounds need to be within curly brackets `{}`. Make sure that the compounds match the compounds in the `&compound` section.
3. The surface area of the active site in m^2
4. The molecular mass of the molecule in Dalton.
5. The characteristic temperature for rotation θ_{rot} in K.
6. The symmetry number, σ, which represent the number of indistinguishable orientations as result of rotation.
7. The sticking coefficient of the molecule. (if unknown, use a value of 1 here)
8. The **desorption** energy in J/mol. (it is defined in such a way that for exothermic adsorption, the value here should be positive positive)

For the elementary reaction steps that occur completely on the catalyst surface, the Arrhenius-type equation is best. Herein, it is assumed that the entropy between the initial, transition and final state does not change significantly. For the Arrhenius equations, the 6 arguments are as follows:

1. Specify the Arrhenius equation with `AR`.
2. The surface reaction (see above).
3. The pre-exponential factor for the forward reaction in s^{-1}.
4. The pre-exponential factor for the backward reaction in s^{-1}.
5. The activation energy for the forward reaction in J/mol.
6. The activation energy for the backward reaction in J/mol.

By using the data as given in Tables 5.2 and 5.3, the adsorption/desorption reactions are specified as given in Listing 5.4.

Important

Always specify Hertz-Knudsen-type elementary reaction steps as adsorptions. In other words, place the gas phase components on the left-hand-side of the equation and the adsorbed species on the right-hand-side.

Listing 5.4: *Adsorption and desorption reaction steps*

```
#The line below tells MKMCXX to index all reaction steps.
&reactions

#Adsorptions/desorption's
#Type   Reaction                m^2     amu  Theta   sigma  stick  J/mol
HK; {CO}    +    {*}=>   {CO*}; 1e-19;  28;  2.8;    1;     1;     80e3
HK; {O2}    +   2{*}=>   2{O*}; 1e-19;  32;  2.08;   2;     1;     40e3
HK; {CO2}   +    {*}=>  {CO2*}; 1e-19;  80;  0.561;  1;     1;     10e3
```

In a similar fashion, the input for the Arrhenius-type of equations is given in Listing 5.5.

Listing 5.5: *Surface reaction*

```
#Surface reactions
#Type   Reaction                                    vf      vb      Eaf     Eab
AR;     {CO*}   +    {O*}   => {CO2*}   +   {*};    10e13;  10e13;  120e3;  180e3
```

5.3.3 Settings

The settings section of the input file is started using the `&settings` keyword. In the settings sections, the program determines what analytical routines are used to evaluate the specified system. The settings are specified using the well-known keyword-value pairing as represented by

`Keyword = new value`.

For a basic simulation without using any of the analytical tools, only the type of simulation and the overall pressure of the system need to be specified. The simulation type is a so-called sequence run and the overall pressure, as given in the example exercise, is 20 bar. The code snippet for these settings is provided in Listing 5.6.

Listing 5.6: *Settings CO*

```
#The line below tells MKMCXX what settings to use

&settings

TYPE = SEQUENCERUN
PRESSURE = 20
```

MKMCXX is highly tunable and offer a much broader set of keywords. In the upcoming sections, the most important analytical tools will be discussed. For a more thorough overview of the possible keywords, we refer to Appendix F on page 211.

5.3.4 Runs

The final (mandatory) section is `&runs`. Herein, the set of simulations are provided. A simulation is the time-integration of the ordinary differential equations underlying the chemokinetic system. To perform this time-integration, the following parameters are required:

1. The temperature in K.
2. The time in s.
3. The absolute tolerance.
4. The relative tolerance.

The example exercise asks us to evaluate the reaction between 400 and 1400 K in steps of 20 K. The simulation time for each of the simulations is set to 1000 s. The sample exercise does not provide any specifications for the tolerances and hence we opt for using the default values. If no values are given, the program automatically resorts to using the default values, which are 10^{-8} for the absolute tolerance and 10^{-12} for the relative tolerances. Here, we are going to use the default values and explicitly provide these as input. This results in the following `&runs` section as provided in Listing 5.7.

Listing 5.7: *Temperature time and tolerance variables for the model.*

```
#The line below tells MKMCXX on what temperatures and how to simulate the catalytic reaction

&runs

#Temp;  Time;   AbsTol; RelTol
400;    1e3;    1e-8;   1e-12
420;    1e3;    1e-8;   1e-12
440;    1e3;    1e-8;   1e-12
# ...
# More desired temperatures.
# ...
1360;   1e3;    1e-8;   1e-12
1380;   1e3;    1e-8;   1e-12
1400;   1e3;    1e-8;   1e-12
```

This concludes the basic input data that is needed for the oxidation reaction of CO to CO_2. The input file is complete and MKMCXX is ready to perform the simulation. We warmly recommend the reader to copy the input above and perform a single simulation before continuing to the data interpretation section. If any errors occur, look into the Common Problems section in Appendix F on page 211.

5.4 Kinetic analysis tools

In this section, we introduce a few kinetic analysis tools to investigate the chemokinetic network. If the reader is curious about interpreting the results of the simulation, he/she is invited to skip this section and immediately go to section 5.5 on page 116.

5.4.1 Reaction order

MKMCXX is able to calculate the reaction order by means of numerical approximation as shown in the previous chapter (see page 94). This is done by performing four additional calculations, each at a slightly different partial pressure of one of the key reactants and finally calculating the derivative using a linear fit. In this section, we will elaborate on how a reaction order analysis is performed using the CO oxidation example.

Listing 5.8: *Code snippet to enable a reaction order analysis.*

```
#The line below tells MKMCXX what settings to use
&settings
TYPE = SEQUENCERUN
PRESSURE = 20

# Specify REAGENTS here
REAGENTS = {CO},{O2}

# Calculate reaction order
ORDER = 1
```

By default, MKMCXX does not calculate the reaction order of a reaction. Evaluation of the reaction orders is specified in the `&settings` section by setting `ORDER = 1`. Furthermore, the user needs to set for which reactants the reaction order should be evaluated. This is shown in Listing 5.8.

Note that the settings section has been slightly altered. First the `REAGENTS` were specified. This tells MKMCXX which compounds should be evaluated when calculating the reaction order. Multiple gas phase compounds can be added to this section and are delimited by a comma. Remember to use the curly brackets to sandwich the compounds!

5.4.2 Apparent activation energy

The effect of temperature on the overall rate of the reaction can be determined by calculating the apparent activation energy as discussed in chapter 4.4 on page 96.

The apparent activation energy can be calculated in MKMCXX by setting the `EAPP` keyword to unity. The program simulates four additional points at slightly different temperatures. After calculating these 5 points, the apparent activation energy is found by performing a linear fit on the following equation:

$$E_{\text{act}}^{\text{app}} = -R\frac{\partial \ln r}{\partial \frac{1}{T}} = RT^2\frac{\partial \ln r^+}{\partial T} \tag{5.6}$$

In equation 5.6, the rate r refers to the rate of a key component. One can easily imagine that in parallel reaction networks, the apparent activation energy is not necessarily the same for each reactant or each product. In principle, there is no such thing as a unique apparent activation energy for a reaction. Thus, to calculate the apparent activation energy, we need to specify the key component for which the apparent activation energy is evaluated. The corresponding `&settings` section of the input file is shown in Listing 5.9.

Listing 5.9: *Code snippet to enable apparent activation energy analysis.*

```
#The line below tells MKMCXX what settings to use
&settings
TYPE = SEQUENCERUN
PRESSURE = 20

# Specify key components
KEYCOMPONENTS = {CO}

# Calculate apparent activation energy
EACT = 1
```

Please note the inclusion of the `KEYCOMPONENTS` keyword. Multiple key components can be specified and these components are delimited by using a comma. By setting `EACT = 1`, MKMCXX will calculate the apparent activation energy for each of the key components.

5.4.3 Degree of rate control

To investigate the influence each elementary reaction step has on the overall reaction, we can perform a degree of rate control analysis. The degree of rate control, as explained in chapter 4, probes the effect of increasing or decreasing the barrier of the elementary reaction step on the overall reaction rate (of a designated key component).

MKMCXX evaluates the degree of rate control by performing 4 additional calculations with slightly different prefactors (ν_f **and** ν_b) while keeping the equilibrium (K_i) of all reactions constant. Because the DRC analysis is relatively expensive, you need to specifically set for which elementary reaction steps the analysis needs to be performed. This is done by appending a `0` or a `1` after the elementary reaction step. The procedure is shown in Listing 5.10.

Listing 5.10: *Enabling degree of rate control analysis for the elementary reaction steps. Note that ";1" after each elementary reaction step.*

```
#The line below tells MKMCXX to index all reaction steps.
&reactions
#Adsorptions/desorption's
#Type   Reaction                            m^2         amu     K       sigma
     sticking    J/mol   DRC
HK;     {CO}    +    {*}    =>   {CO*};     1e-19;      28;     2.8;    1;      1;
             80e3;   1
HK;     {O2}    +   2{*}    =>   2{O*};     1e-19;      32;     2.08;   2;      1;
             40e3;   1
HK;     {CO2}   +    {*}    =>  {CO2*};     1e-19;      80;     0.561;  1;      1;
             10e3;   1

#Surface reactions
#Type   Reaction                                    vf      vb      Eaf     Eab
     DRC
AR;     {CO*}   +    {O*}   => {CO2*}   +   {*};    10e13;  10e13;  120e3;  180e3;
     1
```

In the `&settings` section of the input file, the keyword `DRC` needs to be set to one and the `KEYCOMPONENTS` need to be set. This is shown in Listing 5.11.

Listing 5.11: *Degree of rate control settings*

```
#The line below tells MKMCXX what settings to use
&settings
TYPE = SEQUENCERUN
PRESSURE = 20

# Specify key components
KEYCOMPONENTS = {CO}

# Perform degree of control analysis
DRC = 1
```

5.5 Data interpretation

If you completed the procedure as shown in section 5.3, your calculation should now be up and running (if not, consult the Troubleshooting section in the Appendix on page 211). If you have also added the kinetic analysis tools of the previous section to your simulation, you should now have calculated the steady-state rates of adsorption, desorption and production at a series of temperatures, the reaction order for the compounds CO and O_2, the apparent activation energy and the degree of rate control for the oxidation of CO to CO_2. In this section, we are going to investigate the results from the simulation.

MKMCXX will create a folder called `TYPE_OF_RUN_'date'_'time'` to store all output files in, where 'date' and 'time' have been replaced by the current system date and time. In the example above, this will results in a folder called `SEQUENCERUN_'date'_'time'`. In this folder, a subfolder is created for every temperature as specified in the `&runs` section. Furthermore, there is a folder called `graphs`, a folder called `networkplots` and a folder called `range`. Lastly, there are four text files which are: `compounds.log`, `input.log`, `reactions.log` and `warnings.log`.

Each temperature folder contains the fractional surface coverages at that temperature as a function of the simulation time as well as the consumption and production of gas phase reactants and products. These files are tab-delimited text files and can be opened in a Spreadsheet program such as Microsoft Excel.

The `graphs` folder contains graphs which can be used to quickly evaluate the calculated data. These graphs are automatically generated using the Cairo library[3] and are specifically not intended for reproduction in papers or reports, although this up to discretion of the user. We always recommend remaking the graphs to suit your (or the journal's) style using a proper tool such as Origin, Excel or the `matplotlib` module in Python.[4] In Figure 5.1, an example is shown of a typical graph generated by MKMCXX depicting the production of CO_2 and the consumption of CO and O_2 as function of the temperature. Figure 5.2 shows the same data, but then remade using `matplotlib`.[5] Arguably, there is quite some difference in quality between Figures 5.1 and 5.2 and the latter Figure can furthermore be altered or tuned to your specifications. Throughout this chapter, we will opt for using `matplotlib` to generate our figures.

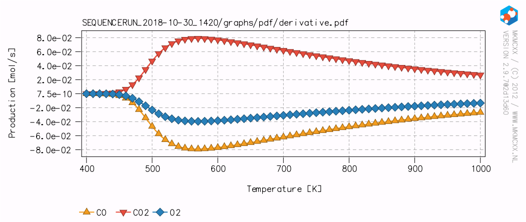


Figure 5.1: *Production of* CO_2 *as function of temperature, the MKMCXX figure.*

The `networkplots` folder contains files which can be visualized using the program GraphViz[6] and these files visualize the network of elementary reaction steps and their reaction rates. Unfortunately, the procedure only works (at the moment) on Linux and hence we will not further discuss it here. The user is advised to consult the online Wiki.[7]

The `range` folder contains the fractional coverage of surface intermediates and the consumption and production rates of gas phase reactants and products as a function of temperature (i.e. the range refers here to the range of temperatures). Furthermore, this subfolder holds the calculated values of the reaction rate constants k, the prefactors and the rates of the elementary reaction steps. If the reaction orders, apparent activation energy and degree of rate control are calculated, each will get their own sub folder respectively.

---

[3] See: `https://www.cairographics.org/`

[4] The main reason for this is that the plotting tool is not exactly smart and it uses some default settings for the visualization. These settings are not universal and we anticipate that for production data some fine-tuning is necessary.

[5] See `https://matplotlib.org/` for more information about using matplotlib to generate graphs.

[6] See `https://www.graphviz.org/` for more information about GraphViz.

[7] See `https://wiki.mkmcxx.nl`.

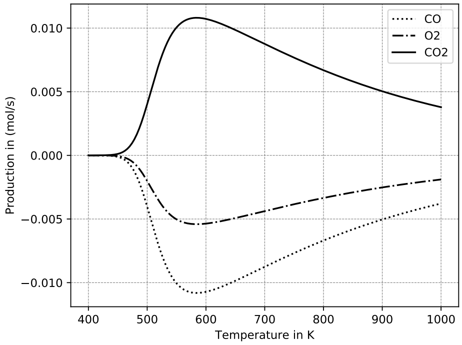


Figure 5.2: *Production of* CO_2 *as function of temperature plotted with Spyder3.*

The file `compounds.log` contains an overview of the compounds in the system and whether they occupy a site. The file `input.log` contains an exact copy of the `input.mkm` file which functions as a backup for future reference. Please do not see this as an excuse to neglect performing every individual simulation in a separate folder. The `reactions.log` file contains the elementary reaction steps and the rate constants as a function of temperature. Finally, the `warnings.log` file reports problems or errors from the simulation. Always consult this file carefully, but be mindful that sometimes false positives are triggered. This means that if a warning is generated, it does not necessarily imply that your calculation is erroneous.

5.5.1 Operating temperature and production

The adsorption equilibria of the compounds of a system depend on the temperature. In Figure 5.3, the coverage of the compounds is plotted as a function of the temperature.

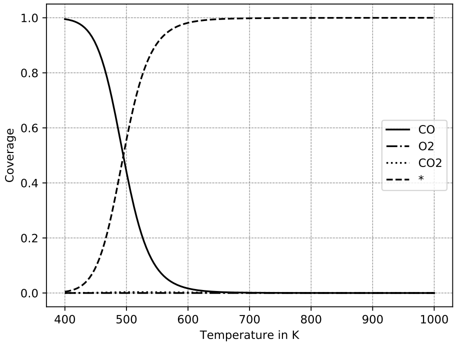


Figure 5.3: *Surface coverage of the compound* CO *as a function of temperature.*

Figure 5.3 shows that with temperatures below 550 K, CO is the most abundant reaction intermediate (MARI). With increasing temperature, the equilibrium of CO adsorption shifts to the gas phase side and hence the amount of free catalyst sites increases. Comparing these results with Figure 5.4, we see that with decreasing surface coverage of CO, the production of

CO_2 increases. This result can be rationalized as with an increasing number of free surface sites, there are more available sites for dissociative adsorption of O_2. Further increasing the temperature above 600 K reduces the coverage of CO to nearly 0 and hence negatively impacts the production of CO_2.

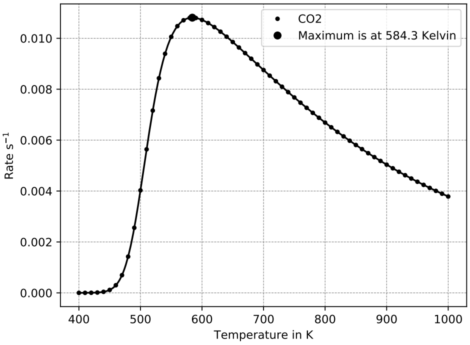


Figure 5.4: *Optimal operation temperature with the respect to the production of* CO_2.

Using Figure 5.4, we are able to answer the first question of the example exercise. From this Figure, it can be seen that the optimal operating temperature of our catalyst (i.e. the temperature at which the activity is highest) is at approximately 570 K.

5.5.2 Reaction orders

The reaction order in CO and O_2 as function of temperature is shown in Figure 5.5. The graph generated by MKMCXX can be found in the `graphs` folder after the simulation. The corresponding numeric data can be found in the `graphs/order` subfolder.

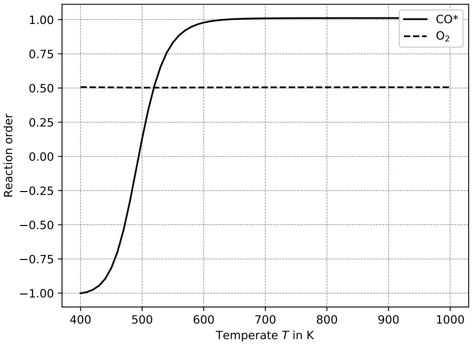


Figure 5.5: *Reaction order of* CO *and* O_2 *as function of temperature.*

From the Figure 5.5, it can be seen that the reaction order in CO is around -1 at very low temperature. From the definition of the reaction order, this implies that a doubling of the partial pressure of CO will result in halving the rate for CO_2 production. Furthermore, it can be seen that the reaction order of O_2 is independent of the temperature. We can now readily answer the second part of the example exercise. The reaction order for O_2 is a constant value of 0.5 and therefore doubling the partial pressure of O_2 will increase the rate of the reaction by a factor $\sqrt{2}$. The reaction order for CO is not constant and increases with increasing temperature. For low temperatures doubling the partial pressure will halve the rate of the reaction as the surface is already poisoned by CO as can also be readily seen in Figure 5.3. For higher temperatures, doubling the partial pressure of CO will double the rate of the reaction.

Another way of interpreting these results is as follows. At elevated temperatures, the catalytic surface is nearly empty. When the surface is empty, there is insufficient amount of reactant on the catalytic surface. Increasing the partial pressure of CO will thus increase the impingement rate of CO with the surface and hence increase the overall reaction rate. A similar reasoning applies to O_2, but with the notable difference that only a single oxygen atom of the oxygen molecule is required. This leads to a reaction order of a half.

5.5.3 Apparent activation energy

The graph for the apparent activation energy, as generated by MKMCXX, can be found in the `graphs/eact` subfolder of the simulation. The corresponding numeric data calculated can be found in the subfolder `range/eact`. The apparent activation energy for CO oxidation as function of temperature is plotted in Figure 5.6.

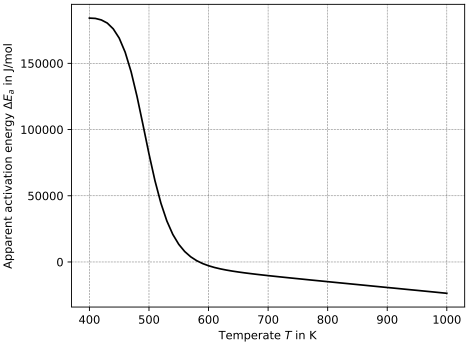


Figure 5.6: *Apparent activation energy for CO as function of temperature.*

Careful examination of Figure 5.6 shows that the apparent activation energy for CO oxidation is negative above 570 K. As the highest activity is observed around 570 K, this implies (form the definition of the apparent activation energy) that the apparent activation energy at that point is 0. Above 570 K, this leads to negative apparent activation energies as one needs to decrease the temperature in order to increase the rate. *Vice versa*, below 570 K, the apparent activation energy is positive as one needs to increase the temperature to increase the rate.

5.5.4 Degree of rate control

The graph for the degree of rate control analysis can be found in the `drc` subfolder. The results for the degree of rate control analysis are shown in Figure 5.7.

In the example exercise, we were asked to determine the rate controlling step. As expected, the dominant rate controlling step for the oxidation of CO is the recombination of CO and O on the surface. This elementary reaction step has a DRC coefficient of unity, independent of the temperature. In other words, it is the **rate-determining** step (as opposed to having multiple rate-controlling steps).

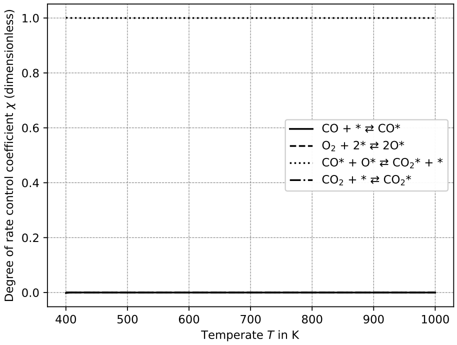


Figure 5.7: *Degree of rate control as function of temperature.*

5.6 Convergence

The program MKMCXX is capable of performing microkinetic simulations for large complex catalytic reactions, nevertheless it is important that the compounds of the reaction have converged at the end of the simulation time. In other words, we are typically seeking the steady-state solution thus we integrate in time sufficiently long that we expect this solution to be reached. This is of course not guaranteed and it can be the case, especially at low temperatures, that the calculation is not yet converged with respect to time-integration. MKMCXX will issue a warning for most convergence problems, however it is important to note that the generated data should always be scrutinized by the user to check for convergence.

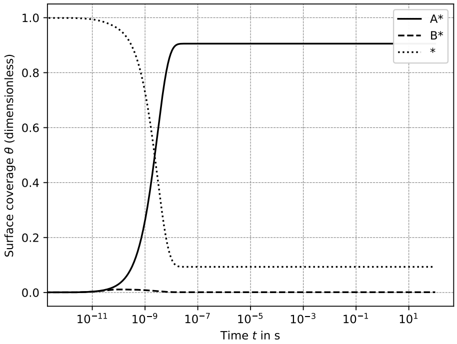


Figure 5.8: *Surface coverage versus time at 450 K.*

Figure 5.8 shows the surface coverage of the catalyst with respect to the time for the simulation at 450 K. Evaluating this Figure shows that the components of the CO oxidation are converged after $1 \cdot 10^{-7}$ seconds.

Due to the significant difference of the rates of the individual elementary reaction steps, the time-integration of the chemokinetic networks typically shows three characteristic regimes:

1. Reactant adsorption onto the surface site.
2. Surface reaction initiation.

3. Reaction propagation.

The last two step may occur simultaneously if the initial reaction steps are rate controlling or the reaction network consists of no serial reaction steps.

☁ Recall

Recall from section 1.5.2 on page 19 that this is exactly the reason why we are allowed to use the quasi-equilibrium assumption. The rates for adsorption/desorption are much faster that the rates for the surface reactions. Thus, adsorption/desorption is already pseudo-equilibrated with respect to the other elementary reaction steps.

⚠ Important

Be careful with assuming a reaction has converged just because the concentration does not change anymore. Always carefully check your data and perform additional calculations at somewhat longer time scales.

5.7 Numerical versus analytical

In the previous sections we explained how to model a microkinetic network using the program MKMCXX. We showed how to model a heterogeneous catalytic reaction and how to interpret the numerical output data. In this section we will derive an analytical solution for same the chemokinetic network and compare the results with the numerical solution of MKMCXX. We will highlight when such a procedure is possible and what additional insights can be gained from deriving an analytical solution.

Assuming that the surface reaction from CO to CO_2 is the rate determining step[8], and furthermore using the pseudo-equilibrium assumption and the zero conversion assumption, we obtain the following equations for the site-balance and the surface coverage of CO:

$$\theta_{\mathrm{CO}} + \theta_{\mathrm{O}} + \theta_{*} = 1 \tag{5.7}$$

$$\theta_{\mathrm{CO}} = \frac{K_{\mathrm{CO}} p_{\mathrm{CO}}}{1 + K_{\mathrm{CO}} p_{\mathrm{CO}} + \sqrt{K_{\mathrm{O_2}} p_{\mathrm{O_2}}}} \tag{5.8}$$

Because zero conversion was assumed, the overall rate is equal to the forward rate of the rate-determining step.

$$r_{\mathrm{rds}} = \frac{k_{\mathrm{rds}} K_{\mathrm{CO}} p_{\mathrm{CO}} \sqrt{K_{\mathrm{O_2}} p_{\mathrm{O_2}}}}{(1 + K_{\mathrm{CO}} p_{\mathrm{CO}} + \sqrt{K_{\mathrm{O_2}} p_{\mathrm{O_2}}})^2} \tag{5.9}$$

In chapter 3, the general rate of adsorption and desorption known as the Hertz-Knudsen equations was derived. Here, we repeat the formula for convenience.

$$k_{\mathrm{ads}} = \frac{p_i A_i}{\sqrt{2\pi m_i k_b T}} \tag{5.10}$$

$$k_{\mathrm{des}} = \frac{k_b T^3}{h^3} \frac{A_i (2\pi m_i k_b)}{\sigma_i \theta_{\mathrm{rot},i}} \exp\left(\frac{-E_{\mathrm{des},i}}{k_b T}\right), \tag{5.11}$$

---

[8] This is already confirmed by the simulation, but it is good to mention it here again as an assumption.

wherein i represents the molecule adsorbing onto the catalyst site. From equations 5.10 and 5.11, we can readily calculate the equilibrium constant for adsorption

$$K = \frac{k_{\text{ads}}}{k_{\text{des}}} \tag{5.12}$$

$$= \frac{\frac{p_i A_i}{\sqrt{2\pi m_i k_b T}}}{\frac{k_b T^3}{h^3} \frac{A_i (2\pi m_i k_b)}{\sigma \theta_{\text{rot}}} \exp\left(\frac{-E_{\text{des},i}}{k_b T}\right)} \tag{5.13}$$

$$= \frac{p_i h^3 \sigma_i \theta_{\text{rot},i}}{k_b T^2 (2\pi m_i k_b T)^{1.5}} \exp\left(\frac{E_{\text{des},i}}{k_b T}\right) \tag{5.14}$$

Using the obtained expression for the equilibrium constant of the adsorption/desorption reactions, the overall rate of the reaction can be calculated. In Figure 5.9 the analytical solutions of the overall rate using the Hertz-Knudsen equations are plotted against the numerically calculated solutions of MKMCXX.

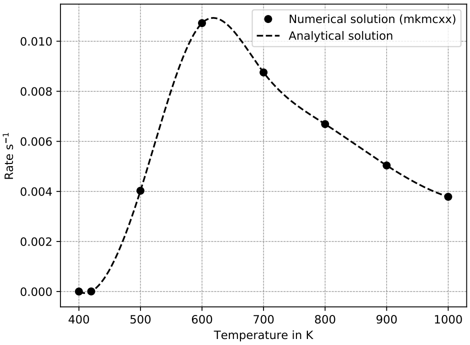


Figure 5.9: *Analytical solution versus numerical solution*

Figure 5.9 shows that the numerical and analytical solution perfectly match. The reason for this match is that the fundamental assumptions behind the analytical derivation remain valid over the whole temperature range. This is more of an exception than a rule.

The same procedure can be repeated for the reaction order and the apparent activation energy. This is basically already covered in section 4.7 on page 101.

5.8 Exercises

The answers to the exercises are given at the end of this book in Appendix C (page 135).

The exercises are marked by a number of gears to indicate their difficulty levels.

Exercise 5.1 ⚙

Consider the CO oxidation reaction as discussed in Chapter 5 on 108.

The input file for this simulation can be found using the link below: `https://www.mkmcxx.nl/downloads/input/input_ex1.mkm`

The input file contains everything needed for this exercise and in principle needs no altering. However, we always encourage to alter some values to get some more feeling for performing microkinetic simulations.

a) Run the simulation using the provided input file in MKMCXX. What is the optimal temperature for CO oxidation?

b) Which of the elementary reaction steps is the rate-determining step?

Exercise 5.2

Consider the following overall reaction which converts reactants A and B to product C, as given by

$$\mathrm{A} + \mathrm{B} \rightarrow \mathrm{C}. \tag{5.15}$$

The chemokinetic network consists of the following four elementary reaction steps

$$\begin{aligned} \mathrm{A} + * &\leftrightarrows \mathrm{A}* \\ \mathrm{B} + * &\leftrightarrows \mathrm{B}* \\ \mathrm{A} * + \mathrm{B}* &\leftrightarrows \mathrm{C} * + * \\ \mathrm{C} + * &\leftrightarrows \mathrm{C}* \end{aligned}$$

In Table 5.4 and 5.5, the kinetic parameters for the elementary reaction steps are given.

Table 5.4: *Kinetic parameters for the adsorption and desorption steps*

Compound	A [m^2]	m (a.u.)	σ [-]	θ_{rot} [K]	E_{ads} [kJ/mol]
A	$1 \cdot 10^{-20}$	40	1	2.92	50
B	$1 \cdot 10^{-20}$	16	1	1.66	100
C	$1 \cdot 10^{-20}$	63	1	0.601	5

a) The total gas pressure is 30 bar and the reactants are fed stoichiometrically. Perform a microkinetic simulation using MKMCXX between 500 K and 1500 K in steps of 50 K. What is the surface composition of where the production of C is the highest? At what temperature does this occur?

b) Calculate the forward reaction rate constant of the adsorption reaction of compound A using the expression generated by MKMCXX at $T = 750$ K.

Table 5.5: *Kinetic parameters for the surface reaction.*

Reaction	ν_f[s^{-1}]	ν_b[s^{-1}]	E_a^f[kJ/mol]	E_a^b[kJ/mol]
$\mathrm{A}^* + \mathrm{B}^* \longrightarrow \mathrm{C}^* + *$	20^{13}	10^{13}	90	320

Exercise 5.3 ⚙⚙

Consider the following overall reaction

$$A_2 + B \rightarrow E \tag{5.16}$$

The relevant kinetic parameters for the rate expressions can be found in Tables 5.6 and 5.7.

Table 5.6: *Parameters for the adsorption and desorption steps*

Compound	A [m^2]	m (a.u.)	σ [-]	θ_{rot} [K]	E_{ads} [kJ/mol]
A_2	$1 \cdot 10^{-20}$	32	1	1	100
B	$1 \cdot 10^{-20}$	15	1	1	110
E	$1 \cdot 10^{-20}$	10	1	1	50

a) Construct the set of elementary reactions steps that describes the reaction mechanism as given by the overall reaction.

b) What is the expected rate-determining step on the basis of the kinetic parameters?

c) Construct an input file for MKMCXX to perform a microkinetic simulation between T =500-1500 K. What is the rate-determining step and how does this change with respect to temperature?

■

Exercise 5.4 ⚙⚙⚙

Consider the following parallel reaction network, wherein A can be converted to both E_2 as well as F as given by

$$A \rightarrow E_2 \tag{5.17}$$

$$A \rightarrow F \tag{5.18}$$

The reaction proceeds via the following set of elementary reaction steps

Table 5.7: *Parameters for the surface reaction.*

Reaction	ν_f[s^{-1}]	ν_b[s^{-1}]	E_a^f[kJ/mol]	E_a^b[kJ/mol]
$A^* + B^* \longrightarrow C^* + *$	10^{13}	10^{13}	100	50
$A^* \longrightarrow D^*$	10^{13}	10^{13}	75	120
$C^* + D^* \longrightarrow E^*$	10^{13}	10^{13}	50	50

$$\begin{aligned}
A + * &\leftrightarrows A* \\
A* &\leftrightarrows 2B* \\
B* &\leftrightarrows C* \\
C* &\leftrightarrows E* \\
2E* &\leftrightarrows E_2 + 2* \\
B* &\leftrightarrows D* \\
2D* &\leftrightarrows F* \\
F* &\leftrightarrows F
\end{aligned} \tag{5.19}$$

The input file for MKMCXX containing the relevant parameters for the rate expressions is found using the following link:
`https://www.mkmcxx.nl/downloads/input/input_ex4.mkm`

a) Assume that the dissociation of A into 2B is rate controlling at 1400 K. Calculate the rate and compare this with the rate as calculated by MKMCXX.

b) What is the most abundant reaction intermediate between 600 and 800 K?

c) Evaluate the results of the DRC analysis. At lower temperature, the DRC (with respect to component A) of $B* \leftrightarrows D*$ is negative. How should this result be interpreted?

d) The current simulation favors the production of E_2. What would you change in the parameters to increase the selectivity towards F?

■

APPENDIX

A

FUNDAMENTAL CONSTANTS

Constant	Symbol	Value	Units
Speed of light	c	$2.99792458 \cdot 10^{8}$	$\mathrm{m} \cdot \mathrm{s}^{-1}$
Planck's constant	h	$6.2606957 \cdot 10^{-34}$	$\mathrm{J} \cdot \mathrm{s}$
Boltzmann's constant	k_b	$1.3806488 \cdot 10^{-23}$	$\mathrm{J} \cdot \mathrm{K}^{-1}$
Avogadro's constant	N_A	$6.02214129 \cdot 10^{23}$	mol^{-1}
Gas constant	R	8.3144621	$\mathrm{J} \cdot \mathrm{K}^{-1} \cdot \mathrm{mol}^{-1}$
Atomic mass constant	m_u	$1.660538921 \cdot 10^{-27}$	kg

APPENDIX B

MATHEMATICS

Contents

B.1 Stirling Approximation

Stirling's theorem states:

$$\sqrt{2\pi} n^{n+\frac{1}{2}} e^{-n} < n! < \sqrt{2\pi} n^{n+\frac{1}{2}} e^{-n} \left(1 + \frac{1}{4n}\right) \tag{B.1}$$

Therefore,

$$\ln(n!) = (n + \frac{1}{2}) \ln(n) - n + C \tag{B.2}$$

where C is a number inbetween 0.9189 and 0.9189 + ln $\left(1 + \frac{1}{4n}\right)$. For large values of n this reduces to the simpler form,

$$\ln(n!) \approx n \ln(n) - n \tag{B.3}$$

B.2 Gaussian integrals

$$\int_{-\infty}^{\infty} \exp^{-x^2} \, \mathrm{d}x = \sqrt{\pi} \tag{B.4}$$

$$\int_{0}^{\infty} x^{2n} \exp^{-x^2/a^2} \, \mathrm{d}x = \sqrt{\pi}\frac{(2n)!}{n!}\left(\frac{a}{2}\right)^{2n+1} \tag{B.5}$$

$$\int_{0}^{\infty} x^{2n+1} \exp^{-x^2/a^2} \, \mathrm{d}x = \frac{n!}{2}a^{2n+2} \tag{B.6}$$

B.3 Taylor expansion for the exponential function

A Taylor series is a representation of a function as an infinite sum of terms that are calculated from the values of the function's derivatives at a single point. Mathematically, the Taylor series is given by the following formula

$$f(x) = \sum_{n=0}^{\infty} \frac{f^{(n)}(a)}{n!}(x-a)^n \tag{B.7}$$

where $f(x)$ is the function we wish to approximate, $f^{(n)}$ is the nth order derivative of $f(x)$ and a is the point from which we wish to evaluate the derivatives. When $a = 0$ is chosen, the series is also called a Maclaurin series. Here, we are going to apply the above formula to derive a Maclaurin series for the exponential function.

$$\begin{aligned}
\exp x &= \sum_{n=0}^{\infty} \frac{f^{(n)}(a)}{n!}(x-a)^n && \text{(B.8)}\\
&= \sum_{n=0}^{\infty} \frac{\frac{\mathrm{d}\exp x}{\mathrm{d}x}|_{x=0}}{n!}x^n && \text{(B.9)}\\
&= \sum_{n=0}^{\infty} \frac{x^n}{n!} && \text{(B.10)}\\
&= \frac{1^0}{0!} + \frac{1^1}{1!} + \frac{1^2}{2!} + \frac{1^3}{3!} + \cdots && \text{(B.11)}\\
&= 1 + x + \frac{x^2}{2!} + \frac{x^3}{3!} + \cdots && \text{(B.12)}
\end{aligned}$$

From the factorial in the denominator, you can already guess that this series converges quite rapidly. Furthermore, when x is much smaller than one, only the first few terms have to be considered of this series. If we for instance only take the first term into consideration, we say that we cut the series off at the linear term so that our Taylor approximation becomes

$$\exp x \approx 1 + x \quad \text{for } x \ll 1. \tag{B.13}$$

B.4 Geometric series

In mathematics, a geometric series is a series with a constant ratio between successive terms. Here, we will derive an expression for a special case of an infinite geometric series.

Consider the geometric series

$$a + ar + ar^2 + ar^3 + \cdots = \sum_{k=0}^{\infty} ar^k. \tag{B.14}$$

Such a series can converge when the absolute value of r is sufficiently small as

$$\sum_{k=0}^{\infty} ar^k = \frac{a}{1-r}\text{ , for } |r| < 1. \tag{B.15}$$

B.5 Lagrange's method of undetermined multipliers

When optimizing a (multivariable) function f under a constraint, we can use Lagrange's method of undetermined multipliers. We introduce for each constraint a new variable (λ_i) called a Lagrange multiplier and study the Lagrange function

$$\mathcal{L}(x_1, x_2, \cdots, x_i, \lambda_1, \lambda_2, \cdots, \lambda_i) = f(x_1, x_2, \cdots, x_i) - \sum_i \lambda_i \cdot g_i(x_1, x_2, \cdots, x_i), \tag{B.16}$$

where g_i is a function representing constraint i. The constrained extrema of f are then the critical points of the Lagrangian $\mathcal{L}$. Thus we solve

$$\nabla \mathcal{L}(x_1, x_2, \cdots, x_i, \lambda_1, \lambda_2, \cdots, \lambda_i) = 0. \tag{B.17}$$

Let us illustrate the above procedure with an example as shown in Figure B.1.

Suppose we wish to maximize

$$f(x, y) = x + 3y \tag{B.18}$$

subject to the constraint

$$x^2 + y^2 = 1. \tag{B.19}$$

The Lagrangian for this problem is

$$\mathcal{L}(x, y, \lambda) = x + 3y - \lambda\left(x^2 + y^2 - 1\right). \tag{B.20}$$

This leads to

$$\nabla \mathcal{L}(x, y, \lambda) = \begin{pmatrix} \frac{\partial \mathcal{L}}{\partial x} \\ \frac{\partial \mathcal{L}}{\partial y} \\ \frac{\partial \mathcal{L}}{\partial \lambda} \end{pmatrix} = \begin{pmatrix} 1 + 2\lambda x \\ 3 + 2\lambda y \\ x^2 + y^2 - 1 \end{pmatrix} = 0. \tag{B.21}$$

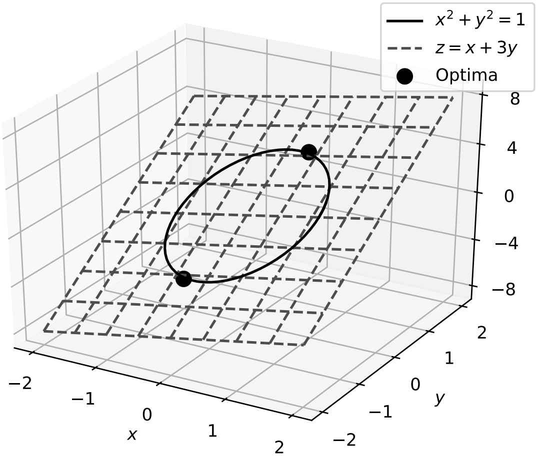


Figure B.1: *Illustration of the constrained optimization problem using Lagrange's method of undetermined multipliers. The objective function f is depicted by the dashed surface and the projected constraint function g is depicted by the black curve.*

This set of equations has two solutions as given by

$$\lambda = \pm\sqrt{2}, \tag{B.22}$$

which implies that the stationary points are

$$\mathcal{L}_{0,1} = \left(-\frac{1}{2\sqrt{2}}, -\frac{3}{2\sqrt{2}}, \sqrt{2}\right) \tag{B.23}$$

and

$$\mathcal{L}_{1,1} = \left(\frac{1}{2\sqrt{2}}, \frac{3}{2\sqrt{2}}, -\sqrt{2}\right). \tag{B.24}$$

Evaluating the objective function yields

$$f\left(\pm\frac{1}{2\sqrt{2}}, \pm\frac{3}{2\sqrt{2}}\right) = \pm\frac{5}{\sqrt{2}}, \tag{B.25}$$

where the positive solution corresponds to a maximum and the negative solution to a minimum.

B.6 l'Hôspital's Rule

When evaluating a limit that is the quotient of two functions and the limit of those functions are either zero or infinity, then l'Hôspital's Rule states that

$$\lim_{x \to a} \frac{f(x)}{g(x)} = \lim_{x \to a} \frac{f'(x)}{g'(x)}. \tag{B.26}$$

The differentiation of the numerator and denominator often simplifies the quotient or converts it to a limit that can be evaluated directly.

For example:

$$\lim_{x \to \infty} \frac{\exp(x) - 1}{x^2 + x} = \lim_{x \to \infty} \frac{\exp(x)}{2x + 1} \tag{B.27}$$

$$= \frac{1}{2 \cdot 0 + 1} \tag{B.28}$$

$$= 1 \tag{B.29}$$

B.7 Matrix diagonalization

A square matrix A can be diagonalized if there exists an invertible matrix P such that

$$D = P^{-1} A P, \tag{B.30}$$

where D is a diagonal matrix. The values on the diagonal are then the eigenvalues, whereas the columns in P are the corresponding right-eigenvectors. For many applications, the square matrix A is a real-symmetric matrix (i.e. all values are real and $A_{i,j} = A_{j,i}$). In such a case, the inverse of the matrix P equals its transpose $P^{-1} = P^{\mathsf{T}}$.

For example, consider the matrix

$$A = \begin{pmatrix} -2 & -2 & 1 \\ -1 & 3 & -1 \\ 2 & -4 & 3 \end{pmatrix}. \tag{B.31}$$

This matrix can be diagonalized with a matrix

$$P = \begin{pmatrix} 2 & -1 & 1 \\ 1 & 0 & -1 \\ 0 & 1 & 2 \end{pmatrix} \tag{B.32}$$

and a diagonal matrix

$$D = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 6 \end{pmatrix}. \tag{B.33}$$

The eigenvalues are thus $\lambda_1 = 1$, $\lambda_2 = 1$ and $\lambda_3 = 6$ with corresponding eigenvectors as columns in matrix P.

B.8 Sum of degree of rate control coefficients

Assume that we can write the rate of an overall reaction as a sum of the rates of its constituting elementary reaction steps multiplied by an (as yet unknown) contribution constant n_i as

$$r_{\text{overall}} = \sum_i n_i \left(k_i^+ \prod_j c_{ij} - k_i^- \prod_j c_{ij} \right) \tag{B.34}$$

$$= \sum_i n_i k_i \left(\prod_j c_{ij} - K_i^{-1} \prod_j c_{ij} \right), \tag{B.35}$$

where $n_i \in \mathbb{R}$.

To obtain the contribution of an elementary reaction step to the overall reaction, we can use the DRC analysis as given by

$$\chi_i = \frac{\partial \ln r_{\text{overall}}}{\partial \ln k_i} \tag{B.36}$$

$$= \frac{\partial r_{\text{overall}}}{\partial k_i} \frac{k_i}{r_{\text{overall}}} \tag{B.37}$$

$$= \frac{\partial \sum_j n_j k_j \left(\prod_k c_{jk} - K_j^{-1} \prod_k c_{jk} \right)}{\partial k_i} \frac{k_i}{\sum_j n_j k_j \left(\prod_k c_{jk} - K_j^{-1} \prod_k c_{jk} \right)} \tag{B.38}$$

$$= \frac{n_i k_i \left(\prod_j c_{ij} - K_i^{-1} \prod_j c_{ij} \right)}{\sum_j n_j k_j \left(\prod_k c_{jk} - K_j^{-1} \prod_k c_{jk} \right)}. \tag{B.39}$$

Since $n_i \in \mathbb{R}$, this gives $\chi_i \in \mathbb{R}$. When $\chi_i > 0$, the reaction contributes to the overall reaction and is rate-limiting. When $\chi_i < 0$, the reaction reduces the overall reaction and is rate-limiting.

Summing over χ_i gives

$$\sum_i \chi_i = \frac{\sum_i n_i k_i \left(\prod_j c_{ij} - K_i^{-1} \prod_j c_{ij} \right)}{\sum_j n_j k_j \left(\prod_k c_{jk} - K_j^{-1} \prod_k c_{jk} \right)} \tag{B.40}$$

$$= 1 \tag{B.41}$$

APPENDIX C

SOLUTIONS

Contents

C.1 Solutions of Chapter 1

C.1.1 Solutions to exercises

The solution below pertain to the exercises of Chapter 1 on page 28 and further.

Solution 1.1

$$\frac{\mathrm{d}[\mathrm{CH_4}]}{\mathrm{d}t} = k_2[\mathrm{CH_3}*][\mathrm{CH_3CHO}] \tag{C.1}$$

The target is to express short-lived intermediates (such as radicals) in terms of gas-phase concentrations. Here, the unknown variable is $[\mathrm{CH_3}*]$ and can be found by using the steady state approximation. In the steady-state approximation, the time-derivative of one or more compounds, typically the reaction intermediates, is set to zero. We apply this approximation to $\frac{\mathrm{d}[CH_3*]}{\mathrm{d}t}$ and $\frac{\mathrm{d}[CH_3CO*]}{\mathrm{d}t}$.

$$\begin{aligned}\frac{\mathrm{d}[CH_3*]}{\mathrm{d}t} =& k_1[CH_3CHO] - k_2[CH_3*][CH_3CHO] \\ &+ k_3[CH_3CO*] - 2k_4[CH_3*]^2 = 0 \end{aligned} \tag{C.2}$$

and

$$\frac{\mathrm{d}[CH_3CO*]}{\mathrm{d}t} = k_2[CH_3*][CH_3CHO] - k_3[CH_3CO*] = 0 \tag{C.3}$$

Combining equations C.2 and C.3 yields

$$[CH_3*] = \sqrt{\frac{k_1}{2k_4}}[CH_3CHO]^{1/2}. \tag{C.4}$$

Inserting equation C.4 into equation C.1 gives

$$\frac{\mathrm{d}[CH_4]}{\mathrm{d}t} = k_2\sqrt{\frac{k_1}{2k_4}}[CH_3CHO]^{3/2}. \tag{C.5}$$

and the rate of formation for $[C_2H_6]$ becomes

$$\frac{\mathrm{d}[C_2H_6]}{\mathrm{d}t} = k_4[CH_3*]^2 = \frac{k_1}{2}[CH_3CHO] \tag{C.6}$$

■

Solution 1.2

The problem in the exercise can be solved by either applying the steady-state approximation or by assuming a pre-equilibrium. Here, we have applied the former as such an approximation is more general and also better exemplifies the mathematical procedure. Obviously, a derivation based on the pre-equilibrium assumption is also valid.

$$\frac{\mathrm{d}[O_2]}{\mathrm{d}t} = k_2[NO_2][NO_3] \tag{C.7}$$

Applying the steady-state approximation to NO and NO_3 yield

$$\frac{\mathrm{d}[NO]}{\mathrm{d}t} = k_2[NO_2][NO_3] - k_3[NO][NO_3] = 0 \tag{C.8}$$

and

$$\frac{\mathrm{d}[NO_3]}{\mathrm{d}t} = k_1^+[N_2O_5] - k_1^-[NO_2][NO_3] - k_2[NO_2][NO_3] - k_3[NO][NO_3] = 0. \tag{C.9}$$

By subtracting equation C.8 from C.9, we obtain

$$[\mathrm{NO_2}][\mathrm{NO_3}] = \frac{k_1^+}{k_1^- + 2k_2}[\mathrm{N_2O_5}] \tag{C.10}$$

which we can readily insert into the rate equation of O_2 formation, resulting in

$$\frac{\mathrm{d}[\mathrm{O_2}]}{\mathrm{d}t} = \frac{k_1^+ k_2}{k_1^- + 2k_2}[\mathrm{N_2O_5}]. \tag{C.11}$$

Think deeper...

- The reason why the reaction order is unity, rather than two, is because the overall reaction is not an elementary reaction step.
- For NO_2, the rate equation is

$$\frac{\mathrm{d}[\mathrm{NO_2}]}{\mathrm{d}t} = k_1^+[\mathrm{N_2O_5}] - k_1^-[\mathrm{NO_2}][\mathrm{NO_3}] + 2k_3[\mathrm{NO}][\mathrm{NO_3}]. \tag{C.12}$$

Inserting equations C.8 and C.10 to C.12 gives

$$\begin{aligned}
\frac{\mathrm{d}[\mathrm{NO_2}]}{\mathrm{d}t} &= k_1^+[\mathrm{N_2O_5}] - \frac{k_1^+ k_1^-}{k_1^- + 2k_2}[\mathrm{N_2O_5}] + \frac{2k_1^+ k_2}{k_1^- + 2k_2}[\mathrm{N_2O_5}] && \text{(C.13)}\\
&= \left(k_1^+ - \frac{k_1^+ k_1^-}{k_1^- + 2k_2} + \frac{2k_1^+ k_2}{k_1^- + 2k_2}\right)[\mathrm{N_2O_5}] && \text{(C.14)}\\
&= \frac{k_1^+}{k_1^- + 2k_2}\left(k_1^- + 2k_2 - k_1^- + 2k_2\right)[\mathrm{N_2O_5}] && \text{(C.15)}\\
&= \frac{k_1^+}{k_1^- + 2k_2}4k_2[\mathrm{N_2O_5}] && \text{(C.16)}\\
&= 4\frac{\mathrm{d}[\mathrm{O_2}]}{\mathrm{d}t}. && \text{(C.17)}
\end{aligned}$$

■

Solution 1.3

Applying the steady-state approximation to $[N_2O_2]$ gives

$$\frac{\mathrm{d}[\mathrm{N_2O_2}]}{\mathrm{d}t} = k_1^+[\mathrm{NO}]^2 - k_1^-[\mathrm{N_2O_2}] - k_2[\mathrm{N_2O_2}][\mathrm{H_2}] = 0. \tag{C.18}$$

From this expression, we can equate the $[N_2O_2]$ to

$$[\mathrm{N_2O_2}] = \frac{k_1^+[\mathrm{NO}]^2}{k_1^- + k_2^+[\mathrm{H_2}]}. \tag{C.19}$$

The rate of formation of $[N_2O]$ is then found to be

$$\frac{d[N_2O]}{dt} = k_2[N_2O_2][H_2] = \frac{k_2 k_1^+ [NO]^2 [H_2]}{k_1^- + k_2^+ [H_2]} \tag{C.20}$$

$$= \frac{k_1^+ [NO]^2}{1 + k_1^- / k_2 [H_2]}. \tag{C.21}$$

■

Solution 1.4

In the overall chain reaction, the elementary reaction steps are denoted as

$Br_2 \rightarrow 2Br^*$	initiation
$CH_4 + Br^* \rightarrow CH_3{}^* + HBr$	propagation
$CH_3{}^* + Br_2 \rightarrow CH_3Br + Br^*$	propagation
$2Br^* \rightarrow Br_2$	termination

The steady-state approximation can be readily applied to the reaction rates of the intermediates.

$$\frac{d[Br^*]}{dt} = 2k_1[Br_2] - k_2[CH_4][Br^*] + k_3[CH_3{}^*][Br_2] - 2k_4[Br^*]^2 = 0 \tag{C.22}$$

$$\frac{d[CH_3{}^*]}{dt} = k_2[CH_4][Br^*] - k_3[CH_3{}^*][Br_2] = 0 \tag{C.23}$$

Inserting equation C.22 in C.23 results in

$$[Br^*] = \left(\frac{k_1}{k_4}[Br_2]\right)^{1/2}. \tag{C.24}$$

Applying equation C.24 to C.23 yields

$$[CH_3{}^*] = \frac{k_2[CH_4]\left(\frac{k_1}{k_4}[Br_2]\right)^{1/2}}{k_3[Br_2]}$$

$$= \frac{k_2 k_1^{1/2} [CH_4]}{k_3 k_4^{1/2} [Br_2]^{1/2}}. \tag{C.25}$$

Finally substituting the result of equation C.25 for the concentration of $[CH_3{}^*]$ in the formation rate of $[CH_3Br]$ results in

$$\frac{d[CH_3Br]}{dt} = k_3[CH_3{}^*][Br_2] = \frac{k_2 k_1^{1/2}}{k_4^{1/2}}[CH_4][Br_2]^{1/2}. \tag{C.26}$$

■

Solution 1.5

a) The elementary reaction step for CO adsorption is

$$\mathrm{CO} + * \leftrightarrows \mathrm{CO}* \tag{C.27}$$

Assuming an equilibrium of the above reaction and only one type of surface site yields

$$K_{\mathrm{CO}} = \frac{\theta_{\mathrm{CO}}}{p_{\mathrm{CO}}\theta_*}. \tag{C.28}$$

Furthermore, we can apply the site-balance defined as

$$\theta_* + \theta_{\mathrm{CO}} = 1. \tag{C.29}$$

Hence,

$$\theta_{\mathrm{CO}} = K_{\mathrm{CO}}p_{\mathrm{CO}}\theta_* = K_{\mathrm{CO}}p_{\mathrm{CO}}(1-\theta_{\mathrm{CO}}) \tag{C.30}$$

$$\theta_{\mathrm{CO}}(1+K_{\mathrm{CO}}p_{\mathrm{CO}}) = K_{\mathrm{CO}}p_{\mathrm{CO}} \tag{C.31}$$

$$\theta_{\mathrm{CO}} = \frac{K_{\mathrm{CO}}p_{\mathrm{CO}}}{1+K_{\mathrm{CO}}p_{\mathrm{CO}}}. \tag{C.32}$$

b) The elementary reaction step for dissociative CO adsorption is

$$\mathrm{CO} + 2* \leftrightarrows \mathrm{C}* + \mathrm{O}*. \tag{C.33}$$

Assuming equilibrium of the above reaction and only one type of surface site gives us

$$K_{\mathrm{CO}} = \frac{\theta_{\mathrm{C}}\theta_{\mathrm{O}}}{p_{\mathrm{CO}}\theta_*^2}. \tag{C.34}$$

For the mass balance (or site balance), we get

$$\theta_* + \theta_{\mathrm{C}} + \theta_{\mathrm{O}} = 1. \tag{C.35}$$

Because the surface fraction of C and O are equal

$$K_{\mathrm{CO}} = \frac{\theta_{\mathrm{C}}^2}{p_{\mathrm{CO}}\theta_*^2}. \tag{C.36}$$

Thus,

$$\theta_C = \sqrt{K_{CO}p_{CO}}\theta_* = \sqrt{K_{CO}p_{CO}}(1-2\theta_C) \tag{C.37}$$

$$\theta_C(1+2\sqrt{K_{CO}p_{CO}}) = \sqrt{K_{CO}p_{CO}} \tag{C.38}$$

$$\theta_C = \frac{\sqrt{K_{CO}p_{CO}}}{1+2\sqrt{K_{CO}p_{CO}}}. \tag{C.39}$$

c) The two elementary reaction steps for co-adsorption are

$$\mathrm{CO} + * \leftrightarrows \mathrm{CO}* \tag{C.40}$$

$$\mathrm{H}_2 + 2* \leftrightarrows 2\mathrm{H}*. \tag{C.41}$$

Assuming pre-equilibrium of these two elementary reaction steps gives

$$K_{CO} = \frac{\theta_{CO}}{p_{CO}\theta_*} \tag{C.42}$$

and

$$K_{H_2} = \frac{\theta_H^2}{p_{H_2}\theta_*^2} \tag{C.43}$$

and thus for the fractional coverages in terms of the fraction of free sites

$$\theta_H = \sqrt{K_{H_2}p_{H_2}}\theta_* \tag{C.44}$$

$$\theta_{CO} = K_{CO}p_{CO}\theta_* \tag{C.45}$$

Using the site balance,

$$\theta_{CO} + \theta_H + \theta_* = 1 \tag{C.46}$$

and inserting the equation for the surface fraction into the equation

$$(1 + K_{CO}p_{CO} + \sqrt{K_{H_2}p_{H_2}})\theta_* = 1 \tag{C.47}$$

and rearranging for θ_* finally yields

$$\theta_* = \frac{1}{1 + K_{CO}p_{CO} + \sqrt{K_{H_2}p_{H_2}}}. \tag{C.48}$$

This equation can be reinserted into the equations for the surface fractions to obtain

$$\theta_H = \frac{\sqrt{K_{H_2}p_{H_2}}}{1 + K_{CO}p_{CO} + \sqrt{K_{H_2}p_{H_2}}} \tag{C.49}$$

$$\theta_{CO} = \frac{K_{CO}p_{CO}}{1 + K_{CO}p_{CO} + \sqrt{K_{H_2}p_{H_2}}} \tag{C.50}$$

(C.51)

d) 💬 *Write down the mechanism.*
The mechanism is given by

1. $CO + * \leftrightarrows CO*$
2. $H_2 + 2* \leftrightarrows 2H*$
3. $CO* + H* \leftrightarrows HCO* + *$
4. $HCO* + H* \leftrightarrows H_2CO* + *$
5. $H_2CO* + H* \leftrightarrows H_3CO* + *$
6. $H_3CO* + H* \leftrightarrows H_3COH* + *$
7. $H_3COH + * \leftrightarrows H_3COH*$

💬 *Reason why you only need to take the surface coverages of CO, H and CH_3COH into account.*
For the construction of the site balance, we only need to take into account those compounds of which we can reasonably expect that they have a non-negligible surface coverage. These are always those compounds before the rate-determining step (i.e. CO and H_2). In addition, the question states that we can consider the RDS to be irreversible and that all steps after the RDS, except the last step, are very fast. From this piece of information, we can assume that once CO reacts with H on the surface, methanol is formed rapidly in the subsequent hydrogenation steps. Desorption of methanol is considered to be in equilibrium though, thus we anticipate that methanol has a non-negligible surface coverage. Conclusively, for the construction of the site-balance, we only need to consider CO, H_2 and CH_3OH.

💬 *Derive an expression for the reaction rate.*
The third step is considered to be the rate-determining step. This gives the following expression for the overall rate

$$r = k_3^+ \theta_{CO} \theta_H. \tag{C.52}$$

We here use the result of question 5c and note that besides CO and H_2, methanol is also equilibrated with the surface. Hence the Langmuir isotherms of CO and H_2 are

$$\theta_H = \frac{\sqrt{K_{H_2} p_{H_2}}}{1 + K_{CO} p_{CO} + \sqrt{K_{H_2} p_{H_2}} + K_{CH_3OH} p_{CH_3OH}} \tag{C.53}$$

$$\theta_{CO} = \frac{K_{CO} p_{CO}}{1 + K_{CO} p_{CO} + \sqrt{K_{H_2} p_{H_2}} + K_{CH_3OH} p_{CH_3OH}}. \tag{C.54}$$

And the overall rate is

$$r = \frac{k_3^+ \sqrt{K_{H_2} p_{H_2}} K_{CO} p_{CO}}{\left(1 + K_{CO} p_{CO} + \sqrt{K_{H_2} p_{H_2}} + K_{CH_3OH} p_{CH_3OH}\right)^2}. \tag{C.55}$$

💬 *Give the limits (the domain) of the reaction orders for H_2, CO and methanol.*
To obtain the reaction order for CO, H_2 and methanol, one needs to solve the following differential:

$$n_{H_2} = p_{H_2} \frac{\partial \ln(r^+)}{\partial p_{H_2}} \tag{C.56}$$

$$= D_1 - 2D_2 \tag{C.57}$$

Here, we are going to split up the complex differential into two smaller (and hopefully simpler) differentials:

$$D_1 = p_{H_2} \frac{\partial \left[\ln k_3^+ + \frac{1}{2}\ln K_{H_2} + \frac{1}{2}\ln p_{H_2} + \ln K_{CO} + \ln p_{CO}\right]}{\partial p_{H_2}} \tag{C.58}$$

$$D_2 = p_{H_2} \frac{\partial \ln\left(1 + K_{CO}p_{CO} + \sqrt{K_{H_2}p_{H_2}} + K_{CH_3OH}p_{CH_3OH}\right)}{\partial p_{H_2}} \tag{C.59}$$

D_1 can be readily solved as all the terms except the $\ln p_{H_2}$ cancel out giving

$$D_1 = p_{H_2} \frac{\partial \frac{1}{2}\ln p_{H_2}}{\partial p_{H_2}} \tag{C.60}$$

$$= \frac{1}{2} p_{H_2} \frac{1}{p_{H_2}} \tag{C.61}$$

$$= \frac{1}{2} \tag{C.62}$$

D_2 is a bit more complex and requires applying the chain-rule

$$D_2 = p_{H_2} \frac{\partial \ln(a)}{\partial a} \frac{\partial a}{\partial p_{H_2}} \tag{C.63}$$

where

$$a = 1 + K_{CO}p_{CO} + \sqrt{K_{H_2}p_{H_2}} + K_{CH_3OH}p_{CH_3OH} \tag{C.64}$$

Thus

$$D_2 = p_{H_2} \frac{1}{a} \frac{\partial \left(1 + K_{CO}p_{CO} + \sqrt{K_{H_2}p_{H_2}} + K_{CH_3OH}p_{CH_3OH}\right)}{\partial p_{H_2}} \tag{C.65}$$

$$= p_{H_2} \frac{1}{a} \left(\frac{1}{2}\sqrt{K_{H_2}p_{H_2}^{-1/2}}\right) \tag{C.66}$$

$$= \frac{1}{2} \left(\frac{\sqrt{K_{H_2}p_{H_2}}}{1 + K_{CO}p_{CO} + \sqrt{K_{H_2}p_{H_2}} + K_{CH_3OH}p_{CH_3OH}}\right) \tag{C.67}$$

$$= \frac{1}{2}\theta_H \tag{C.68}$$

and the final result is

$$n_{H_2} = p_{H_2} \frac{\partial \ln(r^+)}{\partial p_{H_2}} \tag{C.69}$$

$$= \frac{1}{2} - \theta_H \tag{C.70}$$

We can now easily establish the lower and upper limit of the reaction order in H_2:

$$\theta_H \in [0, 1] \to n_{H_2} \in [-\frac{1}{2}, \frac{1}{2}]. \tag{C.71}$$

The derivations for the reaction order in CO and methanol are quite similar to the one for H_2 and result in:

$$n_{CO} = p_{CO} \frac{\partial \ln(r^+)}{\partial p_{CO}} \tag{C.72}$$

$$= 1 - 2\theta_{CO} \tag{C.73}$$

and

$$n_{CH_3OH} = p_{CH_3OH} \frac{\partial \ln(r^+)}{\partial p_{CH_3OH}} \tag{C.74}$$

$$= -2\theta_{CH_3OH} \tag{C.75}$$

This gives for the lower and upper limits for CO and methanol:

$$\theta_{CO} \in [0, 1] \to n_{CO} \in [-1, 1] \tag{C.76}$$

and

$$\theta_{CH_3OH} \in [0, 1] \to n_{CH_3OH} \in [-2, 0] \tag{C.77}$$

■

Solution 1.6

a) The three steps leading to oxygen removal are:

8. $H_2O + * \leftrightarrows H_2O*$
9. $H_2O* + * \leftrightarrows OH* + H*$
10. $OH* + * \leftrightarrows O* + H*$

(C.78)

b) The reaction order is determined by the rate-limiting step and all the steps that are in equilibrium before it. This is most likely step (5) as it involves a hydrogenation step subsequent to two other hydrogenation steps.

c) The overall rate equation, based on the rate-determining step, is given by

$$r = k_5 \theta_{H_2COO} \theta_H \tag{C.79}$$

We need to substitute the surface coverages by expressions that only contain gas-phase pressures and reaction rate constants. To start, we assume quasi-equilibrium of all elementary reaction steps before the rate-determining step.

$$\theta_H = \sqrt{K_1 p_{H_2}} \theta_* \tag{C.80}$$

$$\theta_{CO_2} = K_2 p_{CO_2} \theta_* \tag{C.81}$$

$$\theta_{HCOO} = \frac{K_3 \theta_{CO_2} \theta_H}{\theta_*} \tag{C.82}$$

$$\theta_{H_2COO} = \frac{K_4 \theta_{HCOO} \theta_H}{\theta_*} \tag{C.83}$$

By substituting the expressions for θ_H and θ_{CO_2} in equation C.82, we get

$$\theta_{HCOO} = K_3 \sqrt{K_1 p_{H_2}} K_2 p_{CO_2} \theta_* \tag{C.84}$$

This result can be readily inserted into equation C.83 to obtain

$$\theta_{H_2COO} = K_4 K_3 K_2 p_{CO_2} K_1 p_{H_2} \theta_* \tag{C.85}$$

Now, we need to use the above expressions in combination with the site-balance to construct the expression for the free sites

$$\theta_H + \theta_{CO_2} + \theta_{HCOO} + \theta_{H_2COO} + \theta_* = 1 \tag{C.86}$$

$$\theta_* \left(1 + \sqrt{K_1 p_{H_2}} + K_2 p_{CO_2} + K_3 \sqrt{K_1 p_{H_2}} K_2 p_{CO_2} + K_4 K_3 K_2 p_{CO_2} K_1 p_{H_2} \right) = 1 \tag{C.87}$$

This leads to

$$\theta_* = \frac{1}{1 + \sqrt{K_1 p_{H_2}} + K_2 p_{CO_2} + K_3 \sqrt{K_1 p_{H_2}} K_2 p_{CO_2} + K_4 K_3 K_2 p_{CO_2} K_1 p_{H_2}} \tag{C.88}$$

Using equations C.80, C.85, and C.88, we can construct the overall rate equation

$$
\begin{aligned}
r &= k_5 \theta_{\mathrm{H_2COO}} \theta_{\mathrm{H}} && \text{(C.89)}\\
&= k_5 K_4 K_3 K_2 p_{\mathrm{CO_2}} K_1 p_{\mathrm{H_2}} \sqrt{K_1 p_{\mathrm{H_2}}} \theta_*^2 && \text{(C.90)}\\
&= \frac{k_5 K_4 K_3 K_2 p_{\mathrm{CO_2}} K_1 p_{\mathrm{H_2}} \sqrt{K_1 p_{\mathrm{H_2}}}}{\left(1 + \sqrt{K_1 p_{\mathrm{H_2}}} + K_2 p_{\mathrm{CO_2}} + K_3 \sqrt{K_1 p_{\mathrm{H_2}}} K_2 p_{\mathrm{CO_2}} + K_4 K_3 K_2 p_{\mathrm{CO_2}} K_1 p_{\mathrm{H_2}}\right)^2} && \text{(C.91)}\\
&= \frac{k_5 K_4 K_3 K_2 p_{\mathrm{CO_2}} \left(K_1 p_{\mathrm{H_2}}\right)^{3/2}}{\left(1 + \sqrt{K_1 p_{\mathrm{H_2}}} + K_2 p_{\mathrm{CO_2}} + K_3 \sqrt{K_1 p_{\mathrm{H_2}}} K_2 p_{\mathrm{CO_2}} + K_4 K_3 K_2 p_{\mathrm{CO_2}} K_1 p_{\mathrm{H_2}}\right)^2} && \text{(C.92)}
\end{aligned}
$$

Let us now check whether our hypothesis that the order in H_2 is $3/2$ is correct. To make things a bit easier, let us assume that the surface is nearly empty and that $\theta_* \approx 1$, the rate equation then is

$$
r \approx k_5 K_4 K_3 K_2 p_{\mathrm{CO_2}} \left(K_1 p_{\mathrm{H_2}}\right)^{3/2} \tag{C.93}
$$

and

$$
n_{\mathrm{H_2}} = p_{\mathrm{H_2}} \frac{\partial \ln p_{\mathrm{H_2}}^{3/2}}{\partial p_{\mathrm{H_2}}} = 3/2 \tag{C.94}
$$

☁ Think deeper...

In order to find the optimal fraction, we define the constant α which is the ratio between the partial pressure of $\mathrm{H_2}$ and $\mathrm{CO_2}$.

$$
\alpha = \frac{p_{\mathrm{H_2}}}{p_{\mathrm{CO_2}}} \tag{C.95}
$$

From this, the total pressure becomes

$$
p_{\mathrm{T}} = p_{\mathrm{CO_2}} + p_{\mathrm{H_2}} = p_{\mathrm{CO_2}} + \alpha p_{\mathrm{CO_2}} = (1+\alpha) p_{\mathrm{CO_2}} \tag{C.96}
$$

and we can relate the partial pressure of $\mathrm{H_2}$ and $\mathrm{CO_2}$ to the total pressure as

$$
\begin{aligned}
p_{\mathrm{H2}} &= \frac{\alpha p_{\mathrm{T}}}{1+\alpha} && \text{(C.97)}\\
p_{\mathrm{CO2}} &= \frac{p_{\mathrm{T}}}{1+\alpha} && \text{(C.98)}\\
& && \text{(C.99)}
\end{aligned}
$$

Filling out these new expressions and assuming that the surface is nearly empty results in

$$
r = k_5 K_4 K_3 K_2 \frac{p_{\mathrm{T}}}{1+\alpha} \left(K_1 \frac{\alpha p_{\mathrm{T}}}{1+\alpha}\right)^{3/2} \tag{C.100}
$$

To find out the optimal value in α, we need to take the first derivative towards α and equate this to zero. Therefore, we can simplify the above equation by collecting all variables that do not depend on α

$$r = c\frac{\alpha^{3/2}}{(1+\alpha)^{5/2}} \tag{C.101}$$

where c is a factor that does not depend on α.

$$\frac{\partial r}{\partial \alpha} = \frac{\frac{3}{2}\alpha^{1/2}(1+\alpha)^{5/2} - \frac{5}{2}\alpha^{3/2}(1+\alpha)^{3/2}}{(1+\alpha)^5} = 0 \tag{C.102}$$

To find the value for α, only the numerator of the above expression is relevant and we can ignore the denominator

$$\begin{aligned}
\frac{3}{2}\alpha^{1/2}(1+\alpha)^{5/2} - \frac{5}{2}\alpha^{3/2}(1+\alpha)^{3/2} &= 0 && \text{(C.103)}\\
\frac{3}{2}\alpha^{1/2}(1+\alpha)^{5/2} &= \frac{5}{2}\alpha^{3/2}(1+\alpha)^{3/2} && \text{(C.104)}\\
1+\alpha &= \frac{5}{3}\alpha && \text{(C.105)}\\
\alpha &= \frac{3}{2} && \text{(C.106)}
\end{aligned}$$

This result is to be expected, as the best ratio between the partial pressures of the reactants is of course the ratio between the reaction orders of said reactants. The fraction of CO_2 in terms of the total pressure is then $\frac{2}{5}$ and the fraction of H_2 is then $\frac{3}{5}$.

■

Solution 1.7

a) We assume the steady-state approximation on θ_O. Furthermore, we assume that $\theta_\text{CO} \gg \theta_\text{O}$ and that CO is in quasi-equilibrium with the surface.

b) First, we apply the quasi-equilibrium assumption to CO giving

$$\theta_\text{CO} = K_1 p_\text{CO} \theta_* \tag{C.107}$$

Next, we apply the steady-state assumption to θ_O

$$\frac{\mathrm{d}\theta_\text{O}}{\mathrm{d}t} = 2k_2^+ p_{\text{O}_2} \theta_*^2 - k_3^+ \theta_\text{CO} \theta_\text{O} = 0 \tag{C.108}$$

Note that the second and third elementary reaction step in our mechanism are irreversible, significantly reducing the complexity of the equation. The above result gives us an expression for the partial coverage of O as

$$\theta_O = \frac{2k_2^+ p_{O_2}}{k_3^+ \theta_{CO}} \theta_*^2 \tag{C.109}$$

To obtain the expression for the free site coverage we assume that $\theta_{CO} \gg \theta_O$ giving

$$\begin{aligned} \theta_{CO} + \theta_* &= 1 && \text{(C.110)} \\ \theta_* \left(1 + K_1 p_{CO}\right) &= 1 && \text{(C.111)} \\ \theta_* &= \frac{1}{1 + K_1 p_{CO}} && \text{(C.112)} \end{aligned}$$

Plugging this result into the overall rate equation yields

$$\begin{aligned} r &= k_3^+ \theta_{CO} \theta_O && \text{(C.113)} \\ &= k_3^+ \frac{K_1 p_{CO}}{1 + K_1 p_{CO}} \frac{2k_2^+ p_{O_2}}{k_3^+ \theta_{CO}} \theta_*^2 && \text{(C.114)} \\ &= k_3^+ \frac{K_1 p_{CO}}{1 + K_1 p_{CO}} \frac{2k_2^+ p_{O_2}}{k_3^+} \left(\frac{1}{1 + K_1 p_{CO}} \right)^2 \left(\frac{K_1 p_{CO}}{1 + K_1 p_{CO}} \right)^{-1} && \text{(C.115)} \\ &= \frac{2k_2^+ p_{O_2}}{\left(1 + K_1 p_{CO}\right)^2} && \text{(C.116)} \end{aligned}$$

Note that from the above expression, we can easily see that the order in O_2 is +1 and the order in CO is between -2 and 0.

Solution 1.8

a) Synthesis gas is a mixture of CO and H_2. It is used in Fischer-Tropsch catalysis and in methanol formation. The former reaction is typically performed over a Fe or Co catalyst. The latter reaction is typically performed over a Cu catalyst.

b) In order to further increase the production of H_2, CO can be mixed with H_2O to give CO_2 and H_2. This reaction is called water-gas shift.

c) From the reaction equation ($CH_4 + H_2O \leftrightarrows CO + 3H_2$) we can see that the reaction produces more moles of gas than are consumed. Hence, in principle the reaction should be performed at low pressure to drive the equilibrium to the right hand side of the equation. However, in a typical reactor a moderate pressure is used as to reduce the reactor volume.

Furthermore, the reaction needs to be performed at high temperature, because this reaction is strongly endothermic. Again, the high temperature pushes the equilibrium to the right hand side of the equation.

d) To start, we need to propose a reaction mechanism in terms of a set of elementary reaction steps. To convert methane and water into synthesis gas, a set of 10 elementary reaction steps is necessary.

1. $CH_4 + 2^* \leftrightarrows CH_3{}^* + H^*$
2. $CH_3{}^* + {}^* \leftrightarrows CH_2{}^* + H^*$
3. $CH_2{}^* + {}^* \leftrightarrows CH^* + H^*$
4. $CH^* + {}^* \leftrightarrows C^* + H^*$
5. $H_2O + {}^* \leftrightarrows H_2O^*$
6. $H_2O^* + {}^* \leftrightarrows OH^* + H^*$
7. $OH^* + {}^* \leftrightarrows O^* + H^*$
8. $H_2 + 2^* \leftrightarrows 2H^*$
9. $C^* + O^* \leftrightarrows CO^* + {}^*$
10. $CO + {}^* \leftrightarrows CO^*$

We assume that all the above steps, except the rate-limiting step (9) are in quasi-equilibrium. As such, we can express all surface coverages by one or more equilibrium constants as follows

$$\theta_{\mathrm{CO}} = K_{10} p_{\mathrm{CO}} \theta_* \tag{C.117}$$

$$\theta_{\mathrm{H}} = \sqrt{K_8 p_{\mathrm{H_2}}}\, \theta_* \tag{C.118}$$

$$\theta_{\mathrm{H_2O}} = K_5 p_{\mathrm{H_2O}} \theta_* \tag{C.119}$$

$$\theta_{\mathrm{OH}} = \frac{K_6 \theta_{\mathrm{H_2O}} \theta_*}{\theta_{\mathrm{H}}} = \frac{K_5 K_6 p_{\mathrm{H_2O}}}{\sqrt{K_8 p_{\mathrm{H_2}}}} \theta_* \tag{C.120}$$

$$\theta_{\mathrm{O}} = \frac{K_7 \theta_{\mathrm{OH}} \theta_*}{\theta_{\mathrm{H}}} = \frac{K_7 \frac{K_5 K_6 p_{\mathrm{H_2O}}}{\sqrt{K_8 p_{\mathrm{H_2}}}} \theta_*^2}{\sqrt{K_8 p_{\mathrm{H_2}}}\, \theta_*} = \frac{K_5 K_6 K_7}{K_8} \frac{p_{\mathrm{H_2O}}}{p_{\mathrm{H_2}}} \theta_* \tag{C.121}$$

In the above expressions for O and OH, we have applied subsequent substitution of the surface coverages in such a way that we can express every surface coverage in terms of the partial pressures of the reactants or products and the equilibrium constants. These equilibrium constants correspond to the elementary reaction steps that connect the partial pressures with the surface coverages. Below, the same is done for the surface coverages of the CH_x intermediates

$$\theta_{\mathrm{CH_3}} = \frac{K_1 p_{\mathrm{CH_4}}}{\sqrt{K_8 p_{\mathrm{H_2}}}} \theta_* \tag{C.122}$$

$$\theta_{\mathrm{CH_2}} = \frac{K_1 K_2 p_{\mathrm{CH_4}}}{K_8 p_{\mathrm{H_2}}} \theta_* \tag{C.123}$$

$$\theta_{\mathrm{CH}} = \frac{K_1 K_2 K_3 p_{\mathrm{CH_4}}}{\left(K_8 p_{\mathrm{H_2}}\right)^{3/2}} \theta_* \tag{C.124}$$

$$\theta_{\mathrm{C}} = \frac{K_1 K_2 K_3 K_4 p_{\mathrm{CH_4}}}{\left(K_8 p_{\mathrm{H_2}}\right)^2} \theta_* \tag{C.125}$$

Now we can construct the site-balance

$$\theta_{\mathrm{CO}} + \theta_{\mathrm{H}} + \theta_{\mathrm{H_2O}} + \theta_{\mathrm{OH}} + \theta_{\mathrm{O}} + \theta_{\mathrm{CH_3}} + \theta_{\mathrm{CH_2}} + \theta_{\mathrm{CH}} + \theta_{\mathrm{C}} + \theta_* = 1 \tag{C.126}$$

and plug the above equations for the surface coverages into it

$$\theta_* = \Bigg(1 + K_{10}p_{\mathrm{CO}} + \sqrt{K_8 p_{\mathrm{H_2}}} + K_5 p_{\mathrm{H_2O}} + \frac{K_5K_6p_{\mathrm{H_2O}}}{\sqrt{K_8p_{\mathrm{H_2}}}} + \frac{K_5K_6K_7}{K_8}\frac{p_{\mathrm{H_2O}}}{p_{\mathrm{H_2}}} + \frac{K_1p_{\mathrm{CH_4}}}{\sqrt{K_8p_{\mathrm{H_2}}}} \cdots$$
$$\cdots + \frac{K_1K_2p_{\mathrm{CH_4}}}{K_8p_{\mathrm{H_2}}} + \frac{K_1K_2K_3p_{\mathrm{CH_4}}}{\left(K_8p_{\mathrm{H_2}}\right)^{3/2}} + \frac{K_1K_2K_3K_4p_{\mathrm{CH_4}}}{\left(K_8p_{\mathrm{H_2}}\right)^{2}}\Bigg)^{-1} \tag{C.127}$$

Since the overall rate is determined by the rate of step 9 we can construct the following expression

$$r = k_9^+\theta_{\mathrm{C}}\theta_{\mathrm{O}} - k_9^-\theta_{\mathrm{CO}}\theta_* \tag{C.128}$$
$$= k_9^+\theta_{\mathrm{C}}\theta_{\mathrm{O}} - \frac{k_9^+}{K_9}\theta_{\mathrm{CO}}\theta_* \tag{C.129}$$

If we assume that there is an equilibrium $r = 0$, we can express K_9 as

$$K_9 = \frac{\theta_{\mathrm{CO}}\theta_*}{\theta_{\mathrm{C}}\theta_{\mathrm{O}}} = \frac{p_{\mathrm{CO}}p_{\mathrm{H_2}}^3}{p_{\mathrm{H_2O}}p_{\mathrm{CH_4}}}\frac{K_8^3K_{10}}{K_1K_2K_3K_4K_5K_6K_7} = \frac{p_{\mathrm{CO}}p_{\mathrm{H_2}}^3}{p_{\mathrm{H_2O}}p_{\mathrm{CH_4}}}\frac{1}{K_{\mathrm{eq}}} \tag{C.130}$$

and using this result for K_9 for our overall rate expression results in

$$r = k_9^+\theta_{\mathrm{C}}\theta_{\mathrm{O}} - k_9^-\theta_{\mathrm{CO}}\theta_* \tag{C.131}$$
$$= k_9^+\theta_{\mathrm{C}}\theta_{\mathrm{O}}\left(1 - \frac{1}{K_9}\frac{\theta_{\mathrm{CO}}\theta_*}{\theta_{\mathrm{C}}\theta_{\mathrm{O}}}\right) \tag{C.132}$$
$$= k_9^+\frac{K_1K_2K_3K_4K_5K_6K_7p_{\mathrm{CH_4}}p_{\mathrm{H_2O}}}{\left(K_8p_{\mathrm{H_2}}\right)^3}\left(1 - \frac{1}{K_9}\frac{p_{\mathrm{CO}}p_{\mathrm{H_2}}^3}{p_{\mathrm{H_2}}p_{\mathrm{CH_4}}}\frac{1}{K_{\mathrm{eq}}}\right)\theta_*^2 \tag{C.133}$$

Further assuming that O is the MARI, we can use the following equation for the free sites

$$\theta_* = \left(1 + \frac{K_5K_6K_7}{K_8}\frac{p_{\mathrm{H_2O}}}{p_{\mathrm{H_2}}}\right)^{-1} \tag{C.134}$$

giving

$$r = k_9^+\frac{\dfrac{K_1K_2K_3K_4K_5K_6K_7p_{\mathrm{CH_4}}p_{\mathrm{H_2O}}}{\left(K_8p_{\mathrm{H_2}}\right)^3}\left(1 - \dfrac{1}{K_9}\dfrac{p_{\mathrm{CO}}p_{\mathrm{H_2}}^3}{p_{\mathrm{H_2}}p_{\mathrm{CH_4}}}\dfrac{1}{K_{\mathrm{eq}}}\right)}{\left(1 + \dfrac{K_5K_6K_7}{K_8}\dfrac{p_{\mathrm{H_2O}}}{p_{\mathrm{H_2}}}\right)^2} \tag{C.135}$$

For low conversions, the second term between parentheses in the numerator can be neglected, further simplifying the equation to

$$r = k_9^+ \frac{K_1 K_2 K_3 K_4 K_5 K_6 K_7 p_{CH_4} p_{H_2O}}{(K_8 p_{H_2})^3} \left(1 + \frac{K_5 K_6 K_7}{K_8} \frac{p_{H_2O}}{p_{H_2}}\right)^{-2} \tag{C.136}$$

e) Note that for CH_4 and CO, there are no dependencies in the term between parentheses, so we only need to evaluate the derivative for the part in front of the parentheses. Again, we apply the same trick as in the previous exercise, so that we obtain:

$$n_{CH_4} = p_{CH_4} \frac{\partial \ln(r^+)}{\partial p_{CH_4}} = 1 \tag{C.137}$$

$$n_{CO} = p_{CO} \frac{\partial \ln(r^+)}{\partial p_{CO}} = 0 \tag{C.138}$$

The reaction order in H_2O and H_2 is a bit more complicated but with some rewriting the derivatives equate to

$$\begin{aligned} n_{H_2O} = p_{H_2O} \frac{\partial \ln(r^+)}{\partial p_{H_2O}} &= 1 - 2 p_{H_2O} \frac{K_5 K_6 K_7}{K_8} \frac{\partial p_{H_2O}/\partial p_{H_2O}}{1 + \frac{K_5 K_6 K_7}{K_8 p_{H_2}} \frac{p_{H_2O}}{p_{H_2}}} && \text{(C.139)} \\ &= 1 - 2 \frac{K_5 K_6 K_7}{K_8} \frac{p_{H_2O}}{p_{H_2}} \left(1 + \frac{K_5 K_6 K_7}{K_8 p_{H_2}} \frac{p_{H_2O}}{p_{H_2}}\right)^{-1} && \text{(C.140)} \\ &= 1 - 2\theta_O && \text{(C.141)} \end{aligned}$$

and similarly for H_2

$$n_{H_2} = p_{H_2} \frac{\partial \ln(r^+)}{\partial p_{H_2}} = -3 + 2\theta_O \tag{C.142}$$

From the above expressions for the order, we note that the experimental results are not within the limits of the reaction orders. Consequently, the proposed reaction mechanism is not in agreement with the experiment and needs to be revised.

f) Applying the same procedure as previously, the reaction rate now equates to

$$r = k_1^+ \frac{p_{CH_4}}{\left(1 + \frac{K_5 K_6 K_7}{K_8 p_{H_2}} \frac{p_{H_2O}}{p_{H_2}}\right)^2} \tag{C.143}$$

Note that steps 2-4 do not appear in the rate equation, because only the first dissociative methane adsorption step is kinetically relevant. The equilibrium constants for steps 5-8 appear in the denominator because they control the amount of O on the surface.

From the above rate equation, we can establish the reaction orders to be

$$n_{CH_4} = p_{CH_4} \frac{\partial \ln(r^+)}{\partial p_{CH_4}} = 1 \tag{C.144}$$

$$n_{CO} = p_{CO} \frac{\partial \ln(r^+)}{\partial p_{CO}} = 0 \tag{C.145}$$

$$n_{H_2O} = p_{H_2O} \frac{\partial \ln(r^+)}{\partial p_{H_2O}} = -2\theta_O \tag{C.146}$$

$$n_{H_2} = p_{H_2} \frac{\partial \ln(r^+)}{\partial p_{H_2}} = 2\theta_O \tag{C.147}$$

These results are consistent with the experimental observation.

■

Solution 1.9

a) C_2H_6 adsorption coincides with D_2 adsorption. Upon adsorption, the hydrogen in the C_2H_6 complex can be exchanged for a deuterium by successive dehydrogenation, deuteration and a desorption step.

b)

$$r = k_2^+ \theta_{C_2H_5} \theta_H - k_2^- \theta_{CH_3}^2 \tag{C.148}$$

c) The steady state equation applied to elementary reaction steps 1,3 and 4 and considering competitive adsorption, the Langmuir isotherms for ethyl, methyl and hydrogen become as follows

$$\theta_{C_2H_5} = \frac{K_1 p_{C_2H_6}}{\theta_H} \theta_*^2 \tag{C.149}$$

$$\theta_{CH_3} = \frac{p_{CH_4}}{K_3 \theta_H} \theta_*^2 \tag{C.150}$$

$$\theta_H = \sqrt{K_4 p_{H_2}} \theta_* \tag{C.151}$$

Plugging equation C.151 into C.149 and into C.150, gives

$$\theta_{C_2H_5} = \frac{K_1 p_{C_2H_6}}{\sqrt{K_4 p_{H_2}}} \theta_* \tag{C.152}$$

and

$$\theta_{CH_3} = \frac{p_{CH_4}}{K_3\sqrt{K_4 p_{H_2}}}\theta_* \tag{C.153}$$

Using the site balance, we obtain the following equations

$$\theta_* = \frac{1}{1 + \frac{K_1 p_{C_2H_6}}{\sqrt{K_4 p_{H_2}}} + \frac{p_{CH_4}}{K_3\sqrt{K_4 p_{H_2}}} + \sqrt{K_4 p_{H_2}}} \tag{C.154}$$

$$\theta_{C_2H_5} = \frac{\frac{K_1 p_{C_2H_6}}{\sqrt{K_4 p_{H_2}}}}{1 + \frac{K_1 p_{C_2H_6}}{\sqrt{K_4 p_{H_2}}} + \frac{p_{CH_4}}{K_3\sqrt{K_4 p_{H_2}}} + \sqrt{K_4 p_{H_2}}} \tag{C.155}$$

$$\theta_{CH_3} = \frac{\frac{p_{CH_4}}{K_3\sqrt{K_4 p_{H_2}}}}{1 + \frac{K_1 p_{C_2H_6}}{\sqrt{K_4 p_{H_2}}} + \frac{p_{CH_4}}{K_3\sqrt{K_4 p_{H_2}}} + \sqrt{K_4 p_{H_2}}} \tag{C.156}$$

$$\theta_{H} = \frac{\sqrt{K_4 p_{H_2}}}{1 + \frac{K_1 p_{C_2H_6}}{\sqrt{K_4 p_{H_2}}} + \frac{p_{CH_4}}{K_3\sqrt{K_4 p_{H_2}}} + \sqrt{K_4 p_{H_2}}} \tag{C.157}$$

d) Plugging the above equations into the overall rate equation yields

$$r = \frac{k_2^+ K_1 p_{C_2H_6}\left(1 - \frac{p_{CH_4}^2}{K_1 K_2 K_3^2 K_4 p_{C_2H_6} p_{H_2}}\right)}{\left(1 + \frac{K_1 p_{C_2H_6}}{\sqrt{K_4 p_{H_2}}} + \frac{p_{CH_4}}{K_3\sqrt{K_4 p_{H_2}}} + \sqrt{K_4 p_{H_2}}\right)^2} \tag{C.158}$$

e) Applying the MARI approximation and assuming low conversion simplifies the overall rate equation to

$$r = \frac{k_2^+ K_1 p_{C_2H_6}}{\left(1 + \sqrt{K_4 p_{H_2}}\right)^2} \tag{C.159}$$

Think deeper...

The apparent activation energy can be readily evaluated to

$$\begin{aligned}
\Delta E_{act}^{app} &= RT^2 \frac{\partial \ln(r^+)}{\partial T} && \text{(C.160)}\\
&= RT^2\left(\frac{\partial \ln k_2^+}{\partial T} + \frac{\partial \ln K_1}{\partial T} - 2\frac{\partial \ln\left(1 + \sqrt{K_4 p_{H_2}}\right)}{\partial T}\right) && \text{(C.161)}\\
&= E_{act}^{(2)} + \Delta H_{ads}^{(1)} - \theta_H \Delta H_{ads}^{(4)} && \text{(C.162)}
\end{aligned}$$

■

Solution 1.10

a) From the quasi-equilibrated steps (1), (2) and (4), it follows that

$$\theta_{NO} = K_1 p_{NO} \theta_* \tag{C.163}$$

$$\theta_{CO} = K_2 p_{CO} \theta_* \tag{C.164}$$

$$\theta_N = \sqrt{K_4 p_{N_2}} \theta_* \tag{C.165}$$

To derive the surface coverage of O*, we apply the steady-state approximation to this surface intermediate

$$2k_3^+ p_{O_2} \theta_*^2 - k_6^+ \theta_{CO} \theta_O = 0 \tag{C.166}$$

Note that we have neglected the term $k_5^+ \theta_{CO} \theta_O$, because we assume that NO dissociation is rate-determining. Therefore, this term is negligible compared to the other two terms.

It follows then that

$$\theta_O = \frac{2k_3^+ p_{O_2}}{k_6^+ \theta_{CO}} \theta_*^2 \tag{C.167}$$

Combining this expression with the expression for θ_{CO}, we obtain

$$\theta_O = \frac{2k_3^+ p_{O_2}}{k_6^+ K_2 p_{CO} \theta_*} \theta_*^2 = \frac{2k_3^+ p_{O_2}}{k_6^+ K_2 p_{CO}} \theta_* \tag{C.168}$$

Applying the site balance for all surface intermediates yields

$$\theta_* = \frac{1}{1 + K_1 p_{NO} + K_2 p_{CO} + \frac{2k_3^+ p_{O_2}}{k_6^+ K_2 p_{CO}} + \sqrt{K_4 p_{N_2}}} \tag{C.169}$$

Finally, we can evaluate the rate of N_2 and CO_2 production

$$r_{N_2} = \frac{1}{2} r_5 = \frac{1}{2} k_5^+ \theta_{NO} \theta_* = \frac{\frac{1}{2} k_5^+ K_1 p_{NO}}{\left(1 + K_1 p_{NO} + K_2 p_{CO} + \frac{2k_3^+ p_{O_2}}{k_6^+ K_2 p_{CO}} + \sqrt{K_4 p_{N_2}}\right)^2} \tag{C.170}$$

$$r_{CO_2} = r_6 = k_6^+ \theta_{CO}\theta_O = \frac{2k_3^+ p_{O_2}}{\left(1 + K_1 p_{NO} + K_2 p_{CO} + \frac{2k_3^+ p_{O_2}}{k_6^+ K_2 p_{CO}} + \sqrt{K_4 p_{N_2}}\right)^2} \tag{C.171}$$

Think deeper...

This catalytic reaction pertains to three-way catalytic convertors for environmental pollution control.

■

Solution 1.11

a)

$$1. C_2H_4 + * \leftrightarrows C_2H_4* \tag{C.172}$$
$$2. O_2 + 2* \leftrightarrows 2O* \tag{C.173}$$
$$3. C_2H_4* + O* \rightarrow C_2H_4O + 2* \tag{C.174}$$
$$\tag{C.175}$$

Applying a quasi-equilibrium approximation, we obtain the following expressions for the partial coverages as a function of the partial pressures and equilibrium constants

$$\theta_{C_2H_4} = K_1 p_{C_2H_4} \theta_* \tag{C.176}$$

and

$$\theta_O = \sqrt{K_2 p_{O_2}}\theta_* \tag{C.177}$$

Note that because ethylene-oxide desorbs rapidly, the surface coverage of ethylene-oxide is negligible. Thus, we obtain by constructing a site-balance (not shown here), the following Langmuir-Hinshelwood isotherms:

$$\theta_{C_2H_4} = \frac{K_1 p_{C_2H_4}}{1 + K_1 p_{C_2H_4} + \sqrt{K_2 p_{O_2}}} \tag{C.178}$$

and

$$\theta_O = \frac{\sqrt{K_2 p_{O_2}}}{1 + K_1 p_{C_2H_4} + \sqrt{K_2 p_{O_2}}}. \tag{C.179}$$

b)

$$r_{C_2H_4O} = k_3\theta_{C_2H_4}\theta_O \tag{C.180}$$

$$= \frac{k_3K_1p_{C_2H_4}\sqrt{K_2p_{O_2}}}{\left(1+K_1p_{C_2H_4}+\sqrt{K_2p_{O_2}}\right)^2} \tag{C.181}$$

c) If oxygen strongly adsorbs, we can assume that oxygen is the MARI and hence the overall rate expression simplifies to

$$r_{C_2H_4O} = \frac{k_3K_1p_{C_2H_4}\sqrt{K_2p_{O_2}}}{\left(1+\sqrt{K_2p_{O_2}}\right)^2} \tag{C.182}$$

The reaction orders in oxygen and ethylene are

$$n_{C_2H_4} = p_{C_2H_4}\frac{\partial \ln(r^+)}{\partial p_{C_2H_4}} \tag{C.183}$$

$$= 1 \tag{C.184}$$

$$n_{O_2} = p_{O_2}\frac{\partial \ln(r^+)}{\partial p_{O_2}} \tag{C.185}$$

$$= \frac{1}{2} - \theta_O \tag{C.186}$$

d) The surface is predominantly occupied with adsorbed O.

e)

$$\Delta E_{act}^{app} = RT^2\frac{\partial \ln(r^+)}{\partial T} \tag{C.187}$$

$$= E_{act}^{(3)} + \Delta H_{ads}^{(1)} + \left(\frac{1}{2}-\theta_O\right)\Delta H_{ads}^{(2)} \tag{C.188}$$

■

Solution 1.12

a)

$$1. SO_2 + * \leftrightarrows SO_2* \tag{C.189}$$

$$2. O_2 + 2* \leftrightarrows 2O* \tag{C.190}$$

$$3. SO_2* + O* \rightarrow SO_3* + * \tag{C.191}$$

$$4. SO_3 + * \leftrightarrows SO_3* \tag{C.192}$$

b)

$$r_{SO_3} = k_3 \theta_{SO_2} \theta_O \tag{C.193}$$

Applying the pre-equilibrium, the irreversible step and the rate-limiting step approximation we can derive the following expression for the free sites and for the overall reaction rate.

$$\theta_* = \frac{1}{1 + K_1 p_{SO_2} + \sqrt{K_2 p_{O_2}} + K_4 p_{SO_3}} \tag{C.194}$$

$$r_{SO_3} = \frac{k_3 K_1 p_{SO_2} \sqrt{K_2 p_{O_2}}}{\left(1 + K_1 p_{SO_2} + \sqrt{K_2 p_{O_2}} + K_4 p_{SO_3}\right)^2} \tag{C.195}$$

c) From the form of the overall reaction equation, the limits of the reaction orders can be established as

$$n_{SO_2} \in [-1, 1] \tag{C.196}$$

$$n_{SO_3} \in [-2, 0] \tag{C.197}$$

$$n_{O_2} \in [-\frac{1}{2}, \frac{1}{2}] \tag{C.198}$$

d) If O_2 strongly adsorbs, then we can apply the MARI approximation for O. This gives the following expression for the rate and the reaction orders

$$r_{SO_3} = \frac{k_3 K_1 p_{SO_2} \sqrt{K_2 p_{O_2}}}{\left(1 + \sqrt{K_2 p_{O_2}}\right)^2} \tag{C.199}$$

$$n_{SO_2} = 1 \tag{C.200}$$

$$n_{SO_3} = 0 \tag{C.201}$$

$$n_{O_2} = \frac{1}{2} - \theta_O \tag{C.202}$$

e)

$$\Delta E_{act}^{app} = RT^2 \frac{\partial \ln(r^+)}{\partial T} \tag{C.203}$$

$$= E_{act}^{(3)} + \Delta H_{ads}^{(1)} + \left(\frac{1}{2} - \theta_O\right) \Delta H_{ads}^{(2)} \tag{C.204}$$

f) From the form of the equation, it is clear that two different types of Langmuir isotherms are present. This indicates that there are two different types of surface sites that have particular adsorbates that adsorb on these sites. The rate-determining step proceeds between two species that are adsorbed on these two different sites.

■

Solution 1.13

a)

$$1.C_2H_5OH + * \leftrightarrows C_2H_5OH* \tag{C.205}$$

$$2.O_2 + 2* \leftrightarrows 2O* \tag{C.206}$$

$$3.C_2H_5OH* + O* \rightarrow C_2H_4O + H_2O + 2* \tag{C.207}$$

$$\theta_{C_2H_5OH} = \frac{K_1 p_{C_2H_5OH}}{1 + K_1 p_{C_2H_5OH} + \sqrt{K_2 p_{O_2}}} \tag{C.208}$$

$$\theta_O = \frac{\sqrt{K_2 p_{O_2}}}{1 + K_1 p_{C_2H_5OH} + \sqrt{K_2 p_{O_2}}} \tag{C.209}$$

b)

$$r = k_3 \theta_{C_2H_5OH} \theta_O = \frac{k_3 K_1 p_{C_2H_5OH} \sqrt{K_2 p_{O_2}}}{\left(1 + K_1 p_{C_2H_5OH} + \sqrt{K_2 p_{O_2}}\right)^2} \tag{C.210}$$

c)

$$r = k_3 \theta_{C_2H_5OH} \theta_O = \frac{k_3 K_1 p_{C_2H_5OH} \sqrt{K_2 p_{O_2}}}{\left(1 + K_1 p_{C_2H_5OH}\right)^2} \tag{C.211}$$

$$n_{C_2H_5OH} \in [-1, 1] \tag{C.212}$$

$$n_{O_2} = \frac{1}{2} \tag{C.213}$$

d)

$$\Delta E_{act}^{app} = RT^2 \frac{\partial \ln(r^+)}{\partial T} \tag{C.214}$$

$$= E_{act}^{(3)} + \left(1 - 2\theta_{C_2H_5OH}\right) \Delta H_{ads}^{(1)} + \frac{1}{2} \Delta H_{ads}^{(2)} \tag{C.215}$$

The apparent activation energy depends on the reaction barrier of the rate-determining step and all kinetically relevant steps that proceed before the rate-determining step (which are at equilibrium). In this particular case, this means that the apparent activation energy is decreased due to the release of energy by the O_2 adsorption and is increased in the case that there is a high surface coverage of ethanol. When the surface coverage of ethanol is high, one ethanol molecule needs to desorb in order to form a vacant site necessary for this reaction to occur. If on the other hand the surface coverage of ethanol is very low (and a sufficiently large amount of free sites are present), the apparent activation energy is decreased even more as the adsorption heat of ethanol further decreases the apparent activation energy.

e) In the case of elevated temperatures, both ethanol and oxygen only sporadically adsorb on the surface as these compounds have a higher entropy in the gas phase than adsorbed on the surface. Consequently, the catalytic surface is predominantly empty.

■

Solution 1.14

a)

$$r = k_3^+ \theta_O \theta_H - k_3^- \theta_{OH} \theta_* \tag{C.216}$$

b) The surface concentrations of θ_H, θ_O, θ_{OH} and θ_* can be found using the pre-equilibrium approximation. In that way, we can express these surface concentrations as a function of the partial pressures and the equilibrium constants.

$$\theta_H = \sqrt{K_1 p_{H_2}} \theta_* \tag{C.217}$$

$$\theta_O = \sqrt{K_2 p_{O_2}} \theta_* \tag{C.218}$$

$$\theta_{H_2O} = K_5 p_{H_2O} \theta_* \tag{C.219}$$

$$\theta_{OH} = \frac{\theta_{H_2O}\theta_*}{K_4 \theta_H} \tag{C.220}$$

(C.221)

Substituting these surface concentrations into the rate equation yields

$$r = k_3^+ \sqrt{K_1 p_{H_2}} \theta_* \sqrt{K_2 p_{O_2}} \theta_* - k_3^- \frac{\theta_{H_2O}\theta_*}{K_4 \theta_H} \theta_* \tag{C.222}$$

$$= k_3^+ \sqrt{K_1 K_2 p_{H_2} p_{O_2}} \theta_*^2 - k_3^- \frac{K_5 p_{H_2O} \theta_*^2}{K_4 \sqrt{K_1 p_{H_2}} \theta_*} \theta_* \tag{C.223}$$

$$= k_3^+ \sqrt{K_1 K_2 p_{H_2} p_{O_2}} \theta_*^2 - k_3^- \frac{K_5 p_{H_2O}}{K_4 \sqrt{K_1 p_{H_2}}} \theta_*^2 \tag{C.224}$$

$$= k_3^+ \sqrt{K_1 K_2 p_{H_2} p_{O_2}} \theta_*^2 \left(1 - k_3^- \frac{K_5 p_{H_2O}}{k_3^+ K_4 K_1 p_{H_2} \sqrt{K_2 p_{O_2}}}\right) \tag{C.225}$$

$$= k_3^+ \sqrt{K_1 K_2 p_{H_2} p_{O_2}} \theta_*^2 \left(1 - \frac{p_{H_2O}}{K_{eq} p_{H_2} \sqrt{p_{O_2}}}\right) \tag{C.226}$$

From the last two expressions, it is clear that the equilbrium constant has to be

$$K_{eq} = \frac{K_1 \sqrt{K_2} K_3 K_4}{K_5} \tag{C.227}$$

c) The free site coverage can be readily obtained from the expressions of the surface coverages in terms of equilibrium constants and the site balance:

$$\theta_* = \frac{1}{1 + \sqrt{K_1 p_{H_2}} + \sqrt{K_2 p_{O_2}} + \frac{K_5 p_{H_2O}}{K_4 \sqrt{K_1 p_{H_2}}} + K_5 p_{H_2O}} \tag{C.228}$$

This expression simplifies by applying the MARI approximation (alternatively, you can start by defining a site balance only containing O* and then derive the expression below).

$$\theta_* = \frac{1}{1+\sqrt{K_2 p_{O_2}}} \tag{C.229}$$

d) To establish the reaction order, first fill out the expression for the free sites in the overall rate equation

$$r = k_3^+ \sqrt{K_1 K_2 p_{H_2} p_{O_2}} \left(1 - \frac{p_{H_2O}}{K_{eq} p_{H_2} \sqrt{p_{O_2}}}\right) \cdot \left(\frac{1}{1+\sqrt{K_2 p_{O_2}}}\right)^2 \tag{C.230}$$

Because we assume that the reaction is far from equilibrium, we can neglect the second term between the first set of brackets giving

$$r = \frac{k_3^+ \sqrt{K_1 K_2 p_{H_2} p_{O_2}}}{\left(1+\sqrt{K_2 p_{O_2}}\right)^2} \tag{C.231}$$

From the above expression, the following reaction orders can be derived (please refer to the previous answers for a more thorough derivation).

$$n_{H_2} = \frac{1}{2} \tag{C.232}$$

$$n_{O_2} = \frac{1}{2} - \theta_O \tag{C.233}$$

$$n_{H_2O} = 0 \tag{C.234}$$

e) For very low surface coverage, the rate equals to

$$r = k_3^+ \sqrt{K_1 K_2 p_{H_2} p_{O_2}} \tag{C.235}$$

Plugging in the following expressions for p_{H_2} and p_{O_2}

$$p_{H_2} = \alpha \cdot p_T \tag{C.236}$$

$$p_{O_2} = (1-\alpha) \cdot p_T \tag{C.237}$$

we obtain

$$r = k_3^+ \sqrt{K_1 K_2 \alpha (1-\alpha)} p_T \tag{C.238}$$

Taking the first derivative and equating to zero yields ($\frac{\partial r}{\partial \alpha} = 0$):

$$\alpha = \frac{1}{2} \tag{C.239}$$

In other words: the partial pressure of hydrogen and of oxygen need to be equal.

Think deeper...

The apparent activation energy is

$$\Delta E_{\text{act}}^{\text{app}} = RT^2 \frac{\partial \ln(r^+)}{\partial T} = E_{\text{act}}^{(3)} + \frac{1}{2}\Delta H_{\text{ads}}^{(1)} + \frac{1}{2}\Delta H_{\text{ads}}^{(2)} \tag{C.240}$$

The reaction takes place on a nearly empty surface. For the reaction to take place we need to have one H and one O to be adsorbed. Their adsorption facilitates the process (lowers the apparent activation energy) by half the adsorption enthalpy of the corresponding molecule. The only positive contribution to the apparent activation energy originates from the barrier of elementary reaction step #3.

■

Solution 1.15

a)

$$\frac{1}{2} r_{N_2} = r_5 = k_5^+ \theta_{NO}\theta_* - k_5^- \theta_N \theta_O \tag{C.241}$$

Because all other steps are quasi-equilibrated, we can write

$$\theta_{NO} = K_1 p_{NO} \theta_* \tag{C.242}$$

$$\theta_{CO} = K_2 p_{CO} \theta_* \tag{C.243}$$

$$\theta_{N_2} = K_3 p_{N_2} \theta_* \tag{C.244}$$

$$\theta_N = \sqrt{K_4 \theta_{N_2} \theta_*} = \sqrt{K_4 K_3 p_{N_2} \theta_* \theta_*} = \sqrt{K_3 K_4 p_{N_2}}\theta_* \tag{C.245}$$

$$\theta_O = \frac{\theta_{CO_2}\theta_*}{K_6 \theta_{CO}} = \frac{K_7 p_{CO_2}\theta_*\theta_*}{K_6 K_2 p_{CO}\theta_*} = \frac{K_7 p_{CO_2}}{K_2 K_6 p_{CO}}\theta_* \tag{C.246}$$

$$\theta_{CO_2} = K_7 p_{CO_2} \theta_* \tag{C.247}$$

Using the site balance, this results in

$$\theta_* = \frac{1}{1 + K_1 p_{NO} + K_2 p_{CO} + K_3 p_{N_2} + \sqrt{K_3 K_4 p_{N_2}} + \frac{K_7 p_{CO_2}}{K_2 K_6 p_{CO}} + K_7 p_{CO_2}} \tag{C.248}$$

Plugging this into the overall rate expression and defining an overall reaction equilibrium constant we obtain

$$r_5 = \frac{k_5^+ K_1 p_{NO}\left(1 - \frac{\sqrt{p_{N_2}}p_{CO_2}}{p_{CO}p_{NO}}\frac{1}{K_{\text{eq}}}\right)}{\left(1 + K_1 p_{NO} + K_2 p_{CO} + K_3 p_{N_2} + \sqrt{K_3 K_4 p_{N_2}} + \frac{K_7 p_{CO_2}}{K_2 K_6 p_{CO}} + K_7 p_{CO_2}\right)^2} \tag{C.249}$$

where

$$K_{\text{eq}} = \frac{K_1 K_2 K_5 K_6}{\sqrt{K_4}\sqrt{K_3} K_7} \tag{C.250}$$

b) If O is the MARI, then the overall rate equation simplifies to

$$r_5 = \frac{k_5^+ K_1 p_{\text{NO}} \left(1 - \frac{\sqrt{p_{\text{N}_2}} p_{\text{CO}_2}}{p_{\text{CO}} p_{\text{NO}}} \frac{1}{K_{\text{eq}}}\right)}{\left(1 + \frac{K_7 p_{\text{CO}_2}}{K_2 K_6 p_{\text{CO}}}\right)^2} \tag{C.251}$$

Note that the reaction order is always defined by the derivative of the **forward** direction of the rate. Hence we do not have to take the second term within the brackets in the nominator into account. In other words

$$r^+ = \frac{k_5^+ K_1 p_{\text{NO}}}{\left(1 + \frac{K_7 p_{\text{CO}_2}}{K_2 K_6 p_{\text{CO}}}\right)^2} \tag{C.252}$$

We obtain the following reaction orders

$$n_{\text{N}_2} = 0 \tag{C.253}$$
$$n_{\text{NO}} = 1 \tag{C.254}$$
$$n_{\text{CO}} = 2\theta_{\text{O}} \tag{C.255}$$
$$n_{\text{CO}_2} = -2\theta_{\text{O}} \tag{C.256}$$

The surface contains only O* and *. There is no N_2* on the surface, so lowering or increasing the partial pressure of N_2 has no effect on the overall rate. Hence the reaction order in N_2 is 0. The rate scales linearly with the partial pressure in NO because its partial pressure directly controls the amount of surface NO and accordingly, the overall rate. If we increase the CO partial pressure, the CO coverage increases which lowers the amount of O* on the surface and results in more sites for NO adsorption. In constrast, adding CO_2 will increase the surface coverage of CO_2 and in turn the O* coverage. This leads to a lower NO surface coverage and hence the rate decreases. Hence, the order in CO_2 is negative.

c) The apparent activation energy for the nearly empty surface yields

$$\Delta E_{\text{act}}^{\text{app}} = RT^2 \frac{\partial \ln(r^+)}{\partial T} = E_{\text{act}}^{(5)} + \Delta H_{\text{ads}}^{(1)} \tag{C.257}$$

The surface is nearly empty and one way to increase the rate, is to adsorb more NO. The latter depends on its adsorption energy, hence the negative contribution of the adsorption energy to the apparent activation energy. (note that adsorption energies are always negative, so the (+)-sign in the equation in conjunction with the negative energy results in a negative contribution)

Alternatively, the barrier for the rate-determining elementary reaction step could be lowered. Note that this is purely hypothetical. In practice this could perhaps be done using promotors, but it turns out that lowering the barrier of an elementary reaction step in practive is very difficult to say the least. Nevertheless, if possible, then a lowering of the barrier of the elementary reaction step results in a lowering of the apparent activation energy and hence in an increase of the overall rate.

☁ **Think deeper...**

The apparent activation energy in this particular situation would be

$$\Delta E_{\text{act}}^{\text{app}} = RT^2 \frac{\partial \ln(r^+)}{\partial T} = E_{\text{act}}^{(5)} + \Delta H_{\text{ads}}^{(1)} + 2\theta_{\text{O}} \left(\Delta H_{\text{ads}}^{(2)} + \Delta H_{\text{ads}}^{(6)} - \Delta H_{\text{ads}}^{(7)} \right) \tag{C.258}$$

Note that the complete derivation of the above expression is more a test of mathematical stamina than of chemical understanding.

■

Solution 1.16

a) If the third elementary reaction step is the RDS, the overall rate towards H_2O_2 is given by the following equation:

$$r_{\text{H}_2\text{O}_2} = k_3^+ \theta_{\text{O}_2} \theta_{\text{H}} - k_3^- \theta_{\text{OOH}} \theta_*. \tag{C.259}$$

We assume that all other steps are quasi-equilibrated, hence

$$\begin{aligned}
\theta_{\text{H}} &= \sqrt{K_1 p_{\text{H}_2}} \theta_* && \text{(C.260)}\\
\theta_{\text{O}_2} &= K_2 p_{\text{O}_2} \theta_* && \text{(C.261)}\\
\theta_{\text{OOH}} &= \frac{\theta_{\text{H}_2\text{O}_2}}{K_4 \theta_{\text{H}}} \theta_* && \text{(C.262)}\\
&= \frac{K_5 p_{\text{H}_2\text{O}_2}}{K_4 \sqrt{K_1 p_{\text{H}_2}}} \theta_* && \text{(C.263)}\\
\theta_{\text{H}_2\text{O}_2} &= K_5 p_{\text{H}_2\text{O}_2} \theta_* && \text{(C.264)}
\end{aligned}$$

By applying the site balance, we can derive the following expression for the free sites

$$\theta_* = \frac{1}{1 + \sqrt{K_1 p_{\text{H}_2}} + K_2 p_{\text{O}_2} + \frac{K_5 p_{\text{H}_2\text{O}_2}}{K_4 \sqrt{K_1 p_{\text{H}_2}}} + K_5 p_{\text{H}_2\text{O}_2}} \tag{C.265}$$

Plugging this into the overall rate expression and introducing an equilibrium constant for the reverse reaction yields

$$r = r_{H_2O_2} = \frac{k_3^+ K_2 p_{O_2} \sqrt{K_1 p_{H_2}} \left(1 - \frac{1}{K_{eq}} \frac{p_{H_2O_2}}{p_{O_2} p_{H_2}}\right)}{\left(1 + \sqrt{K_1 p_{H_2}} + K_2 p_{O_2} + \frac{K_5 p_{H_2O_2}}{K_4 \sqrt{K_1 p_{H_2}}} + K_5 p_{H_2O_2}\right)^2} \tag{C.266}$$

b) If O* is the MARI and we assume a low conversion, the above expression simplifies to

$$r = \frac{k_3^+ K_2 p_{O_2} \sqrt{K_1 p_{H_2}}}{\left(1 + K_2 p_{O_2}\right)^2} \tag{C.267}$$

The reaction orders are

$$n_{H_2} = \frac{1}{2} \tag{C.268}$$

$$n_{O_2} = 1 - 2\theta_O \tag{C.269}$$

$$n_{H_2O_2} = 0 \tag{C.270}$$

c) The apparent activation energy is given by

$$\Delta E_{act}^{app} = RT^2 \frac{\partial \ln(r^+)}{\partial T} = E_{act}^{(3)} + (1 - 2\theta_{O_2}) \Delta H_{ads}^{(2)} + \frac{1}{2} \Delta H_{ads}^{(1)} \tag{C.271}$$

For a more thorough description how this answer is obtained, please look at the results of the previous questions.

d) In the high temperature regime, the surface is nearly empty and the rate is then given by

$$r = k_3^+ K_2 p_{O_2} \sqrt{K_1 p_{H_2}} \tag{C.272}$$

and the apparent activation energy becomes

$$\Delta E_{act}^{app} = RT^2 \frac{\partial \ln(r^+)}{\partial T} = E_{act}^{(3)} + \Delta H_{ads}^{(2)} + \frac{1}{2} \Delta H_{ads}^{(1)} \tag{C.273}$$

The apparent activation energy constitutes all kinetically relevant steps, which is the rate-limiting elementary reaction step and the two adsorption steps that precede the rate-limiting step. The apparent activation energy is set by the barrier of the rate-limiting step and is lowered (in the case of an empty surface) by the adsorption energy of O_2 and half the adsorption energy of H_2. Note that in this particular case, if the absolute value of the sum of the adsorption terms is larger than the barrier of the elementary reaction step, that the apparent activation energy becomes negative. This essentially means that the reaction rate is increased with decreasing temperature. This is readily seen if one considers the Sabatier's Principle. At the high temperature limit, we have an empty surface. By decreasing the temperature, more adsorbates will stick to the surface, hence enhancing the overall rate. In other words, by decreasing the temperature, we are moving our reaction towards the Sabatier's optimum.

■

Solution 1.17

a) The set of elementary reaction steps that describe the dual-site kinetic network is:

$$\begin{aligned}
&1.\ \mathrm{CO} + * \leftrightarrows \mathrm{CO}* && \text{(C.274)}\\
&2.\ \mathrm{H_2} + 2* \leftrightarrows 2\mathrm{H}* && \text{(C.275)}\\
&3.\ \mathrm{H_2} + 2\# \leftrightarrows 2\mathrm{H}\# && \text{(C.276)}\\
&4.\ \mathrm{CO} * + \mathrm{H}\# \leftrightarrows \mathrm{HCO} * + \# && \text{(C.277)}\\
&5.\ \mathrm{HCO} * + \mathrm{H}\# \leftrightarrows \mathrm{H_2CO} * + \# && \text{(C.278)}\\
&6.\ \mathrm{H_2CO} * + \mathrm{H}\# \leftrightarrows \mathrm{H_3CO} * + \# && \text{(C.279)}\\
&7.\ \mathrm{H_3CO} * + \mathrm{H}\# \leftrightarrows \mathrm{H_3COH} * + \# && \text{(C.280)}\\
&8.\ \mathrm{H_3COH} + * \leftrightarrows \mathrm{H_3COH}* && \text{(C.281)}
\end{aligned}$$

b) From elementary reaction step (3) and the site balance for τ, we obtain in a similar fashion as shown in previous exercises the following Langmuir isotherm for H on τ sites.

$$\tau_{\mathrm{H}} = \frac{\sqrt{K_3 p_{\mathrm{H_2}}}}{1 + \sqrt{K_3 p_{\mathrm{H_2}}}} \tag{C.282}$$

c) The rate-determining step approximation allows us to construct the following rate expression:

$$r = k_5 \theta_{\mathrm{HCO}} \tau_{\mathrm{H}}. \tag{C.283}$$

By applying a zero-conversion and irreversible step approximation, we only need to derive Langmuir expressions for H, CO, and HCO on θ sites. Using the pseudo-equilibrium approximation, we obtain the following expressions:

$$\begin{aligned}
\theta_{\mathrm{CO}} &= K_1 p_{\mathrm{CO}} \theta_* && \text{(C.284)}\\
\theta_{\mathrm{H}} &= \sqrt{K_2 p_{\mathrm{H_2}}}\,\theta_* && \text{(C.285)}\\
\theta_{\mathrm{HCO}} &= K_1 \sqrt{K_3} K_4 p_{\mathrm{CO}} \sqrt{p_{\mathrm{H_2}}}\,\theta_* && \text{(C.286)}\\
& && \text{(C.287)}
\end{aligned}$$

Using the site balance $\theta_{\mathrm{CO}} + \theta_{\mathrm{H}} + \theta_{\mathrm{HCO}} + \theta_* = 1$, gives

$$\theta_* = \frac{1}{1 + K_1 p_{\mathrm{CO}} + \sqrt{K_2 p_{\mathrm{H_2}}} + K_1 \sqrt{K_3} K_4 p_{\mathrm{CO}} \sqrt{p_{\mathrm{H_2}}}}. \tag{C.288}$$

Using these expressions, we obtain the following final expression for the rate

$$r = k_5 \left(\frac{K_1 \sqrt{K_3} K_4 p_{\mathrm{CO}} \sqrt{p_{\mathrm{H_2}}}}{1 + K_1 p_{\mathrm{CO}} + \sqrt{K_2 p_{\mathrm{H_2}}} + K_1 \sqrt{K_3} K_4 p_{\mathrm{CO}} \sqrt{p_{\mathrm{H_2}}}} \right) \left(\frac{\sqrt{K_3 p_{\mathrm{H_2}}}}{1 + \sqrt{K_3 p_{\mathrm{H_2}}}} \right) \tag{C.289}$$

d) The reaction order in H_2 is given by

$$n_{\mathrm{H_2}} = 1 - \frac{1}{2}\theta_{\mathrm{H}} - \frac{1}{2}\theta_{\mathrm{HCO}} - \frac{1}{2}\tau_{\mathrm{H}} \tag{C.290}$$

and the reaction order for CO is given by

$$n_{\mathrm{CO}} = 1 - \theta_{\mathrm{CO}} - \theta_{\mathrm{HCO}} \tag{C.291}$$

Note that in contrast to single-site kinetic networks, in dual-site catalysis the effect of competitive adsorptions is decreased leading to an increase of the lower limit in the reaction order. This shows that such systems suffer to a lesser extend from poisoning conditions.

e) The apparent activation energy is given by

$$\begin{aligned} \Delta E_{\mathrm{act}}^{\mathrm{app}} = \Delta E_{\mathrm{act}}^{(3)} &+ \Delta H_1 \left(1 - \theta_{\mathrm{CO}} - \theta_{\mathrm{HCO}}\right) \\ &+ \Delta H_2 \left(-\theta_{\mathrm{H}}\right) \\ &+ \Delta H_3 \left(1 - \frac{1}{2}\tau_{\mathrm{H}} - \frac{1}{2}\theta_{\mathrm{HCO}}\right) \\ &+ \Delta H_4 \left(1 - \theta_{\mathrm{HCO}}\right). \end{aligned} \tag{C.292}$$

■

C.2 Solutions of Chapter 2

C.2.1 Solutions to questions

a) For chemistry, the translational, rotational and vibrational partition functions are the most relevant. These partition functions differ in the nature of the configurational freedom that the complex has given a particular energy. A translational degree of freedom indicates that the system can freely translate in one dimension without the energy of the complex changing. Similarly, a rotational degree of freedom indicates the complex can rotate without its energy changing. Finally, a vibrational degree of freedom can be seen as a hindered translation. The molecule can perturb in a specific direction, but this results in an energy increase. As such, vibrational degrees of freedom arise from bound states and the corresponding costs of perturbing from the equilibrium position of these bound states.

b) The partition function is dimensionless and has no unit. This is both evident from the meaning of the partition function (it represents the average number of possible configurations given a particular energy, configuration and temperature) as well as from the various equations wherein the partition function is used (i.e. it is used inside a logarithm).

C.2.2 Solutions to exercises

The solution below pertain to the exercises of Chapter 2 on page 67 and further.

Solution 2.1

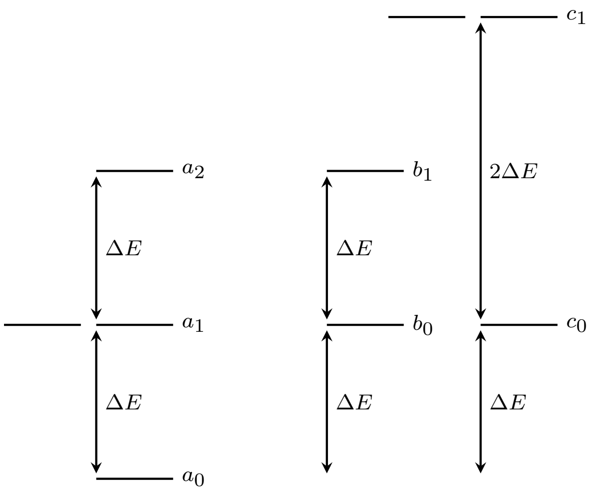


Figure C.1: *Energy level diagram of A, B, and C.*

a) The equilibrium constant in terms of the partition functions is given by

$$K = \prod_i q_i^{\nu_i} = \frac{q_\text{B} q_\text{C}}{q_\text{A}} \tag{C.293}$$

b)

$$q_\text{A} = \sum_{j=0}^{2} \exp\left(-\frac{\epsilon_j}{k_b T}\right) \tag{C.294}$$

$$= 1 + 2\exp\left(-\frac{\Delta E}{k_b T}\right) + \exp\left(-\frac{2\Delta E}{k_b T}\right) \tag{C.295}$$

$$q_{\mathrm{B}} = \exp\left(-\frac{\Delta E}{k_b T}\right) + \exp\left(-\frac{2\Delta E}{k_b T}\right) \tag{C.296}$$

$$q_{\mathrm{C}} = \exp\left(-\frac{\Delta E}{k_b T}\right) + 2\exp\left(-\frac{3\Delta E}{k_b T}\right) \tag{C.297}$$

$$K = \frac{\left(\exp\left(-\frac{\Delta E}{k_b T}\right) + \exp\left(-\frac{2\Delta E}{k_b T}\right)\right)\left(\exp\left(-\frac{\Delta E}{k_b T}\right) + 2\exp\left(-\frac{3\Delta E}{k_b T}\right)\right)}{1 + 2\exp\left(-\frac{\Delta E}{k_b T}\right) + \exp\left(-\frac{2\Delta E}{k_b T}\right)} \tag{C.298}$$

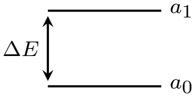
c)

$$\lim_{T \to 0} K = \frac{0 \cdot 0}{1} = 0 \tag{C.299}$$

$$\lim_{T \to \infty} K = \frac{2 \cdot 3}{4} = \frac{3}{2} \tag{C.300}$$

■

Solution 2.2



a)

The partition function for molecule A is

$$q_{\mathrm{A}} = \sum_{i=0}^{1} \exp\left(-\frac{\epsilon_i}{k_b T}\right) \tag{C.301}$$

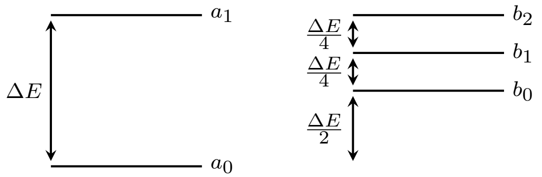
$$= 1 + \exp\left(-\frac{\Delta E}{k_b T}\right) \tag{C.302}$$

The partition function at $T \to 0$ gives

$$\lim_{T \to 0} q_{\mathrm{A}} = 1 \tag{C.303}$$

The partition function at $T \to \infty$ gives

$$\lim_{T \to \infty} q_{\mathrm{A}} = 2 \tag{C.304}$$



b)

The partition function for molecule B is

$$q_{\mathrm{B}} = \sum_{i=0}^{2} \exp\left(-\frac{\epsilon_i}{k_b T}\right) \tag{C.305}$$

$$= \exp\left(-\frac{\Delta E}{2k_b T}\right) + \exp\left(-\frac{3\Delta E}{4k_b T}\right) + \exp\left(-\frac{\Delta E}{k_b T}\right) \tag{C.306}$$

The equilibrium between A and B is given by

$$K = \prod_{i=0}^{1} q_i^{\nu_i} \tag{C.307}$$

$$= \frac{q_{\mathrm{B}}}{q_{\mathrm{A}}} \tag{C.308}$$

$$= \frac{\exp\left(-\frac{\Delta E}{2k_b T}\right) + \exp\left(-\frac{3\Delta E}{4k_b T}\right) + \exp\left(-\frac{\Delta E}{k_b T}\right)}{1 + \exp\left(-\frac{\Delta E}{k_b T}\right)} \tag{C.309}$$

The equilibrium constant for $T \to 0$ yields

$$\lim_{T \to 0} K = \frac{0}{1} = 0 \tag{C.310}$$

The equilibrium constant for $T \to \infty$ yields

$$\lim_{T \to \infty} K = \frac{3}{2} \tag{C.311}$$

■

Solution 2.3

Note that the spectroscopically determined energy levels of A and B are an infinite series of energy levels. The energy levels of A and B have the same energetic separation (ΔE). The difference though is that the series of molecule B starts somewhat higher ($\Delta E/2$)

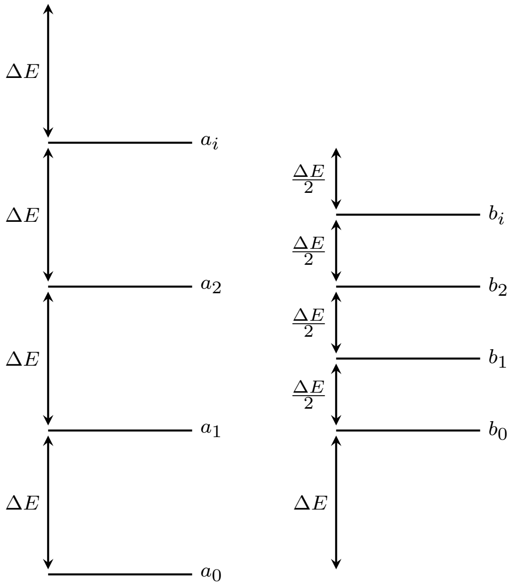


Figure C.2: *Energy level diagram of the spectroscopically determined energy levels of A and B.*

The partition function for A yields

$$q_{\mathrm{A}} = \sum_{i=0}^{\infty} \exp\left(-\frac{\epsilon_i}{k_b T}\right) \tag{C.312}$$

$$q_{\mathrm{A}} = \sum_{i=0}^{\infty} \exp\left(-i\frac{\Delta E}{k_b T}\right) \tag{C.313}$$

$$= \sum_{i=0}^{\infty} \exp\left(-\frac{\Delta E}{k_b T}\right)^i \tag{C.314}$$

The partition function for B yields

$$q_{\mathrm{B}} = \sum_{j=0}^{\infty} \exp\left(-\frac{\epsilon_j}{k_b T}\right) \tag{C.315}$$

$$= \sum_{j=0}^{\infty} \exp\left(-(\frac{j}{2}+1)\frac{\Delta E}{k_b T}\right) \tag{C.316}$$

$$= \exp\left(-\frac{\Delta E}{k_b T}\right) \sum_{j=0}^{\infty} \exp\left(-\frac{\Delta E}{2k_b T}\right)^j \tag{C.317}$$

The above sums are geometric series (see Appendix B.4 on page 131). These series can be simplified using the formula below

$$\sum_{k=0}^{\infty} ar^k = \frac{a}{1-r} \text{ for } |r| < 1 \tag{C.318}$$

Thus we can write

$$q_{\mathrm{A}} = \frac{1}{1 - \exp\left(-\frac{\Delta E}{k_b T}\right)} \tag{C.319}$$

and

$$q_{\mathrm{B}} = \frac{\exp\left(-\frac{\Delta E}{k_b T}\right)}{1 - \exp\left(-\frac{\Delta E}{2k_b T}\right)} \tag{C.320}$$

This gives for the equilibrium constant

$$K = \frac{q_{\mathrm{B}}}{q_{\mathrm{A}}} = \frac{\exp\left(-\frac{\Delta E}{k_b T}\right)\left(1 - \exp\left(-\frac{\Delta E}{k_b T}\right)\right)}{1 - \exp\left(-\frac{\Delta E}{2k_b T}\right)} \tag{C.321}$$

The values for the equilibrium constant K are then:

$$K(T = 0.1\Delta E/k_b) = 0.000045 \tag{C.322}$$
$$K(T = 2\Delta E/k_b) = 1.079 \tag{C.323}$$
$$K(T = 10\Delta E/k_b) = 1.766 \tag{C.324}$$
$$K(T \to \infty) = 2 \tag{C.325}$$

In other words, at very low temperature, only levels of A are occupied. Hence, at low temperature the equilibrium condition states that nearly all species will be in the A configuration. With increasing temperature, more and more levels of B are occupied and the equilibrium shifts to the situation where A and B states have same occupational fraction. Due to the fact that there are twice as many levels of B (because of its separation which is half the separation of the energy levels of A); the equilibrium constant yields 2 at infinite temperature.
To solve for the limiting case ($T \to \infty$), it can help to employ l'Hôspital's rule (see Appendix B.6 on 133), which states

$$\lim_{x \to a} \frac{f(x)}{g(x)} = \lim_{x \to a} \frac{f'(x)}{g'(x)} \tag{C.326}$$

Applying this rule, yields

$$K(T \to \infty) = \lim_{T\to\infty} \left[\frac{\exp\left(-\frac{\Delta E}{k_b T}\right)\left(1 - \exp\left(-\frac{\Delta E}{k_b T}\right)\right)}{1 - \exp\left(-\frac{\Delta E}{2k_b T}\right)} \right] \tag{C.327}$$

$$= \lim_{T\to\infty} \left[\frac{\frac{\Delta E}{k_b T^2}\left(\exp\left(-\frac{\Delta E}{k_b T}\right)\left(1 - \exp\left(-\frac{\Delta E}{k_b T}\right)\right) - \exp\left(-\frac{2\Delta E}{k_b T}\right)\right)}{-\frac{\Delta E}{2k_b T^2}\exp\left(-\frac{\Delta E}{2k_b T}\right)} \right] \tag{C.328}$$

$$= \lim_{T\to\infty} \left[\frac{\frac{\Delta E}{k_b T^2}\left(1 \cdot 0 - 1\right)}{\frac{-\Delta E}{2k_b T^2}} \right] \tag{C.329}$$

$$= \lim_{T\to\infty} \left[\frac{-\frac{\Delta E}{k_b T^2}}{\frac{-\Delta E}{2k_b T^2}} \right] \tag{C.330}$$

$$= 2 \tag{C.331}$$

■

Solution 2.4

a) The translational partition function in three dimensions using the ideal gas law is:

$$q_\mathrm{T} = V \frac{\left(2\pi m k_b T\right)^{3/2}}{h^3} \tag{C.332}$$

$$= \frac{k_b T}{P} \frac{\left(2\pi m k_b T\right)^{3/2}}{h^3} \tag{C.333}$$

Plugging in the values gives

$$q_\mathrm{T} = \frac{1.3806488 \cdot 10^{-23}\mathrm{J} \cdot \mathrm{K}^{-1} \cdot 298\ \mathrm{K}}{1.01325 \cdot 10^5\ \mathrm{Pa}} \frac{\left(2\pi 28 \cdot 10^{-3}\mathrm{kg}/6.0221409 \cdot 10^{23} \cdot 1.3806488 \cdot 10^{-23}\mathrm{J} \cdot \mathrm{K}^{-1} \cdot 298\ \mathrm{K}\right)^{3/2}}{(6.62607004 \cdot 10^{-34}\mathrm{m}^2 \cdot \mathrm{kg} \cdot \mathrm{s}^{-1})^3} \tag{C.334}$$

$$= 5.8163 \cdot 10^6 \tag{C.335}$$

This answer means that an N_2 molecule, given these temperature and pressure conditions, has almost 6 million different translational configurations.

b) q_T increases to the power of $5/2$ with temperature. At higher temperature, more states can be populated, hence increasing the partition function. q_T also increases with volume, but only linearly. A higher volume gives more space per molecule, hence more accessible states. In contrast, q_T decreases with increasing pressure as the volume per particle decreases with pressure.

c)

$$q_\mathrm{V} = \frac{1}{1 - \exp\left(-\frac{h\nu}{k_b T}\right)} \tag{C.336}$$

$$= \frac{1}{1 - \exp\left(-\frac{6.62607004 \cdot 10^{-34} \mathrm{m}^2 \cdot \mathrm{kg} \cdot \mathrm{s}^{-1} \cdot 299792458 \cdot \mathrm{m} \cdot \mathrm{s}^{-1} \cdot 233000\ \mathrm{m}^{-1}}{1.3806488 \cdot 10^{-23} \mathrm{J} \cdot \mathrm{K}^{-1} \cdot 298\ \mathrm{K}}\right)} \tag{C.337}$$

$$\approx 1 \tag{C.338}$$

Note that the vibrational partition function under typical atmospheric conditions usually equals unity.

d) The rotational partition function is given by:

$$q_\mathrm{R} = \frac{8\pi^2 I k_b T}{\sigma h^2} \tag{C.339}$$

Please note that this partition function represents rotation for a diatomic molecule in two dimensions. In other words, this partition function represents two degrees of freedom!

Plugging in the values yields

$$q_\mathrm{R} = \frac{8\pi^2 \cdot 1.407 \cdot 10^{-46} \mathrm{kg} \cdot \mathrm{m}^2 1.3806488 \cdot 10^{-23} \mathrm{J} \cdot \mathrm{K}^{-1} \cdot 298\ \mathrm{K}}{2(6.62607004 \cdot 10^{-34} \mathrm{m}^2 \cdot \mathrm{kg} \cdot \mathrm{s}^{-1})^2} \tag{C.340}$$

$$= 52.05 \tag{C.341}$$

e)

$$Q = q_\mathrm{T} q_\mathrm{V} q_\mathrm{R} \tag{C.342}$$

$$= 5.8163 \cdot 10^6 \cdot 1 \cdot 52.05 \tag{C.343}$$

$$= 3.03 \cdot 10^8 \tag{C.344}$$

Note that the translational partition function represents 3 degrees of freedom, the rotational partition function 2 degrees of freedom and the vibrational partition function 1 degree of freedom. Summing up these numbers gives a total of 6 degrees of freedom, exactly what we would expect from a diatomic molecule!

■

Solution 2.5

a) The Maxwell-Boltzmann distribution expresses the partial fraction of a set of species given their velocity and is given by the following expression

$$f = 4\pi \left(\frac{m}{2\pi k_b T}\right)^{3/2} v^2 \exp\left(\frac{-mv^2}{2k_b T}\right) \tag{C.345}$$

To calculate the average velocity of an ensemble, you simply have to multiply the Maxwell-Boltzmann distribution with the velocity v and integrate over all possible velocities

$$\bar{v} = \int_0^\infty 4\pi \left(\frac{m}{2\pi k_b T}\right)^{3/2} v^2 \exp\left(\frac{-mv^2}{2k_b T}\right) v\mathrm{d}v \tag{C.346}$$

$$= 4\pi \left(\frac{m}{2\pi k_b T}\right)^{3/2} \int_0^\infty v^3 \exp\left(\frac{-mv^2}{2k_b T}\right) \mathrm{d}v \tag{C.347}$$

$$= 4\pi \left(\frac{m}{2\pi k_b T}\right)^{3/2} \frac{1}{2}\left(\frac{2k_b T}{m}\right)^2 \tag{C.348}$$

$$= \left(\frac{8k_b T}{\pi m}\right)^{1/2} \tag{C.349}$$

Note that in the above formula, the mass m is the mass for a single particle. If you want to use the molecular mass in kg/mol, you have to substitute the Boltzmann constant k_b for the gas constant R. Furthermore, to solve the improper integral, we have used the standard integral as defined below. Alternatively, you can use the method of integration by parts.

$$\int_0^\infty x^{2n+1} \exp\left(-\frac{x^2}{a^2}\right) \mathrm{d}x = \frac{n!}{2} a^{2n+2} \tag{C.350}$$

Calculating the average speed for a set of N_2 molecules at room temperature gives

$$\bar{v} = \left(\frac{8RT}{\pi M}\right)^{1/2} \tag{C.351}$$

$$= \left(\frac{8 \cdot 8.3145 \text{ J mol}^{-1} \text{ K}^{-1} \cdot 298\text{K}}{\pi \; 28 \cdot 10^{-3}\text{kg} \cdot \text{mol}^{-1}}\right)^{1/2} \tag{C.352}$$

$$= 475 \text{ m} \cdot \text{s}^{-1} \tag{C.353}$$

Note that you can remember as a rule of thumb that the speed of sound is roughly 70% of the average velocity of the molecules the medium is made of.

b)

$$\bar{v}_{N_2}/\bar{v}_{He} = 1 = \frac{\left(\frac{8k_b T_1}{\pi m_{N_2}}\right)^{1/2}}{\left(\frac{8k_b T_2}{\pi m_{He}}\right)^{1/2}} \tag{C.354}$$

Rearranging yields

$$T_1 = T_2 \cdot \frac{m_{N_2}}{m_{He}} = 2090\text{K} \tag{C.355}$$

c) In a similar manner as in *a*, we can find the translational energy by integrating the following expression

$$\bar{\epsilon}_{\mathrm{t}} = \int_0^\infty 4\pi \left(\frac{m}{2\pi k_b T}\right)^{3/2} v^2 \exp\left(\frac{-mv^2}{2k_b T}\right)\frac{1}{2}mv^2 \mathrm{d}v \tag{C.356}$$

$$= 2m\pi \left(\frac{m}{2\pi k_b T}\right)^{3/2} \int_0^\infty v^4 \exp\left(\frac{-mv^2}{2k_b T}\right)\mathrm{d}v \tag{C.357}$$

$$= 2m\pi \left(\frac{m}{2\pi k_b T}\right)^{3/2} \cdot \sqrt{\pi}\cdot 12 \cdot \left(\frac{k_b T}{2m}\right)^{5/2} \tag{C.358}$$

$$= \frac{3}{2}k_b T \tag{C.359}$$

Note that in the above expression, ϵ_{t} is the average translational energy per particle, not per mole of particles. To get the average energy per mole, we need to substitute k_b for R. Furthermore, to solve the improper integral, we have used the standard integral as defined below (this one differs from the one proposed above!). Alternatively, you can use the method of integration by parts.

$$\int_0^\infty x^{2n} \exp^{-x^2/a^2} \mathrm{d}x = \sqrt{\pi}\frac{(2n)!}{n!}\left(\frac{a}{2}\right)^{2n+1} \tag{C.360}$$

Plugging in the values for 1 mol of N_2 at 100, 298 and 1000 K yields

$$\bar{\epsilon}_{\mathrm{t}}(T = 100\ \mathrm{K}) = 1.247\ \mathrm{kJ}\cdot\mathrm{mol}^{-1} \tag{C.361}$$

$$\bar{\epsilon}_{\mathrm{t}}(T = 298\ \mathrm{K}) = 3.71\ \mathrm{kJ}\cdot\mathrm{mol}^{-1} \tag{C.362}$$

$$\bar{\epsilon}_{\mathrm{t}}(T = 1000\ \mathrm{K}) = 12.47\ \mathrm{kJ}\cdot\mathrm{mol}^{-1} \tag{C.363}$$

■

Solution 2.6

a) Using the ideal gas law, we can write for the particle density

$$\rho = \frac{n}{V} = \frac{P}{k_b T} \tag{C.364}$$

Plugging in the numbers yields

$$\rho = \frac{P}{k_b T} = \frac{1\cdot 10^5\ \mathrm{Pa}}{1.3806488\cdot 10^{-23}\mathrm{J}\cdot\mathrm{K}^{-1}\cdot 298.15\mathrm{K}} \tag{C.365}$$

$$= 2.43\cdot 10^{25}\ \text{particles}\cdot\mathrm{m}^{-3} \tag{C.366}$$

Because the partial pressure of N_2 is $\frac{1}{4}$ of the total pressure and the partial pressure of H_2 is $\frac{3}{4}$ of the partial pressure, their respective number densities are

$$\rho_{N_2} = \frac{1}{4} \cdot 2.43 \cdot 10^{25} = 6.1 \cdot 10^{24} \text{ particles} \cdot \text{m}^{-3} \tag{C.367}$$

$$\rho_{H_2} = \frac{3}{4} \cdot 2.43 \cdot 10^{25} = 1.8 \cdot 10^{25} \text{ particles} \cdot \text{m}^{-3} \tag{C.368}$$

b) The collision density is given by equation 2.113 on 57:

$$Z = 2\left(\frac{\pi k_B T}{m}\right)^{1/2} \sigma^2 n^2 = 2\left(\frac{\pi RT}{M}\right)^{1/2} \sigma^2 n^2. \tag{C.369}$$

(note that in the above formula, σ is the collision **radius**)

Plugging in the values yields

$$Z(H_2, H_2) \tag{C.370}$$

$$= 2\left(\frac{\pi \cdot 8.3145 \cdot 298 \text{ K}}{2 \cdot 10^{-3} \text{ kg} \cdot \text{mol}^{-1}}\right)^{1/2} \cdot \left(\frac{2.71 \cdot 10^{-10}}{2} \text{ m}\right)^2 \cdot \left(1.8 \cdot 10^{25} \text{ particles} \cdot \text{m}^{-3}\right)^2 \tag{C.371}$$

$$= 2.35 \cdot 10^{34} \text{ collision} \cdot \text{m}^{-3}\text{s}^{-1} \tag{C.372}$$

Note that due to the large difference in the smallest and largest numbers (10^{-23} and 10^{25}), some calculators have numerical problems (that do not raise an error...) resulting in wrongly calculated numbers.

Perform this calculation on Wolfram Alpha: `https://www.wolframalpha.com/input/?i=2+*+(pi+*+8.3145+*+298+%2F+(2e-3))%5E0.5+*+(2.71e-10+%2F+2)%5E2+*(1.8e25)%5E2`

c) Similar to the above results, we can calculate for the collision between N_2 and N_2

$$Z(N_2, N_2) \tag{C.373}$$

$$= 2\left(\frac{\pi \cdot 8.3145 \cdot 298 \text{ K}}{28 \cdot 10^{-3} \text{ kg} \cdot \text{mol}^{-1}}\right)^{1/2} \cdot \left(\frac{3.73 \cdot 10^{-10}}{2} \text{ m}\right)^2 \cdot \left(6.1 \cdot 10^{24} \text{ particles} \cdot \text{m}^{-3}\right)^2 \tag{C.374}$$

$$= 1.36 \cdot 10^{33} \text{ collision} \cdot \text{m}^{-3}\text{s}^{-1} \tag{C.375}$$

Perform this calculation on Wolfram Alpha: `https://www.wolframalpha.com/input/?i=2+*+(pi+*+8.3145+*+298+%2F+(28e-3))%5E0.5+*+(3.73e-10+%2F+2)%5E2+*(6.1e24)%5E2`

d) We can calculate the number of collisions between N_2 and H_2 by plugging in the effective diameter $d = (d_1 + d_2)/2$, we then obtain:

$$Z(\mathrm{N_2}, \mathrm{H_2}) = \left(\frac{8\pi k_B T}{\mu}\right)^{1/2} \sigma_{AB}^2 N_A N_B \tag{C.376}$$

$$= \left(\frac{8 \cdot \pi \cdot 8.3145 \cdot 298\ \mathrm{K}}{1.86 \cdot 10^{-3}\ \mathrm{kg} \cdot \mathrm{mol}^{-1}}\right)^{1/2} \cdot \left(\frac{(2.71 + 3.73) \cdot 10^{-10}}{4}\ \mathrm{m}\right)^2 \cdot \left(1.8 \cdot 10^{25}\ \text{particles} \cdot \mathrm{m}^{-3}\right) \cdot \left(6.1 \cdot 10^{24}\ \text{particles} \cdot \mathrm{m}^{-3}\right) \tag{C.377}$$

$$= 1.64 \cdot 10^{34}\ \text{collision} \cdot \mathrm{m}^{-3}\mathrm{s}^{-1} \tag{C.378}$$

Perform this calculation on Wolfram Alpha: `https://www.wolframalpha.com/input/?i=(8+*+pi+*+8.3145+*+298+%2F+(1.86e-3))%5E0.5+*+((2.71+%2B+3.73)*1e-10+%2F+4)%5E2+*1.8e25+*+6.1e24`

e) The number of collision is just the sum of all possible sets of collisions yielding

$$Z_{\text{total}} = 4.13 \cdot 10^{34}\ \text{collision} \cdot \mathrm{m}^{-3}\mathrm{s}^{-1} \tag{C.379}$$

■

Solution 2.7

a) From the formula, the pre-exponential factor and the activation energy can be easily extracted

$$\nu = 2 \cdot 10^{15} \tag{C.380}$$

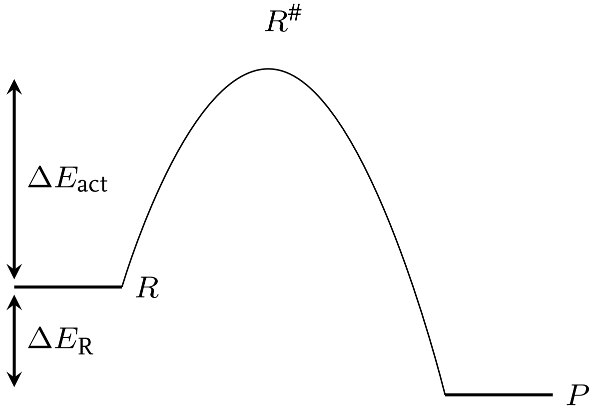
$$\Delta E_{\text{act}} = 274\ \mathrm{kJ} \cdot \mathrm{mol}^{-1} \tag{C.381}$$

b) Draw an reaction energy diagram with three states (initial, transition and final state). Make the height of the transition state higher than the initial and final states.

c) A cyclopropane molecule can be thermally excited by collission with another cyclopropane molecule or another molecule in the same gaseous phase. If the pressure would be significantly lowered, the reaction rate would be lower because there are fewer collisions.

■

Solution 2.8



a) The general reaction equation being used is

$$\mathrm{R} \underset{k_1^-}{\overset{k_1^+}{\rightleftarrows}} \mathrm{R}^{\#} \underset{k_2}{\longrightarrow} \mathrm{P} \tag{C.382}$$

This gives the following rate expression

$$r = k_2 K_1 [\mathrm{R}] \tag{C.383}$$

b) The general expression is

$$r = \frac{k_b T}{h} \frac{Q^{\#\#}}{Q} \exp\left(-\frac{\Delta E_{\text{a}}}{k_b T}\right) [\mathrm{R}] \tag{C.384}$$

Note that in the above expression, $Q^{\#\#}$ denotes the total partition function of the transition state **without** the partition function corresponding to the imaginary frequency.

c) Transition State theory takes all degrees of freedom (rotational, translational as well as vibrational) into account and not just the translational degrees of freedom in collision theory (rendering the latter theory inconsistent with thermodynamics).

■

Solution 2.9

a) The main assumptions of transition state theory are

- There exists an equilibrium between the initial and the transition state
- The crossing of a species from the transition state to the final state is **for the calculation of the rate constant** assumed to be irreversible and corresponds to a particular frequency
- The frequency of transmission or crossing can be modeled as an ultrasoft vibrational mode (other alternatives are possible, but are mathematically more complicated)

b) The general expression is

$$k = \frac{k_b T}{h} \frac{Q^{\#\#}}{Q} \exp\left(-\frac{\Delta E_{\mathrm{a}}}{k_b T}\right) \tag{C.385}$$

Note that in the above expression, $Q^{\#\#}$ denotes the total partition function of the transition state **without** the partition function corresponding to the imaginary frequency.

c) The first term in the equation ($\frac{k_b T}{h}$) is a frequency factor (its dimension is in reciprocal seconds), corresponding to the number of species crossing the barrier in the transition state in a given time frame. The second term is the quotient of the total partition functions in the transition and initial state (please note the comment above regarding the transition state). The last part relates to the difference in electronic energy between the initial and transition state, commonly expressed as the activation energy. Loosely speaking, this term is the obtained result when dividing the electronic partition functions of the transition and initial state.

d) Assuming that all entropy is lost in the transition state, we can formulate the following identities

$$K_1 = \exp\left(-\frac{\Delta G}{k_b T}\right) = \exp\left(-\frac{\Delta H}{k_b T}\right) \cdot \exp\left(\frac{\Delta S}{k_b}\right) = \frac{k_1^+}{k_1^-} \tag{C.386}$$

$$\tag{C.387}$$

The forward and backward rate constants are defined as

$$k_1^+ = \nu_{\text{forward}} \exp\left(-\frac{\Delta E_{\text{act}}^{\text{forward}}}{k_b T}\right) = \frac{k_b T}{h} \frac{Q^{\#\#}}{Q} \exp\left(-\frac{\Delta E_{\text{act}}^{\text{forward}}}{k_b T}\right) \tag{C.388}$$

and

$$k_1^- = \nu_{\text{backward}} \exp\left(-\frac{\Delta E_{\text{act}}^{\text{backward}}}{k_b T}\right) = \frac{k_b T}{h} \exp\left(-\frac{\Delta E_{\text{act}}^{\text{backward}}}{k_b T}\right) \tag{C.389}$$

Dividing these two yields

$$\exp\left(-\frac{\Delta H}{k_bT}\right)\cdot\exp\left(\frac{\Delta S}{k_b}\right)=\frac{\frac{k_bT}{h}\frac{Q^{\#\#}}{Q}\exp\left(-\frac{\Delta E_{\text{act}}^{\text{forward}}}{k_bT}\right)}{\frac{k_bT}{h}\exp\left(-\frac{\Delta E_{\text{act}}^{\text{backward}}}{k_bT}\right)} \tag{C.390}$$

If we assume that all entropy is lost in the transition state, than the difference between forward and backward activation energies is equal to the reaction enthalpy.

$$\exp\left(\frac{\Delta S}{k_b}\right)=\frac{Q^{\#\#}}{Q} \tag{C.391}$$

$$\nu_{\text{forward}}=\frac{k_bT}{h}\exp\left(\frac{-130\ \text{J/mol}}{R}\right)=2.701\cdot10^{6}\text{s}^{-1} \tag{C.392}$$

Note that I have replaced the Boltzmann constant for the gas constant, because the energy was given in a per mole basis. Furthermore, note that the result is quite a low value for a chemical reaction. Typically, chemical reactions have a pre-exponential factor around 10^{13}. The reason is the significant reduction in the number of degrees of freedom upon dissociative adsorption.

e)

$$r=\frac{k_bT}{h}\exp\left(\frac{-130\ \text{J/mol}}{R}\right)\exp\left(\frac{50\cdot10^{3}\ \text{J/mol}}{R\cdot800\ \text{K}}\right)=1469\text{s}^{-1} \tag{C.393}$$

■

Solution 2.10

a)

$$r=\frac{k_bT}{h}\frac{Q^{\#\#}}{Q}\exp\left(-\frac{\Delta E_{\text{a}}}{k_bT}\right)=\frac{k_bT}{h}\frac{\left(q_{\text{R}}^{(2)}q_{\text{T}}^{(3)}\right)^{\#\#}}{q_{\text{V}}^{(1)}q_{\text{R}}^{(2)}q_{\text{T}}^{(3)}}\exp\left(-\frac{\Delta E_{\text{a}}}{k_bT}\right) \tag{C.394}$$

b) To write down the above expression in Arrhenius-form, normally we are allowed to neglect the vibrational partition functions. Here, such an assumption is not given, thus we have to evaluate this expression. Luckily, because the number of translational and rotational partition functions is similar for the transition state as for the initial state, we do not have to evaluate these.

$$\Delta E_{\text{act}}^{\text{arrhenius}}=k_bT^2\frac{\ln\partial r}{\partial T} \tag{C.395}$$

$$=\Delta E_{\text{a}}+k_bT^2\frac{\partial\ln\frac{k_bT}{h}}{\partial T}+k_bT^2\frac{\partial\ln\left(1-\exp\left(-\frac{h\nu}{k_bT}\right)\right)}{\partial T} \tag{C.396}$$

$$=\Delta E_{\text{a}}+k_bT+\frac{h\nu\exp\left(-\frac{h\nu}{k_bT}\right)}{\left(1-\exp\left(-\frac{h\nu}{k_bT}\right)\right)} \tag{C.397}$$

Applying a Taylor approximation to the last term and neglecting all quadratic terms gives

$$\frac{h\nu \exp\left(-\frac{h\nu}{k_bT}\right)}{\left(1-\exp\left(-\frac{h\nu}{k_bT}\right)\right)} \approx \frac{h\nu(1-\frac{h\nu}{k_bT})}{1-1+\frac{h\nu}{k_bT}} \tag{C.398}$$

This we can further simplify this equation by assuming that $\frac{h\nu}{k_bT} \ll 1$.

$$\frac{h\nu(1-\frac{h\nu}{k_bT})}{1-1+\frac{h\nu}{k_bT}} = k_bT(1-\frac{h\nu}{k_bT}) \approx k_bT \tag{C.399}$$

And thus finally obtaining

$$\Delta E_{\text{act}}^{\text{arrhenius}} = \Delta E_{\text{a}} + 2k_bT \tag{C.400}$$

■

Solution 2.11

a) The second derivative of the energy (potential) can be calculated using a numerical derivative as follows

$$k = \frac{\partial^2 V}{\partial x^2} = \frac{V_{x=h} - 2V_{x=0} + V_{x=-h}}{h^2} \tag{C.401}$$

The direction in which we pertubate the system is given by

$$q_1 = r_{BC} - r_{AB} \tag{C.402}$$

$$q_2 = r_{BC} + r_{AB} \tag{C.403}$$

where q_1 is a vector in the direction of the reaction coordinate and q_2 is a vector perpendicular to the direction of the reaction coordinate.

From Figure 2.4, we see that the energy in the direction of the reaction coordinate at $V_{x=-h} = V_{x=h} = 11.00$ a.u., where $h = 0.152$ Å. The energy at the transition state is $V_{x=0} = 11.35$ a.u.

Thus,

$$\begin{aligned} k_{\|} = \frac{\partial^2 V}{\partial x^2} &= -49.38 \text{ a.u. / Å}^2 \qquad (C.404) \\ &= -2125 \text{ J / m}^2 \qquad (C.405) \end{aligned}$$

In the direction perpendicular to the reaction coordinate, we find $V(x=-h) = V(x=h) = 12.00$ a.u., where $h = 0.239$ Å, thus

$$k_\perp = \frac{\partial^2 V}{\partial x^2} = 341.1 \text{ a.u. / Å}^2 \tag{C.406}$$

$$= 14870 \text{ J / m}^2 \tag{C.407}$$

b)

$$\omega_\| = \sqrt{\frac{k}{m}} \tag{C.408}$$

$$= 1.127 \cdot 10^{15}\sqrt{-1}\text{s}^{-1} \tag{C.409}$$

$$= 33.59i \text{ cm}^{-1} \tag{C.410}$$

$$\omega_\perp = \sqrt{\frac{k}{m}} \tag{C.411}$$

$$= 2.982 \cdot 10^{15}\text{s}^{-1} \tag{C.412}$$

$$= 99.47 \text{ cm}^{-1} \tag{C.413}$$

Note that the wavenumber in the direction of the reaction coordinate is very low and **imaginary**. In contrast, the wavenumber perpendicular to the direction of the reaction coordinate is **real** and has a higher force constant.

c) A transition state on the multi-dimensional potential energy surface is characterized by one imaginary frequency in the direction of the reaction coordinate and real frequencies in all other directions. In other words, a transition state is a maximum in energy in one direction and a minimum in energy in all other directions. Such a point is considered stable as the forces (the first derivative of the energy) is zero as given by

$$\frac{\partial V}{\partial q_i} = 0 \text{ for all } i. \tag{C.414}$$

Note though that such a state is meta stable in the sense that a small pertubation in the direction of the reaction coordinate would propagate this system either towards the initial or the final state due to the particular shape of the potential energy curve around this point.

■

Solution 2.12

a) The vibrational frequency correlates with the strength of a bond. So a stronger bond has a higher vibrational frequency.

b) The bond between two atoms in the transition state is relatively weak, as such, the frequency of this bond is weak (or loose) as well.

c) From statistical thermodynamics, we can express K as the quotient of the molecular partition function in the transition and initial state:

$$K = \frac{Z^{\dagger}}{Z} \tag{C.415}$$

where $Z^{\dagger}$ is the molecular partition function in the transition state and Z is the molecular partition function in the initial state. The molecular partition function is the product of the electronic, vibrational, translational and rotational partition functions. We can extract the electronic partition function from the above equation and use it to define the electronic reaction barrier as follows

$$K = \frac{Q^{\dagger}}{Q}\left(\exp\left(\frac{-\epsilon^{\dagger}}{k_bT}\right) / \exp\left(\frac{-\epsilon}{k_bT}\right)\right) \tag{C.416}$$

$$K = \frac{Q^{\dagger}}{Q}\exp\left(\frac{-(\epsilon^{\dagger}-\epsilon)}{k_bT}\right) \tag{C.417}$$

$$K = \frac{Q^{\dagger}}{Q}\exp\left(\frac{-\Delta E_{\mathrm{a}}}{k_bT}\right) \tag{C.418}$$

where where $Q^{\dagger\dagger}$ is the configurational partition function in the transition state and Q the configurational partition function in the initial state. The configurational partition function is the product of the rotational, translational and vibrational partition functions. From the configurational partition function in the transition state, we are going to extract the partition function corresponding to the loose vibration, this yields

$$K = \frac{Q^{\dagger}}{Q}\exp\left(\frac{-\Delta E_{\mathrm{a}}}{k_bT}\right) \tag{C.419}$$

$$K = \frac{1}{1-\exp\left(-\frac{h\omega}{k_bT}\right)}\frac{Q^{\dagger\dagger}}{Q}\exp\left(\frac{-\Delta E_{\mathrm{a}}}{k_bT}\right) \tag{C.420}$$

$$K = \frac{1}{1-\exp\left(-\frac{h\omega}{k_bT}\right)}\frac{\prod_i f_i}{\prod_j f_j}\exp\left(\frac{-\Delta E_{\mathrm{a}}}{k_bT}\right) \tag{C.421}$$

d) The vibrational partition function for a loose vibration (i.e. the vibration in the direction of the reaction coordinate at the transition state) is

$$f_{\mathrm{vib}}^{\dagger} = \frac{1}{1-\exp\left(-\frac{h\omega}{k_bT}\right)} \tag{C.422}$$

$$= \frac{1}{1-1+\frac{h\omega}{k_bT}} \tag{C.423}$$

$$= \frac{1}{\frac{h\omega}{k_bT}} \tag{C.424}$$

$$= \frac{k_bT}{h\omega} \tag{C.425}$$

Note that in the above expression, i runs overall the configurational degrees of freedom of the transition state minus the degree of freedom corresponding to the loose vibration in the direction of the reaction coordinate and j runs over all the degrees of freedom of the initial state.

e) Plugging the result for the loose vibration into the formula for the rate constant and using $\nu = \omega$ gives

$$
\begin{aligned}
k &= \nu K && \text{(C.426)}\\
&= \frac{k_b T}{h\omega}\nu\frac{\prod_i f_i}{\prod_j f_j}\exp\left(-\frac{E_a}{k_b T}\right) && \text{(C.427)}\\
&= \frac{k_b T}{h}\frac{\prod_i f_i}{\prod_j f_j}\exp\left(-\frac{E_a}{k_b T}\right) && \text{(C.428)}\\
&= \frac{k_b T}{h}\frac{Q^{\dagger\dagger}}{Q}\exp\left(-\frac{E_a}{k_b T}\right) && \text{(C.429)}
\end{aligned}
$$

where $Q^{\dagger\dagger}$ is the configurational partition function in the transition state without the partition function corresponding to the loose vibration (hence the double †) and Q the configurational partition function in the initial state. Here, the configurational partition function is the product of the rotational, translational and vibrational partition functions.

■

C.2.3 Solution to challenges

C.2.4 Challenge: Maxwell-Boltzmann distribution

The total set of macrostates and the corresponding number of microstates for each macrostate is schematically represented in Figure C.3. The number of microstates were calculated using equation 2.162 on page 72. For example, the number of microstates for macrostate 4 is given by:

$$\Omega_4 = \frac{5!}{0!\cdot 0!\cdot 1!\cdot 0!\cdot 0!\cdot 2!\cdot 2!} = \frac{120}{4} = 30. \tag{C.430}$$

We calculated the average number of particles per energy state using equation 2.164 on page 73. We obtained the following numbers as given in Table C.1.

Table C.1: *Average number of particles n_i per energy level i.*

i	n_i
0	2.000
1	1.333
2	0.833
3	0.476
4	0.238
5	0.095
6	0.023

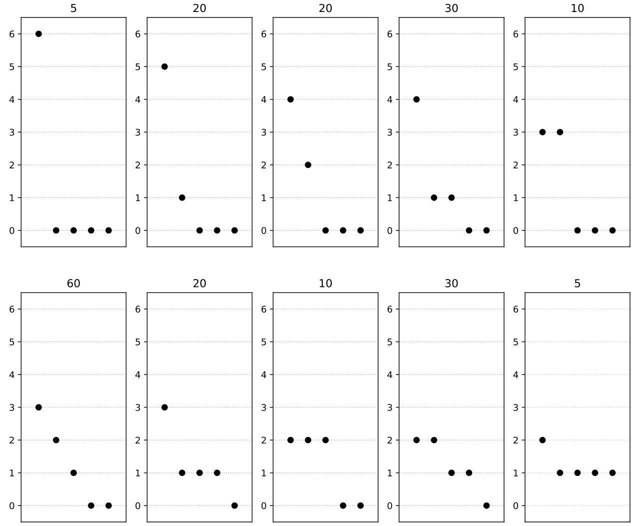


Figure C.3: *Schematic depiction of all macrostates for distributing 6 units of energy over 5 particles. Above each subfigure is the number of microstates for that particular macrostate given.*

The average number of particles in energy state i is shown in Figure C.4. We used a simple curve fitting procedure to fit the data as shown in Table C.1 to equation 2.165 on page 73. The result of this fit is shown in the same Figure. Note that the distribution we derived using only five particles and six energy units approximates the exact Maxwell-Boltzmann distribution to a very large extend. Increasing the number of particles would result in a better match with respect to the exact solution. Typically, you would consider a number of particles in the order of 10^{23}, which would give the exact solution.[1]

We obtained a value of $A = 2.05028583$ and $c = 0.488230$. From this, the temperature is easily calculated as

$$T = \frac{\Delta E}{R} \cdot c \approx 587 \text{ K}. \tag{C.431}$$

---

[1] Although figuring out all the macrostates and number of microstates would become nearly impossible, but that is exactly why we employ statistics.

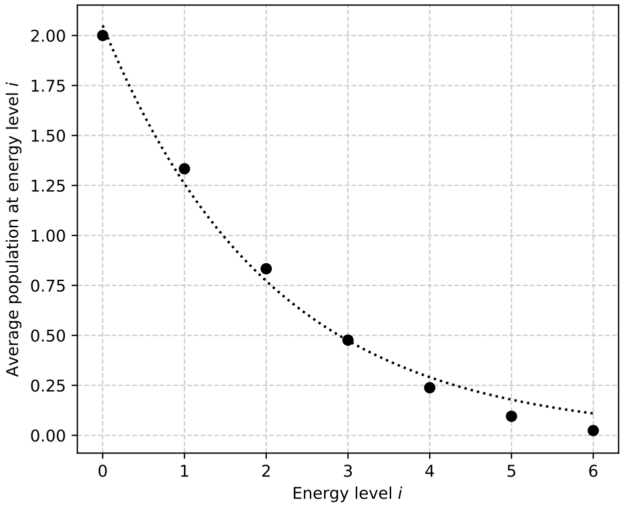


Figure C.4: *Average number of particles as a function of the energy level. The dotted line represents the curve fit.*

C.3 Solutions of Chapter 3

C.3.1 Solutions to questions

1. The difference between a rotational degree of freedom and a hindered rotor is the extend by which both can freely rotate. If a complex can freely rotate without the energy of the system increasing or decreasing, then the complex has a rotational degree of freedom. In contrast, if such a rotation is hindered, then the degree of freedom can be approximated as a hindered rotor. In fact, if the rotation is severely hindered (for instance by a harmonic potential), then the degree of freedom can be modeled by a vibration.

2. The zero point energy can be calculated by

$$E_{\text{ZPE}} = \frac{h\frac{k}{m}}{2k_bT} \tag{C.432}$$

from which it can be seen that the mass m is in the denominator and thus is inversely proportional to the zero point energy. Thus, atoms with a low mass have a more pronounced effect on the zero point energy than atoms with a high mass. For this reason, substitution of a hydrogen atom by a deuterium atom has a very strong effect in the evaluation of many kinetic properties.

C.3.2 Solutions to exercises

The solution below pertain to the exercises of Chapter 3 on page 81 and further.

Solution 3.1

a) We assume that this reaction occurs over a surface and that the corresponding partition functions are vibrational. Furthermore, we assume that the separation of the vibrational levels is thus high that only the ground state is occupied. Furthermore, we assume that we can neglect the ZPE correction. In that case, the reaction rate in the forward and backward direction are

$$\begin{aligned}
k_{\text{forward}} &= \frac{k_bT}{h}\exp\left(\frac{-\Delta E_{\text{act}}}{k_bT}\right) && \text{(C.433)}\\
&= \frac{k_bT}{h}\exp\left(\frac{-\Delta E_{\text{act}}}{RT}\right) && \text{(C.434)}\\
&= 4.84 \cdot 10^4 \text{s}^{-1} && \text{(C.435)}
\end{aligned}$$

and

$$\begin{aligned}
k_{\text{backward}} &= \frac{k_bT}{h}\exp\left(\frac{-\Delta E_{\text{act}}}{k_bT}\right) && \text{(C.436)}\\
&= \frac{k_bT}{h}\exp\left(\frac{-\Delta E_{\text{act}}}{RT}\right) && \text{(C.437)}\\
&= 3.21 \text{s}^{-1}. && \text{(C.438)}
\end{aligned}$$

b) The surface area A of the adsorption site is calculated by

$$
\begin{aligned}
A &= \frac{1}{2} l^2 && \text{(C.439)}\\
&= \frac{1}{2} (2.71\ \text{Å})^2 && \text{(C.440)}\\
&= 3.67205\ \text{Å}^2 && \text{(C.441)}\\
&= 3.67205 \cdot 10^{-20}\ \text{m}^2 && \text{(C.442)}
\end{aligned}
$$

The rate constant for CO desorption is calculated as

$$
\begin{aligned}
k &= \frac{k_b T^3}{h^3} \frac{A\,(2\pi m k_b)}{\sigma \theta_{\text{rot}}} \exp\left(\frac{-E_{\text{des}}}{k_b T}\right) && \text{(C.443)}\\
&= 1.08 \cdot 10^5\ \text{s}^{-1} && \text{(C.444)}
\end{aligned}
$$

c) The rate constant for the adsorption of CO is calculated by

$$
\begin{aligned}
k_{\text{ads}} &= \frac{PA}{\sqrt{2\pi m k_b T}} && \text{(C.445)}\\
&= 6.16 \cdot 10^{-3}\ \text{s}^{-1} && \text{(C.446)}
\end{aligned}
$$

d) Despite that the adsorption reaction has no activation energy, for the desorption reaction the transition state has more entropy than the initial state, whereas for adsorption the transition state has less entropy than the initial state. As such, at relatively high temperature, the desorption becomes several orders of magnitude faster than the adsorption rate.

■

Solution 3.2

a) The forward rate is given by

$$
\begin{aligned}
k_{\text{forward}} &= \frac{k_b T}{h} \frac{Q^{\dagger\dagger}}{Q} \exp\left(\frac{-\Delta E_{\text{act}}}{RT}\right) && \text{(C.447)}\\
&= \frac{k_b T}{h} \frac{(2\pi)^{3/2} l}{h} \sqrt{3 k_b m_{\text{H}} T} \exp\left(\frac{-\Delta E_{\text{act}}}{RT}\right) && \text{(C.448)}\\
&= 1.16717 \cdot 10^9\ \text{s}^{-1}. && \text{(C.449)}
\end{aligned}
$$

Here, we have assumed that all vibrational partition functions have a value of unity. To avoid confusion, we have used l, rather than R for the C-H bond length.

b) From equation C.449, we can calculate the apparent activation energy by

$$E_{\text{act}}^{\text{app}} = RT^2 \frac{\partial \ln r}{\partial T} \tag{C.450}$$

$$= k_b T^2 \frac{\partial \ln k}{\partial T} \tag{C.451}$$

$$= k_b T + \frac{1}{2} k_b T + \Delta E_{\text{act}} \tag{C.452}$$

Thus, the apparent activation energy is higher by $\frac{3}{2} k_b T$, which is about 6.2 kJ/mol at 500K. In other words, the correction of the zero point energy correction is relatively small as compared to the electronic activation energy. Nevertheless, for reactions with small barriers (e.g. for some hydrogenation reactions), the correction can be significant.

■

C.4 Solutions of Chapter 4

C.4.1 Solutions to questions

1. A power law describing a reaction has the following form $r = k \prod_i c_i \nu_i$, where k is the rate constant of the reaction, c_i are the concentrations of compounds i and ν_i are the stoichiometric coefficients of the reaction. If the reaction is an elementary reaction step, then k represents the rate by which the reactants are converted to the product state when they meet. The product $\prod_i$ then represents the chance that these reactants meet. Logically, that chance is correlated to the concentration of the reactants. Furthermore, if for the reaction two or more of the same reactants are required, then this concentration is raised to a power equal to the stoichiometric coefficient.

2. A valid set of elementary reaction steps is

$$\begin{aligned}
\mathrm{CO} + * &\leftrightarrows \mathrm{CO}* && \text{(C.453)}\\
\mathrm{CO}* + * &\leftrightarrows \mathrm{C}* + \mathrm{O}* && \text{(C.454)}\\
\mathrm{C}* + \mathrm{H}* &\leftrightarrows \mathrm{CH}* + * && \text{(C.455)}\\
\mathrm{CH}* + \mathrm{H}* &\leftrightarrows \mathrm{CH_2}* + * && \text{(C.456)}\\
\mathrm{CH_2}* + \mathrm{H}* &\leftrightarrows \mathrm{CH_3}* + * && \text{(C.457)}\\
\mathrm{CH_3}* + \mathrm{H}* &\leftrightarrows \mathrm{CH_4} + 2* && \text{(C.458)}\\
\mathrm{O}* + \mathrm{H}* &\leftrightarrows \mathrm{OH}* + * && \text{(C.459)}\\
\mathrm{OH}* + \mathrm{H}* &\leftrightarrows \mathrm{H_2O}* + * && \text{(C.460)}\\
\mathrm{H_2O} + * &\leftrightarrows \mathrm{H_2O}*, && \text{(C.461)}
\end{aligned}$$

   though more sets can be valid. For instance, the CO dissociation can be hydrogen-assisted (where first CO is hydrogenated prior to C-O bond scission). Alternatively, water can be formed by migration of a hydrogen atom between two hydroxyl species.

3. Hydrogenation of $\mathrm{CH_3}$ to methane forms a stable molecule (one that fulfills the octet rule for C) and consequently such a stable molecule is no longer covalently interacts with the surface. In fact, such a complex has only a weak interaction with the surface due to Van der Waals interactions. In contrast, ammonia has a lone pair which can still interact with the surface to form a metal-nitrogen bond.

4. The reaction order or apparent activation energy are obtained by calculating the first derivative of the *logarithm* of the rate towards the pressure or the temperature, respectively. For an overall reaction wherein there is only one type of product, the rate of consumption of any of the reactants can be expressed by the rate of the product multiplied by some constant that can be derived from the stoichiometric coefficients. For example, in the reaction $\mathrm{A} + 2\mathrm{B} + 3\mathrm{C} \rightarrow \mathrm{D}$, the rate of consumption and production of all the compounds are related by the following expression

$$r_D = -r_A = -2r_B = -3r_C \qquad \text{(C.462)}$$

   Thus, we can express the rate of consumption of any of the rate constant by calculating the quotient of the corresponding stoichiometric coefficient. As this constant has no dependency on either the pressure or on the temperature, it drops out of the logarithm as follows

$$\begin{aligned}\frac{\partial \ln r}{\partial x} &= \frac{\partial \ln (cr)}{\partial x} &\text{(C.463)}\\ &= \frac{\partial \ln (r)}{\partial x} + \frac{\partial \ln (r)}{\partial x} &\text{(C.464)}\\ &= \frac{\partial \ln (r)}{\partial x}, &\text{(C.465)}\end{aligned}$$

where x denotes either the partial pressure for the reaction order or the temperature for the apparent activation energy.

5. The surface coverage of O is determined by adsorption energies of CO, O and CO_2. Because the adsorption energy of CO is so high, the surface is predominantly covered with CO by which there are no free sites available for O or CO_2 to adsorb.

C.4.2 Solutions to exercises

The solution below pertain to the exercises of Chapter 4 on page 106 and further.

Solution 4.1

a) As evident by the assumption used in the derivation, the DRC coefficient voor CO dissociation is unity, whereas all other DRC coefficients are zero.

b)

$$\begin{aligned}n_{O_2} &= p_{O_2} \frac{\partial \ln r}{\partial p_{O_2}} &\text{(C.466)}\\ &= p_{O_2} \frac{\partial \ln \left(\dfrac{k_{\mathrm{rds}} K_{\mathrm{CO}} p_{\mathrm{CO}} \sqrt{K_{O_2} p_{O_2}}}{\left(1 + K_{\mathrm{CO}} p_{\mathrm{CO}} + \sqrt{K_{O_2} p_{O_2}}\right)^2} \right)}{\partial p_{\mathrm{CO}}} &\text{(C.467)}\\ &= D_1 + \frac{1}{2} D_2 - 2 D_3, &\text{(C.468)}\end{aligned}$$

where

$$\begin{aligned}D_1 &= p_{O_2} \frac{\partial \ln \left(k_{\mathrm{rds}} K_{\mathrm{CO}} p_{\mathrm{CO}}\right)}{\partial p_{\mathrm{CO}}} &\text{(C.469)}\\ D_2 &= p_{O_2} \frac{\partial \ln \left(\sqrt{K_{O_2} p_{O_2}} \right)}{\partial p_{O_2}} &\text{(C.470)}\\ D_3 &= p_{O_2} \frac{\partial \ln \left(1 + K_{\mathrm{CO}} p_{\mathrm{CO}} + \sqrt{K_{O_2} p_{O_2}} \right)}{\partial p_{O_2}}. &\text{(C.471)}\end{aligned}$$

The terms D_i can be readily solved, which give

$$D_1 = 0 \tag{C.472}$$

$$D_2 = \frac{1}{2} \tag{C.473}$$

$$D_3 = \frac{1}{2}\frac{\sqrt{K_{\mathrm{O}_2} p_{\mathrm{O}_2}}}{1 + K_{\mathrm{CO}} p_{\mathrm{CO}} + \sqrt{K_{\mathrm{O}_2} p_{\mathrm{O}_2}}} \tag{C.474}$$

and combining these three terms results in

$$n_{\mathrm{CO}} = \frac{1}{2} - \theta_{\mathrm{O}} \tag{C.475}$$

■

Solution 4.2

To proof that the sum-rule for the degree of selectivity holds, we need to convert the sum of degree of selectivity coefficients to a sum of degree of rate control coefficients.

$$\begin{aligned}
\sum_{i,c} \epsilon_{i,c} &= \sum_{i,c} \frac{\partial \eta_c}{\partial \ln k_i} && \text{(C.476)}\\
&= \sum_{i,c} \eta_c \frac{\partial \ln \eta_c}{\partial \ln k_i} && \text{(C.477)}\\
&= \sum_{i,c} \eta_c \frac{\partial \ln r_c / r_r}{\partial \ln k_i} && \text{(C.478)}\\
&= \sum_{i,c} \eta_c \left(\frac{\partial \ln r_c}{\partial \ln k_i} - \frac{\partial \ln r_r}{\partial \ln k_i} \right) && \text{(C.479)}\\
&= \sum_{i,c} \eta_c \left(\chi_c - \chi_r \right) && \text{(C.480)}\\
&= \sum_{c} \eta_c \sum_{i} \left(\chi_{c,i} - \chi_{r,i} \right) && \text{(C.481)}\\
&= \sum_{c} \eta_c \left(\sum_{i} \chi_{c,i} - \sum_{i} \chi_{r,i} \right) && \text{(C.482)}\\
&= \sum_{c} \eta_c \left(1 - 1 \right) && \text{(C.483)}\\
&= 0 && \text{(C.484)}
\end{aligned}$$

From a conceptual point of view, the above can be rationalized. Due to conservation of mass, you can only generate more of one particular product in expense of another product. So if one particular elementary reaction steps favors the product of a compound, there are other elementary reaction steps that favor another product by the same magnitude.

■

C.5 Solutions of Chapter 5

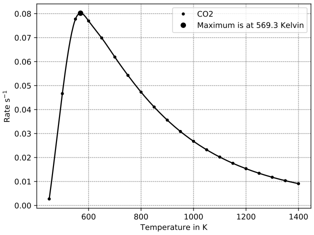
C.5.1 Solutions to Exercises

Solution 5.1

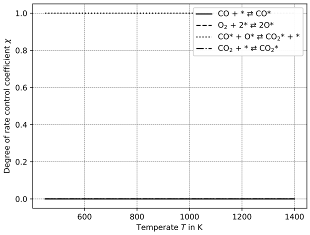
The input file for this simulation can be found using the link below:
https://www.mkmcxx.nl/downloads/input/input_ex1.mkm

a) The optimal temperature for the production of CO_2 can be found, for instance, by investigating `derivative.dat` or `derivative.png`. The results are visualized using `matplotlib` in Figure C.5a. From this Figure, it can be seen that the optimal temperature is around $T = 580$ K.

b) The rate determining step is evaluated using a degree of rate control (DRC) analysis. This analysis is visualized in Figure C.5b. From this Figure, it can be seen that the rate determining step is the surface reaction: $\mathrm{CO}*+\mathrm{O}* \leftrightarrows \mathrm{CO_2}*+*$.



(a) *Rate of production of* CO_2



(b) *Degree of rate control for* CO *oxidation*

■

Solution 5.2

The input file for this simulation can be found using the link below:
https://www.mkmcxx.nl/downloads/input/input_ex2.mkm

a) The optimal coverage is found by comparing the derivative graph with the coverage graph. The optimal coverage for the reaction is when $\theta_{\mathrm{B}} = 0.5$ corresponding with an optimal temperature around 600 K.

b) The `reaction.log` file contains the equations of the rate constants and their dependence on the temperature. This results in

$$k_A^+ = \frac{4.16595 \cdot 10^9}{\sqrt{T}} = 1.5212 \cdot 10^8 (s^{-1}) \tag{C.485}$$

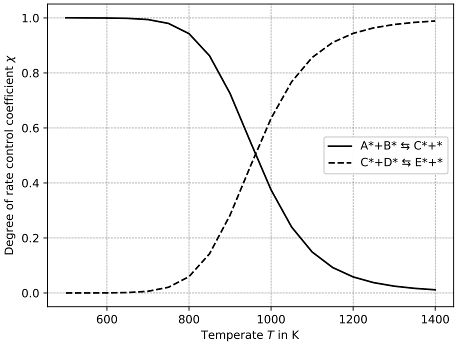


Figure C.6: *Degree of rate control*

■

Solution 5.3

The input file for this simulation can be found using the link below:
`https://www.mkmcxx.nl/downloads/input/input_ex3.mkm`

a) The set of elementary reaction steps is as follows:

$$\begin{aligned} A_2 + 2* &\leftrightarrows 2A* \\ B + * &\leftrightarrows B* \\ A * + B* &\leftrightarrows C * + * \\ A* &\leftrightarrows D* \\ C * + D* &\leftrightarrows E * + * \\ E* &\leftrightarrows E + * \end{aligned}$$

Note that compound A_2 adsorbs dissociatively onto the catalyst surface. If component A_2 would not have adsorbed dissociatively, an extra surface reaction for the dissociation of A_2 would have been added to Table 5.7.

b) From Tables ?? and ??, the following can be observed. (1) The forward reaction of $A*+B* \leftrightarrows C*+*$ has a high barrier whereas the backward reaction has a low barrier. (2) The adsorption rates of compounds A_2 and B are comparable. (3) The backward reaction of $A* \leftrightarrows D*$ has a high activation barrier, which could lead to surface poisoning by compound $D*$.

From the above, we conclude that elementary reaction step $A* + B* \leftrightarrows C* + *$ will, most likely, be significantly rate-controlling.

c) Figure C.6 shows that for the lower temperature regime the rate controlling step is $A* + B* \leftrightarrows C*+*$, however for higher temperatures the elementary reaction step $C*+D* \leftrightarrows E*+*$ becomes rate controlling.

■

Solution 5.4

The input file for this simulation can be found using the link below:
`https://www.mkmcxx.nl/downloads/input/input_ex4.mkm`

a) If elementary reaction step $\mathrm{A}* \leftrightarrows 2\mathrm{B}*$ is rate-controlling and we assume zero conversion, the site balance becomes

$$\theta_A + \theta_* = 1 \tag{C.486}$$

with θ_A being

$$\theta_A = K_A p_A \theta_* \tag{C.487}$$

Note that for calculating the equilibrium constant of A, the Hertz-Knudsen equations are used. This results in the following overall reaction rate

$$r_{RDS} = \frac{k_B^+ K_A p_A}{1 + K_A p_A} = 9.44 \cdot 10^5 (mol/s) \tag{C.488}$$

This rate is consistent with the result as obtained using MKMCXX. This confirms that the analytic expression is valid as long as the underlying assumptions are valid.

b) In `coverage.png` it can be seen that the most abundant reaction intermediate is $\mathrm{D}*$.

c) A negative DRC coefficient implies that the elementary reaction step is rate-inhibiting and therefore that increasing the reaction barrier will increase the rate of the overall reaction. The forward activation barrier for $\mathrm{B}* \leftrightarrows \mathrm{D}*$ is low compared to the backward activation barrier. Furthermore the forward activation barrier for $2\mathrm{D}* \leftrightarrows \mathrm{F}* + *$ is also relatively high. As such, for lower temperatures component $\mathrm{D}*$ poisons the catalyst surface and slows down the overall reaction rate.

d) There are several options to increase the selectivity towards component F. Some are:

(a) Decreasing the forward activation barrier for $2\mathrm{D}* \leftrightarrows \mathrm{F}* + *$.
(b) Increasing the forward activation barrier for $\mathrm{B}* \leftrightarrows \mathrm{D}*$.
(c) Decreasing the backward activation barrier for $\mathrm{B}* \leftrightarrows \mathrm{D}*$.
(d) Increasing the forward activation barrier for $\mathrm{B}* \leftrightarrows \mathrm{C}*$.
(e) Increasing the forward activation barrier for $\mathrm{C}* \leftrightarrows \mathrm{E}*$.

■

APPENDIX D

EXAM PRACTICE QUESTIONS

D.1 Explanation

The set of questions introduced here can be used as practice material for the examination of the course 6A5X0. The difficulty of these questions is expressed by the number of stars, where 3 stars (***) is considered average and 5 stars (*****) is the highest difficulty level. Solutions to these questions are provided in the next chapter on page 201.

D.2 Kinetics

Exam Practice Question D.1 | Kinetics 1

A novel route for the selective oxidation of methane towards methanol is to use sulfur-trioxide (SO_3) as an oxidant. In this reaction, adsorbed SO_3 is in equilibrium with adsorbed oxygen and SO_2 in the gas phase.

$$SO_3* \leftrightarrows SO_2 + O* \tag{D.1}$$

Methane adsorbs molecularly after which it can react with adsorbed oxygen to form methanol on the catalytic surface. This reaction is considered to be the rate-determining step. Adsorbed methanol is in equilibrium with methanol in the gas phase.

a) Provide all elementary reaction steps for the overall reaction $CH_4 + SO_3 \rightarrow CH_3OH + SO_2$

b) Derive an expression for the surface coverage of methane, methanol, sulfur-trioxide and oxygen as a function of the relevant equilibrium constants and partial pressures.

c) Derive an expression for the rate of formation of methanol as function of the partial pressures of methane, methanol, sulfur-trioxide, sulfur-dioxide and oxygen.

For the next subquestions, assume that at low temperature methanol adsorbs significantly stronger on the catalytic surface than any of the other surface intermediates.

d) Describe how the surface looks given the above assumption. Which species is the MARI (most abundant reaction intermediate)?

e) Derive an expression for the rate of formation of methanol. Deduce the reaction orders in methanol and methane.

f) Derive an expression for the apparent activation energy and connect the terms to the physical process. In other words, rationalize your obtained expression.

■

Exam Practice Question D.2 Kinetics 2

Ethylene (CH_2CH_2) can be oxidized to epoxide (CH_2CH_2O) using N_2O. This process proceeds over an Fe catalyst. In this process, ethylene adsorbs molecularly whereas N_2O adsorbs dissociatively according to the following reaction equation

$$N_2O + * \leftrightarrows N_2 + O* \tag{D.2}$$

Two elementary reaction steps occur on the catalytic surface, which is the selective oxidation of ethylene towards epoxide

$$C_2H_4 * + O* \rightarrow C_2H_4O * + * \tag{D.3}$$

and the recombination of two surface oxygen atoms to molecular oxygen in the gas phase

$$2O* \rightarrow O_2 + 2* \tag{D.4}$$

Assume that these processes occur on a catalytic surface with only one type of surface sites. Further assume that adsorbed ethylene is in equilibrium with gas phase ethylene and adsorbed epoxide is in equilibrium with gas phase epoxide. Finally, assume that both reactions D.3 and D.4 are rate-determining for the formation of epoxide and oxygen, respectively.

a) Write down all elementary reaction steps for the above mechanism.

b) Derive an expression for the rate of formation of gas phase epoxide.

c) Derive an expression for the rate of formation of gas phase molecular oxygen.

d) Deduce the lower and upper limit for the reaction orders in oxygen, nitrogen, nitrous oxide, ethylene and epoxide for both rate expressions.

Assume that for the next subquestions, ethylene and epoxide adsorb very weak as compared to dissociative adsorption of nitrous oxide.

e) Derive an expression for the rate of formation of epoxide and molecular oxygen and relate the reaction orders in oxygen, nitrogen, nitrous oxide, ethylene and epoxide to the surface coverages.

f) Derive an expression for the apparent activation energy for the formation of epoxide and molecular oxygen.

■

D.3 Statistical Thermodynamics

Exam Practice Question D.3 Statistical Thermodynamics 1

Consider the following reaction which is at equilibrium:

$$\mathrm{A} + \mathrm{B} \leftrightharpoons \mathrm{C} + \mathrm{D} \tag{D.5}$$

- Molecule A has three energetic states. The ground state of A lies ΔE higher than the ground state of B and the excited states are separated by $2\Delta E$.
- Molecule B also has three energetic states. The two excited states are degenerate (i.e. they have the same energy) and lie $3\Delta E$ above the ground state.
- Molecule C only has a single energetic state which lies equal in energy as compared to the ground state of A.
- Finally, Molecule D has three energetic states. Its ground state equals that of the ground state of C in energy. Its two excited states lie $4\Delta E$ above the ground state.

a) Draw a schematic representation of the distribution of the energetic states over the four molecules. In this drawing, the separation in energy between the states within the same molecule as well as the separation in energy between the ground states of the different molecules should be clearly conveyed.

b) Construct the partition function for each of the molecules A, B, C, D.

c) Derive the equilibrium constant K as function of the previously defined partition functions.

d) Calculate the limits of the equilibrium constant for $T \rightarrow 0$ and $T \rightarrow \infty$. Provide a physical interpretation of your results (i.e. rationalize the obtained values).

■

Exam Practice Question D.4 Statistical Thermodynamics 2

Consider the following reaction which is at equilibrium:

$$\mathrm{A} + \mathrm{B} \leftrightharpoons \mathrm{C} + \mathrm{D} \tag{D.6}$$

- Molecule A has five energetic states. The ground state of A lies ΔE higher than the ground state of B and the excited states are separated by $2\Delta E$.
- Molecule B also has three energetic states. The two excited states are degenerate (i.e. they have the same energy) and lie $3\Delta E$ above the ground state.
- Molecule C only has a single energetic state which lies equal in energy as compared to the ground state of A.
- Finally, Molecule D has three energetic states. Its ground state equals that of the ground state of C in energy. Its two excited states lie $4\Delta E$ above the ground state.

a) Draw a schematic representation of the distribution of the energetic states over the four molecules. In this drawing, the separation in energy between the states within the same molecule as well as the separation in energy between the ground states of the different molecules should be clearly conveyed.

b) Construct the partition function for each of the molecules A, B, C, D.

c) Calculate the average energy of molecule B at $T \to 0$ and $T \to \infty$. Rationalize this results on the basis of the partial occupation of the states of A at these two temperature extremes.

d) Derive the equilibrium constant K as function of the previously defined partition functions.

e) Calculate the limits of the equilibrium constant for $T \to 0$ and $T \to \infty$. Provide a physical interpretation of your results (i.e. rationalize the obtained values).

■

D.4 Collision theory

Exam Practice Question D.5 Collision theory 1

Consider the following reaction

$$H_2 + Br_2 \to 2HBr \tag{D.7}$$

which occurs at $T = 450K$. Consider this reaction to be an elementary reaction step. The rate equation is hence given by

$$r = k_{\text{reaction}}[H_2][Br_2] \tag{D.8}$$

Collision theory can be utilized to calculate the collision frequency. The frequency is given by

$$k_{\text{collisions}} = \pi d^2 \left(\frac{8 k_b T}{\pi \mu} \right)^{1/2} \tag{D.9}$$

The masses of atomic hydrogen and bromine are 1.008 Da and 79.904 Da, respectively. A Dalton equals $1.66054 \cdot 10^{-27}$ kg. The effective collision diameter of H_2 and Br_2 are 1.5 Å and 2.8 Å, respectively. The Boltzmann constant is given by $k_b = 1.38064852 \cdot 10^{-23}$ m^2 kg s^{-2} K^{-1}.

a) Calculate the value for the collision frequency between H_2 and Br_2 using collision theory given the above conditions.

b) What are the dimensions of $k_{\text{collision}}$?

c) Explain in the context of collision theory why the number of collisions that results in a reaction is very low and why this number increases rapidly with temperature.

d) How does the number of effective collisions (i.e. that lead to a reaction) scale with respect to temperature? Choose between constant, linear, quadratic, exponential and logarithmic scaling and rationalize, on the basis of statistical thermodynamics, your choice.

e) Provide an expression for the rate constant k_{reaction} and calculate its value at $T = 450K$. Assume that the activation energy is $\Delta E_a = 200$ kJ/mol.

f) Besides collision theory, there also exists transition state theory. Why do these two theories not give the same equilibrium constant when applying these to the same reaction? Consider the nature of the degrees of freedom involved in both theories.

■

D.5 Transition state theory

Exam Practice Question D.6 | Transition State Theory 1

Ozone (O_3) can adsorb on a metal surface. Upon adsorption, the molecule can neither translate nor rotate on the surface. Assume that all vibrational partition functions equal unity, with exception of the one corresponding to the reaction coordinate. We consider two situations:

1. O_3 dissociates to O and O_2, where the O_2 immediately desorbs from the surface: $O_3* \rightarrow O_2 + O*$
2. O_3 dissociates to adsorbed O and adsorbed O_2: $O_3* \rightarrow O_2 * + O*$

a) Provide a schematic depiction of the reaction for situation (1) (i.e. make a drawing of the reacting fragments on the catalytic surface). Clearly indicate the reaction coordinate. The O_2 fragment cannot translate in the transition state, but it is able to rotate. Derive an expression for the reaction rate of this dissociation reaction within the framework of transition state theory. Pay careful attention to the number and nature of the involved partition functions.

b) Use the expression obtained in the previous subquestion and compare it to the Arrhenius expression. Assuming that both expressions give the same rate, what would be the activation energy and the pre-exponential factor of the Arrhenius equation if the previously obtained equation is cast to the Arrhenius formulation?

c) Provide a schematic depiction of the reaction for situation (2). In the transition state, O_2 can neither rotate, nor translate. Derive an expression for the reaction rate of this dissociation reaction within the framework of transition state theory. Pay careful attention to the number and nature of the involved partition functions.

d) What is in situation (2) the activation energy and pre-exponential factor if the rate expression of the previous subquestion is cast to Arrhenius form?

e) In which of the two situations will the reaction rate for dissociation be the largest if we assume that the activation energy for situation (1) and (2) is identical? Rationalize your result using the concept of entropy and relate this to the partition functions.

■

Exam Practice Question D.7 | Transition State Theory 2

In this question, you are going to derive the Eyring expression from basic principles. The Eyring expression describes the rate of change between two stable states (i.e. initial and final state) via a transition state that connects these two states.

a) What are the fundamental assumptions of the Eyring equation and use these assumptions to construct the following equation:

$$k = \kappa K, \tag{D.10}$$

where k is the rate constant, κ is a prefactor with dimensionality s^{-1} and K is an equilibrium constant (dimensionless). Explain which equilibrium the equilibrium constant K represents.

b) Express the equilibrium constant as a function of the partition functions of the involved states. For the time being, do not make any assumptions about the number and nature of the degrees of freedom.

c) We assume that the motion over the transition state can be modeled as a very weak vibration. Show (i.e. provide a clear and detailed derivation) that using this assumption we are able to derive the following expression for the reaction rate constant:

$$k = \kappa \frac{1}{1 - \exp\left(\frac{-h\nu}{k_b T}\right)} \frac{Q^{\dagger}_{\text{TS}}}{Q_{\text{IS}}} \exp\left(\frac{-\Delta E_{\text{act}}}{k_b T}\right), \tag{D.11}$$

where Q is the product of the partition functions of one or more degrees of freedom, the subscripts *IS* and *TS* refer to initial and final state, respectively, and ν is the frequency of the vibration (in s^{-1}). **Please note the dagger superscript (†) in $Q^{\dagger}_{\text{TS}}$!**

d) Provide a supporting motivation for the assumption that the vibration over the transition state is weak. Use in your explanation the concept that a vibrational degree of freedom corresponds to a chemical bond.

e) When $\left|\frac{-h\nu}{k_b T}\right| \ll 1$, the expression for the vibrational partition function can be simplified. Use the Taylor-expansion of the exponential function:

$$\exp x = 1 + x + \frac{x^2}{2!} + \frac{x^3}{3!} + \frac{x^4}{4!} \cdots \tag{D.12}$$

to show that the vibrational partition function can be simplified to

$$q_v = \frac{k_b T}{h\nu} \tag{D.13}$$

by excluding all terms in the Taylor expression beyond the linear term (i.e. discard all quadratic and higher order terms).

f) Finally, which two variables need to be equal to obtain the general Eyring equation as given by

$$k = \frac{k_b T}{h} \frac{Q^{\dagger}_{\text{TS}}}{Q_{\text{IS}}} \exp\left(\frac{-\Delta E_{\text{act}}}{k_b T}\right) \tag{D.14}$$

■

APPENDIX

E

EXAM QUESTION SOLUTIONS

E.1 Introduction

Below, the solutions to the exam practice questions are provided. These solutions are written in a concise fashion, sometimes omitting trivial steps in the derivation. If you are unable to follow some or more of the derivations, it is recommended that you look back at one of the earlier exercises of the corresponding chapter. More elaborate solutions are provided there which might help you in understanding.

E.2 Kinetics

Exam Solution E.1 Kinetics 1

a) The set of elementary reaction steps is given below. Herein, equation E.4 is the rate-determining step.

1. $SO_3{*} \leftrightarrows SO_2 + O\,{*}$ (E.1)
2. $CH_4 + {*} \leftrightarrows CH_4\,{*}$ (E.2)
3. $SO_3 + {*} \leftrightarrows SO_3\,{*}$ (E.3)
4. $CH_4\,{*} + O{*} \leftrightarrows CH_3OH\,{*} + {*}$ (E.4)
5. $CH_3OH + {*} \leftrightarrows CH_3OH{*}$ (E.5)

b) Assume a quasi-equilibrium for all the elementary reaction steps before the rate-determining step. From these, the following Langmuir adsorption isotherms can be derived.

$$\theta_{CH_4} = \frac{K_2 p_{CH_4}}{1 + K_2 p_{CH_4} + K_3 p_{SO_3} + K_5 p_{CH_3OH} + \frac{K_1 K_3 p_{SO_3}}{p_{SO_2}}} \tag{E.6}$$

$$\theta_{SO_3} = \frac{K_3 p_{SO_3}}{1 + K_2 p_{CH_4} + K_3 p_{SO_3} + K_5 p_{CH_3OH} + \frac{K_1 K_3 p_{SO_3}}{p_{SO_2}}} \tag{E.7}$$

$$\theta_{CH_3OH} = \frac{K_5 p_{CH_3OH}}{1 + K_2 p_{CH_4} + K_3 p_{SO_3} + K_5 p_{CH_3OH} + \frac{K_1 K_3 p_{SO_3}}{p_{SO_2}}} \tag{E.8}$$

$$\theta_{O} = \frac{\frac{K_1 K_3 p_{SO_3}}{p_{SO_2}}}{1 + K_2 p_{CH_4} + K_3 p_{SO_3} + K_5 p_{CH_3OH} + \frac{K_1 K_3 p_{SO_3}}{p_{SO_2}}} \tag{E.9}$$

(E.10)

c) The rate of formation for methanol can be directly found by plugging in the relevant Langmuir isotherms in the rate expression for elementary reaction step (4)

$$r_{CH_3OH} = k_4 \theta_{CH_4} \theta_O = \frac{k_4 K_2 p_{CH_4} \frac{K_1 K_3 p_{SO_3}}{p_{SO_2}}}{\left(1 + K_2 p_{CH_4} + K_3 p_{SO_3} + K_5 p_{CH_3OH} + \frac{K_1 K_3 p_{SO_3}}{p_{SO_2}}\right)^2} \tag{E.11}$$

d) Adsorbed methanol is the MARI, hence the surface mainly contains methanol and vacant sites.

e) Applying the MARI enables us to neglect those coverage terms in the denominator which do **not** correspond to the MARI. Next, the differential for the reaction is solved for the simplified rate expression to obtain the reaction order in methanol and methane.

$$r_{CH_3OH} = k_4 \theta_{CH_4} \theta_O = \frac{k_4 K_2 p_{CH_4} \frac{K_1 K_3 p_{SO_3}}{p_{SO_2}}}{\left(1 + K_5 p_{CH_3OH}\right)^2} \tag{E.12}$$

$$n_{CH_3OH} = p_{CH_3OH} \frac{\partial \ln r}{\partial p_{CH_3OH}} = -2\theta_{CH_3OH} \tag{E.13}$$

$$n_{CH_4} = p_{CH_4} \frac{\partial \ln r}{\partial p_{CH_4}} = 1 \tag{E.14}$$

f) The apparent activation energy is given by

$$\Delta E_{act}^{app} = RT^2 \frac{\partial \ln r}{\partial T} = \Delta E_{act}^{(4)} + \Delta H_1 + \Delta H_2 + \Delta H_3 - 2\theta_{CH_3OH} \Delta H_5 \tag{E.15}$$

The apparent activation energy is the amount of energy which needs to invested for the overall reaction to occur. This energy is equal to the activation energy of the rate-determining step and is reduced by the adsorption energy of particular components when the surface is vacant but increased when the surface is poisoned. The latter can be interpreted in the sense that some energy needs to be invested to remove a component from the surface. In this particular case, the reaction can be inhibited by methanol as is seen from the (negative) dependence on the methanol surface coverage.

■

Exam Solution E.2 Kinetics 2

a)

$$\begin{aligned}
&1.\ N_2O + * \leftrightarrows N_2 + O* && \text{(E.16)}\\
&2.\ C_2H_4 + * \leftrightarrows C_2H_4* && \text{(E.17)}\\
&3.\ C_2H_4 * + O* \leftrightarrows C_2H_4O* && \text{(E.18)}\\
&4.\ O_2 + 2* \leftrightarrows 2O* && \text{(E.19)}\\
&5.\ C_2H_4O + * \leftrightarrows C_2H_4O* && \text{(E.20)}
\end{aligned}$$

b)

$$r_{C_2H_4O} = k_3 \theta_{C_2H_4} \theta_O \tag{E.21}$$

$$= k_3 \frac{K_1 \frac{p_{N_2O}}{p_{N_2}} K_2 p_{C_2H_4}}{\left(1 + K_1 \frac{p_{N_2O}}{p_{N_2}} + K_2 p_{C_2H_4} + K_5 p_{C_2H_4O}\right)^2} \tag{E.22}$$

(E.23)

c)

$$r_{O_2} = k_4 \theta_O^2 \tag{E.24}$$

$$= k_4 \frac{\left(K_1 \frac{p_{N_2O}}{p_{N_2}}\right)^2}{\left(1 + K_1 \frac{p_{N_2O}}{p_{N_2}} + K_2 p_{C_2H_4} + K_5 p_{C_2H_4O}\right)^2} \tag{E.25}$$

d)

reaction orders	O_2	N_2	N_2O	C_2H_4	C_2H_4O
$r_{C_2H_4O}$	0	-1,1	-1,1	-1,1	-2,0
r_{O_2}	0	-2,0	0,2	-2,0	-2,0

e)

$$r_{C_2H_4O} = k_3 \frac{K_1 \frac{p_{N_2O}}{p_{N_2}} K_2 p_{C_2H_4}}{\left(1 + K_1 \frac{p_{N_2O}}{p_{N_2}}\right)^2} \tag{E.26}$$

$$r_{O_2} = k_4 \frac{\left(K_1 \frac{p_{N_2O}}{p_{N_2}}\right)^2}{\left(1 + K_1 \frac{p_{N_2O}}{p_{N_2}}\right)^2} \tag{E.27}$$

We obtain the the following reaction order for the epoxide

$$n_{O_2} = 0 \tag{E.28}$$
$$n_{N_2} = -1 + 2\theta_O \tag{E.29}$$
$$n_{N_2O} = 1 - 2\theta_O \tag{E.30}$$
$$n_{C_2H_4} = 1 \tag{E.31}$$
$$n_{C_2H_4O} = 0 \tag{E.32}$$

and for molecular oxygen

$$n_{O_2} = 0 \tag{E.33}$$
$$n_{N_2} = -2 + 2\theta_O \tag{E.34}$$
$$n_{N_2O} = 2 - 2\theta_O \tag{E.35}$$
$$n_{C_2H_4} = 0 \tag{E.36}$$
$$n_{C_2H_4O} = 0 \tag{E.37}$$

f) The apparent activation energy for epoxide formation is

$$\Delta E_{\text{act}}^{\text{app}} = \Delta E_3 + \Delta H_1 (1 - 2\theta_O) + \Delta H_2 \tag{E.38}$$

and for the formation of molecular oxygen

$$\Delta E_{\text{act}}^{\text{app}} = \Delta E_4 + \Delta H_1 (2 - 2\theta_O) \tag{E.39}$$

■

E.3 Statistical Thermodynamics

Exam Solution E.3 Statistical Thermodynamics 1

a)

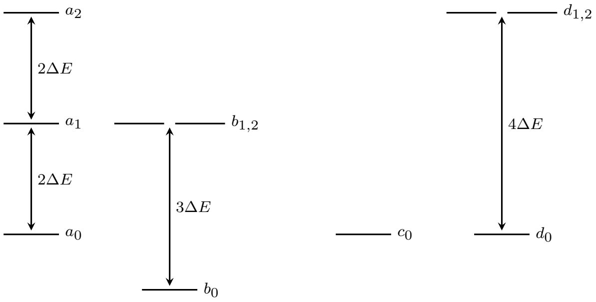


Figure E.1: *Energy level diagram of A, B, C, and D.*

b) Set the energy level of b_0 to the global ground state (i.e. zero):

$$q_A = \exp\left(\frac{-\Delta E}{k_b T}\right) + \exp\left(\frac{-3\Delta E}{k_b T}\right) + \exp\left(\frac{-5\Delta E}{k_b T}\right) \tag{E.40}$$

$$q_B = 1 + 2\exp\left(\frac{-3\Delta E}{k_b T}\right) \tag{E.41}$$

$$q_C = \exp\left(\frac{-\Delta E}{k_b T}\right) \tag{E.42}$$

$$q_D = \exp\left(\frac{-\Delta E}{k_b T}\right) + 2\exp\left(\frac{-5\Delta E}{k_b T}\right) \tag{E.43}$$

c) The equilibrium constant K for the above reaction is

$$K = \frac{q_C q_D}{q_A q_B} \tag{E.44}$$

d) When $T \to 0$, all exponentials go to zero, whereas at $T \to \infty$, all exponentials go to unity. Thus:

$$K(T \to 0) = \lim \frac{0 \cdot 0}{1 \cdot 0} = 0 \tag{E.45}$$

$$K(T \to \infty) = \lim \frac{1 \cdot 3}{3 \cdot 3} = \frac{1}{3} \tag{E.46}$$

At $T \to 0$, only the lowest state is occupied, which is b_0. Hence, the equilibrium constant is 0. At $T \to \infty$, all states are equally likely to be occupied. Hence, our equilibrium constant should resemble the ratio of the products of the number of states of each component (which is basically the definition of the partition function at infinitely high temperature).

■

Exam Solution E.4 Statistical Thermodynamics 2

a)

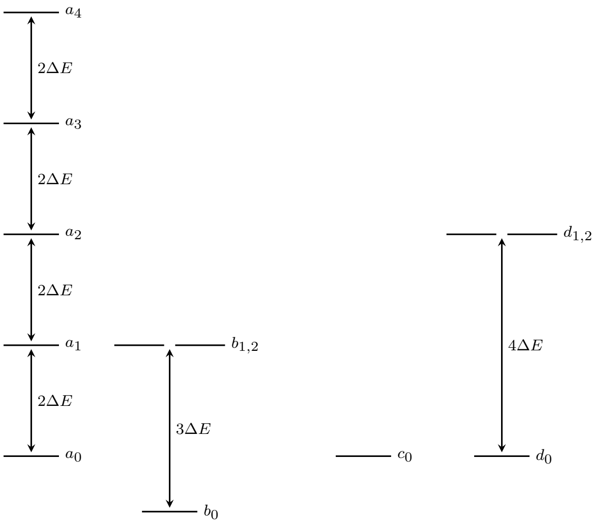


Figure E.2: *Energy level diagram of A, B, C, and D.*

b) Set the energy level of b_0 to the global ground state (i.e. zero):

$$\begin{aligned} q_A =& \exp\left(\frac{-\Delta E}{k_b T}\right) + \exp\left(\frac{-3\Delta E}{k_b T}\right) + \exp\left(\frac{-5\Delta E}{k_b T}\right) \cdots \\ & \cdots + \exp\left(\frac{-7\Delta E}{k_b T}\right) + \exp\left(\frac{-9\Delta E}{k_b T}\right) \end{aligned} \tag{E.47}$$

$$q_B = 1 + 2\exp\left(\frac{-3\Delta E}{k_b T}\right) \tag{E.48}$$

$$q_C = \exp\left(\frac{-\Delta E}{k_b T}\right) \tag{E.49}$$

$$q_D = \exp\left(\frac{-\Delta E}{k_b T}\right) + 2\exp\left(\frac{-5\Delta E}{k_b T}\right) \tag{E.50}$$

c) The equilibrium constant K for the above reaction is

$$K = \frac{q_C q_D}{q_A q_B} \tag{E.51}$$

d) The average energy of molecule B is given by

$$\overline{\epsilon_B} = k_b T^2 \frac{\partial \ln q_B}{\partial T} \tag{E.52}$$

$$= \frac{2 \cdot 3\Delta E \cdot \exp\left(\frac{-3\Delta E}{k_b T}\right)}{1 + 2\exp\left(\frac{-3\Delta E}{k_b T}\right)} \tag{E.53}$$

At $T \to 0$, $\overline{\epsilon_A} = 0$ as only the ground state is occupied which has an energy value of 0.

At $T \to \infty$, $\overline{\epsilon_A} = 2\Delta E$, as all its states are equally occupied. Hence, we get the arithmetic average of the energy values of all these states.

e) When $T \to 0$, all exponentials go to zero, whereas at $T \to \infty$, all exponentials go to unity. Thus:

$$K(T \to 0) = \lim \frac{0 \cdot 0}{1 \cdot 0} = 0 \tag{E.54}$$

$$K(T \to \infty) = \lim \frac{1 \cdot 3}{5 \cdot 3} = \frac{1}{5} \tag{E.55}$$

At $T \to 0$, only the lowest state is occupied, which is b_0. Hence, the equilibrium constant is 0. At $T \to \infty$, all states are equally likely to be occupied. Hence, our equilibrium constant should resemble the ratio of the products of the number of states of each component (which is basically the definition of the partition function at infinitely high temperature).

E.4 Collision theory

Exam Solution E.5 Collision theory 1

a)

$$d^2 = \left(\frac{1.5 \cdot 10^{-10} + 2.8 \cdot 10^{-10}}{2} \right)^2 = 4.6 \cdot 10^{-20} \text{ m}^2 \tag{E.56}$$

$$\mu = \frac{1.008 \cdot 2 \cdot 79.904 \cdot 2}{1.008 \cdot 2 + 79.904 \cdot 2} \cdot 1.66 \cdot 10^{-27} = 3.30 \cdot 10^{-27} \text{ kg} \tag{E.57}$$

$$k = \pi \cdot 4.6 \cdot 10^{-20} \left(\frac{8k_b \cdot 450}{\pi \cdot 3.30 \cdot 10^{-27}} \right)^{1/2} = 3.16 \cdot 10^{-16} \text{ collisions} \cdot \text{m}^3 \cdot \text{s}^{-1} \tag{E.58}$$

b) The unit is collisions $\cdot\, \text{m}^3 \cdot \text{s}^{-1}$.

c) Not every collision immediately results in a reaction. Only those collisions where the particles have sufficient kinetic energy, i.e. equal or larger than the activation energy, will result in a reaction. The number of particles that meets this criterion increases with temperature.

d) The average kinetic energy of the particles in the ensemble increases exponentially with temperature, as can be seen from the Maxwell-Boltzmann velocity distribution and the related average kinetic energy expression.

e)

$$k_{\text{reaction}} = k_{\text{collision}} \cdot \exp\left(\frac{-\Delta E_a}{RT} \right) = 3.16 \cdot 10^{-16} \cdot \exp\left(\frac{-200 \cdot 10^3}{R \cdot 450} \right) \tag{E.59}$$

$$= 6.1880452 \cdot 10^{-40} \text{ m}^3 \cdot \text{s}^{-1} \tag{E.60}$$

Note that this is the reaction rate constant on a per-particle basis. On a per molecule basis, the number is much larger (by about 23 orders of magnitude).

f) In collision theory, only translational degrees of freedom are taken into account, whereas in transition state theory, also rotational and vibrational degrees of freedom are considered. (Note that despite this discrepancy in collision theory, since translational degrees of freedom give the largest partition functions as compared to rotational and vibrational degrees of freedom, collision theory remains fairly accurate.)

■

E.5 Transition state theory

Exam Solution E.6 Transition State Theory 1

a)

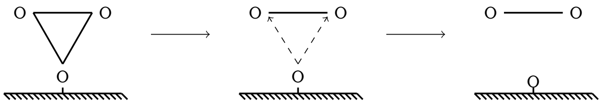


Figure E.3: *Schematic depiction of the initial, transition and final state of* O_3 *dissociation over a catalytic surface. Note that this is a side view, where the viewing direction is parallel to the catalytic surface. The reaction coordinate is shown as a dashed arrow in the image for the transition state.*

$$k = \frac{k_bT}{h}\frac{q_v^{(7)}\,q_r^{(1)}}{q_v^{(9)}}\exp\left(\frac{-\Delta E_{\text{act}}}{k_bT}\right) = \frac{k_bT}{h} q_r \exp\left(\frac{-\Delta E_{\text{act}}}{k_bT}\right) \tag{E.61}$$

In the transition state, the complex has in total 9 degrees of freedom. One degree of freedom (DOF) corresponds to the imaginary frequency and is in the direction of the reaction coordinate. This DOF is represented by $\frac{k_bT}{h}$. Another DOF is the rotational DOF and all other DOFs are vibrational. In the initial state, all DOFs are of a vibrational nature.

b) The Arrhenius-form activation energy is given by

$$\Delta E_{\text{act}}^{\text{arrhenius}} = RT^2\frac{\partial \ln k}{\partial T} \tag{E.62}$$

Plugging the above rate expression into this formula yields for the activation energy:

$$\Delta E_{\text{act}}^{\text{arrhenius}} = \Delta E_{\text{act}} + 2k_bT \tag{E.63}$$

If the two forms (Arrhenius and Eyring) are equal, this yields the following expression for the pre-exponential factor:

$$\nu_{\text{arrhenius}} = \frac{k_bT}{h}\cdot e^2\cdot q_r \tag{E.64}$$

c)

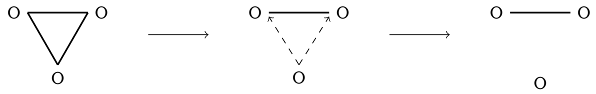


Figure E.4: *Schematic depiction of the initial, transition and final state of* O_3 *dissociation over a catalytic surface. Note that this is a top view, where the viewing direction is perpendicular to the catalytic surface. The reaction coordinate is shown as a dashed arrow in the image for the transition state.*

$$k = \frac{k_b T}{h} \frac{q_v^{(8)}}{q_v^{(9)}} \exp\left(\frac{-\Delta E_{\text{act}}}{k_b T}\right) = \frac{k_b T}{h} \exp\left(\frac{-\Delta E_{\text{act}}}{k_b T}\right) \tag{E.65}$$

In the transition state, the complex has in total 9 degrees of freedom. One degree of freedom (DOF) corresponds to the imaginary frequency and is in the direction of the reaction coordinate. This DOF is represented by $\frac{k_b T}{h}$. All other DOFs are vibrational. In the initial state, all DOFs are of a vibrational nature.

d) The Arrhenius-form activation energy is:

$$\Delta E_{\text{act}}^{\text{arrhenius}} = \Delta E_{\text{act}} + k_b T \tag{E.66}$$

And the corresponding pre-exponential factor becomes:

$$\nu_{\text{arrhenius}} = \frac{k_b T}{h} \cdot e \tag{E.67}$$

e) The important difference between situation (1) and (2) is that in situation the O_2 fragment in the transition state has a rotational degree of freedom. Rotational degrees of freedom have more configurational freedom as compared to vibrational degrees of freedom. Hence, the transition state of situation (1) is higher in entropy and thus lower in Gibbs free energy (recall that $\Delta G = \Delta H - T\Delta S$) as compared to situation (2). We can thus conclude that the reaction of situation (1) will proceed faster than situation (2).

■

Exam Solution E.7 Transition State Theory 2

a) We assume that the initial state is in thermal equilibrium with the transition state. Hence, we introduce an equilibrium constant K. To determine the rate constant to go from the initial to the final state, we introduce a crossing frequency κ that represents the number of species that goes to the final state once that species is at the transition state. This requires us to define another assumption, which states that once a species has crossed the transition state, it will always go to the final state. (it can of course go back to the initial state, but that is captured in the rate expression for the backward reaction)

b) The equilibrium constant is given by

$$K = \frac{Q_{\text{TS}}}{Q_{\text{IS}}} \tag{E.68}$$

c) The total partition function Q is the product of the molecular partition functions representing vibrational, rotational and translations degrees of freedom and the electronic partition function. If we extract the weak vibrational partition function and the electronic partition function, we can rewrite the above equation to

$$K = q_{v,\text{weak}} \cdot \frac{Q^{\dagger}_{\text{TS}}}{Q_{\text{IS}}} \cdot \frac{q_{\text{TS},e}}{q_{\text{IS},e}}, \tag{E.69}$$

wherein the † indicates that we have extracted the partition function corresponding to the reaction coordinate and we have redefined Q to only consist of molecular degrees of freedom (i.e. without the electronic partition function). The quotient of the electronic partition functions can be rewritten using the Boltzmann formula and we can plug in the formula for the vibrational partition function to obtain

$$k = \kappa \frac{1}{1 - \exp\left(\frac{-h\nu}{k_b T}\right)} \frac{Q^{\dagger}_{\text{TS}}}{Q_{\text{IS}}} \exp\left(\frac{-\Delta E_{\text{act}}}{k_b T}\right) \tag{E.70}$$

d) Upon bond-breaking or formation, there exist a transition state wherein the bond is elongated with respect to the most stable state (i.e. the bonded state). In the transition state, it is thus expected that the bond is weaker. A weaker bond is represented by a shallower potential, hence elongation or shortening of the bond will not result in a significant change in the energy. Hence, the force constant representing the vibrational degree of freedom will be relatively small, thus rationalizing the assumption to model the transition as a weak vibration.

e)

$$q_v = \frac{1}{1 - \exp\left(\frac{-h\nu}{k_b T}\right)} \tag{E.71}$$

$$\approx \frac{1}{1 - 1 + \left(\frac{-h\nu}{k_b T}\right)} \tag{E.72}$$

$$\approx \frac{k_b T}{h\nu} \tag{E.73}$$

f) To obtain the general expression for the Eyring equation, the identify $\nu = \kappa$ needs to be true in order to cancel out the κ in the equation.

■

APPENDIX F

MKMCXX

F.1 Settings

The settings section of the input file offers the option to change a lot of default values. In Table F.1, the most relevant settings are given. Most settings are to turn certain functions on or off. Use 0 to turn a feature off and 1 to turn a feature on.

F.2 Troubleshooting

If the input file contains an error, MKMCXX will return one of the following error messages.

- Terminal output: 'The system cannot find the path specified.'

  Make sure the MKMCXX.exe file is present in the bin folder. Also check if the run.bat is in the right sub folder.

- Terminal output: 'Error, could not allocate compound.'

  MKMCXX can't find all compounds specified in the reactions section. Check if all compounds are listed in the compound section and that there are no mistakes in the reaction section.

- Terminal output: 'No conservation of sites for run X: (Variables)'

  Check the elementary reaction steps in the reaction section. Make sure every reaction step is balanced.

- Terminal output: 'Caught signal seg 11. You broke MKMCXX!!!'

  Check the input data in the run section for mistakes. Also make sure the tolerances are reasonable, e.g. $1e-10$ and not $1e10$.

- Terminal output: 'ERROR: RUN (line X): Temperature terminate called after throwing an instance of 'std::runtime_error.'

  Make sure that the temperature on the given line is correct en is a real number.

The input file can also be incomplete or contain other problems, as listed below.

Table F.1: *Settings for MKMCXX*

Keyword	Value	Explanation
TYPE	-	Type run used for the simulation. Default = sequence run.
PRESSURE	# bar	Sets the overall pressure for the system.
ORDERS	0 or 1	Calculate reaction order. Default = 0.
EACT	0 or 1	Calculate apparent activation energy. Default = 0.
DRC	0 or 1	Calculate degree of rate control. Default = 0.
REACTANTS	Compound	Specify reactant for reaction order.
KEYCOMPONENT	Compound	Specify components for E_{app} and DRC.
USETIMESTAMP	0 or 1	Should MKMCXX add a timestamps or not. Default = 1.
MAKEPLOTS	0 or 1	Should MKMCXX make preliminary plots. Default = 1.
GRAPHDATA	0 or 1	If MKMCXX does not need to create plots, MKMCXX can still create the data for the plots. Default = 0
GRAPHFILTER	0 or 1	If MKMCXX should remove small value from preliminary plots. Default = 1
NETWORK	0 or 1	Should MKMCXX add network graphs. Default = 1.
NETWORK_RATES	0 or 1	Should MKMCXX incorporate forward and backward rates. Default = 0.
COLORBLIND	0 or 1	MKMCXX can use improved colors to counter colorblindness. Default = 0.
DEBUG	0 or 1	Generate more convergence data. Default = 0.
NPAR	1 - 8	Amount threads of the processor MKMCXX is aloud to use. Default = 1.
SOLSTOPTIME	0 or 1	The solver is forced to evaluate dydt/jac at t out or allowed to extrapolate backwards. Default = 1.
SOLMAXSTEP	1 - ∞	Amount internal steps solver may take before t_{out} is reached. Default = 5000.
SOLTESTFAIL	1 - ∞	Maximum amount of error test failures per step are aloud. Default = 70.
SOLCONVFAIL	1 - ∞	Maximum amount of convergence test failure per step are aloud. Default = 100.
PRECISION	0 - ∞	Amount of decimals in the output files. Default = 10

- The simulation runs, but the output shows no production.

  Make sure all elementary reaction steps are listed in the reactions sections. Also check if the chosen reaction network is complete, in other words check if you can fully go from reactant to product by following your network.

- The simulation runs, but for some temperature one or multiple compounds have not converged.

  Convergence problems can be solved using the following steps.

  - First of all, increase the simulation time for the specific run. It is possible that the system has not achieved steady state yet, and this can be achieved by increasing the simulation time up until $t = 1e12$.
  - If the simulation time does not solve the problem, try to tighten the tolerances. Tightening the absolute tolerance up until $AbsTol = 1e - 45$ can solve the

convergence problem. The relevant tolerances can be tightened up until $RelTol = 1e-16$.

  - If the specific temperature is not important for the simulation, try removing it.
  - If the specific temperature is important for the simulation, try adjusting the temperature with a few degrees. This may fix the problem if you happen to be at a bifurcation point.

- The reaction order is not calculated by MKMCXX.

  Check the reactants specified by the reactants in the settings, make sure all the reactants are specified. Also make sure the key components, often products, are correctly specified.

- The apparent activation energy is not calculated by MKMCXX, or not correctly.

  If the apparent activation energy is not calculated correctly by MKMCXX, check the specified compound by the keycompounds in the settings section.

- The degree of rate control is not calculated by MKMCXX.

  The sum of the degree of rate control should always be one. It is possible to have a negative degree of rate control. If the sum is not 1, make sure the right elementary reaction steps are taken into account when calculating the degree of rate control. Also make sure the right compounds are specified by the keycompounds.

The program MKMCXX offers a debug mode which offers messages in the terminal. The debug mode produces more data on the relative derivatives (dydt/y) to check for the convergence. The debug mode is enabled by

Listing F.1: *Enabling debug mode.*

```
&settings

# Enable debug mode.
DEBUG = 1
```

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