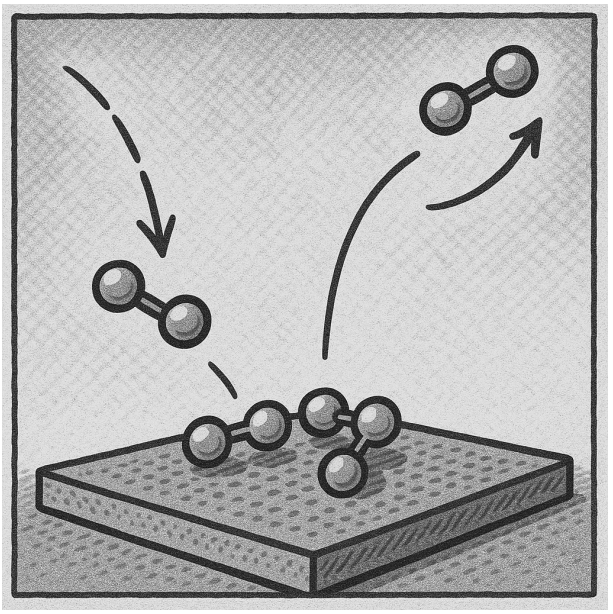
Introduction to Microkinetic Modeling



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

■

Preface to version 1.6

A lot of new content was added to the book in version 1.6. A more thorough introduction of statistical thermodynamics is given. A detailed derivation of various thermodynamic constants and their calculation from the canonical partition function is added. The molecular partition functions is also discussed in more details and their contribution to the heat capacity and entropy is shown. This led to so much more content of what was previously Chapter 2, that that chapter was split up into three chapters. Chapter 5 has also received a massive overhaul. The reaction rate constants are derived from fundamental principles and the number of cases which are shown has doubled.

The book has also received an upgrade in terms of the lay-out. The styling for exercises has been changed and the solutions to the exercises are now provided directly after the exercises. Also, quite some new exercises (and corresponding solutions) have been added to give the reader some options to practice with the material. Throughout the text, you will notice ⚙-boxes telling you which exercises match the contents you have just read.

The number of pages has grown from about 200 to over 300 pages, so I hope that there is much more content for you to enjoy. I have received a lot of feedback on the previous iteration and I have tried to incorporate as much of it as possible in this iteration; please keep sharing your opinion, it is highly valued. As usual, you can find the names of the people who contributed to this work on the next page.

Ivo Filot

Geldrop, 7th January 2020

■

Preface to version 1.7

This book has steadily been growing over the past years on the basis of valuable input from both students as well as colleagues. Looking back at the original version which was only about 90 pages, the book has almost quadrupled in size. In Figure 1, you can find the number of pages for each edition of the book. Besides a lot of additional exercise and detailed workouts, a lot of content was added as well. In this version, I have expanded upon the collision theory section which was a bit lacking in the previous edition. Furthermore, a couple of exercises were modified to better accommodate the content of the corresponding chapter. Because of three very critical students, a lot of spelling, grammar and mathematical errors were found and fixed. Anne Slegers, Iris Nogueroles Langa and Ronald Smits, a bit shout-out to you for your valuable feedback. All the other students who made contributions can be found in the acknowledgements section on the next page. The list is starting to become quite big.

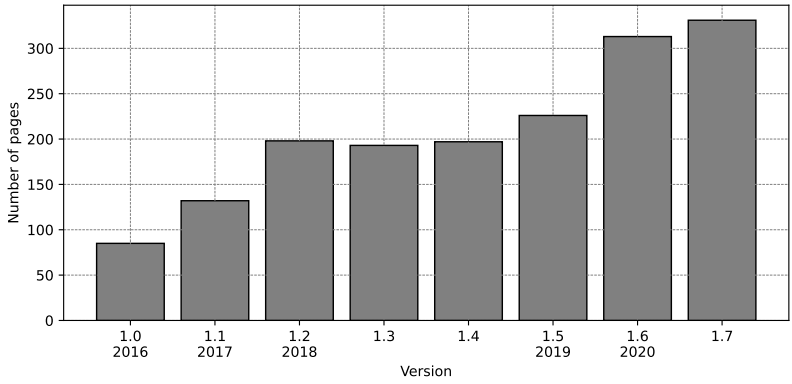

Figure 1: *Number of pages for each version of the book.*

Ivo Filot

Geldrop, 7th December 2020

Preface to version 1.8

The previous academic year proved to be exceptionally difficult due to the - by now - infamous global pandemic. It put a lot of pressure on us as teachers to develop online educational resources, but also a lot of pressure on the students, who were forced to work more independently and isolated than ever before. Such an environment is far from ideal but also shows what items in the lecture material are subpar and need to be improved. We took the suggestions and feedback received from the students to heart and have attempted to implement as many of them into this new iteration. The biggest change noticeable is the vast increase in the number of exam level exercises, including the highly appreciated workouts. This alone encompasses about 80 additional pages to the book. The book always contained a lot of exercises, but the demand for exam level exercises, basically enabling the student to assess their skill level at exam level difficulty, remained quite popular. We hope that this large set will quench your educational thirst. The list of students who contributed to this book has also grown as can be seen on the acknowledgement page. One person deserves special attention, which is Andra Olaru. Andra has worked very hard and with a lot of dedication incorporating all the additional exam level questions. This has been highly appreciated and hopefully not only by me, but by you, the student who is going to use these exercises and workouts, as well. I sincerely hope this iteration of the book will guide you through the topic of kinetics with ease and efficiency.

Ivo Filot — Geldrop, 10th August 2021

■

Preface to version 1.9

With version 1.9, the book has undergone a modest yet important restructuring. The most significant change is the removal of Chapter 7, which previously contained tutorials and explanations related to MKMCXX version 2. MKMCXX, the microkinetics software suite that I have developed, has since evolved considerably, and version 3 is now available. As a result, the content of Chapter 7 had become outdated and no longer reflected the current state of the software.

For future versions, all MKMCXX-related tutorials, examples, and explanations will be published on the website rather than in this book. This shift will allow for more flexibility in keeping the material aligned with ongoing software developments, while the book itself will remain focused on the theoretical and conceptual framework of kinetics and catalysis.

Although this update is smaller in scope than some previous ones, it represents an important step toward maintaining the relevance and clarity of the book. The remaining chapters have been slightly adjusted to ensure a smooth progression of topics.

As always, I am very grateful for the continued feedback and enthusiasm from students and colleagues. Your input remains invaluable in refining both the educational content and the tools that support it. Please continue to share your thoughts and suggestions; they are always welcome.

Ivo Filot — Geldrop, 24th October 2025

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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:

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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. In this respect, the counterpart of kinetics is thermodynamics, which deals with the *static* point of view on chemistry. Whereas thermodynamics is mainly interested in the initial and final states of a system, within kinetics we are interested in the complete mechanism and the time by which the system is converted from one state to another. Thermodynamics seeks to find a description of equilibria, whereas in kinetics equilibrium is a special situation wherein the forward and backward rates are equal to each other. In a way,

kinetics can be seen as a more fundamental science than thermodynamics. That being said, 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 emphasis on heterogeneous catalysis. This chapter serves as an overview and sets the stage for the contents of the upcoming chapters. In Chapter 1 we will treat the concept of an elementary reaction simply as the fundamental building block within a kinetic mechanism. This concept is vastly expanded in Chapter 4 and treated from the perspective of transition state theory wherein the effect of configurational degrees of freedom are treated using a statistical thermodynamics approach. Chapters 2 and 3 serve herein to provide the necessary background to properly introduce transition state theory. Finally, Chapters 5, 6 and 7 explain how the theory can be brought into practice and introduces the field of microkinetic modelling.

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 (analytical) rate expressions for typical chemical processes and derive such expressions on the basis of a reaction mechanism and intelligently chosen assumptions. 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

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

where $[X]$ is the concentration of component X and r is the reaction rate. Expression 1.2 derives from the **law of mass action**, which is the proposition that the rate of a chemical reaction is directly proportional to the product of the activities or concentrations of the reactants. This law holds in principle only for so-called elementary reaction steps. A detailed discussion on what exactly entails an elementary reaction step is given further on in this book[1], 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.

[1] A concise definition would be as follows: An elementary reaction step corresponds to a minimum energy pathway over the potential energy between two local minima, i.e. stable states, wherein this minimum energy pathway only has a single transition state with an imaginary frequency in the direction of the reaction coordinate.

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

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

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

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

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

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

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

$$r_x = \frac{d[X]}{dt} = \nu_x \left(k^+ \prod_{i \in \text{reactants}} [X_i]^{\nu_i} - k^- \prod_{i \in \text{products}} [X_i]^{\nu_i} \right). \tag{1.6}$$

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

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

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

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

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

$$r_j = \left(k^+ \prod_{i \in \text{reactants}} [X_i]^{\nu_i} - k^- \prod_{i \in \text{products}} [X_i]^{\nu_i} \right). \tag{1.10}$$

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.

1.2.1 Time-evaluation of a first-order 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.

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[2] In that scenario, we can rewrite the above equation to

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

This gives us the following differential equations[3] for compounds A and B

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

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

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 $[B]_{t=0} = 0$.

[2] 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.

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

Thus we obtain the following expression for A

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

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

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

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

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

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

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

and similarly, the following expression for B

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

$$\frac{d[B]}{dt} = k \exp(-kt) \tag{1.23}$$

$$d[B] = k \exp(-kt)\, dt \tag{1.24}$$

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

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

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

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,

$$\frac{d[\mathrm{R}]}{dt} = -k'[\mathrm{R}] \tag{1.33}$$
$$\frac{d[\mathrm{A}]}{dt} = k'[\mathrm{R}] - k'[\mathrm{A}] \tag{1.34}$$
$$\frac{d[\mathrm{B}]}{dt} = k'[\mathrm{A}] - k'[\mathrm{B}] \tag{1.35}$$
$$\frac{d[\mathrm{C}]}{dt} = k'[\mathrm{B}] - k'[\mathrm{C}] \tag{1.36}$$
$$\frac{d[\mathrm{P}]}{dt} = k'[\mathrm{C}] \tag{1.37}$$
$$\tag{1.38}$$

In a similar fashion as the previous subsection, 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.[4] 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, the

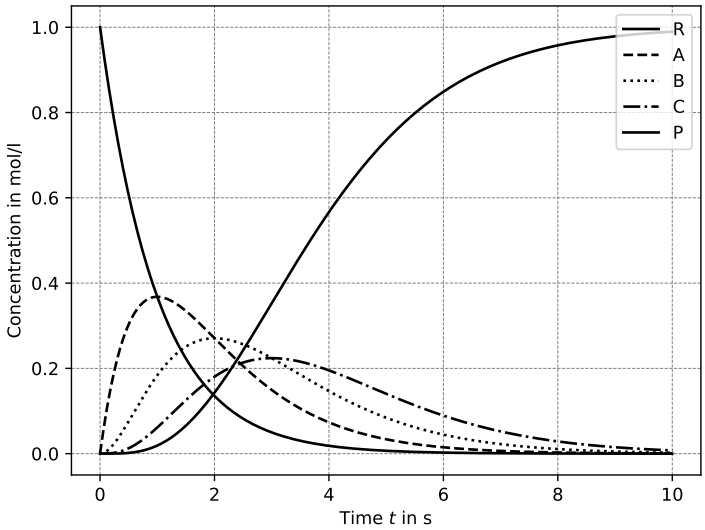


Figure 1.1: *Concentration as a function of time. At $t = 0$, $R_{t=0} = 1$. The system converges to the final result where $P = 1$ at $t \to \infty$.*

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 compound X is simply the sum of all the rates of change of all elementary reaction steps wherein compound X takes part:

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

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:

$$\frac{d[\mathrm{X}]}{dt} = \sum_j \left(\nu_{X,j} \left(k^+ \prod_{i \in \text{reactants}} [X_i]^{\nu_i} - k^- \prod_{i \in \text{products}} [X_i]^{\nu_i} \right) \right). \tag{1.47}$$

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

The steady state approximation

The procedure shown in the previous subsection 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[5], 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

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

[5] 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**.

Practice your understanding

Exercises 1.1 and 1.2

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

$$\frac{d[\mathrm{Cl}\cdot]}{dt} = 0 \tag{1.63}$$
$$\frac{d[\mathrm{H}\cdot]}{dt} = 0. \tag{1.64}$$

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)

$$\frac{d[\mathrm{Cl_2}]}{dt} = -k_1[\mathrm{Cl_2}] - k_3[\mathrm{H}\cdot][\mathrm{Cl_2}] + k_4[\mathrm{Cl}\cdot]^2 \tag{1.65}$$
$$\frac{d[\mathrm{H_2}]}{dt} = -k_2[\mathrm{Cl}\cdot][\mathrm{H_2}] \tag{1.66}$$
$$\frac{d[\mathrm{HCl}]}{dt} = k_2[\mathrm{Cl}\cdot][\mathrm{H_2}] + k_3[\mathrm{H}\cdot][\mathrm{Cl_2}] \tag{1.67}$$
$$\frac{d[\mathrm{Cl}\cdot]}{dt} = 2k_1[\mathrm{Cl_2}] - k_2[\mathrm{Cl}\cdot][\mathrm{H_2}] + k_3[\mathrm{H}\cdot][\mathrm{Cl_2}] - 2k_4[\mathrm{Cl}\cdot]^2 = 0 \tag{1.68}$$
$$\frac{d[\mathrm{H}\cdot]}{dt} = k_2[\mathrm{Cl}\cdot][\mathrm{H_2}] - k_3[\mathrm{H}\cdot][\mathrm{Cl_2}] = 0. \tag{1.69}$$

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:

$$\frac{d[\mathrm{HCl}]}{dt} = 2k_2\sqrt{\frac{k_1}{k_4}}[\mathrm{H_2}][\mathrm{Cl_2}]^{\frac{1}{2}} \tag{1.72}$$

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

$$\frac{d[\mathrm{HCl}]}{dt} = 2k[\mathrm{H_2}][\mathrm{Cl_2}]. \tag{1.73}$$

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.

Practice your understanding

Exercises 1.3 and 1.4

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

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

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 $(1-\theta_R)$ 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

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

and for the rate of change of product P

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

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:

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

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

$$V\frac{d[P]}{dt} = Nk_2^+\frac{\frac{k_1^+[R]}{k_1^-+k_2^+}}{1+\frac{k_1^+[R]}{k_1^-+k_2^+}}. \tag{1.81}$$

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.[6]

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

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[7] for the rate of change in the surface coverage of A:

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

If we assume that the catalytic surface is composed of only one type of site, then 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

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

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

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

[6] 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.

[7] 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.

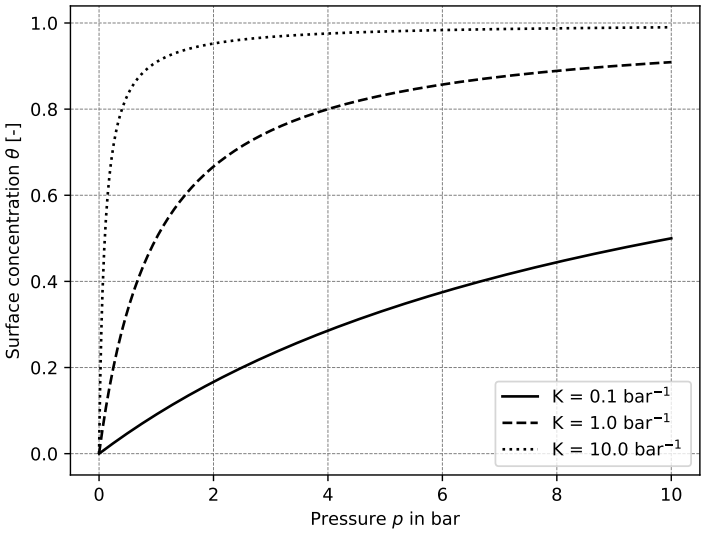


Figure 1.2: *Langmuir adsorption isotherms. The top line corresponds to an equilibrium constant of K=10 bar^{-1}, the middle one has an equilibrium constant of 1 bar^{-1} and the bottom line has an equilibrium constant of 0.1 bar^{-1}.*

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.

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

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

and the corresponding differential equation is

$$\frac{d\theta_A}{dt} = 2p_{A_2}k^+\left(1-\theta_A\right)^2 - 2k^-\theta_A^2. \tag{1.89}$$

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

$$\theta_A = \frac{\sqrt{Kp_{A_2}}}{1+\sqrt{Kp_{A_2}}}. \tag{1.90}$$

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

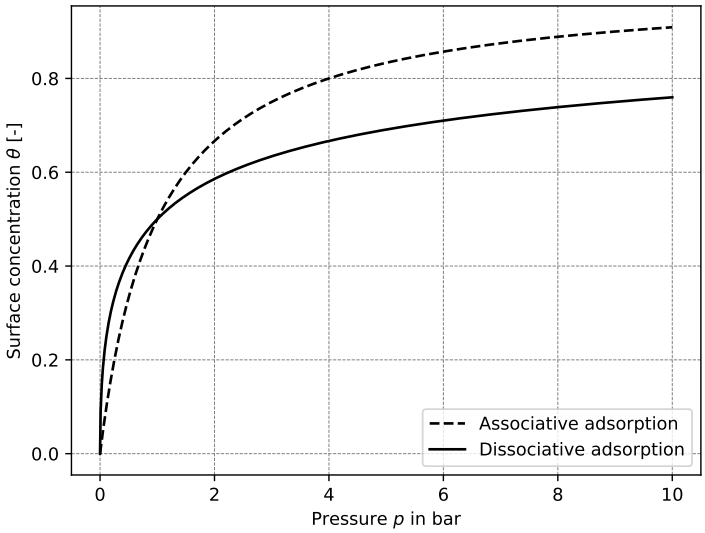


Figure 1.3: *Langmuir adsorption isotherms of associative versus dissociative adsorption. The dashed line corresponds to associative adsorption whereas the solid line represents dissociative adsorption. The equilibrium constant K is the same for both isotherms.*

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

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

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

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

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

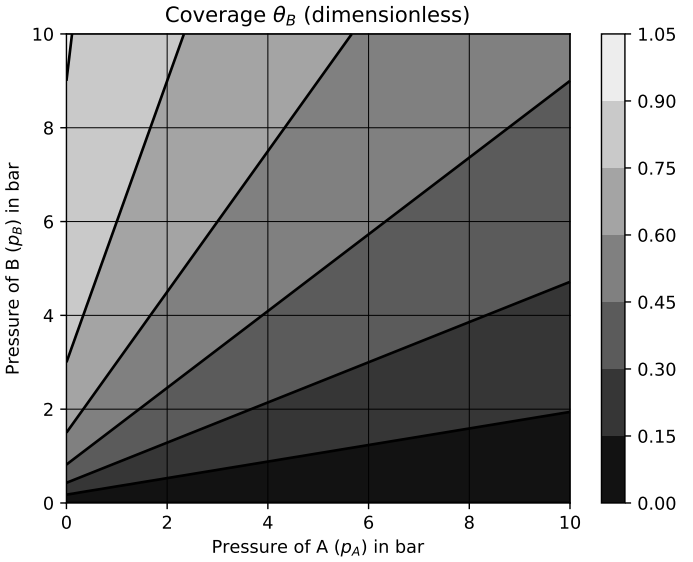


Figure 1.4: *Langmuir adsorption isotherms of competitive adsorption of A and B.*

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

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

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:[8]

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

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[9] and that the nitrogen dissociation actually proceeds in two elementary reaction steps:

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

[9] 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.

$$N_2 + * \leftrightarrows N_2* \tag{1.109}$$

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

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 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

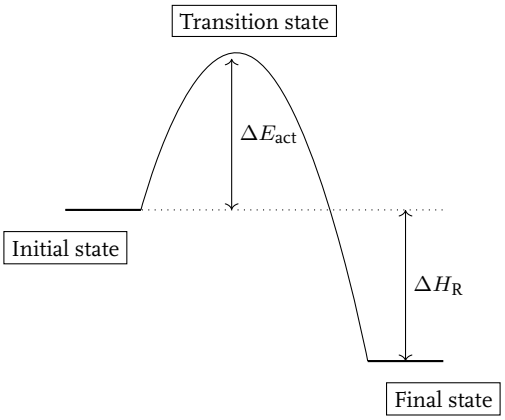


Figure 1.5: *Potential energy diagram of a single elementary reaction step*

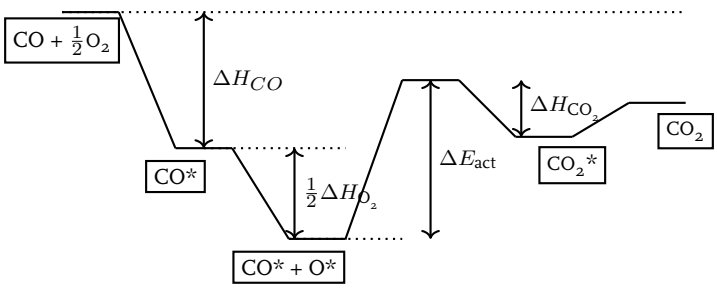


Figure 1.6: *Conceptual potential energy diagram for the CO oxidation reaction. ΔH_X corresponds to the adsorption energy of compound X. ΔE_{act} is the activation energy for the recombination reaction between adsorbed CO and O.*

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 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 and CO_2:

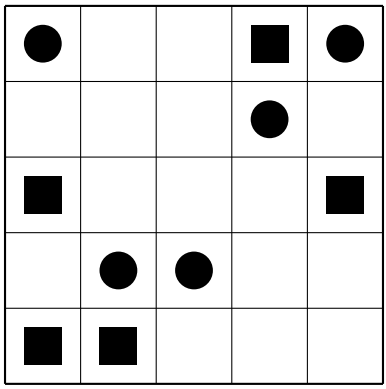


Figure 1.7: *Schematic depiction of a surface catalyst. A catalytic surface can be modelled as a square lattice where each lattice point corresponds to an active site. On these active sites, a single species can adsorb. In the mean-field approximation, it is assumed that there is no interaction between the adsorbed species and all species are distributed randomly over the surface.*

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

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

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

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.[10] Thus, we see a term in the denominator

[10] In principle, all elementary reaction steps are reversible because of the principle of microscopic reversibility. (see section 1.5.1 on page 19) This assumption merely states that under the given conditions, the barrier for the reverse reaction is significantly high and that we can therefore assume that the rate in the reverse direction is negligible.

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,

$$K_{CO} p_{CO} \gg \sqrt{K_{O_2} p_{O_2}}, K_{CO_2} p_{CO_2} \tag{1.126}$$

and the above equation then simplifies to

$$r_{CO_2} = \frac{k_3^+ K_{CO} p_{CO} \sqrt{K_{O_2} p_{O_2}}}{\left(1 + K_{CO} p_{CO}\right)^2}. \tag{1.127}$$

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

$$r_{CO_2} = \frac{k_3^+ \sqrt{K_{O_2} p_{O_2}}}{K_{CO} p_{CO}}. \tag{1.128}$$

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 Thermodynamic limitations

In the previous subsection, we derived the overall reaction rate under the zero-conversion limit. This assumption greatly simplifies the mathematics, however, it blinds us from the important principle that any chemical reaction proceeds towards equilibrium, but can never surpass the equilibrium condition. As such, we will derive the overall rate equation for a simple chemical

system, but without invoking the zero-conversion limit. It will hence be seen that the limiting equilibrium condition arises naturally in the final result.

Assume the same set of elementary reaction steps as in the previous subsection:

$$\mathrm{CO} + * \leftrightarrows \mathrm{CO}* \tag{1.129}$$

$$\mathrm{O_2} + 2* \leftrightarrows 2\mathrm{O}* \tag{1.130}$$

$$\mathrm{CO}* + \mathrm{O}* \leftrightarrows \mathrm{CO_2} * + * \tag{1.131}$$

$$\mathrm{CO_2} + * \leftrightarrows \mathrm{CO_2}* \tag{1.132}$$

The overall reaction rate, including the reverse reaction is given by

$$r_{\mathrm{CO_2}} = k_3^+ \theta_{\mathrm{CO}} \theta_{\mathrm{O}} - k_3^- \theta_{\mathrm{CO_2}} \theta_* \tag{1.133}$$

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

$$\cdots - k_3^- \frac{K_{\mathrm{CO_2}} p_{\mathrm{CO_2}}}{\left(1 + K_{\mathrm{CO}} p_{\mathrm{CO}} + \sqrt{K_{\mathrm{O_2}} p_{\mathrm{O_2}}} + K_{\mathrm{CO_2}} p_{\mathrm{CO_2}}\right)^2} \tag{1.134}$$

Note that equation 1.134 only differs in form, but is the same as equation 1.123. We can rewrite equation 1.134 as

$$r_{\mathrm{CO_2}} = k_3^+ \frac{K_{\mathrm{CO}} p_{\mathrm{CO}} \sqrt{K_{\mathrm{O_2}} p_{\mathrm{O_2}}}}{\left(1 + K_{\mathrm{CO}} p_{\mathrm{CO}} + \sqrt{K_{\mathrm{O_2}} p_{\mathrm{O_2}}} + K_{\mathrm{CO_2}} p_{\mathrm{CO_2}}\right)^2} \left(1 - \frac{k_3^- K_{\mathrm{CO_2}} p_{\mathrm{CO_2}}}{k_3^+ K_{\mathrm{CO}} p_{\mathrm{CO}} \sqrt{K_{\mathrm{O_2}} p_{\mathrm{O_2}}}}\right) \tag{1.135}$$

$$= k_3^+ \frac{K_{\mathrm{CO}} p_{\mathrm{CO}} \sqrt{K_{\mathrm{O_2}} p_{\mathrm{O_2}}}}{\left(1 + K_{\mathrm{CO}} p_{\mathrm{CO}} + \sqrt{K_{\mathrm{O_2}} p_{\mathrm{O_2}}} + K_{\mathrm{CO_2}} p_{\mathrm{CO_2}}\right)^2} \left(1 - \frac{k_3^- K_{\mathrm{CO_2}}}{k_3^+ K_{\mathrm{CO}} \sqrt{K_{\mathrm{O_2}}}} \frac{p_{\mathrm{CO_2}}}{p_{\mathrm{CO}} \sqrt{p_{\mathrm{O_2}}}}\right) \tag{1.136}$$

$$= k_3^+ \frac{K_{\mathrm{CO}} p_{\mathrm{CO}} \sqrt{K_{\mathrm{O_2}} p_{\mathrm{O_2}}}}{\left(1 + K_{\mathrm{CO}} p_{\mathrm{CO}} + \sqrt{K_{\mathrm{O_2}} p_{\mathrm{O_2}}} + K_{\mathrm{CO_2}} p_{\mathrm{CO_2}}\right)^2} \left(1 - \frac{K_{\mathrm{CO_2}}}{K_3 K_{\mathrm{CO}} \sqrt{K_{\mathrm{O_2}}}} \frac{p_{\mathrm{CO_2}}}{p_{\mathrm{CO}} \sqrt{p_{\mathrm{O_2}}}}\right) \tag{1.137}$$

The last two quotient terms in equation 1.137 are important in our analysis. The second to last quotient

$$\frac{K_{\mathrm{CO_2}}}{K_3 K_{\mathrm{CO}} \sqrt{K_{\mathrm{O_2}}}} = \frac{1}{K_{\mathrm{eq}}} \tag{1.138}$$

is the inverse of the equilibrium constant for the overall reaction. This constant only depends on temperature, which we here assume to be constant. The other term,

$$\frac{p_{\mathrm{CO_2}}}{p_{\mathrm{CO}} \sqrt{p_{\mathrm{O_2}}}} \tag{1.139}$$

corresponds to the quotient of the pressures of the reactants and products. This term, as seen in equation 1.139, equals the equilibrium constant K_{eq} when the reaction is at equilibrium. It can now readily be seen that at chemical equilibrium, the product of these last two terms equals one, by which the term within the round brackets equals zero and thus the overall reaction rate equals zero.[11]

Conclusively, all chemical reactions proceed towards chemical equilibrium, but can never surpass this equilibrium. Another way of saying this, is noting that at chemical equilibrium, the forward and backward reaction rates are equal. It should be mentioned that a chemical equilibrium is a dynamic equilibrium in the sense that reactants are converted to products and *vice versa*. The system is not stagnant, but is in a state where no net change is observed.

1.6 Dependencies in pressure and temperature

The overall reaction rate critically depends on the applied pressure and the operating temperature. This dependency can be probed by investigating the *reaction order* or the *apparent activation energy*. The former probes the effect on the overall reaction rate due to an infinitesimal change to the pressure, relative to a preset working point of given reaction rate and pressure. Similarly, the apparent activation energy probes the effect of an infinitesimal change in temperature. These analytical tools provide us with important information under the working state of the catalyst. We will treat these concepts in this section.

1.6.1 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[12]

$$n_X = \frac{\partial r^+ / r^+}{\partial p_X / p_X} \tag{1.140}$$

$$= p_X \frac{\partial \ln r^+}{\partial p_X}. \tag{1.141}$$

The plus sign in r^+ is to indicate that we are only considering the reaction in the forward direction in this analysis. Considering only the forward direction is synonymous to performing the analysis at low conversion.

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

[11] Since K_{eq} depends on temperature, it is also evident that temperature plays a very important role in chemical equilibria. By carefully chosing the temperature of the reaction, any thermodynamically limiting conditions can potentially be avoided.

[12] Note that the reaction order probes relative changes, as can be seen by the division of r^+ in the numerator and p_X in the denominator. This formula can be rewritten as the derivative of the natural logarithm. As will become clear in this section, the application of a natural logarithm allows for efficient evaluation of the reaction orders.

$$
\begin{aligned}
n_{CO} =& p_{CO} \frac{\partial \ln r^+}{\partial p_{CO}} && \text{(1.142)}\\
=& p_{CO} \frac{\partial \ln \frac{k_3^+ K_{CO} p_{CO} \sqrt{K_{O_2} p_{O_2}}}{(1+K_{CO} p_{CO})^2}}{\partial p_{CO}} && \text{(1.143)}\\
=& p_{CO} \frac{\partial}{\partial p_{CO}} \left(\ln k_3^+ + \ln K_{CO} + \ln p_{CO} + \frac{1}{2} \ln K_{O_2} + \frac{1}{2} \ln p_{O_2} - 2 \ln (1 + K_{CO} p_{CO}) \right) && \text{(1.144)}\\
=& p_{CO} \frac{\partial}{\partial p_{CO}} \left(\ln p_{CO} - 2 \ln (1 + K_{CO} p_{CO}) \right) && \text{(1.145)}\\
=& 1 - 2 p_{CO} \frac{\partial \ln (1 + K_{CO} p_{CO})}{\partial p_{CO}} && \text{(1.146)}\\
=& 1 - 2 \frac{p_{CO}}{(1 + K_{CO} p_{CO})} \frac{\partial (1 + K_{CO} p_{CO})}{\partial p_{CO}} && \text{(1.147)}\\
=& 1 - 2 \frac{K_{CO} p_{CO}}{(1 + K_{CO} p_{CO})} && \text{(1.148)}\\
=& 1 - 2\theta_{CO} && \text{(1.149)}\\
& && \text{(1.150)}
\end{aligned}
$$

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.

$$
r_{CO_2} = \frac{k_3^+ K_{CO} p_{CO} \sqrt{K_{O_2} p_{O_2}}}{\left(1 + K_{CO} p_{CO} + \sqrt{K_{O_2} p_{O_2}} + K_{CO_2} p_{CO_2}\right)^2} \qquad \text{(1.151)}
$$

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

$$
\begin{aligned}
n_{CO} =& 1 - 2\theta_{CO} && \text{(1.152)}\\
n_{O_2} =& \frac{1}{2} - \theta_O && \text{(1.153)}\\
n_{CO_2} =& -2\theta_{CO_2} && \text{(1.154)}
\end{aligned}
$$

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

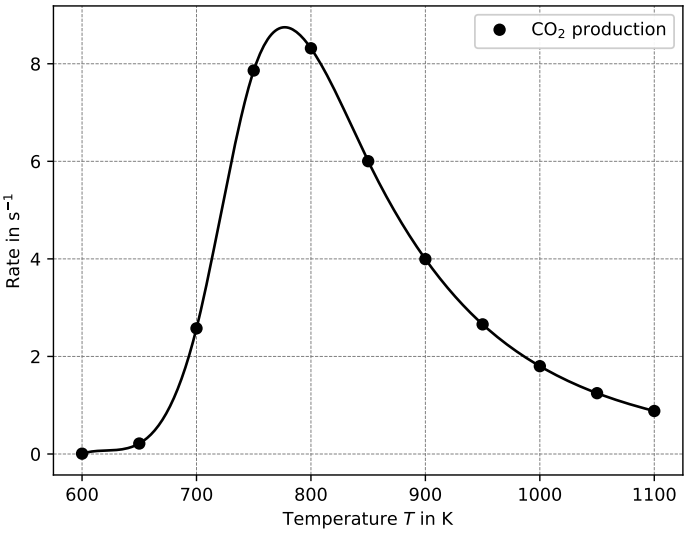


Figure 1.8: *Rate of CO_2 formation as a function of temperature*

the temperature range under consideration, its corresponding reaction order is constant and amounts to $n_{O_2} = \frac{1}{2}$ for the whole range.

Practice your understanding

Exercises 1.5, 1.6, 1.7, 1.8, 1.9, and 1.10

1.6.2 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[13]

$$\Delta E_{\text{act}}^{\text{app}} = RT^2 \frac{\partial \ln r^+}{\partial T}, \tag{1.155}$$

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

[13] Although not explicitly shown here, the apparent activation energy also probes a *relative* change, similar to the reaction order. This gives rise to the logarithmic term as shown in equation 1.155.

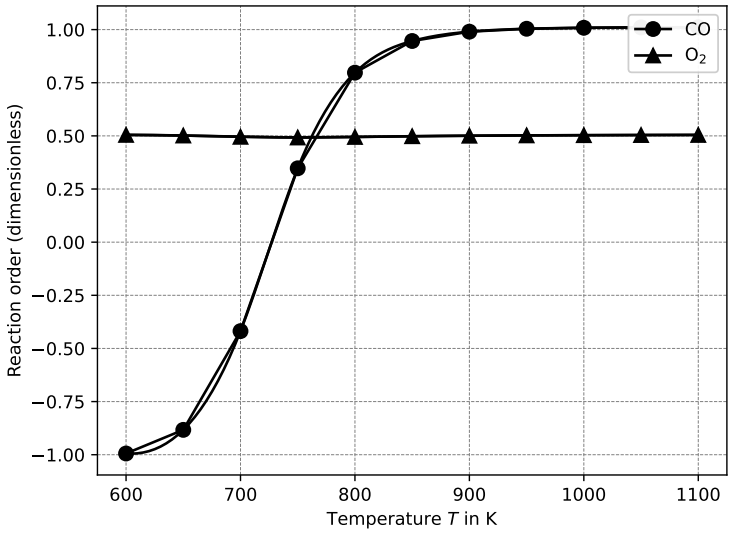


Figure 1.9: *Reaction order in* CO *and* O_2 *as a function of temperature*

$$\Delta E_{\text{act}}^{\text{app}} = RT^2 \frac{\partial \ln \left(\frac{k_3^+ K_{\text{CO}} p_{\text{CO}} \sqrt{K_{\text{O}_2} p_{\text{O}_2}}}{(1+K_{\text{CO}} p_{\text{CO}})^2} \right)}{\partial T} \tag{1.156}$$

$$= RT^2 \frac{\partial}{\partial T} \left(\ln k_3^+ + \ln K_{\text{CO}} + \ln p_{\text{CO}} + \frac{1}{2} \ln K_{\text{O}_2} + \frac{1}{2} \ln p_{\text{O}_2} - 2 \ln \left(1 + K_{\text{CO}} p_{\text{CO}}\right) \right) \tag{1.157}$$

$$= RT^2 \frac{\partial}{\partial T} \left(\ln k_3^+ + \ln K_{\text{CO}} + \frac{1}{2} \ln K_{\text{O}_2} - 2 \ln \left(1 + K_{\text{CO}} p_{\text{CO}}\right) \right) \tag{1.158}$$

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 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:

$$k = \nu \exp \left(\frac{-\Delta E_{\text{act}}}{RT} \right), \tag{1.159}$$

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

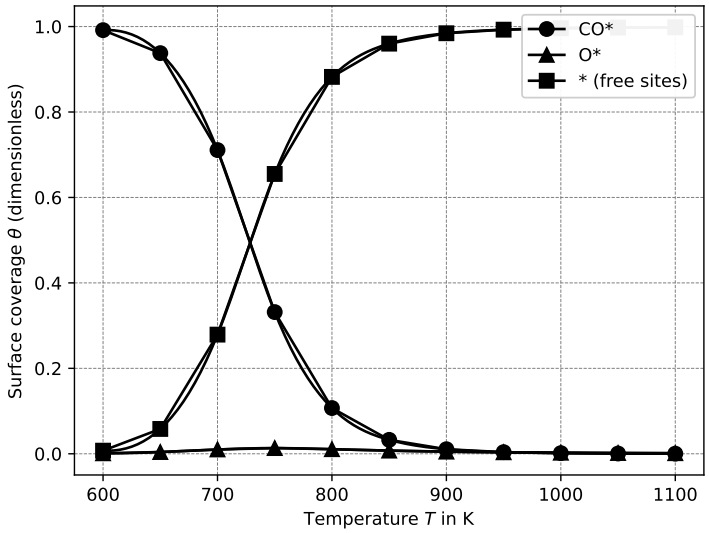


Figure 1.10: *Surface coverage of* CO *and* O *as a function of temperature*

$$\frac{\partial}{\partial T}\ln\left(\nu\exp\left(\frac{-\Delta E_{\text{act}}}{RT}\right)\right)=\frac{\partial}{\partial T}\left(\ln(\nu)+\frac{-\Delta E_{\text{act}}}{RT}\right) \tag{1.160}$$

$$=\frac{\Delta E_{\text{act}}}{RT^2}. \tag{1.161}$$

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

$$K=\exp\left(\frac{-\Delta G_{\text{R}}}{RT}\right)=\exp\left(\frac{-\Delta H_{\text{R}}+T\Delta S_{\text{R}}}{RT}\right)=\exp\left(\frac{-\Delta H_{\text{R}}}{RT}\right)\exp\left(\frac{\Delta S_{\text{R}}}{R}\right), \tag{1.162}$$

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 1.158

$$\frac{\partial}{\partial T}\ln\left(\exp\left(\frac{-\Delta H_{\text{R}}}{RT}\right)\exp\left(\frac{\Delta S_{\text{R}}}{R}\right)\right) \tag{1.163}$$

$$=\frac{\partial}{\partial T}\left[\ln\left(\exp\left(\frac{-\Delta H_{\text{R}}}{RT}\right)\right)+\ln\left(\exp\left(\frac{\Delta S_{\text{R}}}{R}\right)\right)\right] \tag{1.164}$$

$$=\frac{\partial}{\partial T}\left(\frac{-\Delta H_{\text{R}}}{RT}+\frac{\Delta S_{\text{R}}}{R}\right) \tag{1.165}$$

$$=\frac{\Delta H_{\text{R}}}{RT^2} \tag{1.166}$$

Finally, we have to solve for the fourth term in Equation 1.158 which can be done by using the chain rule and applying the result of Equation 1.166.

$$\frac{\partial}{\partial T}\left(2\ln\left(1+K_{\mathrm{CO}}p_{\mathrm{CO}}\right)\right) = 2\,\frac{\partial}{\partial T}\left(\ln\left(1+K_{\mathrm{CO}}p_{\mathrm{CO}}\right)\right) \tag{1.167}$$

$$= 2\,\frac{\partial \ln\alpha}{\partial\alpha}\frac{\partial\alpha}{\partial T} \text{ with } \alpha = 1+K_{\mathrm{CO}}p_{\mathrm{CO}} \tag{1.168}$$

$$= 2\,\frac{1}{\alpha}\frac{\partial\alpha}{\partial T} \text{ with } \alpha = 1+K_{\mathrm{CO}}p_{\mathrm{CO}} \tag{1.169}$$

$$= 2\,\frac{p_{\mathrm{CO}}}{1+K_{\mathrm{CO}}p_{\mathrm{CO}}}\frac{\partial K_{\mathrm{CO}}}{\partial T} \tag{1.170}$$

$$= 2\,\frac{p_{\mathrm{CO}}}{1+K_{\mathrm{CO}}p_{\mathrm{CO}}}\frac{\partial \exp\left(\frac{-\Delta H_{\mathrm{R}}}{RT}\right)\exp\left(\frac{\Delta S_{\mathrm{R}}}{R}\right)}{\partial T} \tag{1.171}$$

$$= 2\,\frac{p_{\mathrm{CO}}K_{\mathrm{CO}}}{1+K_{\mathrm{CO}}p_{\mathrm{CO}}}\frac{\Delta H_{\mathrm{CO}}}{RT^2} \tag{1.172}$$

Note that the term $\frac{p_{\mathrm{CO}}K_{\mathrm{CO}}}{1+K_{\mathrm{CO}}p_{\mathrm{CO}}}$ 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

$$\frac{\partial}{\partial T}\left(2\ln\left(1+K_{\mathrm{CO}}p_{\mathrm{CO}}\right)\right) = 2\,\theta_{\mathrm{CO}}\frac{\Delta H_{\mathrm{CO}}}{RT^2} \tag{1.173}$$

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

$$\Delta E_{\mathrm{act}}^{\mathrm{app}} = RT^2\frac{\partial}{\partial T}\left(\ln k_3^{+} + \ln K_{\mathrm{CO}} + \frac{1}{2}\ln K_{\mathrm{O_2}} - 2\ln\left(1+K_{\mathrm{CO}}p_{\mathrm{CO}}\right)\right) \tag{1.174}$$

$$= \Delta E_{\mathrm{act}} + \Delta H_{CO} + \frac{1}{2}\Delta H_{\mathrm{O_2}} - 2\Delta H_{CO}\theta_{CO} \tag{1.175}$$

$$= \Delta E_{\mathrm{act}} + \Delta H_{CO}\left(1-2\theta_{CO}\right) + \frac{1}{2}\Delta H_{\mathrm{O_2}} \tag{1.176}$$

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.

Practice your understanding

Exercises 1.11, 1.12, 1.13, 1.14, 1.15 and 1.16

1.7 Differentiating between catalytic mechanisms

The apparent activation energy and the reaction order are two ways by which a (catalytic) reaction can be experimentally probed. By proposing a particular reaction mechanism and assuming a rate-determining step, it is possible to falsify a postulated reaction mechanism by means of an experiment. This has become a very important technique in the elucidation of reaction mechanisms. In this section, we will provide a simple example how this procedure works. We will herein focus on the reaction order, but similar strategies are possible for the apparent activation energy.

Consider the CO oxidation reaction. We can postulate this overall reaction to proceed in the following two ways:

1. CO and O_2 both adsorb on the catalytic surface. CO adsorbs molecularly and O_2 adsorbs dissociatively. Adsorbed CO and adsorbed O can react to form CO_2 which can leave the surface.

2. O_2 adsorbs dissociatively on the catalytic surface and CO reacts, directly from the gas phase and without first adsorbing on the surface, with an adsorbed oxygen. This result in C-O bond formation and an adsorbed CO_2 molecule which can finally desorb from the surface.

Reactions wherein all adsorbates first have to adsorb on the catalytic surface before they can react (situation 1) are termed **Langmuir-Hinshelwood** type of reaction mechanisms. In contrast, reaction mechanisms wherein one of the reactants directly react from the gas phase (situation 2) are known as **Eley-Rideal** type of mechanisms.

Let us assume that in both cases the reaction that results in the formation of adsorbed CO_2 is the rate-determining step. Furthermore, we assume a quasi-equilibrium for all elementary reaction steps before the rate-determining step and further operate under the zero-conversion limit. With these assumptions in place, we can readily derive an equation for the rate of formation of CO_2 as function of the partial pressures of CO and O_2.

For a Langmuir-Hinshelwood mechanism, the overall reaction rate was already derived in previous sections and corresponds to

$$r_{\mathrm{LH}} = k^{+} \frac{K_{\mathrm{CO}} p_{\mathrm{CO}} \sqrt{K_{\mathrm{O_2}} p_{\mathrm{O_2}}}}{\left(1 + K_{\mathrm{CO}} p_{\mathrm{CO}} + \sqrt{K_{\mathrm{O_2}} p_{\mathrm{O_2}}}\right)^2}. \tag{1.177}$$

For the Eley-Rideal type of mechanism, the situation is a bit different. Let us derive it starting from the fundamental rate equation for the rate-determining step.

$$r_{\mathrm{ER}} = k_2 \theta_{\mathrm{O}} p_{\mathrm{CO}}. \tag{1.178}$$

Only for O_2 adsorption a corresponding Langmuir adsorption isotherm is needed to obtain an overall rate expression as function of partial pressures, equilibrium constants and reaction rate constants. Plugging the Langmuir adsorption isotherm for O_2 in the above equation yields

$$r_{\mathrm{ER}} = k^{+} \frac{p_{\mathrm{CO}} \sqrt{K_{\mathrm{O_2}} p_{\mathrm{O_2}}}}{\left(1 + K_{\mathrm{CO}} p_{\mathrm{CO}} + \sqrt{K_{\mathrm{O_2}} p_{\mathrm{O_2}}}\right)}. \tag{1.179}$$

The most salient difference between equation 1.177 and 1.179 is the lack of a Langmuir adsorption isotherm for CO in the latter equation and consequently no longer the squaring of the denominator. This latter aspect should be clear; in an Eley-Rideal type of mechanism, only a single active site on the catalyst is required whereas in a Langmuir-Hinshelwood type of mechanism, two such sites are necessary for the reaction to proceed.

Let us derive the reaction orders in CO for these two mechanisms. For the Langmuir-Hinshelwood mechanism, this has already been done in previous sections and the result is

$$n_{\mathrm{CO,LH}} = 1 - 2\theta_{\mathrm{CO}}. \tag{1.180}$$

For the Eley-Rideal mechanism, the result is

$$n_{CO,ER} = 1 - \theta_{CO}. \tag{1.181}$$

For the Langmuir-Hinshelwood mechanism, the reaction order in CO will thus be between 1 and -1, whereas for the Eley-Rideal mechanism, it will be between 1 and 0. Thus if an experimental situation is produced wherein the CO coverage is high and a negative reaction order in CO is found, this would be in favor for rejecting the hypothesis wherein an Eley-Rideal mechanism is postulated. Furthermore, this result also nicely shows that in an Eley-Rideal mechanism, surface poisoning by CO is impossible as CO is not required to adsorb on the surface.

Conclusively, by postulating a reaction mechanism and deriving analytical expressions for the reaction rate and subsequently for the reaction orders allows for a combined theoretical/experimental procedure to falsify reaction mechanisms.

Practice your understanding

Exercises 1.17

1.8 Multi-site mechanisms

So far, we have dealt with catalytic surfaces harboring only a single type of active site. We can readily extend this methodology for two or even multiple types of active sites. These different active sites can for instance have different preferences for which compounds can be readily adsorbed. To obtain analytical solutions, it is nevertheless required that the fundamental assumptions such as the rate-determining step approximation and pseudo-equilibrium approximation remain in place. To illustrate the principle, let us consider an example.

We revisit the pedagogical problem of CO oxidation. Let us assume that CO adsorbs on one type of active site, denoted by * and O adsorbs on another type of active sites, denoted by #. The rate-determining step is the recombination of CO with O utilizing the two different types of active sites. We assume that the resulting CO_2 can only be adsorbed on a * type of active site. Following these assumptions, the set of elementary reaction steps would then be

$$CO + * \rightleftarrows CO* \tag{1.182}$$
$$O_2 + 2\# \rightleftarrows 2O\# \tag{1.183}$$
$$CO* + O\# \rightarrow CO_2 * + \# \tag{1.184}$$
$$CO_2 + * \rightleftarrows CO_2* \tag{1.185}$$

Assuming a pseudo-equilibrium, the following Langmuir adsorption isotherms would be obtained

$$\theta_{CO} = \frac{K_{CO} p_{CO}}{1 + K_{CO} p_{CO} + K_{CO_2} p_{CO_2}} \tag{1.186}$$
$$\theta_{CO_2} = \frac{K_{CO_2} p_{CO_2}}{1 + K_{CO} p_{CO} + K_{CO_2} p_{CO_2}} \tag{1.187}$$
$$\tau_O = \frac{\sqrt{K_{O_2} p_{O_2}}}{1 + \sqrt{K_{O_2} p_{O_2}}}, \tag{1.188}$$

wherein we use τ to denote the fractional coverage of # types of active sites and wherein we have applied distinct site balances (see e.g. eqaution 1.95) for the θ- and #-type of active sites. From the rate-determining step approximation, we can now readily derive the overall reaction rate as function of the partial pressures, equilibrium and reaction rate constants.

$$r = k^{+}\theta_{CO}\tau_{O} \tag{1.189}$$

$$= k^{+}\frac{K_{CO}p_{CO}\sqrt{K_{O_2}p_{O_2}}}{\left(1 + K_{CO}p_{CO} + K_{CO_2}p_{CO_2}\right)\left(1 + \sqrt{K_{O_2}p_{O_2}}\right)} \tag{1.190}$$

Comparing equation 1.190 with 1.177 readily shows the result of utilizing different types of active sites with respect to the overall reaction rate. Instead of a denominator wherein only the terms corresponding to a single type of active site is found, for a multi-site mechanism, all sites that participate in the reaction mechanism are found. These differences can have a profound effect on the catalytic mechanism. In a single-site mechanism, there is a strong competition between adsorbates that require the same type of active site whereas in a multi-site mechanism, such competition is partially mitigated. This can be readily seen from the reaction orders.

For a single site mechanism, the reaction orders in CO and O_2 were established to be

$$n_{CO,\text{single-site}} = 1 - 2\theta_{CO} \tag{1.191}$$

$$n_{O_2,\text{single-site}} = 1 - \theta_{O_2} \tag{1.192}$$

.

For the dual-site mechanism, these reaction orders are

$$n_{CO,\text{dual-site}} = 1 - \theta_{CO} \tag{1.193}$$

$$n_{O_2,\text{dual-site}} = \frac{1}{2} - \frac{1}{2}\tau_{O}. \tag{1.194}$$

Clearly, at very high coverages of CO, the single-site mechanism is prone to poisoning due to CO preventing the adsorption of O_2 as found from negative reaction orders. On the other hand, for the dual-site mechanism, the reaction order in CO can never become negative as # types of active sites always remain accessible for O_2 to adsorb on as on this type of active site, there is no co-adsorption of CO and O. Furthermore, as the different types of mechanism are expected to show a different kinetic response under the right catalytic conditions, the reaction order can be utilized to differentiate between the two mechanism, in line with what was shown in the previous section.

Practice your understanding

Exercises 1.18

1.9 Exercises

The answers to the exercises can be found at the end of this Chapter on page 43. The exercises are marked by a number of gears to indicate their difficulty levels.

EXERCISE 1.1

The decomposition of acetaldehyde

$$CH_3CHO \rightarrow CH_4 + CO \tag{1.195}$$

proceeds in the gas phase via methyl radicals according to

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. $2CH_3{}^* \rightarrow C_2H_6$ (1.196)

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

$$2N_2O_5 \rightarrow 4NO_2 + O_2 \tag{1.197}$$

proceeds according to the following rate equation

$$r = \frac{d[O_2]}{dt} = k[N_2O_5] \tag{1.198}$$

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.

1. $N_2O_5 \leftrightarrows NO_2 + NO_3$
2. $NO_2 + NO_3 \rightarrow NO + NO_2 + O_2$
3. $NO + NO_3 \rightarrow 2NO_2$ (1.199)

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

$$2NO + H_2 \rightarrow N_2O + H_2O \tag{1.200}$$

using the steady-state approximation. 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_3OH 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

$$CO_2 + 3H_2 \rightarrow CH_3OH + H_2O \tag{1.201}$$

The mechanism is thought to proceed in the following manner

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. $H_3COH + * \leftrightarrows H_3COH*$

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. Assume that the reaction is operated under zero conversion.

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:

$$\begin{aligned} &1.\ \mathrm{CO} + * \leftrightarrows \mathrm{CO}* \\ &2.\ \mathrm{O_2} + 2* \rightarrow 2\mathrm{O}* \\ &3.\ \mathrm{CO}* + \mathrm{O}* \rightarrow \mathrm{CO_2} + 2* \end{aligned} \tag{1.202}$$

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:

$$\mathrm{CH_4} + \mathrm{H_2O} \rightarrow \mathrm{CO} + 3\mathrm{H_2} \tag{1.203}$$

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

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

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 $\mathrm{H_2}$, for instance in ammonia production, what other important chemical reaction can be utilized to increase the amount of $\mathrm{H_2}$ 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 $\mathrm{CH_4}$ is dissociative, whereas the adsorption of $\mathrm{H_2O}$ 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. $C_2H_5* + H* \leftrightarrows 2CH_3*$
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, explicitly 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

$$SO_2 + \frac{1}{2}O_2 \rightarrow SO_3 \tag{1.204}$$

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 is strongly adsorbed whereas SO_2 and SO_3 are only weakly adsorbed.[14]

[14] Note that O_2 adsorbs dissociatively, so it is the oxygen atom that adsorbs strongly.

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

$$r = k \left(\frac{K_{SO_2} p_{SO_2}}{1 + K_{SO_2} p_{SO_2} + K_{SO_3} p_{SO_3}} \right) \left(\frac{K_{O_2}^{1/2} p_{O_2}^{1/2}}{1 + K_{O_2}^{1/2} p_{O_2}^{1/2}} \right) \tag{1.205}$$

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.

$$C_2H_5OH^* + O^* \rightarrow C_2H_4O + H_2O + 2^* \tag{1.206}$$

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:

1. $H_2 + 2* \leftrightarrows 2H*$
2. $O_2 + 2* \leftrightarrows 2O*$
3. $O* + H* \leftrightarrows OH* + *$
4. $OH* + H* \leftrightarrows H_2O* + *$
5. $H_2O + * \leftrightarrows H_2O*$

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.

$$r = k_3^+ \sqrt{K_1 K_2 p_{H_2} p_{O_2}} \left(1 - \frac{p_{H_2O}}{K_{\text{equilibrium}} p_{H_2} \sqrt{p_{O_2}}}\right) \theta_*^2 \tag{1.207}$$

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.

$$
\begin{aligned}
&1.\ \mathrm{NO} + * \leftrightarrows \mathrm{NO}* \\
&2.\ \mathrm{CO} + * \leftrightarrows \mathrm{CO}* \\
&3.\ \mathrm{N_2} + * \leftrightarrows \mathrm{N_2}* \\
&4.\ \mathrm{N_2}* + * \leftrightarrows 2\mathrm{N}* \\
&5.\ \mathrm{NO}* + * \leftrightarrows \mathrm{N}* + \mathrm{O}* \\
&6.\ \mathrm{CO}* + \mathrm{O}* \leftrightarrows \mathrm{CO_2}* + * \\
&7.\ \mathrm{CO_2} + * \leftrightarrows \mathrm{CO_2}*
\end{aligned}
\tag{1.208}
$$

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:

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

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

The hydrogenation of acetylene can occur via two different mechanisms: Langmuir-Hinshelwood or Eley-Rideal. The former assumes that both acetylene and hydrogen adsorb on neighboring sites before (two-fold) hydrogenation takes place, whereas the latter assumes that hydrogen directly reacts from the gas phase with adsorbed acetylene.

Assume that the rate-determining step of each mechanism is

- Langmuir-Hinshelwood: $C_2H_2* + H* \rightarrow CH_2CH* + *$
- Eley-Rideal: $C_2H_2* + H_2 \rightarrow C_2H_4*$

When constructing the mechanism, assume that hydrogen adsorbs dissociatively in both mechanisms. Furthermore, despite that hydrogen adsorption is not needed in the Eley-Rideal mechanism, allow hydrogen to co-adsorb. To simplify upon the mathematics, assume that the reaction is conducted at zero-conversion.

a) Write down the elementary reaction steps for both mechanisms.

b) Show that these mechanisms can be differentiated by their reaction orders. Mention what conditions are required to show this difference.

EXERCISE 1.18

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.

1.10 Solutions

The solutions below pertain to the exercises of Chapter 1 on page 33 and further.

SOLUTION 1.1

$$\frac{\mathrm{d}[CH_4]}{\mathrm{d}t} = k_2[CH_3{}^*][CH_3CHO] \tag{1.209}$$

The target is to express short-lived intermediates (such as radicals) in terms of gas-phase concentrations. Here, the unknown variable is $[CH_3{}^*]$ 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 $\frac{\mathrm{d}[CH_3CO^*]}{\mathrm{d}t}$.

$$\begin{aligned}\frac{\mathrm{d}[CH_3{}^*]}{\mathrm{d}t} =& k_1[CH_3CHO] - k_2[CH_3{}^*][CH_3CHO] \\ &+ k_3[CH_3CO^*] - 2k_4[CH_3{}^*]^2 = 0\end{aligned} \tag{1.210}$$

and

$$\frac{\mathrm{d}[CH_3CO^*]}{\mathrm{d}t} = k_2[CH_3{}^*][CH_3CHO] - k_3[CH_3CO^*] = 0 \tag{1.211}$$

Combining Equations 1.210 and 1.211 yields

$$[CH_3{}^*] = \sqrt{\frac{k_1}{2k_4}}[CH_3CHO]^{1/2}. \tag{1.212}$$

Inserting Equation 1.212 into Equation 1.209 gives

$$\frac{\mathrm{d}[\mathrm{CH_4}]}{\mathrm{d}t} = k_2\sqrt{\frac{k_1}{2k_4}}[\mathrm{CH_3CHO}]^{3/2}. \tag{1.213}$$

and the rate of formation for $[\mathrm{C_2H_6}]$ becomes

$$\frac{\mathrm{d}[\mathrm{C_2H_6}]}{\mathrm{d}t} = k_4[\mathrm{CH_3}^*]^2 = \frac{k_1}{2}[\mathrm{CH_3CHO}] \tag{1.214}$$

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.

$$\frac{\mathrm{d}[\mathrm{O_2}]}{\mathrm{d}t} = k_2[\mathrm{NO_2}][\mathrm{NO_3}] \tag{1.215}$$

Applying the steady-state approximation to NO and $\mathrm{NO_3}$ yield

$$\frac{\mathrm{d}[\mathrm{NO}]}{\mathrm{d}t} = k_2[\mathrm{NO_2}][\mathrm{NO_3}] - k_3[\mathrm{NO}][\mathrm{NO_3}] = 0 \tag{1.216}$$

and

$$\frac{\mathrm{d}[\mathrm{NO_3}]}{\mathrm{d}t} = k_1^+[\mathrm{N_2O_5}] - k_1^-[\mathrm{NO_2}][\mathrm{NO_3}] - k_2[\mathrm{NO_2}][\mathrm{NO_3}] - k_3[\mathrm{NO}][\mathrm{NO_3}] = 0. \tag{1.217}$$

By subtracting Equation 1.216 from 1.217, we obtain

$$[\mathrm{NO_2}][\mathrm{NO_3}] = \frac{k_1^+}{k_1^- + 2k_2}[\mathrm{N_2O_5}] \tag{1.218}$$

which we can readily insert into the rate equation of $\mathrm{O_2}$ formation, resulting in

$$\frac{\mathrm{d}[\mathrm{O_2}]}{\mathrm{d}t} = \frac{k_1^+ k_2}{k_1^- + 2k_2}[\mathrm{N_2O_5}]. \tag{1.219}$$

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

$$\frac{d[NO_2]}{dt} = k_1^+[N_2O_5] - k_1^-[NO_2][NO_3] + 2k_3[NO][NO_3]. \tag{1.220}$$

Inserting Equations 1.216 and 1.218 into 1.220 gives

$$\begin{aligned}\frac{d[NO_2]}{dt} =& k_1^+[N_2O_5] - \frac{k_1^+k_1^-}{k_1^- + 2k_2}[N_2O_5] + \frac{2k_1^+k_2}{k_1^- + 2k_2}[N_2O_5] && (1.221)\\ =& \left(k_1^+ - \frac{k_1^+k_1^-}{k_1^- + 2k_2} + \frac{2k_1^+k_2}{k_1^- + 2k_2}\right)[N_2O_5] && (1.222)\\ =& \frac{k_1^+}{k_1^- + 2k_2}\left(k_1^- + 2k_2 - k_1^- + 2k_2\right)[N_2O_5] && (1.223)\\ =& \frac{k_1^+}{k_1^- + 2k_2} 4k_2[N_2O_5] && (1.224)\\ =& 4\frac{d[O_2]}{dt}. && (1.225)\end{aligned}$$

SOLUTION 1.3

Applying the steady-state approximation to $[N_2O_2]$ gives

$$\frac{d[N_2O_2]}{dt} = k_1^+[NO]^2 - k_1^-[N_2O_2] - k_2[N_2O_2][H_2] = 0. \tag{1.226}$$

From this expression, we can equate the $[N_2O_2]$ to

$$[N_2O_2] = \frac{k_1^+[NO]^2}{k_1^- + k_2[H_2]}. \tag{1.227}$$

The rate of formation of $[N_2O]$ is then found to be

$$\begin{aligned}\frac{d[N_2O]}{dt} =& k_2[N_2O_2][H_2] = \frac{k_2k_1^+[NO]^2[H_2]}{k_1^- + k_2[H_2]} && (1.228)\\ =& \frac{k_1^+[NO]^2}{1 + k_1^-/(k_2[H_2])}. && (1.229)\end{aligned}$$

SOLUTION 1.4

In the overall chain reaction, the elementary reaction steps are denoted as

$$\begin{aligned} \mathrm{Br_2} &\rightarrow 2\mathrm{Br}^* && \text{initiation} \\ \mathrm{CH_4} + \mathrm{Br}^* &\rightarrow \mathrm{CH_3}^* + \mathrm{HBr} && \text{propagation} \\ \mathrm{CH_3}^* + \mathrm{Br_2} &\rightarrow \mathrm{CH_3Br} + \mathrm{Br}^* && \text{propagation} \\ 2\mathrm{Br}^* &\rightarrow \mathrm{Br_2} && \text{termination} \end{aligned}$$

The steady-state approximation can be readily applied to the reaction rates of the intermediates.

$$\frac{\mathrm{d}[\mathrm{Br}^*]}{\mathrm{d}t} = 2k_1[\mathrm{Br_2}] - k_2[\mathrm{CH_4}][\mathrm{Br}^*] + k_3[\mathrm{CH_3}^*][\mathrm{Br_2}] - 2k_4[\mathrm{Br}^*]^2 = 0 \tag{1.230}$$

$$\frac{\mathrm{d}[\mathrm{CH_3}^*]}{\mathrm{d}t} = k_2[\mathrm{CH_4}][\mathrm{Br}^*] - k_3[\mathrm{CH_3}^*][\mathrm{Br_2}] = 0 \tag{1.231}$$

Inserting Equation 1.230 in 1.231 results in

$$[\mathrm{Br}^*] = \left(\frac{k_1}{k_4}[\mathrm{Br_2}]\right)^{1/2}. \tag{1.232}$$

Applying Equation 1.232 to 1.231 yields

$$\begin{aligned} [\mathrm{CH_3}^*] &= \frac{k_2[\mathrm{CH_4}]\left(\frac{k_1}{k_4}[\mathrm{Br_2}]\right)^{1/2}}{k_3[\mathrm{Br_2}]} \\ &= \frac{k_2 k_1^{1/2}[\mathrm{CH_4}]}{k_3 k_4^{1/2}[\mathrm{Br_2}]^{1/2}}. \end{aligned} \tag{1.233}$$

Finally substituting the result of Equation 1.233 for the concentration of $[\mathrm{CH_3}^*]$ in the formation rate of $[\mathrm{CH_3Br}]$ results in

$$\frac{\mathrm{d}[\mathrm{CH_3Br}]}{\mathrm{d}t} = k_3[\mathrm{CH_3}^*][\mathrm{Br_2}] = \frac{k_2 k_1^{1/2}}{k_4^{1/2}}[\mathrm{CH_4}][\mathrm{Br_2}]^{1/2}. \tag{1.234}$$

SOLUTION 1.5

a) The elementary reaction step for CO adsorption is

$$\mathrm{CO} + * \leftrightarrows \mathrm{CO}* \tag{1.235}$$

Assuming an equilibrium of the above reaction and only one type of surface site yields

$$K_{\mathrm{CO}} = \frac{\theta_{\mathrm{CO}}}{p_{\mathrm{CO}}\theta_*}. \tag{1.236}$$

Furthermore, we can apply the site-balance defined as

$$\theta_* + \theta_{\mathrm{CO}} = 1. \tag{1.237}$$

Hence,

$$\theta_{\mathrm{CO}} = K_{\mathrm{CO}}p_{\mathrm{CO}}\theta_* = K_{\mathrm{CO}}p_{\mathrm{CO}}(1 - \theta_{\mathrm{CO}}) \tag{1.238}$$

$$\theta_{\mathrm{CO}}(1 + K_{\mathrm{CO}}p_{\mathrm{CO}}) = K_{\mathrm{CO}}p_{\mathrm{CO}} \tag{1.239}$$

$$\theta_{\mathrm{CO}} = \frac{K_{\mathrm{CO}}p_{\mathrm{CO}}}{1 + K_{\mathrm{CO}}p_{\mathrm{CO}}}. \tag{1.240}$$

b) The elementary reaction step for dissociative CO adsorption is

$$\mathrm{CO} + 2* \leftrightarrows \mathrm{C}* + \mathrm{O}*. \tag{1.241}$$

Assuming equilibrium of the above reaction and only one type of surface site gives us

$$K_{\mathrm{CO}} = \frac{\theta_{\mathrm{C}}\theta_{\mathrm{O}}}{p_{\mathrm{CO}}\theta_*^2}. \tag{1.242}$$

For the mass balance (or site balance), we get

$$\theta_* + \theta_{\mathrm{C}} + \theta_{\mathrm{O}} = 1. \tag{1.243}$$

Because the surface fraction of C and O are equal

$$K_{\mathrm{CO}} = \frac{\theta_{\mathrm{C}}^2}{p_{\mathrm{CO}}\theta_*^2}. \tag{1.244}$$

Thus,

$$\theta_C = \sqrt{K_{CO} p_{CO}}\theta_* = \sqrt{K_{CO} p_{CO}}(1 - 2\theta_C) \tag{1.245}$$

$$\theta_C(1 + 2\sqrt{K_{CO} p_{CO}}) = \sqrt{K_{CO} p_{CO}} \tag{1.246}$$

$$\theta_C = \frac{\sqrt{K_{CO} p_{CO}}}{1 + 2\sqrt{K_{CO} p_{CO}}}. \tag{1.247}$$

c) The two elementary reaction steps for co-adsorption are

$$CO + * \leftrightarrows CO* \tag{1.248}$$

$$H_2 + 2* \leftrightarrows 2H*. \tag{1.249}$$

Assuming pre-equilibrium of these two elementary reaction steps gives

$$K_{CO} = \frac{\theta_{CO}}{p_{CO}\theta_*} \tag{1.250}$$

and

$$K_{H_2} = \frac{\theta_H^2}{p_{H_2}\theta_*^2} \tag{1.251}$$

and thus for the fractional coverages in terms of the fraction of free sites

$$\theta_H = \sqrt{K_{H_2} p_{H_2}}\theta_* \tag{1.252}$$

$$\theta_{CO} = K_{CO} p_{CO}\theta_* \tag{1.253}$$

Using the site balance,

$$\theta_{CO} + \theta_H + \theta_* = 1 \tag{1.254}$$

and inserting the equation for the surface fraction into the equation

$$(1 + K_{CO} p_{CO} + \sqrt{K_{H_2} p_{H_2}})\theta_* = 1 \tag{1.255}$$

and rearranging for θ_* finally yields

$$\theta_* = \frac{1}{1 + K_{CO} p_{CO} + \sqrt{K_{H_2} p_{H_2}}}. \tag{1.256}$$

This equation can be reinserted into the equations for the surface fractions to obtain

$$\theta_H = \frac{\sqrt{K_{H_2} p_{H_2}}}{1 + K_{CO} p_{CO} + \sqrt{K_{H_2} p_{H_2}}} \tag{1.257}$$

$$\theta_{CO} = \frac{K_{CO} p_{CO}}{1 + K_{CO} p_{CO} + \sqrt{K_{H_2} p_{H_2}}} \tag{1.258}$$

$$\tag{1.259}$$

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_3OH 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

$$r = k_3^+ \theta_{CO} \theta_H. \tag{1.260}$$

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

$$\theta_H = \frac{\sqrt{K_{H_2} p_{H_2}}}{1 + K_{CO} p_{CO} + \sqrt{K_{H_2} p_{H_2}} + K_{CH_3OH} p_{CH_3OH}} \tag{1.261}$$

$$\theta_{CO} = \frac{K_{CO} p_{CO}}{1 + K_{CO} p_{CO} + \sqrt{K_{H_2} p_{H_2}} + K_{CH_3OH} p_{CH_3OH}}. \tag{1.262}$$

And the overall rate is

$$r = \frac{k_3^+ \sqrt{K_{H_2} p_{H_2}} K_{CO} p_{CO}}{\left(1 + K_{CO} p_{CO} + \sqrt{K_{H_2} p_{H_2}} + K_{CH_3OH} p_{CH_3OH}\right)^2}. \tag{1.263}$$

💬 *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:

$$n_{H_2} = p_{H_2} \frac{\partial \ln(r^+)}{\partial p_{H_2}} \tag{1.264}$$

$$= D_1 - 2D_2 \tag{1.265}$$

Here, we are going to split up the complex differential into two smaller (and hopefully simpler) differentials:

$$D_1 = p_{H_2} \frac{\partial \left[\ln k_3^+ + \frac{1}{2} \ln K_{H_2} + \frac{1}{2} \ln p_{H_2} + \ln K_{CO} + \ln p_{CO} \right]}{\partial p_{H_2}} \tag{1.266}$$

$$D_2 = p_{H_2} \frac{\partial \ln \left(1 + K_{CO} p_{CO} + \sqrt{K_{H_2} p_{H_2}} + K_{CH_3OH} p_{CH_3OH} \right)}{\partial p_{H_2}} \tag{1.267}$$

D_1 can be readily solved as all the terms except the $\ln p_{H_2}$ cancel out giving

$$D_1 = p_{H_2} \frac{\partial \frac{1}{2} \ln p_{H_2}}{\partial p_{H_2}} \tag{1.268}$$

$$= \frac{1}{2} p_{H_2} \frac{1}{p_{H_2}} \tag{1.269}$$

$$= \frac{1}{2} \tag{1.270}$$

D_2 is a bit more complex and requires applying the chain-rule

$$D_2 = p_{H_2} \frac{\partial \ln(a)}{\partial a} \frac{\partial a}{\partial p_{H_2}} \tag{1.271}$$

where

$$a = 1 + K_{CO} p_{CO} + \sqrt{K_{H_2} p_{H_2}} + K_{CH_3OH} p_{CH_3OH} \tag{1.272}$$

Thus

$$D_2 = p_{H_2} \frac{1}{a} \frac{\partial \left(1 + K_{CO} p_{CO} + \sqrt{K_{H_2} p_{H_2}} + K_{CH_3OH} p_{CH_3OH} \right)}{\partial p_{H_2}} \tag{1.273}$$

$$= p_{H_2} \frac{1}{a} \left(\frac{1}{2} \sqrt{K_{H_2}} p_{H_2}^{-1/2} \right) \tag{1.274}$$

$$= \frac{1}{2} \left(\frac{\sqrt{K_{H_2} p_{H_2}}}{1 + K_{CO} p_{CO} + \sqrt{K_{H_2} p_{H_2}} + K_{CH_3OH} p_{CH_3OH}} \right) \tag{1.275}$$

$$= \frac{1}{2} \theta_H \tag{1.276}$$

and the final result is

$$n_{H_2} = p_{H_2} \frac{\partial \ln(r^+)}{\partial p_{H_2}} \tag{1.277}$$

$$= \frac{1}{2} - \theta_H \tag{1.278}$$

We can now easily establish the lower and upper limit of the reaction order in H_2:

$$\theta_H \in [0, 1] \rightarrow n_{H_2} \in [-\frac{1}{2}, \frac{1}{2}]. \tag{1.279}$$

The derivations for the reaction order in CO and methanol are quite similar to the one for H_2 and result in:

$$n_{CO} = p_{CO} \frac{\partial \ln(r^+)}{\partial p_{CO}} \tag{1.280}$$

$$= 1 - 2\theta_{CO} \tag{1.281}$$

and

$$n_{CH_3OH} = p_{CH_3OH} \frac{\partial \ln(r^+)}{\partial p_{CH_3OH}} \tag{1.282}$$

$$= -2\theta_{CH_3OH} \tag{1.283}$$

This gives for the lower and upper limits for CO and methanol:

$$\theta_{CO} \in [0, 1] \rightarrow n_{CO} \in [-1, 1] \tag{1.284}$$

and

$$\theta_{CH_3OH} \in [0, 1] \rightarrow n_{CH_3OH} \in [-2, 0] \tag{1.285}$$

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. $OH* + * \leftrightarrows O* + H*$

(1.286)

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

$$r = k_5^+ \theta_{H_2COO} \theta_H \tag{1.287}$$

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.

$$\theta_H = \sqrt{K_1 p_{H_2}}\,\theta_* \tag{1.288}$$

$$\theta_{CO_2} = K_2 p_{CO_2} \theta_* \tag{1.289}$$

$$\theta_{HCOO} = \frac{K_3 \theta_{CO_2} \theta_H}{\theta_*} \tag{1.290}$$

$$\theta_{H_2COO} = \frac{K_4 \theta_{HCOO} \theta_H}{\theta_*} \tag{1.291}$$

By substituting the expressions for θ_H and θ_{CO_2} in Equation 1.290, we get

$$\theta_{HCOO} = K_3 \sqrt{K_1 p_{H_2}} K_2 p_{CO_2} \theta_* \tag{1.292}$$

This result can be readily inserted into Equation 1.291 to obtain

$$\theta_{H_2COO} = K_4 K_3 K_2 p_{CO_2} K_1 p_{H_2} \theta_* \tag{1.293}$$

Now, we need to use the above expressions in combination with the site-balance to construct the expression for the free sites

$$\theta_H + \theta_{CO_2} + \theta_{HCOO} + \theta_{H_2COO} + \theta_* = 1 \tag{1.294}$$

$$\theta_* \left(1 + \sqrt{K_1 p_{H_2}} + K_2 p_{CO_2} + K_3 \sqrt{K_1 p_{H_2}} K_2 p_{CO_2} + K_4 K_3 K_2 p_{CO_2} K_1 p_{H_2}\right) = 1 \tag{1.295}$$

This leads to

$$\theta_* = \frac{1}{1 + \sqrt{K_1 p_{H_2}} + K_2 p_{CO_2} + K_3 \sqrt{K_1 p_{H_2}} K_2 p_{CO_2} + K_4 K_3 K_2 p_{CO_2} K_1 p_{H_2}} \tag{1.296}$$

Using Equations 1.288, 1.293, and 1.296, we can construct the overall rate equation

$$r = k_5^+ \theta_{H_2COO} \theta_H \tag{1.297}$$

$$= k_5^+ K_4 K_3 K_2 p_{CO_2} K_1 p_{H_2} \sqrt{K_1 p_{H_2}} \theta_*^2 \tag{1.298}$$

$$= \frac{k_5^+ K_4 K_3 K_2 p_{CO_2} K_1 p_{H_2} \sqrt{K_1 p_{H_2}}}{\left(1 + \sqrt{K_1 p_{H_2}} + K_2 p_{CO_2} + K_3 \sqrt{K_1 p_{H_2}} K_2 p_{CO_2} + K_4 K_3 K_2 p_{CO_2} K_1 p_{H_2}\right)^2} \tag{1.299}$$

$$= \frac{k_5^+ K_4 K_3 K_2 p_{CO_2} \left(K_1 p_{H_2}\right)^{3/2}}{\left(1 + \sqrt{K_1 p_{H_2}} + K_2 p_{CO_2} + K_3 \sqrt{K_1 p_{H_2}} K_2 p_{CO_2} + K_4 K_3 K_2 p_{CO_2} K_1 p_{H_2}\right)^2} \tag{1.300}$$

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

$$r \approx k_5^+ K_4 K_3 K_2 p_{CO_2} \left(K_1 p_{H_2}\right)^{3/2} \tag{1.301}$$

and

$$n_{H_2} = p_{H_2} \frac{\partial \ln p_{H_2}^{3/2}}{\partial p_{H_2}} = 3/2 \tag{1.302}$$

Think deeper...

In order to find the optimal fraction, we define the constant α which is the ratio between the partial pressure of H_2 and CO_2.

$$\alpha = \frac{p_{H_2}}{p_{CO_2}} \tag{1.303}$$

From this, the total pressure becomes

$$p_T = p_{CO_2} + p_{H_2} = p_{CO_2} + \alpha p_{CO_2} = (1 + \alpha) p_{CO_2} \tag{1.304}$$

and we can relate the partial pressure of H_2 and CO_2 to the total pressure as

$$p_{H2} = \frac{\alpha p_T}{1 + \alpha} \tag{1.305}$$

$$p_{CO2} = \frac{p_T}{1 + \alpha} \tag{1.306}$$

$$\tag{1.307}$$

Filling out these new expressions and assuming that the surface is nearly empty results in

$$r = k_5^+ K_4 K_3 K_2 \frac{p_T}{1 + \alpha} \left(K_1 \frac{\alpha p_T}{1 + \alpha}\right)^{3/2} \tag{1.308}$$

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

$$r = c\frac{\alpha^{3/2}}{(1+\alpha)^{5/2}} \tag{1.309}$$

where c is a factor that does not depend on α.

$$\frac{\partial r}{\partial \alpha} = \frac{\frac{3}{2}\alpha^{1/2}(1+\alpha)^{5/2} - \frac{5}{2}\alpha^{3/2}(1+\alpha)^{3/2}}{(1+\alpha)^5} = 0 \tag{1.310}$$

To find the value for α, only the numerator of the above expression is relevant and we can ignore the denominator

$$\frac{3}{2}\alpha^{1/2}(1+\alpha)^{5/2} - \frac{5}{2}\alpha^{3/2}(1+\alpha)^{3/2} = 0 \tag{1.311}$$

$$\frac{3}{2}\alpha^{1/2}(1+\alpha)^{5/2} = \frac{5}{2}\alpha^{3/2}(1+\alpha)^{3/2} \tag{1.312}$$

$$1+\alpha = \frac{5}{3}\alpha \tag{1.313}$$

$$\alpha = \frac{3}{2} \tag{1.314}$$

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 $\theta_{CO} \gg \theta_O$ and that CO is in quasi-equilibrium with the surface.

b) First, we apply the quasi-equilibrium assumption to CO giving

$$\theta_{CO} = K_1 p_{CO} \theta_* \tag{1.315}$$

Next, we apply the steady-state assumption to θ_O

$$\frac{\mathrm{d}\theta_O}{\mathrm{d}t} = 2k_2^+ p_{O_2} \theta_*^2 - k_3^+ \theta_{CO} \theta_O = 0 \tag{1.316}$$

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

$$\theta_O = \frac{2k_2^+ p_{O_2}}{k_3^+ \theta_{CO}} \theta_*^2 \tag{1.317}$$

To obtain the expression for the free site coverage we assume that $\theta_{CO} \gg \theta_O$ giving

$$\theta_{CO} + \theta_* = 1 \tag{1.318}$$

$$\theta_* \left(1 + K_1 p_{CO}\right) = 1 \tag{1.319}$$

$$\theta_* = \frac{1}{1 + K_1 p_{CO}} \tag{1.320}$$

Plugging this result into the overall rate equation yields

$$r = k_3^+ \theta_{CO} \theta_O \tag{1.321}$$

$$= k_3^+ \frac{K_1 p_{CO}}{1 + K_1 p_{CO}} \frac{2k_2^+ p_{O_2}}{k_3^+ \theta_{CO}} \theta_*^2 \tag{1.322}$$

$$= k_3^+ \frac{K_1 p_{CO}}{1 + K_1 p_{CO}} \frac{2k_2^+ p_{O_2}}{k_3^+} \left(\frac{1}{1 + K_1 p_{CO}}\right)^2 \left(\frac{K_1 p_{CO}}{1 + K_1 p_{CO}}\right)^{-1} \tag{1.323}$$

$$= \frac{2k_2^+ p_{O_2}}{\left(1 + K_1 p_{CO}\right)^2} \tag{1.324}$$

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

$$\theta_{CO} = K_{10} p_{CO} \theta_* \tag{1.325}$$

$$\theta_{H} = \sqrt{K_8 p_{H_2}}\, \theta_* \tag{1.326}$$

$$\theta_{H_2O} = K_5 p_{H_2O} \theta_* \tag{1.327}$$

$$\theta_{OH} = \frac{K_6 \theta_{H_2O} \theta_*}{\theta_H} = \frac{K_5 K_6 p_{H_2O}}{\sqrt{K_8 p_{H_2}}} \theta_* \tag{1.328}$$

$$\theta_{O} = \frac{K_7 \theta_{OH} \theta_*}{\theta_H} = \frac{K_7 \frac{K_5 K_6 p_{H_2O}}{\sqrt{K_8 p_{H_2}}} \theta_*^2}{\sqrt{K_8 p_{H_2}} \theta_*} = \frac{K_5 K_6 K_7}{K_8} \frac{p_{H_2O}}{p_{H_2}} \theta_* \tag{1.329}$$

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

$$\theta_{CH_3} = \frac{K_1 p_{CH_4}}{\sqrt{K_8 p_{H_2}}} \theta_* \tag{1.330}$$

$$\theta_{CH_2} = \frac{K_1 K_2 p_{CH_4}}{K_8 p_{H_2}} \theta_* \tag{1.331}$$

$$\theta_{CH} = \frac{K_1 K_2 K_3 p_{CH_4}}{\left(K_8 p_{H_2}\right)^{3/2}} \theta_* \tag{1.332}$$

$$\theta_{C} = \frac{K_1 K_2 K_3 K_4 p_{CH_4}}{\left(K_8 p_{H_2}\right)^{2}} \theta_* \tag{1.333}$$

Now we can construct the site-balance

$$\theta_{CO} + \theta_H + \theta_{H_2O} + \theta_{OH} + \theta_O + \theta_{CH_3} + \theta_{CH_2} + \theta_{CH} + \theta_C + \theta_* = 1 \tag{1.334}$$

and plug the above equations for the surface coverages into it

$$\theta_* = \left(1 + K_{10}p_{CO} + \sqrt{K_8 p_{H_2}} + K_5 p_{H_2O} + \frac{K_5K_6p_{H_2O}}{\sqrt{K_8p_{H_2}}} + \frac{K_5K_6K_7}{K_8}\frac{p_{H_2O}}{p_{H_2}} + \frac{K_1p_{CH_4}}{\sqrt{K_8p_{H_2}}} \cdots \right.$$
$$\left. \cdots + \frac{K_1K_2p_{CH_4}}{K_8p_{H_2}} + \frac{K_1K_2K_3p_{CH_4}}{(K_8p_{H_2})^{3/2}} + \frac{K_1K_2K_3K_4p_{CH_4}}{(K_8p_{H_2})^2}\right)^{-1} \tag{1.335}$$

Since the overall rate is determined by the rate of step 9 we can construct the following expression

$$r = k_9^+\theta_C\theta_O - k_9^-\theta_{CO}\theta_* \tag{1.336}$$
$$= k_9^+\theta_C\theta_O - \frac{k_9^+}{K_9}\theta_{CO}\theta_* \tag{1.337}$$

If we assume that there is an equilibrium $r = 0$, we can express K_9 as

$$K_9 = \frac{\theta_{CO}\theta_*}{\theta_C\theta_O} = \frac{p_{CO}p_{H_2}^3}{p_{H_2O}p_{CH_4}}\frac{K_8^3K_{10}}{K_1K_2K_3K_4K_5K_6K_7} = \frac{p_{CO}p_{H_2}^3}{p_{H_2O}p_{CH_4}}\frac{1}{K_{eq}} \tag{1.338}$$

and using this result for K_9 for our overall rate expression results in

$$r = k_9^+\theta_C\theta_O - k_9^-\theta_{CO}\theta_* \tag{1.339}$$
$$= k_9^+\theta_C\theta_O\left(1 - \frac{1}{K_9}\frac{\theta_{CO}\theta_*}{\theta_C\theta_O}\right) \tag{1.340}$$
$$= k_9^+\frac{K_1K_2K_3K_4K_5K_6K_7p_{CH_4}p_{H_2O}}{(K_8p_{H_2})^3}\left(1 - \frac{1}{K_9}\frac{p_{CO}p_{H_2}^3}{p_{H_2}p_{CH_4}}\frac{1}{K_{eq}}\right)\theta_*^2 \tag{1.341}$$

Further assuming that O is the MARI, we can use the following equation for the free sites

$$\theta_* = \left(1 + \frac{K_5K_6K_7}{K_8}\frac{p_{H_2O}}{p_{H_2}}\right)^{-1} \tag{1.342}$$

giving

$$r = k_9^+\frac{\frac{K_1K_2K_3K_4K_5K_6K_7p_{CH_4}p_{H_2O}}{(K_8p_{H_2})^3}\left(1 - \frac{1}{K_9}\frac{p_{CO}p_{H_2}^3}{p_{H_2O}p_{CH_4}}\frac{1}{K_{eq}}\right)}{\left(1 + \frac{K_5K_6K_7}{K_8}\frac{p_{H_2O}}{p_{H_2}}\right)^2} \tag{1.343}$$

For low conversions, the second term between parentheses in the numerator can be neglected, further simplifying the equation to

$$r = k_9^+ \frac{K_1 K_2 K_3 K_4 K_5 K_6 K_7 p_{CH_4} p_{H_2O}}{\left(K_8 p_{H_2}\right)^3} \left(1 + \frac{K_5 K_6 K_7}{K_8} \frac{p_{H_2O}}{p_{H_2}}\right)^{-2} \tag{1.344}$$

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:

$$n_{CH_4} = p_{CH_4} \frac{\partial \ln(r^+)}{\partial p_{CH_4}} = 1 \tag{1.345}$$

$$n_{CO} = p_{CO} \frac{\partial \ln(r^+)}{\partial p_{CO}} = 0 \tag{1.346}$$

The reaction order in H_2O and H_2 is a bit more complicated but with some rewriting the derivatives equate to

$$n_{H_2O} = p_{H_2O} \frac{\partial \ln(r^+)}{\partial p_{H_2O}} = 1 - 2 p_{H_2O} \frac{K_5 K_6 K_7}{K_8} \frac{\partial p_{H_2O} / \partial p_{H_2O}}{1 + \frac{K_5 K_6 K_7}{K_8} \frac{p_{H_2O}}{p_{H_2}}} \tag{1.347}$$

$$= 1 - 2 \frac{K_5 K_6 K_7}{K_8 p_{H_2}} p_{H_2O} \left(1 + \frac{K_5 K_6 K_7}{K_8} \frac{p_{H_2O}}{p_{H_2}}\right)^{-1} \tag{1.348}$$

$$= 1 - 2\theta_O \tag{1.349}$$

and similarly for H_2

$$n_{H_2} = p_{H_2} \frac{\partial \ln(r^+)}{\partial p_{H_2}} = -3 + 2\theta_O \tag{1.350}$$

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

$$r = k_1^+ \frac{p_{CH_4}}{\left(1 + \frac{K_5 K_6 K_7}{K_8} \frac{p_{H_2O}}{p_{H_2}}\right)^2} \tag{1.351}$$

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

$$n_{CH_4} = p_{CH_4} \frac{\partial \ln(r^+)}{\partial p_{CH_4}} = 1 \tag{1.352}$$

$$n_{CO} = p_{CO} \frac{\partial \ln(r^+)}{\partial p_{CO}} = 0 \tag{1.353}$$

$$n_{H_2O} = p_{H_2O} \frac{\partial \ln(r^+)}{\partial p_{H_2O}} = -2\theta_O \tag{1.354}$$

$$n_{H_2} = p_{H_2} \frac{\partial \ln(r^+)}{\partial p_{H_2}} = 2\theta_O \tag{1.355}$$

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)

$$r = k_2^+ \theta_{C_2H_5} \theta_H - k_2^- \theta_{CH_3}^2 \tag{1.356}$$

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

$$\theta_{C_2H_5} = \frac{K_1 p_{C_2H_6}}{\theta_H} \theta_*^2 \tag{1.357}$$

$$\theta_{CH_3} = \frac{p_{CH_4}}{K_3 \theta_H} \theta_*^2 \tag{1.358}$$

$$\theta_H = \sqrt{K_4 p_{H_2}} \theta_* \tag{1.359}$$

Plugging Equation 1.359 into 1.357 and into 1.358, gives

$$\theta_{C_2H_5} = \frac{K_1 p_{C_2H_6}}{\sqrt{K_4 p_{H_2}}} \theta_* \tag{1.360}$$

and

$$\theta_{CH_3} = \frac{p_{CH_4}}{K_3\sqrt{K_4 p_{H_2}}}\theta_* \tag{1.361}$$

Using the site balance, we obtain the following equations

$$\theta_* = \frac{1}{1 + \frac{K_1 p_{C_2H_6}}{\sqrt{K_4 p_{H_2}}} + \frac{p_{CH_4}}{K_3\sqrt{K_4 p_{H_2}}} + \sqrt{K_4 p_{H_2}}} \tag{1.362}$$

$$\theta_{C_2H_5} = \frac{\frac{K_1 p_{C_2H_6}}{\sqrt{K_4 p_{H_2}}}}{1 + \frac{K_1 p_{C_2H_6}}{\sqrt{K_4 p_{H_2}}} + \frac{p_{CH_4}}{K_3\sqrt{K_4 p_{H_2}}} + \sqrt{K_4 p_{H_2}}} \tag{1.363}$$

$$\theta_{CH_3} = \frac{\frac{p_{CH_4}}{K_3\sqrt{K_4 p_{H_2}}}}{1 + \frac{K_1 p_{C_2H_6}}{\sqrt{K_4 p_{H_2}}} + \frac{p_{CH_4}}{K_3\sqrt{K_4 p_{H_2}}} + \sqrt{K_4 p_{H_2}}} \tag{1.364}$$

$$\theta_H = \frac{\sqrt{K_4 p_{H_2}}}{1 + \frac{K_1 p_{C_2H_6}}{\sqrt{K_4 p_{H_2}}} + \frac{p_{CH_4}}{K_3\sqrt{K_4 p_{H_2}}} + \sqrt{K_4 p_{H_2}}} \tag{1.365}$$

d) Plugging the above equations into the overall rate equation yields

$$r = \frac{k_2^+ K_1 p_{C_2H_6}\left(1 - \frac{p_{CH_4}^2}{K_1 K_2 K_3^2 K_4 p_{C_2H_6} p_{H_2}}\right)}{\left(1 + \frac{K_1 p_{C_2H_6}}{\sqrt{K_4 p_{H_2}}} + \frac{p_{CH_4}}{K_3\sqrt{K_4 p_{H_2}}} + \sqrt{K_4 p_{H_2}}\right)^2} \tag{1.366}$$

e) Applying the MARI approximation and assuming low conversion simplifies the overall rate equation to

$$r = \frac{k_2^+ K_1 p_{C_2H_6}}{\left(1 + \sqrt{K_4 p_{H_2}}\right)^2} \tag{1.367}$$

Think deeper...

The apparent activation energy can be readily evaluated to

$$\Delta E_{act}^{app} = RT^2 \frac{\partial \ln(r^+)}{\partial T} \tag{1.368}$$

$$= RT^2\left(\frac{\partial \ln k_2^+}{\partial T} + \frac{\partial \ln K_1}{\partial T} - 2\frac{\partial \ln\left(1 + \sqrt{K_4 p_{H_2}}\right)}{\partial T}\right) \tag{1.369}$$

$$= E_{act}^{(2)} + \Delta H_{ads}^{(1)} - \theta_H \Delta H_{ads}^{(4)} \tag{1.370}$$

SOLUTION 1.10

From the quasi-equilibrated steps (1), (2) and (4), it follows that

$$\theta_{NO} = K_1 p_{NO} \theta_* \tag{1.371}$$

$$\theta_{CO} = K_2 p_{CO} \theta_* \tag{1.372}$$

$$\theta_N = \sqrt{K_4 p_{N_2}}\, \theta_* \tag{1.373}$$

To derive the surface coverage of O*, we apply the steady-state approximation to this surface intermediate

$$2k_3^+ p_{O_2} \theta_*^2 - k_6^+ \theta_{CO} \theta_O = 0 \tag{1.374}$$

Note that we have neglected the term $k_5^+ \theta_{NO} \theta_O$, because we assume that NO dissociation is rate-determining. Therefore, this term is negligible compared to the other two terms.

It follows then that

$$\theta_O = \frac{2k_3^+ p_{O_2}}{k_6^+ \theta_{CO}} \theta_*^2 \tag{1.375}$$

Combining this expression with the expression for θ_{CO}, we obtain

$$\theta_O = \frac{2k_3^+ p_{O_2}}{k_6^+ K_2 p_{CO} \theta_*} \theta_*^2 = \frac{2k_3^+ p_{O_2}}{k_6^+ K_2 p_{CO}} \theta_* \tag{1.376}$$

Applying the site balance for all surface intermediates yields

$$\theta_* = \frac{1}{1 + K_1 p_{NO} + K_2 p_{CO} + \frac{2k_3^+ p_{O_2}}{k_6^+ K_2 p_{CO}} + \sqrt{K_4 p_{N_2}}} \tag{1.377}$$

Finally, we can evaluate the rate of N_2 and CO_2 production

$$r_{N_2} = \frac{1}{2} r_5 = \frac{1}{2} k_5^+ \theta_{NO} \theta_* = \frac{\frac{1}{2} k_5^+ K_1 p_{NO}}{\left(1 + K_1 p_{NO} + K_2 p_{CO} + \frac{2k_3^+ p_{O_2}}{k_6^+ K_2 p_{CO}} + \sqrt{K_4 p_{N_2}}\right)^2} \tag{1.378}$$

$$r_{CO_2} = r_6 = k_6^+ \theta_{CO} \theta_O = \frac{2k_3^+ p_{O_2}}{\left(1 + K_1 p_{NO} + K_2 p_{CO} + \frac{2k_3^+ p_{O_2}}{k_6^+ K_2 p_{CO}} + \sqrt{K_4 p_{N_2}}\right)^2} \tag{1.379}$$

Think deeper...

This catalytic reaction pertains to three-way catalytic convertors for environmental pollution control.

SOLUTION 1.11

a)

$$1.\mathrm{C_2H_4} + * \leftrightarrows \mathrm{C_2H_4}* \tag{1.380}$$
$$2.\mathrm{O_2} + 2* \leftrightarrows 2\mathrm{O}* \tag{1.381}$$
$$3.\mathrm{C_2H_4}* + \mathrm{O}* \rightarrow \mathrm{C_2H_4O} + 2* \tag{1.382}$$
$$\tag{1.383}$$

Applying a quasi-equilibrium approximation, we obtain the following expressions for the partial coverages as a function of the partial pressures and equilibrium constants

$$\theta_{\mathrm{C_2H_4}} = K_1 p_{\mathrm{C_2H_4}} \theta_* \tag{1.384}$$

and

$$\theta_{\mathrm{O}} = \sqrt{K_2 p_{\mathrm{O_2}}}\,\theta_* \tag{1.385}$$

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:

$$\theta_{\mathrm{C_2H_4}} = \frac{K_1 p_{\mathrm{C_2H_4}}}{1 + K_1 p_{\mathrm{C_2H_4}} + \sqrt{K_2 p_{\mathrm{O_2}}}} \tag{1.386}$$

and

$$\theta_{\mathrm{O}} = \frac{\sqrt{K_2 p_{\mathrm{O_2}}}}{1 + K_1 p_{\mathrm{C_2H_4}} + \sqrt{K_2 p_{\mathrm{O_2}}}}. \tag{1.387}$$

b)

$$r_{\mathrm{C_2H_4O}} = k_3 \theta_{\mathrm{C_2H_4}} \theta_{\mathrm{O}} \tag{1.388}$$
$$= \frac{k_3 K_1 p_{\mathrm{C_2H_4}} \sqrt{K_2 p_{\mathrm{O_2}}}}{\left(1 + K_1 p_{\mathrm{C_2H_4}} + \sqrt{K_2 p_{\mathrm{O_2}}}\right)^2} \tag{1.389}$$

c) If oxygen strongly adsorbs, we can assume that oxygen is the MARI and hence the overall rate expression simplifies to

$$r_{\mathrm{C_2H_4O}} = \frac{k_3 K_1 p_{\mathrm{C_2H_4}} \sqrt{K_2 p_{\mathrm{O_2}}}}{\left(1 + \sqrt{K_2 p_{\mathrm{O_2}}}\right)^2} \tag{1.390}$$

The reaction orders in oxygen and ethylene are

$$n_{C_2H_4} = p_{C_2H_4} \frac{\partial \ln(r^+)}{\partial p_{C_2H_4}} \tag{1.391}$$

$$= 1 \tag{1.392}$$

$$n_{O_2} = p_{O_2} \frac{\partial \ln(r^+)}{\partial p_{O_2}} \tag{1.393}$$

$$= \frac{1}{2} - \theta_O \tag{1.394}$$

d) The surface is predominantly occupied with adsorbed O.

e)

$$\Delta E_{act}^{app} = RT^2 \frac{\partial \ln(r^+)}{\partial T} \tag{1.395}$$

$$= E_{act}^{(3)} + \Delta H_{ads}^{(1)} + \left(\frac{1}{2} - \theta_O\right) \Delta H_{ads}^{(2)} \tag{1.396}$$

SOLUTION 1.12

a)

$$1.SO_2 + * \leftrightarrows SO_2* \tag{1.397}$$

$$2.O_2 + 2* \leftrightarrows 2O* \tag{1.398}$$

$$3.SO_2* + O* \rightarrow SO_3* + * \tag{1.399}$$

$$4.SO_3 + * \leftrightarrows SO_3* \tag{1.400}$$

b)

$$r_{SO_3} = k_3 \theta_{SO_2} \theta_O \tag{1.401}$$

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.

$$\theta_* = \frac{1}{1 + K_1 p_{SO_2} + \sqrt{K_2 p_{O_2}} + K_4 p_{SO_3}} \tag{1.402}$$

$$r_{SO_3} = \frac{k_3 K_1 p_{SO_2} \sqrt{K_2 p_{O_2}}}{\left(1 + K_1 p_{SO_2} + \sqrt{K_2 p_{O_2}} + K_4 p_{SO_3}\right)^2} \tag{1.403}$$

c) From the form of the overall reaction equation, the limits of the reaction orders can be established as

$$n_{SO_2} \in [-1, 1] \tag{I.404}$$
$$n_{SO_3} \in [-2, 0] \tag{I.405}$$
$$n_{O_2} \in [-\frac{1}{2}, \frac{1}{2}] \tag{I.406}$$

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

$$r_{SO_3} = \frac{k_3 K_1 p_{SO_2} \sqrt{K_2 p_{O_2}}}{\left(1 + \sqrt{K_2 p_{O_2}}\right)^2} \tag{I.407}$$

$$n_{SO_2} = 1 \tag{I.408}$$
$$n_{SO_3} = 0 \tag{I.409}$$
$$n_{O_2} = \frac{1}{2} - \theta_O \tag{I.410}$$

e)

$$\Delta E_{act}^{app} = RT^2 \frac{\partial \ln(r^+)}{\partial T} \tag{I.411}$$
$$= E_{act}^{(3)} + \Delta H_{ads}^{(1)} + \left(\frac{1}{2} - \theta_O\right) \Delta H_{ads}^{(2)} \tag{I.412}$$

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)

$$1.\ C_2H_5OH + * \leftrightarrows C_2H_5OH* \tag{I.413}$$
$$2.\ O_2 + 2* \leftrightarrows 2O* \tag{I.414}$$
$$3.\ C_2H_5OH* + O* \rightarrow C_2H_4O + H_2O + 2* \tag{I.415}$$

$$\theta_{C_2H_5OH} = \frac{K_1 p_{C_2H_5OH}}{1 + K_1 p_{C_2H_5OH} + \sqrt{K_2 p_{O_2}}} \tag{I.416}$$

$$\theta_O = \frac{\sqrt{K_2 p_{O_2}}}{1 + K_1 p_{C_2H_5OH} + \sqrt{K_2 p_{O_2}}} \tag{I.417}$$

b)

$$r = k_3 \theta_{C_2H_5OH} \theta_O = \frac{k_3 K_1 p_{C_2H_5OH} \sqrt{K_2 p_{O_2}}}{\left(1 + K_1 p_{C_2H_5OH} + \sqrt{K_2 p_{O_2}}\right)^2} \tag{I.418}$$

c)

$$r = k_3 \theta_{C_2H_5OH} \theta_O = \frac{k_3 K_1 p_{C_2H_5OH} \sqrt{K_2 p_{O_2}}}{\left(1 + K_1 p_{C_2H_5OH}\right)^2} \tag{I.419}$$

$$n_{C_2H_5OH} \in [-1, 1] \tag{I.420}$$

$$n_{O_2} = \frac{1}{2} \tag{I.421}$$

d)

$$\Delta E_{act}^{app} = RT^2 \frac{\partial \ln(r^+)}{\partial T} \tag{I.422}$$

$$= E_{act}^{(3)} + \left(1 - 2\theta_{C_2H_5OH}\right) \Delta H_{ads}^{(1)} + \frac{1}{2} \Delta H_{ads}^{(2)} \tag{I.423}$$

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)

$$r = k_3^+ \theta_O \theta_H - k_3^- \theta_{OH} \theta_* \tag{I.424}$$

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.

$$\theta_{\mathrm{H}} = \sqrt{K_1 p_{\mathrm{H_2}}}\theta_* \tag{1.425}$$

$$\theta_{\mathrm{O}} = \sqrt{K_2 p_{\mathrm{O_2}}}\theta_* \tag{1.426}$$

$$\theta_{\mathrm{H_2O}} = K_5 p_{\mathrm{H_2O}}\theta_* \tag{1.427}$$

$$\theta_{\mathrm{OH}} = \frac{\theta_{\mathrm{H_2O}}\theta_*}{K_4\theta_{\mathrm{H}}} \tag{1.428}$$

$$\tag{1.429}$$

Substituting these surface concentrations into the rate equation yields

$$r = k_3^+ \sqrt{K_1 p_{\mathrm{H_2}}}\theta_* \sqrt{K_2 p_{\mathrm{O_2}}}\theta_* - k_3^- \frac{\theta_{\mathrm{H_2O}}\theta_*}{K_4\theta_{\mathrm{H}}}\theta_* \tag{1.430}$$

$$= k_3^+ \sqrt{K_1 K_2 p_{\mathrm{H_2}} p_{\mathrm{O_2}}}\theta_*^2 - k_3^- \frac{K_5 p_{\mathrm{H_2O}}\theta_*^2}{K_4\sqrt{K_1 p_{\mathrm{H_2}}}\theta_*}\theta_* \tag{1.431}$$

$$= k_3^+ \sqrt{K_1 K_2 p_{\mathrm{H_2}} p_{\mathrm{O_2}}}\theta_*^2 - k_3^- \frac{K_5 p_{\mathrm{H_2O}}}{K_4\sqrt{K_1 p_{\mathrm{H_2}}}}\theta_*^2 \tag{1.432}$$

$$= k_3^+ \sqrt{K_1 K_2 p_{\mathrm{H_2}} p_{\mathrm{O_2}}}\theta_*^2 \left(1 - k_3^- \frac{K_5 p_{\mathrm{H_2O}}}{k_3^+ K_4 K_1 p_{\mathrm{H_2}}\sqrt{K_2 p_{\mathrm{O_2}}}}\right) \tag{1.433}$$

$$= k_3^+ \sqrt{K_1 K_2 p_{\mathrm{H_2}} p_{\mathrm{O_2}}}\theta_*^2 \left(1 - \frac{p_{\mathrm{H_2O}}}{K_{\mathrm{eq}} p_{\mathrm{H_2}}\sqrt{p_{\mathrm{O_2}}}}\right) \tag{1.434}$$

From the last two expressions, it is clear that the equilbrium constant has to be

$$K_{\mathrm{eq}} = \frac{K_1\sqrt{K_2}K_3 K_4}{K_5} \tag{1.435}$$

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:

$$\theta_* = \frac{1}{1 + \sqrt{K_1 p_{\mathrm{H_2}}} + \sqrt{K_2 p_{\mathrm{O_2}}} + \frac{K_5 p_{\mathrm{H_2O}}}{K_4\sqrt{K_1 p_{\mathrm{H_2}}}} + K_5 p_{\mathrm{H_2O}}} \tag{1.436}$$

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).

$$\theta_* = \frac{1}{1 + \sqrt{K_2 p_{\mathrm{O_2}}}} \tag{1.437}$$

d) To establish the reaction order, first fill out the expression for the free sites in the overall rate equation

$$r = k_3^+ \sqrt{K_1 K_2 p_{\mathrm{H_2}} p_{\mathrm{O_2}}} \left(1 - \frac{p_{\mathrm{H_2O}}}{K_{\mathrm{eq}} p_{\mathrm{H_2}}\sqrt{p_{\mathrm{O_2}}}}\right) \cdot \left(\frac{1}{1 + \sqrt{K_2 p_{\mathrm{O_2}}}}\right)^2 \tag{1.438}$$

Because we assume that the reaction is far from equilibrium, we can neglect the second term between the first set of brackets giving

$$r = \frac{k_3^+ \sqrt{K_1 K_2 p_{H_2} p_{O_2}}}{\left(1 + \sqrt{K_2 p_{O_2}}\right)^2} \tag{I.439}$$

From the above expression, the following reaction orders can be derived (please refer to the previous answers for a more thorough derivation).

$$n_{H_2} = \frac{1}{2} \tag{I.440}$$

$$n_{O_2} = \frac{1}{2} - \theta_O \tag{I.441}$$

$$n_{H_2O} = 0 \tag{I.442}$$

e) For very low surface coverage, the rate equals to

$$r = k_3^+ \sqrt{K_1 K_2 p_{H_2} p_{O_2}} \tag{I.443}$$

Plugging in the following expressions for p_{H_2} and p_{O_2}

$$p_{H_2} = \alpha \cdot p_T \tag{I.444}$$

$$p_{O_2} = (1 - \alpha) \cdot p_T \tag{I.445}$$

we obtain

$$r = k_3^+ \sqrt{K_1 K_2 \alpha (1 - \alpha)} p_T \tag{I.446}$$

Taking the first derivative and equating to zero yields ($\frac{\partial r}{\partial \alpha} = 0$):

$$\alpha = \frac{1}{2} \tag{I.447}$$

In other words: the partial pressure of hydrogen and of oxygen need to be equal.

Think deeper...

The apparent activation energy is

$$\Delta E_{act}^{app} = RT^2 \frac{\partial \ln(r^+)}{\partial T} = E_{act}^{(3)} + \frac{1}{2}\Delta H_{ads}^{(1)} + \frac{1}{2}\Delta H_{ads}^{(2)} \tag{I.448}$$

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)

$$r_{N_2} = \frac{1}{2} r_5 = \frac{1}{2}\left(k_5^+ \theta_{NO}\theta_* - k_5^- \theta_N \theta_O\right) \tag{1.449}$$

Because all other steps are quasi-equilibrated, we can write

$$\theta_{NO} = K_1 p_{NO}\theta_* \tag{1.450}$$
$$\theta_{CO} = K_2 p_{CO}\theta_* \tag{1.451}$$
$$\theta_{N_2} = K_3 p_{N_2}\theta_* \tag{1.452}$$
$$\theta_N = \sqrt{K_4\theta_{N_2}\theta_*} = \sqrt{K_4 K_3 p_{N_2}\theta_*\theta_*} = \sqrt{K_3 K_4 p_{N_2}}\theta_* \tag{1.453}$$
$$\theta_O = \frac{\theta_{CO_2}\theta_*}{K_6\theta_{CO}} = \frac{K_7 p_{CO_2}\theta_*\theta_*}{K_6 K_2 p_{CO}\theta_*} = \frac{K_7 p_{CO_2}}{K_2 K_6 p_{CO}}\theta_* \tag{1.454}$$
$$\theta_{CO_2} = K_7 p_{CO_2}\theta_* \tag{1.455}$$

Using the site balance, this results in

$$\theta_* = \frac{1}{1 + K_1 p_{NO} + K_2 p_{CO} + K_3 p_{N_2} + \sqrt{K_3 K_4 p_{N_2}} + \frac{K_7 p_{CO_2}}{K_2 K_6 p_{CO}} + K_7 p_{CO_2}} \tag{1.456}$$

Plugging this into the overall rate expression and defining an overall reaction equilibrium constant we obtain

$$r_5 = \frac{k_5^+ K_1 p_{NO}\left(1 - \frac{\sqrt{p_{N_2}}p_{CO_2}}{p_{CO}p_{NO}}\frac{1}{K_{eq}}\right)}{\left(1 + K_1 p_{NO} + K_2 p_{CO} + K_3 p_{N_2} + \sqrt{K_3 K_4 p_{N_2}} + \frac{K_7 p_{CO_2}}{K_2 K_6 p_{CO}} + K_7 p_{CO_2}\right)^2} \tag{1.457}$$

where

$$K_{eq} = \frac{K_1 K_2 K_5 K_6}{\sqrt{K_4}\sqrt{K_3 K_7}} \tag{1.458}$$

b) If O is the MARI, then the overall rate equation simplifies to

$$r_5 = \frac{k_5^+ K_1 p_{NO}\left(1 - \frac{\sqrt{p_{N_2}}p_{CO_2}}{p_{CO}p_{NO}}\frac{1}{K_{eq}}\right)}{\left(1 + \frac{K_7 p_{CO_2}}{K_2 K_6 p_{CO}}\right)^2} \tag{1.459}$$

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 numerator into account. In other words

$$r^+ = \frac{k_5^+ K_1 p_{NO}}{\left(1 + \frac{K_7 p_{CO_2}}{K_2 K_6 p_{CO}}\right)^2} \tag{1.460}$$

We obtain the following reaction orders

$$n_{N_2} = 0 \tag{1.461}$$
$$n_{NO} = 1 \tag{1.462}$$
$$n_{CO} = 2\theta_O \tag{1.463}$$
$$n_{CO_2} = -2\theta_O \tag{1.464}$$

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

$$\Delta E_{act}^{app} = RT^2 \frac{\partial \ln(r^+)}{\partial T} = E_{act}^{(5)} + \Delta H_{ads}^{(1)} \tag{1.465}$$

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 practice 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

$$\Delta E_{act}^{app} = RT^2 \frac{\partial \ln(r^+)}{\partial T} = E_{act}^{(5)} + \Delta H_{ads}^{(1)} + 2\theta_O \left(\Delta H_{ads}^{(2)} + \Delta H_{ads}^{(6)} - \Delta H_{ads}^{(7)}\right) \tag{1.466}$$

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:

$$r_{H_2O_2} = k_3^+ \theta_{O_2} \theta_H - k_3^- \theta_{OOH} \theta_* . \tag{1.467}$$

We assume that all other steps are quasi-equilibrated, hence

$$\theta_H = \sqrt{K_1 p_{H_2}} \theta_* \tag{1.468}$$

$$\theta_{O_2} = K_2 p_{O_2} \theta_* \tag{1.469}$$

$$\theta_{OOH} = \frac{\theta_{H_2O_2}}{K_4 \theta_H} \theta_* \tag{1.470}$$

$$= \frac{K_5 p_{H_2O_2}}{K_4 \sqrt{K_1 p_{H_2}}} \theta_* \tag{1.471}$$

$$\theta_{H_2O_2} = K_5 p_{H_2O_2} \theta_* \tag{1.472}$$

By applying the site balance, we can derive the following expression for the free sites

$$\theta_* = \frac{1}{1 + \sqrt{K_1 p_{H_2}} + K_2 p_{O_2} + \frac{K_5 p_{H_2O_2}}{K_4 \sqrt{K_1 p_{H_2}}} + K_5 p_{H_2O_2}} \tag{1.473}$$

Plugging this into the overall rate expression and introducing an equilibrium constant for the reverse reaction yields

$$r = r_{H_2O_2} = \frac{k_3^+ K_2 p_{O_2} \sqrt{K_1 p_{H_2}} \left(1 - \frac{1}{K_{eq}} \frac{p_{H_2O_2}}{p_{O_2} p_{H_2}}\right)}{\left(1 + \sqrt{K_1 p_{H_2}} + K_2 p_{O_2} + \frac{K_5 p_{H_2O_2}}{K_4 \sqrt{K_1 p_{H_2}}} + K_5 p_{H_2O_2}\right)^2} \tag{1.474}$$

b) If O_2* is the MARI and we assume a low conversion, the above expression simplifies to

$$r = \frac{k_3^+ K_2 p_{O_2} \sqrt{K_1 p_{H_2}}}{\left(1 + K_2 p_{O_2}\right)^2} \tag{1.475}$$

The reaction orders are

$$n_{H_2} = \frac{1}{2} \tag{1.476}$$

$$n_{O_2} = 1 - 2\theta_{O_2} \tag{1.477}$$

$$n_{H_2O_2} = 0 \tag{1.478}$$

c) The apparent activation energy is given by

$$\Delta E_{\text{act}}^{\text{app}} = RT^2 \frac{\partial \ln(r^+)}{\partial T} = E_{\text{act}}^{(3)} + (1 - 2\theta_{O_2})\Delta H_{\text{ads}}^{(2)} + \frac{1}{2}\Delta H_{\text{ads}}^{(1)} \tag{1.479}$$

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

$$r = k_3^+ K_2 p_{O_2} \sqrt{K_1 p_{H_2}} \tag{1.480}$$

and the apparent activation energy becomes

$$\Delta E_{\text{act}}^{\text{app}} = RT^2 \frac{\partial \ln(r^+)}{\partial T} = E_{\text{act}}^{(3)} + \Delta H_{\text{ads}}^{(2)} + \frac{1}{2}\Delta H_{\text{ads}}^{(1)} \tag{1.481}$$

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) Langmuir-Hinshelwood

$$C_2H_2 + * \rightleftarrows C_2H_2* \tag{1.482}$$
$$H_2 + 2* \rightleftarrows 2H* \tag{1.483}$$
$$C_2H_2* + H* \rightarrow C_2H_3* + * \tag{1.484}$$
$$C_2H_3* + H* \rightleftarrows C_2H_4* + * \tag{1.485}$$
$$C_2H_4 + * \rightleftarrows C_2H_4* \tag{1.486}$$

Eley-Rideal:

$$C_2H_2 + * \rightleftarrows C_2H_2* \tag{1.487}$$
$$H_2 + 2* \rightleftarrows 2H* \tag{1.488}$$
$$C_2H_2* + H_2 \rightarrow C_2H_4* \tag{1.489}$$
$$C_2H_4 + * \rightleftarrows C_2H_4* \tag{1.490}$$

b) First, the reaction order of the Langmuir-Hinshelwood mechanism will be derived.

In order to obtain the reaction order, the reaction rate expression must first be determined. By applying the rate-determining step assumption, the following rate expressions can be determined

$$r = k_3^+ \theta_{C_2H_2} \theta_H - k_3^- \theta_{C_2H_4} \theta_*, \tag{1.491}$$

which can be simplified using the zero-conversion approximation

$$r = k_3^+ \theta_{C_2H_2} \theta_H. \tag{1.492}$$

To find an expression for the reaction rate, one must first find an expression for the fractional surface coverages of the different compounds.The individual surface coverages can be derived from the rates of formation of the corresponding elementary reaction steps.

$$\frac{d\theta_{C_2H_2*}}{dt} = k_1^+ p_{C_2H_2} \theta_* - k_1^- \theta_{C_2H_2} \tag{1.493}$$

$$\frac{d\theta_{H*}}{dt} = 2k_2^+ p_{H_2} \theta_*^2 - 2k_2^- \theta_H^2 \tag{1.494}$$

By applying that $K_x = \frac{k_1^+}{k_1^-}$ and the steady-state approximation, the following expressions for the surface coverages can be derived:

$$\theta_{C_2H_2} = K_1 p_{C_2H_2} \theta_* \tag{1.495}$$

$$\theta_H = \sqrt{K_2 p_{H_2}} \theta_* \tag{1.496}$$

The total balance of all the coverages equals

$$\theta_* + \theta_{C_2H_2} + \theta_H = 1. \tag{1.497}$$

By substituting the individual expressions into the total balance and rewriting the equation for θ_*, the following equation is obtained:

$$\theta_* = \frac{1}{1 + K_1 p_{C_2H_2} + \sqrt{K_2 p_{H_2}}}. \tag{1.498}$$

Substituting this expression back into the equations for the fractional surface coverages of carbon monoxide and oxygen, and consequently substituting these equations into the overall reaction rate equation yields

$$r_{LH} = \frac{k_3^+ K_1 p_{C_2H_2} \sqrt{K_2 p_{H_2}}}{\left(1 + K_1 p_{C_2H_2} + \sqrt{K_2 p_{H_2}}\right)^2}. \tag{1.499}$$

Note that denominator is squared, which shows that two active sides are required. From the rate expression, the reaction order can be readily derived.

$$n_{C_2H_2} = p_{C_2H_2} \frac{\partial \ln(r)}{\partial p_{C_2H_2}} \tag{1.500}$$

$$= p_{C_2H_2} \frac{\partial}{\partial p_{C_2H_2}} \left(\ln \left(\frac{k_3^+ K_1 p_{C_2H_2} \sqrt{K_2 p_{H_2}}}{\left(1 + K_1 p_{C_2H_2} + \sqrt{K_2 p_{H_2}}\right)^2} \right) \right) \tag{1.501}$$

By applying that $\ln(ab) = \ln(a) + \ln(b)$ and that $\ln\left(\frac{a}{b}\right) = \ln(a) - \ln(b)$, we can rewrite this to:

$$n_{C_2H_2} = p_{C_2H_2} \frac{\partial}{\partial p_{C_2H_2}} \left(\ln(k_3^+ K_1 \sqrt{K_2 p_{H_2}}) + \ln(p_{C_2H_2}) - \ln\left(\left(1 + K_1 p_{C_2H_2} + \sqrt{K_2 p_{H_2}}\right)^2 \right) \right) \tag{1.502}$$

Since the first term of the derivative has no dependency on $p_{C_2H_2}$, it can be crossed out. Furthermore, we can rewrite the last term by applying $\frac{\partial \ln(x)}{\partial p_{C_2H_2}} = \frac{\partial \ln(x)}{\partial \alpha} \frac{\partial \alpha}{\partial p_{C_2H_2}}$. Then, we obtain:

$$n_{C_2H_2} = p_{C_2H_2} \left(\frac{\partial \ln(p_{C_2H_2})}{\partial p_{C_2H_2}} - \frac{\partial \ln\left((1 + K_1 p_{C_2H_2} + \sqrt{K_2 p_{H_2}} + K_5 p_{C_2H_4})^2 \right)}{\partial (1 + K_1 p_{C_2H_2} + \sqrt{K_2 p_{H_2}})} \cdots \right. \tag{1.503}$$

$$\left. \cdots \frac{\partial (1 + K_1 p_{C_2H_2} + \sqrt{K_2 p_{H_2}})}{\partial p_{C_2H_2}} \right) \tag{1.504}$$

$$= p_{C_2H_2} \left(\frac{K_1}{p_{C_2H_2}} - 2 \frac{1}{1 + K_1 p_{C_2H_2} + \sqrt{K_2 p_{H_2}}} \right) \tag{1.505}$$

$$= 1 - 2\theta_{C_2H_2} \tag{1.506}$$

By working out the equation for the other compounds, we obtain the following reaction orders for the Langmuir-Hinshelwood mechanism:

$$n_{C_2H_2}^{LH} = 1 - 2\theta_{C_2H_2}$$

$$n_{H_2}^{LH} = \frac{1}{2} - \theta_H \tag{1.507}$$

$$\tag{1.508}$$

Following the same strategy for the Eyel-Rideal mechanism, the following reaction rate equation and corresponding reaction orders can be obtained:

$$r_{ER} = \frac{k_3^+ K_1 p_{C_2H_2} p_{H_2}}{\left(1 + K_1 p_{C_2H_2} + \sqrt{K_2 p_{H_2}}\right)}. \tag{1.509}$$

Note how the denominator is not squared here, indicating only a single reaction site is required. From the above reaction equation, we can readily derive the reaction orders using the same strategy as shown for the Langmuir-Hinshelwood mechanism.

$$n^{\mathrm{ER}}_{\mathrm{C_2H_2}} = 1 - \theta_{\mathrm{C_2H_2}}$$

$$n^{\mathrm{ER}}_{\mathrm{H_2}} = 1 - \frac{1}{2}\theta_{\mathrm{H}} \tag{1.510}$$

(1.511)

To conclude, the two mechanisms can be differentiated by their reaction orders because they have different expressions for them. This difference is from an experimental point of view most easily probed at high pressure or at low temperature. Under these conditions, it is expected that the surface coverages are high which is expected to result in the largest difference between equations 1.508 and 1.511.

SOLUTION 1.18

a) The set of elementary reaction steps that describe the dual-site kinetic network is:

$$1.\ \mathrm{CO} + * \leftrightarrows \mathrm{CO}* \tag{1.512}$$
$$2.\ \mathrm{H_2} + 2* \leftrightarrows 2\mathrm{H}* \tag{1.513}$$
$$3.\ \mathrm{H_2} + 2\# \leftrightarrows 2\mathrm{H}\# \tag{1.514}$$
$$4.\ \mathrm{CO} * + \mathrm{H}\# \leftrightarrows \mathrm{HCO} * + \# \tag{1.515}$$
$$5.\ \mathrm{HCO} * + \mathrm{H}\# \rightarrow \mathrm{H_2CO} * + \# \tag{1.516}$$
$$6.\ \mathrm{H_2CO} * + \mathrm{H}\# \leftrightarrows \mathrm{H_3CO} * + \# \tag{1.517}$$
$$7.\ \mathrm{H_3CO} * + \mathrm{H}\# \leftrightarrows \mathrm{H_3COH} * + \# \tag{1.518}$$
$$8.\ \mathrm{H_3COH} + * \leftrightarrows \mathrm{H_3COH}* \tag{1.519}$$

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.

$$\tau_{\mathrm{H}} = \frac{\sqrt{K_3 p_{\mathrm{H_2}}}}{1 + \sqrt{K_3 p_{\mathrm{H_2}}}} \tag{1.520}$$

c) The rate-determining step approximation allows us to construct the following rate expression:

$$r = k_5 \theta_{\mathrm{HCO}} \tau_{\mathrm{H}}. \tag{1.521}$$

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:

$$\theta_{CO} = K_1 p_{CO} \theta_* \tag{1.522}$$

$$\theta_H = \sqrt{K_2 p_{H_2}}\,\theta_* \tag{1.523}$$

$$\theta_{HCO} = K_1 \sqrt{K_3} K_4 p_{CO} \sqrt{p_{H_2}}\,\theta_* \tag{1.524}$$

Using the site balance $\theta_{CO} + \theta_H + \theta_{HCO} + \theta_* = 1$, gives

$$\theta_* = \frac{1}{1 + K_1 p_{CO} + \sqrt{K_2 p_{H_2}} + K_1 \sqrt{K_3} K_4 p_{CO} \sqrt{p_{H_2}}}. \tag{1.525}$$

Using these expressions, we obtain the following final expression for the rate

$$r = k_5 \left(\frac{K_1 \sqrt{K_3} K_4 p_{CO} \sqrt{p_{H_2}}}{1 + K_1 p_{CO} + \sqrt{K_2 p_{H_2}} + K_1 \sqrt{K_3} K_4 p_{CO} \sqrt{p_{H_2}}} \right) \left(\frac{\sqrt{K_3 p_{H_2}}}{1 + \sqrt{K_3 p_{H_2}}} \right) \tag{1.526}$$

d) The reaction order in H_2 is given by

$$n_{H_2} = 1 - \frac{1}{2}\theta_H - \frac{1}{2}\theta_{HCO} - \frac{1}{2}\tau_H \tag{1.527}$$

and the reaction order for CO is given by

$$n_{CO} = 1 - \theta_{CO} - \theta_{HCO} \tag{1.528}$$

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 pertaining to the rate expression as given in equation 1.526 is derived as follows. The first step is to split up the complex equation into smaller parts by making use of the natural logarithm.

$$\Delta E_{act}^{app} = RT^2 \frac{\partial}{\partial T} \ln(r^+) \tag{1.529}$$

$$= RT^2 \frac{\partial}{\partial T} \left\{ \ln\left(k_5 K_1 \sqrt{K_3} K_4\right) - \ln(\alpha) + \ln\left(\sqrt{K_3}\right) - \ln(\beta) \right\}, \tag{1.530}$$

wherein

$$\alpha = 1 + K_1 p_{CO} + \sqrt{K_2 p_{H_2}} + K_1 \sqrt{K_3} K_4 p_{CO} \sqrt{p_{H_2}} \tag{1.531}$$

$$\beta = 1 + \sqrt{K_3 p_{H_2}}. \tag{1.532}$$

Note that in equation 1.530, we have already omitted all terms that do not explicitly depend on the temperature, i.e. the partial pressures in CO and H_2. We will now derive all four terms in equation 1.530, one-by-one.

For the first term, we split up the logarithm containing a product of equilibrium constants into a sum of logarithms each containing only a single equilibrium constant, and solve these terms.

$$RT^2 \frac{\partial}{\partial T} \ln\left(k_5 K_1 \sqrt{K_3} K_4\right) = RT^2 \frac{\partial}{\partial T} \left\{\ln k_5 + \ln K_1 + \frac{1}{2} \ln K_3 + \ln K_4\right\} \tag{1.533}$$

$$= \Delta E_{\text{act}}^{(5)} + \Delta H_1 + \frac{1}{2}\Delta H_3 + \Delta H_4 \tag{1.534}$$

For the second term, we have to use the chain-rule to solve the differential.

$$RT^2 \frac{\partial \ln \alpha}{\partial \alpha} \frac{\partial \alpha}{\partial T} \tag{1.535}$$

$$= RT^2 \frac{1}{\alpha} \frac{\partial \alpha}{\partial T} \tag{1.536}$$

$$= RT^2 \frac{1}{\alpha} \frac{\partial \alpha}{\partial T} \left\{K_1 p_{\text{CO}} + \sqrt{K_2 p_{\text{H}_2}} + K_1 \sqrt{K_3} K_4 p_{\text{CO}} \sqrt{p_{\text{H}_2}}\right\} \tag{1.537}$$

$$= \frac{1}{\alpha} \left\{\Delta H_1 K_1 p_{\text{CO}} + \frac{1}{2}\Delta H_2 \sqrt{K_2 p_{\text{H}_2}} + \left(\Delta H_1 + \frac{1}{2}\Delta H_3 + \Delta H_4\right) K_1 \sqrt{K_3} K_4 p_{\text{CO}} \sqrt{p_{\text{H}_2}}\right\} \tag{1.538}$$

$$= \frac{\Delta H_1 K_1 p_{\text{CO}} + \frac{1}{2}\Delta H_2 \sqrt{K_2 p_{\text{H}_2}} + \left(\Delta H_1 + \frac{1}{2}\Delta H_3 + \Delta H_4\right) K_1 \sqrt{K_3} K_4 p_{\text{CO}} \sqrt{p_{\text{H}_2}}}{1 + K_1 p_{\text{CO}} + \sqrt{K_2 p_{\text{H}_2}} + K_1 \sqrt{K_3} K_4 p_{\text{CO}} \sqrt{p_{\text{H}_2}}} \tag{1.539}$$

$$= \Delta H_1 \theta_{\text{CO}} + \frac{1}{2}\Delta H_2 \theta_{\text{H}} + \left(\Delta H_1 + \frac{1}{2}\Delta H_3 + \Delta H_4\right) \theta_{\text{HCO}} \tag{1.540}$$

In a similar fashion, we obtain the following two results for the third and fourth term.

$$RT^2 \frac{\partial}{\partial T} \ln\left(\sqrt{K_3}\right) = RT^2 \frac{\partial}{\partial T} \frac{1}{2} \ln\left(K_3\right) \tag{1.541}$$

$$= \frac{1}{2}\Delta H_3 \tag{1.542}$$

and

$$RT^2 \frac{\partial \ln \beta}{\partial \beta} \frac{\partial \beta}{\partial T} = RT^2 \frac{1}{\beta} \frac{\partial \beta}{\partial T} \tag{1.543}$$

$$= RT^2 \frac{1}{\beta} \frac{\partial \beta}{\partial T} \left\{\sqrt{K_3 p_{\text{H}_2}}\right\} \tag{1.544}$$

$$= \frac{1}{2}\Delta H_3 \tau_{\text{H}} \tag{1.545}$$

Finally combining all terms and factoring everything in terms of the enthalpies for the individual elementary reaction steps gives

$$\begin{aligned}\Delta E_{\text{act}}^{\text{app}} = \Delta E_{\text{act}}^{(5)} &+ \Delta H_1 \left(1 - \theta_{\text{CO}} - \theta_{\text{HCO}}\right) \\ &+ \Delta H_2 \left(-\frac{1}{2}\theta_{\text{H}}\right) \\ &+ \Delta H_3 \left(1 - \frac{1}{2}\tau_{\text{H}} - \frac{1}{2}\theta_{\text{HCO}}\right) \\ &+ \Delta H_4 \left(1 - \theta_{\text{HCO}}\right). \end{aligned} \tag{1.546}$$

CHAPTER 2

STATISTICAL THERMODYNAMICS

Contents

2.1 Introduction

In the previous chapter, we discussed kinetics from a general point of view wherein the values for the reaction rate constants and equilibrium constants were assumed to be known. In this and the following chapters, we aim to obtain numeric values for these constants from *first principles*. Thus, our problem is to calculate macroscopic properties, i.e. chemical equilibria and reaction rate constants, from molecular properties. As the number of molecules involved in typical reaction mixtures easily exceeds 10^{20}, we should employ some clever strategy to average out irrelevant details to obtain the relevant observables of interest. In this chapter, we are going to introduce statistical thermodynamics which describes how the properties of individual molecules propagate to observables at the macroscale by means of statistical averaging.

Table 2.1: *Number of students with a given grade.*

Grade	0	1	2	3	4	5	6	7	8	9	10
Number of students	1	1	1	1	2	2	0	3	2	2	1

We start this chapter by giving a short summary of the statistical method. Next, we introduce the postulates of thermodynamics. We derive the Maxwell-Boltzmann equation and introduce the concept of partition functions. From these partition functions, *mechanical* properties such as pressure, energy, volume and the number of molecules can be computed. By making the connection with classical thermodynamics, also *non-mechanical* properties such as temperature, entropy, free energy and chemical potential can be calculated.

2.2 Probability theory

Because of the statistical interpretation we are going to employ to treat thermodynamics, we will briefly discuss probability theory in this section using a couple of examples. Consider a class of sixteen students, whose grades for the kinetics course are as given in Table 2.1.

The total number of students in the class is given by

$$N = \sum_{i}^{\infty} n(i), \tag{2.1}$$

which in our example equals 16. In Figure 2.1, a histogram of the above data is depicted.

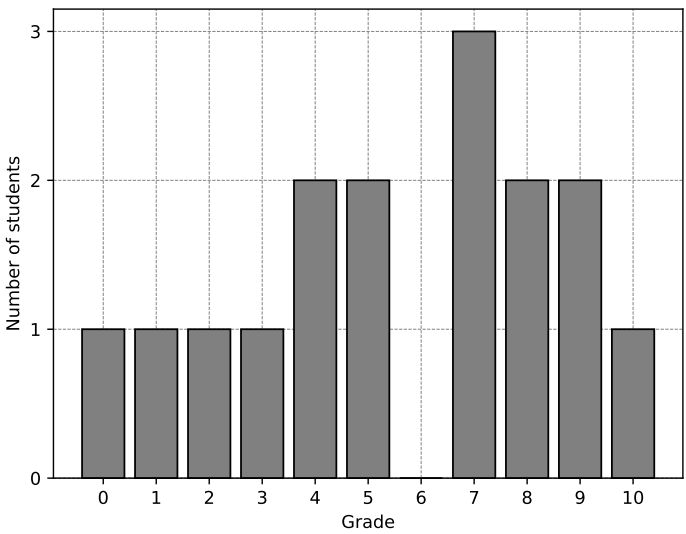


Figure 2.1: *Histogram showing the number of students, $n(i)$ with grade i.*

Let us now ask the following questions

1. What is the chance that when I select a student at random from this class, that his/her grade will be a 10?

2. What is the most probable grade?
3. What is the median grade?
4. What is the average grade?
5. What is the average of the square of the grades?

Let us answer these questions one by one.
The chance or **probability** to obtain a particular student with a grade i is given by

$$P_i(i) = \frac{n(i)}{N}. \tag{2.2}$$

For the case of a grade of 10, this chance equals

$$P_{10} = \frac{1}{16}. \tag{2.3}$$

The **most probable**[1] grade is found by evaluating at which grade i, $n(i)$ has the largest value. This corresponds to a grade of 7.

The **median** grade corresponds to that grade for which the probability of getting a larger result is equal to getting a smaller result. This would be a grade of 6, as 8 students have a lower grade and 8 students have a higher grade than a 6.

The **average**[2] grade can be found by evaluating

$$\langle i \rangle = \sum_{i=0}^{\infty} \frac{in(i)}{N} = \frac{0+1+2+3+2\cdot 4+2\cdot 5+3\cdot 7+2\cdot 8+2\cdot 9+10}{16} = \frac{89}{16} \approx 5.6. \tag{2.4}$$

Finally, the average of the square of the grades can be found by evaluating

$$\left\langle i^2 \right\rangle = \sum_{i=0}^{\infty} \frac{i^2 n(i)}{N} \approx 39.5625. \tag{2.5}$$

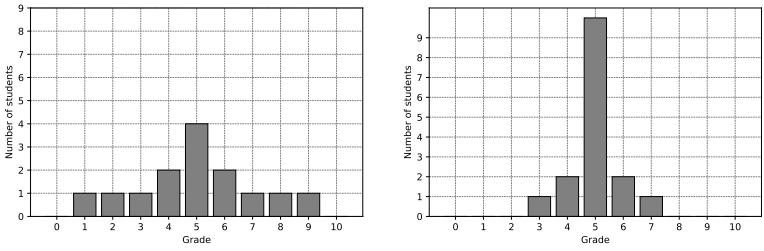


Figure 2.2: *Two histograms with the same median, average and most probable value, but showing a vastly different distribution.*

In principle, two distributions can have the same average, but still look vastly different. For example, let us consider the two histograms as given in Figure 2.2. The most notable difference

[1] Sometimes also called the **mode** in statistics.
[2] Sometimes termed the **expectation value**.

is the amount of spread in each distribution. The one of the left has a significantly larger spread than the one on the right. To quantify the spread, you can use the **variance** of the distribution σ^2 as given by

$$\sigma^2 = \left\langle (\Delta i)^2 \right\rangle. \tag{2.6}$$

Note that the square root of the variance σ is known as the **standard deviation**, which can be written as

$$\sigma = \sqrt{\langle i^2 \rangle - \langle i \rangle^2}. \tag{2.7}$$

So far, we have been dealing with discrete variables, but the above can be generalized to *continuous* distributions. A continuous distribution has infinitesimal intervals by which the probability is proportional to the length of the interval. Because of the infinitesimal intervals, we can no longer speak about the probability, but have to introduce the concept of a probability density $\rho(x)$. The probability that x lies between a and b, a finite interval, is then given by the integral

$$P_{ab} = \int_a^b \rho(x)dx. \tag{2.8}$$

The previously obtained formulas for discrete distributions can now be cast into continuous form. An important feature of the probability density and thus of distribution functions is that they are normalized in the sense that

$$\int_{-\infty}^{\infty} \rho(x)dx = 1, \tag{2.9}$$

to ensure that the probability density integrated over all possible space equals unity, as the object to which the probability refers has to be *somewhere*. For the average of x, we evaluate

$$\langle x \rangle = \int_{-\infty}^{\infty} x\rho(x)dx. \tag{2.10}$$

And for the variance we evaluate

$$\sigma^2 = \left\langle x^2 \right\rangle - \langle x \rangle^2. \tag{2.11}$$

Once the distribution function of a system is given, we can readily evaluate the average value of some observable property of interest. For example, consider a ball bouncing between two walls separated by a distance $2L$ on either side of the origin of the coordinate system as shown in Figure 2.3.

The probability density to find the ball at position x on the interval $[-L, L]$ is constant and equal to some value A and outside this interval the probability density to find the ball is equal to zero. To find the value of A, we can use Equation 2.9.

$$\int_{-\infty}^{\infty} \rho(x)dx = \int_{-L}^{L} Adx = A2L = 1 \tag{2.12}$$

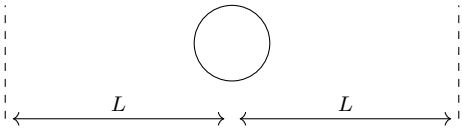


Figure 2.3: *Schematic depiction of a ball, located at the origin, bouncing between two walls (dashed lines). The complete domain has length $2L$ and is centered around the origin.*

From this equation, it follows that $A = \frac{1}{2L}$ and that the distribution function for the ball is given by

$$\rho(x) = \frac{1}{2L} \text{ for } -L \leq x \leq L. \tag{2.13}$$

We can intuitively guess what the average value for the position x of the ball would be. Since the probability function is symmetrical around the origin, the average position of the ball would be at $x = 0$. If we apply Equation 2.10, we indeed obtain this result.

$$\langle x \rangle = \int_{-\infty}^{\infty} x\rho(x)dx = \int_{-L}^{L} \frac{x}{2L}dx = \frac{x^2}{4L}\Big|_{-L}^{L} = \frac{L^2 - (-L)^2}{4L} = 0 \tag{2.14}$$

For the average squared value of the position, we need to evaluate

$$\left\langle x^2 \right\rangle = \int_{-\infty}^{\infty} x^2\rho(x)dx = \int_{-L}^{L} \frac{x^2}{2L}dx = \frac{x^3}{6L}\Big|_{-L}^{L} = \frac{L^3 - (-L)^3}{6L} = \frac{L^2}{3}. \tag{2.15}$$

And from this result, we can readily obtain the standard deviation

$$\sigma = \sqrt{\left\langle x^2 \right\rangle - \langle x \rangle^2} = \sqrt{\frac{L^2}{3}} = \frac{L}{\sqrt{3}}. \tag{2.16}$$

In general, if we are interested in evaluating some property a, we need to cast our distribution function in such a way that the probability density ρ is expressed as a function of a. Next, to obtain an expression for the average value of a, we need to evaluate

$$\boxed{\langle a \rangle = \int_{-\infty}^{\infty} a\rho(a)da.} \tag{2.17}$$

Equation 2.17 together with Equation 2.9 will be used extensively in this chapter and forms the basis for evaluating many properties in statistical thermodynamics.

2.3 Ensembles and postulates

In the previous section, we discussed the statistical background necessary to calculate average properties of molecules. Before we do so, we first need to introduce two important concepts in statistical thermodynamics: **ensembles** and the fundamental **postulates**. An ensemble is a (mental) collection of a very large number $\mathcal{N}$ of systems. Each of these systems is constructed in such a way that it resembles the thermodynamic properties of the actual thermodynamic system we are studying. It is possible to define several types of ensembles, however, in this chapter we are going to focus on the so-called *canonical ensemble*.

The **canonical ensemble** is a supersystem consisting of $\mathcal{N}$ subsystems wherein each subsystem has a fixed number of particles (e.g. atoms or molecules) N, a fixed volume V and a fixed temperature T. Each of these subsystems acts as a representative ensemble for our prototype system for which we wish to calculate mechanical and thermodynamic properties. A schematic depiction of the canonical ensemble is provided in Figure 2.4. Each of the subsystems is placed in a lattice and is compartmentalized by impermeable, heat conducting walls. In other words, the particles in the subsystems are **not** allowed to leave the system, but the subsystems are allowed to exchange energy via the walls. Observe that each of the subsystems is essentially immersed in a large heat bath at temperature T of the other $\mathcal{N}-1$ subsystems in the ensemble as is required for the subsystem to be representative of the original thermodynamic (i.e. prototype) system. The supersystem (i.e. the canonical ensemble) itself is placed in complete thermal insulation, by which its constraints are a fixed number of particles $\mathcal{N}N$, a fixed volume $\mathcal{N}V$ and a fixed energy E. We assume that the number of systems $\mathcal{N}$ is very large (i.e. $\mathcal{N} \gg 10^{20}$) by which we are allowed to explore the limit of $\mathcal{N} \to \infty$.

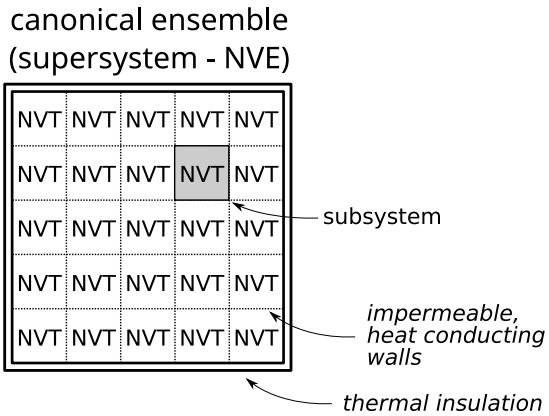


Figure 2.4: *Schematic depiction of the canonical ensemble.*

Next, we introduce the two fundamental postulates. The **first postulate** states that *the long-time average of a mechanical variable M in the thermodynamic system of interest is equal to the ensemble average of M, in the limit that $\mathcal{N} \to \infty$, provided that the systems of the ensemble replicate the thermodynamic state and environment of the actual system of interest.*[2] In other words, we are allowed to replace a time-average for an ensemble-average. So if we observe a single subsystem in the canonical ensemble for a very long time, its time average would be equal to the ensemble average of the supersystem probed at a single point in time. The first postulate by itself is however insufficient to calculate any properties, hence we will introduce the second postulate.

The **second postulate** states that *in an ensemble $\mathcal{N} \to \infty$ representative of an isolated thermodynamic system, the (sub)systems of 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].

In other words, if I select a subsystem at random from the ensemble, the chance to find it in any particular quantum state is the same for all possible (i.e. allowed) quantum states. This means that each quantum state is represented by the same number of systems in the ensemble.

Connecting the first and second postulates, we can infer that the **supersystem spends equal amounts of time, over a long time period, in each of the available quantum states**. The latter is known as the **quantum ergodic hypothesis**, while the second postulate is known as the **principle of equal *a priori* probabilities.**[2]

Let us explore these concepts by means of a simple example. Assume that we have a canonical ensemble consisting of four subsystems (A, B, C, D) and where each subsystem can be in one of four possible energy states $E_0 - E_3$, where the index of the energy state ($0 - 3$) corresponds to how many units of energy that energy state contains (e.g. $E_0 = 0, E_1 = 1 \cdots$).[3] The total energy E of the canonical ensemble is set at $E_{\text{total}} = 4$ in the sense that

$$E_A + E_B + E_C + E_D = E_{\text{total}} = 4 \tag{2.18}$$

We now define a **distribution** or **macrostate** as the number of energy states n_i present in the supersystem for each energy state E_i. Given these constraints, there are four different distributions or macrostates as given by

1. $n_0 = 2, n_1 = 1, n_2 = 0, n_3 = 1$
2. $n_0 = 2, n_1 = 0, n_2 = 2, n_3 = 0$
3. $n_0 = 1, n_1 = 2, n_2 = 1, n_3 = 0$
4. $n_0 = 0, n_1 = 4, n_2 = 0, n_3 = 0$

where each distribution complies with

$$E_{\text{total}} = \sum_i n_i E_i \tag{2.19}$$

consistent with Equation 2.18.

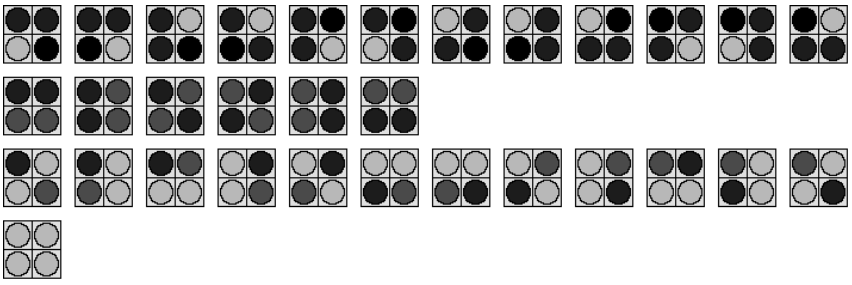


Figure 2.5: *Schematic depiction of a canonical ensemble of only four subsystems. Each subsystem is only allowed to be in one of four energy states. Each row corresponds to a different macrostate, each image in the row to a different microstate. The shades of gray of the circles represent the different energy states.*

For each macrostate, there are one or more ways the energy levels can be arranged among the different subsystems as depicted in Figure 2.5 by the various configurations which are ordered in rows per possible macrostate. A single **arrangement** is termed a **microstate** and what is referred

[3] In this discussion, it does not matter what a "unit of energy" actually is.

to as the *possible quantum states* in the second postulate. The second postulate now dictates that the probability for each of these microstates is equal in the sense that the supersystem spends equal amounts of time in each of the possible microstates. A critical implication of the second postulate is that the **number of microstates** dictates the chance (or weight) to find the system in a particular **macrostate** in the sense that

$$w_i = \frac{\Omega_i}{\sum_j \Omega_j}, \tag{2.20}$$

where Ω_i is the number of microstates for macrostate i. For instance, in our example the chance to find the supersystem in the fourth macrostate (all systems are in energy state E_1) is twelve times less likely than to find the supersystem in the first macrostate (two systems in energy state E_0, one system in energy state E_1 and one system in energy state E_3).

The number of microstates for each macrostate can be calculated using the following combinatorial formula

$$\Omega_i = \frac{\mathcal{N}!}{\prod_i n_i!}. \tag{2.21}$$

For example, the number of microstates for the third macrostate is given by

$$\Omega_3 = \frac{4!}{1! \cdot 2! \cdot 1!} = \frac{24}{2} = 12, \tag{2.22}$$

consistent with Figure 2.5. The number of microstates for each macrostate not only defines the chance to encounter a particular macrostate, it also defines the chance to encounter a particular energy state in any of the subsystems by

$$P_i = \frac{1}{\mathcal{N}} \frac{\sum_j \Omega_j n_{i,j}}{\sum_j \Omega_j}, \tag{2.23}$$

where $n_{i,j}$ is the number of systems in energy state E_i for macrostate j.

Observe that Equation 2.23 is similar to Equation 2.4. The chance for example to encounter any of the subsystems in energy state E_0 is given by

$$P_0 = \frac{1}{4} \frac{12 \cdot 2 + 6 \cdot 2 + 12 \cdot 1 + 1 \cdot 0}{12 + 6 + 12 + 1} = \frac{48}{124} = \frac{12}{31}. \tag{2.24}$$

Furthermore, note that Equation 2.23 is consistent with

$$\sum_i P_i = 1, \tag{2.25}$$

as is to be expected. With this framework in place, we are able to calculate any desired ensemble average. For example, the average energy of the system is given by

$$\langle E \rangle = \sum_i P_i E_i = \sum_i \left[\frac{1}{\mathcal{N}} \frac{\sum_j \Omega_j n_i}{\sum_j \Omega_j} E_i \right] = 1. \tag{2.26}$$

and $\left\langle E^2 \right\rangle$ is given by

$$\left\langle E^2 \right\rangle = \sum_i P_i E_i^2 = \sum_i \left[\frac{1}{\mathcal{N}} \frac{\sum_j \Omega_j n_i}{\sum_j \Omega_j} E_i^2 \right] = \frac{61}{31}. \tag{2.27}$$

Technically, Equation 2.23 is sufficient to calculate canonical ensemble averages of mechanical variables, however, for very large systems (i.e. realistic systems we are typically dealing with), summing over the vast array of possible macrostates is far from feasible. Thus, we wish to obtain a more explicit expression for P_i. In the next section, we will elaborate on how we can simplify Equation 2.23 by considering the hypothesis that a single macrostate has a weight $w \to 1$ in the limit $\mathcal{N} \to \infty$.

2.4 Macrostate dominance

Let us explore what happens in the example of the previous section in the limit of $\mathcal{N} \to \infty$. If the total energy remains limited to $E_{\text{total}} = 4$, the number of possible *macrostates* remains the same, however the number of microstates per macrostate will increase. Increasing the total number of systems $\mathcal{N}$ effectively results in adding systems with an energy level of E_0 to the set.[4] Thus the possible configurations (macrostates) as function of $\mathcal{N}$ become

1. $n_0 = \mathcal{N} - 2, n_1 = 1, n_2 = 0, n_3 = 1$
2. $n_0 = \mathcal{N} - 2, n_1 = 0, n_2 = 2, n_3 = 0$
3. $n_0 = \mathcal{N} - 3, n_1 = 2, n_2 = 1, n_3 = 0$
4. $n_0 = \mathcal{N} - 4, n_1 = 4, n_2 = 0, n_3 = 0$

From this, we can readily calculate the number of microstates per macrostate by application of Equation 2.21 which gives for $\mathcal{N} \geq 4$

$$\Omega_1 = \frac{\mathcal{N}!}{(\mathcal{N}-2)!} = \mathcal{N}(\mathcal{N}-1) \tag{2.28}$$

$$\Omega_2 = \frac{\mathcal{N}!}{(\mathcal{N}-2)!2!} = \frac{1}{2}\mathcal{N}(\mathcal{N}-1) \tag{2.29}$$

$$\Omega_3 = \frac{\mathcal{N}!}{(\mathcal{N}-3)!2!} = \frac{1}{2}\mathcal{N}(\mathcal{N}-1)(\mathcal{N}-2) \tag{2.30}$$

$$\Omega_4 = \frac{\mathcal{N}!}{(\mathcal{N}-4)!4!} = \frac{1}{24}\mathcal{N}(\mathcal{N}-1)(\mathcal{N}-2)(\mathcal{N}-3) \tag{2.31}$$

$$\tag{2.32}$$

and the chance to encounter (or the weight of) macrostate i can be calculated from Equation 2.23 which gives after some careful algebra

$$w_1 = \frac{24}{\mathcal{N}^2 + 7\mathcal{N} + 18} \tag{2.33}$$

$$w_2 = \frac{12}{\mathcal{N}^2 + 7\mathcal{N} + 18} \tag{2.34}$$

$$w_3 = \frac{12\mathcal{N} - 24}{\mathcal{N}^2 + 7\mathcal{N} + 18} \tag{2.35}$$

$$w_4 = \frac{\mathcal{N}^2 - 5\mathcal{N} + 6}{\mathcal{N}^2 + 7\mathcal{N} + 18}. \tag{2.36}$$

[4] Check this for yourself: Start by listing all the possible macrostate configurations for $\mathcal{N} = 5$, then for $\mathcal{N} = 6$, and $\mathcal{N} = 7$. Do you see a pattern arising?

Note that the sum of the numerators is equal to the denominator

$$24 + 12 + [12\mathcal{N} - 24] + \left[\mathcal{N}^2 - 5\mathcal{N} + 6\right] = \mathcal{N}^2 + 7\mathcal{N} + 18, \tag{2.37}$$

in agreement with Equation 2.25. The probabilities to encounter each macrostate are depicted in Figure 2.6. From this picture, it can be readily observed that even for a relatively few number of systems $\mathcal{N}$, with increasing number of systems, the probability of a single macrostate goes to unity by which this macrostate becomes the **dominant macrostate**.

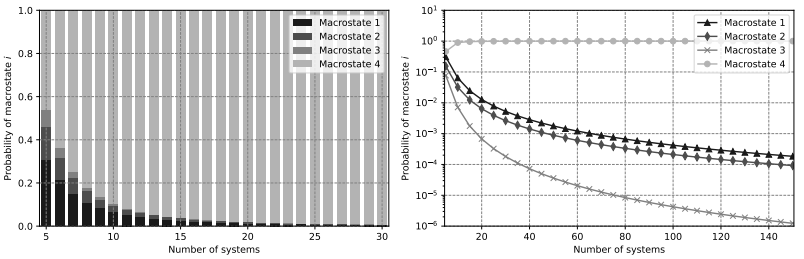


Figure 2.6: *Weight of each macrostate as function of the number of systems $\mathcal{N}$.*

Although we here demonstrated the **principle of macrostate dominance** for a relatively few allowed energy states, the result can be readily extended towards canonical ensembles which have many possible energy states E_i. This result enables us to greatly simplify the calculation of ensemble averages, as we only have to take the dominant macrostate into account as the weight of all other macrostates will become negligibly small for sufficiently large systems. Equation 2.23 thus simplifies to

$$P_i = \frac{n_i}{\mathcal{N}}, \tag{2.38}$$

where n_i is the number of systems in energy state E_i **for the dominant macrostate only**.

Practice your understanding

Exercise 2.1

2.5 Maxwell-Boltzmann distribution law

In the previous section we have seen that there is a single macrostate that has so many microstates that its weight towards the ensemble average dominates. Thus, our objective is to find the configuration of n_i that maximizes Ω for that macrostate. From here on, we define the number of microstates corresponding to the *dominant macrostate* by the variable Ω_D.[5] Furthermore, instead of Equation 2.21 wherein we iterated over the number of subsystems, we will here iterate over the set of possible energy states E_i, taking explicitly the degeneracy factor g_i of each energy state into account as given by

$$\Omega_D = \mathcal{N}! \prod_i \frac{(g_i)^{n_i}}{n_i!}. \tag{2.39}$$

[5]The 'D' refers to distinguishable.

In this formula, the degeneracy factor g_i corresponds to the number of quantum states that have the same energy.[6] To optimize a function, we can take its first derivative and set this equal to 0. For the multi-variable function $\Omega_D(n_i)$, this gives

$$\frac{\partial \Omega_D}{\partial n_i} = 0, \tag{2.40}$$

for all n_i and corresponding to a maximum for Ω_D under the restriction that the values for n_i adhere to Equations 2.41 and 2.42.

$$n_1 + n_2 + ... \equiv \sum_i n_i = \mathcal{N} \tag{2.41}$$

$$n_1 E_1 + n_2 E_2 + ... \equiv \sum_i n_i E_i = E \tag{2.42}$$

where $\mathcal{N}$ is the number of subsystems in the canonical ensemble and E the total energy of the system. By changing the values of $n_1, n_2, \cdots n_i$ by a small amount ∂n_i, the value Ω_D is changed by the small amount $\partial \Omega_D$:

$$\partial \Omega_D = \left(\frac{\partial \Omega_D}{\partial n_1}\right) \partial n_1 + \left(\frac{\partial \Omega_D}{\partial n_2}\right) \partial n_2 + \cdots + \left(\frac{\partial \Omega_D}{\partial n_i}\right) \partial n_i. \tag{2.43}$$

According to Equation 2.41, the above gives

$$\partial n_1 + \partial n_2 + \cdots + \partial n_i + \cdots = 0 \tag{2.44}$$

and similarly Equation 2.42 yields

$$E_1 \partial n_1 + E_2 \partial n_2 + \cdots + E_i \partial n_i + \cdots = 0. \tag{2.45}$$

Maximizing Ω_D subject to these restrictive conditions can be done by means of Lagrange's method of undetermined multipliers.[7] We therefore introduce two new variables β and γ, the Lagrange multipliers, by which we obtain

$$\begin{aligned} \partial \Omega_D = &\left(\frac{\partial \Omega_D}{\partial n_1} - \gamma - \beta E_1\right) \partial n_1 + \left(\frac{\partial \Omega_D}{\partial n_2} - \gamma - \beta E_2\right) \partial n_2 \\ &+ \cdots + \left(\frac{\partial \Omega_D}{\partial n_i} - \gamma - \beta E_i\right) \partial n_i. \end{aligned} \tag{2.46}$$

When Ω_D has a maximum value, i.e.

$$\partial \Omega_D = 0, \tag{2.47}$$

[6] In quantum mechanics, an energy level is degenerate if it corresponds to two or more different measurable states of a quantum system. Conversely, two or more different states of a quantum mechanical system are said to be degenerate if they give the same value of energy upon measurement.

[7] See Appendix B.6 on page 280.

the values of n_i must therefore be such that the left-hand side of Equation 2.46 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 2.44 and 2.45 hold. Since Equation 2.46 holds for any γ and β, let us choose values for γ and β such that:

$$\frac{\partial \Omega_D}{\partial n_1} - \gamma - \beta E_1 = 0 \tag{2.48}$$

$$\frac{\partial \Omega_D}{\partial n_2} - \gamma - \beta E_2 = 0 \tag{2.49}$$

The only way to ensure that the right-hand side of Equation 2.46 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

$$\frac{\partial \Omega_D}{\partial n_i} - \gamma - \beta E_i = 0 \ (i = 1, 2, 3, \cdots). \tag{2.50}$$

The distribution function that gives the largest Ω_D is also the distribution giving the largest $\ln \Omega_D$, since $\ln x$ increases monotonically with x. It turns out to be more convenient to maximize $\ln \Omega_D$ instead of Ω_D, thus we will focus on solving Equation 2.51 instead of 2.50.

$$\frac{\partial \ln(\Omega_D)}{\partial n_i} - \gamma - \beta E_i = 0 \tag{2.51}$$

By applying Stirling's approximation (see appendix B.2) to Equation 2.51 we obtain the following equation

$$\ln \Omega_D = N \ln N - N + \sum_i (n_i \ln g_i) - \sum_i (n_i \ln n_i - n_i) \tag{2.52}$$

and taking the first derivative of the above yields

$$\frac{\partial \ln \Omega_D}{\partial n_i} = \ln g_i - \ln n_i. \tag{2.53}$$

By combining expression 2.51 and 2.53 this yields

$$\ln g_i - \ln n_i - \gamma - \beta E_i = 0 \tag{2.54}$$

and with some rearranging, this gives

$$\ln n_i = \ln g_i - \gamma - \beta E_i. \tag{2.55}$$

Finally taking the exponent on both sides, we obtain

$$n_i = g_i \exp(-\gamma) \exp(-\beta E_i). \tag{2.56}$$

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 systems among the energy levels (i.e. the

dominant macrostate). On the basis of Equation 2.44, the sum of the most probable distribution of systems should be equal to unity, thus giving:

$$\sum_i n_i* = \mathcal{N}, \tag{2.57}$$

where n_i* is the number of subsystems in state i for the most probable distribution Ω_D. Furthermore,

$$\begin{aligned} N &= g_1 \exp(-\gamma) \exp(-\beta E_1) + g_2 \exp(-\gamma) \exp(-\beta E_2) + \cdots + g_i \exp(-\gamma) \exp(-\beta E_i) + \cdots \\ &= \exp(-\gamma) \left(g_1 \exp(-\beta E_1) + g_2 \exp(-\beta E_2) + \cdots + g_i \exp(-\beta E_i) + \cdots \right) \\ &= \exp(-\gamma) \sum_i g_i \exp(-\beta E_i) \end{aligned} \tag{2.58}$$

Hence,

$$\exp(-\gamma) = \frac{N}{\sum_i g_i \exp(-\beta E_i)} = \frac{N}{q}, \tag{2.59}$$

where

$$q = \sum_i g_i \exp(-\beta E_i). \tag{2.60}$$

The sum q is coined by Planck as the *Zustandssumme*, but is also called the **molecular partition function** or sum-over-states. So far, we have been talking about *subsystems and supersystems* (i.e. the canonical ensemble), but what are now these systems and subsystems. Given the thermodynamic system of interest which is represented by the canonical ensemble (e.g. a set of molecules in a container), the subsystems can be (but are certainly not limited to)

- Different molecules.
- Different degrees of freedom in the same molecule (wherein the supersystem is a set of identical molecules).
- Molecules adsorbed on different active sites on a catalytic surface.

For example, let us consider the subsystems to be the same molecule (particle) which can be in each of two possible energy states. The term partition function becomes obvious when one wants to evaluate the fraction of molecules in each of the energy states, for example:

$$\boxed{\frac{n_i*}{n_j*} = \frac{g_i \exp(-\beta E_i)}{g_j \exp\left(-\beta E_j\right)}} \tag{2.61}$$

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.

In principle, we can drop the degeneracy factor g_i by including the degenerate states as separate (though identical in energy) states in the summation. Using this approach, the probability to encounter the system in state i is then given by

$$P_i = \frac{\exp\left(-\beta E_i\right)}{\sum_j \exp\left(-\beta E_j\right)}. \tag{2.62}$$

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. We will derive an expression for β in the upcoming section.

Practice your understanding

Exercise 2.2

2.6 Thermodynamic variables

In Figure 2.7, the general procedure for obtaining any thermodynamic property, both *mechanical* as well as *non-mechanical,* is shown. In the previous sections, we showed how we can utilize probability theory to calculate averages from the canonical ensemble. From the definition of the partition function as given in Equation 2.61, we are able to calculate a probability density or distribution function using the approach as shown in section 2.2. In turn, from this distribution function, we can calculate the average value for a *mechanical* thermodynamic property using the discrete form of Equation 2.17 as given by

$$\langle M \rangle = \sum_i M_i P_i, \tag{2.63}$$

where M_i is a *mechanical* thermodynamic value M for state i and P_i is the probability of state i.

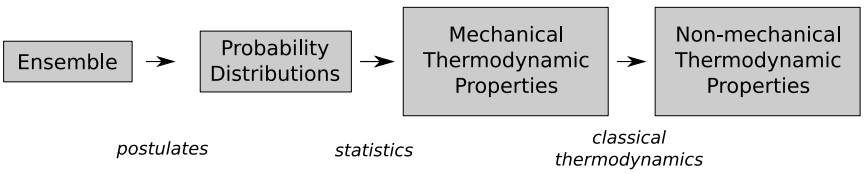


Figure 2.7: *Flow diagram of the general procedure to obtain mechanical and non-mechanical thermodynamic properties from the canonical ensemble.*

By appealing to classical thermodynamics we can also calculate *non-mechanical* thermodynamic properties **from the mechanical thermodynamic properties**. In the upcoming subsections, we will derive expressions for the total energy, pressure, heat capacity, the entropy and enthalpy, the chemical potential and the Helmholtz free energy from the (canonical) partition function as given in Equation 2.60.

2.6.1 Internal energy and heat capacity

The total energy E for a system can thus be readily calculated by application of Equation 2.63.

$$\langle E\rangle = \sum_i P_i E_i \tag{2.64}$$

$$= \frac{\sum_i E_i \exp\left(\frac{-E_i}{k_B T}\right)}{\sum_i \exp\left(\frac{-E_i}{k_B T}\right)} \tag{2.65}$$

$$= \frac{\sum_i E_i \exp\left(\frac{-E_i}{k_B T}\right)}{q} \tag{2.66}$$

$$= k_B T^2 \frac{\partial \ln q}{\partial T}. \tag{2.67}$$

Once we have obtained an expression for $\langle E\rangle$, we can also calculate the heat capacity at constant volume C_v by

$$C_v = \frac{\partial \langle E\rangle}{\partial T}. \tag{2.68}$$

Note that the heat capacity is a *non-mechanical* property and we calculate its value from the average energy, which is a *mechanical* thermodynamic property. In other words, we have derived a *non-mechanical* thermodynamic property from a *mechanical* one by using *classical thermodynamics*.

2.6.2 Entropy

The average energy E is given by

$$\langle E\rangle = \sum_i P_i E_i. \tag{2.69}$$

Taking the differential of $\langle E\rangle$ gives

$$d\langle E\rangle = \sum_i E_i dP_i + \sum_i P_i dE_i \tag{2.70}$$

$$= -\frac{1}{\beta}\sum_i (\ln P_i + \ln q)\, dP_i + \sum_i P_i \left(\frac{\partial E_i}{\partial V}\right)_N dV. \tag{2.71}$$

Using the equalities

$$\sum_i P_i = 1, \qquad \sum_i dP_i = 0 \tag{2.72}$$

and

$$d\left(\sum_i P_i \ln P_i\right) = \sum_i \ln P_i dP_i, \tag{2.73}$$

we can rewrite Equation 2.71 to

$$-\frac{1}{\beta}d\left(\sum_i P_i \ln P_i\right) = d\langle E\rangle + \langle p\rangle\, dV. \tag{2.74}$$

This result can be readily associated to the following expression in classical thermodynamics

$$T\, dS = dE + p\, dV, \tag{2.75}$$

where T is the temperature, S the entropy, p the pressure and V the volume. Thus we obtain the following association

$$TdS \longleftrightarrow -\frac{1}{\beta}d\left(\sum_i P_i \ln P_i\right), \tag{2.76}$$

which can be rewritten as

$$dS \longleftrightarrow \frac{1}{\beta T}dG, \tag{2.77}$$

wherein

$$G = -\left(\sum_i P_i \ln P_i\right). \tag{2.78}$$

From classical thermodynamics we know that the left side of Equation 2.77 is an exact differential[8], hence the right side of the equation also has to be an exact differential. This condition will be met if $\frac{1}{\beta T}$ is any function of G, in such a way that

$$dS \longleftrightarrow \phi(G)dG = df(G), \tag{2.79}$$

where

$$f(G) = \int \phi(G)dG \tag{2.80}$$

and

$$\phi(G) = \frac{df(G)}{dG}. \tag{2.81}$$

Integrating Equation 2.79 then yields

$$S \longleftrightarrow f(G) + c, \tag{2.82}$$

[8] A differential is said to be exact if the corresponding vector field is conservative. The thermodynamic function G is a so-called *state function*, which holds the property that a change of a state function during a process depends only on the initial and final states of the system, not on the path of the process.

where c is an integration constant *independent* of G and therefore independent of the variables on which G depends. From experiment, it is known that the entropy always involves the difference in entropy between two states. Therefore, the constant c will cancel out upon calculation of such a difference and we are thus allowed to set $c = 0$ for convenience.

We now wish to obtain an expression for the function $f(G)$. From thermodynamics, it is known that the entropy is an additive property in the sense that

$$S(A \cap B) = S(A) + S(B). \tag{2.83}$$

Thus the function $f(G)$ should also have this property in the sense that,

$$f(G_A + G_B) = f(G_A) + f(G_B). \tag{2.84}$$

or in more general terms

$$f(x + y) = f(x) + f(y). \tag{2.85}$$

Differentiating Equation 2.85 gives

$$\frac{df(x+y)}{d(x+y)}\frac{\partial(x+y)}{\partial x} = \frac{df(x+y)}{d(x+y)} = \frac{df(x)}{dx} \tag{2.86}$$

$$\frac{df(x+y)}{d(x+y)}\frac{\partial(x+y)}{\partial y} = \frac{df(x+y)}{d(x+y)} = \frac{df(y)}{dy}, \tag{2.87}$$

hence

$$\frac{df(x)}{dx} = \frac{df(y)}{dy}. \tag{2.88}$$

In other words, a function of x is equal to the same function of y. The only function that satisfies this property is a constant. Thus

$$\frac{df(x)}{dx} = k \tag{2.89}$$

and

$$f(x) = kx + c, \tag{2.90}$$

where c is another constant. In order to satisfy Equation 2.85, we have to set this constant to $c = 0$ and $f(x) = kx$. Plugging this result into Equation 2.82 yields

$$S \longleftrightarrow f(G) = kG \tag{2.91}$$

$$S \longleftrightarrow -k\sum_i P_i \ln P_i. \tag{2.92}$$

Furthermore, from Equation 2.79 we have

$$\phi(G) = \frac{df(G)}{dG} = k = \frac{1}{\beta T}, \tag{2.93}$$

or

$$\frac{1}{T} \longleftrightarrow \beta k, \qquad \frac{1}{kT} \longleftrightarrow \beta. \tag{2.94}$$

The constant k is at this point still unknown, but can be derived from experiment. Typically, it is derived from the pressure of an ideal gas by which it can be found that $k = k_\mathrm{B}$. Thus we obtain the following expressions for calculating the entropy from the partition function:

$$S = -k_\mathrm{B} \sum_i \frac{\exp\left(-\frac{E_i}{k_\mathrm{B}T}\right)}{q} \ln\left(\frac{\exp\left(-\frac{E_i}{k_\mathrm{B}T}\right)}{q}\right) \tag{2.95}$$

$$= k_\mathrm{B} \sum_i P_i \frac{E_i}{k_\mathrm{B}T} + k_\mathrm{B} \sum_i P_i \ln(q) \tag{2.96}$$

$$= k_\mathrm{B} \left(\frac{\langle E \rangle}{k_\mathrm{B}T} + \ln(q)\right) \tag{2.97}$$

$$= k_\mathrm{B}T \left(\frac{\partial \ln q}{\partial T}\right) + k_\mathrm{B} \ln q \tag{2.98}$$

$$= \frac{\partial}{\partial T} \left(k_\mathrm{B}T \ln q\right). \tag{2.99}$$

2.6.3 Free energy and the chemical potential

If we substitute Equation 2.62 into Equation 2.92, we obtain

$$S = \frac{\langle E \rangle}{T} + k_\mathrm{B} \ln q = \frac{E}{T} - \frac{A}{T}, \tag{2.100}$$

where A corresponds to the Helmholtz free energy as given by the classical thermodynamical expression

$$dA = -SdT - pdV + \sum_i \mu_i dN_i. \tag{2.101}$$

By rewriting Equation 2.100 and inserting the expressions for the internal energy and the entropy (Equations 2.67 and 2.99), we can derive an expression for the Helmholtz free energy by

$$A = E - TS \tag{2.102}$$

$$= k_\mathrm{B}T^2 \frac{\partial \ln q}{\partial T} - T \frac{\partial}{\partial T} \left(k_\mathrm{B}T \ln q\right) \tag{2.103}$$

$$= k_\mathrm{B}T^2 \frac{\partial \ln q}{\partial T} - k_\mathrm{B}T^2 \frac{\partial \ln q}{\partial T} - k_\mathrm{B}T \ln q \tag{2.104}$$

and by noting that the first two terms cancel each other out, we obtain

$$A = -k_\mathrm{B}T \ln q. \tag{2.105}$$

From the Helmholtz free energy, we can derive an expression for the pressure as

$$p = -\left(\frac{\partial A}{\partial V}\right)_{T,N} = k_B T \left(\frac{\partial \ln q}{\partial V}\right)_{T,N}. \tag{2.106}$$

And for the chemical potential we have

$$\mu = \left(\frac{\partial A}{\partial N}\right)_{T,V} = -k_B T \left(\frac{\partial \ln q}{\partial N}\right)_{T,V}. \tag{2.107}$$

Finally, for the enthalpy we obtain

$$H = E + pV = k_B T^2 \frac{\partial \ln q}{\partial T} + k_B T \left(\frac{\partial \ln q}{\partial V}\right)_{T,N} V. \tag{2.108}$$

2.7 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[9] is given by

$$Q = \prod_i q_i. \tag{2.109}$$

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

$$Q = q^N. \tag{2.110}$$

If the subsystems are identical particles[10], which are impossible to distinguish from each other, the partition function is calculated by

$$Q = \prod_i \frac{q_i^{N_i}}{N_i!}, \tag{2.111}$$

which reduces to

$$Q = \frac{q^N}{N!}, \tag{2.112}$$

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

[9] Sometimes a capital Q is used to distinguish the partition function pertaining to an ensemble versus the partition function of a single species or a single subsystem. In other cases, subscripted labels will be used to indicate the meaning. It should be clear from the context what is exactly meant.

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

2.7.1 Gibbs Paradox

At this point, you might wonder where the $1/N!$ correction in Equation 2.112 comes from. The $1/N!$ correction is best explained using Gibbs paradox, which is a semi-classical derivation of the entropy that does not take into account the indistinguishability of particles, yielding an expression for the entropy which is not extensive (thus a paradox). The paradox goes as follows: Consider an ideal gas of N (indistinguishable) particles in a container with a fixed volume V. A partition separates the container into two sections with volumes V_1 and V_2 in such a way that

$$V_1 + V_2 = V. \tag{2.113}$$

Also, there are N_1 particles in the volume V_1 and N_2 particles in the volume V_2. It is assumed that the number density is the same throughout the system as given by

$$\rho = \frac{N_1}{V_1} = \frac{N_2}{V_2}. \tag{2.114}$$

Consider what would happen to the *total* entropy if the partition would be removed. Since the particles are identical, the total entropy should not increase upon removal of the divisor as the particles cannot be distinguished from each other. Let us first calculate the entropy without the $1/N!$ factor and then calculate the entropy with the $1/N!$ factor.

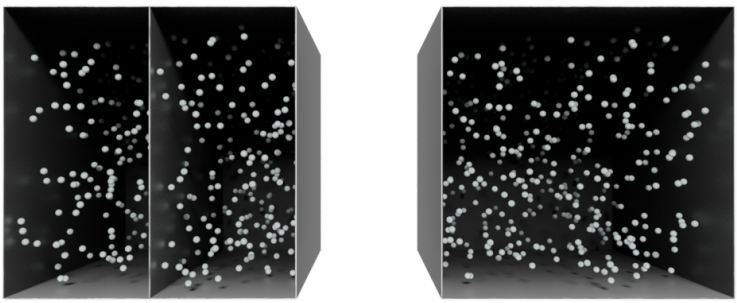


Figure 2.8: *Gibbs Paradox: What would happen to the total entropy when going from the left situation to the right? The entropy of the particles in the container on the left is the same as that for the particles in the container on the right.*

The total entropy without the $1/N!$ factor is given by

$$S = \frac{\partial}{\partial T}\left(k_{\mathrm{B}} T \ln q\right) \tag{2.115}$$

$$= \frac{\partial}{\partial T}\left(N k_{\mathrm{B}} T \ln q(V)\right) \tag{2.116}$$

$$= N k_{\mathrm{B}} T \frac{\partial}{\partial T} \ln q(V) + N k_{\mathrm{B}} \ln q(V). \tag{2.117}$$

Thus the total entropy before and after are

$$S_{\text{before}} = N_1 k_{\mathrm{B}} \left[T \frac{\partial}{\partial T} \ln q\left(V_1\right) + \ln q(V_1)\right] + N_2 k_{\mathrm{B}} \left[T \frac{\partial}{\partial T} \ln q\left(V_2\right) + \ln q(V_2)\right], \tag{2.118}$$

and

$$S_{\text{after}} = k_{\text{B}} \left(N_1 + N_2\right) \left(T \frac{\partial}{\partial T} \ln q \left(V_1 + V_2\right) + \ln q \left(V_1 + V_2\right)\right), \tag{2.119}$$

respectively. Thus, the difference in entropy ΔS is given by

$$\Delta S = S_{\text{after}} - S_{\text{before}} \tag{2.120}$$

$$= k_{\text{B}} N_1 \left[T \frac{\partial}{\partial T} \ln \left(\frac{q(V)}{q(V_1)}\right) + \ln \left(\frac{q(V)}{q(V_1)}\right)\right] + k_{\text{B}} N_2 \left[T \frac{\partial}{\partial T} \ln \left(\frac{q(V)}{q(V_2)}\right) + \ln \left(\frac{q(V)}{q(V_2)}\right)\right]. \tag{2.121}$$

Since the volume V is constant, V cannot be a function of T. Furthermore, q scales linearly with V in the sense that V is only a multiplicative factor in the partition function q. Thus, the term V cancels out when taking the derivative of q towards T and the following identity holds[11]

$$\frac{\partial}{\partial T} \ln q \left(V_1\right) = \frac{\partial}{\partial T} \ln q \left(V_2\right) = \frac{\partial}{\partial T} \ln q \left(V_1 + V_2\right). \tag{2.122}$$

Using the identity above, we can further simplify the expression for ΔS as

$$\Delta S = k_{\text{B}} N_1 \ln \left(\frac{q(V)}{q(V_1)}\right) + k_{\text{B}} N_2 \ln \left(\frac{q(V)}{q(V_2)}\right) \neq 0. \tag{2.123}$$

Since the entropy is an extensive property, ΔS should be equal to zero. Let us now introduce the correction factor $1/N!$ and apply the Stirling approximation $\ln N! \approx N \ln N - N$. We then obtain for S_1 and S_2

$$S_1 = N_1 k_{\text{B}} \left[T \frac{\partial}{\partial T} \ln q(V_1) + \ln q(V_1) - \ln N_1 + 1\right] \tag{2.124}$$

$$S_2 = N_2 k_{\text{B}} \left[T \frac{\partial}{\partial T} \ln q(V_2) + \ln q(V_2) - \ln N_2 + 1\right] \tag{2.125}$$

and for the situation after the divisor has been removed

$$S_{\text{after}} = k_{\text{B}} \left(N_1 + N_2\right) \left(T \frac{\partial}{\partial T} \ln q \left(V_1 + V_2\right) + \ln q \left(V_1 + V_2\right) - \ln \left(N_1 + N_2\right) + 1\right). \tag{2.126}$$

Taking the difference between these two and using the identity as shown in Equation 2.122 yields the following expression for the change in entropy upon removal of the divisor

$$\Delta S = S_{\text{before}} - S_{\text{after}} \tag{2.127}$$

$$= k_{\text{B}} N_1 \ln \left(\frac{q(V)}{q(V_1)}\right) + k_{\text{B}} N_2 \ln \left(\frac{q(V)}{q(V_2)}\right) - k_{\text{B}} N_1 \ln \left(\frac{N}{N_1}\right) - k_{\text{B}} N_2 \ln \left(\frac{N}{N_2}\right) \tag{2.128}$$

$$= k_{\text{B}} N_1 \ln \left(\frac{q(V)}{N} \frac{N_1}{q(V_1)}\right) + k_{\text{B}} N_2 \ln \left(\frac{q(V)}{N} \frac{N_2}{q(V_2)}\right). \tag{2.129}$$

[11] In Chapter 3, the translational partition function will be shown to be $q_{\text{T}} = \left(\frac{2\pi m k_{\text{B}} T}{h^2}\right)^{3/2} V$ by which you can verify that this statement is indeed valid.

We already stated earlier that q scales linearly with V. Since all other properties upon which q depend are the same because the gas particles are the same, this implies that the only difference between the partition functions comes from the value of V. In other words,

$$\frac{q(V)}{q(V_1)} = \frac{(V)}{V_1}. \tag{2.130}$$

Using this equality gives

$$\Delta S = k_\mathrm{B} N_1 \ln\left(\frac{V}{N}\frac{N_1}{V_1}\right) + k_\mathrm{B} N_2 \ln\left(\frac{V}{N}\frac{N_2}{V_2}\right). \tag{2.131}$$

Since the number density is the same in both partitions of the volume as given by

$$\rho = \frac{N_1}{V_1} = \frac{N_2}{V_2} = \frac{N}{V}, \tag{2.132}$$

this implies that

$$\Delta S = k_\mathrm{B} N_1 \ln\left(\frac{\rho}{\rho}\right) + k_\mathrm{B} N_2 \ln\left(\frac{\rho}{\rho}\right), \tag{2.133}$$

by which the logarithmic terms vanish as $\ln(1) = 0$, giving the expected result of $\Delta S = 0$. Thus, it seems that the $1/N!$ term is absolutely necessary to resolve the paradox.

2.7.2 Quantum mechanical explanation

Although we have now found a practical way to resolve the entropy problem, it does not readily explain why the factor of $1/N!$ is required. The answer to that question originates from quantum mechanics. From a quantum-mechanical point of view, the arrangement of the particles is operationally indistinguishable from any other arrangement as the particles *themselves* are indistinguishable. In our formulation of the partition functions as shown in Equation 2.60, we sum over the particles but we *should* sum over all the quantum states of the system. If two indistinguishable particles are swapped, no one would be able to tell. In fact, all possible permutations of the indistinguishable particles pertain to the same **single** quantum state and should thus only be counted once.

Thus, if we know the total number of possible permutations that leave the system in the same state, we can calculate the correction factor. Consider a system of only five particles. How many different permutations are possible? The answer to this question is relatively straightforward. We can place the first particle in any of the five options, for the next particle, only four options remain. For the third particle, there are only three options left and so on. Thus, the total number of possible arrangements is $5 \cdot 4 \cdot 3 \cdot 2 \cdot 1 = 5! = 120$. In general, there are $N!$ possible arrangements for N particles and from this we can readily see that the correction factor to resolve the over-counting is $1/N!$. [12]

[12] It should be noted here that this correction factor is only valid in the limit where the number of available states is significantly larger than the number of particles by which we can safely assume that two particles rarely find themselves in the same state. If this assumption cannot be made, Bose-Einstein or Fermi-Dirac statistics has to be used of which the Boltzmann statistics as presented here is a limiting case.

2.8 Equilibrium constants

Consider the arbitrary reaction that proceeds in a closed vessel at constant volume V and pressure p as given by the following reaction equation

$$\nu_A A + \nu_B B \underset{k^-}{\overset{k^+}{\rightleftharpoons}} \nu_C C + \nu_D D. \tag{2.134}$$

The Gibbs free energy of this reaction is defined as

$$\Delta G = \sum_i \nu_i \mu_i = \nu_C \mu_C + \nu_D \mu_D - \nu_A \mu_A - \nu_B \mu_B. \tag{2.135}$$

At equilibrium, the Gibbs free energy is equal to zero. By insertion of Equation 2.107 in Equation 2.135 and using Equation 2.112 (because molecules are indistinguishable particles), we obtain

$$\sum_i -\nu_i k_\mathrm{B} T \frac{\partial}{\partial N_i} \left[\ln \left(\frac{q_i^{N_i}}{N_i!} \right) \right] = 0, \tag{2.136}$$

where q_i is the partition function of molecule i and N_i is the total number of molecules i. Because the $k_\mathrm{B}T$ term does not depend on the index i, we can drop it. Furthermore, we can also drop the minus sign.[13] Thus, we can rewrite the above equation to[14]

$$0 = \sum_i -\nu_i k_\mathrm{B} T \frac{\partial}{\partial N_i} \left[\ln \left(\frac{q_i^{N_i}}{N_i!} \right) \right] \tag{2.137}$$

$$= \sum_i \nu_i \frac{\partial}{\partial N_i} \left[\ln \left(\frac{q_i^{N_i}}{N_i!} \right) \right] \tag{2.138}$$

$$= \sum_i \nu_i \frac{\partial}{\partial N_i} \left[N_i \ln (q_i) - \ln (N_i!) \right] \tag{2.139}$$

$$= \sum_i \nu_i \frac{\partial}{\partial N_i} \left[N_i \ln (q_i) - N_i \ln (N_i) + N_i \right] \tag{2.140}$$

$$= \sum_i \nu_i \left[\ln (q_i) - \ln (N_i) - \frac{N_i}{N_i} + 1 \right] \tag{2.141}$$

$$= \sum_i \nu_i \left[\ln (q_i) - \ln (N_i) \right] \tag{2.142}$$

$$= \ln \left(\prod_i q_i^{\nu_i} \right) - \ln \left(\prod_i N_i^{\nu_i} \right) \tag{2.143}$$

$$= \left(\prod_i q_i^{\nu_i} \right) - \left(\prod_i N_i^{\nu_i} \right) = 0 \tag{2.144}$$

[13] Because the equation is equal to zero, we are allowed to multiply both sides by -1.

[14] Note that in the derivation, we have used Stirling's approximation to simplify the ln $(N!)$ term. More information about Stirling's approximation can be found in Appendix B.2 on page 278.

by which we obtain

$$K_n(T,V) = \prod_i q_i^{\nu_i} = \prod_i N_i^{\nu_i}, \tag{2.145}$$

wherein K_n is a **number-based** equilibrium constant that depends on temperature and volume. Applying the above formula to our example reaction yields

$$K_n(T,V) = \frac{N_C^{\nu_C} N_D^{\nu_D}}{N_A^{\nu_A} N_B^{\nu_B}} = \frac{q_C^{\nu_C} q_D^{\nu_D}}{q_A^{\nu_A} q_B^{\nu_B}}, \tag{2.146}$$

thus the number of molecules at equilibrium is related to their corresponding partition functions. It is often convenient to express the equilibrium constants in terms of concentrations or *number densities*. We can do this by dividing both q and N by the volume V such that $\rho = N/V$, by which we obtain

$$\frac{\left(N_C/V\right)^{\nu_C}\left(N_D/V\right)^{\nu_D}}{\left(N_A/V\right)^{\nu_A}\left(N_B/V\right)^{\nu_B}} = \frac{\left(q_C/V\right)^{\nu_C}\left(q_D/V\right)^{\nu_D}}{\left(q_A/V\right)^{\nu_A}\left(q_B/V\right)^{\nu_B}}, \tag{2.147}$$

which is equal to

$$\frac{\rho_C^{\nu_C}\rho_D^{\nu_D}}{\rho_A^{\nu_A}\rho_B^{\nu_B}} = \frac{\left(q_C/V\right)^{\nu_C}\left(q_D/V\right)^{\nu_D}}{\left(q_A/V\right)^{\nu_A}\left(q_B/V\right)^{\nu_B}} = K_c(T), \tag{2.148}$$

wherein $K_c(T)$ is a **number-density-based** equilibrium constant that only depends on the temperature T. Multiplying all terms by $k_\mathrm{B}T$ and assuming the ideal gas law, yields

$$\frac{p_C^{\nu_C} p_D^{\nu_D}}{p_A^{\nu_A} p_B^{\nu_B}} = \frac{\left(q_C k_\mathrm{B}T/V\right)^{\nu_C}\left(q_D k_\mathrm{B}T/V\right)^{\nu_D}}{\left(q_A k_\mathrm{B}T/V\right)^{\nu_A}\left(q_B k_\mathrm{B}T/V\right)^{\nu_B}} = K_p(T), \tag{2.149}$$

by which we can define a **pressure-based** equilibrium constant $K_p(T)$.

The various kinds of equilibrium constants can be connected to the standard Gibbs free energy of reaction as follows. First, we need to define the so-called **thermodynamic equilibrium constant**[3] as given by

$$\boxed{K \equiv \prod_i \left(a_i\right)^{\nu_i} = \exp\left(-\frac{\Delta G_\mathrm{r}^\ominus}{k_\mathrm{B}T}\right),} \tag{2.150}$$

Next, the chemical potential μ is related to the standard chemical potential $\mu^\ominus$ by

$$\mu_i = \mu_i^\ominus + k_\mathrm{B}T\ln\left(a_i\right) = \mu_i^\ominus + k_\mathrm{B}T\ln\left(\phi_i\frac{p_i}{p^\ominus}\right), \tag{2.151}$$

wherein $\mu_i^\ominus$ is the standard chemical potential for the pure phase, which is the chemical potential under specified standard conditions (i.e. being in the standard state; typically p = 1 atm and T = 298.15K), a_i the activity of component i, $p^\ominus$ is the standard pressure and ϕ_i the fugacity coefficient of component i, which from here onwards we will consider to be unity.

Insertion of Equation 2.151 into Equation 2.150 and expanding the natural logarithms gives

$$\ln(K) = \ln\left(\prod_i \left(p_i/p^{\ominus}\right)^{\nu_i}\right) \tag{2.152}$$

$$= \sum_i \nu_i \ln\left(p_i/p^{\ominus}\right) \tag{2.153}$$

$$= \sum_i \nu_i \frac{\mu_i - \mu_i^{\ominus}}{k_B T} \tag{2.154}$$

$$= -\frac{\Delta G^{\ominus}}{k_B T}. \tag{2.155}$$

From this, we can readily relate the thermodynamic equilibrium constant, to the other equilibrium constants, essentially connecting these to the Gibbs free energy of the reaction. For the **pressure-based** equilibrium constant we obtain

$$K_p(T) = \prod_i (p_i)^{\nu_i} = \prod_i (q_i k_B T/V)^{\nu_i} = K\left(p^{\ominus}\right)^{\Delta\nu} = \left(p^{\ominus}\right)^{\Delta\nu} \exp\left(-\frac{\Delta G_r^{\ominus}}{k_B T}\right), \tag{2.156}$$

where

$$\Delta\nu = \sum_i \nu_i. \tag{2.157}$$

For the **number-based** equilibrium constant we obtain

$$K_n(T,V) = \prod_i N_i^{\nu_i} = \prod_i q_i^{\nu_i} = \left(\frac{k_B T}{V}\right)^{\Delta\nu} K_p = \left(\frac{p^{\ominus} V}{k_B T}\right)^{\Delta\nu} \exp\left(-\frac{\Delta G_r^{\ominus}}{k_B T}\right), \tag{2.158}$$

and for the **number-density-based** equilibrium constant

$$K_c(T) = \prod_i \rho_i^{\nu_i} = \prod_i (q_i/V)^{\nu_i} = (k_B T)^{\Delta\nu} K_p = \left(\frac{p^{\ominus}}{k_B T}\right)^{\Delta\nu} \exp\left(-\frac{\Delta G_r^{\ominus}}{k_B T}\right). \tag{2.159}$$

In summary, we have defined three different variants of the equilibrium constant, which differ only by the variables of interest that we use. These are the *number*-based equilibrium

constant $K_n(T, V)$, the *number-density* based equilibrium constant $K_c(T)$ and a *pressure*-based equilibrium constant $K_p(T)$. These three different types of equilibrium constants can in turn be connected to the standard Gibbs free energy of the reaction via the thermodynamic equilibrium constant.

2.9 Application of partition functions

Let us consider a simple example to illustrate the theory shown in this chapter. Consider two systems (A and B) which each have two states separated by an energy ΔE and where the ground state energy of A lies ΔE lower in energy than system B. The partition function for system A is then given by

$$q_A = \sum_i g_i \exp\left(-\frac{\Delta E_i}{k_\mathrm{B} T}\right) \tag{2.160}$$

$$= 1 + \exp\left(-\frac{\Delta E}{k_\mathrm{B} T}\right) \tag{2.161}$$

and for system B by

$$q_B = \sum_i g_i \exp\left(-\frac{\Delta E_i}{k_\mathrm{B} T}\right) \tag{2.162}$$

$$= \exp\left(-\frac{\Delta E}{k_\mathrm{B} T}\right) + \exp\left(-\frac{2\Delta E}{k_\mathrm{B} T}\right). \tag{2.163}$$

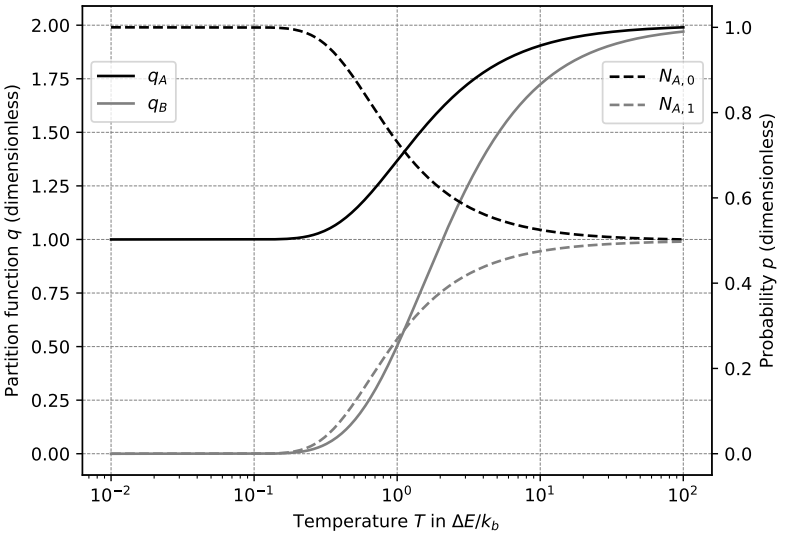


Figure 2.9: *Partition function q for system with particles A and B and the occupancies of the energy states of A as function of temperature.*

In Figure 2.9, 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 function 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.

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

$$K = \frac{q_B}{q_A} = \frac{\exp\left(-\frac{\Delta E}{k_B T}\right) + \exp\left(-\frac{2\Delta E}{k_B T}\right)}{1 + \exp\left(-\frac{\Delta E}{k_B T}\right)}. \tag{2.164}$$

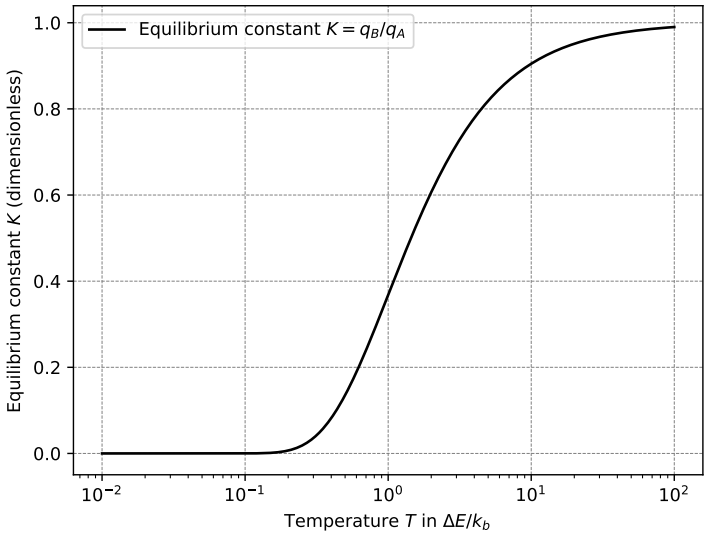


Figure 2.10: *Equilibrium constant K between A and B as function of temperature.*

The value for the equilibrium constant K as function of temperature is depicted in Figure 2.10. 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 total energy, which for system A would be

$$E_A = k_B T^2 \left(\frac{\partial \ln q}{\partial T} \right) \tag{2.165}$$

$$= \frac{\exp\left(-\frac{\Delta E}{k_B T}\right) \cdot \Delta E}{1 + \exp\left(-\frac{\Delta E}{k_B T}\right)} \tag{2.166}$$

and for system B

$$E_B = k_B T^2 \left(\frac{\partial \ln q}{\partial T} \right) \tag{2.167}$$

$$= \frac{\exp\left(-\frac{\Delta E}{k_B T}\right) \cdot \Delta E + \exp\left(-\frac{2\Delta E}{k_B T}\right) \cdot 2\Delta E}{\exp\left(-\frac{\Delta E}{k_B T}\right) + \exp\left(-\frac{2\Delta E}{k_B T}\right)}. \tag{2.168}$$

Careful examination of the above two formula shows that the total 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 total energy. At the lowest temperature, the total energy of a molecule corresponds to the energy of the ground state and with increasing temperature, the total 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 section 3.3, we will calculate heat capacities using molecular partition functions and in section 4.2, partition functions are used to construct expressions for the reaction rate constants.

Practice your understanding

Exercise 2.3, 2.4, 2.5 and 2.6

Challenges

Exercise 2.7

2.10 Exercises

The answers to the exercises can be found at the end of this Chapter on page 111. The exercises are marked by a number of gears to indicate their difficulty levels.

EXERCISE 2.1

Consider a canonical ensemble of $\mathcal{N} = 5$ subsystems. There are six allowed energy levels $E_0, E_1, E_2, E_3, E_4, E_5$, where the index i in E_i corresponds to how many units of energy are in the energy state E_i. The total energy of the canonical ensemble is set at $E_{\text{total}} = 5$.

a) List the set of different macrostate configurations. How many macrostates are there in total?

b) How many microstates are there for each macrostate? You are not expected to list all the possible configurations.

c) Which macrostate will be the dominant macrostate in the limit $\mathcal{N} \to \infty$?

EXERCISE 2.2

In NMR spectroscopy, a magnetic field is applied to create an energetic difference between spin-up (α) and spin-down (β) protons, creating a two-level system. Assume that the spin-up protons are aligned with the magnetic field (more favorable and thus exothermic) and spin-down protons are oppositely aligned (less favorable and therefore endothermic). Their energies are then given by

$$E_\alpha = -\frac{1}{2}\gamma_N B_0 \hbar \tag{2.169}$$

$$E_\beta = +\frac{1}{2}\gamma_N B_0 \hbar \tag{2.170}$$

Calculate the distribution of protons that are in the excited state as given by the ratio $\frac{n_\beta}{n_\alpha}$ at room temperature. Assume that the NMR has a magnetic field strength of 1.4 Tesla. The gyromagnetic ratio γ_N of a proton is 42.577 MHz / Tesla.

EXERCISE 2.3

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

$$A \leftrightarrows B + C \tag{2.171}$$

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 2.4

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 2.5

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

$$E_i^A = i\Delta E \tag{2.172}$$

$$E_j^B = \left(\frac{j}{2} + 1\right)\Delta E \tag{2.173}$$

with $i, j = 0, 1, 2, 3, \ldots$.

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 $T = 0.1\Delta E/k_\mathrm{B}$, $T = 2\Delta E/k_\mathrm{B}$, and $T = 10\Delta E/k_\mathrm{B}$ 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.5 on page 279.

EXERCISE 2.6

Consider the equilibrium:

$$\mathrm{A} + \mathrm{B} \rightleftarrows \mathrm{C} + 3\mathrm{D}. \tag{2.174}$$

Assume that:

- A has three energy levels separated by ΔE.
- B has two energy levels, all separated by ΔE and the ground state at the same level as the ground state of A.

- C and D both have only a double-degenerate ground state located $2\Delta E$ above the ground state of A.

a) Draw a schematic representation of the energy levels of all the molecules.

b) Derive the partition function for each of the molecules.

c) Derive the equilibrium constant for this system.

d) What is the value for the equilibrium constant at very low and very high temperature? Provide a chemical interpretation for your findings.

EXERCISE 2.7 ✪✪✪✪

In this exercise, 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. For example, 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 called 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.[15] If the particles 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 2.11. In this Figure, three macrostates and their corresponding number of microstates are given.

Within a Maxwell-Boltzmann distribution, all particles are distinguishable from each other. Hence, for the first macrostate as shown in Figure 2.11, 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

$$\Omega_i = \frac{N!}{\prod_i n_i!}, \tag{2.175}$$

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).

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

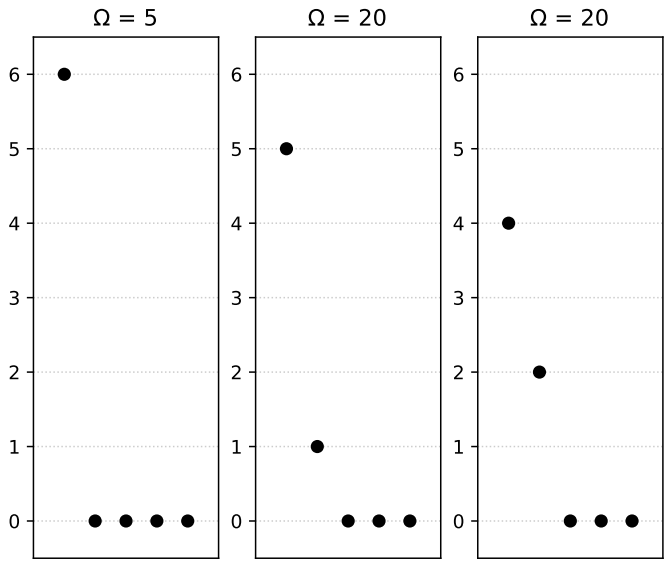


Figure 2.11: *Schematic depiction of the first three macrostates for distributing 6 units of energy over 5 particles. Above each subfigure is the number of microstates for that particular macrostate given.*

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 2.11, 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 2.11 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

$$\Omega(N,q) = \binom{q+N-1}{q} = \frac{(q+N-1)!}{q!\,(N-1)!}. \tag{2.176}$$

Again, you only have to show that Equation 2.176 is valid for this example.

d) Calculate the average number of particles in each energy level using the following formula

$$n_j = \sum_i \frac{\Omega_i}{\Omega} n_{i,j}, \tag{2.177}$$

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

$$n_i = A \cdot \exp\left(-c \cdot E_i\right) \tag{2.178}$$

where E_i is the total energy of the system using arbitrary "units of energy" ΔE.

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 2 kJ/mol.

2.11 Solutions

The solutions below pertain to the exercises of Chapter 2 on page 107 and further.

SOLUTION 2.1

a) In total, there are 7 possible macrostates. These are

(a) $(4, 0, 0, 0, 0, 1)$

(b) $(3, 1, 0, 0, 1, 0)$

(c) $(3, 0, 1, 1, 0, 0)$

(d) $(2, 2, 0, 1, 0, 0)$

(e) $(2, 1, 2, 0, 0, 0)$

(f) $(1, 3, 1, 0, 0, 0)$

(g) $(0, 5, 0, 0, 0, 0)$

In this notation, a macrostate is given by

$$(n_0, n_1, n_2, n_3, n_4, n_5)\,, \tag{2.179}$$

where n_i is the number of systems in quantum state i. Note that for each macrostate, it can be found that

$$\mathcal{N} = \sum_{i=0}^{5} n_i = 5 \tag{2.180}$$

and

$$E_\mathrm{t} = \sum_{i=0}^{5} n_i \cdot E_i = 5. \tag{2.181}$$

b) The number of microstates per macrostate can be calculated using Equation 2.21. These are $\Omega_1 = 5$, $\Omega_2 = 20$, $\Omega_3 = 20$, $\Omega_4 = 30$, $\Omega_5 = 30$, $\Omega_6 = 20$, $\Omega_7 = 1$.

c) Expanding the size of the ensemble beyond $\mathcal{N} = 5$ does not provide any new macrostate configurations, but only adds additional states of E_0 to the configurations. The macrostate which will become the dominant macrostate is that state which has the **least amount** of subsystems with energy E_0. This corresponds to $\mathcal{S}_7$, which will have $\mathcal{N} - 5$ subsystems with energy E_0, whereas all other macrostates have $n_0 > \mathcal{N} - 5$.

SOLUTION 2.2

The energy difference can be calculated using the given formula.

$$\Delta E = \gamma_N B_0 \hbar = \frac{\gamma_N B_0 h}{2\pi} \tag{2.182}$$

From this, the distribution can be readily calculated, giving

$$\frac{n_\beta}{n_\alpha} = \exp\left(\frac{-\Delta E}{k_\mathrm{B} T}\right) \tag{2.183}$$

$$= \exp\left(\frac{-\gamma_N B_0 h}{2\pi k_\mathrm{B} T}\right) \tag{2.184}$$

$$= 0.999998472 \tag{2.185}$$

In conclusion, there is a slightly smaller fraction of H-nuclei in the excited spin-state.

SOLUTION 2.3

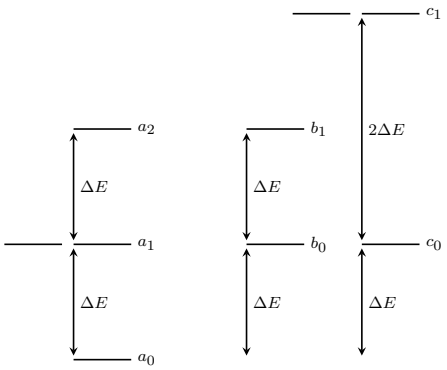


Figure 2.12: *Energy level diagram of A, B, and C.*

a) The equilibrium constant in terms of the partition functions is given by

$$K = \prod_i q_i^{\nu_i} = \frac{q_\mathrm{B} q_\mathrm{C}}{q_\mathrm{A}} \tag{2.186}$$

b)

$$q_\mathrm{A} = \sum_{j=0}^{2} g_j \exp\left(-\frac{\epsilon_j}{k_\mathrm{B}T}\right) \tag{2.187}$$

$$= 1 + 2\exp\left(-\frac{\Delta E}{k_\mathrm{B}T}\right) + \exp\left(-\frac{2\Delta E}{k_\mathrm{B}T}\right) \tag{2.188}$$

$$q_\mathrm{B} = \exp\left(-\frac{\Delta E}{k_\mathrm{B}T}\right) + \exp\left(-\frac{2\Delta E}{k_\mathrm{B}T}\right) \tag{2.189}$$

$$q_\mathrm{C} = \exp\left(-\frac{\Delta E}{k_\mathrm{B}T}\right) + 2\exp\left(-\frac{3\Delta E}{k_\mathrm{B}T}\right) \tag{2.190}$$

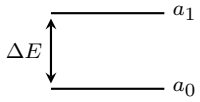
$$K = \frac{\left(\exp\left(-\frac{\Delta E}{k_\mathrm{B}T}\right) + \exp\left(-\frac{2\Delta E}{k_\mathrm{B}T}\right)\right)\left(\exp\left(-\frac{\Delta E}{k_\mathrm{B}T}\right) + 2\exp\left(-\frac{3\Delta E}{k_\mathrm{B}T}\right)\right)}{1 + 2\exp\left(-\frac{\Delta E}{k_\mathrm{B}T}\right) + \exp\left(-\frac{2\Delta E}{k_\mathrm{B}T}\right)} \tag{2.191}$$

c)

$$\lim_{T\to 0} K = \frac{0 \cdot 0}{1} = 0 \tag{2.192}$$

$$\lim_{T\to \infty} K = \frac{2 \cdot 3}{4} = \frac{3}{2} \tag{2.193}$$

SOLUTION 2.4



a)

The partition function for molecule A is

$$q_{\mathrm{A}} = \sum_{i=0}^{1} \exp\left(-\frac{\epsilon_i}{k_{\mathrm{B}}T}\right) \tag{2.194}$$

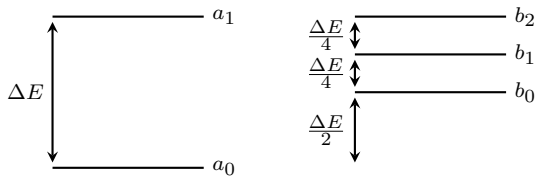
$$= 1 + \exp\left(-\frac{\Delta E}{k_{\mathrm{B}}T}\right) \tag{2.195}$$

The partition function at $T \to 0$ gives

$$\lim_{T\to 0} q_{\mathrm{A}} = 1 \tag{2.196}$$

The partition function at $T \to \infty$ gives

$$\lim_{T\to \infty} q_{\mathrm{A}} = 2 \tag{2.197}$$



b)

The partition function for molecule B is

$$q_{\mathrm{B}} = \sum_{i=0}^{2} \exp\left(-\frac{\epsilon_i}{k_{\mathrm{B}}T}\right) \tag{2.198}$$

$$= \exp\left(-\frac{\Delta E}{2k_{\mathrm{B}}T}\right) + \exp\left(-\frac{3\Delta E}{4k_{\mathrm{B}}T}\right) + \exp\left(-\frac{\Delta E}{k_{\mathrm{B}}T}\right) \tag{2.199}$$

The equilibrium between A and B is given by

$$K = \prod_{i=0}^{1} q_i^{\nu_i} \tag{2.200}$$

$$= \frac{q_{\mathrm{B}}}{q_{\mathrm{A}}} \tag{2.201}$$

$$= \frac{\exp\left(-\frac{\Delta E}{2k_{\mathrm{B}}T}\right) + \exp\left(-\frac{3\Delta E}{4k_{\mathrm{B}}T}\right) + \exp\left(-\frac{\Delta E}{k_{\mathrm{B}}T}\right)}{1 + \exp\left(-\frac{\Delta E}{k_{\mathrm{B}}T}\right)} \tag{2.202}$$

The equilibrium constant for $T \to 0$ yields

$$\lim_{T\to 0} K = \frac{0}{1} = 0 \tag{2.203}$$

The equilibrium constant for $T \to \infty$ yields

$$\lim_{T\to \infty} K = \frac{3}{2} \tag{2.204}$$

SOLUTION 2.5

Note that the spectroscopically determined energy levels of A and B are an infinite series of energy levels. The series of molecule B starts somewhat higher (ΔE) than the series of molecule A and furthermore, the energy separation of molecule B is half the size of that of molecule A.

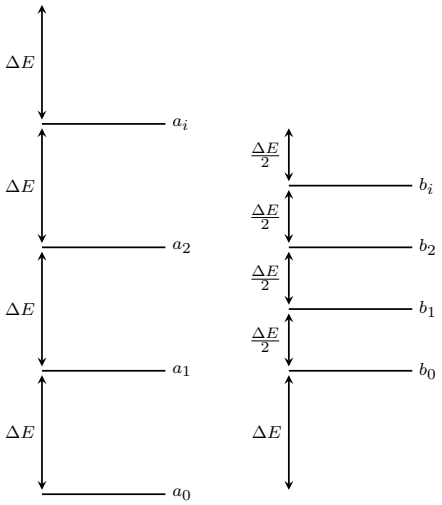


Figure 2.13: *Energy level diagram of the spectroscopically determined energy levels of A and B.*

The partition function for A yields

$$q_{\mathrm{A}} = \sum_{i=0}^{\infty} \exp\left(-\frac{E_i^A}{k_{\mathrm{B}}T}\right) \tag{2.205}$$

$$q_{\mathrm{A}} = \sum_{i=0}^{\infty} \exp\left(-i\frac{\Delta E}{k_{\mathrm{B}}T}\right) \tag{2.206}$$

$$= \sum_{i=0}^{\infty} \exp\left(-\frac{\Delta E}{k_{\mathrm{B}}T}\right)^i \tag{2.207}$$

The partition function for B yields

$$q_{\mathrm{B}} = \sum_{j=0}^{\infty} \exp\left(-\frac{E_j^B}{k_{\mathrm{B}}T}\right) \tag{2.208}$$

$$= \sum_{j=0}^{\infty} \exp\left(-\left(\frac{j}{2}+1\right)\frac{\Delta E}{k_{\mathrm{B}}T}\right) \tag{2.209}$$

$$= \exp\left(-\frac{\Delta E}{k_{\mathrm{B}}T}\right) \sum_{j=0}^{\infty} \exp\left(-\frac{\Delta E}{2k_{\mathrm{B}}T}\right)^j \tag{2.210}$$

The above sums are geometric series (see Appendix B.5 on page 279). These series can be simplified using the formula below

$$\sum_{k=0}^{\infty} ar^k = \frac{a}{1-r} \text{ for } |r| < 1 \tag{2.211}$$

Thus we can write

$$q_{\mathrm{A}} = \frac{1}{1-\exp\left(-\frac{\Delta E}{k_{\mathrm{B}}T}\right)} \tag{2.212}$$

and

$$q_{\mathrm{B}} = \frac{\exp\left(-\frac{\Delta E}{k_{\mathrm{B}}T}\right)}{1-\exp\left(-\frac{\Delta E}{2k_{\mathrm{B}}T}\right)} \tag{2.213}$$

This gives for the equilibrium constant

$$K = \frac{q_{\mathrm{B}}}{q_{\mathrm{A}}} = \frac{\exp\left(-\frac{\Delta E}{k_{\mathrm{B}}T}\right)\left(1-\exp\left(-\frac{\Delta E}{k_{\mathrm{B}}T}\right)\right)}{1-\exp\left(-\frac{\Delta E}{2k_{\mathrm{B}}T}\right)} \tag{2.214}$$

The values for the equilibrium constant K are then:

$$K(T = 0.1\Delta E/k_{\mathrm{B}}) = 0.000045 \tag{2.215}$$

$$K(T = 2\Delta E/k_{\mathrm{B}}) = 1.079 \tag{2.216}$$

$$K(T = 10\Delta E/k_{\mathrm{B}}) = 1.766 \tag{2.217}$$

$$K(T \to \infty) = 2 \tag{2.218}$$

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'Hôpital's rule (see Appendix B.7 on 281), which states

$$\lim_{x \to a} \frac{f(x)}{g(x)} = \lim_{x \to a} \frac{f'(x)}{g'(x)} \tag{2.219}$$

Applying this rule, yields

$$K(T \to \infty) = \lim_{T \to \infty} \left[\frac{\exp\left(-\frac{\Delta E}{k_\mathrm{B} T}\right)\left(1 - \exp\left(-\frac{\Delta E}{k_\mathrm{B} T}\right)\right)}{1 - \exp\left(-\frac{\Delta E}{2 k_\mathrm{B} T}\right)} \right] \tag{2.220}$$

$$= \lim_{T \to \infty} \left[\frac{\frac{\Delta E}{k_\mathrm{B} T^2}\left(\exp\left(-\frac{\Delta E}{k_\mathrm{B} T}\right)\left(1 - \exp\left(-\frac{\Delta E}{k_\mathrm{B} T}\right)\right) - \exp\left(-\frac{2\Delta E}{k_\mathrm{B} T}\right)\right)}{-\frac{\Delta E}{2 k_\mathrm{B} T^2} \exp\left(-\frac{\Delta E}{2 k_\mathrm{B} T}\right)} \right] \tag{2.221}$$

$$= \lim_{T \to \infty} \left[\frac{\frac{\Delta E}{k_\mathrm{B} T^2}\left(1 \cdot 0 - 1\right)}{\frac{-\Delta E}{2 k_\mathrm{B} T^2}} \right] \tag{2.222}$$

$$= \lim_{T \to \infty} \left[\frac{-\frac{\Delta E}{k_\mathrm{B} T^2}}{\frac{-\Delta E}{2 k_\mathrm{B} T^2}} \right] \tag{2.223}$$

$$= 2 \tag{2.224}$$

SOLUTION 2.6

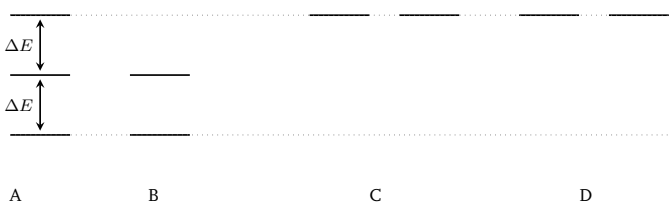


Figure 2.14: *Energy level diagram of the A, B, C and D.*

a)

b)

$$q_\mathrm{A} = 1 + \exp\left(-\frac{\Delta E}{k_\mathrm{B} T}\right) + \exp\left(-\frac{2\Delta E}{k_\mathrm{B} T}\right) \tag{2.225}$$

$$q_\mathrm{B} = 1 + \exp\left(-\frac{\Delta E}{k_\mathrm{B} T}\right) \tag{2.226}$$

$$q_\mathrm{C} = 2 \exp\left(-\frac{2\Delta E}{k_\mathrm{B} T}\right) \tag{2.227}$$

$$q_\mathrm{D} = 2 \exp\left(-\frac{2\Delta E}{k_\mathrm{B} T}\right) \tag{2.228}$$

c)

$$K = \frac{q_C q_D^3}{q_A q_B} \tag{2.229}$$

$$= \frac{16 \exp\left(-\frac{8\Delta E}{k_B T}\right)}{\left(1 + \exp\left(-\frac{\Delta E}{k_B T}\right) + \exp\left(-\frac{2\Delta E}{k_B T}\right)\right)\left(1 + \exp\left(-\frac{\Delta E}{k_B T}\right)\right)} \tag{2.230}$$

d) Taking the limits, yields the following results for the equilibrium constant:

$$K(T \to 0) = \frac{0}{1 \cdot 1} = 0 \tag{2.231}$$

$$K(T \to \infty) = \frac{16}{3 \cdot 2} = \frac{8}{3} \tag{2.232}$$

At zero temperature, only the ground states of A and B are occupied. At infinite temperature, all states have equal probability to be occupied and hence the equilibrium constant should reflect the quotient of the product of states of both sides of the equation, which corresponds to $2 \cdot 2^3$ states on the right hand side and $3 \cdot 2$ states on the left hand side.

SOLUTION 2.7

a) The total set of macrostates and the corresponding number of microstates for each macrostate is schematically represented in Figure 2.15. The number of microstates were calculated using Equation 2.175 on page 109. For example, the number of microstates for macrostate 4 is given by:

$$\Omega_4 = \frac{5!}{0! \cdot 0! \cdot 1! \cdot 0! \cdot 0! \cdot 2! \cdot 2!} = \frac{120}{4} = 30. \tag{2.233}$$

b) The total set of possible macrostates is shown in Figure 2.15. Each subfigure represents one particular macrostate. Above each subfigure the number of microstates is given.

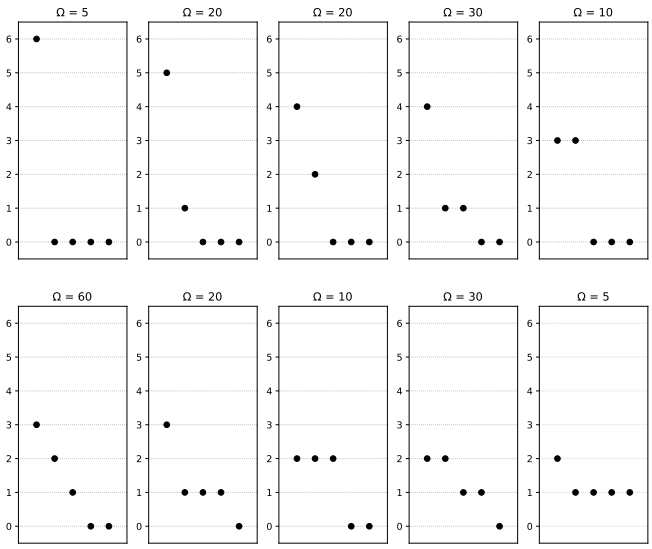


Figure 2.15: *Schematic depiction of all macrostates for distributing 6 units of energy over 5 particles.*

c) The total number of microstates is calculated as

$$\Omega(N, q) = \frac{(6 + 5 - 1)!}{6!\,(5 - 1)!} = \frac{3628800}{720 \cdot 24} = 210 \tag{2.234}$$

d) We calculated the average number of particles per energy state using Equation 2.177 on page 111. We obtained the following numbers as given in Table 2.2.

Table 2.2: *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	0.024

e) The average number of particles in energy state i is shown in Figure 2.16. We used a simple curve fitting procedure to fit the data as shown in Table 2.2 to Equation 2.178 on page 111. 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 extent. 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.[16]

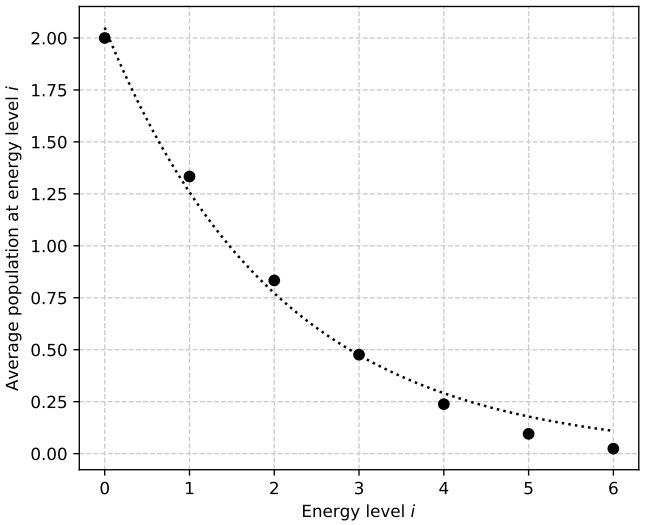


Figure 2.16: *Average number of particles as a function of the energy level. The dotted line represents the curve fit.*

We obtained a value of $A = 2.15$ and $c = 0.538$. From this, the temperature is easily calculated (using $\Delta E = 2000$ J) as

$$T = \frac{\Delta E}{R \cdot c} \approx 447 \text{ K}. \tag{2.235}$$

Reproduce the results of subquestions d) and e) by reviewing this Google Spreadsheet[a]: https://docs.google.com/spreadsheets/d/1KBcp0AJVm7aIDCqA6RI9KVDe9Ewr4DqNnS7vb51XcPw/edit?usp=sharing

[a] Credit to Douwe Orij for creating this Spreadsheet.

[16] Although figuring out all the macrostates and number of microstates would become nearly impossible, but that is exactly why we employ statistics.

CHAPTER 3

MOLECULAR PARTITION FUNCTIONS

Contents

3.1 Introduction

In the previous chapter, we covered the fundamentals of statistical thermodynamics. The concept of partition functions was introduced and we showed how important thermodynamic variables can be readily calculated from these partition functions. The partition functions employed were quite

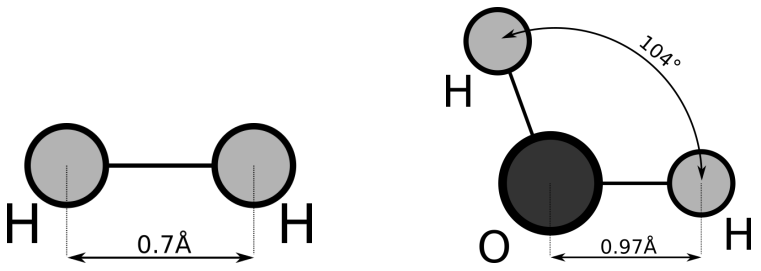
general. In this chapter, we will derive specific expressions for the canonical partition functions for molecular systems. Herein, we will utilize the principle of independent subsystems. We start this chapter by first introducing the concept of the potential energy surface and the identification of important points on this surface, as it helps in the understanding of the association of degrees of freedom to the partition functions. Thereafter, the molecular partition functions are derived and a few applications of these are shown. This chapter acts as the foundation of the next chapter which treats transition state theory and the chapter thereafter, which applies the concepts of molecular partition functions and transition state theory to calculate rate expressions from first principles.

3.2 The potential energy surface

As mentioned in the introduction, before we continue with looking in more detail into the relevant partition functions pertaining to molecules, we first make a brief excursion to the concept of the potential energy surface (PES). Many important concepts that might appear to be mathematically challenging can be more easily understood with the insights provided by the idea of the PES. Indeed, the PES is a powerful concept on which we can build when explaining the contents of the upcoming sections of this chapter and the following chapter.

3.2.1 Visualization and interpretation

Consider the dihydrogen molecule as shown in Figure 3.1a. We can express its potential energy as a function of its interatomic distance. This is schematically depicted in Figure 3.2. The graph as shown in Figure 3.2 is called a **potential energy surface**, although for a one-dimensional system it can be called a **potential energy curve**. From this Figure, it can be seen that the potential energy of H_2 shows a minimum as function of the H-H distance. This minimum corresponds to the equilibrium bond distance of H_2. Furthermore, we can observe that upon compressing the H_2 molecule, the potential energy rapidly increases due to Pauli repulsion. Elongation of the H-H bond also leads to an increase of the potential energy, albeit less steeply, due to the lack of favorable orbital overlap. At a very large H-H bond distance, dihydrogen dissociates into its two H-atom fragments. As the potential energy is given with respect to all atoms at infinite separation, the potential energy converges to zero at very large interatomic distances.



(a) H_2 **(b)** H_2O

Figure 3.1: *Schematic depiction of the molecular structures of H_2 and H_2O. H_2 has a single internal degree of freedom (DOF), which is the H-H bond distance. H_2O has two internal degrees of freedom when it is constrained to its C_{2v} symmetry. A bond distance and an angle.*

In general terms, the potential energy of a **diatomic** molecule is a function that depends only on a single variable r, as given by

$$E = f(r), \tag{3.1}$$

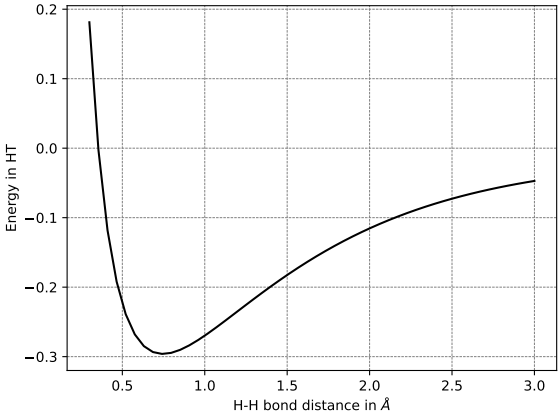


Figure 3.2: *Potential energy curve of the dihydrogen molecule. Dihydrogen has only a single degree of freedom (DOF) and hence its energy can be given as function of only the interatomic distance.*

where E is the potential energy and r the interatomic distance. From our chemical intuition, we know that translation or rotation of the molecule does not change its energy.[1] Another way of saying this is that **the potential energy of a molecule or atom is invariant under translations or rotations**. Thus, the only way by which the potential energy can be changed is by changing the distances between the atoms. Hence, the potential energy of a **diatomic** molecule is a one-dimensional function depending only on the interatomic distance. Another way of saying this is that the potential energy of a diatomic molecule has only a single **degree of freedom**. In more mathematical terms, the function f is a so-called map as given by

$$f : \mathbb{R}_{\geq 0} \mapsto \mathbb{R}, \tag{3.2}$$

where $\mathbb{R}_{\geq 0}$ means the set of real numbers greater than or equal to 0.[2]

A map is a way of associating unique objects to every element in a given set. In the case of potential energy surfaces, we associate a potential energy to a geometry as described by a set of variables. Maps allow us to look at functions in a more abstract sense. Maps such as the one in Equation 3.2 are typically depicted in a graph by a single curve. It is easy to conceive a molecular system with two or more degrees of freedom. Let us consider H_2O constrained to its C_{2v} symmetry as shown in Figure 3.1b. Under this constraint, we are only allowed to change the O-H bond distance of the two O-H bonds **simultaneously** and change the H-O-H dihedral angle.[3] Thus, given these restrictions, H_2O has two degrees of freedom and its potential energy becomes a function of two coordinates as given by

$$E = f(r, \theta), \tag{3.3}$$

where r is the O-H bond distance and θ the H-O-H dihedral angle. Herein, f is a map[4] that

[1] From the perspective of this theoretical analysis, it is considered to be in full vacuum.

[2] Distances between atoms correspond to vector lengths and these cannot be negative. As such, the function f always takes a non-zero value as its input.

[3] Convince yourself that changing only one of the two O-H bond distances would result in a breaking of the C_{2v} symmetry.

[4] This map takes two values as an input and a single value as an output. The input values are the set of non-negative real numbers and an angle. Because of symmetry constraints, we only need to supply the angles on the interval $[0, \pi]$.

associates a scalar (i.e. the potential energy) to an interatomic bond distance and an angle as given by

$$f : \left\{ \mathbb{R}_{\geq 0}, [0, \pi] \right\} \mapsto \mathbb{R}. \tag{3.4}$$

Clearly, we can no longer construct a potential energy *curve* for this system, but we are able to depict the potential energy using a contour plot as given in Figure 3.3. On the left hand side in Figure 3.3, the potential energy as function of the O-H bond distance r and the H-O-H dihedral angle θ is shown. In the contour plot, darker shaded areas indicate a lower potential energy, lighter shaded areas indicate a higher potential energy.[5] From this plot, it can thus already be seen that the minimum energy configuration of H_2O corresponds to r= 0.97 Å and θ = 103.6°. A perhaps more elegant way to visualize the same result is by using a polar plot. Herein, the polar angle in the plot corresponds to the H-O-H dihedral angle and the radius to the O-H bond distance. The polar plot readily shows the symmetry of the system as the upper part of the graph (corresponding to $0 < \theta < 180$ °) is a reflection of the lower part.

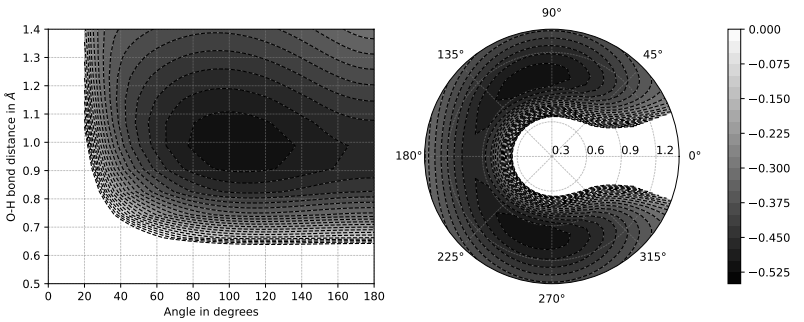


Figure 3.3: *Potential energy surface of H_2O. The minimum energy configuration of H_2O corresponds to $r = 0.974$Å and θ = 103.6°. All energies are given in Ht.*

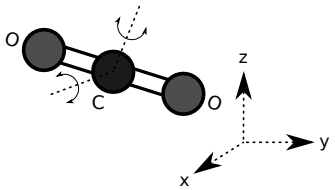
In general, given the geometry of the molecule, an energy corresponding to that specific configuration can be defined or calculated. A system containing N atoms has $3N$ independent coordinates, as each atom can be moved along three of the Cartesian axes. Nevertheless, we saw that for the construction of the PES, fewer degrees of freedom are considered as rotations and translations do not change the potential energy of the molecule. It is therefore useful to be a bit more specific as not all degrees of freedom are the same. A system consisting of N atoms is said to have $3N$ degrees of *configurational* freedom corresponding to the three-dimensional space wherein it exists. The value of $3N$ is easily enough understood as each atom in the system can move alongside each of the three Cartesian direction.

A fewer number than $3N$ is however necessary to construct the potential energy surface of a molecular system and we refer to those degrees of freedom as **internal** degrees of freedom. The number of internal DOFs can then be calculated by subtracting the number of translational and rotational DOFs from the total number of configurational DOFs. The system as a whole can also move along three Cartesian axes, hence any system in three-dimensional space has three translational DOFs.

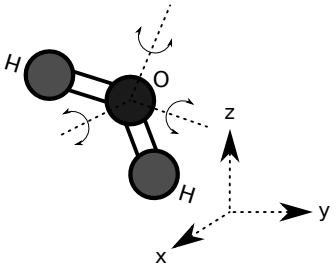
Furthermore, depending on the number of atoms and their configuration, a system in three-dimensional space can have zero, two or three rotational DOFs. Single atoms are considered to be point particles. Since we cannot define a rotation around a single point, a single atom has **zero** rotational degrees of freedom. Linear molecules, such as CO, N_2 or CO_2, have two

[5] Recall that lower potential energies correspond to stabler configurations.

rotational degrees of freedom. The rotational angles of these molecules are perpendicular to the bond axis. This is schematically illustrated in Figure 3.4a for the CO_2 molecule. Non-linear polyatomic molecules, such as H_2O, have three rotational degrees of freedom. This is schematically illustrated in Figure 3.4b.



(a) *Schematic depiction of the rotational and translational axes of the CO_2 molecule. Because CO_2 is a linear molecule, it has only two rotational degrees of freedom and three translational degrees of freedom. As atoms are point particles and a rotational around a point is undefined, CO_2 lacks a rotational axis alongside the O-C-O bond axes.*



(b) *Schematic depiction of the rotational and translational axes of the H_2O molecule. H_2O has three translational and three rotational degrees of freedom.*

In summary, the number of internal degrees of freedom are

$$n_{\text{dof,int}} = 3N - 5, \text{for linear molecules} \tag{3.5}$$
$$n_{\text{dof,int}} = 3N - 6, \text{for non-linear molecules} \tag{3.6}$$

and the function that calculates the potential energy of a polyatomic molecule consisting of N atoms corresponds to a map that associates a scalar to $n = 3N - 5$ or $n = 3N - 6$ internal degrees of freedom as given by

$$f : \mathbb{R}^{3N-5} \mapsto \mathbb{R} \text{ for linear molecules} f : \mathbb{R}^{3N-6} \mapsto \mathbb{R} \text{ for non-linear molecules.} \tag{3.7}$$

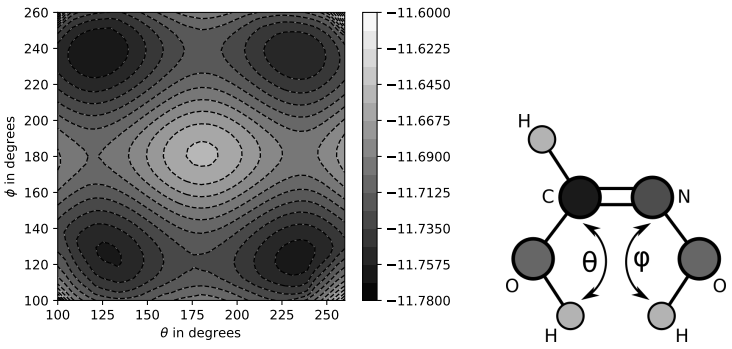
Functions that depend on a single variable are easily plotted in a graph. Two-dimensional functions can be visualized using a contour plot or a heat map as shown in Figures 3.3. For three-dimensional functions you could create an isosurface plot, but for any higher-dimensional function you need to reduce the dimensionality in order to produce a plot. Hence, the full potential energy surfaces can rarely be depicted in a single graph. The reason we were able to do so for H_2 or H_2O was because the number of internal degrees of freedom was either very low ($n \leq 2$) or because we applied a symmetry constraint to reduce the number of (relevant) degrees of freedom.

3.2.2 Stable points

Using the PES, we can define what it means for a molecular system to be considered stable. Chemical stability is closely connected to the potential energy of the molecular system. A molecule is considered stable when it resides in a so-called **local minimum** on the PES. The term *local* refers to the possibility that several such minima exist on the PES, of which only one is the lowest. This lowest minimum is referred to as the **global minimum**. You can imagine these local minima as valleys on the potential energy landscape that are separated by mountainous regions. Once a molecular geometry lies within such a valley, it is considered stable, as energy must be supplied to move the system out of that valley.[6]

[6] For example, by heating or excitation with photons.

An example of multiple minima on the PES is shown in Figure 3.5a. Here, the various isomers of hydroxyformaldoxime are explored as a function of the C–O–H (θ) and N–O–H (ϕ) dihedral angles. These isomers correspond to local minima on the potential energy surface, and the mountainous regions dividing them represent the minimum energy required to move from one configuration to another.[7]



(a) *Potential energy surface.* **(b)** *Chemical structure.*

Figure 3.5: *Potential energy surface (PES) and chemical structure of hydroxyformaldoxime. The PES shows four minima, but only one corresponds to the global minimum. All energies are given in HT.*

From a more intuitive perspective, the molecules encountered in everyday life generally reside in relatively deep valleys on their PES. Molecules such as H_2O and CO_2 are particularly stable and correspond to very deep minima. It is well known that a significant amount of energy is required to make H_2O or CO_2 react.[8] A chemical reaction can therefore be envisioned as a transition from one valley to another, requiring the system to cross the energetic mountain separating them. These ideas will be further developed in Chapter 4.2, where transition state theory is discussed.

Before doing so, let us examine how these stable points on the PES can be identified mathematically. We will use the H_2 molecule as an example. The minimum energy configuration of H_2 corresponds to its equilibrium bond length, which represents an extremum (a point of zero slope) on its potential energy curve (PEC).[9] To locate such points, we take the first derivative of the energy with respect to its degrees of freedom (DOFs) and set it equal to zero. Figure 3.6 shows the potential energy E, the first derivative $\left(\frac{\partial E}{\partial r}\right)$, and the second derivative $\left(\frac{\partial^2 E}{\partial r^2}\right)$ as a function of the bond distance r. The local minimum on the PEC is indicated by a black circle in all three graphs. From the left and center panels, it can be seen that the local minimum in E corresponds to $\left(\frac{\partial E}{\partial r}\right) = 0$. This condition only tells us that the point is an extremum. To determine whether it is a minimum or a maximum, we inspect the second derivative: a negative value corresponds to a maximum, while a positive value indicates a minimum. From the right panel, we observe that the second derivative is positive, and thus this extremum is a local minimum.

The above reasoning can be extended to polyatomic molecules, i.e., to higher-dimensional space. Consider the function f that calculates the potential energy as a function of n degrees of

[7] See exercise 3.2 on page 153.
[8] This is, of course, why catalysts are often used.
[9] The other kind of extremum is a maximum.

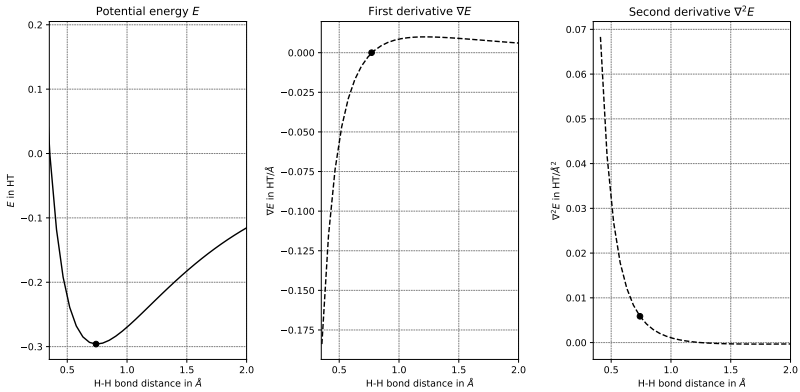


Figure 3.6: *Potential energy curve of H_2 and its first and second derivatives with respect to the interatomic bond distance.*

freedom of a molecular system, as given by

$$f : \mathbb{R}^n \mapsto \mathbb{R}. \tag{3.8}$$

The gradient of the scalar-valued differentiable function f is given by

$$\nabla f(\vec{r}) = \sum_{i=1}^{n} \frac{\partial f}{\partial x_i}(\vec{r})\, \mathbf{e}_i \tag{3.9}$$

and defines the vector field of f as

$$f : \mathbb{R}^n \to \mathbb{R}, \qquad \nabla f : \mathbb{R}^n \to \mathbb{R}^n. \tag{3.10}$$

A point where

$$\nabla f\,(\vec{r}) = 0 \tag{3.11}$$

is called a **critical point** (or stationary point) of f. To determine whether this point is a minimum, maximum, or saddle point, we must consider the second derivatives, which are collected in the **Hessian** matrix:

$$\mathbf{H}(\vec{r}) = \nabla^2 f(\vec{r}) \tag{3.12}$$

$$= \left[\frac{\partial^2 f}{\partial x_i \partial x_j}(\vec{r}) \right]_{i,j=1}^{n}. \tag{3.13}$$

From the definition of the ∇ operator, it is clear that the second derivatives form a matrix termed the **Hessian** matrix, with each element given by

$$H_{ij} = \frac{\partial^2 f}{\partial x_i \partial x_j}. \tag{3.14}$$

Thus, for a system with n DOFs, the second derivatives form the $n \times n$ matrix $\mathbf{H}$. $\mathbf{H}$ describes the local curvature around the point $\vec{r}$ and is symmetric in the sense that

$$H_{ij} = H_{ji}. \tag{3.15}$$

If all eigenvalues[10] of $\mathbf{H}$ are positive, the critical point $\vec{r}$ corresponds to a local minimum; if all are negative, it corresponds to a maximum; and if both positive and negative eigenvalues are present, it corresponds to a saddle point. In principle, one could attempt to assess this property by calculating the determinant and trace of $\mathbf{H}$, since $\det(\mathbf{H})$ is the product and $\mathrm{Tr}(\mathbf{H})$ the sum of its eigenvalues. However, this approach is only valid in two dimensions. For higher dimensions, positive determinant and trace do not guarantee that all eigenvalues are positive. The rigorous condition for a minimum is that $\mathbf{H}$ is **positive definite**.

In practice, we directly evaluate the eigenvalues (and corresponding eigenvectors) of the molecular system and ignore any eigenvalues very close to zero, as these correspond to rotations and translations.[11] Because calculating the eigenvalues also forms the basis for determining vibrational frequencies—and since constructing the Hessian matrix is the most computationally expensive step—the nature of stable points on the PES is identified through a so-called **frequency analysis**.

3.2.3 Frequency analysis

Let us explore the relatively complex mathematical concepts of the previous section by an example. Let us revisit the H_2O molecule, but now we are going to constrain the geometry of H_2O to the two-dimensional plane as shown in Figure 3.7. In other words, all atoms of the H_2O are fixed on the xy-plane. The total number of DOFs is thus $2N = 6$. The point $\vec{r}$ on the PES can be defined by six coordinates and the Hessian matrix $\mathbf{H}$ will be a 6x6 square symmetric matrix. Let us consider the situation wherein we have optimized[12] the geometry in the sense that we have found the most stable configuration of H_2O corresponding to a point $\vec{r}$ on the PES. We can probe the curvature of the PES around this point by systematically moving all the atoms in both the positive and negative x- and y-direction by a small amount and evaluating the effect on the potential energy. For our example system, it turns out that the Hessian matrix[13] looks as shown in Equation 3.16.

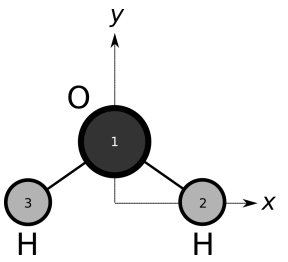


Figure 3.7: *H_2O molecule constrained to the xy-plane.*

[10] See Appendix B.8 on page 282 for a brief explanation of the matrix diagonalization procedure and the concept of eigenvalues.

[11] Think about this: the second derivative of the energy resembles a force constant. If the energy does not change as a function of a particular degree of freedom, that degree of freedom would have a force constant of zero.

[12] The exact procedure behind the geometry optimization of the molecule is outside the scope of this textbook.

[13] All values are given in HT/bohr^2

$$\mathbf{H} = \begin{pmatrix} 0.621 & 0.000 & -0.310 & 0.245 & -0.310 & -0.245 \\ 0.000 & 0.427 & 0.187 & -0.214 & -0.187 & -0.214 \\ -0.310 & 0.187 & 0.341 & -0.216 & -0.031 & 0.029 \\ 0.245 & -0.214 & -0.216 & 0.203 & -0.029 & 0.010 \\ -0.310 & -0.187 & -0.031 & -0.029 & 0.341 & 0.216 \\ -0.245 & -0.214 & 0.029 & 0.010 & 0.216 & 0.203 \end{pmatrix} \tag{3.16}$$

Each of the elements in the Hessian matrix how the i-th component of the force changes when the j-th coordinate is displaced. This perhaps sounds relatively complicated, but let us look into a couple of values. First, we need to define which elements of $\mathbf{H}$ correspond to which atoms and which directions. The elements are given in the following order: O(1)$_x$, O(1)$_y$, H(2)$_x$, H(2)$_y$, H(3)$_x$, H(3)$_y$. So the first element H_{11} probes the force on the oxygen atom in the x-direction when perturbing the oxygen atom an infinitesimal amount in the x-direction. The positive value in the matrix tells us that movement of the oxygen atom increases the force in the x-direction. The second element $H_{12} = H_{21}$, which is the first off-diagonal element, probes the effect on the force on the oxygen atom in the y-direction when perturbing the oxygen in the x-direction or alternatively, it probes the force in the x-direction when perturbing the oxygen atom an infinitesimal amount in the y-direction.[14] The value of zero shows that a perturbation in the x-direction has no effect on the force in the y-direction for the O atom, and *vice versa*. As a final example, let us consider an interaction between two different atoms. The element $H_{13} = H_{31}$ probes the effect on the force on the oxygen atom in the x-direction upon perturbing the H(2) atom in the x-direction. The negative second derivative shows that this perturbation leads to a force in the opposite direction, that is, the force in the negative x-direction for the H(2) increases when perturbing the O atom in the positive x-direction.

The reason the Hessian matrix $\mathbf{H}$ was constructed was to explore the nature of the critical point $\vec{r}$ on the PES. In the previous section it was explained that we can assess the nature by calculating the eigenvalues of the Hessian matrix $\mathbf{H}$. Calculation of the eigenvalues proceeds by performing a so-called matrix diagonalization. The procedure is briefly explained in Appendix B.8 on 282. The eigenvalues of $\mathbf{H}$ in Equation 3.16 are

$$\lambda = \begin{pmatrix} 1.125 \\ 0.857 \\ 0.157 \\ 0.000 \\ 0.000 \\ 0.000 \end{pmatrix}. \tag{3.17}$$

Typically, we order the eigenvalues from high to low. Note that the three lowest eigenvalues are zero. These pertain to two translations and one rotation. As the system is constrained to the plane, there are two translational and one rotational degrees of freedom with zero curvature, consistent with the invariance of the potential energy under translation and rotation in the plane. The other three eigenvalues pertain to the internal degrees of freedom of the molecule and are thus of interest for our analysis. Since the remaining (non-zero) eigenvalues are positive, we can conclude that the point $\vec{r}$ on the PES corresponds to a minimum.

From the Hessian matrix $\mathbf{H}$, it is possible to construct the vibrational spectrum of the molecule under the harmonic approximation. This is termed a (harmonic) frequency analysis. The frequency analysis provides us with vibrational frequencies (i.e. the strengths of the vibrations) as well as the vibrational modes (i.e. the direction of the vibrations). The result of this analysis can directly be compared to an infrared (IR) measurement. The procedure is as follows.

[14] Note that because the matrix is symmetric, we are allowed to swap the x and y direction.

Using a Taylor expansion[15], we can construct Equation 3.18 for the *potential* energy around a critical point $\vec{r}_0$ on the potential energy surface. Note that we are going to use V instead of E for the potential energy as we are going to use E for the total energy.

$$V(\vec{r}) = V_0 + \sum_{i}^{3N} \left(\frac{\partial V}{\partial x_i} \right) \left(x_i - x_{i,0} \right) + \frac{1}{2!} \sum_{i,j}^{3N} \left(\frac{\partial^2 V}{\partial x_i x_j} \right) \left(x_i - x_{i,0} \right) \left(x_j - x_{j,0} \right) + \cdots , \quad (3.18)$$

wherein V corresponds to the potential energy, V_0 is the potential energy at the critical point $\vec{r}$, and x_i are the Cartesian directions in which we can perturb the atoms. Within the harmonic approximation, we retain only the second-order term, neglecting all higher-order contributions. Furthermore, since we are assessing a critical point on the PES, the linear term is equal to zero.[16] Thus, the equation simplifies to

$$V(\vec{r}) = V_0 + \frac{1}{2!} \sum_{i,j}^{3N} \left(\frac{\partial^2 V}{\partial x_i \partial x_j} \right) \left(x_i - x_{i,0} \right) \left(x_j - x_{j,0} \right) . \quad (3.19)$$

To calculate the normal modes, we consider that the total vibrational energy is always conserved according to

$$E = T + V, \quad (3.20)$$

wherein T is the kinetic energy and V the potential energy.

For a system of N atoms, this gives the following expression for the vibrational energy around a critical point on the potential energy surface with respect to the electronic ground state at that critical point[17]

$$E = \frac{1}{2} \sum_{i}^{N} m_i \left| \vec{v} \right|^2 + \frac{1}{2} \sum_{i,j}^{3N} \left(\frac{\partial^2 V}{\partial x_i \partial x_j} \right) \left(x_i - x_{i,0} \right) \left(x_j - x_{j,0} \right) . \quad (3.21)$$

We now introduce a change of coordinates. Instead of using the spatial coordinates x_i, we are going to use root-mass-weighted coordinates with respect to the critical point $\vec{r}$ as given by

$$\xi_i = \sqrt{m_i} \left(x_i - x_{i,0} \right) , \quad (3.22)$$

wherein $x_{i,0}$ is the equilibrium position of the atom i in the direction of i. Applying this coordinate transformation to Equation 3.21, results in

$$E = \underbrace{\frac{1}{2} \sum_{i}^{3N} \left(\dot{\xi}_i \right)^2}_{\text{kinetic energy}} + \underbrace{\frac{1}{2} \sum_{i,j}^{3N} \left(\frac{\partial^2 V}{\partial \xi_i \partial \xi_j} \right) \xi_i \xi_j}_{\text{potential energy}} . \quad (3.23)$$

Equation 3.23 can be rewritten as a matrix equation as given by

$$E(\vec{\xi}) = \frac{1}{2} \dot{\boldsymbol{\xi}}^{\mathsf{T}} \dot{\boldsymbol{\xi}} + \frac{1}{2} \vec{\xi} \mathbf{H} \vec{\xi}, \quad (3.24)$$

[15] See Appendix B.4 on page 278.

[16] Recall that $\nabla V = 0$ at a critical point.

[17] In other words, the expression for E as shown in equation 3.21 has its zero-of-energy set at the level of the electronic ground state implying that $V_0 = 0$

where $\boldsymbol{\xi}$ and $\dot{\boldsymbol{\xi}}$ are the vectors consisting of the root-mass-weighted coordinates and the first derivatives, respectively and $\mathbf{H}$ is the mass-weighted Hessian matrix. Each element in the Hessian matrix is given by:

$$\mathbf{H}_{ij} = \left(\frac{\partial^2 V}{\partial \xi_i \partial \xi_j} \right). \tag{3.25}$$

The matrix Equation 3.24 can be written in diagonal form[18]

$$E(\mathbf{q}) = \frac{1}{2}\dot{\mathbf{q}}^{\mathsf{T}}\dot{\mathbf{q}} + \frac{1}{2}\vec{q}\mathbf{L}\vec{q}, \tag{3.26}$$

wherein $\mathbf{L}$ is a diagonal matrix and $\mathbf{q}$ a matrix consisting of orthogonal column vectors. Each q_i corresponds to a single oscillator as described by

$$q_i(t) = A\cos\left(\omega_i t + \phi_i\right), \tag{3.27}$$

wherein

$$\omega_i = \sqrt{\frac{k_i}{\mu_i}}, \tag{3.28}$$

where ω_i is the angular frequency, k_i the force constant and μ_i the reduced mass.

Note that due to the choice of coordinates in the matrix $\mathbf{H}$, the elements on the diagonal of $\mathbf{L}$ are the squared angular frequencies (ω_i^2) of the harmonic oscillators and the eigenvalues of $\mathbf{H}$. $\mathbf{L}$ and $\mathbf{q}$ can be obtained from $\mathbf{H}$ by the process of a matrix diagonalization according to

$$\mathbf{L} = \mathbf{A}^{\mathsf{T}}\mathbf{H}\mathbf{A}. \tag{3.29}$$

The column vectors in $\mathbf{A}$ are herein the eigenvectors as given by

$$q_j = \sum_{i}^{3N} A_{ij}\xi_i. \tag{3.30}$$

The above derivation might look complicated, especially if you are not used to the mathematics behind it. The main idea behind the procedure is to obtain so-called **normal modes**. A normal mode is an independent, synchronous motion of atoms that may be excited without leading to the excitation of any other normal mode.[19] This property can be readily assessed from the orthogonality property of the eigenvectors. If you would excite the molecular system with an amount of energy corresponding to the strength of the oscillator, the atoms in the molecule would start to vibrate according to the eigenvector corresponding to that harmonic oscillator.

The procedure behind the frequency analysis can be summarized in the following set of steps.

1. Find a critical point on the PES.
2. Construct the Hessian matrix.

[18] This is yet another coordinate transformation, but in such a way that the matrix $\mathbf{H}$ has only non-zero terms on its diagonal.

[19] This independence is important when constructing the vibrational partition functions in section 3.7 on page 146.

3. Convert the Hessian matrix to a root-mass-weighted Hessian matrix.

4. Perform a matrix diagonalization to obtain eigenvectors and eigenvalues.

Let us look back to the example with which we started this section. In Equation 3.16 the Hessian matrix for H_2O is given. The next step is to convert this matrix to a mass-weighted Hessian matrix. This can be done by dividing each element of the matrix by the masses of its corresponding atoms, as given by

$$H'_{ij} = \frac{H_{ij}}{\sqrt{m_i m_j}}, \tag{3.31}$$

where H'_{ij} is an element of the mass-weighted Hessian matrix, H_{ij} is the regular Hessian matrix and m_i and m_j are the masses of the atoms i and j. Note that from here on, we are going to drop the prime for the mass-weighted Hessian matrix.

For the first element H_{ij} in Equation 3.16, we have to divide by the mass of the oxygen atom. It is convenient to use atomic units for the masses as the matrix elements are given in units of HT/bohr^2. The mass of oxygen is 16 amu, by which the value for the element H'_{11} in the mass-weighted Hessian matrix becomes

$$H'_{11} = \frac{0.621}{\sqrt{16 \cdot 16}} = 0.0388. \tag{3.32}$$

The units for the mass-weighted Hessian matrix are in HT/bohr^2/amu, where amu is the atomic mass unit. For the first interatomic element, the value becomes

$$H'_{13} = \frac{-0.310}{\sqrt{16 \cdot 1}} = -0.0776. \tag{3.33}$$

Applying the procedure for all elements in Equation 3.16 gives the mass-weighted Hessian matrix as given in Equation 3.34.

$$\mathbf{H} = \begin{pmatrix} 0.039 & 0.000 & -0.078 & 0.061 & -0.078 & -0.061 \\ 0.000 & 0.027 & 0.047 & -0.053 & -0.047 & -0.053 \\ -0.078 & 0.047 & 0.341 & -0.216 & -0.031 & 0.029 \\ 0.061 & -0.053 & -0.216 & 0.203 & -0.029 & 0.010 \\ -0.078 & -0.047 & -0.031 & -0.029 & 0.341 & 0.216 \\ -0.061 & -0.053 & 0.029 & 0.010 & 0.216 & 0.203 \end{pmatrix} \tag{3.34}$$

The eigenvalues (λ) of this matrix correspond to the squared angular frequencies (ω_i^2) and are

$$\lambda = \begin{pmatrix} 0.542 \\ 0.515 \\ 0.00976 \\ 0.000 \\ 0.000 \\ 0.000 \end{pmatrix}. \tag{3.35}$$

The eigenvalues are in the same units as the original elements (HT/bohr^2/amu). Converting these to SI-units and taking the square root gives us units of angular frequency (rad $\cdot$ s^{-1}). These

can be converted to vibrational frequency (in s^{-1} or Hz) by dividing by 2π. As the value of the vibrational frequency is typically in the order of 10^{12}, they are often given in THz.

The angular frequencies for the three strongest oscillators (i.e. the three largest eigenvalues) are

$$\omega_1 = 713 \cdot 10^{12} \text{ rad} \cdot \text{s}^{-1} \tag{3.36}$$
$$\omega_2 = 695 \cdot 10^{12} \text{ rad} \cdot \text{s}^{-1} \tag{3.37}$$
$$\omega_3 = 303 \cdot 10^{12} \text{ rad} \cdot \text{s}^{-1}. \tag{3.38}$$

The corresponding ordinary frequencies are ($\nu = \frac{\omega}{2\pi}$)

$$\nu_1 = 114 \text{ THz} \tag{3.39}$$
$$\nu_2 = 111 \text{ THz} \tag{3.40}$$
$$\nu_3 = 48.1 \text{ THz}. \tag{3.41}$$

Vibrational frequencies can be probed using infrared (IR) spectroscopy. Herein, the oscillator strength is typically given in wavenumbers ($\overline{\nu}$)in cm^{-1}, which we can obtain by multiplying the vibrational frequency ν by the conversion factor 33.35641.[20] For our H_2O example, this gives the following wavenumbers

$$\overline{\nu}_1 = 3772 \text{ cm}^{-1} \tag{3.42}$$
$$\overline{\nu}_2 = 3674 \text{ cm}^{-1} \tag{3.43}$$
$$\overline{\nu}_3 = 1601 \text{ cm}^{-1}. \tag{3.44}$$

Besides the oscillator strength, we can also obtain the eigen*vectors* corresponding to the eigenvalues. These eigenvectors pertain to the normal modes. The three eigenvectors for the three strongest oscillators are

$$\vec{v}_1 = \begin{pmatrix} -0.267 \\ 0.000 \\ 0.535 \\ -0.422 \\ 0.535 \\ 0.422 \end{pmatrix},$$
$$\vec{v}_2 = \begin{pmatrix} 0.000 \\ -0.195 \\ -0.574 \\ 0.390 \\ 0.574 \\ 0.390 \end{pmatrix}, \tag{3.45}$$
$$\vec{v}_3 = \begin{pmatrix} 0.000 \\ 0.270 \\ -0.414 \\ -0.541 \\ 0.414 \\ -0.541 \end{pmatrix}.$$

[20] We leave it as an exercise to the reader to derive this conversion factor.

A schematic depiction of the three vibrational modes is given in Figure 3.8. The strongest two oscillators correspond to the asymmetric and symmetric stretch. The weakest oscillator of the three is the bending mode.

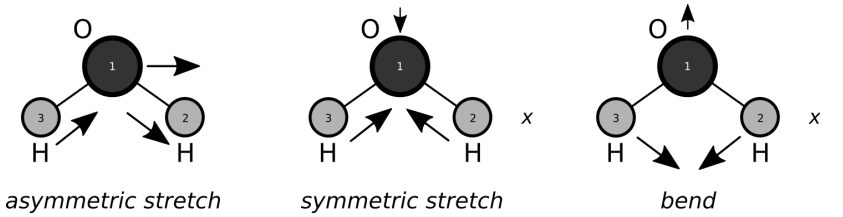


Figure 3.8: *The three vibrational modes of the H_2O molecule.*

In summary, in this section we have introduced the concept of the potential energy surface and a number of mathematical techniques how we can describe such a surface. Local minima on the PES correspond to stable states of the molecules. In order to assess whether a critical point on the PES is a local minimum, we can perform a frequency analysis. If all non-zero eigenvalues of the mass-weighted Hessian are positive, the critical point corresponds to a local minimum. If one or more eigenvalues are negative, the point is a saddle point or transition state.

Practice your understanding

Exercises 3.1 and 3.2

3.2.4 The transition state

So far, we have seen that local minima on the potential energy surface (PES) correspond to stable molecular configurations. These minima represent equilibrium geometries, for which the potential energy increases when the nuclear coordinates are slightly perturbed. However, not all stationary points on the PES are minima. Between two neighboring local minima there typically exists another special kind of stationary point, located at the highest energy along the path of lowest possible energy connecting the two minima. Such a point is known as a **transition state**, or more generally, a **saddle point**.

From a mathematical point of view, a transition state is a *critical point* on the PES, meaning that the first derivatives of the potential energy with respect to all nuclear coordinates vanish:

$$\nabla V(\vec{r}_{\mathrm{TS}}) = 0, \tag{3.46}$$

where $\vec{r}_{\mathrm{TS}}$ denotes the position of the transition state on the PES. Whether this critical point corresponds to a minimum, a maximum, or a saddle point is determined by the curvature of the PES in the vicinity of $\vec{r}_{\mathrm{TS}}$, which is described by the Hessian matrix $\mathbf{H}(\vec{r}_{\mathrm{TS}})$.

At a transition state, the Hessian matrix has **exactly one negative eigenvalue**. This means that there is one direction in configuration space along which the potential energy decreases when the system is displaced away from the transition state. This direction is known as the **reaction coordinate**. Along all other directions, the curvature of the PES is positive, so the energy increases upon displacement. In this sense, the transition state is a maximum along the reaction coordinate, but a minimum with respect to all directions perpendicular to it.

Physically, the transition state represents the *energy barrier* that must be crossed for a chemical reaction to occur. In a one-dimensional reaction coordinate diagram, it appears as the peak separating two valleys corresponding to the reactant and product minima. The energy difference between the transition state and the reactant minimum is called the **activation energy** (ΔE_{act}):

$$\Delta E_{\mathrm{act}} = E_{\mathrm{TS}} - E_{\mathrm{reactants}}. \tag{3.47}$$

Within the harmonic approximation, introduced in Section 3.2.3, the curvature of the PES is directly related to the vibrational motion of the system. The eigenvalues of the mass-weighted Hessian correspond to the squared angular frequencies of the normal modes. A negative eigenvalue at the transition state therefore leads to an *imaginary vibrational frequency*. This reflects the fact that the transition state is not mechanically stable: even an infinitesimally small displacement along the reaction coordinate causes the system to move away from the transition state and descend the PES toward either the reactant or the product minimum. For this reason, the transition state represents a fleeting configuration that can only be located by imposing the condition that the forces vanish.

In practice, this property provides a simple and powerful computational criterion: a stationary structure that exhibits one and only one imaginary vibrational frequency is identified as a transition state.

These ideas are summarized in the following formal definition.

Definition (Transition State). A *transition state* is a first-order saddle point on the potential energy surface (PES). It is a stationary configuration $\vec{r}_{\mathrm{TS}}$ satisfying

$$\nabla V(\vec{r}_{\mathrm{TS}}) = 0,$$

for which the Hessian matrix has exactly one negative eigenvalue. Equivalently, within the harmonic approximation, the vibrational spectrum of a transition state contains one and only one imaginary frequency.
The corresponding eigenmode defines the reaction coordinate and points along the *minimum energy path* connecting two adjacent local minima corresponding to the reactant and product states. All remaining normal modes have real frequencies and describe stable vibrations orthogonal to the reaction pathway.

The transition state thus forms the bottleneck along the minimum energy path and plays a central role in determining reaction rates. The quantitative connection between the properties of the transition state and the rate of a chemical reaction will be developed in Section 4.2, which introduces transition state theory.

3.3 Molecular partition functions

In the previous sections, we introduced the concept of the potential energy surface (PES) and discussed how its local curvature around a minimum defines the **normal modes** of vibration of a molecule. Each normal mode represents an independent, quantized motion of the nuclei about the equilibrium geometry. The frequencies of these normal modes are obtained from the eigenvalues of the mass-weighted Hessian matrix $\mathbf{H}$. As such, the PES not only determines the equilibrium structure of a molecule but also the spectrum of possible vibrational energy levels.

These normal modes, together with the translational and rotational degrees of freedom that correspond to zero eigenvalues of $\mathbf{H}$, form the basis for constructing the **molecular partition function**. Each type of motion, translation, rotation, and vibration, contributes independently to the total partition function of a molecule. In other words, the curvature of the PES defines the quantized energy levels associated with these motions, and the statistical distribution of molecules among these levels gives rise to the thermodynamic properties of the system.

With this connection established between the PES and the quantized energy levels of a molecule, we can now evaluate the partition function for a *single* molecule. Once the partition function of a molecule is known, many important thermodynamic properties can be readily calculated.

Energies must always be defined with respect to a reference state.[21] Several conventions are commonly used. One approach defines all energies with respect to the separated atoms

[21] There is no such thing as an absolute energy.

($\vec{r} \to \infty$) at rest, while another defines the zero of energy relative to the electronic ground state of the molecule. The different choices are illustrated in Figure 3.9. In this figure, the zero of energy corresponds to the situation where the atoms are infinitely far apart and at rest. An alternative reference is the depth of the potential well, denoted by D_e. Although the choice of the zero of energy affects the absolute form of the energy expressions and hence the mathematical form of the partition functions, it has no influence on the resulting thermodynamic quantities (such as equilibrium constants) as long as the same energy reference is used consistently for all (sub)systems.

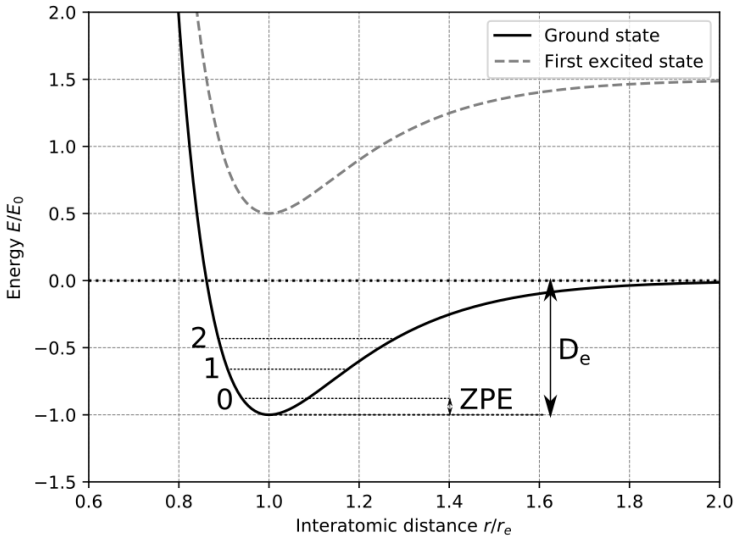


Figure 3.9: *Ground state (and first excited) state of the electronic energy E as function of the internuclear separation. E_0 refers to the energy of the electronic ground state and r_e to the equilibrium interatomic distance. A few vibrational energy levels are denoted.*

For the different energy terms that constitute the total molecular energy, we make the following assumptions

- The electronic energy is only a function of the positions of the nuclei.
- The molecule is allowed to move freely, i.e. without any change in its corresponding energy, inside a volume V and once the center of mass is outside of this box, we assume that the energy becomes infinite. In other words, the molecule can never leave the box.
- We assume rotational and vibrational motions to be decoupled. The rotational motion is considered to be that of a rigid, free rotator.
- Vibrational motions are considered to correspond to a set of simple harmonic oscillators as described by the normal modes.

Under these assumptions, the total molecular energy E_t is composed of the following series of energy terms, each corresponding to *independent* subsystems, as given by

$$E_{\mathrm{t}} = E_{\mathrm{trans}} + E_{\mathrm{rot}} + E_{\mathrm{vib}} + E_{\mathrm{el}} + E_{\mathrm{nuc}}, \tag{3.48}$$

where E_{trans}, E_{rot}, E_{vib}, E_{el}, and E_{nuc} are the translational, rotational, vibrational, electronic and nuclear energies, respectively. The translational, rotational, vibrational, electronic and nuclear energies can each be associated to a partition function by which we obtain translational, rotational, vibrational, nuclear and electronic partition functions, by means of the following (general) equation

$$q_k = \sum_i \exp\left(\frac{-E_i^k}{k_{\mathrm{B}}T}\right), \tag{3.49}$$

where k can be any of the above mentioned types. The total molecular partition function q_{mol} can be calculated using Equation 2.109 which gives

$$q_{\mathrm{mol}} = \prod_i q_i = q_{\mathrm{trans}} q_{\mathrm{rot}} q_{\mathrm{vib}} q_{\mathrm{elec}} q_{\mathrm{nuc}}. \tag{3.50}$$

For the partition function of an ensemble of N molecules, we have to divide by the factor $1/N!$ to account for the indistinguishability of the molecules, which gives

$$Q = \frac{1}{N!} q_{\mathrm{mol}}^N, \tag{3.51}$$

where Q is the partition function for an ensemble of N identical molecules and q_{mol} the total molecular partition function.[22]

3.4 Electronic and nuclear partition functions

For the construction of the molecular partition function, we can neglect the contribution of the excited states of the nuclear and electronic subsystems. As the energy difference between excited *nuclear* states and the nuclear ground state is extremely large, for almost all terrestrial purposes (i.e. 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, corresponding to

$$q_{\mathrm{nuc}} = 1 \tag{3.52}$$

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

$$q_{\mathrm{elec}} = \omega_{e,0} \exp\left(\frac{D_e}{k_{\mathrm{B}}T}\right), \tag{3.53}$$

[22] Sometimes a capital Q is used to distinguish the partition function pertaining to an ensemble versus the partition function of a single species or a single subsystem. In other cases, subscripted labels will be used to indicate the meaning. It should be clear from the context what is exactly meant.

where $\omega_{e,0}$ is the degeneracy of the electronic ground state and D_e is depth of the potential energy well (as shown in Figure 3.9).[23] For most molecules, $\omega_{e,0} = 1$. A notable exception is for instance O_2, which has a degenerate ground state. If we express the electronic partition function however with respect to the depth of the energy well, it simplifies to

$$q_{\text{elec}} = \omega_{e,0}. \tag{3.54}$$

3.5 Translational partition function

The translational partition function corresponds to the number of energy states associated with the movement of the center of mass of the molecule. Herein, we assume that the molecule exists within a volume defined by a rectangular box of dimensions $a \times b \times c$ wherein the potential energy of the molecule does not change and wherein interactions with other molecules or atoms are being neglected. This corresponds to the quantum mechanical textbook problem[24] of a particle in a three-dimensional box of which the solutions are known to be

$$E_{p,r,s} = \frac{h^2}{8m}\left(\frac{p^2}{a^2} + \frac{r^2}{b^2} + \frac{s^2}{c^2}\right), \tag{3.55}$$

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

$$q_{\text{trans}} = q_x q_y q_z = \sum_p e^{-E_x(p)/k_{\text{B}}T} \sum_r e^{-E_y(r)/k_{\text{B}}T} \sum_s e^{-E_z(s)/k_{\text{B}}T} \tag{3.56}$$

Combining the two Equations 3.55 and 3.56 yields

$$q_{\text{trans}} = \sum_{p=1} e^{-Ap^2} \sum_{r=1} e^{-Br^2} \sum_{s=1} e^{-Cs^2} \tag{3.57}$$

where A, B, C are

$$A = \frac{h^2}{8ma^2k_{\text{B}}T} \tag{3.58}$$

$$B = \frac{h^2}{8mb^2k_{\text{B}}T} \tag{3.59}$$

$$C = \frac{h^2}{8mc^2k_{\text{B}}T} \tag{3.60}$$

We can replace the sum in Equation 3.57 by an integral if, in passing from one energy level to the next higher level, $\Delta E \ll k_{\text{B}}T$, for in this case the summand will change its value essentially continuously with as function of p, r and q. We then obtain

$$q_{\text{trans}} = \int_0^\infty e^{-Ap^2}\,dp \int_0^\infty e^{-Br^2}\,dr \int_0^\infty e^{-Cs^2}\,ds. \tag{3.61}$$

By applying the standard integral

[23] Note that D_e corresponds to the electronic binding energy for polyatomic molecules.
[24] See for instance *Introduction to Quantum Mechanics* of Griffiths.

$$I = \int_0^\infty e^{-cz^2}\, dz = \frac{1}{2}\left(\frac{\pi}{c}\right)^{\frac{1}{2}} \tag{3.62}$$

the expression for the translational partition function becomes

$$q_{\text{trans}} = \frac{(2\pi m k_{\text{B}} T)^{\frac{3}{2}}\, abc}{h^3} = \frac{(2\pi m k_{\text{B}} T)^{\frac{3}{2}}\, V}{h^3}. \tag{3.63}$$

The above formula corresponds to the three-dimensional translational partition function. As the energy levels for translation in one direction are independent of the energy levels for translation in any of the two other direction (if they are orthogonal to each other and to the first direction), we can define the partition functions for one translational degree of freedom as shown in Equation 3.64.

$$\boxed{q_{\text{trans}} = \frac{L\sqrt{2\pi m k_{\text{B}} T}}{h}} \tag{3.64}$$

3.5.1 Thermodynamic properties

Mono-atomic gases only have translational degrees of freedom.[25] Thus, we can readily calculate the average energy (Equation 2.67) and heat capacity (Equation 2.68) of a mono-atomic gas. The total energy of a mono-atomic gas is given by[26]

$$\langle E\rangle = k_{\text{B}} T^2 \frac{\partial \ln q}{\partial T} \tag{3.65}$$

$$= k_{\text{B}} T^2 \frac{\partial \ln\left(\frac{1}{N!}\left(\frac{(2\pi m k_{\text{B}} T)^{\frac{3}{2}} V}{h^3}\right)^N\right)}{\partial T}. \tag{3.66}$$

$$= N k_{\text{B}} T^2 \frac{\partial \ln\left(\frac{(2\pi m k_{\text{B}} T)^{\frac{3}{2}} V}{h^3}\right)}{\partial T}. \tag{3.67}$$

$$= \frac{3}{2} N k_{\text{B}} T. \tag{3.68}$$

or simply

$$\langle E\rangle = \frac{3}{2} k_{\text{B}} T, \tag{3.69}$$

per atom.
From this, we can calculate the heat capacity as

$$C_v = \frac{\partial \langle E\rangle}{\partial T} = \frac{3}{2} k_{\text{B}}, \tag{3.70}$$

[25] Recall that we cannot rotate around a point particle, so there are no rotational degrees of freedom. Furthermore, there are no chemical bonds in atoms, so there are no vibrational degrees of freedom either.

[26] Recall that atoms are indistinguishable particles, so we have to apply Equation 2.112 to get the partition function of the full ensemble (i.e. many atoms).

which for one mole of gas results in

$$C_{v,m} = \frac{3}{2} k_B N_a = \frac{3}{2} R = 12.47 \text{ J/mol/K}. \tag{3.71}$$

We can readily compare this result with the molar heat capacities of gases such as Ar, He, and Kr, which have values of 12.55, 12.64, and 12.48 J/mol/K, respectively.

3.6 Rotational partition function

For the construction of the rotational partition function, we differentiate between diatomic (and linear) molecules and the more general situation of polyatomic molecules.

3.6.1 Diatomic molecules

The rotational energy for a diatomic molecule is given by

$$E_{\text{rot}(J)} = \frac{J(J+1)h^2}{8\pi^2 I} \tag{3.72}$$

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 center of mass of the molecule. As the energy level $E_{\text{rot}(J)}$ is degenerate with degeneracy $g_{\text{rot}} = 2J + 1$, the rotational partition function is

$$q_{\text{rot}} = \sum_{J=0}^{\infty} (2J+1) \exp\left(\frac{-J(J+1)h^2}{8\pi^2 I k_B T}\right). \tag{3.73}$$

In Figure 3.10, the contribution of rotational energy level J to the total rotational partition function for a N_2 molecule at room temperature is shown. The contributions pass through a maximum as the population decreases exponentially while the degeneracy increases linearly.

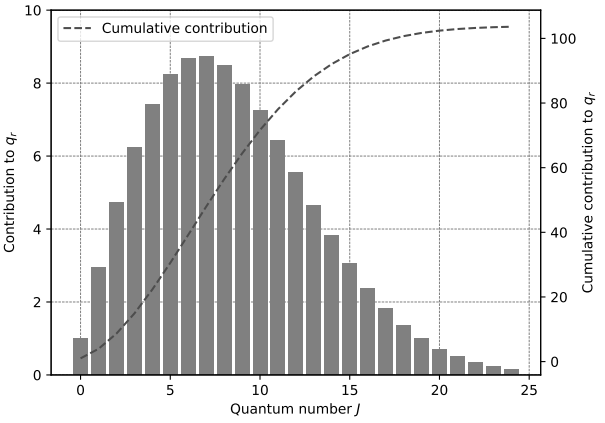


Figure 3.10: *Contribution of rotational energy level J to the total rotational partition function for a N_2 molecule at room temperature. The vibrational temperature of N_2 is 2.88 K.*

Similar to the derivation of the translational partition function, we replace the sum over states by an integral, thus obtaining

$$q_{\text{rot}} = \int_0^\infty (2J+1) \exp\left(\frac{-J(J+1)h^2}{8\pi^2 I k_{\text{B}} T}\right) dJ \tag{3.74}$$

yielding

$$q_{\text{rot}} = \frac{8\pi^2 I k_{\text{B}} T}{h^2}, \tag{3.75}$$

wherein I is the moment of inertia about the center of mass as defined as

$$I = \frac{\sum_i m_i r_i^2}{\sum_i m_i}. \tag{3.76}$$

Equation 3.75 is derived for a **diatomic molecule**.[27] In that case, the moment of inertia can be further simplified to

$$I_{\text{diatomic}} = \frac{m_1 m_2 R^2}{m_1 + m_2} = \mu R^2, \tag{3.77}$$

wherein R is the interatomic distance between atoms 1 and 2 and μ is called the **reduced mass** and is defined as

$$\mu = \frac{m_1 m_2}{m_1 + m_2}. \tag{3.78}$$

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

$$\Theta_{\text{rot}} = \frac{h^2}{8\pi^2 I k_{\text{B}}} \tag{3.79}$$

which turns Equation 3.75 into

$$q_{\text{rot}} = \frac{T}{\Theta_{\text{rot}}} \tag{3.80}$$

For a homonuclear diatomic molecule, rotating the molecule by 180 degrees brings the molecule into a configuration which is *indistinguishable* from the original configuration. This leads to an overcounting of the accessible states, hence we need to correct this by introducing a correction factor σ which is termed the symmetry number.[28] The symmetry number corresponds to the number of distinct ways by which a molecule can be brought into identical configuration by a rotation. For a homonuclear diatomic molecule (e.g. H_2, N_2, O_2, the symmetry numbers equals $\sigma = 2$, whereas for a heteronuclear diatomic molecule (e.g. CO, NO, CN), $\sigma = 1$ as given by

$$\sigma = \begin{cases} 2 \text{ for homonuclear diatomic molecules} \\ 1 \text{ for heteronuclear diatomic molecules} \end{cases} \tag{3.81}$$

[27] Please note that Equation 3.75 contains both rotational degrees of freedom.

[28] A detailed explanation of the origin of the symmetry number and the calculation of its value is provided in section 3.6.2 on page 144.

Thus, the final result becomes

$$\boxed{q_{\text{rot,diatom}} = \frac{8\pi^2 I k_B T}{\sigma h^2}} \tag{3.82}$$

Note that the above formula is only valid at sufficiently high temperature, i.e. $T \gg \Theta_{\text{rot}}$. If this is not the case, you can use the following formula

$$\boxed{q_{\text{rot,diatom}} = \frac{T}{\Theta_{\text{rot}}}\left(1 + \frac{\Theta_{\text{rot}}}{3T} + \cdots\right).} \tag{3.83}$$

or use Equation 3.73 explicitly, but limit the number of terms.

3.6.2 Polyatomic molecules

To derive the rotational partition function for a polyatomic molecule, we first have to evaluate its principal moments of inertia I_A, I_B and I_C. A rather elegant way of describing the principal moments of inertia is as follows.[29] Locate the center of mass of the equilibrium configuration of the molecule. Next, consider any straight line passing through the center of mass. A moment of inertia can be calculated about this line: $I = \sum_i m_i d_i^2$, where d_i is the perpendicular distance of the mass m_i from the line. On this line, mark off a distance on both sides of the center of mass proportional to $I^{-1/2}$ calculated about the line. Now choose other lines through the center of mass and on each of these lines mark off distances proportional to $I^{-1/2}$ about the line. The loci of the marks will form an ellipsoid, called the ellipsoid of inertia. The longest line corresponds to a principal axis of the ellipsoid, and the associated moment of inertia I is the smallest of the three principal moments. The shortest line likewise defines a principal axis, and its associated moment of inertia is the largest. The third principal moment of inertia corresponds to the axis perpendicular to the first two.

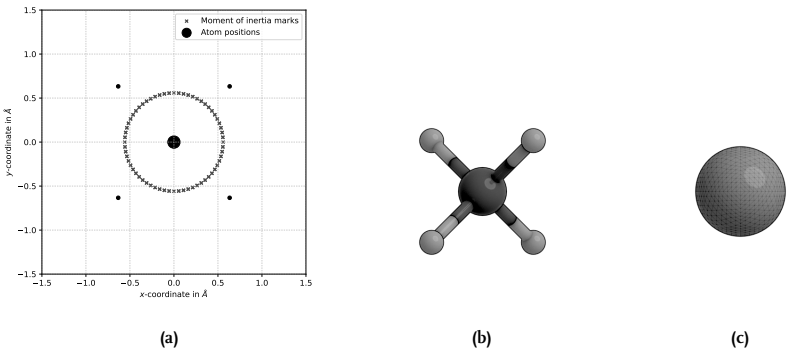


Figure 3.11: ***(a)*** *Atomic positions and moment of inertia marks of CH_4.* ***(b,c)*** *Three-dimensional render of the molecular configuration and the ellipsoid of inertia.*

In Figures 3.11, 3.12, and 3.13, this procedure is shown for methane, ammonia and caffeine. Different shapes of molecules give different ellipsoids of inertia. For a highly symmetrical

[29] See *An introduction to Statistical Thermodynamics* by Hill, Dover.

molecule such as methane, we obtain a sphere corresponding to three equal moments of inertia, whereas for low symmetrical molecule such as caffeine, we obtain an ellipsoid with three different moments of inertia.

The mathematical procedure for calculating the moments of inertia is as follows. Given the set of coordinates that defines the positions of the atoms, we first center the molecule around its center of mass. The center of mass for a polyatomic molecule is defined as the point for which the following identities hold.

$$\sum_i m_i x_i = \sum_i m_i y_i = \sum_i m_i z_i \tag{3.84}$$

Next, we construct the inertia tensor as given by

$$\mathbf{I} = \begin{pmatrix} I_{xx} & I_{xy} & I_{xz} \\ I_{xy} & I_{yy} & I_{yz} \\ I_{xz} & I_{yz} & I_{zz} \end{pmatrix}, \tag{3.85}$$

where

$$I_{xx} = \sum_i m_i \left(y_i^2 + z_i^2\right) \tag{3.86}$$

$$I_{yy} = \sum_i m_i \left(x_i^2 + z_i^2\right) \tag{3.87}$$

$$I_{zz} = \sum_i m_i \left(x_i^2 + y_i^2\right) \tag{3.88}$$

$$I_{xy} = -\sum_i m_i \left(x_i y_i\right) \tag{3.89}$$

$$I_{yz} = -\sum_i m_i \left(y_i z_i\right) \tag{3.90}$$

$$I_{xz} = -\sum_i m_i \left(x_i z_i\right) \tag{3.91}$$

To obtain the moments of inertia and the axes of inertia, we perform a matrix diagonalization procedure on the inertia tensor. The resulting eigenvalues correspond to the principal moments of inertia and the eigenvectors to the principal moments of inertia. For example, the three moments of inertia of methane each have a value of $I_A = I_B = I_C = 3.20$ amu Å^2. The moments of inertia for ammonia are $I_A = 1.73$ amu Å^2, $I_B = 1.73$ amu Å^2, and $I_C = 2.66$ amu Å^2. Two of the principal moments of inertia of ammonia thus have the same value. The moments of inertia for caffeine are $I_A = 479$ amu Å^2, $I_B = 722$ amu Å^2 and $I_C = 1192$ amu Å^2.

If all three moments of inertia are the same, the molecule is called a **spherical top**. If only two out of the three moments of inertia are the same, the molecule is a **symmetric top**. If all three moments of inertia are different, the molecule is an **asymmetric top**.

Once the principal moments of inertia are established, we can readily calculate the rotational partition function for a polyatomic molecule. Without any further derivation, the rotational partition function for a polyatomic molecule is given by

$$q_{\text{rot,asym}} = \frac{\sqrt{\pi}}{\sigma}\sqrt{\frac{8\pi^2 I_A k_B T}{h^2}}\sqrt{\frac{8\pi^2 I_B k_B T}{h^2}}\sqrt{\frac{8\pi^2 I_C k_B T}{h^2}} \tag{3.92}$$

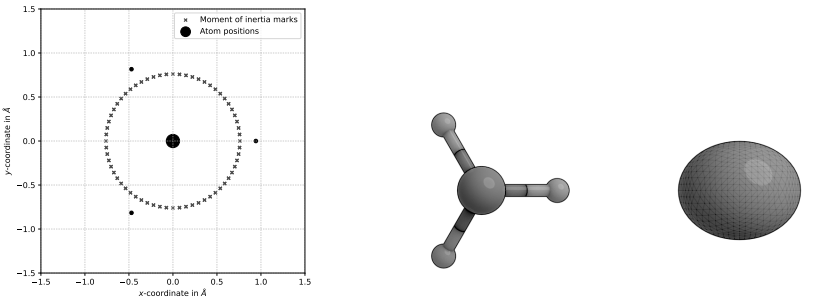


Figure 3.12: ***(a)*** *Atomic positions and moment of inertia marks of NH_3.* ***(b,c)*** *Three-dimensional render of the molecular configuration and the ellipsoid of inertia.*

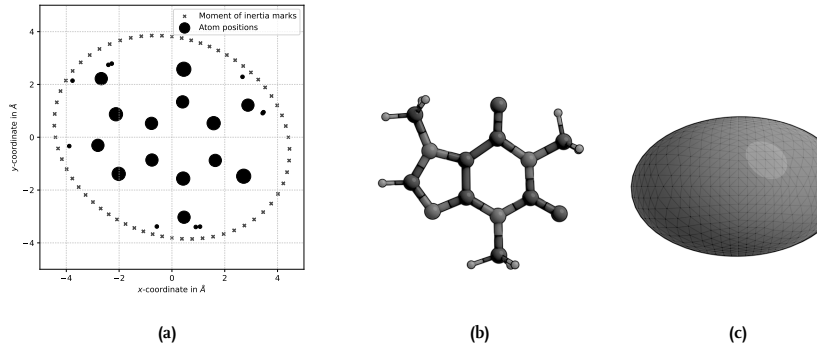


Figure 3.13: ***(a)*** *Atomic positions and moment of inertia marks of caffeine ($C_8H_{10}N_4O_2$).* ***(b,c)*** *Three-dimensional render of the molecular configuration and the ellipsoid of inertia. The moment of inertia marks and the ellipsoid have been scaled by a factor of 100.*

which can also be written as

$$q_{\text{rot,asym}} = \frac{\sqrt{\pi}}{\sigma}\sqrt{\frac{T^3}{\Theta_A\Theta_B\Theta_C}} \tag{3.93}$$

using Equation 3.79 for the rotational temperatures.

Symmetry number

Similar to the result obtained for the diatomic molecules, also for polyatomic molecules there is a symmetry number σ corresponding to the number of distinct ways the molecule can be rotated onto itself. The fundamental origin of the symmetry number relates to the number of forbidden rotational states due to symmetry constraints.[30] This is best explained using the (simple) example of $^{16}O_2$. Because the ^{16}O nucleus is a boson, its **total wave function** should be

[30] The explanation relates to that given in section 2.7.2 on page 100.

symmetrical under interchange of the two nuclei.[31] The total wave function is the *product* of the nuclear, electronic, rotational, vibrational and translational wave function as given by

$$\psi_{\text{total}} = \psi_{\text{nuc}} \times \psi_{\text{elec}} \times \psi_{\text{trans}} \times \psi_{\text{rot}} \times \psi_{\text{vib}}. \tag{3.94}$$

Under exchange of the nuclei, the electronic ground state for $^{16}O_2$ is odd[32], the nuclear spin wave function is even[33], the vibrational wave function is also even and the translational wave function only depends on the motion of the center of mass and therefore has no effect on the overall symmetry. Thus, in order for the total wave function for O_2 to be even, the rotational wave functions **have to be odd**. In other words, the even rotational wave functions are forbidden.

In the construction of the diatomic rotational partition function as provided in Equation 3.82, we integrated over all rotational levels, but for O_2, only half of the values of J are allowed (i.e. only the odd values). To correct for this, we have to divide by a factor of 2.[34]

For polyatomic molecules, the situation can be significantly more complicated because there can be more than two identical nuclei, the vibrational wave function are not necessarily all symmetrical and the rotational wave function are more complicated for polyatomic molecules.[35] Luckily, there is an easy way to calculate the symmetry number of a molecule by considering its point group. The symmetry number σ is then equal to the **number of rotational operators in the point group**. An overview of the σ value for common point groups is provided in Table 3.1

Table 3.1: *Rotational symmetry number σ of the most common point groups in chemistry. Table taken from reference [5].*

Point group	σ
C_1	1
C_s	1
C_2	2
C_{2v}	2
C_{3v}	3
$C_{\infty v}$	1
D_{2h}	4
D_{3h}	6
D_{5h}	10
$D_{\infty h}$	2
D_{3d}	6
T_d	12
O_h	24

Let us consider a couple of examples. Methane corresponds to the T_d point group and thus

[31] For fermions, e.g. ^1H, the nuclear wave function is antisymmetrical under exchange.

[32] This is actually a rare exception. Most diatomic molecules have the symmetric $^1\Sigma_g^+$ electronic ground state. O_2 however has the anti-symmetric $^3\Sigma_g^-$ ground state.

[33] Because it is composed of bosons.

[34] It has to be noted that at low temperature, this trick is only approximately correct as we are still including the inaccessible $J = 0$ state. Because at low temperature only a few rotational energy levels are populated, this leads to a relatively large error in the rotational partition function. Nevertheless, the classical approximation is in general quite good, especially at elevated temperature (i.e. above room temperature). The main exception here is H_2 below room temperature.

[35] In principle, one has to evaluate the correct nuclear degeneracy for each rovibrational state by the evaluation of the direct product between the permutation group symmetries of the rovibrational states and the nuclear spin wave functions.[4, 5]

has a symmetry number of 12. The water molecule with C_{2v} symmetry has a symmetry number of 2 and the methyl radical with the D_{3h} point group has a rotational symmetry number of 6.

3.6.3 Thermodynamic properties

From the rotational partition function, we can readily calculate the contribution of rotations to for instance the energy or the molar heat capacity using Equations 2.67 and 2.68. For a polyatomic molecule with three rotational degrees of freedom, these are[36]

$$\langle E_{\text{rot}} \rangle = \frac{3}{2} N k_{\text{B}} T \tag{3.95}$$

and

$$C_{v,\text{rot},m} = \frac{3}{2} N k_{\text{B}} = \frac{3}{2} R. \tag{3.96}$$

For a diatomic molecule, we obtain very similar results, which are

$$\langle E_{\text{rot}} \rangle = N k_{\text{B}} T \tag{3.97}$$

and

$$C_{v,\text{rot},m} = N k_{\text{B}} = R. \tag{3.98}$$

From these results, we can conclude that each rotational degree of freedom (similar to each translational degree of freedom), contributes $\frac{1}{2} N k_{\text{B}} T$ to the total energy and $\frac{1}{2} N k_{\text{B}}$ to the molar heat capacity.

3.7 Vibrational partition function

To obtain an expression for the vibrational partition function, we will first elaborate how the vibrational partition function is obtained for a diatomic molecule and continue to extend this result to polyatomic molecules.

3.7.1 Diatomic molecules

Let the equilibrium internuclear distance be r_e. Then according to Hooke's law, contraction or elongation of the interatomic distance results in an increase of the potential energy of the molecule as given by:

$$V = \frac{1}{2} k \left(r - r_e \right)^2 \tag{3.99}$$

where k is the force constant which can be calculated from the PES as shown in section 3.2.3. The variation of r with time is in classical mechanics the simple harmonic motion, for which the angular frequency ω is given by

$$\omega = \sqrt{\frac{k}{\mu}} \tag{3.100}$$

where μ is the reduced mass of the molecule, which for a diatomic molecule is given by

[36] We leave the derivation as an exercise to the reader.

$$\mu = \frac{m_A m_B}{m_A + m_B}, \tag{3.101}$$

wherein m_A and m_B are the masses of the two nuclei. The permitted vibrational energy levels are found, according to quantum mechanics, to be

$$E_{\text{vib}} = \left(i + \frac{1}{2}\right)\hbar\omega = \left(i + \frac{1}{2}\right)h\nu \tag{3.102}$$

where ω is the angular frequency in rad $\cdot$ s^{-1}, i is the vibrational quantum number which can have any non-negative integer value, $\hbar$ is Planck's constant divided by 2π and ν the vibrational frequency in s^{-1}. In Figure 3.14, the potential energy curves for CO and N_2 are given including the harmonic approximation of their vibrational mode. From the bottom two graphs in this figure, it can be seen that the harmonic approximation is a reasonable fit of the potential energy close to the equilibrium position. The gray lines in the harmonic approximation correspond to the first 25 vibrational energy levels. The stronger N-N bond as compared to the C-O bond is reflected by the steeper increase in the potential energy (and thus a larger force constant) as well as by the greater distance between the vibrational energy levels for N_2 as compared to CO.

The above energy levels are defined with respect to the electronic ground state. The energy difference between the electronic ground state and the lowest vibrational state is termed the zero point energy[37] and is given by

$$E_{\text{zpe}} = \frac{\hbar\omega}{2}. \tag{3.103}$$

If we express the vibrational energy levels with respect to the lowest vibrational energy level, we can omit the term $\frac{1}{2}$ in the value for the vibrational energy E_{vib} by which we obtain

$$E_{\text{vib}} = i\hbar\omega = ih\nu, \tag{3.104}$$

hence the partition function for a diatomic molecule is

$$q_{\text{vib}} = \sum_{i=0}^{\infty} \exp\left(-ih\nu/k_{\text{B}}T\right). \tag{3.105}$$

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

$$\exp\left(-ih\nu/k_{\text{B}}T\right) = x^i \tag{3.106}$$

and Equation 3.105 can be written as

$$q_{\text{vib}} = \sum_{i=0}^{\infty} x^i = 1 + x + x^2 + x^3 + x^4 + \cdots \tag{3.107}$$

This type of an infinite series is known as the geometric series[38], which converges to

[37] The reason why the lowest vibrational state lies E_{zpe} above the electronic ground state has its origins in quantum mechanics. If the lowest vibrational state would be at the electronic ground state, this would imply that its momentum is zero and that the uncertainty of measuring both the position and momentum is also zero. This is a direct violation of the Heisenberg uncertainty principle, which states that $\Delta x \Delta p \geq \hbar/2$.

[38] See Appendix B.5 on page 279.

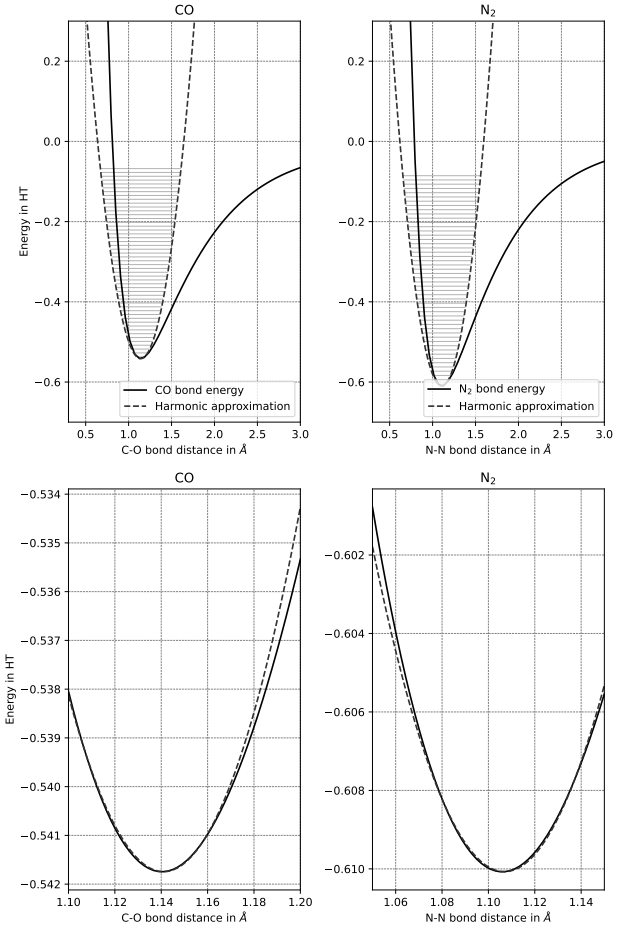


Figure 3.14: *(top) The potential energy curve of CO and N_2 and the first 25 vibrational energy levels under the harmonic approximation. (bottom) Close-up of the potential energy curve and the harmonic approximation around the equilibrium position.*

$$q_{\text{vib}} = \frac{1}{1 - \exp\left(-h\nu/k_{\text{B}}T\right)} \tag{3.108}$$

The quantity $h\nu/k_{\text{B}}$ 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

$$\boxed{q_{\text{vib}} = \frac{1}{1 - \exp\left(-\Theta/T\right)}} \tag{3.109}$$

or with respect to the electronic ground state as

$$q_{\text{vib}} = \frac{\exp\left(-\frac{1}{2}\Theta/T\right)}{1-\exp\left(-\Theta/T\right)}. \tag{3.110}$$

Practice your understanding

Exercise 3.3

3.7.2 Polyatomic molecules

The question that now arises is how to define Equation 3.109 for a polyatomic molecule. For any given (non-linear) polyatomic molecule with a fixed center of mass, $n = 3N - 6$ independent coordinates can be given for the relative position of each atom with respect to one another, where N is the number of atoms within the molecule.[39] Similar to how the three-dimensional translational partition functions can be decomposed into three independent one-dimensional partition functions (with orthogonal translational directions), we would like to decompose the molecule into a set of independent vibrational modes. As demonstrated in section 3.2.3, this is possible by the construction of the normal modes, which are defined as independent, synchronous motions of atoms that may be excited without leading to the excitation of any of the other normal modes. Within this framework, the contribution to the potential energy of one normal mode is independent of the other normal modes by which we can express the total potential energy as the following sum

$$V = V_1 + V_2 + V_3 + \cdots + V_{3N-6} = \sum_{i=1}^{3N-6} V_i. \tag{3.111}$$

The normal modes are constructed by a change of basis, wherein we can express the contribution to the potential energy of a single normal mode by

$$V_i = \frac{1}{2} k_i \left(q_i - q_i^0\right)^2 \tag{3.112}$$

wherein k_i is the force constant of the normal mode, q_i is a coordinate in the new basis, and q_i^0 the equilibrium value of q_i.

Coordinates q_i chosen in such a way that Equations 3.111 and 3.112 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 3.104. Considering that we are dealing with $n = 3N - 6$ normal modes for a given polyatomic molecule, we can rewrite Equation 3.109 for the full vibrational partition function as:

$$q_{\text{vib}} = \prod_{i}^{3N-6} \frac{1}{1-\exp\left(-\Theta/T\right)} \tag{3.113}$$

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

[39] For a linear molecule we obtain $n = 3N - 5$ independent coordinates.

$$q_{\text{vib},i} = \frac{1}{1 - \exp\left(-h\nu_i/k_\text{B}T\right)}, \tag{3.114}$$

which is essentially the same formula as given for the vibrational partition function of a diatomic molecule. Equation 3.114 is defined with respect to the zero point energy state. With respect to the electronic ground state, we have to correct the partition function by a factor $\exp\left(-\frac{1}{2}h\nu/k_\text{B}T\right)$, which gives:

$$q_{\text{vib},i} = \frac{\exp\left(-\frac{1}{2}h\nu_i/k_\text{B}T\right)}{1 - \exp\left(-h\nu_i/k_\text{B}T\right)} \tag{3.115}$$

3.7.3 Thermodynamic properties

Using the expressions for the vibrational partition function, we can readily derive expressions for important thermodynamic properties. The contributions to the total energy for a non-linear polyatomic molecule by the vibrational partition function, with respect to **all atoms at infinite distance and at rest**, is given by[40]

$$\langle E_\text{vib}\rangle = Nk_\text{B}T \sum_{i=1}^{3N'-6} \left(\frac{h\nu_i}{2k_\text{B}T} + \frac{h\nu_i/k_\text{B}T}{\left(\exp\left(h\nu_i/k_\text{B}T\right) - 1\right)} \right) \tag{3.116}$$

and the contributions to the the molar heat capacity are[41]

$$C_{v,\text{vib},m} = R \sum_{i=1}^{3N'-6} \left(\frac{h\nu_i}{k_\text{B}T}\right)^2 \frac{\exp\left(h\nu_i/k_\text{B}T\right)}{\left(\exp\left(h\nu_i/k_\text{B}T\right) - 1\right)^2}. \tag{3.117}$$

Thus, the total energy from all contributions (i.e. translational, rotational and vibrational) is

$$\langle E\rangle = Nk_\text{B}T \left[\frac{3}{2} + \frac{3}{2} + \sum_{i=1}^{3N'-6} \left(\frac{h\nu_i}{2k_\text{B}T} + \frac{h\nu_i/k_\text{B}T}{\left(\exp\left(h\nu_i/k_\text{B}T\right) - 1\right)} \right) \right] - D_e, \tag{3.118}$$

where D_e is the bonding energy of the molecule.[42] The molar heat capacity from all contributions is

$$C_{v,m} = R \left[\frac{3}{2} + \frac{3}{2} + \sum_{i=1}^{3N'-6} \left(\frac{h\nu_i}{k_\text{B}T}\right)^2 \frac{\exp\left(h\nu_i/k_\text{B}T\right)}{\left(\exp\left(h\nu_i/k_\text{B}T\right) - 1\right)^2} \right]. \tag{3.119}$$

[40] Note that N refers to the total number of molecules and N' (note the prime) refers to the number of atoms within the molecule.

[41] Observe that when calculating *molar* properties that the Nk_B term is replaced for the gas constant R.

[42] This is a positive number for a stable complex. It corresponds to the depth of the potential well on the potential energy surface with respect to the atoms at infinite distance.

For a diatomic molecule, the above equations simplify to

$$\langle E \rangle = N k_\mathrm{B} T \left[\frac{3}{2} + \frac{2}{2} + \left(\frac{h\nu}{2k_\mathrm{B}T} + \frac{h\nu/k_\mathrm{B}T}{\left(\exp\left(h\nu/k_\mathrm{B}T\right) - 1\right)} \right) \right] - D_e, \tag{3.120}$$

and

$$C_{v,m} = R \left[\frac{3}{2} + \frac{2}{2} + \left(\frac{h\nu}{k_\mathrm{B}T} \right)^2 \frac{\exp\left(h\nu/k_\mathrm{B}T\right)}{\left(\exp\left(h\nu/k_\mathrm{B}T\right) - 1\right)^2} \right], \tag{3.121}$$

as a diatomic molecule only has two rotational degrees of freedom and one vibrational degree of freedom.

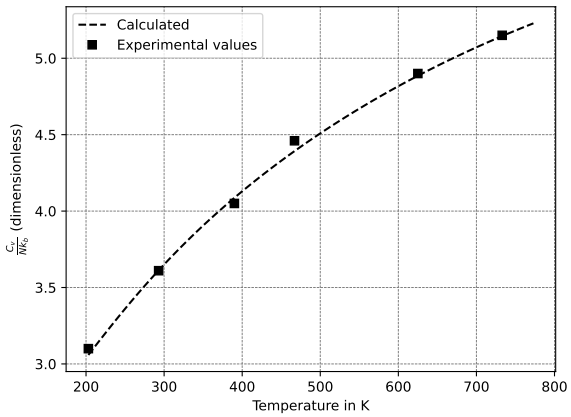


Figure 3.15: *Heat capacity of N_2O as function of temperature. Note that the thermodynamic calculation matches the experimental results quite well.*

Let us compare how Equation 3.119 holds up to experiment. Consider the N_2O molecule, which is a polyatomic linear molecule. It has three translational, two rotational and four vibrational degrees of freedom. The heat capacity of a di- and polyatomic molecule depends on temperature only due to the vibrational degrees of freedom. The contributions to the heat capacity of the translational and rotational degrees of freedom equal $\frac{5}{2}Nk_\mathrm{B}$. For the vibrational contributions, vibrational temperatures of Θ_i of 850, 850, 1840 and 3200 K are used.[43] In Figure 3.15, the calculated heat capacity is compared against experimental values. From this Figure, it can be seen that the computed values are in close agreement with the experiment.

3.8 Final remarks

In this chapter, the molecular partition functions commonly seen in chemical systems were derived. In the next chapter, we will employ these concepts in the derivation of transition state theory. Furthermore, in the chapter thereafter, the molecular partition functions will be used

[43] Note that two of the four vibrational temperatures have the same value, this is not a mistake.

to construct specific expressions for the reaction rate constants in various elementary reaction steps.

Practice your understanding

Exercises 3.4 and 3.5

Challenges

Exercise 3.6 and 3.7

3.9 Exercises

The answers to the exercises can be found at the end of this Chapter on page 156. The exercises are marked by a number of gears to indicate their difficulty levels.

EXERCISE 3.1

The Morse potential is a relatively simple interatomic interaction model for the potential energy of a diatomic molecule. Using the Morse potential, one could build the potential energy curve of a diatomic molecule.

The Morse potential is given by

$$V(r) = D_e \left(1 - \exp\left(-\alpha\left(r - r_e\right)\right)\right)^2, \tag{3.122}$$

where r is the distance between the atoms, r_e the equilibrium distance between the atoms, D_e the well depth and α a parameter that controls the 'width' of the potential.

a) Show that the first derivative of the potential equals zero when $r = r_e$.

b) Calculate the force constant at the equilibrium position of the potential as a function of D_e and α.

c) The Morse potential values for HCl are $D_e = 43291$ cm^{-1} and $\alpha = 1.7314$Å^{-1}. Calculate the vibrational frequency ν in THz and the wavenumber $\overline{\nu}$ of the H-Cl stretching vibration.

Hint: Think about how wavenumbers ($\overline{\nu}$, typically expressed in cm^{-1}) are related to the energy of a wave. Recall that energy (E) can be expressed using the relation

$$E = hc\overline{\nu}, \tag{3.123}$$

where h is Planck's constant and c is the speed of light. This connection hints at how wavenumbers inherently reflect the energy of photons.

d) How does the wavenumber change when you swap the hydrogen atom for a deuterium atom?

EXERCISE 3.2

In Figure 3.5a on page 126, the potential energy surface of hydroxyformaldoxime is drawn as a function of two bond angles.

a) Identify the four local minima on the potential energy surface.

b) Schematically draw the four stable isomers of hydroxyformaldoxime and indicate their positions on the potential energy surface.

c) Draw a path on the potential energy surface that connects the two local minima at the top and bottom left on the potential energy surface. The path has to be constructed in such a fashion that is as low in energy as possible. This path is termed the minimum energy pathway. Indicate the highest point in this path.

d) Schematically draw the potential energy **curve** corresponding to this path. In other words, place the progress along this path on the x-axis and the potential energy on the y-axis.

e) What is the highest point on the potential energy curve called? What would the corresponding structure look like?

f) Determine the energy difference between the lowest and highest point on the potential energy curve. To what kinetic parameter does this value correspond?

EXERCISE 3.3

Calculate the molar fraction of the first four (vibrational) energy levels of Cl_2 at 200, 800, and 1000 K. Assume that Cl_2 has infinitely many vibrational energy levels, each separated by a vibrational temperature defined as $\Theta_{vib} = \frac{h\nu}{k_B} = 810$ K.

EXERCISE 3.4

a) Calculate the translational partition function of a N_2 molecule at $T = 298.15$ K and at $p = 1$ atm. Assume that N_2 can be treated as an ideal gas.

b) 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**.

c) Calculate the moment of inertia of N_2. Assume that the interatomic distance is 1.1069 Å.

d) Calculate the rotational partition function of N_2 at 298.15 K.

e) Calculate the total molecular partition function of N_2.

f) Calculate the molar heat capacity of N_2 at standard conditions.

EXERCISE 3.5

a) Derive the average energy ($\langle E \rangle$) for a mono-atomic ideal gas.

b) Derive the entropy for a mono-atomic ideal gas and substitute the temperature T in this expression for $U = \langle E \rangle$ as constructed in the previous subquestion. Show that the result corresponds to the Sackur-Tetrode equation.

$$\frac{S}{Nk_B} = \ln\left\{\frac{V}{N}\left(\frac{4\pi mU}{3h^2N}\right)^{\frac{3}{2}}\right\} + \frac{5}{2} \tag{3.124}$$

EXERCISE 3.6

a) Derive an expression for the entropy of a diatomic molecule based on its partition functions.

b) Calculate the value for the molar entropy of CO at standard conditions (T = 298.15 K and p = 1 atm). Use a rotational temperature $\Theta_r = 2.77$ K and a vibrational temperature $\Theta_v = 3070$ K. Compare your results to the experimentally obtained result of 197.9 J/mol/K.

EXERCISE 3.7

Equation 3.82 on page 142 works well in the case where $T \gg \Theta_{rot}$. For H_2 however, this is not the case and the explicit form as shown in Equation 3.73 on page 140 has to be used. Furthermore, in H_2, the spin states of the nuclei play a very important role. In this exercise, we will calculate the rotational contribution to the heat capacity of H_2 in the lower temperature limit and show its deviation from an ideal gas $C_{v,rot} = k_B$. We will first start by deriving the rotational contribution to the heat capacity for HD, which is somewhat simpler, after which we will derive it for H_2.

a) Insert Θ_{rot} into Equation 3.73.

b) Calculate the contribution of the rotations to the average (internal) energy E_{rot}. Use Equation 2.67 on page 93.

c) Calculate the contribution of the rotations to the heat capacity $C_{v,rot}$. Use Equation 2.68 on page 93.

d) The answer of the previous question looks quite complicated[44], but if you study it carefully, you will note that a lot of terms are actually the same. Use a spreadsheet program such as Excel and calculate the rotational contribution to the heat capacity as a function of the temperature. You do not have to take a lot of terms J for the answer to converge, about 30 terms should be sufficient.[45] The rotational temperature of HD is 64.0K.

e) The situation for H_2 is a bit more complicated, as H_2 has, because of its identical nuclei, two different forms known as *para*-hydrogen and *ortho*-hydrogen. Para-hydrogen has an antisymmetric (odd) nuclear wave function and ortho-hydrogen has a symmetric (even) nuclear wave function. The total wave function should be anti-symmetric as the two hydrogen atoms are fermions. Thus, for para-hydrogen, only the even rotational wave functions are allowed, whereas for ortho-hydrogen, only the odd rotational wave functions are allowed.[46] Furthermore, the ortho-hydrogen state is triple degenerate as the odd rotational wave functions are triple degenerate.

Calculate the rotational contribution to the heat capacity for para- and ortho-hydrogen. For para-hydrogen, only include the even terms in J (i.e. $J = 0, 2, \cdots$), while for ortho-hydrogen, only the odd terms in J (i.e. $J = 1, 3, 5, \cdots$) should be used.

[44] Feel free to peak at the solutions if you have trouble deriving it. I will not judge you.

[45] Bonus question: How many terms are required for convergence, e.g. up to the fourth decimal?

[46] Note that *odd* × *even* gives *odd*.

f) Finally calculate the rotational contribution to the heat capacity including both even and odd terms, but increase the weight of the odd terms by a factor of 3 to account for the triple degeneracy of the para-hydrogen state. Compare your results with a simple mixture of para- and ortho-hydrogen at a ratio of 1:3 using the results obtained in the previous subquestion. Why is there a significant difference between the two?

3.10 Solutions

The solutions below pertain to the exercises of Chapter 3 on page 153 and further.

SOLUTION 3.1

a) Taking the first derivative of the potential energy towards the internuclear distance, yields

$$\frac{\partial V}{\partial r} = 2D_e\alpha \cdot \exp\left(-\alpha\left(r - r_e\right)\right) \cdot \left(1 - \exp\left(-\alpha\left(r - r_e\right)\right)\right). \tag{3.125}$$

Filling out $r = r_e$ gives

$$\frac{\partial V}{\partial r}(r = r_e) = 2D_e\alpha \cdot 1 \cdot (1 - 1) = 0 \tag{3.126}$$

You would expect this result, as the equilibrium distance is a critical point on the potential energy curve.

b)

$$\frac{\partial^2 V}{\partial r^2} = 2\alpha^2 D_e \exp\left(-\alpha\left(r - r_e\right)\right)\left(2\exp\left(-\alpha\left(r - r_e\right)\right) - 1\right) \tag{3.127}$$

Filling out $r = r_e$ gives

$$\frac{\partial^2 V}{\partial r^2}(r = r_e) = 2\alpha^2 D_e \cdot 1 \cdot (2 - 1) = 2\alpha^2 D_e \tag{3.128}$$

c)

$$k = 2D_e\alpha^2 = 2 \cdot 43291 \cdot h \cdot c \cdot 100 \cdot \left(1.7314 \cdot 10^{10}\right)^2 = 515.6\text{N/m} \tag{3.129}$$

$$\mu = \frac{m_{\text{Cl}} \cdot m_{\text{H}}}{m_{\text{Cl}} + m_{\text{H}}} = 1.614 \cdot 10^{-27}\ \text{kg} \tag{3.130}$$

$$\nu = \frac{1}{2\pi}\sqrt{\frac{k}{\mu}} = 89.95\ \text{THz} \tag{3.131}$$

$$\overline{\nu} = \nu \cdot 10^{-2}/c = 3000\ \text{cm}^{-1} \tag{3.132}$$

d) The wavenumber scales roughly by a factor $1/\sqrt{2}$. Repeating the above calculation gives a value of $\overline{\nu} = 2150\text{cm}^{-1}$.

SOLUTION 3.2

a) The four minima correspond to the four darkly shaded areas on the PES. They are indicated by the arrows in Figure 3.16.

b) In Figure 3.16, a schematic depiction of the four configuration of hydroxyformaldoxime are given and their position on the PES is indicated.

c) The white dotted line in Figure 3.16 corresponds to the minimum energy pathway connecting the two stable states at the bottom left and top right of the PES. The highest point along this minimum energy pathway has been indicated by a circle.

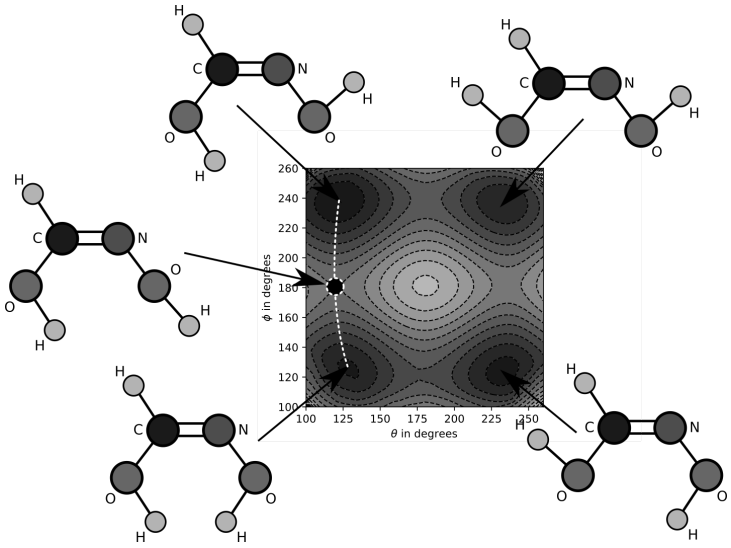


Figure 3.16: *The four local minima of hydroxyformaldoxime and one of the depicted transition states.*

d) The one-dimensional projection of the PES along the minimum energy pathway is shown in Figure 3.17.

e) The highest point along the minimum energy pathway is termed the transition state. In Figure 3.16, a schematic depiction of the transition structure is provided (center structure on the left).

f) The energetic difference is roughly 0.035 HT (which is about 90 kJ/mol). This energetic difference corresponds to the activation energy for crossing the reaction barrier.

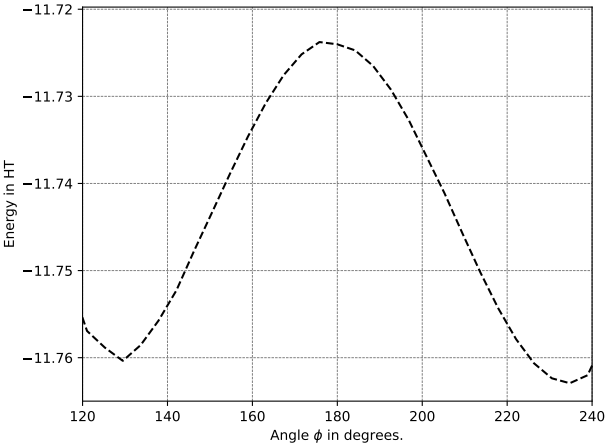


Figure 3.17: *Potential energy curve of hydroxyformaldoxime along the minimum energy path.*

SOLUTION 3.3

The partition function is given by[47]

$$q_{\mathrm{Cl}_2} = \sum_{j=0}^{\infty} \exp\left(-\frac{j\Theta_{\mathrm{vib}}}{T}\right) \tag{3.133}$$

$$= \frac{1}{1-\exp\left(-\Theta_{\mathrm{vib}}/T\right)} \tag{3.134}$$

The molar fraction of energy level i can then be calculated by

$$\eta_i = \frac{\exp\left(-\frac{i\Theta_{\mathrm{vib}}}{T}\right)}{q_{\mathrm{Cl}_2}} = \exp\left(-i\Theta_{\mathrm{vib}}/T\right) \cdot \left(1-\exp\left(-\Theta_{\mathrm{vib}}/T\right)\right) \tag{3.135}$$

which gives the results as presented in Table 3.2.

Table 3.2: *Molar fraction of energy level i as function of T.*

i/T	200 K	800 K	1000 K
0	0.9825	0.6367	0.5551
1	0.0171	0.2313	0.2470
2	0.0002	0.0840	0.1099
3	0.0000	0.0305	0.0489

[47] Similar to 2.5, we used the geometric series to evaluate the infinite sum.

SOLUTION 3.4

a) The translational partition function in three dimensions using the ideal gas law is:

$$q_{\mathrm{T}} = V\frac{(2\pi m k_{\mathrm{B}}T)^{3/2}}{h^3} \tag{3.136}$$

$$= \frac{k_{\mathrm{B}}T}{P}\frac{(2\pi m k_{\mathrm{B}}T)^{3/2}}{h^3} \tag{3.137}$$

Plugging in the values gives

$$q_{\mathrm{T}} = \frac{1.3806488\cdot 10^{-23}\ \mathrm{J\cdot K^{-1}}\cdot 298.15\ \mathrm{K}}{1.01325\cdot 10^{5}\ \mathrm{Pa}} \frac{\left(2\pi\cdot 28\cdot 10^{-3}\mathrm{kg}\ /\ \left(6.0221409\cdot 10^{23}\right)\cdot 1.3806488\cdot 10^{-23}\ \mathrm{J\cdot K^{-1}}\cdot 298.15\ \mathrm{K}\right)^{3/2}}{(6.62607004\cdot 10^{-34}\ \mathrm{m^2\cdot kg\cdot s^{-1}})^3} \tag{3.138}$$

$$= 5.8236\cdot 10^{6} \tag{3.139}$$

b)

$$q_{\mathrm{V}} = \frac{1}{1-\exp\left(-\frac{h\nu}{k_{\mathrm{B}}T}\right)} \tag{3.140}$$

$$= \frac{1}{1-\exp\left(-\frac{6.62607004\cdot 10^{-34}\ \mathrm{m^2\cdot kg\cdot s^{-1}}\cdot 299792458\cdot \mathrm{m\cdot s^{-1}}\cdot 233000\ \mathrm{m^{-1}}}{1.3806488\cdot 10^{-23}\ \mathrm{J\cdot K^{-1}}\cdot 298\ \mathrm{K}}\right)} \tag{3.141}$$

$$= 1.000013 \approx 1 \tag{3.142}$$

Note that the vibrational partition function under typical atmospheric conditions usually equals unity.

c) The moment of inertia is calculated by[48]

$$I = \mu r^2 \tag{3.143}$$

$$= \frac{m_1 m_2}{m_1+m_2}r^2 \tag{3.144}$$

$$= \frac{m}{2}r^2 \tag{3.145}$$

$$= \frac{14}{2}\cdot 10^{-3}\ \mathrm{kg}\ \cdot \left(6.0221409\cdot 10^{23}\right)^{-1}\cdot \left(1.1069\cdot 10^{-10}\mathrm{m}\right)^2 \tag{3.146}$$

$$= 1.424\cdot 10^{-46}\ \mathrm{kg\cdot m^2} \tag{3.147}$$

[48] Note that m represents the mass of a single nitrogen atom, not that of the dinitrogen molecule.

d) The rotational partition function is given by:

$$q_{\mathrm{R}} = \frac{8\pi^2 I k_{\mathrm{B}} T}{\sigma h^2} \tag{3.148}$$

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

$$q_{\mathrm{R}} = \frac{8\pi^2 \cdot 1.424 \cdot 10^{-46}\ \mathrm{kg \cdot m^2} \cdot 1.3806488 \cdot 10^{-23}\ \mathrm{J \cdot K^{-1}} \cdot 298.15\ \mathrm{K}}{2(6.62607004 \cdot 10^{-34}\ \mathrm{m^2 \cdot kg \cdot s^{-1}})^2} \tag{3.149}$$

$$= 52.71 \tag{3.150}$$

e)

$$Q = q_{\mathrm{T}} q_{\mathrm{V}} q_{\mathrm{R}} \tag{3.151}$$

$$= 5.8236 \cdot 10^6 \cdot 1.000013 \cdot 52.71 \tag{3.152}$$

$$= 3.070 \cdot 10^8 \tag{3.153}$$

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!

f) The heat capacity can be calculated using Equation 3.121 on page 151.

$$C_{v,m} = N k_{\mathrm{B}} \left[\frac{3}{2} + \frac{2}{2} + \left(\frac{h\nu}{k_{\mathrm{B}} T} \right)^2 \frac{\exp\left(h\nu / k_{\mathrm{B}} T\right)}{\left(\exp\left(h\nu / k_{\mathrm{B}} T\right) - 1\right)^2} \right] \tag{3.154}$$

$$= R \left[\frac{3}{2} + \frac{2}{2} + \left(\frac{h\nu}{k_{\mathrm{B}} T} \right)^2 \frac{\exp\left(h\nu / k_{\mathrm{B}} T\right)}{\left(\exp\left(h\nu / k_{\mathrm{B}} T\right) - 1\right)^2} \right] \tag{3.155}$$

$$= 20.80\ \mathrm{J/mol/K} \tag{3.156}$$

Perform the above calculations on repl.it:
https://repl.it/@ifilot/N2-partition-functions

SOLUTION 3.5

a) The average energy is given by

$$\langle E \rangle = k_{\mathrm{B}} T^2 \frac{\partial}{\partial T} \ln (Q) \tag{3.157}$$

$$\text{with } Q = \frac{q_T^N}{N!} \tag{3.158}$$

$$\text{and } q_T = \left(\frac{2\pi m k_{\mathrm{B}} T}{h^2} \right)^{\frac{3}{2}} V \tag{3.159}$$

Readily solving the derivative then yields

$$\langle E \rangle = k_{\mathrm{B}} T^2 \frac{\partial}{\partial T} \ln \left\{ \frac{3N}{2} \ln \left(\frac{2\pi m k_{\mathrm{B}} T}{h^2} \right) + \ln (V) - \ln(N!) \right\} \tag{3.160}$$

$$= k_{\mathrm{B}} T^2 \frac{\partial}{\partial T} \left\{ \frac{3}{2} N \ln (T) \right\} \tag{3.161}$$

$$= \frac{3}{2} N k_{\mathrm{B}} T \text{ or } \frac{3}{2} RT \text{ on a per mole basis.} \tag{3.162}$$

$$\tag{3.163}$$

b) The fundamental expression for the entropy is given by

$$S = \frac{\partial}{\partial T} \left\{ k_{\mathrm{B}} T \ln (Q) \right\} \tag{3.164}$$

$$= k_{\mathrm{B}} \ln (Q) + k_{\mathrm{B}} T \frac{\partial \ln (Q)}{\partial T} \tag{3.165}$$

Plugging in the relevant terms and recycling the answer of the previous subquestion readily yields

$$S = N k_{\mathrm{B}} \left\{ \frac{3}{2} \ln \left(\frac{2\pi m k_{\mathrm{B}} T}{h^2} \right) + \ln (V) - \ln (N) + 1 \right\} + \frac{3}{2} N k_{\mathrm{B}} \tag{3.166}$$

$$= N k_{\mathrm{B}} \left\{ \frac{3}{2} \ln \left(\frac{2\pi m k_{\mathrm{B}} T}{h^2} \right) + \ln (V) - \ln (N) + \frac{5}{2} \right\} \tag{3.167}$$

$$\frac{S}{N k_{\mathrm{B}}} = \ln \left(\frac{2\pi m k_{\mathrm{B}} T}{h^2} \right)^{\frac{3}{2}} + \ln (V) - \ln (N) + \frac{5}{2} \tag{3.168}$$

$$= \ln \left\{ \frac{V}{N} \left(\frac{2\pi m k_{\mathrm{B}} T}{h^2} \right)^{\frac{3}{2}} \right\} + \frac{5}{2} \tag{3.169}$$

in which,

$$T = \frac{2}{3} \frac{\langle E \rangle}{N k_{\mathrm{B}}} \tag{3.170}$$

Thus,

$$\frac{S}{Nk_\mathrm{B}} = \ln\left\{\frac{V}{N}\left(\frac{2\pi m k_\mathrm{B}\frac{2\langle E\rangle}{3Nk_\mathrm{B}}}{h^2}\right)^{\frac{3}{2}}\right\} + \frac{5}{2} \tag{3.171}$$

$$= \ln\left\{\frac{V}{N}\left(\frac{4\pi m U}{3h^2 N}\right)^{\frac{3}{2}}\right\} + \frac{5}{2}, \tag{3.172}$$

which is fully consistent with the Sackur-Tetrode equation.

SOLUTION 3.6

a) The entropy can be derived from the partition functions by

$$S = \frac{\partial}{\partial T}\left(k_\mathrm{B} T \ln q\right), \tag{3.173}$$

where

$$q = \frac{1}{N!}\left(q_\mathrm{T} q_\mathrm{R} q_\mathrm{V} q_\mathrm{e}\right)^N, \tag{3.174}$$

where N is the amount of molecules. Note that we have to introduce the $\frac{1}{N!}$ factor because CO molecules are indistinguishable particles. Let us first calculate the individual entropy contributions of translational, rotational, vibrational and electronic partition functions and then combine them into the final formula. Note that we evaluate all partition functions **with respect to the electronic ground state**. We will incorporate the $\frac{1}{N!}$ only in the evaluation of the translational partition function.[49]

Let us start with the most simple contribution, that of the electronic partition function. Since we evaluate all partition function with respect to the electronic ground state and since we assume that only the electronic ground state is occupied, the electronic partition function becomes

$$q_\mathrm{e} = \omega_{\mathrm{e},0}, \tag{3.175}$$

where $\omega_{\mathrm{e},0}$ corresponds to the degeneracy of the electronic ground state.[50] Next, we evaluate the contribution of the translations, which gives

[49] This choice is fully arbitrary here. Yet if we use it for the translational partition functions, we can recycle the result for the derivation of the entropy of a mono-atomic gas.

[50] Which is usually equal to one, so note that the entropic contribution of the electronic ground state is typically zero.

$$S_{\mathrm{t}} = \frac{\partial}{\partial T}\left\{k_{\mathrm{B}}T\ln\left(\frac{q_{\mathrm{T}}^{N}}{N!}\right)\right\} \tag{3.176}$$

$$= k_{\mathrm{B}}T\frac{\partial}{\partial T}\left\{\ln\left(\frac{q_{\mathrm{T}}^{N}}{N!}\right)\right\} + k_{\mathrm{B}}\ln\left(\frac{q_{\mathrm{T}}^{N}}{N!}\right) \tag{3.177}$$

$$= k_{\mathrm{B}}T\frac{\partial}{\partial T}\left\{\ln\left(\frac{1}{N!}\right) + N\ln\left(\left(\frac{2\pi m k_{\mathrm{B}}}{h^2}\right)^{3/2}V\right) + \frac{3}{2}N\ln\left(T\right)\right\} + k_{\mathrm{B}}\ln\left(\frac{q_{\mathrm{T}}^{N}}{N!}\right) \tag{3.178}$$

$$= k_{\mathrm{B}}T\frac{\partial}{\partial T}\left\{\frac{3}{2}N\ln\left(T\right)\right\} + k_{\mathrm{B}}\left(N\ln\left(q_{\mathrm{T}}\right) - \ln\left(N!\right)\right) \tag{3.179}$$

$$= \frac{3}{2}Nk_{\mathrm{B}} + Nk_{\mathrm{B}}\ln q_{\mathrm{T}} - k_{\mathrm{B}}\left(N\ln N - N\right) \tag{3.180}$$

$$= Nk_{\mathrm{B}}\left(\frac{3}{2} + \ln q_{\mathrm{T}} - \ln N + 1\right) \tag{3.181}$$

$$= Nk_{\mathrm{B}}\ln\left(\left(\frac{2\pi m k_{\mathrm{B}}T}{h^2}\right)^{3/2}V\frac{\exp\left(\frac{5}{2}\right)}{N}\right). \tag{3.182}$$

Note that in the derivation above, we applied Stirling's approximation to evaluate $\ln\left(N!\right)$. For the entropy contribution due to rotations, we get

$$S_{\mathrm{r}} = \frac{\partial}{\partial T}\left\{k_{\mathrm{B}}T\ln\left(q_{\mathrm{R}}^{N}\right)\right\} \tag{3.183}$$

$$= k_{\mathrm{B}}T\frac{\partial}{\partial T}\ln\left(q_{\mathrm{R}}^{N}\right) + k_{\mathrm{B}}\ln\left(q_{\mathrm{R}}^{N}\right) \tag{3.184}$$

$$= Nk_{\mathrm{B}}T\frac{\partial}{\partial T}\ln\left(\frac{8\pi^2 I k_{\mathrm{B}}T}{\sigma h^2}\right) + Nk_{\mathrm{B}}\ln\left(q_{\mathrm{R}}\right) \tag{3.185}$$

$$= Nk_{\mathrm{B}}T\frac{\partial}{\partial T}\ln\left(T\right) + Nk_{\mathrm{B}}\ln\left(q_{\mathrm{R}}\right) \tag{3.186}$$

$$= Nk_{\mathrm{B}}\ln\left(\frac{8\pi^2 I k_{\mathrm{B}}T\exp(1)}{\sigma h^2}\right). \tag{3.187}$$

And finally for the vibrational partition function we obtain

$$S_\mathrm{v} = \frac{\partial}{\partial T}\left\{k_\mathrm{B}T\ln\left(q_\mathrm{V}^N\right)\right\} \tag{3.188}$$

$$= k_\mathrm{B}T\frac{\partial}{\partial T}\ln\left(q_\mathrm{V}^N\right) + k_\mathrm{B}\ln\left(q_\mathrm{V}^N\right) \tag{3.189}$$

$$= Nk_\mathrm{B}T\frac{\partial}{\partial T}\ln\left\{\frac{\exp\left(-\frac{h\nu}{2k_\mathrm{B}T}\right)}{1-\exp\left(-\frac{h\nu}{k_\mathrm{B}T}\right)}\right\} + Nk_\mathrm{B}\ln\left(q_\mathrm{V}\right) \tag{3.190}$$

$$= Nk_\mathrm{B}T\frac{\partial}{\partial T}\left\{\left(-\frac{h\nu}{2k_\mathrm{B}T}\right) - \ln\left(1-\exp\left(-\frac{h\nu}{k_\mathrm{B}T}\right)\right)\right\} + Nk_\mathrm{B}\ln\left(q_\mathrm{V}\right) \tag{3.191}$$

$$= Nk_\mathrm{B}T\left\{\left(\frac{h\nu}{2k_\mathrm{B}T^2}\right) + \frac{\frac{h\nu}{k_\mathrm{B}T^2}\exp\left(-\frac{h\nu}{k_\mathrm{B}T}\right)}{1-\exp\left(-\frac{h\nu}{k_\mathrm{B}T}\right)}\right\} + Nk_\mathrm{B}\ln\left(q_\mathrm{V}\right) \tag{3.192}$$

$$= Nk_\mathrm{B}T\left\{\left(\frac{h\nu}{2k_\mathrm{B}T^2}\right) + \frac{\frac{h\nu}{k_\mathrm{B}T^2}}{\exp\left(\frac{h\nu}{k_\mathrm{B}T}\right)-1} - \left(\frac{h\nu}{2k_\mathrm{B}T^2}\right) - \frac{1}{T}\ln\left(1-\exp\left(-\frac{h\nu}{k_\mathrm{B}T}\right)\right)\right\} \tag{3.193}$$

$$= Nk_\mathrm{B}\left(\frac{\frac{h\nu}{k_\mathrm{B}T}}{\exp\left(\frac{h\nu}{k_\mathrm{B}T}\right)-1} - \ln\left(1-\exp\left(-\frac{h\nu}{k_\mathrm{B}T}\right)\right)\right). \tag{3.194}$$

Note that we have multiplied by $\exp\left(+\frac{h\nu}{k_\mathrm{B}T}\right)$ in equation 3.192 to get rid of the exponent in the numerator to obtain equation 3.193. Combining all three results yields

$$\frac{S_\mathrm{m}}{Nk_\mathrm{B}} = \ln\left(\left(\frac{2\pi mk_\mathrm{B}T}{h^2}\right)^{3/2}V\frac{\exp\left(\frac{5}{2}\right)}{N}\right) + \ln\left(\frac{8\pi^2Ik_\mathrm{B}T\exp(1)}{\sigma h^2}\right)\cdots$$
$$\cdots + \frac{\frac{h\nu}{k_\mathrm{B}T}}{\exp\left(\frac{h\nu}{k_\mathrm{B}T}\right)-1} - \ln\left(1-\exp\left(-\frac{h\nu}{k_\mathrm{B}T}\right)\right) + \ln\omega_{\mathrm{e},0}. \tag{3.195}$$

b) Applying the ideal gas law and calculating per mole of molecules gives

$$\frac{S_\mathrm{m}}{R} = \ln\left(\left(\frac{2\pi mk_\mathrm{B}T}{h^2}\right)^{3/2}\frac{k_\mathrm{B}T}{p}\frac{\exp\left(\frac{5}{2}\right)}{1}\right) + \ln\left(\frac{8\pi^2Ik_\mathrm{B}T\exp(1)}{\sigma h^2}\right)\cdots$$
$$\cdots + \frac{\frac{h\nu}{k_\mathrm{B}T}}{\exp\left(\frac{h\nu}{k_\mathrm{B}T}\right)-1} - \ln\left(1-\exp\left(-\frac{h\nu}{k_\mathrm{B}T}\right)\right) + \ln\omega_{\mathrm{e},0}. \tag{3.196}$$

Let us first calculate the values for the translational, rotational and vibrational partition functions, which yield the results at standard conditions

$$q_\mathrm{T} = 5.824\cdot10^6 \tag{3.197}$$

$$q_\mathrm{R} = 1.076\cdot10^2 \tag{3.198}$$

$$q_\mathrm{V} = 1.000. \tag{3.199}$$

From these results, we can already conclude that we are allowed to neglect vibrational contributions[51], significantly simplifying the equation to

$$S_\mathrm{m} = R\left\{\ln\left(\left(\frac{2\pi m k_\mathrm{B}T}{h^2}\right)^{3/2}\frac{k_\mathrm{B}T}{p}\exp\left(\frac{5}{2}\right)\right) + \ln\left(\frac{8\pi^2 I k_\mathrm{B}T\exp(1)}{\sigma h^2}\right)\right\}. \tag{3.200}$$

Identifying the formulas for the partition functions in the above equation gives

$$S_\mathrm{m} = R\left\{\ln\left(q_\mathrm{T}\exp\left(\frac{5}{2}\right)\right) + \ln\left(q_\mathrm{R}\exp(1)\right)\right\}. \tag{3.201}$$

And upon filling out the values for the partition functions we obtain the final result of S_m = 197.52 J/mol/K. This result is in very close agreement to the experimental result of $S_\mathrm{m}^\ominus$ = 197.9 J/mol/K.

SOLUTION 3.7

a)

$$q_\mathrm{rot} = \sum_{J=0}^{\infty}(2J+1)\exp\left(\frac{-J(J+1)\Theta_\mathrm{rot}}{T}\right) \tag{3.202}$$

b)

$$E_\mathrm{rot} = k_\mathrm{B}T^2\frac{\partial}{\partial T}\ln q_\mathrm{rot} \tag{3.203}$$

$$= k_\mathrm{B}\left[\frac{\sum_{J=0}^{\infty}(2J+1)J(J+1)\Theta_\mathrm{rot}\exp\left(\frac{-J(J+1)\Theta_\mathrm{rot}}{T}\right)}{\sum_{J=0}^{\infty}(2J+1)\exp\left(\frac{-J(J+1)\Theta_\mathrm{rot}}{T}\right)}\right] \tag{3.204}$$

[51] Feel free to include the vibrational contribution; you will see it only starts to matter for the final answer at the third digit after the decimal point.

c)

$$C_{\mathrm{v,rot}} = \frac{\partial}{\partial T} E_{\mathrm{rot}} \tag{3.205}$$

$$= \frac{\partial}{\partial T} k_{\mathrm{B}} \left[\frac{\sum_{J=0}^{\infty} (2J+1) J(J+1) \Theta_{\mathrm{rot}} \exp\left(-\frac{J(J+1)\Theta_{\mathrm{rot}}}{T} \right)}{\sum_{J=0}^{\infty} (2J+1) \exp\left(-\frac{J(J+1)\Theta_{\mathrm{rot}}}{T} \right)} \right] \tag{3.206}$$

$$= \frac{k_{\mathrm{B}}}{T^2} \left[\frac{\sum_{J=0}^{\infty} (2J+1) \left(J(J+1)\Theta_{\mathrm{rot}} \right)^2 \exp\left(-\frac{J(J+1)\Theta_{\mathrm{rot}}}{T} \right)}{\sum_{J=0}^{\infty} (2J+1) \exp\left(\frac{-J(J+1)\Theta_{\mathrm{rot}}}{T} \right)} - \cdots \right.$$

$$\left. \cdots \frac{\left(\sum_{J=0}^{\infty} (2J+1) \left(J(J+1)\Theta_{\mathrm{rot}} \right) \exp\left(-\frac{J(J+1)\Theta_{\mathrm{rot}}}{T} \right) \right)^2}{\left(\sum_{J=0}^{\infty} (2J+1) \exp\left(-\frac{J(J+1)\Theta_{\mathrm{rot}}}{T} \right) \right)^2} \right] \tag{3.207}$$

⚠ Note the minus sign between the two terms in the square brackets.

d) You should obtain an answer similar to what is shown in Figure 3.18. Note that the results converges to $C_{\mathrm{v,rot}} = k_{\mathrm{B}}$ at higher temperatures, which is the result obtained for an ideal diatomic gas.

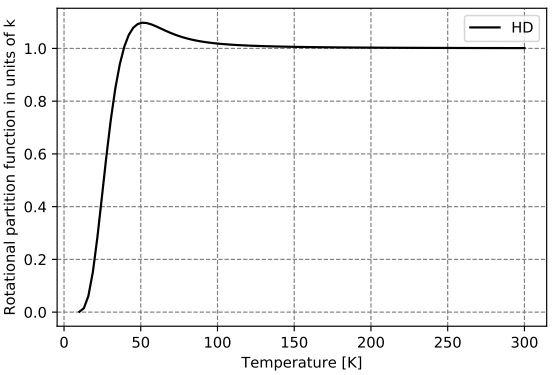


Figure 3.18: *Rotational contribution to the heat capacity in units of k_B for the hydrogen-deuterium molecule.*

e) You should obtain an answer similar to what is shown in Figure 3.19. Note that para-hydrogen is lower in energy (its first allowed rotational energy level is at $J = 0$) and thus its contribution to the heat capacity starts at lower temperature.

f) You should obtain an answer similar to what is shown in Figure 3.20. The main reason for the difference is that the 1:3 mixture is the high-temperature ratio between para- and ortho-hydrogen (corresponding to the degeneracy of their nuclear states). However due to the allowed rotational energy levels, the distribution between ortho- and para- will change as a function of temperature.

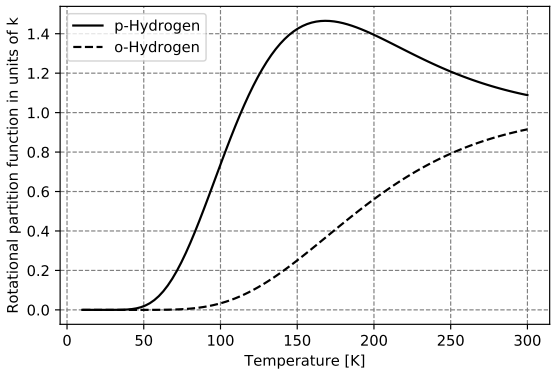


Figure 3.19: *Rotational contribution to the heat capacity in units of k_B for para- and ortho-hydrogen.*

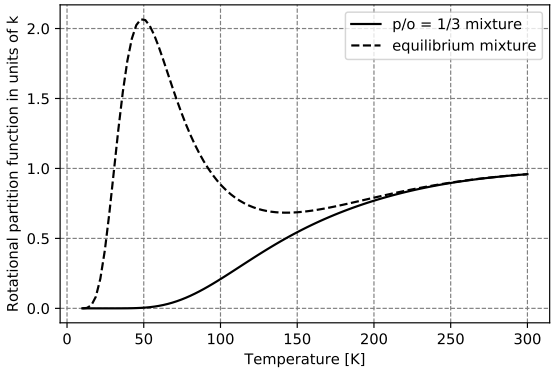


Figure 3.20: *Rotational contribution to the heat capacity in units of k_B for a 1:3 mixture and the equilibrium composition.*

Explore the rotational contribution to the heat capacities of H_2 and HD online using this Wolfram Cloud app:
`https://demonstrations.wolfram.com/LowTemperatureHeatCapacityOfHydrogenMolecules/`

CHAPTER 4

TRANSITION STATE THEORY

Contents

4.1 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.

Our derivation of collision theory proceeds in a couple of steps. First, we estimate the number of collisions as a function of the velocity of a molecule. Next, we derive an equation to calculate the average velocity of a particle as a function of temperature and use this speed distribution to obtain an expression for the average velocity *between* two molecules as a function of temperature. As not all collisions lead to a reaction, we finally introduce a correction factor to account for the collision efficiency.

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

To derive the rate of reaction for the mixture, we first start by calculating the number of collisions per second for a single 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 σ_{AB} of the line of flight of the center of molecule A during the passage of A, wherein σ_{AB} is given by[1]

$$\sigma_{AB} = \frac{d_A + d_B}{2}. \tag{4.1}$$

This is schematically depicted in Figure 4.1.

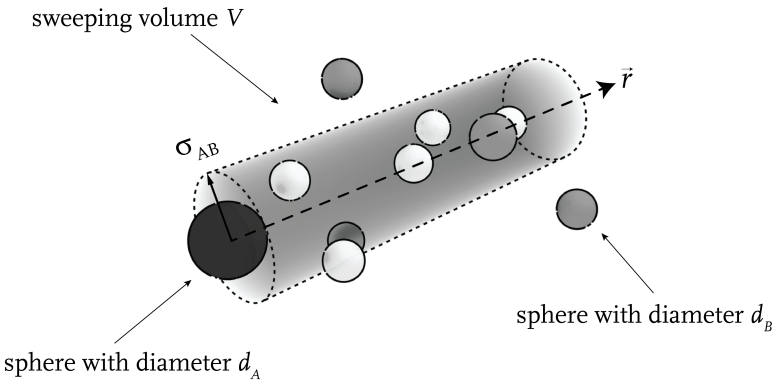


Figure 4.1: *Schematic depiction of the cylinder space swept out by molecule A. All molecules whose center are within the volume as defined by the cylinder will undergo a collision. The radius of this cylinder is equal to half of the sum of the diameters of the two molecules A and B.*

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 cylinder with radius σ_{AB} multiplied by the number of molecules of type B per cubic meter, ρ_B. The required volume is thus

$$V = \pi\sigma_{AB}^2 \overline{r}, \tag{4.2}$$

where $\overline{r}$ is the *mean relative* velocity of molecule A. The number of collisions for a single molecule of A is given by

$$n_{\text{col}} = \pi\sigma_{AB}^2 \overline{r}\rho_B. \tag{4.3}$$

4.1.1 Maxwell-Boltzmann speed distribution

The appropriate mean relative velocity $\overline{r}$ can be calculated from the two-body distribution function of the molecules A and B. This process involves quite some mathematical steps, so let us proceed one step at a time. Let us first establish the distribution function for a **single** molecule and in the next subsection, we will build a two-body distribution function based on the results found in this subsection. The chance to encounter a single particle as function of its energy is given by

[1] In other words, the sweeping radius is essentially the sum of the radii of the potentially colliding particles.

the Boltzmann distribution of energy as given in Equation 2.61. According to this equation, the probability that a molecule has energy E_i is given by

$$p_i = \frac{\exp\left(-\frac{E_i}{k_B T}\right)}{\sum_j \exp\left(-\frac{E_j}{k_B T}\right)} = \frac{\exp\left(-\frac{E_i}{k_B T}\right)}{Z}, \tag{4.4}$$

where Z corresponds to the total translational partition function.

The velocity $\vec{v}$ has three components, i.e. in the v_x, v_y and v_z direction. The translational energy in each of the Cartesian directions is given by

$$E_{t,x} = \frac{1}{2} m v_x^2, \tag{4.5}$$

where $E_{t,x}$ corresponds to the total translational energy in the x-direction, m is the mass of a particle and v_x is the velocity in the x-direction. For all three Cartesian directions, we thus obtain

$$E_i = \frac{1}{2} m \left(v_x^2 + v_y^2 + v_z^2\right). \tag{4.6}$$

We can readily plug Equation 4.6 into Equation 4.4. Furthermore, because $\vec{v}$ can be considered to be a continuous function, we change the finite chance p_i into an *infinitesimal* chance[2] f as given by

$$f(\vec{v}) = Z^{-1} \exp\left(-\frac{m \|\vec{v}\|^2}{2 k_B T}\right) \tag{4.7}$$

$$= Z^{-1} \exp\left(-\frac{m v_x^2}{2 k_B T}\right) \exp\left(-\frac{m v_y^2}{2 k_B T}\right) \exp\left(-\frac{m v_z^2}{2 k_B T}\right), \tag{4.8}$$

where $f(\vec{v})$ is the infinitesimal chance (probability density) to encounter a particle at velocity $\vec{v}$ as function of $\vec{v}$. Because the function $f(\vec{v})$ corresponds to an infinitesimal chance, this function can be interpreted as a distribution function. The function $f(\vec{v})$ is however not yet normalized. To normalize it, we have to integrate[3] over all possible velocities, irrespective of direction, and set the value of Z^{-1} such that this integral over all possible configurations equals unity. Hence,

$$\int f(\vec{v}) = 1 \tag{4.9}$$

$$= Z^{-1} \int_{-\infty}^{\infty} \exp\left(-\frac{m v_x^2}{2 k_B T}\right) dv_x \int_{-\infty}^{\infty} \exp\left(-\frac{m v_y^2}{2 k_B T}\right) dv_y \int_{-\infty}^{\infty} \exp\left(-\frac{m v_z^2}{2 k_B T}\right) dv_z. \tag{4.10}$$

$$= Z^{-1} \left(\frac{2\pi k_B T}{m}\right)^{\frac{3}{2}}. \tag{4.11}$$

From this, it follows that Z^{-1} can be interpreted as a normalization constant to ensure that the integral equals unity. Plugging this normalization constant Z^{-1} back into the original

[2] If you find this step confusing, have another look at section 2.2. Because $\vec{v}$ is considered continuous rather than discrete, to obtain the finite chance (or probability) p from f, we simply integrate f over some domain. In other words, f can be interpreted as a **probability density**.

[3] Have a look at section B.3 in the appendix on page 278 for a handy set of standard integrals.

equations yields the following equation for the infinitesimal chance to encounter a particle at velocity $\vec{v}$:

$$f(\vec{v}) = \left(\frac{m}{2\pi k_B T}\right)^{\frac{3}{2}} \exp\left(-\frac{mv_x^2}{2k_B T}\right) \exp\left(-\frac{mv_y^2}{2k_B T}\right) \exp\left(-\frac{mv_z^2}{2k_B T}\right) \tag{4.12}$$

Equation 4.12 is the Maxwell-Boltzmann speed distribution. Considering our problem formulation wherein we aim to calculate the number of collisions between molecules A and B, we wish to derive a related expression corresponding to the distribution function of a particle that only depends on the magnitude of the velocity $f(\|\vec{v}\|)$ and **irrespective** of the particular direction that the particle is moving in. In other words, we wish to obtain a distribution as function of the particle's speed, rather than its velocity.[4]

To calculate this property, we perform a coordinate transformation from Cartesian to spherical coordinates and integrate out the parts that depend on the polar angle θ and the azimuthal angle ϕ. In spherical coordinates[5], Equation 4.12 is written as

$$f(\|\vec{v}\|, \theta, \phi) = \left(\frac{m}{2\pi k_B T}\right)^{\frac{3}{2}} \exp\left(-\frac{m\|\vec{v}\|^2}{2k_B T}\right) \|\vec{v}\|^2 \sin(\theta). \tag{4.13}$$

Note that the part $||\vec{v}||^2 \sin(\theta)$ corresponds to the Jacobian due to the unit transformation from Cartesian to spherical coordinates. Let us now integrate out the part that depends on the angles θ and ϕ by which we obtain the following results[6]

$$f(\|\vec{v}\|) = \int_0^{2\pi} d\phi \int_0^{\pi} \sin(\theta)\, d\theta \left[\left(\frac{m}{2\pi k_B T}\right)^{\frac{3}{2}} \exp\left(-\frac{m\|\vec{v}\|^2}{2k_B T}\right) |v|^2\right] \tag{4.14}$$

$$= 4\pi \|\vec{v}\|^2 \left(\frac{m}{2\pi k_B T}\right)^{\frac{3}{2}} \exp\left(-\frac{m\|\vec{v}\|^2}{2k_B T}\right) \tag{4.15}$$

Since the speed c corresponds to

$$c = \sqrt{v_x^2 + v_y^2 + v_z^2} = \|\vec{v}\|, \tag{4.16}$$

let us rewrite Equation 4.15 as

$$f(c) = 4\pi c^2 \left(\frac{m}{2\pi k_B T}\right)^{\frac{3}{2}} \exp\left(-\frac{mc^2}{2k_B T}\right) \tag{4.17}$$

Equation 4.17 is the Maxwell-Boltzmann speed distribution, irrespective of the direction of said velocity.

[4] Recall that there is a subtle difference between speed and velocity. Velocity is defined as the speed with a direction, while speed does not have a direction.

[5] See Appendix B.1.3 on page 277.

[6] Observe that this procedure is analogues to calculating the surface of a sphere of radius $r = \|\vec{v}\|$.

As seen in section 2.2, we can calculate the average property given a distribution by multiplying that distribution by the variable of interest and integrating over the whole distribution.[7] From this distribution, we can thus obtain the average speed or average magnitude for the velocity by multiplying the distribution function by c and integrating over the complete configuration space[8] as given by

$$c_{\text{avg}} = \int_0^\infty f(c) \cdot c \, dc = \int_0^\infty 4\pi c^3 \left(\frac{m}{2\pi k_{\text{B}} T}\right)^{\frac{3}{2}} \exp\left(-\frac{mc^2}{2k_{\text{B}}T}\right) dc \tag{4.18}$$

$$= \sqrt{\frac{8k_{\text{B}}T}{\pi m}}. \tag{4.19}$$

In a similar fashion, we can obtain the root-mean-squared speed, which equals

$$c_{\text{rms}} = \left[\int_0^\infty f(c) \cdot c^2 \, dc\right]^{\frac{1}{2}} = \left[\int_0^\infty 4\pi c^4 \left(\frac{m}{2\pi k_{\text{B}} T}\right)^{\frac{3}{2}} \exp\left(-\frac{mc^2}{2k_{\text{B}}T}\right) dc\right]^{\frac{1}{2}} \tag{4.20}$$

$$= \sqrt{\frac{3k_{\text{B}}T}{m}} \tag{4.21}$$

and the most probable speed, which is obtained by solving

$$\frac{df(c)}{dc} = 0 = 4\pi \left(\frac{m}{2\pi k_{\text{B}} T}\right)^{\frac{3}{2}} \frac{\left(2k_{\text{B}}T - mc^2\right) \exp\left(-\frac{mc^2}{2k_{\text{B}}T}\right)}{k_{\text{B}}T}. \tag{4.22}$$

Observing that the term before the fraction cannot be zero, neither the exponent term in the numerator nor the denominator, it follows that

$$2k_{\text{B}}T - mc^2 = 0, \tag{4.23}$$

giving

$$c_{\text{mp}} = \sqrt{\frac{2k_{\text{B}}T}{m}}. \tag{4.24}$$

In Figure 4.2, the speed distribution for a N_2 molecule for two different temperatures is given. Note that at higher temperatures, the magnitude of the velocities are more 'smeared out'. The most probable speed corresponds to the maximum of the speed distribution. The average speed lies at somewhat higher speed than the most probable speed, because the speed distribution tails off at higher speeds.

Practice your understanding

Exercise 4.1

[7] Assuming of course that the distribution is normalized. If not, we have to either normalize the distribution first or divide the result of the integration by the integral of the distribution over its complete function space.

[8] In other words, integrating over all possible values of c.

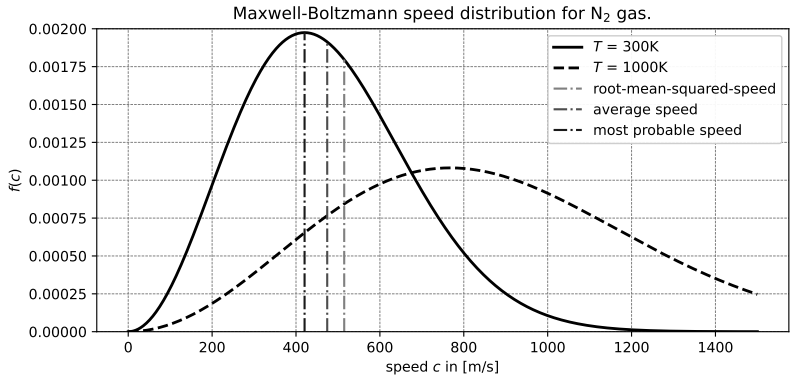


Figure 4.2: *Maxwell-Boltzmann speed distribution for N_2 for $T = 300K$ and $T = 1000K$. The most probable speed, average speed and root-mean-square speed are indicated for $T = 300K$ as well.*

4.1.2 Collision density

In the previous subsection we derived the Maxwell-Boltzmann speed distribution pertaining to a single particle. To obtain the mean *relative* velocity between two particles, we have to construct the distribution for two particles, which is simply the product of two single-particle distribution functions, as given by

$$f\left(\vec{v}_A, \vec{v}_B\right) = f\left(\vec{v}_A\right) \cdot f\left(\vec{v}_B\right) \tag{4.25}$$

$$= \left(\frac{\sqrt{m_A m_B}}{2\pi k_\mathrm{B} T}\right)^3 \exp\left(-\frac{m_A \left\|\vec{v}_A\right\|^2}{2k_\mathrm{B}T}\right) \exp\left(-\frac{m_B \left\|\vec{v}_B\right\|^2}{2k_\mathrm{B}T}\right) \tag{4.26}$$

The (kinetic) energy terms in this distribution is defined with some arbitrary frame of reference and the total energy is herein the sum of the kinetic energy of particle A and particle B. We can introduce a coordinate transformation wherein the total kinetic energy for the two-body system is given as the sum of the kinetic energy due to movement of the center of mass and the kinetic energy due to velocities with respect to the center of mass as given by

$$\frac{m_A \left\|\vec{v}_A\right\|^2}{2} + \frac{m_B \left\|\vec{v}_B\right\|^2}{2} = \frac{1}{2}\left(m_A + m_B\right)\left\|\vec{v}'\right\|^2 + \frac{1}{2}\mu\left\|\vec{r}\right\|^2 \tag{4.27}$$

where $\vec{v}'$ is the velocity of the center of mass, μ the reduced mass and $\vec{r}$ the relative velocity of particle A with respect to particle B. It can be readily seen that Equation 4.27 is valid if we use the following definitions for $\vec{v}'$, μ and $\vec{r}$:

$$\vec{v}' \equiv \frac{m_A \vec{v}_A + m_B \vec{v}_B}{m_A + m_B} \tag{4.28}$$

$$\mu \equiv \frac{m_A m_B}{m_A + m_B} \tag{4.29}$$

$$\vec{r} \equiv \vec{v}_A - \vec{v}_B\,. \tag{4.30}$$

By using the above definitions, we can rewrite Equation 4.26 as

$$f\left(\vec{v}', \vec{r}\right) = f\left(\vec{v}_A\right) \cdot f\left(\vec{v}_B\right) \tag{4.31}$$

$$= \left(\frac{\sqrt{m_A m_B}}{2\pi k_B T}\right)^3 \exp\left(-\frac{\left(m_A + m_B\right)\left\|\vec{v}'\right\|^2}{2k_B T}\right) \exp\left(-\frac{\mu\left\|\vec{r}\right\|^2}{2k_B T}\right). \tag{4.32}$$

From this equation, we can derive an equation for the distribution only as function of the relative velocity $\vec{r}$ and irrespective of the velocity of the center of mass $\vec{v}'$ by integrating over all possible values of $\vec{v}'$. This gives

$$f\left(\vec{r}\right) = \left(\frac{\sqrt{m_A m_B}}{2\pi k_B T}\right)^3 \int_{-\infty}^{\infty} \exp\left(-\frac{\left(m_A + m_B\right) v_x^2}{2k_B T}\right) dv_x \int_{-\infty}^{\infty} \exp\left(-\frac{\left(m_A + m_B\right) v_y^2}{2k_B T}\right) dv_y \cdots \tag{4.33}$$

$$\cdots \int_{-\infty}^{\infty} \exp\left(-\frac{\left(m_A + m_B\right) v_z^2}{2k_B T}\right) dv_z \exp\left(-\frac{\mu\left\|\vec{r}\right\|^2}{2k_B T}\right) \tag{4.34}$$

$$= \left(\frac{\sqrt{m_A m_B}}{2\pi k_B T}\right)^3 \left(\frac{2\pi k_B T}{m_A + m_B}\right)^{3/2} \exp\left(-\frac{\mu\left\|\vec{r}\right\|^2}{2k_B T}\right) \tag{4.35}$$

$$= \left(\frac{\mu}{2\pi k_B T}\right)^{3/2} \exp\left(-\frac{\mu\left\|\vec{r}\right\|^2}{2k_B T}\right). \tag{4.36}$$

As seen in the previous subsection, by performing a coordinate transformation from Cartesian to spherical coordinates and integrating out the angles ϕ and θ, we can cast the above equation into a distribution function that only depends on the magnitude of the relative velocity $||\vec{r}||$ and thus irrespective of the direction. The above distribution function in spherical coordinates is given by

$$f\left(||r||, \theta, \phi\right) = \left(\frac{\mu}{2\pi k_B T}\right)^{3/2} \exp\left(-\frac{\mu||\vec{r}||^2}{2k_B T}\right) ||\vec{r}||^2 \sin\theta. \tag{4.37}$$

Integrating out the angles yields

$$f\left(||\vec{r}||\right) = 4\pi||\vec{r}||^2 \left(\frac{\mu}{2\pi k_B T}\right)^{3/2} \exp\left(-\frac{\mu||\vec{r}||^2}{2k_B T}\right). \tag{4.38}$$

Observe that Equation 4.38 is very similar to Equation 4.17 on page 172. Instead of the speed c, we have the relative speed $||r||$. Similarly to how the mean speed was calculated in Equation 4.19, the mean relative speed can be found to be

$$\overline{r} = \left(\frac{8k_B T}{\pi\mu}\right)^{1/2}, \tag{4.39}$$

where m in Equation 4.19 is replaced by the reduced mass μ. Note that in the special case that $m_A = m_B = m$,

$$\mu = \frac{m}{2} \tag{4.40}$$

and

$$\overline{r} = \sqrt{2}c \tag{4.41}$$

Finally, we can plug Equation 4.39 into Equation 4.3 to obtain the number of collisions of a single molecule of A per second as given by

$$n_{\text{col}} = \left(\frac{8\pi k_{\text{B}} T}{\mu}\right)^{1/2} \sigma_{AB}^2 \rho_B, \tag{4.42}$$

where ρ is the number[9] of molecules per volume as given by

$$\rho = \frac{n}{V}. \tag{4.43}$$

From this, we can calculate the number of collisions per unit volume per molecule of type A with molecule B by multiplying n_{col} by ρ_A which gives

$$\boxed{Z_{AB} = \left(\frac{8\pi k_{\text{B}} T}{\mu}\right)^{1/2} \sigma_{AB}^2 \rho_A \rho_B.} \tag{4.44}$$

In the case that molecule A and B are *like* molecules, the above equation can be further simplified by substituting σ_{AB} for σ and noting that $\rho_A = \rho_B$. Also, we have to introduce a factor of $\frac{1}{2}$ to avoid double counting.[10]

$$\begin{aligned} Z &= \frac{1}{2} Z_{AB} && (4.45)\\ &= \frac{1}{2}\left(\frac{8\pi k_{\text{B}} T}{\mu}\right)^{1/2} \sigma_{AB}^2 \rho_A \rho_B && (4.46)\\ &= \frac{1}{2}\left(\frac{8\pi k_{\text{B}} T}{m/2}\right)^{1/2} \sigma^2 \rho^2 && (4.47)\\ &= 2\left(\frac{\pi k_{\text{B}} T}{m}\right)^{1/2} \sigma^2 \rho^2. && (4.48) \end{aligned}$$

4.1.3 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 relative kinetic energy to overcome some energetic barrier necessary for the reaction to proceed. Consider the situation such as illustrated in Figure 4.3a. Molecule A has some relative velocity $\vec{r}$ with respect to molecule B. This relative velocity $\vec{r}$ is not necessarily oriented in the direction of the vector $\vec{d}_{AB}$ spanned from the center of A to the center of B. For example, the vectors $\vec{r}$ and $\vec{d}_{AB}$ could be oriented at a 90 degrees angle by which the collision is more like a grazing incident by which only a minimum of the total kinetic energy of A is transferred to B.

[9] Please note that we literally mean here the number of molecules, **not** the number of moles of a molecule.

[10] For unlike particles, the number of collisions is counted by considering the volume sweep of molecule A through a gaseous mixture of B (or vice versa, but only counted once). For like particles, the volume sweep is through a gaseous mixture of itself resulting in double counting. If this concept is troubling you, have a look at exercise 4.2 on page 190.

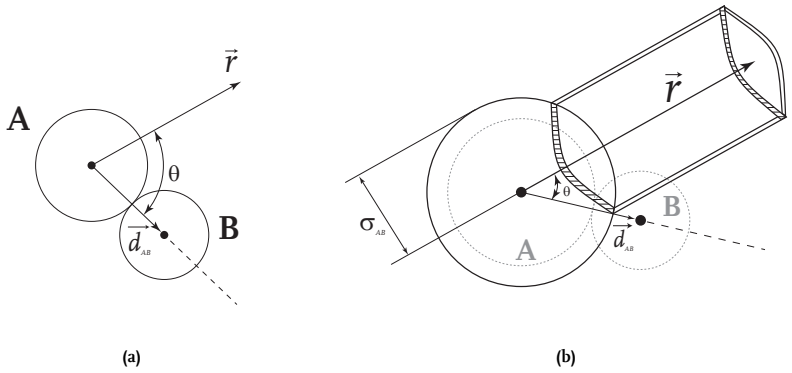


Figure 4.3: *(a) Schematic illustration of a collision between molecules A and B where the relative velocity $\vec{r}$ is oriented at an angle θ with respect to the vector $\vec{d}_{AB}$ pertaining to the line of centers of molecules A of B. Only part of the kinetic energy that corresponds to the component of the velocity projected on $\vec{d}_{AB}$ can be used to overcome the barrier for the reaction. (b) Schematic depiction of the sweeping volume V as function of the relative velocity $\vec{r}$ and the angle θ. The sweeping volume corresponds to a shell (hollow cylinder) with a circumference of $P = 2\pi\sigma_{AB} \sin\theta$, width $\Delta l = \sigma_{AB} d\theta$ and a height $h = ||\vec{r}||$.*

As such, we need to define some effective kinetic energy, which is determined by the component of the relative velocity vector $\vec{r}$ in the direction as given by $\vec{d}_{AB}$. This effective energy is given by

$$E_{\text{kin,eff}} = \frac{1}{2}\mu||\vec{r}||^2 \cos\theta. \tag{4.49}$$

In the situation wherein we neglected to take the effectiveness of a collision into account, as shown in the beginning of this section, the number of collisions was calculated by considering the sweeping volume $V = \pi\sigma_{AB}^2 \bar{r}$, wherein σ_{AB} corresponds to the collision radius and $\bar{r}$ the average relative velocity. We were allowed to consider the average relative velocity because the shape of the sweeping volume given some value for the relative velocity $\vec{r}$ is always a cylinder with a fixed radius. When the orientation of relative velocity $\vec{r}$ starts to play a role, the sweeping volume is given by a **hollow** cylinder (or shell) with a different radius depending on the **value and direction** of $\vec{r}$ as given in Figure 4.3b.

For a given value of $\vec{r}$, the area of contact between molecules A and B for an angle between the vectors $\vec{r}$ and $\vec{d}_{AB}$ between θ and $\theta + d\theta$ corresponds to the circumference

$$P = 2\pi\sigma_{AB} \sin\theta \tag{4.50}$$

multiplied by the infinitesimal width

$$\Delta l = \sigma_{AB} d\theta \tag{4.51}$$

to give

$$A = 2\pi\sigma_{AB}^2 \sin\theta d\theta. \tag{4.52}$$

The sweeping volume corresponding to the above situation, taking the component of the relative velocity $\vec{r}$ in the direction of $\vec{d}_{AB}$ into account, is then given by

$$V = ||\vec{r}||2\pi\sigma_{AB}^2 \sin\theta\cos\theta d\theta. \tag{4.53}$$

Let us take one step back and reflect on what we are trying to derive. We want to calculate the number of collisions between A and B in some mixture with some number density of the molecules A and B given by ρ_A and ρ_B, respectively. To obtain this number, we consider a single molecule of A and construct the volume that if a molecule of B is within this volume, a collision is encountered. By multiplying then this volume V with the number density ρ_B, we would obtain the total number of collisions per molecule of A. In turn multiplying this result by the number density of A, would give the total number of collisions between A and B per volume.

In addition to the situation as sketched in this reflection, we have a set of conditions in place by which the sweeping volume is essentially smaller in size as compared to the situation in the absence of these conditions. We start out by considering a new sweeping volume V, but not for any given molecule A, but a molecule of A that has a relative velocity $\vec{r}$ oriented at an angle θ with respect to $\vec{d}_{AB}$. [11] The volume V as given in Equation 4.53 now corresponds to a molecule of A with an **effective magnitude** $||\vec{r}||$ considering that the vector $\vec{r}$ is oriented at an angle θ with respect to $\vec{d}_{AB}$. To construct the total number of collisions from this value V, we need to integrate over all relevant effective magnitudes $||\vec{r}||$ and all relevant angles θ. Herein, the effective magnitude $||\vec{r}||$ is integrated from the lower bound

$$||\vec{r}||_{\text{min}} = \sqrt{\frac{2\Delta E}{\mu}}, \tag{4.54}$$

where ΔE is the minimum energy to overcome the reaction barrier, and the upper bound of infinity. For the angle θ, we have a lower bound of o and an upper bound as given by

$$\theta_{\text{max}} = \arccos\left(\sqrt{\frac{2E}{\mu||\vec{r}||^2}}\right). \tag{4.55}$$

Because not all values of $||\vec{r}||$ and θ are equally distributed in our mixture, our integral has to take the (normalized) probability of encountering a molecule of A at $||\vec{r}||$ and θ into account, which is given by the two-body distribution function in relative spherical coordinates as given in Equation 4.38. The sweeping volume V is then given by multiplying Equation 4.38 by Equation 4.53 and integrating over $||\vec{r}||$ and θ using the lower and upper bounds as given above, which yields

$$V = 8\pi^2\left(\frac{\mu}{2\pi k_{\text{B}}T}\right)^{3/2}\sigma_{AB}^2\int_{||\vec{r}||_{\text{min}}}^{\infty}\left[||r||^3\exp\left(-\frac{\mu||\vec{r}||^2}{2k_{\text{B}}T}\right)\int_0^{\theta_{\text{max}}}\sin\theta\cos\theta d\theta\right]d||\vec{r}||. \tag{4.56}$$

The integral over θ evaluates to

$$\int_0^{\theta_{\text{max}}}\sin\theta\cos\theta d\theta = \frac{1}{2}\left(1-\frac{2\Delta E}{\mu||\vec{r}||^2}\right) \tag{4.57}$$

[11] Note that we are allowed to consider the vectors $\vec{r}$ and $\vec{d}_{AB}$ to lie on the same plane.

by which Equation 4.56 reduces to

$$V = 4\pi^2 \left(\frac{\mu}{2\pi k_B T}\right)^{3/2} \sigma_{AB}^2 \int_{||\vec{r}||_{\min}}^{\infty} ||\vec{r}||^3 \left(1 - \frac{2\Delta E}{\mu ||\vec{r}||^2}\right) \exp\left(-\frac{\mu ||\vec{r}||^2}{2k_B T}\right) d||\vec{r}||. \quad (4.58)$$

Integrating over $||\vec{r}||$ finally yields

$$V = \left(\frac{8\pi k_B T}{\mu}\right)^{1/2} \sigma_{AB}^2 \exp\left(-\frac{\Delta E}{k_B T}\right). \quad (4.59)$$

From Equation 4.59, the collision number Z_{AB} can be readily established by multiplying the sweeping volume V by the number densities of molecules A and B, giving

$$\boxed{Z_{AB} = \left(\frac{8\pi k_B T}{\mu}\right)^{1/2} \sigma_{AB}^2 \exp\left(-\frac{\Delta E}{k_B T}\right) \rho_A \rho_B.} \quad (4.60)$$

Observe now that Equation 4.60 only differs from Equation 4.44 by the energetic penalty $\xi = \exp\left(-\frac{\Delta E}{k_B T}\right)$, where ξ is always between 0 and 1 as ΔE corresponds to a barrier and is thus guaranteed to be a positive number.

Finally, for like particles, equation 4.60 transform to

$$\boxed{Z = 2\left(\frac{\pi k_B T}{m}\right)^{1/2} \sigma^2 \exp\left(-\frac{\Delta E}{k_B T}\right) \rho^2,} \quad (4.61)$$

where the formula has been adapted to mitigate the double counting of like species, similar to as shown in the derivation of Equation 4.48.

4.1.4 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:

$$A + M \underset{k_1^-}{\overset{k_1^+}{\rightleftharpoons}} A* + M \quad (4.62)$$

$$A* \xrightarrow{k_2^+} P \quad (4.63)$$

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

$$\frac{d[A*]}{dt} = k_1^+[A][M] - k_2^+[A*] - k_1^-[A*][M] = 0 \tag{4.64}$$

$$[A*] = \frac{k_1^+[A][M]}{k_2^+ + k_1^-[M]} \tag{4.65}$$

and hence the rate of reaction becomes

$$\frac{d[P]}{dt} = \frac{k_1^+ k_2^+[A][M]}{k_2^+ + k_1^-[M]}. \tag{4.66}$$

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

$$\frac{d[P]}{dt} = \frac{k_1^+ k_2^+[A]^2}{k_2^+ + k_1^-[A]}. \tag{4.67}$$

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

$$\frac{d[P]}{dt} = \frac{k_1^+ k_2^+[A]^2}{k_2^+ + k_1^-[A]} \approx k_1^+[A]^2. \tag{4.68}$$

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.

Practice your understanding

Exercise 4.2

4.2 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.[6, 7, 8] Here, we will employ a derivation wherein we assume that the reaction coordinate can be modeled as a translation.[12]

4.2.1 Derivation

To derive a general formula for the reaction rate constant, let us introduce a simple model system. In Figure 4.4, 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]

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

[12] There is a somewhat simpler derivation, but we leave this as an exercise to you. See exercise 4.8 on page 195 for an alternative derivation of the Eyring equation.

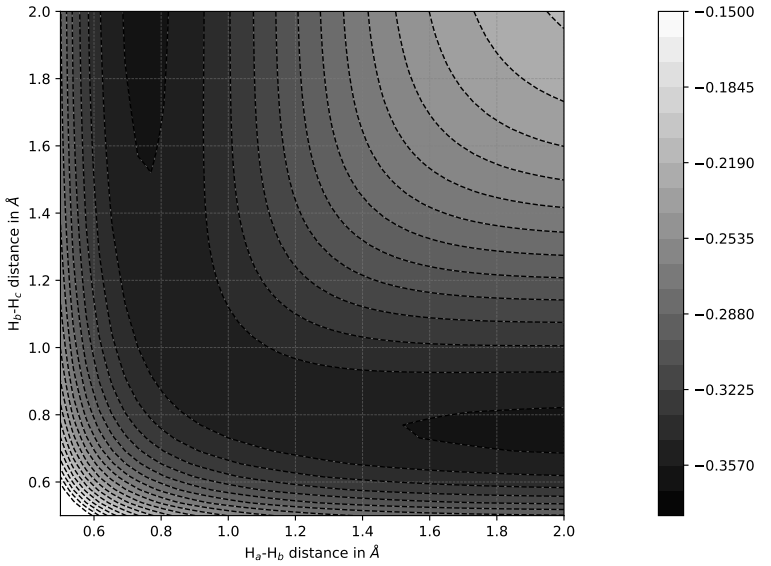


Figure 4.4: *Potential energy surface of the one-dimensional tri-atomic hydrogen system. The white dotted line indicates the reaction coordinate of the elementary reaction step wherein a hydrogen atom is transferred between the two other hydrogen atoms. All energies are given in HT. A surface plot of the same data is provided in Figure 4.5a.*

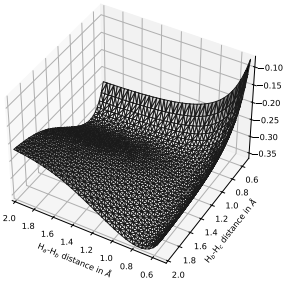
Within this Figure, the two dark regions (denoted by A and B) designate the stable states, being the complex H_A-H_B with the atomic hydrogen H_C far away (state A) and the situation where $H_B - H_C$ are bonded and H_A as atomic hydrogen (state B). One can construct a path of minimum energy between these two states as shown by the white dotted line. This minimum energy path that connects the two stable states, wherein all the points on the path are higher in energy than the two stable states, is termed the **reaction coordinate**. The point highest in energy along this path corresponds to a meta-stable state, which is termed the **transition state** (shown in Figure 4.4 by point 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 coordinate). In mathematical terms, such a point on the potential energy surface, which is a maximum in one direction and a minimum in all other directions, is known as a first-order *saddle point*.[13]

In addition to the contour plot of Figure 4.4, also a surface plot of the potential energy surface is provided in Figure 4.5a. Herein, the minimum energy path that connects the two stable states can be seen as the valley in this plot. The highest point alongside this minimum energy pathway corresponds to the transition state, which is the first-order saddle point. If we imagine a direction orthogonal to the direction of the minimum energy pathway, we can see in Figure 4.5a that this corresponds to a sharp increase in the potential energy, indicating that the transition state is a minimum in this direction.

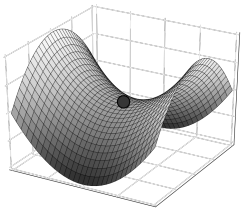
We want to derive a rate constant corresponding to the rate of the conversion of the **number of molecules per unit volume per unit time**.[14] Using a statistical assumption, it is obvious that

[13] Similarly, a second-order saddle point is the highest point on the minimum energy pathway between two first-order saddle points.

[14] Note that for this analysis, you can readily swap states A and B due to the principle of microscopic reversibility. See



(a) *Surface plot of the potential energy landscape of trilinear H_3.*



(b) *Example of a saddle point.*

Figure 4.5: *The transition state of an elementary reaction step corresponds to a saddle point on the potential energy surface. A saddle point is a point of a function where the derivatives in orthogonal directions are all zero (i.e. critical point), but which is not a local extremum of the function. A first-order saddle point is a critical point which is a maximum in one and only one direction and a minimum in all other directions.*

such a rate is proportional to the **number density** of molecules residing in state A.

$$\text{rate} = k\rho_A \tag{4.69}$$

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

1. The transition state and initial state are in thermal equilibrium in such a way that we can define an (number-density based) 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

$$R_{\text{IS}} \rightleftarrows R_{\text{TS}} \xrightarrow[\text{irrev}]{} P \tag{4.70}$$

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

$$k = \nu K, \tag{4.71}$$

where ν is a crossing frequency (in s^{-1}) at which species at the transition state migrate to the final state.[15]

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 4.71 also holds when we study the transient behavior? From

page 19.

[15] 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.

experiment though, it is found that rate constants do not change when the system approaches equilibrium[6], therefore, we believe that Equation 4.71 holds, irrespective of whether our system is in equilibrium or not.

Going back to our model system, for the elementary reaction step $H_2 + H \rightarrow H + H_2$, the *number-density based* equilibrium constant K can be defined as[16]

$$K = \frac{\rho^\dagger}{\rho_{AB}\rho_C} = \frac{(q^\dagger/V)}{(q_{AB}/V)(q_C/V)}, \tag{4.72}$$

wherein $q^\dagger$ corresponds to the molecular partition function in the transition state, q_{AB} to the molecular partition function of the AB complex (H_2) and q_C to the partition function of the single H atom. All three molecular partition functions are defined with respect to the lowest electronic ground state. If we extract the electronic partition functions from the total molecular partition function, we obtain

$$K = \frac{(q'^\dagger/V)}{(q'_{AB}/V)(q'_C/V)} \frac{q_e^\dagger}{(q_{e,AB})(q_{e,C})} \tag{4.73}$$

$$= \frac{(q'^\dagger/V)}{(q'_{AB}/V)(q'_C/V)} \exp\left(-\frac{\Delta E_{a,elec}}{k_B T}\right), \tag{4.74}$$

where the prime in q' indicates that we have omitted the electronic partition function from the total molecular partition function and $\Delta E_{a,elec}$ corresponds to the electronic activation energy as given by

$$\Delta E_{a,elec} = E^\dagger_{elec} + \sum_i^{\text{reactants}} \nu_i E_{i,elec}, \tag{4.75}$$

where $E^\dagger_{elec}$ is the electronic energy of the complex in the transition state, ν_i the stoichiometric coefficient[17], i an iterator for the reactants and $E_{i,elec}$ the electronic energy of reactant i. Note that all electronic energies are defined with the **zero of energy corresponding to all constituting atoms infinitely far apart and at rest**. Furthermore, note that the same holds for the vibrational partition functions in Equation 4.74, thus they contain the zero point energy term $\exp\left(\frac{1}{2}\frac{h\nu}{k_B T}\right)$ as shown in Equation 3.115.

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 $\overline{v}$ of the species, the time τ is given by

$$\tau = \frac{\delta}{\overline{v}}. \tag{4.76}$$

Thus, the reaction rate constant equation so far yields

$$k = \frac{\overline{v}}{\delta} \frac{(q'^\dagger/V)}{(q'_{AB}/V)(q'_C/V)} \exp\left(-\frac{\Delta E_{a,elec}}{k_B T}\right). \tag{4.77}$$

[16] Here, we use a number-density based equilibrium constant as defined in Equation 2.159 on page 103 as we wish to obtain a rate in terms of the number of molecules converted per unit volume and per unit time. If another type of rate expression is used, e.g. based on pressures, a different equilibrium constant can be used. Examples of these types of rates are shown in the next chapter.

[17] Note that these are per definition negative for reactants

Next, we extract the partition function corresponding to the reaction coordinate from the total molecular partition function of the transition state. In this derivation, we model motion along the reaction coordinate as a one-dimensional translation. This approximation treats the transition-state complex as quasi-bound in all coordinates except the reaction coordinate, which is free to move across the dividing surface. By combination of Equation 3.64 and the previous equation we obtain

$$k = \frac{\overline{v}}{\delta} \frac{\delta \sqrt{2\pi m k_\mathrm{B} T}}{h} \frac{(q''^{\dagger}/V)}{(q'_\mathrm{AB}/V)(q'_\mathrm{C}/V)} \exp\left(-\frac{\Delta E_\mathrm{a,elec}}{k_\mathrm{B} T}\right). \tag{4.78}$$

Note that we used an additional prime in q'' to indicate that we have extracted one translational degree of freedom from the partition function of the transition state. The average velocity $\overline{v}$ **in one dimension** can be obtained in a similar fashion as shown for the Maxwell-Boltzmann speed distribution in section 4.1.1, which yields

$$\overline{v} = \frac{\int_0^\infty \exp\left(\frac{-mv^2}{2k_\mathrm{B}T}\right) v dv}{\int_0^\infty \exp\left(\frac{-mv^2}{2k_\mathrm{B}T}\right) dv} \tag{4.79}$$

$$= \sqrt{\frac{2k_\mathrm{B}T}{\pi m}}. \tag{4.80}$$

Plugging this equation into Equation 4.78, 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

$$k = \frac{\sqrt{\frac{2k_\mathrm{B}T}{\pi m}}}{2\delta} \frac{\delta \sqrt{2\pi m k_\mathrm{B} T}}{h} \frac{(q''^{\dagger}/V)}{(q'_\mathrm{AB}/V)(q'_\mathrm{C}/V)} \exp\left(-\frac{\Delta E_\mathrm{a,elec}}{k_\mathrm{B} T}\right). \tag{4.81}$$

The above equation can be rewritten to

$$k^+ = \frac{k_\mathrm{B}T}{h} \frac{(q^{\ddagger}/V)}{(q'_\mathrm{AB}/V)(q'_\mathrm{C}/V)} \exp\left(-\frac{\Delta E_\mathrm{a,elec}}{k_\mathrm{B} T}\right). \tag{4.82}$$

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 and added a + to indicate that this reaction rate constant corresponds to the reaction in the (arbitrarily defined) forward direction. Equation 4.82 is known as the *Eyring equation* or *transition state theory equation*. For the reverse reaction, we would obtain

$$k^- = \frac{k_\mathrm{B}T}{h} \frac{(q^{\ddagger}/V)}{(q_\mathrm{A}/V)(q_\mathrm{BC}/V)} \exp\left(-\frac{\left(\Delta E_\mathrm{a,elec} - \Delta E_\mathrm{r,elec}\right)}{k_\mathrm{B} T}\right), \tag{4.83}$$

where $\Delta E_\mathrm{r,elec}$ corresponds to the electronic energy for the reaction as defined as

$$\Delta E_\mathrm{r,elec} = \sum_i \nu_i E_{i,\mathrm{elec}}. \tag{4.84}$$

Combining Equations 4.82 and 4.83 gives

$$K = \frac{k^+}{k_-} = \frac{(q_A/V)(q_{BC}/V)}{(q_{AB}/V)(q_C/V)} \exp\left(-\frac{\Delta E_{r,elec}}{k_B T}\right), \tag{4.85}$$

which is in agreement with Equation 2.159.[18] Finally, Equations 4.82 and 4.83 pertain to bimolecular reactions. The general expression for transition state theory becomes[19]

$$k = \frac{k_B T}{h} \frac{(q^\ddagger/V)}{\prod_i (q_i/V)} \exp\left(-\frac{\Delta E_{a,elec}}{k_B T}\right). \tag{4.86}$$

The above expression was derived for reactions in the gas phase, where the molecular partition functions are expressed per unit volume. For reactions occurring on surfaces or within condensed phases, the situation is different. In those cases, the reactive species are confined to two (or fewer) spatial dimensions, and the partition functions are expressed per surface area or per adsorption site rather than per volume. Consequently, no volume correction appears in the expression for the surface reaction rate constant, and its dimensionality is typically s^{-1}. The total number of available adsorption sites or surface coverage then replaces the role of V in defining the molecular densities. A detailed treatment of surface reactions is given in Section 5.5.

Furthermore, note that the term $\prod_i (q_i/V)$ ensures that the dimensionality of the reaction rate constant is always consistent with the type of reaction. For example, for a unimolecular reaction, the term $1/V$ cancels out with the $1/V$ term in the numerator of Equation 4.86. Thus we obtain a dimensionality of s^{-1} for the reaction rate constant for a unimolecular reaction. Using the same line of thought, we can deduce that for a bimolecular reaction, the reaction rate constant has a dimensionality of $s^{-1} \cdot m^3$. Thus, transition state theory can be readily applied to all kind of reaction events (including the very unlikely trimolecular reactions).

Practice your understanding

Exercises 4.3, 4.4, 4.5 and 4.6

4.2.2 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

$$I = \sigma_{AB}^2 \frac{m_A m_B}{m_A + m_B} \tag{4.87}$$

[18] Note that the exponential term in Equation 4.85 corresponds to the quotient of the electronic partition functions.

[19] It is important to note that the way the rate was **defined** influences the form of the reaction rate constant. In the derivation used in this chapter, the rate was defined as a function of the reaction rate constant and the **number-densities** of the reactants. If the rate is defined, for instance, as a function of the reaction rate constant and pressures, the expression will differ as a different equilibrium constant between initial and transition state has to be used. In the next chapter, we will showcase a number of situations wherein the rate constant is calculated in different constructions of the rate expression.

and thus k can be written using expression 4.82 as

$$k = \frac{k_B T}{h} \frac{(q^{\ddagger}/V)}{(q'_A/V)(q'_B/V)} \exp\left(\frac{-\Delta E_{a,elec}}{k_B T}\right) \tag{4.88}$$

$$= \frac{k_B T}{h} \frac{q^{3D}_{trans}/V q^{2D}_{rot}}{q^{3D}_{trans}/V q^{3D}_{trans}/V} \exp\left(\frac{-\Delta E_{a,elec}}{k_B T}\right) \tag{4.89}$$

$$= \frac{k_B T}{h} \frac{\frac{(2\pi(m_A+m_B)k_B T)^{3/2}}{h^3} \frac{8\pi^2 \sigma^2_{AB} \frac{m_A m_B}{m_A+m_B} k_B T}{h^2}}{\frac{(2\pi m_A k_B T)^{3/2}}{h^3} \frac{(2\pi m_B k_B T)^{3/2}}{h^3}} \exp\left(\frac{-\Delta E_{a,elec}}{k_B T}\right) \tag{4.90}$$

$$= \left(8\pi k_B T \frac{m_A + m_B}{m_A m_B}\right)^{1/2} \sigma^2_{AB} \exp\left(\frac{-\Delta E_{a,elec}}{k_B T}\right) \tag{4.91}$$

$$= \left(\frac{8\pi k_B T}{\mu}\right)^{1/2} \sigma^2_{AB} \exp\left(-\frac{\Delta E}{k_B T}\right) \tag{4.92}$$

The above formula is equal to Equation 4.60 when multiplied by the number density of A and B $\rho_A \cdot \rho_B$, showing that both theories provide the same rate expression.

4.2.3 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

$$K = \frac{k^+}{k^-} \tag{4.93}$$

$$= \frac{\left(\frac{8\pi k_B T}{\mu_{AB}}\right)^{1/2} \sigma^2_{AB} \exp\left(\frac{-\Delta E_{act,f}}{k_B T}\right)}{\left(\frac{8\pi k_B T}{\mu_{CD}}\right)^{1/2} \sigma^2_{CD} \exp\left(\frac{-\Delta E_{act,b}}{k_B T}\right)} \tag{4.94}$$

$$= \frac{\sigma^2_{AB}}{\sigma^2_{CD}} \sqrt{\frac{\mu_{CD}}{\mu_{AB}}} \exp\left(\frac{-\Delta H}{k_B T}\right). \tag{4.95}$$

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.

4.2.4 Motivation from sequence of successful collisions

In section 4.1.4, it was shown that molecules undergoing chemical reactions are activated by collisions. From transition state theory, it follows that, by assuming thermal equilibrium between the initial and transition state, the reaction rate depends exponentially on $\Delta E_{act}/k_B T$. Transition state theory does not explicitly account for molecular collisions; however, thermal equilibrium can only be established if some form of interaction between molecules exists. Without collisions, there would be no mechanism for energy transfer.

An elegant heuristic argument showing how collisions can give rise to the exponential form of the reaction rate was provided by Hinshelwood in his seminal work *The Kinetics of Chemical Change*.[10, 11] The idea is as follows. In each collision, a molecule may either gain or lose energy.

To reach the minimum energy required to react, a molecule must experience a sequence of "favorable" collisions, i.e. those that increase its energy, until its energy exceeds the activation energy ΔE_a, which is typically much larger than the average thermal energy.

Let the probability that a favorable run is terminated (i.e., that the next collision is unfavorable) be

$$P_{\text{fail}} = \frac{1}{X}, \tag{4.96}$$

so that the probability of continuing the favorable sequence is

$$P_{\text{continue}} = 1 - \frac{1}{X}. \tag{4.97}$$

The probability that a favorable run persists for x successive collisions is then

$$P_{\text{run,continue}}(x) = \left(1 - \frac{1}{X}\right)^x = \left[\left(1 - \frac{1}{X}\right)^X\right]^{x/X}. \tag{4.98}$$

In the limit of many collisions, where $X \to \infty$ while x/X remains finite, we recover

$$\lim_{X\to\infty} P_{\text{run,continue}}(x) = \exp\left(-\frac{x}{X}\right). \tag{4.99}$$

Thus, the probability that a molecule successfully undergoes x favorable collisions before an unfavorable one decays exponentially with the ratio x/X.

In this analogy, x represents the number of successive energy-increasing collisions required for a molecule to reach the transition state and is therefore proportional to the activation energy ΔE_a. The quantity X corresponds to the average number of collisions occurring before an unfavorable one and increases with temperature T. The ratio x/X can therefore be associated with $\Delta E_a/k_B T$, leading to an exponential dependence of the reaction probability on this ratio.

This argument should not be regarded as a rigorous derivation of the Arrhenius form, but rather as an illustrative analogy. It demonstrates that an exponential dependence naturally arises when the probability of completing a long sequence of favorable events is considered.[20]

4.2.5 Comparison with the Arrhenius equation

The Arrhenius equation is an empirical relationship between the rate constant of a chemical reaction and the absolute temperature as given by

$$k = \nu \exp\left(-\frac{\Delta E_{\text{act}}}{RT}\right), \tag{4.100}$$

wherein the pre-exponential factor ν and the activation energy ΔE_{act} are determined by experimental means. The Arrhenius equation works remarkable well and as such it is interesting how it compares to the Eyring equation.

Given a hypothetical gas-phase reaction

$$\text{A} + \text{B} \to \text{C}, \tag{4.101}$$

[20] Hinshelwood explicitly emphasizes the heuristic nature of this reasoning—indeed, twice— in his book, as noted in reference [10].

the reaction rate constant as established from transition theory is given by[21]

$$k = \frac{k_B T}{h} \frac{q^{\dagger}_{\text{trans,3d}} q^{\dagger}_{\text{rot,3d}} q^{\ddagger}_{\text{vib}}}{q_{\text{A,trans,3d}} q_{\text{A,rot,3d}} q_{\text{A,vib}} \times q_{\text{B,trans,3d}} q_{\text{B,rot,3d}} q_{\text{B,vib}}} \times \cdots$$
$$\cdots \exp\left(\frac{-\Delta E_{\text{act,elec+zpe}}}{k_B T}\right)\left(\frac{V}{k_B T}\right) \tag{4.102}$$

wherein $\Delta E_{\text{act,zpe}}$ is the ZPE-corrected activation energy and for simplicity we assume the vibrational modes (where the ZPE contribution has been peeled of) to be equal to 1.

The activation energy from purely theoretical grounds can be calculated using (observe the similarity with the apparent activation energy)

$$\Delta E_{\text{act}} = k_B T \frac{\partial \ln k}{\partial T} \tag{4.103}$$

which yields for Equation 4.102

$$\Delta E_{\text{act}} = k_B T^2 \frac{\partial \ln k}{\partial T} \tag{4.104}$$
$$= E_{\text{act,elec+zpe}} + k_B T \left(1 + \left[\frac{3}{2} + \frac{3}{2}\right] - \left[\frac{3}{2} + \frac{3}{2} + \frac{3}{2} + \frac{3}{2}\right] - 1\right) \tag{4.105}$$
$$= E_{\text{act,elec+zpe}} - 3k_B T \tag{4.106}$$

where the first term within the square brackets corresponds to the derivative of the molecular partition functions for the transition state and the second term between the square brackets those terms for the initial state. Note that the value of $3k_B T$ is the result of the following three set of terms

1. The prefactor $\frac{k_B T}{h}$
2. The difference in translational and rotational degrees of freedom between initial and transition state.
3. The factor $\left(\frac{V}{k_B T}\right)$ that compensates for the difference in the number of gas phase species.

Considering the second item, each degree of freedom contributes a factor of $\frac{1}{2} k_B T$. The initial state has in total 6 translational and 6 rotational degrees of freedom whereas the transition state only has 3 of each. Consequently, there is a difference of 6 degrees of freedom giving a value of $-3k_B T$. Because the contribution due to the first item and the third item cancel out, we obtain a "correction term" of $-3k_B T$.

Since the Arrhenius equation and the Eyring equation aim to model the same chemical process, both equations should yield the same value for k such that

$$k_{\text{eyring}} = k_{\text{arrhenius}}. \tag{4.107}$$

And thus

[21] The full derivation and the assumption that go into this is shown in the next chapter, but is not relevant for the point I want to make here.

$$\nu \exp\left(-\frac{\Delta E_{\text{act}}}{RT}\right) = \frac{k_B T}{h} \frac{q^{\dagger}_{\text{trans,3d}} q^{\dagger}_{\text{rot,3d}} q^{\ddagger}_{\text{vib}}}{q_{\text{A,trans,3d}} q_{\text{A,rot,3d}} q_{\text{A,vib}} \times q_{\text{B,trans,3d}} q_{\text{B,rot,3d}} q_{\text{B,vib}}} \times \cdots$$
$$\cdots \exp\left(\frac{-\Delta E_{\text{act,elec+zpe}}}{k_B T}\right) \left(\frac{V}{k_B T}\right) \tag{4.108}$$

We can establish the value for ν in the Arrhenius equation by substituting ΔE_{act} for the value found in Equation 4.106 which yields after some algebra[22]

$$\nu = \frac{k_B T}{h} \frac{q^{\dagger}_{\text{trans,3d}} q^{\dagger}_{\text{rot,3d}} q^{\ddagger}_{\text{vib}}}{q_{\text{A,trans,3d}} q_{\text{A,rot,3d}} q_{\text{A,vib}} \times q_{\text{B,trans,3d}} q_{\text{B,rot,3d}} q_{\text{B,vib}}} \left(\frac{V}{k_B T}\right) \exp(3). \tag{4.109}$$

Conclusively, it should come as to no surprise that the Arrhenius equation works so well. It only differs from the Eyring equation by a small compensating factor equal to the difference in degrees of freedom and species between the initial and transition state.

Practice your understanding

Exercise 4.7

Challenges

Exercises 4.8 and 4.9

[22] Also see the Transition State Theory Exam Exercises 1 and 4.

4.3 Exercises

The answers to the exercises can be found at the end of this Chapter on page 196. The exercises are marked by a number of gears to indicate their difficulty levels.

EXERCISE 4.1

a) Calculate the average speed of an N_2 molecule at room temperature ($T = 298$K). Make use of the Maxwell-Boltzmann speed distribution as given in Equation 4.17 on page 172. Feel free to directly use Equation B.27 on page 278 to solve the integral.

b) At which temperature is the average speed 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.26 on page 278 to solve the integral.

EXERCISE 4.2

Given a mixture of N_2 and H_2 in a 1:3 ratio at 1.00 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 0.289 nm and the collision diameter of N_2 is 0.364 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 4.3

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 **constant** 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 4.4

Consider the gas phase isomerization of cyclopropane to propylene. We are going to calculate the reaction rate constant according to transition state theory.

a) How many degrees of freedom does cyclopropane have in total?

b) How many translational, rotational, and vibrational degrees of freedom does cyclopropane have?

c) How many translational, rotational, and vibrational degrees of freedom does the complex in the transition state between cyclopropane and propylene have?

d) Construct the expression for the rate constant according to transition state theory.

e) Calculate the activation energy according to the Arrhenius equation.

f) Assume that $\Theta_i \gg T$, where $\Theta_i = \frac{h\nu}{k_B}$. How can you simplify your answer of the previous question?

g) Provide an interpretation of the previous two answers in the context of transition state theory.

EXERCISE 4.5

In the field of astrochemistry, the chemical processes in interstellar dust clouds are being studied. A particular type of regime indicated as the *Cold Neutral Medium* (CNM) exhibits an ambient temperature of about 50-100 K. Under these conditions, the subtle interplay between the electronic activation energy and the number of accessible configurations in the transition state can play an important role in determining the dominant kinetic route in reaction mechanisms between chemical species. In this exercise, we will explore a hypothetical situation wherein a reactant A can isomerize to a product B via two different (parallel) pathways. The first pathway has a lower activation energy than the second, but the second pathway has two rotational degrees of freedom in the transition state, allowing for more accessible configurations. In other words, whereas the first pathway is favored in terms of energy, the second pathway is favored in terms of entropy.
Assume an irreversible isomerization reaction

$$A \rightarrow B, \tag{4.110}$$

that can proceed via two parallel pathways which each have a single transition state between A and B denoted as TS_1 and TS_2.

The properties of TS_1 are

- Zero point energy corrected activation energy $\Delta E^{(1)}_{\text{act,e+zpe}}$
- $3N - 1$ (real) vibrational degrees of freedom
- A single imaginary vibration in the direction of the reaction coordinate

and the properties of TS_2 are

- Zero point energy corrected activation energy $\Delta E^{(2)}_{\text{act,e+zpe}}$
- 2 rotational degrees of freedom with the same rotational temperature Θ
- $3N-3$ (real) vibrational degrees of freedom
- A single imaginary vibration in the direction of the reaction coordinate

Assume that

- $\Delta E^{(1)}_{\text{act,e+zpe}} > \Delta E^{(2)}_{\text{act,e+zpe}}$
- $\left(1-\exp\left(-\frac{h\nu}{k_b T}\right)\right)^{-1} \approx 1$
- The zero point corrected activation energies are given in J/mol (i.e. use R instead of a k_{B})
- The initial state only has vibrational degrees of freedom

(a) Construct the rate expression for both pathways. Assume that each of the rotational partition functions can be modeled using

$$q_{\text{rot}} = \sqrt{\frac{T}{\Theta}}. \tag{4.111}$$

(b) Construct the transcendental expression at which the rate for both pathways is the same.[23]

(c) Express the transcendental equation in the form

$$\exp\left(-\frac{\Delta E_{\text{diff}}}{RT}\right) = f\left(\Theta, T\right), \tag{4.112}$$

where ΔE_{diff} is the difference between the zero point energy corrected activation energies for the first and second pathways as given by

$$\Delta E_{\text{diff}} = \Delta E^{(1)}_{\text{act,e+zpe}} - \Delta E^{(2)}_{\text{act,e+zpe}}. \tag{4.113}$$

Produce an explicit expression $T_e = f(R, \Theta, \Delta E_{\text{diff}})$ for the equivalence temperature T_e by performing a Taylor expansion on the exponential term and cutting this expansion off after the linear term.

(d) Provide a limiting condition with respect to Θ, R and ΔE_{diff} for which a temperature T_e exists.

(e) Derive the cubic equation that results from a second order expansion of the exponent.

(f) Make a plot of T/Θ versus the first and second order expansions of the exponential term and the exponential term itself. Use the following values: Θ=150K and ΔE_{diff} = 0.3 kJ/mol. Highlight where the lines intersect. How well do the first and second order expansions of the exponential term compare to the exponential term?

(g) Calculate the value for T_e using the first and second order expansions of the exponential term and compare this to the exact result. How much do the first and second order solutions differ from each other and how do they compare to the exact solution?[24,25]

[23] A transcendental equation is an equation containing a transcendental function of the variable(s) being solved for. Such equations often do not have closed-form solutions.

[24] Note that your graphical calculator or any modern spreadsheet program have root finding functions by which you can establish the solution to the transcendental equation.

[25] If you want to establish the solution for the cubic equation analytically, have a look at Equation B.60 at page 282.

(h) Produce a graph of the rates of conversion via pathways 1 and 2 versus the temperature. Show that these rates are equal at the equivalence temperature T_e as calculated in the previous subquestion. Produce a secondary graph wherein the ratio k_2/k_1 is shown and show that this ratio equals 1 at the equivalence temperature T_e. Provide an interpretation of your results wherein you elaborate on the subtle interplay between energy and entropy with respect to the reaction rates.

EXERCISE 4.6

a) Derive an expression for the rate constant of O_2 dissociation into two oxygen fragments in the gas phase according to transition state theory. Provide explicit expressions 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.

In your derivation, you will encounter the following term:

$$\frac{h\nu \exp\left(-\frac{h\nu}{k_B T}\right)}{\left(1-\exp\left(-\frac{h\nu}{k_B T}\right)\right)} \tag{4.114}$$

Apply a Taylor expansion to this term, truncating it before the quadratic term, to simplify the resulting expression.

EXERCISE 4.7

In this exercise, we are going to derive the force constants for the linear H_3 system. For your convenience, we have constructed a matrix plot (see Figure 4.6 wherein the values of the potential energy as function of the A-B and B-C distances are shown. This graph uses the same values as those that were used to construct Figure 4.4. All values are given in kJ/mol.

a) Highlight the cells that correspond to the minimum energy pathway that connects the two cells which have a value of 0.0 for the potential energy. The cells wherein the potential energy is zero can be found at positions (2,13) and (13,2).

b) Identify the cell that corresponds to the transition state. What is the value of the potential energy in this cell?

c) Calculate the force constant

$$k = \frac{\partial^2 V}{\partial x^2} \tag{4.115}$$

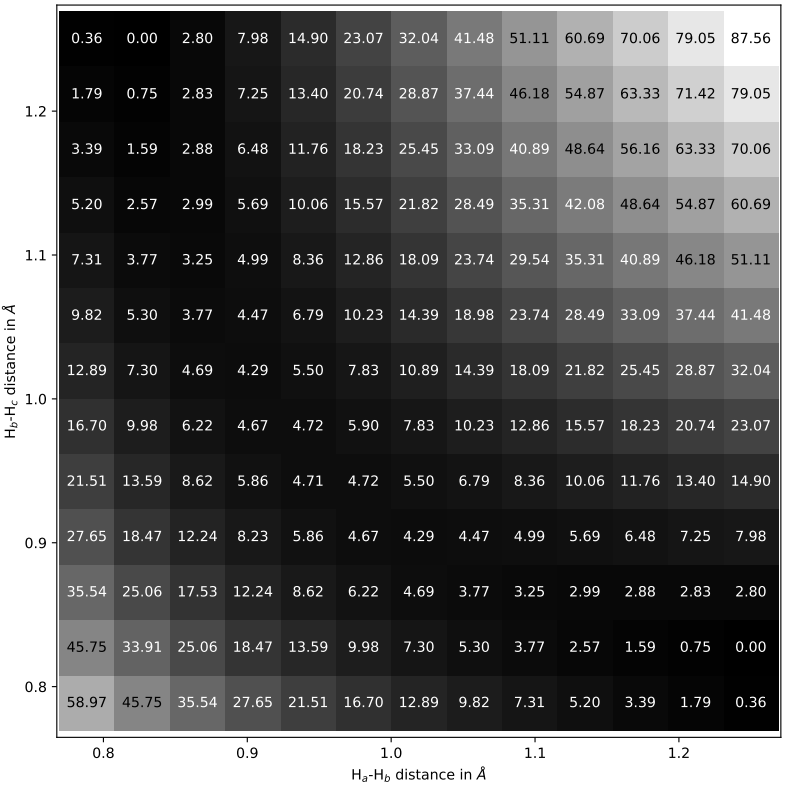


Figure 4.6: *Matrix plot around the transition state of the elementary reaction of proton shuffling in linear H_3. The data corresponds to the same dataset as used in the potential energy surface as shown in Figure 4.4. All values are given in kJ/mol.*

in the direction of the reaction coordinate and the force constant in the direction perpendicular to the reaction coordinate. Use the following numerical approximation to calculate these force constants.

$$k \approx \frac{V\left(\vec{r}_0 - \vec{h}\right) - 2V\left(\vec{r}_0\right) + V\left(\vec{r}_0 + \vec{h}\right)}{||\vec{h}||^2}, \tag{4.116}$$

where $\vec{r}_0$ is the position of the transition state and $||\vec{h}||$ the Euclidean distance (vector norm) between two diagonally adjacent cells. Note that the length of an edge of a cell is 0.0385 Å.

d) Calculate the angular 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?

e) 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 4.8 ✪✪✪✪✪

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 $k = \nu_{\text{crossing}} K$, where k is the rate constant according to transition state theory, ν_{crossing} 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_{crossing} using a different assumption.

Assume that ν_{crossing} corresponds to the vibrational frequency in the direction of the reaction coordinate (note that the frequency factor ν_{crossing} and the vibrational frequency ν 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:

$$K = \frac{1}{1 - \exp\left(-\frac{h\nu}{k_b T}\right)} \cdot \frac{\prod_i q_i}{\prod_j q_j} \exp\left(-\frac{E_{\text{act,zpe}}}{k_b T}\right) \tag{4.117}$$

where q_i are the partition functions in the transition state, q_j the partition functions in the initial state and $E_{\text{act,zpe}}$ the electronic activation energy including zero-point energy correction.

d) Assume that the frequency in the direction of the reaction coordinate is weak and that $\frac{h\nu}{k_b T} \ll 1$. Use a Taylor series (see Appendix section B.4) 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:

$$\frac{k_b T}{h\nu} \tag{4.118}$$

e) Plug the results you have obtained for K in the expression for k and assume that $\nu_{\text{crossing}} = \nu$. 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?

EXERCISE 4.9

In this exercise, we will be comparing the rate constants k as calculated by collision theory with experimental results for the union of H_2 and I_2 and the dissociation of HI. The experimental results are taken from the seminal paper of Bodenstein, written in 1899.[12] His results have been compared earlier using kinetic gas theory by Lewis in 1918[13] and we will use the cross section σ which was used in the latter work.

The elementary reaction step is given by

$$H_2 + I_2 \rightleftarrows 2HI. \tag{4.119}$$

Express all reaction rates in mol / m^3 / s. Assume that the total concentration of the gas phase species is 1000 moles / m^3.

Table 4.1: *Reaction rate constants k for the union of H_2 and I_2. Values taken from references [12] and [13].*

T [K]	556	629	666	700	781
k [mol/m^3/s]	$4.44 \cdot 10^{-5}$	$2.25 \cdot 10^{-3}$	$1.42 \cdot 10^{-2}$	$6.42 \cdot 10^{-2}$	$1.34 \cdot 10^{0}$

Table 4.2: *Reaction rate constants k for the dissociation of HI. Values taken from references [12] and [13].*

T [K]	556	629	666	700	781
k [mol/m^3/s]	$1.76 \cdot 10^{-7}$	$1.51 \cdot 10^{-5}$	$1.10 \cdot 10^{-4}$	$5.79 \cdot 10^{-4}$	$1.98 \cdot 10^{-4}$

a) Provide an expression for the reaction rate constant for the forward reaction (Equation 4.119) using collision theory. Calculate the reaction rate constant as a function of temperature between $T = 550$ K and $T = 800$K. Use a value of $\sigma_{H_2,I_2} = 2$Å and an activation energy of 168 kJ/mol.

b) Provide an expression for the reaction rate constant for the backward reaction (Equation 4.119) using collision theory. Calculate the reaction rate constant as a function of temperature between $T = 550$ K and $T = 800$K. Use a value of $\sigma = 2$Å and an activation energy of 180 kJ/mol.

c) Compare your results with the results obtained from Bodenstein as provided in Tables 4.1 and 4.2 by plotting them in a graph. Use a logarithmic axis for the reaction rate constant k.

4.4 Solutions

The solutions below pertain to the exercises of Chapter 4 on page 190 and further.

SOLUTION 4.1

a) The Maxwell-Boltzmann distribution expresses the partial fraction of a set of species given their speed and is given by the following expression

$$f = 4\pi \left(\frac{m}{2\pi k_B T} \right)^{3/2} c^2 \exp\left(\frac{-mc^2}{2k_B T} \right) \tag{4.120}$$

To calculate the average speed of an ensemble, you simply have to multiply the Maxwell-Boltzmann distribution with the speed c and integrate over all possible velocities

$$\bar{c} = \int_0^\infty 4\pi \left(\frac{m}{2\pi k_\mathrm{B} T}\right)^{3/2} c^2 \exp\left(\frac{-mc^2}{2k_\mathrm{B}T}\right) c \,\mathrm{d}c \tag{4.121}$$

$$= 4\pi \left(\frac{m}{2\pi k_\mathrm{B} T}\right)^{3/2} \int_0^\infty v^3 \exp\left(\frac{-mc^2}{2k_\mathrm{B}T}\right) \mathrm{d}c \tag{4.122}$$

$$= 4\pi \left(\frac{m}{2\pi k_\mathrm{B} T}\right)^{3/2} \frac{1}{2} \left(\frac{2k_\mathrm{B}T}{m}\right)^2 \tag{4.123}$$

$$= \left(\frac{8k_\mathrm{B}T}{\pi m}\right)^{1/2} \tag{4.124}$$

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.

$$\int_0^\infty x^{2n+1} \exp\left(-\frac{x^2}{a^2}\right) \mathrm{d}x = \frac{n!}{2} a^{2n+2} \tag{4.125}$$

Calculating the average speed for a set of N_2 molecules at room temperature gives

$$\bar{c} = \left(\frac{8RT}{\pi M}\right)^{1/2} \tag{4.126}$$

$$= \left(\frac{8 \cdot 8.3145 \text{ J mol}^{-1} \text{ K}^{-1} \cdot 298\text{K}}{\pi \, 28 \cdot 10^{-3} \text{kg} \cdot \text{mol}^{-1}}\right)^{1/2} \tag{4.127}$$

$$= 475 \text{ m} \cdot \text{s}^{-1} \tag{4.128}$$

Note that you can remember as a rule of thumb that the speed of sound is roughly 70% of the average speed of the molecules the medium is made of.

b)

$$\bar{c}_{\mathrm{N}_2} / \bar{c}_\mathrm{He} = 1 = \frac{\left(\frac{8k_\mathrm{B}T_1}{\pi m_{\mathrm{N}_2}}\right)^{1/2}}{\left(\frac{8k_\mathrm{B}T_2}{\pi m_\mathrm{He}}\right)^{1/2}} \tag{4.129}$$

Rearranging yields

$$T_1 = T_2 \cdot \frac{m_{\mathrm{N}_2}}{m_\mathrm{He}} = 2090\text{K} \tag{4.130}$$

c) In a similar manner as in *a*, we can find the translational energy by integrating the following expression

$$\bar{\epsilon_t} = \int_0^\infty 4\pi \left(\frac{m}{2\pi k_B T}\right)^{3/2} c^2 \exp\left(\frac{-mc^2}{2k_B T}\right) \frac{1}{2} mc^2 \mathrm{d}c \tag{4.131}$$

$$= 2m\pi \left(\frac{m}{2\pi k_B T}\right)^{3/2} \int_0^\infty c^4 \exp\left(\frac{-mc^2}{2k_B T}\right) \mathrm{d}c \tag{4.132}$$

$$= 2m\pi \left(\frac{m}{2\pi k_B T}\right)^{3/2} \cdot \sqrt{\pi} \cdot 12 \cdot \left(\frac{k_B T}{2m}\right)^{5/2} \tag{4.133}$$

$$= \frac{3}{2} k_B T \tag{4.134}$$

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.

$$\int_0^\infty x^{2n} \exp^{-x^2/a^2} \mathrm{d}x = \sqrt{\pi} \frac{(2n)!}{n!} \left(\frac{a}{2}\right)^{2n+1} \tag{4.135}$$

Plugging in the values for 1 mol of N_2 at 100, 298 and 1000 K yields

$$\bar{\epsilon_t}(T = 100\ \mathrm{K}) = 1.247\ \mathrm{kJ \cdot mol^{-1}} \tag{4.136}$$

$$\bar{\epsilon_t}(T = 298\ \mathrm{K}) = 3.71\ \mathrm{kJ \cdot mol^{-1}} \tag{4.137}$$

$$\bar{\epsilon_t}(T = 1000\ \mathrm{K}) = 12.47\ \mathrm{kJ \cdot mol^{-1}} \tag{4.138}$$

SOLUTION 4.2

a) Using the ideal gas law, we can write for the particle density

$$\rho = \frac{n}{V} = \frac{P}{k_B T} \tag{4.139}$$

Plugging in the numbers yields

$$\rho = \frac{P}{k_B T} = \frac{1 \cdot 10^5\ \mathrm{Pa}}{1.3806488 \cdot 10^{-23}\ \mathrm{J \cdot K^{-1}} \cdot 298.15\mathrm{K}} \tag{4.140}$$

$$= 2.43 \cdot 10^{25}\ \mathrm{particles \cdot m^{-3}} \tag{4.141}$$

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

$$\rho_{N_2} = \frac{1}{4} \cdot 2.43 \cdot 10^{25} = 6.157 \cdot 10^{24} \text{ particles} \cdot \text{m}^{-3} \tag{4.142}$$

$$\rho_{H_2} = \frac{3}{4} \cdot 2.43 \cdot 10^{25} = 1.847 \cdot 10^{25} \text{ particles} \cdot \text{m}^{-3} \tag{4.143}$$

b) The collision density is given by Equation 4.48 on 176:

$$Z = 2 \left(\frac{\pi k_B T}{m} \right)^{1/2} \sigma^2 \rho^2 = 2 \left(\frac{\pi RT}{M} \right)^{1/2} \sigma^2 \rho^2. \tag{4.144}$$

Note that in the above formula, σ is the collision **radius** as given by

$$\sigma = \frac{d_{H_2} + d_{H_2}}{2} = d_{H_2}. \tag{4.145}$$

Plugging in the values yields

$$Z(H_2, H_2) \tag{4.146}$$

$$= 2 \left(\frac{\pi \cdot 8.3145 \cdot 298 \text{ K}}{2 \cdot 10^{-3} \text{ kg} \cdot \text{mol}^{-1}} \right)^{1/2} \cdot \left(2.89 \cdot 10^{-10} \text{ m} \right)^2 \cdot \left(1.847 \cdot 10^{25} \text{ particles} \cdot \text{m}^{-3} \right)^2 \tag{4.147}$$

$$= 1.124 \cdot 10^{35} \text{ collision} \cdot \text{m}^{-3} \text{s}^{-1} \tag{4.148}$$

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+*+%28pi+*+8.3145+*+298+%2F+%282e-3%29%29%5E0.5+*+%282.89e-10%29%5E2+*+%281.847e25%29%5E2

c) Similar to the above results, we can calculate for the collision between N_2 and N_2

$$Z(N_2, N_2) \tag{4.149}$$

$$= 2 \left(\frac{\pi \cdot 8.3145 \cdot 298 \text{ K}}{28 \cdot 10^{-3} \text{ kg} \cdot \text{mol}^{-1}} \right)^{1/2} \cdot \left(3.64 \cdot 10^{-10} \text{ m} \right)^2 \cdot \left(6.157 \cdot 10^{24} \text{ particles} \cdot \text{m}^{-3} \right)^2 \tag{4.150}$$

$$= 5.297 \cdot 10^{33} \text{ collision} \cdot \text{m}^{-3} \text{s}^{-1} \tag{4.151}$$

Perform this calculation on Wolfram Alpha:
https://www.wolframalpha.com/input/?i=2+*+%28pi+*+8.3145+*+298+%2F+%2828e-3%29%29%5E0.5+*+%283.64e-10%29%5E2+*%286.157e24%29%5E2

d) We can calculate the number of collisions between N_2 and H_2 by plugging in the effective radius

$$\sigma_{AB} = \frac{d_{N_2} + d_{H_2}}{2} = \frac{(2.89 + 3.64) \cdot 10^{-10}}{2} = 3.265 \cdot 10^{-10}\ \text{m} \tag{4.152}$$

from which we find

$$Z(N_2, H_2) = \left(\frac{8\pi k_B T}{\mu}\right)^{1/2} \sigma_{AB}^2 \rho_A \rho_B \tag{4.153}$$

$$= \left(\frac{8 \cdot \pi \cdot 8.3145 \cdot 298\ \text{K}}{1.86 \cdot 10^{-3}\ \text{kg} \cdot \text{mol}^{-1}}\right)^{1/2} \cdot \left(\frac{(2.89 + 3.64) \cdot 10^{-10}}{2}\ \text{m}\right)^2 \cdot$$

$$\left(1.847 \cdot 10^{25}\ \text{particles} \cdot \text{m}^{-3}\right) \cdot \left(6.157 \cdot 10^{24}\ \text{particles} \cdot \text{m}^{-3}\right) \tag{4.154}$$

$$= 7.014 \cdot 10^{34}\ \text{collision} \cdot \text{m}^{-3}\text{s}^{-1} \tag{4.155}$$

Perform this calculation on Wolfram Alpha:
https://www.wolframalpha.com/input?i=%288+*+pi+*+8.3145+*+298+%2F+%281.86e-3%29%29%5E0.5+*+%28%282.89+%2B+3.64%29*1e-10+%2F+2%29%5E2+*1.847e25+*+6.157e24

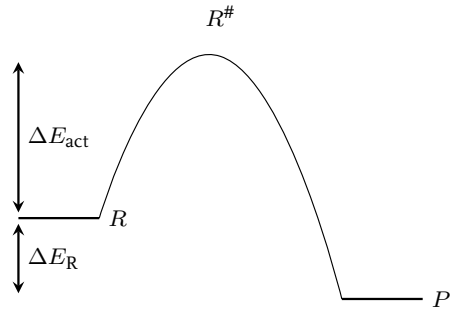
⚠ Note that we directly obtain the total number of collisions between hydrogen and nitrogen by evaluating the above expression. Swapping hydrogen and nitrogen in the above formula gives exactly the same number. Since a collision of hydrogen with nitrogen is also a collision of nitrogen with hydrogen, we only have to evaluate Equation 4.153 once. This principle relates to the motivation why a factor of $\frac{1}{2}$ was introduced in Equation 4.45 on 176.

e) The number of collision is just the sum of all possible sets of collisions yielding

$$Z_{\text{total}} = 1.124 \cdot 10^{35} + 5.297 \cdot 10^{33} + 7.014 \cdot 10^{34} \tag{4.156}$$

$$= 1.878 \cdot 10^{35}\ \text{collision} \cdot \text{m}^{-3}\text{s}^{-1} \tag{4.157}$$

SOLUTION 4.3



a) The general reaction equation being used is

$$\text{R} \underset{k_1^-}{\overset{k_1^+}{\rightleftharpoons}} \text{R}^{\#} \xrightarrow[]{k_2} \text{P} \tag{4.158}$$

This gives the following rate expression

$$r = k_2 K_1 [\text{R}] \tag{4.159}$$

b) The general expression is

$$k = \frac{k_\text{B} T}{h} \frac{(q^{\ddagger}/V)}{\prod_i (q_i/V)} \exp\left(-\frac{\Delta E_{\text{a,elec}}}{k_\text{B} T}\right) \tag{4.160}$$

Note that in the above expression, $q^{\ddagger}$ 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 4.4

a) The chemical formula of cyclopropane is C_3H_6. It thus has nine atoms, giving $n = 3N = 27$ degrees of freedom.

b) Cyclopropane is a non-linear polyatomic molecule (in the gas phase), thus we have to apply $n_v = 27 - 6 = 21$ for the number of vibrational degrees of freedom. Cyclopropane can move in three directions and we can identify three rotational axes, hence cyclopropane has 3 translational and 3 rotational degrees of freedom.

c) The complex in the transition state is still a single gas phase species, so the same rules as above apply with the exception that one of the vibrational modes now corresponds to an imaginary frequency. Thus we 3 translational, 3 rotational, and 21 vibrational degrees of which one has an imaginary frequency. The total number of degrees of freedom remains the same and is $n = 3N = 27$.

d) The general expression is given in Equation 4.86 on page 185. Using the information above, we can readily construct an expression for the rate constant:

$$k = \frac{k_\mathrm{B}T}{h} \frac{(q^\ddagger/V)}{\prod_i (q_i/V)} \exp\left(-\frac{\Delta E_\mathrm{a,e}}{k_\mathrm{B}T}\right) \tag{4.161}$$

$$= \frac{k_\mathrm{B}T}{h} \frac{\left(q^\ddagger_\mathrm{vib}\right)^{(20)} q^\ddagger_\mathrm{rot,3D} q^\ddagger_\mathrm{trans,3D}}{\left(q_\mathrm{vib}\right)^{(21)} q_\mathrm{rot,3D} q_\mathrm{trans,3D}} \exp\left(\frac{-\Delta E_\mathrm{a,e}}{k_\mathrm{B}T}\right), \tag{4.162}$$

where the ‡ symbol indicates the partition function of the transition state complex and $q^{(n)}$ is short-hand notation for $\prod_{i=1}^{n} q_i$. Note that as the activation energy is given with respect to the electronic ground state, the vibrational partition functions are also set with respect to the electronic ground state and thus correspond to Equation 3.115 on page 150.

e) Arrhenius theory is an empirical theory which states that

$$\Delta E^\mathrm{arrhenius}_\mathrm{act} = k_\mathrm{B}T^2 \frac{\partial \ln k}{\partial T}. \tag{4.163}$$

Evaluating the above expression yields

$$= k_{\mathrm{B}}T^2 \frac{\partial}{\partial T} \ln \left\{ \frac{k_{\mathrm{B}}T}{h} \frac{\left(q^{\ddagger}_{\mathrm{vib}}\right)^{(20)} q^{\ddagger}_{\mathrm{rot,3D}} q^{\ddagger}_{\mathrm{trans,3D}}}{\left(q_{\mathrm{vib}}\right)^{(21)} q_{\mathrm{rot,3D}} q_{\mathrm{trans,3D}}} \exp\left(\frac{-\Delta E_{\mathrm{a,e}}}{k_{\mathrm{B}}T}\right) \right\} \tag{4.164}$$

$$= k_{\mathrm{B}}T^2 \frac{\partial}{\partial T} \left\{ \ln(T) + \ln\left(\frac{\left(q^{\ddagger}_{\mathrm{vib}}\right)^{(20)}}{\left(q_{\mathrm{vib}}\right)^{(21)}}\right) + \ln\left(\frac{q^{\ddagger}_{\mathrm{rot,3D}} q^{\ddagger}_{\mathrm{trans,3D}}}{q_{\mathrm{rot,3D}} q_{\mathrm{trans,3D}}}\right) \right\} + \Delta E_{\mathrm{a,e}} \tag{4.165}$$

$$= k_{\mathrm{B}}T^2 \frac{\partial}{\partial T} \left\{ \ln(T) + \ln\left(\frac{\left(q^{\ddagger}_{\mathrm{vib}}\right)^{(20)}}{\left(q_{\mathrm{vib}}\right)^{(21)}}\right) + \ln\left(\frac{T^{6/2}}{T^{6/2}}\right) \right\} + \Delta E_{\mathrm{a,e}} \tag{4.166}$$

$$= k_{\mathrm{B}}T^2 \frac{\partial}{\partial T} \left\{ \ln(T) + \ln\left(\frac{\prod_i^{20} \exp\left(-\frac{h\nu_i^{\ddagger}}{2k_{\mathrm{B}}T}\right)}{\prod_i^{21} \exp\left(-\frac{h\nu_i}{2k_{\mathrm{B}}T}\right)}\right) + \ln\left(\frac{\prod_i^{21}\left(1-\exp\left(-\frac{h\nu_i}{k_{\mathrm{B}}T}\right)\right)}{\prod_i^{20}\left(1-\exp\left(-\frac{h\nu_i^{\ddagger}}{k_{\mathrm{B}}T}\right)\right)}\right) \right\} + \Delta E_{\mathrm{a,e}} \tag{4.167}$$

$$= k_{\mathrm{B}}T^2 \frac{\partial}{\partial T} \left\{ \ln(T) + \ln\left(\frac{\prod_i^{21}\left(1-\exp\left(-\frac{h\nu_i}{k_{\mathrm{B}}T}\right)\right)}{\prod_i^{20}\left(1-\exp\left(-\frac{h\nu_i^{\ddagger}}{k_{\mathrm{B}}T}\right)\right)}\right) \right\} + \Delta E_{\mathrm{a,e+zpe}} \tag{4.168}$$

$$= k_{\mathrm{B}}T^2 \left\{ \frac{1}{T} + \sum_i^{20} \frac{h\nu_i^{\ddagger}}{k_{\mathrm{B}}T^2} \left(\exp\left(+\frac{h\nu_i^{\ddagger}}{k_{\mathrm{B}}T}\right) - 1\right)^{-1} - \sum_i^{21} \frac{h\nu_i}{k_{\mathrm{B}}T^2} \left(\exp\left(+\frac{h\nu_i}{k_{\mathrm{B}}T}\right) - 1\right)^{-1} \right\} + \Delta E_{\mathrm{a,e+zpe}} \tag{4.169}$$

$$= \Delta E_{\mathrm{a,e+zpe}} + k_{\mathrm{B}}T + \sum_i^{20} h\nu_i^{\ddagger} \left(\exp\left(+\frac{h\nu_i^{\ddagger}}{k_{\mathrm{B}}T}\right) - 1\right)^{-1} - \sum_i^{21} h\nu_i \left(\exp\left(+\frac{h\nu_i}{k_{\mathrm{B}}T}\right) - 1\right)^{-1} \tag{4.170}$$

where $\Delta E_{\mathrm{a,e+zpe}}$ corresponds to the zero point energy corrected activation energy as given by

$$\Delta E_{\mathrm{a,e+zpe}} = \Delta E_{\mathrm{a,e}} + \sum_i \epsilon^{\ddagger}_{\mathrm{zpe},i} - \sum_i \epsilon_{\mathrm{zpe},i}, \tag{4.171}$$

where

$$\epsilon_{\mathrm{zpe}} = \frac{h\nu}{2}. \tag{4.172}$$

Note that in the above equation, the T-dependency of the translational and rotational partition functions cancel out. This is not because they are the same, but because their T-dependency is the same (which is what we probe with the apparent activation energy).

f) $\Theta_i \gg T$ is the same as stating that $q_{\text{vib}} \approx 1$. Thus all the terms that depend on the vibrational partition function can be discarded, yielding

$$\Delta E_{\text{act}}^{\text{arrhenius}} = \Delta E_{\text{a,e+zpe}} + k_{\text{B}} T \tag{4.173}$$

g) The activation energy of a reaction corresponds to the difference in energy between the transition state and initial state. As a function of temperature, more and more vibrational energy levels get excited, increasing the energy of the initial or transition state. From the equation, we can observe that the total activation energy is the sum of the electronic activation energy, corrected for the zero-point energies (because these correspond to the lowest occupied vibrational states) and a term corresponding to the average vibrational energy with respect to the lowest vibrational state.

Under typical conditions, the separation in energy between the vibrational energy levels is so high that under terrestrial conditions only the vibrational ground state is occupied. This means, that the term in the exponent is relatively big. Since we are taking the reciprocal of this term, we are multiplying $h\nu_i$ by a very small number and thus we can often neglect the $h\nu_i \left(\exp\left(+\frac{h\nu_i^{\ddagger}}{k_{\text{B}} T} \right) - 1 \right)^{-1}$ terms in the equation.[26]

SOLUTION 4.5

a) Starting at the generalized expression for the Eyring equation and plugging in the partition functions corresponding to the IS and TS for pathway 1 (using shorthand notation), we find

$$k_1 = \frac{k_B T}{h} \frac{Q^{\ddagger}}{Q} \exp\left(-\frac{\Delta E_{\text{act,e}}^{(1)}}{k_B T} \right) \tag{4.174}$$

$$= \frac{k_B T}{h} \frac{q_v^{(3N-1)}}{q_v^{(3N)}} \exp\left(-\frac{\Delta E_{\text{act,e}}^{(1)}}{k_B T} \right) \tag{4.175}$$

We can readily migrate the ZPE component of the vibrational partition function

$$q_v = \left(1 - \exp\left(-\frac{h\nu}{k_B T} \right) \right)^{-1} \underbrace{\exp\left(-\frac{h\nu}{2k_B T} \right)}_{\text{ZPE component}} \tag{4.176}$$

[26] We leave it as an additional exercise to the reader to verify that in the limit of $T \to \infty$, the term $h\nu_i \left(\exp\left(+\frac{h\nu_i^{\ddagger}}{k_{\text{B}} T} \right) - 1 \right)^{-1} \approx k_{\text{B}} T$. The easiest way to see this is by constructing a Taylor expansion of the exponential term and cutting the expansion off after the linear term. The plus and minus one terms cancel out, leaving a single $k_{\text{B}} T$ term.

to the exponent term containing the electronic activation energy, yielding modified $q\prime_v$, resulting in[27]

$$k_1 = \frac{k_B T}{h} \frac{q\prime_v^{(3N-1)}}{q\prime_v^{(3N)}} \exp\left(-\frac{\Delta E^{(1)}_{\text{act,e+zpe}}}{k_B T}\right) \tag{4.177}$$

Given that

$$q_v\prime = \left(1 - \exp\left(\frac{h\nu}{k_B T}\right)\right)^{-1} \approx 1 \; \forall \; \nu \tag{4.178}$$

we can simplify the reaction rate constant equation even further to

$$k_1 = \frac{k_B T}{h} \frac{q\prime_v^{(3N-1)}}{q\prime_v^{(3N)}} \exp\left(-\frac{\Delta E^{(1)}_{\text{act,e+zpe}}}{k_B T}\right) \tag{4.179}$$

$$= \frac{k_B T}{h} \exp\left(-\frac{\Delta E^{(1)}_{\text{act,e+zpe}}}{k_B T}\right). \tag{4.180}$$

In a very similar fashion we find

$$k_2 = \frac{k_B T}{h} \frac{Q^{\ddagger}}{Q} \exp\left(-\frac{\Delta E^{(2)}_{\text{act,e}}}{k_B T}\right) \tag{4.181}$$

$$= \frac{k_B T}{h} \frac{q_v^{(3N-3)} q_r^{(2)}}{q_v^{(3N)}} \exp\left(-\frac{\Delta E^{(2)}_{\text{act,e}}}{k_B T}\right) \tag{4.182}$$

$$= \frac{k_B T}{h} q_r^{(2)} \frac{q\prime_v^{3N-3}}{q\prime_v^{3N}} \exp\left(-\frac{\Delta E^{(2)}_{\text{act,e+zpe}}}{k_B T}\right) \tag{4.183}$$

$$= \frac{k_B T}{h} \frac{T}{\Theta} \exp\left(-\frac{\Delta E^{(2)}_{\text{act,e+zpe}}}{k_B T}\right) \tag{4.184}$$

Finally, since $r_i = k_i \rho_A$, we obtain

$$r_1 = \frac{k_B T}{h} \exp\left(-\frac{\Delta E^{(1)}_{\text{act,e+zpe}}}{k_B T}\right) \rho_A \tag{4.185}$$

$$r_2 = \frac{k_B T}{h} \frac{T}{\Theta} \exp\left(-\frac{\Delta E^{(2)}_{\text{act,e+zpe}}}{k_B T}\right) \rho_A \tag{4.186}$$

[27] Note the primes.

b) To determine the transcendental equation that describes the temperature at which the rate of conversion from A to B would be the same for both pathways, we set

$$r_1 = r_2 \tag{4.187}$$

from which it follows that

$$\exp\left(-\frac{\Delta E^{(1)}_{\text{act,e+zpe}} - \Delta E^{(2)}_{\text{act,e+zpe}}}{RT}\right) = \frac{T}{\Theta} \tag{4.188}$$

c) Equation 4.188 can be written as

$$\exp\left(-\frac{\Delta E_{\text{diff}}}{RT}\right) = \frac{T}{\Theta}. \tag{4.189}$$

Performing a Taylor expansion on the exponential term and cutting this expansion off after the linear term yields

$$1 - \frac{\Delta E_{\text{diff}}}{RT} = \frac{T}{\Theta}. \tag{4.190}$$

This equation can be rewritten into the following form by which we can readily apply the quadratic formula (see Equation B.58 on page 282) to find the two roots of the equation.

$$T_e^2 - \Theta T_e + \Delta E_{\text{diff}} \frac{\Theta}{R} = 0 \tag{4.191}$$

Using the quadratic formula, the temperature of equivalence can be established to be

$$T_e = \frac{\Theta \pm \sqrt{\Theta^2 - 4\Delta E_{\text{diff}} \frac{\Theta}{R}}}{2} \tag{4.192}$$

which can be rewritten to

$$T_e = \frac{\Theta \pm \left[\Theta\sqrt{1 - \frac{4\Delta E_{\text{diff}}}{R\Theta}}\right]}{2}. \tag{4.193}$$

Since $\sqrt{1 - \frac{4\Delta E_{\text{diff}}}{R\Theta}} < 1$, the equivalence temperature T_e is always positive (assuming its non-imaginary) by which both roots of the equation are valid solutions.

d) Because the equivalence temperature T_e needs to be a real-valued number, the part inside the square root has to be positive. Hence the limiting condition by which a solution is found is given by

$$\frac{4\Delta E_{\text{diff}}}{R\Theta} \leq 1. \tag{4.194}$$

If the above condition is not met, this implies that one of the two pathways has a universally (i.e. at all possible temperatures) higher rate as compared to the other.

e) Using a second order expansion implies that the Taylor expansion is cut off after the quadratic term. This yields the following equation:

$$1 - \frac{\Delta E_{\text{diff}}}{RT} + \frac{1}{2}\left(\frac{\Delta E_{\text{diff}}}{RT}\right)^2 = \frac{T}{\Theta}. \tag{4.195}$$

We can rewrite this equation into the standard form of a cubic equation as given by

$$T^3 - \Theta T^2 + \Theta\frac{\Delta E_{\text{diff}}}{R}T - \frac{\Theta}{2}\left(\frac{\Delta E_{\text{diff}}}{R}\right)^2 = 0. \tag{4.196}$$

f)

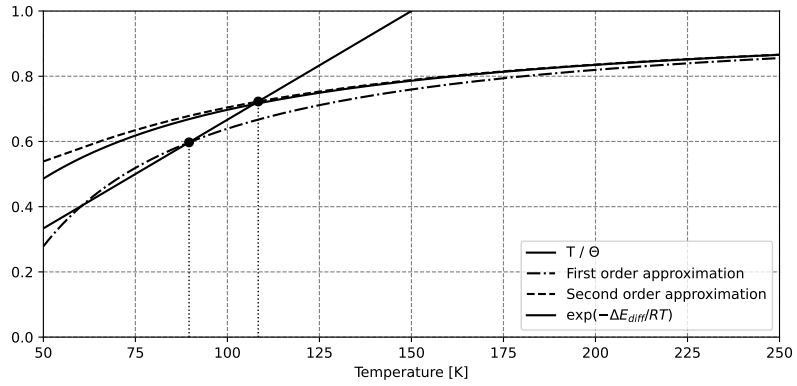


Figure 4.7: *Comparison of the first and second order expansion of the exponential term with the exponential term itself. The points of intersection of the exponential term and its approximations with the line T/Θ are shown.*

g) Solving for the quadratic and cubic equations using equations B.58 and B.60 on page 282, the first and second order approximations to T_e yield the following values[28]

$$T_{e,\text{first}} = 89.5865813 \text{ K} \tag{4.197}$$

$$T_{e,\text{second}} = 108.3727518 \text{ K}. \tag{4.198}$$

[28] We are only showing this many digits after the decimal point for the purpose of comparing the solutions. By no means do we have the impression that one could measure temperatures at this level of accuracy.

The exact result is

$$T_{e,\text{exact}} = 107.09620097 \text{ K}, \tag{4.199}$$

which only starts to differ after the sixth digit after the decimal point with respect to the results as found using the second order approximation. As such, we can readily conclude that the second order expansion of the exponential term is a very accurate approximation, whereas the first order expansion gives a measurable difference with respect to the exact solution.

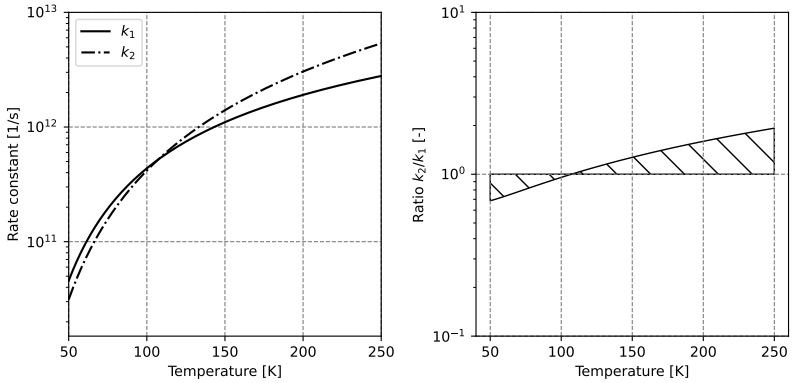


Figure 4.8: *(left) The rate constant in pathways 1 and 2 as a function of the temperature T. (right) The ratio k_2/k_1 as function of temperature. From both figures, it can be observed that below the equivalence temperature T_e, the first pathway (with k_1) has the highest rate, whereas above the equivalence temperature, the second pathway (with k_2) has the highest rate.*

h) In Figure 4.8, a comparison between the two pathways is shown. From this Figure, it can be seen that at $T < T_e$, the first pathway is the dominant pathway, whereas at $T > T_e$, the second pathway dominates. The interpretation of this situation is fairly straightforward. At very low temperature, not that many of the rotational states are accessible and the activation energy (which resides in the exponent), is the most important term for the rate of the reaction. With increasing temperature, more and more of the rotational states in the second transition state become accessible. At temperatures above the equivalence temperature, the number of accessible quantum states in the second transition state outweighs the extra cost to access this transition state with respect to the first transition state. In other words, above the equivalence temperature, the entropic factors are outweighing the energetic factors and in this regime, the second pathway exhibits a higher rate than the first pathway.

SOLUTION 4.6

a) For the initial state, it is assumed that the complex has three translational degrees of freedom, two rotational degrees of freedom and one vibrational degree of freedom corresponding to the O-O stretching frequency. In the transition state, this vibrational mode will correspond to dissociation reaction coordinate and thus this mode becomes an imaginary frequency. Using the Eyring equation, this results in the following expression for the reaction rate constant:

$$k = \frac{k_B T}{h} \frac{(q^{\ddagger}/V)}{\prod_i (q_i/V)} \exp\left(\frac{-\Delta E_{\text{act,elec}}}{k_B T}\right) = \frac{k_B T}{h} \frac{\left(q^{\ddagger}_{\text{r,2D}} q^{\ddagger}_{\text{t,3D}}\right)}{q_v q_{\text{r,2D}} q_{\text{t,3D}}} \exp\left(-\frac{\Delta E_{\text{act,elec}}}{k_B T}\right), \tag{4.200}$$

where the ‡ symbol refers to the partition function of the transition state. Expressions for the translational, rotational and vibrational partition functions can be obtained from Equation 3.64, 3.82 and 3.110 respectively.

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. Fortunately, because the number of translational and rotational partition functions is similar for the transition state as for the initial state, their respective contributions will cancel out and we are allowed to *a priori* neglect these.

$$\Delta E_{\text{act}}^{\text{arrhenius}} = k_B T^2 \frac{\partial \ln k}{\partial T} \tag{4.201}$$

$$= \Delta E_{\text{act,elec}} + k_B T^2 \frac{\partial \ln \frac{k_B T}{h}}{\partial T} - k_B T^2 \frac{\partial}{\partial T} \ln(q_v) \tag{4.202}$$

$$= \Delta E_{\text{act,elec}} + k_B T^2 \frac{\partial \ln \frac{k_B T}{h}}{\partial T} + k_B T^2 \frac{\partial}{\partial T} \ln\left(\frac{1 - \exp\left(-\frac{h\nu}{k_B T}\right)}{\exp\left(-\frac{h\nu}{2k_B T}\right)}\right) \tag{4.203}$$

$$= \Delta E_{\text{act,elec}} + k_B T^2 \frac{\partial \ln \frac{k_B T}{h}}{\partial T} + k_B T^2 \frac{\partial}{\partial T} \left[\ln\left(1 - \exp\left(-\frac{h\nu}{k_B T}\right)\right) + \frac{h\nu}{2k_B T}\right] \tag{4.204}$$

$$= \Delta E_{\text{act,elec}} - \frac{h\nu}{2} + k_B T - \frac{h\nu \exp\left(-\frac{h\nu}{k_B T}\right)}{\left(1 - \exp\left(-\frac{h\nu}{k_B T}\right)\right)} \tag{4.205}$$

$$= \Delta E_{\text{act,zpe}} + k_B T - \frac{h\nu \exp\left(-\frac{h\nu}{k_B T}\right)}{\left(1 - \exp\left(-\frac{h\nu}{k_B T}\right)\right)} \tag{4.206}$$

where $\Delta E_{\text{act,zpe}}$ corresponds to the electronic activation energy including zero-point energy corrections.

ℹ Note that in this derivation, we considered only a single vibrational mode (the O–O stretching vibration) which becomes the reaction coordinate in the transition state. The corresponding zero-point energy term $h\nu/2$ therefore represents the lowest quantized vibrational level associated with this mode. The multiplication of the Boltzmann factor for the electronic activation energy with the exponential term from the vibrational partition function,

$$\exp\left(-\frac{\Delta E_{\text{act,elec}}}{k_B T}\right) \exp\left(-\frac{h\nu}{2k_B T}\right), \tag{4.207}$$

combines into a single exponential through addition of exponents:

$$\exp\left[-\frac{\left(\Delta E_{\text{act,elec}}+\frac{1}{2}h\nu\right)}{k_{\text{B}}T}\right]. \tag{4.208}$$

This shows that the apparent activation energy naturally includes the zero-point energy contribution from this vibrational mode.

For molecules with multiple vibrational degrees of freedom, the same reasoning applies, and the total correction would be the *sum over all vibrational modes*, i.e. the difference in total zero-point energies between the transition and initial states.

Applying a Taylor approximation to the last term, truncating before the quadratic terms, gives

$$\frac{h\nu\exp\left(-\frac{h\nu}{k_{\text{B}}T}\right)}{\left(1-\exp\left(-\frac{h\nu}{k_{\text{B}}T}\right)\right)}\approx\frac{h\nu\left(1-\frac{h\nu}{k_{\text{B}}T}\right)}{1-1+\frac{h\nu}{k_{\text{B}}T}} \tag{4.209}$$

This we can further simplify this equation by assuming that $\frac{h\nu}{k_{\text{B}}T}\ll 1$.

$$\frac{h\nu\left(1-\frac{h\nu}{k_{\text{B}}T}\right)}{1-1+\frac{h\nu}{k_{\text{B}}T}}=k_{\text{B}}T\left(1-\frac{h\nu}{k_{\text{B}}T}\right)\approx k_{\text{B}}T \tag{4.210}$$

And thus finally obtaining

$$\Delta E_{\text{act}}^{\text{arrhenius}}=\Delta E_{\text{act,zpe}} \tag{4.211}$$

SOLUTION 4.7

a) The minimum energy pathway is highlighted in Figure 4.9.

b) The cell at position (5,5) which has a value of 4.71 kJ/mol for the potential energy.

c) The force constant in the direction of the reaction coordinate is

$$k_{\parallel}\approx\frac{V\left(\vec{r}_0-\vec{h}\right)-2V\left(\vec{r}_0\right)+V\left(\vec{r}_0+\vec{h}\right)}{||h||^2} \tag{4.212}$$

$$=\frac{4.67\text{ kJ/mol}-2\cdot 4.71\text{ kJ/mol}+4.67\text{ kJ/mol}}{\left(\sqrt{2}\cdot 0.0385\text{ Å}\right)^2} \tag{4.213}$$

$$=-27.0\text{kJ/mol/Å}^2 \tag{4.214}$$

$$=-4.48\text{N/m}. \tag{4.215}$$

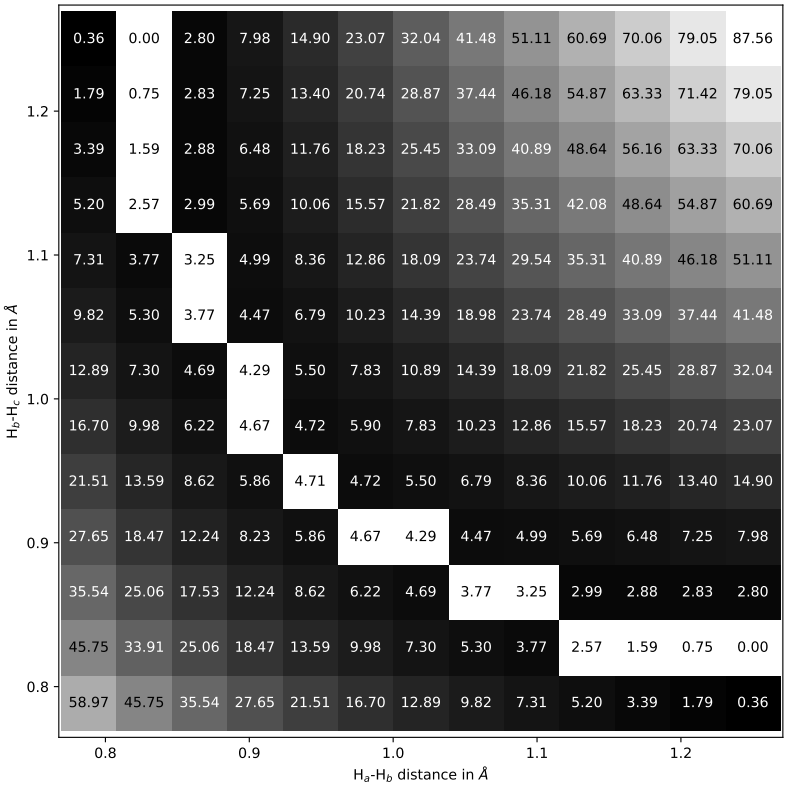


Figure 4.9: *The highlighted cells (in white) correspond to the minimum energy pathway over the potential energy surface.*

The force constant perpendicular to the direction of the reaction coordinate is

$$k_\perp \approx \frac{V\left(\vec{r}_0 - \vec{h}\right) - 2V\left(\vec{r}_0\right) + V\left(\vec{r}_0 + \vec{h}\right)}{||h||^2} \tag{4.216}$$

$$= \frac{8.23\ \text{kJ/mol} - 2 \cdot 4.71\ \text{kJ/mol} + 5.90\ \text{kJ/mol}}{\left(\sqrt{2} \cdot 0.0385\ \text{Å}\right)^2} \tag{4.217}$$

$$= 1589\ \text{kJ/mol/ Å}^2 \tag{4.218}$$

$$= 264\ \text{N/m}. \tag{4.219}$$

Note that $h = \sqrt{2} \cdot 0.0385$ Å because we take the distances across the diagonal of the cells.

d)

$$\omega_{\parallel} = \sqrt{\frac{k_{\parallel}}{\mu}} \tag{4.220}$$

$$= \sqrt{\frac{-4.48 \text{ N/m}}{1.66 \cdot 10^{-27} \text{ kg}}} \tag{4.221}$$

$$= 51.9i \cdot 10^{12} \text{ rad s}^{-1}, \tag{4.222}$$

where $i = \sqrt{-1}$ and

$$\omega_{\perp} = \sqrt{\frac{k_{\perp}}{\mu}} \tag{4.223}$$

$$= \sqrt{\frac{263 \text{ N/m}}{1.66 \cdot 10^{-27} \text{ kg}}} \tag{4.224}$$

$$= 397 \cdot 10^{12} \text{ rad s}^{-1}. \tag{4.225}$$

The angular frequency corresponding to a vibration in the direction of the reaction coordinate is the **imaginary frequency**. This corresponds to the point on the PES to be a maximum in that direction.

e) 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

$$\frac{\partial V}{\partial q_i} = 0 \text{ for all } i. \tag{4.226}$$

Note though that such a state is meta stable in the sense that a small perturbation 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 4.8

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 as

$$K = \frac{\rho^\dagger}{\prod_i \rho_i} = \frac{(q^\dagger/V)}{\prod_i (q_i/V)}, \tag{4.227}$$

wherein we have only assumed that the transition state corresponds to a single complex and where $q^\dagger$ is the **molecular** partition function in the transition state and q_i is the **molecular** partition function of the species in the initial state (i loops here over the species). 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

$$K = \frac{(q'^\dagger/V)}{\prod_i (q'_i/V)} \left(\exp\left(\frac{-E_e^\dagger}{k_B T}\right) / \exp\left(\frac{-E_e}{k_B T}\right) \right) \tag{4.228}$$

$$K = \frac{(q'^\dagger/V)}{\prod_i (q'_i/V)} \exp\left(\frac{-(E_e^\dagger - E_e)}{k_B T}\right) \tag{4.229}$$

$$K = \frac{(q'^\dagger/V)}{\prod_i (q'_i/V)} \exp\left(-\frac{\Delta E_{a,e}}{k_B T}\right) \tag{4.230}$$

where $q'^\dagger$ is the **configurational** partition function in the transition state and q'_i the **configurational** partition function of complex i in the initial state. The configurational partition function is the product of the rotational, translational and vibrational partition functions.

We now transfer the zero point energy from the vibrational partition function to the activation energy, by which we obtain

$$K = \frac{(q'^\dagger/V)}{\prod_i (q'_i/V)} \exp\left(-\frac{\Delta E_{act,zpe}}{k_B T}\right), \tag{4.231}$$

and wherein all q_V are defined according to Equation 3.109 as given on page 148. From the configurational partition function in the transition state, we are going to extract the partition function corresponding to the loose vibration. This yields

$$K = \frac{(q'^\dagger/V)}{\prod_i (q'_i/V)} \exp\left(-\frac{\Delta E_{act,zpe}}{k_B T}\right) \tag{4.232}$$

$$K = \frac{1}{1 - \exp\left(-\frac{h\nu}{k_B T}\right)} \frac{(q''^\dagger/V)}{\prod_i (q'_i/V)} \exp\left(-\frac{\Delta E_{act,zpe}}{k_B T}\right) \tag{4.233}$$

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

$$q^{\dagger}_{\text{vib}} = \frac{1}{1 - \exp\left(-\frac{h\nu}{k_{\text{B}}T}\right)} \tag{4.234}$$

$$= \frac{1}{1 - 1 + \frac{h\nu}{k_{\text{B}}T}} \tag{4.235}$$

$$= \frac{1}{\frac{h\nu}{k_{\text{B}}T}} \tag{4.236}$$

$$= \frac{k_{\text{B}}T}{h\nu} \tag{4.237}$$

e) Plugging the result for the loose vibration into the formula for the rate constant and using $\nu_{\text{crossing}} = \nu$ gives

$$k = \nu_{\text{crossing}} K \tag{4.238}$$

$$= \frac{k_{\text{B}}T}{h\nu} \nu_{\text{crossing}} \frac{(q''^{\dagger}/V)}{\prod_i (q'_i/V)} \exp\left(-\frac{\Delta E_{\text{a,e+zpe}}}{k_{\text{B}}T}\right) \tag{4.239}$$

$$= \frac{k_{\text{B}}T}{h} \frac{(q''^{\dagger}/V)}{\prod_i (q'_i/V)} \exp\left(-\frac{\Delta E_{\text{a,e+zpe}}}{k_{\text{B}}T}\right) \tag{4.240}$$

$$= \frac{k_{\text{B}}T}{h} \frac{(q^{\ddagger}/V)}{\prod_i (q_i/V)} \exp\left(-\frac{\Delta E_{\text{a,e+zpe}}}{k_{\text{B}}T}\right) \tag{4.241}$$

where $q^{\ddagger}$ is the configurational partition function in the transition state without the partition function corresponding to the loose vibration and q_i the configurational partition function of a complex in the initial state with respect to the zpe level. Note that we have dropped all primes.

SOLUTION 4.9

a) The rate constant for union is given in Equation 4.60 on page 179. Expressing this rate in moles / m^3 / s and extracting the reaction rate constant from the expression yields

$$k_{\text{f}} = \frac{1}{N_{\text{a}}} \rho \left(\frac{8\pi k_{\text{B}}T}{\mu}\right)^{1/2} \sigma_{AB}^2 \exp\left(\frac{-\Delta E_{\text{act}}}{k_{\text{B}}T}\right), \tag{4.242}$$

where N_{a} is Avogadro's number and ρ is the total density of gas phase molecules in mol / m^3.

b) Similar to the previous subquestion, from Equation 4.61 on page 179, the reaction rate constant k is given by

$$k_{\text{b}} = \frac{2}{N_{\text{a}}} \rho \left(\frac{\pi k_{\text{B}}T}{m}\right)^{1/2} \sigma^2 \exp\left(\frac{-\Delta E_{\text{act}}}{k_{\text{B}}T}\right). \tag{4.243}$$

c) The comparison between the reaction rate constants as calculated from collision theory versus the experimental results are provided in Figure 4.10. We can readily see from this Figure that the theory is in agreement with experiment. The main reason for this agreement is that small diatomic molecules such as H_2, I_2 and HI can be adequately modeled with the framework of assumptions used in collision theory.

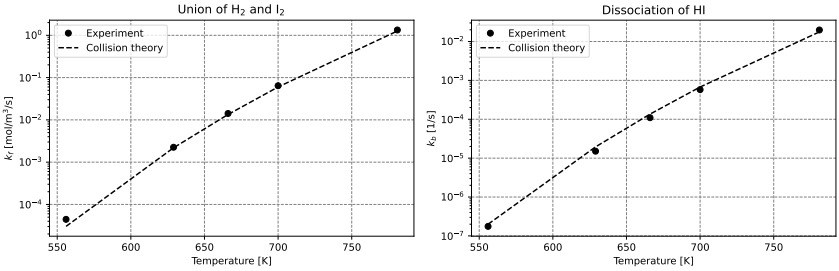


Figure 4.10: *Comparison between reaction rate constants calculated from collision theory versus experiment. Experimental data are taken from references [12] and [13].*

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CHAPTER 5

THE RATES OF ELEMENTARY REACTION STEPS

Contents

5.1 Introduction

In the previous chapters, the important concepts of statistical thermodynamics to calculate rate equations from first principles were discussed. In this chapter, we will build further upon this body of knowledge and derive specific expressions for various types of elementary reaction steps. The derivation will be very similar to the derivation of the Eyring equation as shown in the previous Chapter. In short, we start by constructing an expression for the rate of change as a function of a crossing frequency and a assumed thermal equilibrium between initial and final state.

$$\text{rate} = \nu K^{\dagger}[\text{reactants}] = k[\text{reactants}] \tag{5.1}$$

where ν is the crossing frequency, K the equilibrium constant between initial and transition state, [reactants] the concentration, number density or partial pressure of the reactants and k the reaction rate constants.

Next, we express the equilibrium constant in terms of the partition functions of the initial and transition state and extract one degree of freedom from the transition state to cancel out the crossing frequency to obtain an expression for the reaction rate constants as shown for instance below

$$k = \frac{k_B T}{h} \frac{(q^{\ddagger}/V)}{\prod_i (q_i/V)} \exp\left(\frac{-\Delta E_{a,e}}{k_B T}\right). \tag{5.2}$$

The exact form of the expression for the reaction rate constant may depend on the type of rate that is desired, as will be shown in this chapter. The partition functions that need to be used correspond to the degrees of freedom of the complex in the initial and the transition state. For convenience, we repeat the formulas for the rotational, vibrational and translational partition functions which were derived in Chapter 3 in Table 5.1.

Table 5.1: *Formulas for the translational, vibrational and rotational partition functions.*

Partition function	Formula
Translational (1D)	$\frac{L\sqrt{2\pi m k_B T}}{h}$
Vibrational (single mode, without ZPE)	$\frac{1}{1-\exp\left(\frac{-h\nu}{k_B T}\right)}$
Vibrational (single mode, with ZPE)	$\frac{\exp\left(\frac{-h\nu}{2k_B T}\right)}{1-\exp\left(\frac{-h\nu}{k_B T}\right)}$
Rotational (diatomic)	$\frac{8\pi^2 I k_B T}{h^2}$
Rotational (polyatomic,asymmetric)	$\frac{\sqrt{\pi}}{\sigma}\sqrt{\frac{8\pi^2 I_A k_B T}{h^2}}\sqrt{\frac{8\pi^2 I_B k_B T}{h^2}}\sqrt{\frac{8\pi^2 I_C k_B T}{h^2}}$

We proceed by first treating gas phase reactions. Thereafter, we consider gas-solid interactions and finally we will discuss elementary reaction steps over catalytic surfaces.

5.2 Gas phase reactions

The most simple and straightforward application of transition state theory relates to reactions in the gas phase. We will treat unimolecular and bimolecular reactions. From these two cases, the reader can readily extend the methodology to more complex cases, e.g. trimolecular reactions.

5.2.1 Unimolecular gas phase reactions

A unimolecular gas phase reaction is a reaction wherein a single molecule is being converted as given by

$$A \rightarrow B \tag{5.3}$$

A typical example is an isomerization reaction, for example, between the eclipsed and staggered conformations of ethane. The fundamental expression for the rate of conversion is given by

$$-\left.\frac{\partial p_{\mathrm{A}}}{\partial t}\right|_{+} = +\left.\frac{\partial p_{\mathrm{B}}}{\partial t}\right|_{+} = \nu\frac{N^{\dagger}k_{\mathrm{B}}T}{V} = \nu K^{\dagger}\frac{k_{\mathrm{B}}T}{V}N_{\mathrm{is}}, \tag{5.4}$$

where $N^{\dagger}$ is the number of gas phase molecules in the transition state, N_{is} the number of gas phase molecules in the initial state and ν the crossing frequency factor. Note that we use the subscriptum $\left.\frac{\partial\square}{\partial t}\right|_{+}$ to indicate that we only consider the rate of change due to a single elementary reaction step and only in one direction. Furthermore, in the above equation K denotes a **number-based equilibrium constant** as given by

$$K^{\dagger} = \frac{N^{\dagger}}{N_{\mathrm{is}}}. \tag{5.5}$$

From the treatise as presented in section 2.8 on page 101, the number-based equilibrium constant can be readily related to the partition functions in the initial and transition state, which gives[1]

$$K^{\dagger} = \frac{q^{\dagger}}{q_{\mathrm{is}}}. \tag{5.6}$$

Let us assume that the gas under consideration is a polyatomic and non-linear, its complete molecular partition function is then given by

$$Q_{\mathrm{is}} = \frac{1}{N_{\mathrm{is}}!} \times q_{\mathrm{is,trans,3d}} \times q_{\mathrm{is,rot,3d}} \times q_{\mathrm{is,vib}} \times q_{\mathrm{is,elec}}, \tag{5.7}$$

by which q_{is} in Equation 5.6 is given by[2]

$$Q_{\mathrm{is}} = q_{\mathrm{is,trans,3d}} \times q_{\mathrm{is,rot,3d}} \times q_{\mathrm{is,vib}} \times q_{\mathrm{is,elec}}, \tag{5.8}$$

wherein $q_{\mathrm{is,trans,3d}}$, $q_{\mathrm{is,rot,3d}}$, $q_{\mathrm{is,vib}}$, and $q_{\mathrm{is,elec}}$ are the three-dimensional translational, three-dimensional rotational, $3N_{\mathrm{a}} - 6$-dimensional vibrational partition function and electronic partition function for the complex in the initial state, respectively. Note that N_{a} corresponds to the number of atoms in the molecule. The partition functions are herein given by

$$q_{\mathrm{is,trans,3d}} = \left(\frac{2\pi m k_{\mathrm{B}}T}{h^2}\right)^{3/2} V \tag{5.9}$$

$$q_{\mathrm{is,rot,3d}} = \frac{\sqrt{\pi}}{\sigma}\sqrt{\frac{8\pi^2 I_A k_{\mathrm{B}}T}{h^2}}\sqrt{\frac{8\pi^2 I_B k_{\mathrm{B}}T}{h^2}}\sqrt{\frac{8\pi^2 I_C k_{\mathrm{B}}T}{h^2}} \tag{5.10}$$

$$q_{\mathrm{is,vib}} = \prod_{i}^{3N_{\mathrm{a}}-6} \frac{\exp\left(\frac{-h\nu_i}{2k_{\mathrm{B}}T}\right)}{1-\exp\left(\frac{-h\nu_i}{k_{\mathrm{B}}T}\right)} \tag{5.11}$$

$$q_{\mathrm{is,elec}} = \exp\left(\frac{-\Delta E_{\mathrm{elec,is}}}{k_{\mathrm{B}}T}\right). \tag{5.12}$$

[1] Herein, we thus assume thermal equilibrium between the initial and transition state.

[2] Please note that the factor $\frac{1}{N!}$ corresponding to the correction factor for identical particles in Equation 5.7 and 5.14 drops out by application of Equation 2.107 (page 97) and taking $\mu_{\mathrm{is}} = \mu_{\mathrm{ts}}$. If this goes too quick for you, the procedure is shown more explicitly in section 5.3 in the calculation of the rate for adsorption for a mono-atomic gas. It is also recommended to review section 2.8 on page 101.

For the transition state, the complete molecular partition function is given by

$$Q^\dagger = \frac{1}{N^\dagger!} \times q^\dagger_{\text{trans,3d}} \times q^\dagger_{\text{rot,3d}} \times q^\dagger_{\text{vib}} \times q^\dagger_{\text{elec}}, \tag{5.13}$$

by which $q^\dagger$ in Equation 5.6 is given by

$$q^\dagger = q^\dagger_{\text{trans,3d}} \times q^\dagger_{\text{rot,3d}} \times q^\dagger_{\text{vib}} \times q^\dagger_{\text{elec}}, \tag{5.14}$$

wherein we obtain a similar set of equations. The most notable difference between the partition function for the initial and transition state is in the vibrational and electronic partition functions, which are

$$q_{\text{is,vib}} = \prod_{i=1}^{3N_\text{a}-6} \frac{\exp\left(\frac{-h\nu_i}{2k_\text{B}T}\right)}{1-\exp\left(\frac{-h\nu_i}{k_\text{B}T}\right)} \tag{5.15}$$

$$q^\dagger_{\text{elec}} = \exp\left(\frac{-\Delta E_{\text{elec,ts}}}{k_\text{B}T}\right). \tag{5.16}$$

Note that the quotient

$$\frac{q^\dagger_{\text{elec}}}{q_{\text{is,elec}}} = \exp\left(\frac{-\left[\Delta E_{\text{elec,ts}} - \Delta E_{\text{elec,is}}\right]}{k_\text{B}T}\right) = \exp\left(\frac{-\Delta E_{\text{act}}}{k_\text{B}T}\right), \tag{5.17}$$

which provides the term for the activation energy for isomerization. We can furthermore assume that the translational and rotational partition functions of the initial and transition state are very similar, since the geometry and mass distribution of the molecule change only slightly along the reaction coordinate. Consequently, the moments of inertia (I_A, I_B, and I_C), and therefore q_rot, are nearly identical for both states. These partition functions thus cancel out, yielding the following expression for the equilibrium constant:

$$K = \frac{q^\dagger_{\text{trans,3d}} q^\dagger_{\text{rot,3d}} q^\dagger_{\text{vib}} q^\dagger_{\text{elec}}}{q_{\text{is,trans,3d}} q_{\text{is,rot,3d}} q_{\text{is,vib}} q_{\text{is,elec}}} \tag{5.18}$$

$$= \frac{q^\dagger_{\text{vib}} q^\dagger_{\text{elec}}}{q_{\text{is,vib}} q_{\text{is,elec}}} \tag{5.19}$$

$$= \frac{q^\dagger_{\text{vib}}}{q_{\text{is,vib}}} \exp\left(\frac{-\Delta E_{\text{act}}}{k_\text{B}T}\right) \tag{5.20}$$

$$= \frac{\prod_{j=1}^{3N_\text{a}-6}\left[1-\exp\left(\frac{-h\nu_j}{k_\text{B}T}\right)\right]}{\prod_{i=1}^{3N_\text{a}-6}\left[1-\exp\left(\frac{-h\nu_i}{k_\text{B}T}\right)\right]} \exp\left(\frac{-\left(\Delta E_{\text{act}} + \Delta E_{\text{zpe}}\right)}{k_\text{B}T}\right), \tag{5.21}$$

where j iterates over the vibrational modes in the initial state (numerator) and i loops over the vibrational modes in the transition state (denominator).

Finally, we wish to get rid of the crossing frequency ν, by which we are going to extract the weak vibrational mode in the transition state that corresponds to a degree of freedom in the direction of the reaction coordinate. Plugging Equation 5.21 into Equation 5.4 yields

$$-\left.\frac{\partial p_{\mathrm{A}}}{\partial t}\right|_{+} = \frac{k_{\mathrm{B}}T}{h}\frac{\prod_{j}^{3N_{\mathrm{a}}-6}\left[1-\exp\left(\frac{-h\nu_j}{k_{\mathrm{B}}T}\right)\right]}{\prod_{i}^{3N_{\mathrm{a}}-7}\left[1-\exp\left(\frac{-h\nu_i}{k_{\mathrm{B}}T}\right)\right]}\exp\left(\frac{-\left(\Delta E_{\mathrm{act}}+\Delta E_{\mathrm{zpe}}\right)}{k_{\mathrm{B}}T}\right)\frac{k_{\mathrm{B}}T}{V}N_{\mathrm{is}} \tag{5.22}$$

$$= \frac{k_{\mathrm{B}}T}{h}\frac{\prod_{j}^{3N_{\mathrm{a}}-6}\left[1-\exp\left(\frac{-h\nu_j}{k_{\mathrm{B}}T}\right)\right]}{\prod_{i}^{3N_{\mathrm{a}}-7}\left[1-\exp\left(\frac{-h\nu_i}{k_{\mathrm{B}}T}\right)\right]}\exp\left(\frac{-\left(\Delta E_{\mathrm{act}}+\Delta E_{\mathrm{zpe}}\right)}{k_{\mathrm{B}}T}\right)p_{\mathrm{A}}. \tag{5.23}$$

Note that in Equation 5.23, we loop over $3N_{\mathrm{a}}-7$, instead of $3N_{\mathrm{a}}-6$ vibrational modes for the transition state as we have extracted a single vibrational mode to obtain the $\frac{k_{\mathrm{B}}T}{h}$ term corresponding to the crossing frequency.

On the basis of microscopic reversibility, we can immediately apply Equation 5.23 for the reverse reaction by swapping the partition functions corresponding to the initial state for the final state by which we obtain

$$\left.\frac{\partial p_{\mathrm{B}}}{\partial t}\right|_{+} = -\frac{k_{\mathrm{B}}T}{h}\frac{\prod_{j}^{3N_{\mathrm{a}}-6}\left[1-\exp\left(\frac{-h\nu_j}{k_{\mathrm{B}}T}\right)\right]}{\prod_{i}^{3N_{\mathrm{a}}-7}\left[1-\exp\left(\frac{-h\nu_i}{k_{\mathrm{B}}T}\right)\right]}\exp\left(\frac{-\left(\Delta E_{\mathrm{act,back}}+\Delta E_{\mathrm{zpe,back}}\right)}{k_{\mathrm{B}}T}\right)p_x, \tag{5.24}$$

wherein i thus now iterates over the vibrational modes of the final state. Conclusively, the reaction rate for a unimolecular reaction $A \rightarrow B$, in general terms and without making any explicit assumptions on the nature of the degrees of freedom, is given by

$$\boxed{-\left.\frac{\partial p_{\mathrm{A}}}{\partial t}\right|_{+} = \frac{k_{\mathrm{B}}T}{h}\frac{q'^{\ddagger}}{q'_{\mathrm{is}}}\exp\left(\frac{-\Delta E_{\mathrm{act}}}{k_{\mathrm{B}}T}\right)p_{\mathrm{A}}.} \tag{5.25}$$

In this expression, q' denotes the product of the translational, rotational and vibrational partition functions[3] as given by

$$q' = q_{\mathrm{trans,3d}} \times q_{\mathrm{rot,3d}} \times q_{\mathrm{vib}} \tag{5.26}$$

and the ‡ indicates that we extracted a single DOF from the partition function of the transition state to construct the $\frac{k_{\mathrm{B}}T}{h}$ term for the crossing frequency. Furthermore, note that ΔE_{act} in Equation 5.25 refers to the **electronic activation energy**. This is the activation energy **without the zero-point energy corrections**. These terms have to be calculated from the **vibrational partition functions**. The reader is recommended to start from Equation 5.25 when constructing reaction rates rather than to re-derive this equation from *first principles*. Next, assumptions need to be made to come up with expressions for the partition function q' and finally a detailed rate expression can be constructed.

[3] Thus excluding the electronic partition function as that term is extracted.

5.2.2 Bimolecular gas phase reactions

Consider the bimolecular gas phase reaction between components A and B to give C as given by

$$A + B \rightarrow C. \tag{5.27}$$

An example of a bimolecular reaction is the Diels-Alder dimerization of cyclopentadiene to form dicyclopentadiene. A bimolecular reaction goes via a transition state which is an AB-complex. The most notable difference between a unimolecular and a bimolecular reaction is that the transition state is only a **single** species in the gas phase, whereas the initial state are **two** species in the gas phase. In other words, several translational and rotational degrees of freedom have been converted to vibrational degrees of freedom upon formation of the transition state complex. The number-based equilibrium constant is given by

$$K^\dagger = \frac{N^\dagger_{\mathrm{AB}}}{N_{\mathrm{A}} N_{\mathrm{B}}} = \frac{q^\dagger}{q_{\mathrm{A}} q_{\mathrm{B}}} \tag{5.28}$$

$$= \frac{q^\dagger_{\mathrm{trans,3d}} q^\dagger_{\mathrm{rot,3d}} q^\dagger_{\mathrm{vib}} q^\dagger_{\mathrm{elec}}}{q_{\mathrm{A,trans,3d}} q_{\mathrm{A,rot,3d}} q_{\mathrm{A,vib}} q_{\mathrm{A,elec}} \times q_{\mathrm{B,trans,3d}} q_{\mathrm{B,rot,3d}} q_{\mathrm{B,vib}} q_{\mathrm{B,elec}}} \tag{5.29}$$

$$= \frac{q^\dagger_{\mathrm{trans,3d}} q^\dagger_{\mathrm{rot,3d}} q^\dagger_{\mathrm{vib}}}{q_{\mathrm{A,trans,3d}} q_{\mathrm{A,rot,3d}} q_{\mathrm{A,vib}} \times q_{\mathrm{B,trans,3d}} q_{\mathrm{B,rot,3d}} q_{\mathrm{B,vib}}} \exp\left(\frac{-\Delta E_{\mathrm{act}}}{k_{\mathrm{B}} T}\right) \tag{5.30}$$

We can now construct a rate expression for a bimolecular reaction using

$$-\frac{\partial p_{\mathrm{A}}}{\partial t} = -\frac{\partial p_{\mathrm{B}}}{\partial t} = +\frac{\partial p_{\mathrm{C}}}{\partial t} = \nu K^\dagger \frac{k_{\mathrm{B}} T}{V} N_{\mathrm{A}} N_{\mathrm{B}} \tag{5.31}$$

$$= \nu K \frac{k_{\mathrm{B}} T}{V} \frac{p_{\mathrm{A}} V}{k_{\mathrm{B}} T} \frac{p_{\mathrm{B}} V}{k_{\mathrm{B}} T} \tag{5.32}$$

$$= \frac{k_{\mathrm{B}} T}{h} \frac{q^\dagger_{\mathrm{trans,3d}} q^\dagger_{\mathrm{rot,3d}} q^\ddagger_{\mathrm{vib}}}{q_{\mathrm{A,trans,3d}} q_{\mathrm{A,rot,3d}} q_{\mathrm{A,vib}} \times q_{\mathrm{B,trans,3d}} q_{\mathrm{B,rot,3d}} q_{\mathrm{B,vib}}} \cdots$$

$$\cdots \exp\left(\frac{-\Delta E_{\mathrm{act}}}{k_{\mathrm{B}} T}\right) \left(\frac{V}{k_{\mathrm{B}} T}\right) p_{\mathrm{A}} p_{\mathrm{B}}. \tag{5.33}$$

As the example reaction used in the derivation of transition state theory in section 4.2.1 on page 180 is also a bimolecular reaction, we should be able to convert the result from above to the form found in Equation 4.82. The most notable difference is that we here expressed the rates in terms of **change in pressure per unit of time**, whereas in the example problem for the derivation of transition state theory, we expressed the rate in terms of the **change in the number of molecules per unit of volume per unit of time**. In other words, we use p in the former expression whereas we use ρ in the latter. The pressure p and the number-density ρ are related by the ideal gas law by $p = \rho k_{\mathrm{B}} T$. Thus we can write

$$\left.\frac{\partial p_\mathrm{A}}{\partial t}\right|_+ = k_\mathrm{B}T\frac{\partial \rho_\mathrm{A}}{\partial t} \tag{5.34}$$

$$= \frac{k_\mathrm{B}T}{h}\frac{q^\dagger_{\mathrm{trans,3d}}q^\dagger_{\mathrm{rot,3d}}q^\ddagger_{\mathrm{vib}}}{q_{\mathrm{A,trans,3d}}q_{\mathrm{A,rot,3d}}q_{\mathrm{A,vib}}\times q_{\mathrm{B,trans,3d}}q_{\mathrm{B,rot,3d}}q_{\mathrm{B,vib}}}\cdots$$

$$\cdots\exp\left(\frac{-\Delta E_\mathrm{act}}{k_\mathrm{B}T}\right)\left(\frac{V}{k_\mathrm{B}T}\right)k_\mathrm{B}T\rho_\mathrm{A}k_\mathrm{B}T\rho_\mathrm{B} \tag{5.35}$$

$$k_\mathrm{B}T\frac{\partial \rho_\mathrm{A}}{\partial t} = \frac{k_\mathrm{B}T}{h}\frac{q^\dagger_{\mathrm{trans,3d}}q^\dagger_{\mathrm{rot,3d}}q^\ddagger_{\mathrm{vib}}/V}{q_{\mathrm{A,trans,3d}}q_{\mathrm{A,rot,3d}}q_{\mathrm{A,vib}}/V\times q_{\mathrm{B,trans,3d}}q_{\mathrm{B,rot,3d}}q_{\mathrm{B,vib}}/V}\cdots$$

$$\cdots\exp\left(\frac{-\Delta E_\mathrm{act}}{k_\mathrm{B}T}\right)\rho_\mathrm{A}\rho_\mathrm{B}, \tag{5.36}$$

which is equivalent to Equation 4.82. In conclusion, we have now two types of expressions for the rate of conversion for a bimolecular reaction

$$-\left.\frac{\partial p_\mathrm{A}}{\partial t}\right|_+ = -\frac{\partial p_\mathrm{B}}{\partial t} = \frac{k_\mathrm{B}T}{h}\frac{q'^\ddagger}{q'_\mathrm{A}q'_\mathrm{B}}\exp\left(\frac{-\Delta E_\mathrm{act}}{k_\mathrm{B}T}\right)\left(\frac{V}{k_\mathrm{B}T}\right)p_\mathrm{A}p_\mathrm{B} \tag{5.37}$$

and

$$-\left.\frac{\partial \rho_\mathrm{A}}{\partial t}\right|_+ = -\frac{\partial \rho_\mathrm{B}}{\partial t} = \frac{k_\mathrm{B}T}{h}\frac{\left(q'^\ddagger/V\right)}{\left(q'_\mathrm{is}/V\right)\left(q'_\mathrm{B}/V\right)}\exp\left(\frac{-\Delta E_\mathrm{act}}{k_\mathrm{B}T}\right)\rho_\mathrm{A}\rho_\mathrm{B}, \tag{5.38}$$

where

$$q' = q_{\mathrm{trans,3d}}\times q_{\mathrm{rot,3d}}\times q_{\mathrm{vib}}. \tag{5.39}$$

⚠ Take care

The comparison between the derivation done here and the one done in the previous chapter should highlight that depending on the form of the rate expression, different expressions of the reaction rate constant are possible, but all are based on the same transition state theory.

5.3 Adsorption

Consider a catalytic surface in contact with a gas, such as depicted in Figure 5.1. In the gas phase, any non-linear molecule has three translational degrees of freedom as well as three rotational degrees of freedom.[4] All other degrees of freedom correspond to internal vibrations. However, when the molecule absorbs, it loses several degrees of motional freedom corresponding to a loss in entropy. In general, upon (chemical) adsorption, the molecule no longer has any translational or rotational degrees of freedom and only vibrational degrees of freedom. Let us here derive the full rate expression r_ads for adsorption by which we readily obtain an expression for the reaction rate constant k_ads.

[4] A single atom only has translational degrees of freedom. We will cover this situation specifically.

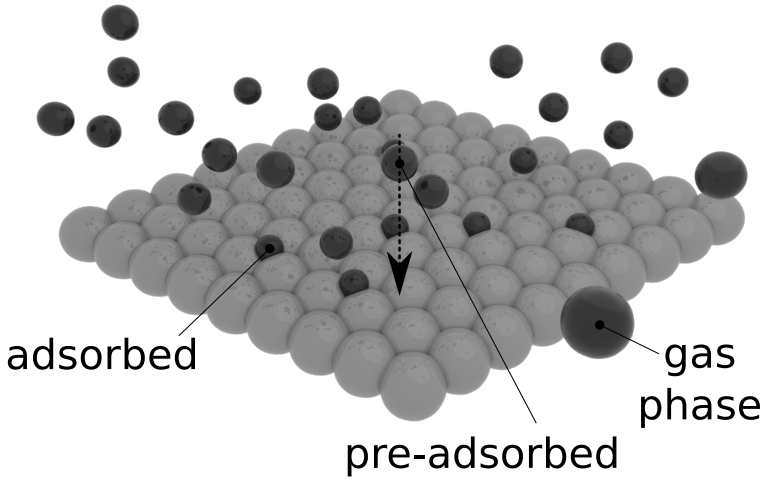


Figure 5.1: *Schematic depiction of a catalytic surface in contact with a mono-atomic gas. The adsorbed state, the pre-adsorbed state and the gas phase state are indicated.*

We wish to obtain the rate of change of the surface coverage of component X as function of the partial pressure of X and the number of free sites on the surface.[5]

$$r_{\text{ads}}^{+} = \left.\frac{\partial \theta_x}{\partial t}\right|_{+} = k p_x \theta_* . \tag{5.40}$$

Let us first write down the fundamental expression for the rate of change of the surface coverage as a function of the number of particles in the transition state for this elementary reaction step.

$$r_{\text{ads}}^{+} = \left.\frac{\partial \theta_x}{\partial t}\right|_{+} = \nu \frac{N^{\dagger}}{\overline{N}} = \nu K^{\dagger} \frac{N_{\text{gas}}}{\overline{N}} \tag{5.41}$$

where $\overline{N}$ is the total number of active (i.e. adsorption) sites on the surface and K a number-based equilibrium constant[6] as given by

$$K^{\dagger} = \frac{N^{\dagger}}{N_{\text{gas}}}. \tag{5.42}$$

In the above equation, $N^{\dagger}$ is the number of particles in the transition state and N_{gas} is the number of particles in the gas phase. We assume thermal equilibrium between the gas phase and the number of particles that hover directly above a free site in the transition state for adsorption. Let us start by finding an expression for the equilibrium constant K from the partition functions. The canonical ensemble partition function for the gas phase species is given by

$$Q_{\text{gas}} = \frac{q_{\text{gas}}^{N}}{N!} \tag{5.43}$$

[5] Note that in the following we only consider the reaction in the forward direction, i.e. we ignore for the moment the part of the reaction corresponding to desorption.

[6] See Equation 2.145 on page 102.

and for the transition state by

$$Q^{\dagger} = \frac{M!}{N^{\dagger}!(M-N^{\dagger})!}\left(q^{\dagger}_{\text{ads}}\right)^{N^{\dagger}}, \tag{5.44}$$

wherein $\frac{M!}{N^{\dagger}!(M-N^{\dagger})!}$ corresponds to the number of possibilities to place $N^{\dagger}$ adsorbates above M available free sites.[7] The chemical potential for the gas phase and the pre-adsorbed state are given by

$$\mu_{\text{gas}} = -k_{\text{B}}T\frac{\partial}{\partial N_{\text{gas}}}\ln\left(\frac{q_{\text{gas}}^{N_{\text{gas}}}}{N_{\text{gas}}!}\right) \tag{5.45}$$

and

$$\mu^{\dagger}_{\text{ads}} = -k_{\text{B}}T\frac{\partial}{\partial N^{\dagger}}\ln\left(\frac{M!}{N^{\dagger}!(M-N^{\dagger})!}\left(q^{\dagger}_{\text{ads}}\right)^{N^{\dagger}}\right). \tag{5.46}$$

Using the Stirling approximation[8], we can simplify Equations 5.45 and 5.46 which gives

$$\ln\left(\frac{q_{\text{gas}}^{N_{\text{gas}}}}{N_{\text{gas}}!}\right) = N_{\text{gas}}\ln\left(q_{\text{gas}}\right) - N_{\text{gas}}\ln N_{\text{gas}} - N_{\text{gas}} \tag{5.47}$$

and

$$\ln\left(\frac{M!}{N^{\dagger}!(M-N^{\dagger})!}\left(q^{\dagger}_{\text{ads}}\right)^{N^{\dagger}}\right) \tag{5.48}$$

$$= M\ln M - M - N^{\dagger}\ln N^{\dagger} + N^{\dagger} - \left(M-N^{\dagger}\right)\ln\left(M-N^{\dagger}\right) + \left(M-N^{\dagger}\right) + N^{\dagger}\ln q^{\dagger}_{\text{ads}} \tag{5.49}$$

$$= M\ln M - N^{\dagger}\ln N^{\dagger} - \left(M-N^{\dagger}\right)\ln\left(M-N^{\dagger}\right) + N^{\dagger}\ln q^{\dagger}_{\text{ads}}, \tag{5.50}$$

which yields the following expression for the chemical potentials

$$\mu_{\text{gas}} = -k_{\text{B}}T\ln\left(\frac{q_{\text{gas}}}{N_{\text{gas}}}\right) \tag{5.51}$$

and

$$\mu^{\dagger}_{\text{ads}} = -k_{\text{B}}T\ln\left(\frac{q^{\dagger}_{\text{ads}}}{N^{\dagger}}\left(M-N^{\dagger}\right)\right). \tag{5.52}$$

[7] Recall that $\theta_{*} \equiv \frac{M}{N}$.

[8] See Appendix B.2 on page 278

For the chemical potential of the pre-adsorbed state, we can assume that the number of molecules in the pre-adsorbed state is much smaller than the number of available active sites ($M \gg N^\dagger$) by which the previous expression simplifies to

$$\mu^\dagger_{\text{ads}} = -k_\text{B}T \ln\left(\frac{M}{N^\dagger} q^\dagger_{\text{ads}}\right). \tag{5.53}$$

From this, by assuming thermal equilibrium and thus setting $\mu_{\text{gas}} = \mu^\dagger_{\text{ads}}$, we obtain the following expression for the equilibrium constant

$$K^\dagger = \frac{N^\dagger}{N_{\text{gas}}} = M \frac{q^\dagger_{\text{ads}}}{q_{\text{gas}}}. \tag{5.54}$$

Plugging the above expression into Equation 5.41 yields

$$r^+_{\text{ads}} = \left.\frac{\partial \theta_x}{\partial t}\right|_+ = \nu \frac{q^\dagger_{\text{ads}}}{q_{\text{gas}}} \frac{M}{\overline{N}} N_{\text{gas}} = \nu \frac{q^\dagger_{\text{ads}}}{q_{\text{gas}}} \theta_* N_{\text{gas}}. \tag{5.55}$$

By the same procedure as shown in section 4.2.1 on page 184, we extract one DOF from the partition function for the pre-adsorbed state to cancel out the crossing frequency ν, by which we obtain

$$r^+_{\text{ads}} = \left.\frac{\partial \theta_x}{\partial t}\right|_+ = \frac{k_\text{B}T}{h} \frac{q^\ddagger_{\text{ads}}}{q_{\text{gas}}} \theta_* N_{\text{gas}}. \tag{5.56}$$

In conclusion, we have the following (general) rate expressions for an adsorption reaction:

$$\boxed{r^+_{\text{ads}} = \left.\frac{\partial \theta_x}{\partial t}\right|_+ = \frac{k_\text{B}T}{h} \frac{q^\ddagger}{q_{\text{gas}}} \theta_* N_{\text{gas}}.} \tag{5.57}$$

If we now wish to obtain the rate of change in the *partial pressure* of component X, we can readily do so by multiplying equation 5.57 by a factor $-\overline{N}\frac{k_\text{B}T}{V}$. Note herein the negative sign as molecules in the gas phase are consumed when this reaction proceeds in the forward direction. Applying now this factor to the left hand side of equation 5.57 yields

$$-\overline{N}\frac{k_\text{B}T}{V} \cdot \left.\frac{\partial \theta_x}{\partial t}\right|_+ = \left.\frac{\partial p_x}{\partial t}\right|_+, \tag{5.58}$$

which is exactly the differential equation we are looking for. Of course, we need to perform the same operation on both sides of the equation is we want to equation to remain valid. Multiplying the right hand side of equation 5.57 by this factor yields

$$r^+_{\text{ads}} = \left.\frac{\partial p_x}{\partial t}\right|_+ = -\overline{N}\frac{k_\text{B}T}{V} \cdot \frac{k_\text{B}T}{h} \frac{q^\ddagger}{q_{\text{gas}}} \theta_* N_{\text{gas}} \tag{5.59}$$

$$= -\overline{N}\frac{k_\text{B}T}{V} \cdot \frac{k_\text{B}T}{h} \frac{q^\ddagger}{q_{\text{gas}}} \theta_* \frac{p_x V}{k_\text{B}T} \tag{5.60}$$

$$= -\frac{k_\text{B}T}{h} \frac{q^\ddagger}{q_{\text{gas}}} \theta_* p_x \overline{N}. \tag{5.61}$$

Thus, the rate of change for the partial pressure in X is given by

$$\boxed{r_{\text{ads}}^{+} = \left.\frac{\partial p_x}{\partial t}\right|_{+} = -\frac{k_{\text{B}}T}{h}\frac{q^{\ddagger}}{q_{\text{gas}}}\theta_* p_x \overline{N}.} \tag{5.62}$$

Comparing Equation 5.57 with Equation 5.62, we observe that the change in the surface density of free sites is related to the change in gas phase components by the factor $\overline{N}$, which is simply the number of active sites in our control volume. The ratio $\overline{N}$ is not easily calculated and depends on a lot of factors such as the accessible surface of the catalyst, the number of active sites per accessible surface of the catalyst and the catalyst loading. Equations 5.57 and 5.62 depend on the details of the adsorption process and various cases can be constructed. In the following subsections, we will consider a couple of cases.

5.3.1 Adsorption of a mono-atomic gas

Let us start with the most simple case: the adsorption of a mono-atomic gas wherein the atom in the gas phase has three translational degrees of freedom of which in the transition state only two translational degrees of freedom remain. This is the situation shown in Figure 5.1. The other translational degree of freedom, which corresponds to a motion in the direction of the reaction coordinate, was extracted to cancel out the crossing frequency ν. Finally, we assume that there is no difference in the electronic energy between the initial and transition state, or in other words, that an adsorption reaction is **not activated**. With these assumptions in mind, let us derive an expression for the adsorption rate starting from Equation 5.57:

$$r_{\text{ads}}^{+} = \left.\frac{\partial \theta_x}{\partial t}\right|_{+} = \frac{k_{\text{B}}T}{h}\frac{q_{\text{ads}}^{\ddagger}}{q_{\text{gas}}}\theta_* N_{\text{gas}} \tag{5.63}$$

$$= \frac{k_{\text{B}}T}{h}\left(\frac{2\pi m k_{\text{B}}T}{h^2}\right)^{2/2}\left(\frac{2\pi m k_{\text{B}}T}{h^2}\right)^{-3/2}\frac{A}{V}\theta_* N_{\text{gas}} \tag{5.64}$$

$$= \frac{k_{\text{B}}T}{h}\frac{hA}{\sqrt{2\pi m k_{\text{B}}T}}\theta_*\frac{p_x}{k_{\text{B}}T} \tag{5.65}$$

$$= \frac{p_x A}{\sqrt{2\pi m k_{\text{B}}T}}\theta_*. \tag{5.66}$$

or alternatively in terms of the rate of the change of the *partial pressure* by

$$r_{\text{ads}}^{+} = -\frac{p_x A}{\sqrt{2\pi m k_{\text{B}}T}}\theta_*\frac{\overline{N}}{V}k_{\text{B}}T, \tag{5.67}$$

wherein we have again multiplied both sides of equation 5.66 by a factor $-\overline{N}\frac{k_{\text{B}}T}{V}$. Note that in the above equations, A corresponds to the area wherein the atom can freely above above the active site. Typically, we set A therefore equal to the area of an active site. We can also readily rationalize the factor $\frac{\overline{N}}{V}k_{\text{B}}T$ in equation 5.66. The fraction $\frac{\overline{N}}{V}$ corresponds to the number of active sites *per volume*. In other words, this is the active site *density* in our control volume. If molecules are adsorbed on those sites, this results in a decrease of the partial pressure. Assuming that gaseous X can be adequately described by the ideal gas law, this process scales linearly with a factor $k_{\text{B}}T$ per molecule of X consumed in this fashion.

Finally, since equation 5.66 can also be written as

$$r_{\text{ads}}^{+} = \left.\frac{\partial \theta_x}{\partial t}\right|_{+} = k\theta_* p_x, \tag{5.68}$$

it follows that

$$k_{\text{ads}} = \frac{A}{\sqrt{2\pi m k_{\text{B}} T}}. \tag{5.69}$$

5.3.2 Adsorption of diatomic gas

Adsorption of a diatomic gas is very similar to a mono-atomic gas. The main difference is that a diatomic gas has rotational degrees of freedom which can either be lost or retained in the transition state (depending on whether the transition state is a mobile or immobile transition state). In the case that the transition state is mobile, the expression for diatomic adsorption is similar to that as for a mono-atomic adsorption.[9] We will not explicitly derive it here.

A diatomic molecule has two rotational degrees of freedom. Let us consider how the rate of adsorption will look like when assuming that both rotational degrees of freedom are converted to vibrational degrees of freedom. We will start the derivation from the general expression as shown in Equation 5.57.

$$r_{\text{ads}}^{+} = \frac{\partial \theta_x}{\partial t} = \frac{k_{\text{B}} T}{h} \frac{q'^{\ddagger}}{q'_{\text{gas}}} \theta_* N_{\text{gas}} \tag{5.70}$$

$$= \frac{k_{\text{B}} T}{h} \frac{q'^{\ddagger}_{\text{trans,2d}} \left(q'^{\ddagger}_{\text{vib}} \right)^{(3)}}{q_{\text{trans,3d}} q_{\text{rot,2d}} q_{\text{vib}}^{(1)}} \theta_* N_{\text{gas}} \tag{5.71}$$

$$= \frac{k_{\text{B}} T}{h} \frac{q'^{\ddagger}_{\text{trans,2d}} \left(q'^{\ddagger}_{\text{vib}} \right)^{(3)}}{q_{\text{trans,3d}} q_{\text{rot,2d}} q_{\text{vib}}^{(1)}} \theta_* \frac{p_x V}{k_{\text{B}} T} \tag{5.72}$$

Observe that the volume V in the numerator of the final term will cancel with the the corresponding V of the three-dimensional translational partition function in the initial state and the $k_{\text{B}} T$ in the denominator will cancel with the $k_{\text{B}} T$ term in the numerator of the crossing frequency term. Furthermore, note that the superscript (3) denotes that we have to consider the vibrational partition function of three vibrational modes. We further assume that only the vibrational ground state is occupied, by which the vibrational partition function simplifies to

$$q_{\text{vib}} = \exp\left(-\frac{h\nu}{2 k_{\text{B}} T} \right), \tag{5.73}$$

corresponding to the partition function of the vibrational zero-point energy only. Combining these two expressions yields

$$r_{\text{ads}}^{+} = \frac{\partial \theta_x}{\partial t} = \underbrace{\frac{A}{\sqrt{2\pi m k_{\text{B}} T}}}_{\text{translations}} \underbrace{\frac{\exp\left(-\sum_{i=1}^{3} \frac{h\nu_i}{2 k_{\text{B}} T} \right)}{\exp\left(-\frac{h\nu}{2 k_{\text{B}} T} \right)}}_{\text{vibrations}} \underbrace{\frac{h^2}{8\pi^2 I k_{\text{B}} T}}_{\text{rotations}} p_x \theta_*, \tag{5.74}$$

wherein the origin of each term is mentioned. The first term originates from the difference between the translational degrees of freedom, which amounts to a single lost translational degree of freedom in the transition state. The second term originates from the difference in the vibrational partition functions, which under the approximation that only the ground state

[9] If we assume that the rotational partition functions and the single vibrational partition function does not change appreciably from the gas phase to the pre-adsorbed state

is occupied, results in the difference in the vibrational zero-point energies. The third and last term corresponds to the difference in the rotational partition function where we observe that all rotational degrees of freedom are lost.

5.4 Desorption

Desorption is the opposite of adsorption: a bound compound leaves the catalytic surface and goes to the gas phase. The rate of change of the surface coverage of component X (θ_{ads}) as function of the coverage of X is given by

$$r_{\text{des}}^{+} = \left.\frac{\partial \theta_{\text{ads}}}{\partial t}\right|_{+} = k\theta_{\text{ads}}. \tag{5.75}$$

Let us first write down the fundamental expression for the rate of change of the surface coverage as a function of the number of particles in the transition state for this elementary reaction step.

$$r_{\text{des}}^{+} = \left.\frac{\partial \theta_{\text{ads}}}{\partial t}\right|_{+} = \nu\theta^{\dagger} = \nu K^{\dagger}\theta_{\text{ads}}, \tag{5.76}$$

wherein

$$K^{\dagger} = \frac{q'^{\dagger}}{q'_{\text{ads}}}. \tag{5.77}$$

From the partition function of the activated complex, a degree of freedom is extracted to get rid of the ν, by which the general expression for the rate for desorption becomes[10]

$$\boxed{r_{\text{des}}^{+} = -\left.\frac{\partial \theta_{\text{ads}}}{\partial t}\right|_{+} = \frac{k_{\text{B}}T}{h}\frac{q^{\ddagger}}{q_{\text{ads}}}\theta_{\text{ads}}} \tag{5.78}$$

and where the exact expression depends on the nature of the degrees of freedom of the activated complex and the complex in the initial state. In the following two subsection, we will explore a couple of cases.

5.4.1 Diatomic desorption

Let us consider the situation wherein a molecule is strongly adsorbed and only has vibrational degrees of freedom. Upon desorption, it already regains two translational degrees of freedom and two rotational degrees of freedom in the activated complex. We furthermore assume that all vibrational partition functions are in their vibrational ground state only. From Equation 5.78, the rate for desorption can then be calculated as

[10] This part of the derivation is exactly the same as what we have seen before for the other types of reactions.

$$r_{\text{des}}^{+} = -\left.\frac{\partial \theta_{\text{ads}}}{\partial t}\right|_{+} \tag{5.79}$$

$$= \frac{k_{\text{B}}T}{h}\frac{q^{\ddagger}}{q_{\text{ads}}}\theta_{\text{ads}} \tag{5.80}$$

$$= \frac{k_{\text{B}}T}{h} q^{\dagger}_{\text{trans,2d}} q^{\dagger}_{\text{rot,2d}} \exp\left(-\frac{\left[\Delta E_{\text{elec,des}} + \Delta E_{\text{zpe,des}}\right]}{k_{\text{B}}T}\right)\theta_{\text{ads}} \tag{5.81}$$

$$= \frac{k_{\text{B}}T}{h} A \frac{2\pi m k_{\text{B}}T}{h^2}\frac{8\pi^2 I k_{\text{B}}T}{\sigma h^2} \exp\left(-\frac{\left[\Delta E_{\text{elec,des}} + \Delta E_{\text{zpe,des}}\right]}{k_{\text{B}}T}\right)\theta_{\text{ads}} \tag{5.82}$$

$$= \frac{k_{\text{B}}T}{h}\frac{A\left(2\pi m k_{\text{B}}T\right)}{h^2}\frac{8\pi^2 I k_{\text{B}}T}{\sigma h^2} \exp\left(-\frac{\left[\Delta E_{\text{elec,des}} + \Delta E_{\text{zpe,des}}\right]}{k_{\text{B}}T}\right)\theta_{\text{ads}} \tag{5.83}$$

$$= \frac{k_{\text{B}}T^3}{h^3}\frac{A\left(2\pi m k_{\text{B}}\right)}{\sigma \Theta_{\text{rot}}} \exp\left(-\frac{\left[\Delta E_{\text{elec,des}} + \Delta E_{\text{zpe,des}}\right]}{k_{\text{B}}T}\right)\theta_{\text{ads}}, \tag{5.84}$$

wherein σ corresponds to the symmetry number for the diatomic rotational partition function as explained on page 144 and Θ_{rot} the rotational temperature as shown in Equation 3.79 on page 141.

5.4.2 Non-linear polyatomic desorption

Let us repeat the case in the previous subsection, but now for a non-linear polyatomic molecule and assuming three rotational degrees of freedom. The result is quite similar

$$r_{\text{des}}^{+} = -\left.\frac{\partial \theta_{\text{ads}}}{\partial t}\right|_{+} \tag{5.85}$$

$$= \frac{k_{\text{B}}T}{h}\frac{q^{\ddagger}}{q_{\text{ads}}}\theta_{\text{ads}} \tag{5.86}$$

$$= \frac{k_{\text{B}}T}{h} q^{\dagger}_{\text{trans,2d}} q^{\dagger}_{\text{rot,3d}} \exp\left(-\frac{\left[\Delta E_{\text{elec,des}} + \Delta E_{\text{zpe,des}}\right]}{k_{\text{B}}T}\right)\theta_{\text{ads}} \tag{5.87}$$

$$= \frac{k_{\text{B}}T}{h}\frac{A\left(2\pi m k_{\text{B}}T\right)}{h^2}\frac{\sqrt{\pi}}{\sigma}\sqrt{\frac{8\pi^2 I_A k_{\text{B}}T}{h^2}}\sqrt{\frac{8\pi^2 I_B k_{\text{B}}T}{h^2}}\sqrt{\frac{8\pi^2 I_C k_{\text{B}}T}{h^2}}\cdots \tag{5.88}$$

$$\cdots \exp\left(-\frac{\left[\Delta E_{\text{elec,des}} + \Delta E_{\text{zpe,des}}\right]}{k_{\text{B}}T}\right)\theta_{\text{ads}} \tag{5.89}$$

$$= \frac{k_{\text{B}}T^{7/2}}{h^3}\frac{A\left(2\pi^{3/2} m k_{\text{B}}\right)}{\sigma \Theta_A \Theta_B \Theta_C} \exp\left(-\frac{\left[\Delta E_{\text{elec,des}} + \Delta E_{\text{zpe,des}}\right]}{k_{\text{B}}T}\right)\theta_{\text{ads}}, \tag{5.90}$$

where $\Theta_A, \Theta_B, \Theta_C$ represent the rotational temperatures corresponding to the three principal moments of inertia of the complex.[11]

[11] See section 3.6.2 on page 142.

5.5 Surface reactions

Complexes absorbed on a catalytic surface typically only have vibrational degrees of freedom. These complexes can associate to form a single new complex (e.g. C* hydrogenation to form CH*) or they can dissociate and form two new complexes (e.g. CO* dissociation to from C* and O*). The general expression for a surface reaction is given by

$$r^{+}_{\text{surf}} = -\left.\frac{\partial \theta_{\text{ads}}}{\partial t}\right|_{+} = \frac{k_{\text{B}}T}{h}\frac{q^{\ddagger}}{\prod_i q_{\text{i}}}\prod_i \theta_i, \tag{5.91}$$

wherein the product Π iterates over the surface complexes i in the reactant state. For a dissociation reaction, there is only a single reactant, whereas for a association reaction, there are two reactants. We assume that there is only a single transition state complex. In the construction of Equation 5.91, a single weak vibrational mode was extracted from the partition function in the transition state to obtain the $\frac{k_{\text{B}}T}{h}$ prefactor as indicated by the $\ddagger$ symbol. Using Equation 5.91, we can readily construct the rate expression for an association and dissociation reaction.

5.5.1 Association reaction

Let us consider the association of two surface complexes, A and B, to form the AB complex. Because all degrees of freedom are vibrational, this implies that complex A has $3N_{\text{A}}$ vibrational modes and similarly, complex B has $3N_{\text{A}}$ vibrational modes. Because of the extraction of the weak vibrational mode corresponding to the reaction coordinate, the transition state complex has one fewer vibrational mode, i.e. $AB^{\dagger}$ has $3(N_{\text{A}}+N_{\text{B}})-1$, for the construction of the vibrational partition functions. From this, the rate expression is

$$\begin{aligned} r^{+}_{\text{surf}} &= \frac{k_{\text{B}}T}{h}\frac{q^{\ddagger}}{\prod_i q_{\text{i}}}\prod_i \theta_i \\ &= \frac{k_{\text{B}}T}{h}\prod_{i=1}^{3(N_{\text{A}}+N_{\text{B}})-1}\left(\frac{\exp\left(-\frac{h\nu_i}{2k_{\text{B}}T}\right)}{1-\exp\left(-\frac{h\nu_i}{k_{\text{B}}T}\right)}\right)\cdots \\ &\cdots\prod_{j=1}^{3N_{\text{A}}}\left(\frac{\exp\left(-\frac{h\nu_j}{2k_{\text{B}}T}\right)}{1-\exp\left(-\frac{h\nu_j}{k_{\text{B}}T}\right)}\right)^{-1}\prod_{k=1}^{3N_{\text{B}}}\left(\frac{\exp\left(-\frac{h\nu_k}{2k_{\text{B}}T}\right)}{1-\exp\left(-\frac{h\nu_k}{k_{\text{B}}T}\right)}\right)^{-1}\cdots \\ &\cdots\exp\left(-\frac{-\Delta E_{\text{act, elec}}}{k_{\text{B}}T}\right)\theta_{\text{A}}\theta_{\text{B}} \end{aligned} \tag{5.92}$$

We can extract the zero point energy contributions from the vibrational partition functions and add these to the electronic activation energy to obtain a zero point energy corrected reaction barrier as given by

$$\Delta E_{\text{act,zpe-corr}} = \Delta E_{\text{act,elec}} + \sum_{i=1}^{3(N_{\text{A}}+N_{\text{B}})-1}\frac{h\nu_i}{2} - \sum_{j=1}^{3N_{\text{B}}}\frac{h\nu_j}{2} - \sum_{k=1}^{3N_{\text{B}}}\frac{h\nu_k}{2}. \tag{5.93}$$

Although for many reactions the zero point energy corrections tend to be in the order of 1-5 kJ/mol, which is relatively small in comparison to the difference in electronic energies which are

roughly in the order of 30-100 kJ/mol, they can become important, especially when dealing with (de-)hydrogenation reactions and thus can no longer be neglected.

We can furthermore simplify Equation 5.92 by assuming that only the vibrational ground state is occupied, which gives

$$\boxed{r^{+}_{\text{surf}} = \frac{k_{\text{B}}T}{h}\exp\left(-\frac{-\Delta E_{\text{act, zpe-corr}}}{k_{\text{B}}T}\right)\theta_{\text{A}}\theta_{\text{B}}.} \tag{5.94}$$

5.5.2 Dissociation reaction

Dissociation reactions are the opposite of association reactions, so we can readily derive the result for these results from the results obtained for the association reaction. These are

$$\begin{aligned}\boxed{r^{+}_{\text{surf}} &= \frac{k_{\text{B}}T}{h}\frac{q^{\ddagger}}{\prod_i q_{\text{i}}}\prod_i \theta_i \\ &= \frac{k_{\text{B}}T}{h}\prod_{i=1}^{3(N_{\text{AB}})-1}\left(\frac{\exp\left(-\frac{h\nu_i}{2k_{\text{B}}T}\right)}{1-\exp\left(-\frac{h\nu_i}{k_{\text{B}}T}\right)}\right)\cdots \\ &\cdots\prod_{j=1}^{3N_{\text{AB}}}\left(\frac{\exp\left(-\frac{h\nu_j}{2k_{\text{B}}T}\right)}{1-\exp\left(-\frac{h\nu_j}{k_{\text{B}}T}\right)}\right)^{-1}\cdots \\ &\cdots\exp\left(-\frac{-\Delta E_{\text{act, elec}}}{k_{\text{B}}T}\right)\theta_{\text{AB}}}\end{aligned} \tag{5.95}$$

which can be simplified, using the same assumptions as provided in the previous subsection, to

$$\boxed{r^{+}_{\text{surf}} = \frac{k_{\text{B}}T}{h}\exp\left(-\frac{-\Delta E_{\text{act, zpe-corr}}}{k_{\text{B}}T}\right)\theta_{\text{AB}}.} \tag{5.96}$$

5.6 Energies, enthalpies and entropies of activation

For a set reaction rate constant k, its enthalpy and entropy of activation are defined as[14]

$$k \equiv \frac{k_{\text{B}}T}{h}\exp\left(-\frac{\Delta H^{\dagger}}{k_{\text{B}}T}\right)\exp\left(\frac{\Delta S^{\dagger}}{k_{\text{B}}}\right). \tag{5.97}$$

Using the above expression, we can readily define the Gibbs free energy, enthalpy and entropy of activation as

$$\boxed{\Delta G^{\ddagger} \equiv G_{\text{ts}} - G_{\text{is}} = -k_{\text{B}}T\ln K^{\ddagger},} \tag{5.98}$$

$$\Delta H^{\ddagger} \equiv H_{\text{ts}} - H_{\text{is}} = k_{\text{B}} T^2 \frac{\partial}{\partial T} \ln K^{\ddagger}, \tag{5.99}$$

and

$$\Delta S^{\ddagger} \equiv S_{\text{ts}} - S_{\text{is}} = \frac{\Delta H^{\ddagger} - \Delta G^{\ddagger}}{T} = \frac{\partial}{\partial T} \left(k_{\text{B}} T \ln K^{\ddagger} \right), \tag{5.100}$$

wherein $K^{\ddagger}$ is the equilibrium constant used, as necessary, to construct the rate expression. The ‡ is to indicate that one degree of freedom has been extracted from this equilibrium constant to construct the $\frac{k_{\text{B}}T}{h}$ pre-factor. Furthermore, the type of the equilibrium constant $K^{\ddagger}$ depends on the rate expression. For example, for an adsorption/desorption step, a number-based equilibrium constant is used, whereas for a gas-phase reaction, a pressure-based equilibrium constant can be used.

⚠ Take care

Because of the free choice wherein the rate expression is constructed, this can lead to different values for the enthalpy, entropy and Gibbs free energy of activation. As such, it is of the utmost importance that a reference state is defined when expressing these values.[15]

Let us now compare the Gibbs free energy for activation between a unimolecular and bimolecular reaction in the gas phase. We assume that the activation energy for both reactions is the same. For the unimolecular reaction, the initial and final state have by approximation the same translational, rotational and vibrational partition functions in the initial and final. For the bimolecular reaction, we assume that the two reactant molecules are of the same type (corresponding to the reaction $2A \rightarrow B$) and that the change in the vibrational partition functions is negligible.

For the unimolecular reaction, the Gibbs free energy of activation is then given by

$$\Delta G^{\ddagger}_{\text{unimolecular}} = \Delta E_{\text{act}}. \tag{5.101}$$

Note that because there is no difference in the *configurational* partition functions between the initial and transition state, a lot of terms simply cancel out. Now let us consider how the Gibbs free energy of activation for the bimolecular looks like

$$\Delta G^{\ddagger}_{\text{bimolecular}} = \Delta E_{\text{act}} - k_{\text{B}} T \ln \left(\frac{q^{\dagger}_{\text{trans}} q^{\dagger}_{\text{rot}}}{(q_{\text{trans}} q_{\text{rot}})^2} \right). \tag{5.102}$$

Clearly, the bimolecular reaction has an additional term corresponding to the difference in the configurational partition functions. Since the denominator is expected to be much larger than the numerator, the additional term in Equation 5.102 as compared to Equation 5.102 gives a positive contribution to the Gibbs free energy of activation, essentially making the reaction more difficult. This can be easily understood as the initial state has many more degrees of freedom as compared to the transition state and thus the change from initial to transition state corresponds

to a significant loss in entropy. However, before we will explicitly calculate the entropy loss, we first calculate the enthalpy of activation.[12]

The pressure-based equilibrium constants for the unimolecular and bimolecular reaction are given by

$$K_p^{\ddagger} = \frac{q^{\ddagger} k_B T/V}{q_{is} k_B T/V} \tag{5.103}$$

$$= \frac{q^{\dagger}}{q_{is}} = 1 \tag{5.104}$$

and

$$K_p^{\ddagger} = \frac{q^{\ddagger} k_B T/V}{\left(q_{is} k_B T/V\right)^2} \tag{5.105}$$

$$= \frac{q^{\dagger}}{q_{is}} \left(\frac{V}{k_B T}\right) \tag{5.106}$$

$$= \frac{q^{\dagger}_{trans} q^{\dagger}_{rot}}{\left(q_{trans} q_{rot}\right)^2} \left(\frac{V}{k_B T}\right) \tag{5.107}$$

From these, we can readily calculate the enthalpy of activation as

$$\Delta H^{\ddagger}_{unimolecular} = \Delta E_{act}. \tag{5.108}$$

Note that because there is no difference in the *configurational* partition functions between the initial and transition state, a lot of terms simply cancel out. Now let us consider how the Gibbs free energy of activation for the bimolecular looks like

$$\Delta H^{\ddagger}_{bimolecular} = \Delta E_{act} + \left(\frac{3}{2} k_B T + \frac{3}{2} k_B T\right) - 2\left(\frac{3}{2} k_B T + \frac{3}{2} k_B T\right) + k_B T \tag{5.109}$$

$$= \Delta E_{act} - 2 k_B T. \tag{5.110}$$

From these two results, we can readily calculate the entropy of activation, which gives

$$\Delta S^{\ddagger}_{unimolecular} = 0 \tag{5.111}$$

and

$$\Delta S^{\ddagger}_{bimolecular} = k_B \ln\left(\frac{q^{\dagger}_{trans} q^{\dagger}_{rot}}{\left(q_{trans} q_{rot}\right)^2}\right) + 2 k_B. \tag{5.112}$$

From the equations above, we can readily see that the bimolecular reaction has a negative entropy of activation, which acts as an additional barrier for the reaction to occur.

It is also possible to directly calculate the Gibbs free energy of activation $G^{\dagger}$ and the enthalpy of activation $H^{\dagger}$ directly from the reaction rate constants using

[12] This is also known as the heat of formation.

$$\Delta G^{\ddagger} \equiv G_{\mathrm{ts}} - G_{\mathrm{is}} = -k_{\mathrm{B}}T\left[\ln k_r - \ln\left(\frac{k_{\mathrm{B}}T}{h}\right)\right] \tag{5.113}$$

and

$$\Delta H^{\ddagger} \equiv H_{\mathrm{ts}} - H_{\mathrm{is}} = k_{\mathrm{B}}T^2\frac{\partial}{\partial T}\ln k_r - k_{\mathrm{B}}T - (n-1)k_{\mathrm{B}}T, \tag{5.114}$$

where n denotes the molecularity of a gas phase reaction. For a unimolecular reaction, $n = 1$ and for a bimolecular reaction $n = 2$.[13]

5.7 Final remarks

The previous sections showed explicit formulas for adsorption, desorption and surface reactions. In principle, you can use these formulas to 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 identifying the applicable partition functions, 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.

Practice your understanding

Exercises 5.1, 5.2 and 5.3

Challenges

Exercise 5.4

[13] Note that for a surface reaction, $n = 1$ and the last $(n - 1)$ term disappears.

5.8 Exercises

The answers to the exercises can be found at the end of this Chapter on page 238. The exercises are marked by a number of gears to indicate their difficulty levels.

EXERCISE 5.1

a) Calculate the rate constant for CO dissociation in the forward and the backward direction using appropriate assumptions (given the limited information provided) 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 5.84. 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. Use the same surface area as you used for the calculation of the desorption rate constant. Assume a mobile transition state, i.e. that no rotational degrees of freedom of CO are lost between the initial and transition state.

d) Why is the rate constant for desorption higher than for adsorption?

EXERCISE 5.2

a) Derive a formula for the entropy of activation for adsorption, assuming that the complex loses one translational degree of freedom between the initial and transition state. You can neglect any differences in the rotational and vibrational partition functions between the initial and transition state. Interpret the final result.

b) Derive a formula for the entropy of activation for desorption, assuming that the complex regains two translational and two rotational degrees of freedom when migrating from the adsorbed state to the activated complex. You can neglect any differences in the vibrational partition functions between initial and transition state. Interpret the final result.

EXERCISE 5.3

Consider the catalytic hydrogenation of $CH_2 \cdot$ over a stepped surface of a Ru catalyst towards $CH_3 \cdot$ as given by

$$CH_2 * + H* \rightarrow CH_3 * + * \tag{5.115}$$

The electronic activation energies in the forward and backward direction of this elementary reaction step are 59.0 and 53.6 kJ/mol, respectively. The zero point energy (ZPE) corrections as given by

$$\Delta_{\text{zpe}} = \sum_i \frac{h\nu_i}{2} \tag{5.116}$$

for initial, transition and final state are 76.9, 75.8 and 81.2 kJ/mol. Assume a reaction temperature of $T = 500$K.

a) Calculate the rate in the forward and in the backward direction with and without the ZPE correction.

b) Calculate the quotient of the rates for including and excluding the ZPE correction.

c) Calculate the quotient of the equilibrium constant for including and excluding the ZPE corrections.

d) Motivate why the difference is relatively large.

EXERCISE 5.4 ✪✪✪✪✪

Consider the dissociative adsorption of methane as given by

$$\mathrm{CH_4} + 2* \rightarrow \mathrm{CH_3} * + \mathrm{H}* \tag{5.117}$$

Assume that in the transition state, all translational and rotational degrees of freedom are lost. Furthermore, assume that $q'_{\mathrm{vib}} = \frac{1}{1-\exp\left(-\frac{h\nu}{k_{\mathrm{B}}T}\right)} = \approx 1$. Use the variable $\Delta E_{\mathrm{e,a}}$ for the electronic activation energy and $\Delta E^{\dagger}_{\mathrm{zpe}}$ for the difference in the zero-point energy between the transition and initial state.

a) Provide the full rate expression and derive from it an expression for the reaction rate constant for dissociative adsorption of methane from transition state theory under the conditions as given above.

b) Calculate the enthalpy of activation using

$$\Delta H^{\dagger} = k_b T^2 \frac{\partial \ln k}{\partial T} - k_b T. \tag{5.118}$$

This expression is very similar to the Arrhenius activation energy, but by subtracting $k_b T$, we exclude the frequency factor $\frac{k_b T}{h}$.

c) Derive an expression for the entropy of activation using

$$\Delta S^{\dagger} = \frac{\partial}{\partial T}\left(k_b T\left(\ln\left(k\right) - \ln\left(\frac{k_b T}{h}\right)\right)\right). \tag{5.119}$$

Similar to the expression for the internal energy of activation, we exclude the frequency factor $\frac{k_b T}{h}$ in the calculation of the entropy of activation.

d) Calculate the Gibbs free energy of activation using

$$\Delta G^{\dagger} = \Delta H^{\dagger} - T\Delta S^{\dagger}. \tag{5.120}$$

and show that the result is consistent with

$$k = \frac{k_b T}{h} \exp\left(-\frac{\Delta G^\dagger}{k_b T}\right). \tag{5.121}$$

in line with Equation 5.97 on page 232.

5.9 Solutions

The solutions below pertain to the exercises of Chapter 5 on page 236 and further.

SOLUTION 5.1

a) We assume that this reaction occurs over a surface and that the corresponding partition functions are vibrational. Moreover, we assume that the separation of the vibrational levels is thus high that only the ground state is occupied and in void of any information, we assume that we can neglect the ZPE correction. In that case, the reaction rate in the forward and backward direction are

$$k_{\text{forward}} = \frac{k_\text{B} T}{h} \exp\left(\frac{-\Delta E_\text{act}}{k_\text{B} T}\right) \tag{5.122}$$

$$= \frac{k_\text{B} T}{h} \exp\left(\frac{-\Delta E_\text{act}}{RT}\right) \tag{5.123}$$

$$= 4.58 \cdot 10^4 \text{s}^{-1} \tag{5.124}$$

Perform this calculation on Wolfram Alpha:
https://www.wolframalpha.com/input/?i=1.38064852E-23+*+500+%2F+6.62607004E-34+*+exp%28-80e3+%2F+%288.3145+*+500%29%29

and

$$k_{\text{backward}} = \frac{k_\text{B} T}{h} \exp\left(\frac{-\Delta E_\text{act}}{k_\text{B} T}\right) \tag{5.125}$$

$$= \frac{k_\text{B} T}{h} \exp\left(\frac{-\Delta E_\text{act}}{RT}\right) \tag{5.126}$$

$$= 3.03 \text{s}^{-1}. \tag{5.127}$$

Perform this calculation on Wolfram Alpha:
https://www.wolframalpha.com/input/?i=1.38064852E-23+*+500+%2F+6.62607004E-34+*+exp%28-120e3+%2F+%288.3145+*+500%29%29

b) The surface area A of the adsorption site (an equilateral triangle) is calculated by

$$A = \frac{\sqrt{3}}{4} l^2 \tag{5.128}$$

$$= \frac{\sqrt{3}}{4} (2.71\ \text{Å})^2 \tag{5.129}$$

$$= 3.18\ \text{Å}^2 \tag{5.130}$$

$$= 3.18 \cdot 10^{-20}\ \text{m}^2 \tag{5.131}$$

The rate constant for CO desorption is calculated as

$$k = \frac{k_\text{B} T^3}{h^3} \frac{A\,(2\pi m k_\text{B})}{\sigma \theta_\text{rot}} \exp\left(\frac{-E_\text{des}}{k_\text{B} T}\right) \tag{5.132}$$

$$= 7.90 \cdot 10^4\ \text{s}^{-1} \tag{5.133}$$

Perform this calculation on Wolfram Alpha:
https://www.wolframalpha.com/input/?i=1.38064852E-23+*+500%5E3+%2F+%286.62607004E-34%29%5E3+*+3.18E-20+*+%282.0+*+3.141527+*+1.66053906660E-27+*+28+*+1.38064852E-23%29+%2F+2.8+*+exp%28-120e3+%2F+%288.3145+*+500%29%29

c) The rate constant for the adsorption of CO is calculated by

$$k_\text{ads} = \frac{A}{\sqrt{2\pi m k_\text{B} T}} \tag{5.134}$$

$$= 7.08 \cdot 10^2\ \text{Pa}^{-1}\ \text{s}^{-1} \tag{5.135}$$

Perform this calculation on Wolfram Alpha:
https://www.wolframalpha.com/input/?i=3.18E-20+%2F+sqrt%282+*+3.141527+*+1.66053906660E-27+*+28+*+1.38064852E-023+*+500%29

d) Despite that the adsorption reaction has no activation energy, the rate for adsorption is lower than for desorption. The reason for this is that in 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 5.2

a) The rate constant is given by

$$k_r = \frac{A}{\sqrt{2\pi m k_\mathrm{B} T}} \tag{5.136}$$

We can calculate the heat of activation by

$$\Delta H^\ddagger = k_\mathrm{B} T^2 \frac{\partial}{\partial T} \ln k_r - k_\mathrm{B} T = -\frac{3}{2} k_\mathrm{B} T. \tag{5.137}$$

The Gibbs free energy of activation is given by

$$\Delta G^\ddagger = -k_\mathrm{B} T \left[\ln k_r - \ln \left(\frac{k_\mathrm{B} T}{h} \right) \right] \tag{5.138}$$

$$= -k_\mathrm{B} T \ln \left(\frac{A}{\sqrt{2\pi m k_\mathrm{B} T}} \frac{h}{k_\mathrm{B} T} \right). \tag{5.139}$$

and thus the entropy of activation is

$$S^\ddagger = \frac{\Delta H^\ddagger - \Delta G^\ddagger}{T} \tag{5.140}$$

$$= \frac{-\frac{3}{2} k_\mathrm{B} T + k_\mathrm{B} T \ln \left(\frac{A}{\sqrt{2\pi m k_\mathrm{B} T}} \frac{h}{k_\mathrm{B} T} \right)}{T} \tag{5.141}$$

$$= k_\mathrm{B} \left[-\frac{3}{2} + \ln \left(\frac{A}{\sqrt{2\pi m k_\mathrm{B} T}} \frac{h}{k_\mathrm{B} T} \right) \right]. \tag{5.142}$$

Note that because $\frac{k_\mathrm{B} T}{h} \approx \mathcal{O}(10^{13})$ and $\frac{A}{\sqrt{2\pi m k_\mathrm{B} T}} \approx \mathcal{O}(10^{2})$, the last term in the brackets gives about 11 negative units of k_B. Thus, the entropy of activation is **negative** as to be expected as we are loosing entropy upon going from the gas phase to the pre-adsorbed state.

b) The rate constant for desorption is given by

$$k_r = \frac{k_\mathrm{B} T^3}{h^3} \frac{2\pi m k_\mathrm{B}}{\sigma \Theta_r} \exp \left(-\frac{\Delta E_\mathrm{des}}{k_\mathrm{B} T} \right) \tag{5.143}$$

We can calculate the heat of activation by

$$\Delta H^{\ddagger} = k_{\mathrm{B}} T^2 \frac{\partial}{\partial T} \ln k_r - k_{\mathrm{B}} T = \Delta E_{\mathrm{des}} + 2 k_{\mathrm{B}} T \tag{5.144}$$

The Gibbs free energy of activation is given by

$$\Delta G^{\ddagger} = -k_{\mathrm{B}} T \left[\ln k_r - \ln \left(\frac{k_{\mathrm{B}} T}{h} \right) \right] \tag{5.145}$$

$$= \Delta E_{\mathrm{des}} - k_{\mathrm{B}} T \ln \left(\frac{T^2}{h^2} \frac{2\pi m k_{\mathrm{B}}}{\sigma \Theta_r} \right). \tag{5.146}$$

and thus the entropy of activation is

$$S^{\ddagger} = \frac{\Delta H^{\ddagger} - \Delta G^{\ddagger}}{T} \tag{5.147}$$

$$= k_{\mathrm{B}} \left[2 + \ln \left(\frac{T^2}{h^2} \frac{2\pi m k_{\mathrm{B}}}{\sigma \Theta_r} \right) \right]. \tag{5.148}$$

For desorption, the entropy of activation is **positive** as the complex regains configurational degrees of freedom upon migrating from the adsorbed state to the activated state.

SOLUTION 5.3

a)

$$k_{\mathrm{f}} = \frac{k_{\mathrm{B}} T}{h} \exp \left(-\frac{\Delta E_{\mathrm{act,f}}}{k_{\mathrm{B}} T} \right) = 7.15 \cdot 10^6 \ \mathrm{s}^{-1} \tag{5.149}$$

Perform this calculation on Wolfram Alpha:
https://www.wolframalpha.com/input/?i=1.38064852E-23*500%2F6.62607004e-34*exp%28-59e3+%2F+%288.3145+*+500%29%29

and

$$k_{\mathrm{f,zpe}} = \frac{k_{\mathrm{B}} T}{h} \exp \left(-\frac{\Delta E_{\mathrm{act,f}} + \Delta E^{\dagger}_{\mathrm{zpe}}}{k_{\mathrm{B}} T} \right) = 9.13 \cdot 10^6 \ \mathrm{s}^{-1} \tag{5.150}$$

Perform this calculation on Wolfram Alpha:
https://www.wolframalpha.com/input/?i=1.38064852E-23*500%2F6.62607004e-34*exp%28-%2859e3+%2B+75.8e3-76.9e3%29+%2F+%288.3145+*+500%29%29

$$k_b = \frac{k_\mathrm{B}T}{h} \exp\left(-\frac{\Delta E_\mathrm{act,b}}{k_\mathrm{B}T}\right) = 2.62 \cdot 10^7 \ \mathrm{s}^{-1} \tag{5.151}$$

Perform this calculation on Wolfram Alpha:
https://www.wolframalpha.com/input/?i=1.38064852E-23*500%2F6.62607004e-34*exp%28-%2853.6e3%29+%2F+%288.3145+*+500%29%29

and

$$k_\mathrm{b,zpe} = \frac{k_\mathrm{B}T}{h} \exp\left(-\frac{\Delta E_\mathrm{act,b} + \Delta E^\dagger_\mathrm{zpe}}{k_\mathrm{B}T}\right) = 9.61 \cdot 10^7 \ \mathrm{s}^{-1} \tag{5.152}$$

Perform this calculation on Wolfram Alpha:
https://www.wolframalpha.com/input/?i=1.38064852E-23*500%2F6.62607004e-34*exp%28-%2853.6e3+%2B+75.8e3-81.2e3%29+%2F+%288.3145+*+500%29%29

b) The quotient of the forward rate is

$$\frac{k_\mathrm{f,zpe}}{k_\mathrm{f}} = \frac{9.13 \cdot 10^6}{7.15 \cdot 10^6} = 1.27 \tag{5.153}$$

and for the backward rate is

$$\frac{k_\mathrm{b,zpe}}{k_b} = \frac{9.61 \cdot 10^7}{2.62 \cdot 10^7} = 3.67 \tag{5.154}$$

c) The quotient of the equilibrium constants is given by

$$\frac{K_{\text{zpe}}}{K} = \frac{k_{\text{f,zpe}}/k_{\text{b,zpe}}}{k_{\text{f}}/k_{\text{b}}} = \frac{1.27}{3.67} = 0.35 \tag{5.155}$$

d) The main reason why the differences are relatively large is because hydrogenation reactions contain light atoms (i.e. hydrogen), which results in relatively large vibrational wave numbers (and thus vibrational frequencies), in turn giving relatively large zero point energy corrections.

SOLUTION 5.4

⚠ In this question, we are often making use of the following mathematical trick

$$\frac{\partial}{\partial x}\ln\left(f(c_i \neq x)x^p\right) = \frac{\partial}{\partial x}\left[\ln\left(f(c_i \neq x)\right) + p\ln x\right] \tag{5.156}$$

$$= \frac{\partial}{\partial x} p\ln x \tag{5.157}$$

$$= \frac{p}{x} \tag{5.158}$$

wherein $f(c_i \neq x)$ represents any function (or collection of variables) that do not explicitly depend on x. We will not explicitly write out this construction in this subquestion and leave it up to the reader to recognize where this has been applied.

a) The full rate expression is given by Equation 5.57 on page 226

$$r^+_{\text{ads}} = \left.\frac{\partial\theta_x}{\partial t}\right|_+ = \frac{k_{\text{B}}T}{h}\frac{q'^{\ddagger}}{q'_{\text{gas}}} p_x \theta_*, \tag{5.159}$$

by which the rate constant k is expressed as

$$k = \frac{k_{\text{B}}T}{h}\frac{q'^{\ddagger}}{q'_{\text{gas}}} \tag{5.160}$$

$$= \frac{k_{\text{B}}T}{h}\left(\frac{2\pi m k_{\text{B}}T}{h^2}\right)^{-3/2} V^{-1}\left(\frac{\pi^{1/2}}{\sigma}\sqrt{\frac{T^3}{\Theta_A\Theta_B\Theta_C}}\right)^{-1}\exp\left(-\frac{\Delta E_{\text{e,a}} + \Delta E_{\text{zpe}}}{k_{\text{B}}T}\right) \tag{5.161}$$

b) The enthalpy of activation is given by

$$U^\dagger = k_{\text{B}}T^2\frac{\partial \ln k}{\partial T} - k_{\text{B}}T \tag{5.162}$$

$$= k_{\text{B}}T^2\frac{\partial}{\partial T}\left[\ln T - \frac{3}{2}\ln T - \frac{3}{2}\ln T + \frac{\Delta E_{\text{e,a}} - \Delta E_{\text{zpe}}}{k_{\text{B}}T}\right] - k_{\text{B}}T \tag{5.163}$$

$$= \Delta E_{\text{e,a}} + \Delta E_{\text{zpe}} - 3k_{\text{B}}T. \tag{5.164}$$

c) The entropy of activation is given by

$$\Delta S^\dagger = \frac{\partial}{\partial T}\left(k_b T\left(\ln(k) - \ln\left(\frac{k_b T}{h}\right)\right)\right) \tag{5.165}$$

$$= \frac{\partial}{\partial T}\left(k_b T\left(\ln\left[\left(\frac{2\pi m k_\mathrm{B} T}{h^2}\right)^{-3/2} V^{-1}\left(\frac{\pi^{1/2}}{\sigma}\sqrt{\frac{T^3}{\Theta_A\Theta_B\Theta_C}}\right)^{-1} \times \cdots\right.\right.\right.$$

$$\left.\left.\left. \cdots \exp\left(-\frac{\Delta E_{\mathrm{e,a}} + \Delta E_{\mathrm{zpe}}}{k_\mathrm{B} T}\right)\right]\right)\right) \tag{5.166}$$

$$= k_\mathrm{B}\left(\ln\left[\left(\frac{2\pi m k_\mathrm{B} T}{h^2}\right)^{-3/2} V^{-1}\left(\frac{\pi^{1/2}}{\sigma}\sqrt{\frac{T^3}{\Theta_A\Theta_B\Theta_C}}\right)^{-1}\right] - \cancel{\frac{\Delta E_{\mathrm{e,a}} + \Delta E_{\mathrm{zpe}}}{k_\mathrm{B} T}}\right) + \cdots$$

$$\cdots k_\mathrm{B} T\left(\cancel{\frac{\Delta E_{\mathrm{e,a}} + \Delta E_{\mathrm{zpe}}}{k_\mathrm{B} T^2}} - \frac{3}{T}\right) \tag{5.167}$$

$$= k_\mathrm{B}\left(\ln\left[\left(\frac{2\pi m k_\mathrm{B} T}{h^2}\right)^{-3/2} V^{-1}\left(\frac{\pi^{1/2}}{\sigma}\sqrt{\frac{T^3}{\Theta_A\Theta_B\Theta_C}}\right)^{-1}\right] - 3\right) \tag{5.168}$$

Note that in the derivation above, the terms corresponding to the electronic activation energy and its zero point energy correction cancel out, as indicated by the diagonal lines through these terms.

d) Finally, the Gibbs free energy of activation is given by

$$\Delta G^\dagger = \Delta H^\dagger - T\Delta S^\dagger \tag{5.169}$$

$$= \Delta E_{\mathrm{e,a}} + \Delta E_{\mathrm{zpe}} - k_\mathrm{B} T\left(\ln\left[\left(\frac{2\pi m k_\mathrm{B} T}{h^2}\right)^{-3/2} V^{-1}\left(\frac{\pi^{1/2}}{\sigma}\sqrt{\frac{T^3}{\Theta_A\Theta_B\Theta_C}}\right)^{-1}\right]\right) \tag{5.170}$$

Plugging this result into Equation 5.97 on page 232 gives

$$k = \frac{k_b T}{h} \exp\left(-\frac{\Delta G^{\dagger}}{k_b T}\right) \tag{5.171}$$

$$= \frac{k_b T}{h} \exp\left(-\frac{\Delta E_{\mathrm{e,a}} + \Delta E_{\mathrm{zpe}} - k_{\mathrm{B}} T \left(\ln\left[\left(\frac{2\pi m k_{\mathrm{B}} T}{h^2}\right)^{-3/2} V^{-1} \left(\frac{\pi^{1/2}}{\sigma}\sqrt{\frac{T^3}{\Theta_A \Theta_B \Theta_C}}\right)^{-1}\right]\right)}{k_b T}\right) \tag{5.172}$$

$$= \frac{k_{\mathrm{B}} T}{h} \left(\frac{2\pi m k_{\mathrm{B}} T}{h^2}\right)^{-3/2} V^{-1} \left(\frac{\pi^{1/2}}{\sigma}\sqrt{\frac{T^3}{\Theta_A \Theta_B \Theta_C}}\right)^{-1} \exp\left(-\frac{\Delta E_{\mathrm{e,a}} + \Delta E_{\mathrm{zpe}}}{k_{\mathrm{B}} T}\right), \tag{5.173}$$

fully consistent with Equation 5.161.

CHAPTER 6

MICROKINETIC MODELING

Contents

6.1 Introduction

In Chapter 1, we introduced the concept of elementary reaction steps and the Langmuir–Hinshelwood–Hougen–Watson (LHHW) formalism, which provides a framework for describing surface reactions at the molecular level. In Chapter 2, we explained how systems containing different chemical compounds can be characterized by a small set of macroscopic parameters, such as temperature, pressure, and concentration. Chapter 3 then detailed how molecular partition functions can be used to relate microscopic molecular properties to macroscopic thermodynamic quantities. In Chapter 4, we introduced transition state theory and derived the Eyring equation, which expresses the rate of interconversion between chemical species once the activation energy and partition functions are known. In Chapter 5, we illustrated how these rate expressions apply to specific types of elementary reaction steps.

In this chapter, we combine these concepts to construct a complete microkinetic model from the ground up. We show how to connect multiple elementary reaction steps into a reaction network, formulate the corresponding set of ordinary differential equations (ODEs), and integrate them in time using appropriate boundary conditions and initial values. Finally, we discuss how

to derive observable quantities from a microkinetic model and how these can be compared with experimental data.

6.2 Microkinetic modeling of a simple catalytic reaction

In this section, we illustrate how to set up a microkinetic model using a simple example of a catalytic reaction. To keep the discussion straightforward, we will restrict ourselves to unimolecular elementary reaction steps. More complex chemical systems will be introduced later in this chapter. The most effective way to understand how microkinetic simulations work is to build one yourself. To facilitate this, we provide a small set of Python scripts that gradually introduce the underlying methodology. These scripts are not intended to be the most efficient implementation, but they serve as a convenient learning tool to grasp the fundamental principles of microkinetic modeling. We recommend running the scripts in a Python IDE such as **Spyder**.[1]

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).

6.2.1 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.

$$\mathrm{A} \longrightarrow \mathrm{A}* \longrightarrow \mathrm{B}* \longrightarrow \mathrm{B}. \tag{6.1}$$

The overall reaction for this chemokinetic network is

$$\mathrm{A} \longrightarrow \mathrm{B}, \tag{6.2}$$

which is composed of the following three elementary reaction steps

$$\mathrm{A} + * \leftrightarrows \mathrm{A}* \tag{6.3}$$
$$\mathrm{B} + * \leftrightarrows \mathrm{B}* \tag{6.4}$$
$$\mathrm{A}* \leftrightarrows \mathrm{B} * . \tag{6.5}$$

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 5.69 and 5.84 on pages 228 and 230, respectively). Furthermore, we will use the assumptions as discussed in section 5.5 on page 231 for the surface reactions. The parameters for the adsorption and desorption steps are given in Tables 6.1 and 6.2, respectively.

[1] More information about Spyder can be found at `https://www.spyder-ide.org/`.

Table 6.1: *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 6.2: *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]
A* $\longrightarrow$ 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 6.1 and 6.2, 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 6.1.

The function `calc_k_arr` as shown in Listing 6.1 calculates the Arrhenius-type rate constant as given by Equation 5.91 on page 231. The functions `calc_kads` and `calc_kdes` calculate the reaction rates for adsorption and desorption, respectively. These functions are based on Equations 5.69 and 5.84 on pages 228 and 230, 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 $X = 0$.[2] 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 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[3]

[2] This is often termed as that one operates the reaction at **differential conditions**.

[3] Recall that for constructing an analytical expression, we require a series of assumptions.

Listing 6.1: *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))
```

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.[4]

The set of ordinary differential equations for this system to solve is given in Equations 6.6 - 6.8. Please note that in these equations k_b refers to the reaction rate constant in the backward direction and not to the Boltzmann constant.

$$\frac{\partial \theta_\mathrm{A}}{\partial t} = k_{\mathrm{ads,A}} \cdot p_\mathrm{A} \cdot \theta_* - k_{\mathrm{des,A}} \cdot \theta_\mathrm{A} - k_f \cdot \theta_\mathrm{A} + k_b \cdot \theta_\mathrm{B} \tag{6.6}$$

$$\frac{\partial \theta_\mathrm{B}}{\partial t} = k_{\mathrm{ads,B}} \cdot p_\mathrm{B} \cdot \theta_* - k_{\mathrm{des,B}} \cdot \theta_\mathrm{B} + k_f \cdot \theta_\mathrm{A} - k_b \cdot \theta_\mathrm{B} \tag{6.7}$$

$$\frac{\partial \theta_*}{\partial t} = -k_{\mathrm{ads,A}} \cdot p_\mathrm{A} \cdot \theta_* + k_{\mathrm{des,A}} \cdot \theta_\mathrm{A} - k_{\mathrm{ads,B}} \cdot p_\mathrm{B} \cdot \theta_* + k_{\mathrm{des,B}} \cdot \theta_\mathrm{B} \tag{6.8}$$

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 6.2. 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 6.3.

Listing 6.3: *Python functions to perform the time-integration of the set of ordinary differential equation.*

```
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()
```

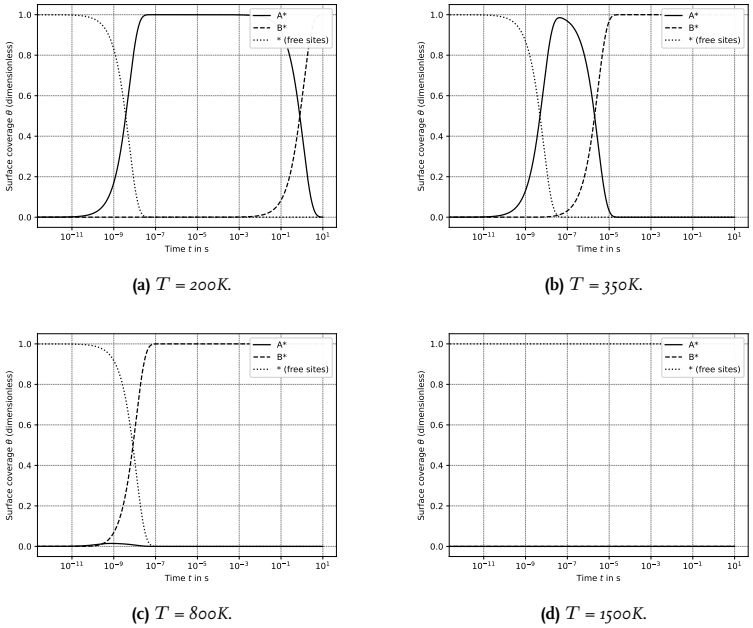
The ODE solver is constructed using a generic interface as explained in detail on its webpage.[5] First, we need to construct a function that takes as input the two parameters t (time) and y (surface concentrations). Optionally, a list of parameters can be provided. Here, we provide as additional parameters 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 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.[6]

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

[4] `https://docs.scipy.org/doc/scipy/reference/generated/scipy.integrate.ode.html`
[5] `https://docs.scipy.org/doc/scipy/reference/generated/scipy.integrate.ode.html`
[6] Consult the web page of SciPy for more information how this is done.

Listing 6.2: *Python functions to perform the time-integration of the set of ordinary differential equation.*

```
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
```



(a) $T = 200K$. **(b)** $T = 350K$.

(c) $T = 800K$. **(d)** $T = 1500K$.

Figure 6.1: *Surface coverage as a function of time for the unimolecular catalytic surface reaction.*

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:

$$\theta_A, \theta_B, \theta_* \in [0, 1] \tag{6.9}$$

under the constraint (remember that there is conservation of mass)

$$\theta_A + \theta_B + \theta_* = 1 \tag{6.10}$$

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:

$$\frac{\partial \theta_i}{\partial t} = 0 \tag{6.11}$$

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 6.1a-6.1d, 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 6.1a-6.1c, a

similar final result is obtained, which is the catalytic surface fully covered with B. Note that in Figure 6.1a, 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 (6.1b-6.1d), 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 6.1d (i.e., at a significantly high temperature, does not converge to a similar-steady solution as the other Figures. In 6.1d, 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 5.69 and 5.84 on pages 228 and 230, 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.

In Figure 6.2, 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 $T \approx 1175K$).

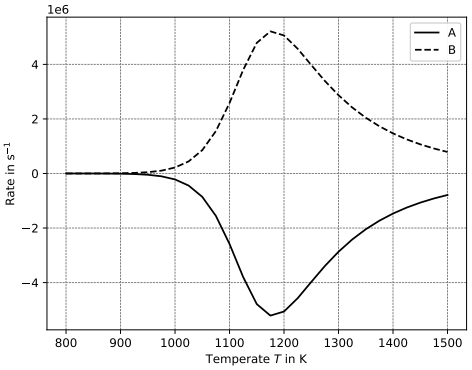


Figure 6.2: *Production rates of compounds A and B as a function of temperature.*

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.

6.2.2 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

$$2CO + O_2 \rightarrow 2CO_2 \tag{6.12}$$

and constitutes the following elementary reaction steps

$$CO + * \leftrightarrows CO* \tag{6.13}$$
$$O_2 + 2* \leftrightarrows 2O* \tag{6.14}$$
$$CO* + O* \leftrightarrows CO_2* + * \tag{6.15}$$
$$CO_2 + * \leftrightarrows CO_2* \tag{6.16}$$

These elementary reaction steps lead to the following set of ordinary differential equations

$$\frac{\partial \theta_{CO}}{\partial t} = k_{1,ads}\theta_* - k_{1,des}\theta_{CO} - k_{3,f}\theta_{CO}\theta_O + k_{3,b}\theta_{CO_2}\theta_* \tag{6.17}$$
$$\frac{\partial \theta_O}{\partial t} = 2k_{2,ads}\theta_*^2 - 2k_{2,des}\theta_O^2 - k_{3,f}\theta_{CO}\theta_O + k_{3,b}\theta_{CO_2}\theta_* \tag{6.18}$$
$$\frac{\partial \theta_{CO_2}}{\partial t} = k_{4,ads}\theta_* - k_{4,des}\theta_{CO_2} + k_{3,f}\theta_{CO}\theta_O - k_{3,b}\theta_{CO_2}\theta_* \tag{6.19}$$
$$\frac{\partial \theta_*}{\partial t} = -k_{1,ads}\theta_* + k_{1,des}\theta_{CO} - 2k_{2,ads}\theta_*^2 + 2k_{2,des}\theta_O^2 + k_{3,f}\theta_{CO}\theta_O - k_{3,b}\theta_{CO_2}\theta_* - k_{4,ads}\theta_* + k_{4,des}\theta_{CO_2} \tag{6.20}$$

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 6.3 and 6.4.

Table 6.3: *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

Combining the data in Tables 6.3 and 6.4 and the set of ordinary differential equations leads to the Python code as shown in Listing 6.4. Note that we have introduced two auxiliary variables

Table 6.4: *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

Listing 6.4: *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.*

```
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
```

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.

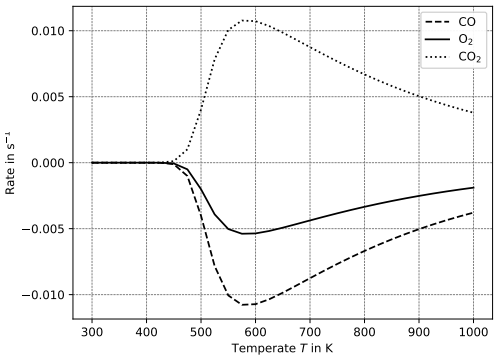


Figure 6.3: *Production rate of* CO_2 *and consumption rates of* CO *and* O_2 *as a function of temperature.*

The result for this simulation is given in Figure 6.3. 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.

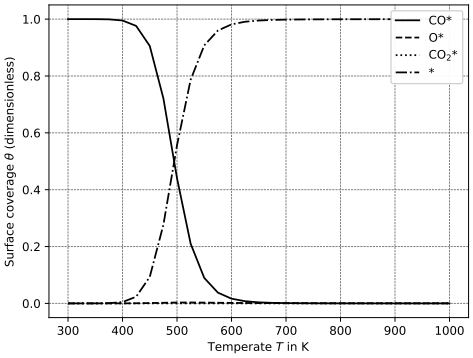


Figure 6.4: *Surface coverage as a function of temperature.*

In Figure 6.4, 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 temperatures, the CO coverage decreases even more and the surface becomes empty. At that point, the overall rate decreases again.

6.3 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 1.6.1 on page 24):

$$n_i = p_i \frac{\partial \ln r^+}{\partial p_i}, \tag{6.21}$$

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 6.5. At the end of this chapter, we will also show that for some systems, an analytical expression can be derived.

In Listing 6.5, 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.

The reaction orders of CO and O_2 as function of temperature is found in Figure 6.5. 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 $\sqrt{2}$.

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

$$r = c p_{\mathrm{CO}}^{\nu_{\mathrm{CO}}} p_{\mathrm{O_2}}^{\nu_{\mathrm{O_2}}}, \tag{6.22}$$

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

Listing 6.5: *Python functions to calculate the reaction order of CO at temperature T.*

```
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)
```

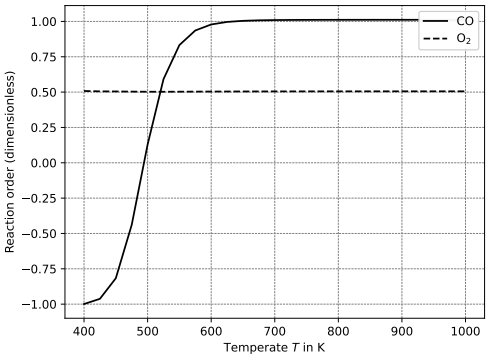


Figure 6.5: *Reaction orders in CO and O_2 as a function of temperature.*

realize is that the above expression is limited to a fairly small region in temperature as is evident from Figure 6.5. 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.

6.4 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 1.6.2 on page 26):

$$\Delta E_{\text{act}}^{\text{app}} = RT^2 \frac{\partial \ln r^+}{\partial T}. \tag{6.23}$$

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 6.23 as shown in Listing 6.6. 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 6.6: *Python functions to calculate the apparent activation energy at temperature T.*

```
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)
```

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 is increased. In contrast, a negative energy indicates that the overall reaction rate would be decreased as a result of an increase in temperature. Consequently, if the apparent activation energy is zero, this means that the reaction is at an optimum with respect to temperature.

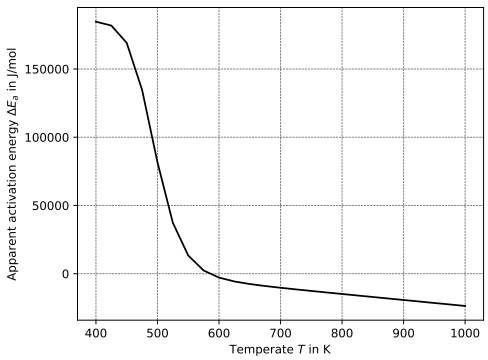


Figure 6.6: *Apparent activation energy as a function of temperature.*

In Figure 6.6, 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 6.4) 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 6.3, 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 6.23 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:

$$r_j = \nu \exp\left(\frac{\Delta E_{\text{act}}^{\text{app}}}{RT}\right) \prod_i p_i^{\nu_i}, \tag{6.24}$$

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 6.6, 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.

6.5 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

$$\chi_i = \left(\frac{\partial \ln r}{\partial \ln k_i}\right)_{k_j \neq k_i, K_i}, \tag{6.25}$$

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

$$K_i = \frac{k_i^+}{k_i^-}. \tag{6.26}$$

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 6.7.

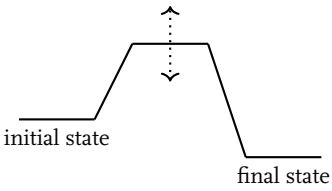


Figure 6.7: *Schematic representation of varying the reaction barrier of an elementary reaction step while keeping the Gibbs free energy of the reaction constant.*

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[7] as given by

$$\sum_i \chi_i = 1. \tag{6.27}$$

The DRC analysis for CO oxidation is given in Figure 6.8. 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.

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.

6.6 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

[7] The proof for this equality is given in section B.10 of the Appendix.

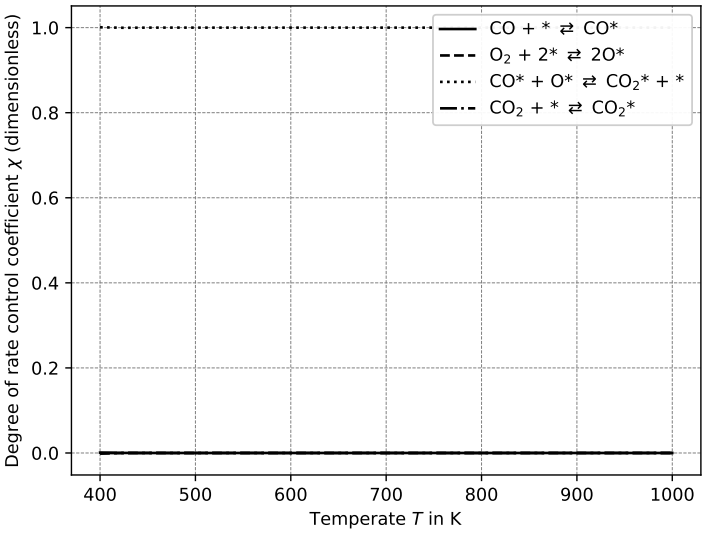


Figure 6.8: *Degree of rate control coefficient as function of temperature.*

evaluation, one solves the following differential

$$\epsilon_{i,c} = \left(\frac{\partial \eta_c}{\partial \ln k_i} \right)_{k_j \neq k_i, K_i}, \tag{6.28}$$

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:

$$\epsilon_{i,c} = \left(\frac{\partial \eta_c}{\partial \ln k_i} \right)_{k_j \neq k_i, K_i} \tag{6.29}$$

$$= \eta_c \left(\frac{\partial \ln \eta_c}{\partial \ln k_i} \right)_{k_j \neq k_i, K_i} \tag{6.30}$$

$$= \eta_c \left(\frac{\partial \ln r_c / r_r}{\partial \ln k_i} \right)_{k_j \neq k_i, K_i} \tag{6.31}$$

$$= \eta_c \left(\left(\frac{\partial \ln r_c}{\partial \ln k_i} \right)_{k_j \neq k_i, K_i} - \left(\frac{\partial \ln r_r}{\partial \ln k_i} \right)_{k_j \neq k_i, K_i} \right) \tag{6.32}$$

$$= \eta_c \left(\chi_{c,i} - \chi_{r,i} \right) \tag{6.33}$$

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

$$\sum_{i,c} \epsilon_{i,c} = 0. \tag{6.34}$$

6.7 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 $CO* + O* \rightarrow CO_2 * + *$ 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,

$$CO + * \leftrightarrows CO* \tag{6.35}$$

$$O_2 + 2* \leftrightarrows 2O* \tag{6.36}$$

and consequently

$$K_{CO} = \frac{\theta_{CO}}{p_{CO}\theta_*} \tag{6.37}$$

$$K_{O_2} = \frac{\theta_O^2}{p_{O_2}\theta_*^2}, \tag{6.38}$$

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, [8]

$$\theta_{CO} + \theta_O + \theta_* = 1, \tag{6.39}$$

we can calculate the fraction of free sites as a function of the equilibrium constants and the partial pressures.

$$1 = \theta_{CO} + \theta_O + \theta_* \tag{6.40}$$

$$= K_{CO}p_{CO}\theta_* + \sqrt{K_{O_2}p_{O_2}}\theta_* + \theta_* \tag{6.41}$$

$$= \left(1 + K_{CO}p_{CO} + \sqrt{K_{O_2}p_{O_2}}\right)\theta_* \tag{6.42}$$

$$\theta_* = \frac{1}{1 + K_{CO}p_{CO} + \sqrt{K_{O_2}p_{O_2}}} \tag{6.43}$$

[8] 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.

We can use this result to explicitly calculate the coverages for θ_{CO} and θ_{O_2},

$$\theta_{CO} = \frac{K_{CO}p_{CO}}{1 + K_{CO}p_{CO} + \sqrt{K_{O_2}p_{O_2}}} \tag{6.44}$$

$$\theta_{O} = \frac{\sqrt{K_{O_2}p_{O_2}}}{1 + K_{CO}p_{CO} + \sqrt{K_{O_2}p_{O_2}}}. \tag{6.45}$$

At zero coverage, the overall rate is given by the *forward* rate of the rate-determining elementary reaction step as

$$r = k_{rds}\theta_{CO}\theta_{O_2} \tag{6.46}$$

$$= \frac{k_{rds}K_{CO}p_{CO}\sqrt{K_{O_2}p_{O_2}}}{\left(1 + K_{CO}p_{CO} + \sqrt{K_{O_2}p_{O_2}}\right)^2}. \tag{6.47}$$

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.

$$n_{CO} = p_{CO}\frac{\partial \ln r}{\partial p_{CO}} \tag{6.48}$$

$$= p_{CO}\frac{\partial \ln\left(\frac{k_{rds}K_{CO}p_{CO}\sqrt{K_{O_2}p_{O_2}}}{\left(1+K_{CO}p_{CO}+\sqrt{K_{O_2}p_{O_2}}\right)^2}\right)}{\partial p_{CO}} \tag{6.49}$$

$$= D_1 + \frac{1}{2}D_2 - 2D_3, \tag{6.50}$$

where

$$D_1 = p_{CO}\frac{\partial \ln\left(k_{rds}K_{CO}p_{CO}\right)}{\partial p_{CO}} \tag{6.51}$$

$$D_2 = p_{CO}\frac{\partial \ln\left(K_{O_2}p_{O_2}\right)}{\partial p_{CO}} \tag{6.52}$$

$$D_3 = p_{CO}\frac{\partial \ln\left(1 + K_{CO}p_{CO} + \sqrt{K_{O_2}p_{O_2}}\right)}{\partial p_{CO}}. \tag{6.53}$$

The terms D_i can be readily solved, which give

$$D_1 = 1 \tag{6.54}$$

$$D_2 = 0 \tag{6.55}$$

$$D_3 = \frac{K_{CO}p_{CO}}{1 + K_{CO}p_{CO} + \sqrt{K_{O_2}p_{O_2}}} \tag{6.56}$$

and combining these three terms results in

$$n_{CO} = 1 - 2\theta_{CO}. \tag{6.57}$$

In a similar fashion, we obtain

$$n_{O_2} = \frac{1}{2} - \theta_O. \tag{6.58}$$

These results are completely in line with the numerical results as shown in Figure 6.5, 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 $n_{CO} = 1 - 2 \cdot 1 = -1$. With decreasing surface coverage, the reaction order increases and finally at low surface coverage of CO, the reaction order becomes 1.

For n_{O_2}, we can see from Figure 6.4 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 $n_{O_2} = \frac{1}{2} - 1 \cdot 0 = \frac{1}{2}$. This confirms our results as seen in Figure 6.5 where indeed a reaction order of $\frac{1}{2}$ is seen for O_2.

The apparent activation energy can also be readily derived.

$$\Delta E_{act}^{app} = RT^2 \frac{\partial \ln r}{\partial T} \tag{6.59}$$

$$= RT^2 \frac{\partial \ln \left(\frac{k_{rds} K_{CO} p_{CO} \sqrt{K_{O_2} p_{O_2}}}{\left(1 + K_{CO} p_{CO} + \sqrt{K_{O_2} p_{O_2}}\right)^2} \right)}{\partial T} \tag{6.60}$$

$$= D_1 + D_2 + \frac{1}{2} D_3 - 2D_4 \tag{6.61}$$

where

$$D_1 = RT^2 \frac{\ln k_{rds}}{\partial T} \tag{6.62}$$

$$D_2 = RT^2 \frac{\ln K_{CO}}{\partial T} \tag{6.63}$$

$$D_3 = RT^2 \frac{\ln K_O}{\partial T} \tag{6.64}$$

$$D_4 = RT^2 \frac{\partial \ln \left(1 + K_{CO} p_{CO} + \sqrt{K_{O_2} p_{O_2}}\right)}{\partial T}. \tag{6.65}$$

which resolve to

$$D_1 = \Delta E_{rds} \tag{6.66}$$

$$D_2 = \Delta H_{CO} \tag{6.67}$$

$$D_3 = \Delta H_O \tag{6.68}$$

$$D_4 = \Delta H_{CO} \frac{K_{CO} p_{CO}}{1 + K_{CO} p_{CO} + \sqrt{K_{O_2} p_{O_2}}} + \frac{1}{2} \Delta H_{O_2} \frac{\sqrt{K_{O_2} p_{O_2}}}{1 + K_{CO} p_{CO} + \sqrt{K_{O_2} p_{O_2}}}. \tag{6.69}$$

Combining these terms gives

$$\Delta E_{\text{act}}^{\text{app}} = \Delta E_{\text{rds}} + \Delta H_{\text{CO}} \left(1 - 2\theta_{CO}\right) + \Delta H_{\text{O}_2} \left(\frac{1}{2} - \theta_{\text{O}}\right). \tag{6.70}$$

Note that in the above expression, the part between the round brackets are equal to the reaction orders:

$$\Delta E_{\text{act}}^{\text{app}} = \Delta E_{\text{rds}} + \Delta H_{\text{CO}} \left(n_{\text{CO}}\right) + \Delta H_{\text{O}_2} \left(n_{\text{O}_2}\right). \tag{6.71}$$

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

$$\begin{aligned}
\Delta E_{\text{act}}^{\text{app}} &= \Delta E_{\text{rds}} + \Delta H_{\text{CO}} \left(n_{\text{CO}}\right) + \Delta H_{\text{O}_2} \left(n_{\text{O}_2}\right) && (6.72)\\
&= 120\text{kJ/mol} + 80\text{kJ/mol} - 0.5 \cdot 40\text{kJ/mol} && (6.73)\\
&= 180\text{kJ/mol} && (6.74)
\end{aligned}$$

From Figure 6.6 we can see that around 400K, the apparent activation energy indeed has a value of around 180 kJ/mol. Furthermore, from Figure 6.4 we see that this situation corresponds to a surface nearly fully covered with CO. Indeed, from the coverages as obtained from Figure 6.4 and using the formula for the apparent activation energy, Figure 6.6 can be completely reproduced.

Practice your understanding

Exercise 6.1 and 6.2

6.8 Exercises

The answers to the exercises can be found at the end of this Chapter on page 269. The exercises are marked by a number of gears to indicate their difficulty levels.

EXERCISE 6.1 ⚙⚙

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 6.47.

b) Derive the reaction order for O_2 in the CO oxidation reaction and show that your result matches that of Equation 6.58. *Hint: You need to use the chain-rule.*

EXERCISE 6.2 ⚙⚙

a) Show that Equation 6.34 holds using the proof for the sum rule of the degree of rate control coefficients (eq. 6.27).

6.9 Solutions

The solutions below pertain to the exercises of Chapter 6 on page 269 and further.

SOLUTION 6.1

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)

$$n_{O_2} = p_{O_2} \frac{\partial \ln r}{\partial p_{O_2}} \tag{6.75}$$

$$= p_{O_2} \frac{\partial \ln \left(\frac{k_{rds} K_{CO} p_{CO} \sqrt{K_{O_2} p_{O_2}}}{\left(1 + K_{CO} p_{CO} + \sqrt{K_{O_2} p_{O_2}}\right)^2} \right)}{\partial p_{CO}} \tag{6.76}$$

$$= D_1 + \frac{1}{2} D_2 - 2D_3, \tag{6.77}$$

where

$$D_1 = p_{O_2} \frac{\partial \ln \left(k_{rds} K_{CO} p_{CO} \right)}{\partial p_{CO}} \tag{6.78}$$

$$D_2 = p_{O_2} \frac{\partial \ln \left(\sqrt{K_{O_2} p_{O_2}} \right)}{\partial p_{O_2}} \tag{6.79}$$

$$D_3 = p_{O_2} \frac{\partial \ln \left(1 + K_{CO} p_{CO} + \sqrt{K_{O_2} p_{O_2}} \right)}{\partial p_{O_2}}. \tag{6.80}$$

The terms D_i can be readily solved, which give

$$D_1 = 0 \tag{6.81}$$

$$D_2 = \frac{1}{2} \tag{6.82}$$

$$D_3 = \frac{1}{2} \frac{\sqrt{K_{O_2} p_{O_2}}}{1 + K_{CO} p_{CO} + \sqrt{K_{O_2} p_{O_2}}} \tag{6.83}$$

and combining these three terms results in

$$n_{CO} = \frac{1}{2} - \theta_O \tag{6.84}$$

SOLUTION 6.2

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.

$$\sum_{i,c} \epsilon_{i,c} = \sum_{i,c} \frac{\partial \eta_c}{\partial \ln k_i} \tag{6.85}$$

$$= \sum_{i,c} \eta_c \frac{\partial \ln \eta_c}{\partial \ln k_i} \tag{6.86}$$

$$= \sum_{i,c} \eta_c \frac{\partial \ln r_c / r_r}{\partial \ln k_i} \tag{6.87}$$

$$= \sum_{i,c} \eta_c \left(\frac{\partial \ln r_c}{\partial \ln k_i} - \frac{\partial \ln r_r}{\partial \ln k_i} \right) \tag{6.88}$$

$$= \sum_{i,c} \eta_c \left(\chi_c - \chi_r \right) \tag{6.89}$$

$$= \sum_{c} \eta_c \sum_{i} \left(\chi_{c,i} - \chi_{r,i} \right) \tag{6.90}$$

$$= \sum_{c} \eta_c \left(\sum_{i} \chi_{c,i} - \sum_{i} \chi_{r,i} \right) \tag{6.91}$$

$$= \sum_{c} \eta_c \left(1 - 1 \right) \tag{6.92}$$

$$= 0 \tag{6.93}$$

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.

APPENDIX

APPENDIX A

DATA COMPENDIUM

A.1 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	$6.62606957 \cdot 10^{-34}$	$\mathrm{J} \cdot \mathrm{s}$
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 (amu)	m_u	$1.660538921 \cdot 10^{-27}$	kg

A.2 Clebsch-Gordan Coefficients

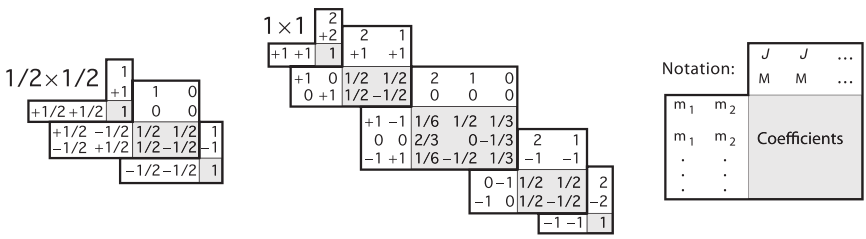


Figure A.1: *Clebsch-Gordan Coefficients for two spin-$\frac{1}{2}$ and two spin-1 particles.*

Appendix A

APPENDIX B

MATHEMATICS

Contents

B.1 Coordinate systems

B.1.1 Cartesian coordinates

Gradient operator:

$$\nabla f\left(x,y,z\right)=\frac{\partial f}{\partial x}+\frac{\partial f}{\partial y}+\frac{\partial f}{\partial z} \tag{B.1}$$

Laplacian operator:

$$\nabla^2 f\left(x,y,z\right)=\frac{\partial^2 f}{\partial x^2}+\frac{\partial^2 f}{\partial y^2}+\frac{\partial^2 f}{\partial z^2} \tag{B.2}$$

Jacobian (differential volume):

$$dV=dx\,dy\,dz \tag{B.3}$$

B.1.2 Cylindrical coordinates

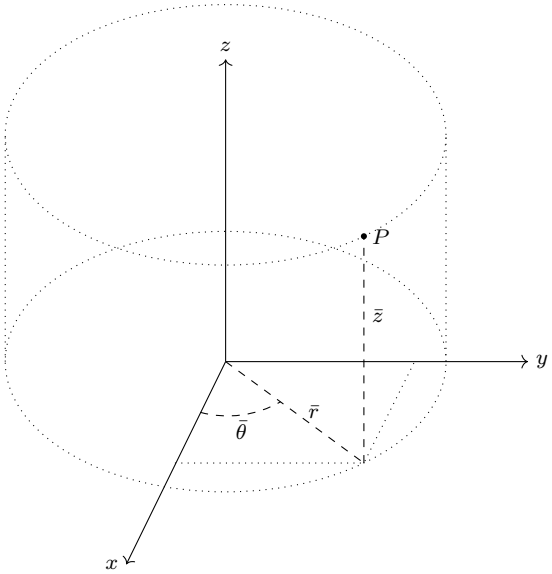


Figure B.1: *Cylindrical coordinate system.*

The cylindrical coordinates (see Figure B.1) are related to the Cartesian coordinates by means of the following unit transformation

$$x = \rho \cos\theta \tag{B.4}$$
$$y = \rho \sin\theta \tag{B.5}$$
$$z = z \tag{B.6}$$

and

$$\rho = \sqrt{x^2 + y^2} \tag{B.7}$$
$$\theta = \arctan\left(\frac{y}{x}\right) \tag{B.8}$$
$$z = z \tag{B.9}$$

Gradient operator:

$$\nabla f(\rho, \theta, z) = \frac{\partial f}{\partial \rho} + \frac{1}{\rho}\frac{\partial f}{\partial \theta} + \frac{\partial f}{\partial z} \tag{B.10}$$

Laplacian operator:

$$\nabla^2 f(\rho, \theta, z) = \frac{1}{\rho}\frac{\partial}{\partial \rho}\left(\frac{\partial f}{\partial \rho}\right) + \frac{1}{\rho^2}\frac{\partial^2 f}{\partial \theta^2} + \frac{\partial^2 f}{\partial z^2} \tag{B.11}$$

Jacobian (differential volume):

$$dV = \rho \, d\rho \, d\phi \, dz \tag{B.12}$$

B.1.3 Spherical coordinates

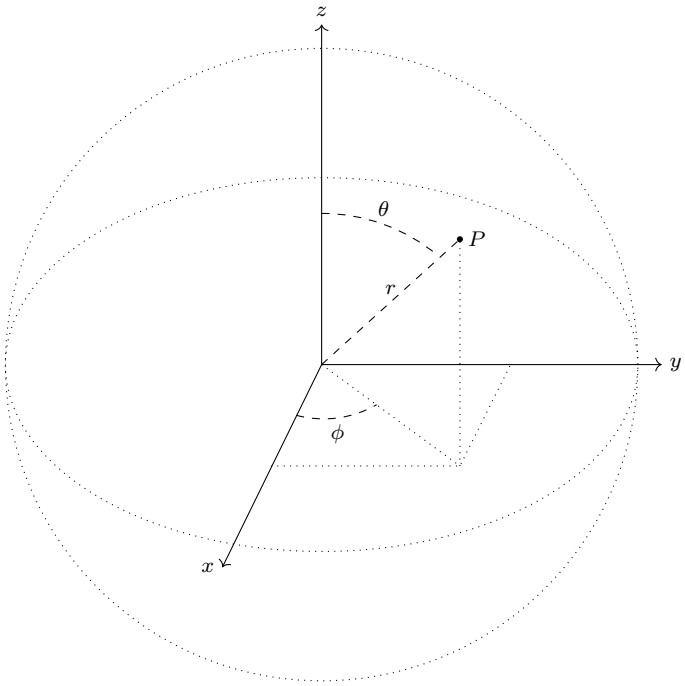


Figure B.2: *Spherical coordinate system. Note that the physics convention is used for the coordinate symbols, as set in ISO 80000-2:2019.*

The spherical coordinates (see Figure B.2) are related to the Cartesian coordinates by means of the following unit transformation

$$x = r \sin\theta \cos\phi \tag{B.13}$$
$$y = r \sin\theta \sin\phi \tag{B.14}$$
$$z = r \cos\theta \tag{B.15}$$

and

$$r = \sqrt{x^2 + y^2 + z^2} \tag{B.16}$$
$$\theta = \arctan\left(\frac{\sqrt{x^2 + y^2}}{z}\right) \tag{B.17}$$
$$\phi = \arctan\left(\frac{y}{x}\right) \tag{B.18}$$

Gradient operator:

$$\nabla f\,(r, \theta, \phi) = \frac{\partial f}{\partial r} + \frac{1}{r}\frac{\partial f}{\partial \theta} + \frac{1}{r \sin\theta}\frac{\partial f}{\partial \phi} \tag{B.19}$$

Laplacian operator:

$$\nabla^2 f\,(r,\theta,\phi) = \frac{1}{r^2}\left(r^2\frac{\partial f}{\partial r}\right) + \frac{1}{r^2\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial f}{\partial\theta}\right) + \frac{1}{r^2\sin^2\theta}\frac{\partial^2 f}{\partial\varphi^2} \tag{B.20}$$

Jacobian (differential volume):

$$dV = r^2\sin\theta\; dr\; d\theta\; d\phi \tag{B.21}$$

B.2 Stirling Approximation

Stirling's theorem states:

$$\sqrt{2\pi}n^{n+\frac{1}{2}}e^{-n} < n! < \sqrt{2\pi}n^{n+\frac{1}{2}}e^{-n}\left(1+\frac{1}{4n}\right) \tag{B.22}$$

Therefore,

$$\ln(n!) = (n+\frac{1}{2})\ln(n) - n + C \tag{B.23}$$

where C is a number between 0.9189 and $0.9189 + \ln\left(1+\frac{1}{4n}\right)$. For large values of n, this reduces to the simpler form,

$$\ln(n!) \approx n\ln(n) - n \tag{B.24}$$

B.3 Gaussian integrals

$$\int_{-\infty}^{\infty} \exp^{-x^2}\,\mathrm{d}x = \sqrt{\pi} \tag{B.25}$$

$$\int_0^{\infty} x^{2n}\exp^{-x^2/a^2}\,\mathrm{d}x = \sqrt{\pi}\frac{(2n)!}{n!}\left(\frac{a}{2}\right)^{2n+1} \tag{B.26}$$

$$\int_0^{\infty} x^{2n+1}\exp^{-x^2/a^2}\,\mathrm{d}x = \frac{n!}{2}a^{2n+2} \tag{B.27}$$

B.4 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

$$f(x) = \sum_{n=0}^{\infty}\frac{f^{(n)}(a)}{n!}(x-a)^n \tag{B.28}$$

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.

$$\exp x = \sum_{n=0}^{\infty} \frac{f^{(n)}(a)}{n!}(x-a)^n \tag{B.29}$$

$$= \sum_{n=0}^{\infty} \frac{\frac{\mathrm{d}\exp x}{\mathrm{d}x}|_{x=0}}{n!}x^n \tag{B.30}$$

$$= \sum_{n=0}^{\infty} \frac{x^n}{n!} \tag{B.31}$$

$$= \frac{x^0}{0!} + \frac{x^1}{1!} + \frac{x^2}{2!} + \frac{x^3}{3!} + \cdots \tag{B.32}$$

$$= 1 + x + \frac{x^2}{2!} + \frac{x^3}{3!} + \cdots \tag{B.33}$$

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

$$\exp x \approx 1 + x \quad \text{for } x \ll 1. \tag{B.34}$$

B.5 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

$$a + ar + ar^2 + ar^3 + \cdots = \sum_{k=0}^{\infty} ar^k. \tag{B.35}$$

Such a series can converge when the absolute value of r is sufficiently small as

$$\sum_{k=0}^{\infty} ar^k = \frac{a}{1-r}\text{ , for } |r| < 1. \tag{B.36}$$

Consider also the following two converging series

$$\sum_{k=1}^{\infty} ak \cdot r^k = \frac{ar}{(r-1)^2}\text{ , for } |r| < 1 \tag{B.37}$$

and

$$\sum_{k=1}^{\infty} ak \cdot (1-k) \cdot r^{k-1} = -\frac{a}{r-1}\text{ , for } |r| < 1. \tag{B.38}$$

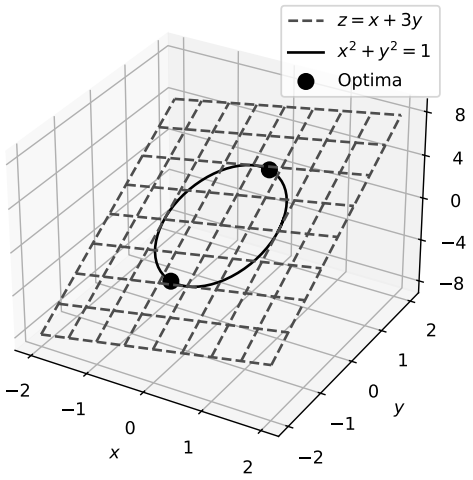


Figure B.3: *Illustration of the constrained optimization problem using Lagrange's method of undetermined multipliers. The objective function f is depicted by the dashed surface and the projected constraint function g is depicted by the black curve.*

B.6 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

$$\mathcal{L}(x_1, x_2, \cdots, x_i, \lambda_1, \lambda_2, \cdots, \lambda_i) = f(x_1, x_2, \cdots, x_i) - \sum_i \lambda_i \cdot g_i(x_1, x_2, \cdots, x_i), \quad \text{(B.39)}$$

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

$$\nabla \mathcal{L}(x_1, x_2, \cdots, x_i, \lambda_1, \lambda_2, \cdots, \lambda_i) = 0. \quad \text{(B.40)}$$

Let us illustrate the above procedure with an example as shown in Figure B.3. Suppose we wish to maximize

$$f(x, y) = x + 3y \quad \text{(B.41)}$$

subject to the constraint

$$x^2 + y^2 = 1. \quad \text{(B.42)}$$

The Lagrangian for this problem is

$$\mathcal{L}(x, y, \lambda) = x + 3y - \lambda \left(x^2 + y^2 - 1 \right). \quad \text{(B.43)}$$

This leads to

$$\nabla \mathcal{L}(x, y, \lambda) = \begin{pmatrix} \frac{\partial \mathcal{L}}{\partial x} \\ \frac{\partial \mathcal{L}}{\partial y} \\ \frac{\partial \mathcal{L}}{\partial \lambda} \end{pmatrix} = \begin{pmatrix} 1 - 2\lambda x \\ 3 - 2\lambda y \\ x^2 + y^2 - 1 \end{pmatrix} = 0. \tag{B.44}$$

This set of equations has two solutions as given by

$$x = \frac{1}{2\lambda}, \quad y = \frac{3}{2\lambda}, \tag{B.45}$$

which, substituted into the constraint $x^2 + y^2 = 1$, yields

$$\lambda = \pm \frac{\sqrt{10}}{2}. \tag{B.46}$$

which implies that the stationary points are

$$(x, y, \lambda) = \left(\frac{1}{\sqrt{10}}, \frac{3}{\sqrt{10}}, \frac{\sqrt{10}}{2} \right) \quad \text{and} \quad \left(-\frac{1}{\sqrt{10}}, -\frac{3}{\sqrt{10}}, -\frac{\sqrt{10}}{2} \right). \tag{B.47}$$

Evaluating the objective function yields

$$f(x, y) = x + 3y = \pm\sqrt{10}, \tag{B.48}$$

where the positive solution corresponds to a maximum and the negative solution to a minimum.

B.7 l'Hôpital'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'Hôpital's Rule states that

$$\lim_{x \to a} \frac{f(x)}{g(x)} = \lim_{x \to a} \frac{f'(x)}{g'(x)}. \tag{B.49}$$

The differentiation of the numerator and denominator often simplifies the quotient or converts it to a limit that can be evaluated directly.

For example:

$$\lim_{x \to 0} \frac{\exp(x) - 1}{x^2 + x} = \lim_{x \to 0} \frac{\exp(x)}{2x + 1} \tag{B.50}$$

$$= \frac{1}{2 \cdot 0 + 1} \tag{B.51}$$

$$= 1 \tag{B.52}$$

B.8 Matrix diagonalization

A square matrix A can be diagonalized if there exists an invertible matrix P such that

$$\mathbf{D} = \mathbf{P}^{-1}\mathbf{A}\mathbf{P}, \tag{B.53}$$

where $\mathbf{D}$ 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 $\mathbf{P}$ equals its transpose $\mathbf{P}^{-1} = \mathbf{P}^{\mathsf{T}}$.

For example, consider the matrix

$$\mathbf{A} = \begin{pmatrix} -2 & -2 & 1 \\ -1 & 3 & -1 \\ 2 & -4 & 3 \end{pmatrix}. \tag{B.54}$$

This matrix can be diagonalized with a matrix

$$\mathbf{P} = \begin{pmatrix} 2 & -1 & 1 \\ 1 & 0 & -1 \\ 0 & 1 & 2 \end{pmatrix} \tag{B.55}$$

and a diagonal matrix

$$\mathbf{D} = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 6 \end{pmatrix}. \tag{B.56}$$

The eigenvalues are thus $\lambda_1 = 1$, $\lambda_2 = 1$ and $\lambda_3 = 6$ with corresponding eigenvectors as columns in matrix P.

B.9 Roots of quadratic and cubic equations

The roots of the quadratic equation

$$ax^2 + bx + c = 0 \tag{B.57}$$

are given by

$$x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a}. \tag{B.58}$$

The roots of the cubic equation

$$ax^3 + bx^2 + cx + d = 0 \tag{B.59}$$

are given by

$$x = \sqrt[3]{q + s} + \sqrt[3]{q - s} + p, \tag{B.60}$$

where

$$p = \frac{-b}{3a} \tag{B.61}$$

$$q = p^3 + \frac{bc - 3ad}{6a^2} \tag{B.62}$$

$$r = \frac{c}{3a} \tag{B.63}$$

$$s = \sqrt{q^2 + (r - p^2)^3} \tag{B.64}$$

B.10 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

$$r_{\text{overall}} = \sum_i n_i \left(k_i^+ \prod_j c_{ij} - k_i^- \prod_j c_{ij} \right) \tag{B.65}$$

$$= \sum_i n_i k_i \left(\prod_j c_{ij} - K_i^{-1} \prod_j c_{ij} \right), \tag{B.66}$$

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

$$\chi_i = \frac{\partial \ln r_{\text{overall}}}{\partial \ln k_i} \tag{B.67}$$

$$= \frac{\partial r_{\text{overall}}}{\partial k_i} \frac{k_i}{r_{\text{overall}}} \tag{B.68}$$

$$= \frac{\partial \sum_j n_j k_j \left(\prod_k c_{jk} - K_j^{-1} \prod_k c_{jk} \right)}{\partial k_i} \frac{k_i}{\sum_j n_j k_j \left(\prod_k c_{jk} - K_j^{-1} \prod_k c_{jk} \right)} \tag{B.69}$$

$$= \frac{n_i k_i \left(\prod_j c_{ij} - K_i^{-1} \prod_j c_{ij} \right)}{\sum_j n_j k_j \left(\prod_k c_{jk} - K_j^{-1} \prod_k c_{jk} \right)}. \tag{B.70}$$

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

$$\sum_i \chi_i = \frac{\sum_i n_i k_i \left(\prod_j c_{ij} - K_i^{-1} \prod_j c_{ij} \right)}{\sum_j n_j k_j \left(\prod_k c_{jk} - K_j^{-1} \prod_k c_{jk} \right)} \tag{B.71}$$

$$= 1 \tag{B.72}$$

APPENDIX C

EXAM PRACTICE EXERCISES

C.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 gears, where three gears (⚙⚙⚙) is considered average and five gears (⚙⚙⚙⚙⚙) is the highest difficulty level. Solutions to these questions are provided in the next chapter on page 309.

C.2 Kinetics

EXAM PRACTICE QUESTION Kinetics 1 ⚙⚙⚙

CO oxidation proceeds by molecular adsorption of CO and dissociative adsorption of O_2, followed by recombination of CO and O on the catalytic surface, and finally by desorbing CO_2 from the catalyst. Recombination of CO and O on the surface is considered to be the rate-determining step. You are not allowed to use the zero-conversion approximation in this exercise.

a) Show the four elementary reaction steps that represent this process.

b) Derive the Langmuir adsorption isotherms of CO and O. Which assumption are you required to employ?

c) Derive the expression for the rate of formation of CO_2 as a function of the gas phase pressures of the relevant compounds. Assume that the rate-determining step is irreversible.

Assume for the remainder of this question that CO adsorbs much stronger than any of the other compounds.

d) What approximation are we allowed to use given the above assumption?

e) Derive the reaction order in CO. What are the limits of the reaction order in CO?

f) Derive the apparent activation energy for CO_2 formation.

g) Why is the apparent activation energy negative at very high temperature?

EXAM PRACTICE QUESTION Kinetics 2 ✿✿✿

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.

$$SO_3* \leftrightarrows SO_2 + O* \tag{C.1}$$

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 and furthermore assumed to be irreversible. 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 Kinetics 3 ✿✿✿

Ethylene (C_2H_4) can be oxidized to epoxide (C_2H_4O) 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

$$N_2O + * \leftrightarrows N_2 + O* \tag{C.2}$$

Two elementary reaction steps occur on the catalytic surface, which is the selective oxidation of ethylene towards epoxide

$$C_2H_4 * + O* \rightarrow C_2H_4O * + * \tag{C.3}$$

and the recombination of two surface oxygen atoms to molecular oxygen in the gas phase

$$2O* \rightarrow O_2 + 2* \tag{C.4}$$

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 C.3 and C.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 weakly 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.

EXAM PRACTICE QUESTION Kinetics 4 ✿✿✿✿✿

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.

EXAM PRACTICE QUESTION Kinetics 5

Ethylene oxide is an important chemical feedstock for the synthesis of ethylene glycol, glycol ethers, ethanolamines, ethoxylates and acrylonitrile. Ethylene oxide is industrially produced by oxidation of ethylene in the presence of a silver catalyst.

The catalytic mechanism is envisioned to proceed by the molecular adsorption of ethylene as well as the dissociative adsorption of oxygen, followed by recombination of adsorbed ethylene and an adsorbed oxygen atom to form adsorbed ethylene epoxide and finally desorption of the epoxide.

Unless stated otherwise, assume in the following questions that:

- The surface recombination of adsorbed ethylene and the oxygen atom is the rate-determining step.
- The rate-determining step is irreversible.
- The reaction is operating at a finite conversion. This means that you are not allowed to assume a zero-conversion approximation.

a) Construct the set of four elementary reaction steps that describe the catalytic oxidation of ethylene to form ethylene epoxide. Clearly indicate which step is the rate-determining step.

b) Derive an expression for the rate of formation of ethylene epoxide.

c) How does the rate expression derived in the previous question change when you can apply a zero-conversion approximation?

d) In addition to the zero-conversion approximation, also assume that C_2H_4 adsorbs much stronger than all other surface intermediates. Which component is the MARI under these conditions? Simplify the rate expression even further using these assumptions.

e) Derive the reaction orders in C_2H_4, O_2 and C_2H_4O as function of the relevant surface coverages under these conditions. What are the minimum and maximum reaction orders for C_2H_4, O_2 and C_2H_4O?

f) Derive an expression for the apparent activation energy as function of the relevant surface coverages.

g) Why is the apparent activation energy negative at very high temperature?

h) Detailed experiments have revealed that the reaction rate turns out to be

$$r = \frac{k_3 K_1 p_{C_2H_4} \sqrt{K_2 p_{O_2}}}{(1 + K_1 p_{C_2H_4})(1 + \sqrt{K_2 p O_2})} \tag{C.5}$$

Provide an explanation in terms of the underlying catalytic mechanism why the above rate expression is observed.

EXAM PRACTICE QUESTION Kinetics 6

Consider a catalytic termolecular reaction as given by

$$A + B + C \rightarrow D \tag{C.6}$$

where A,B and C all occupy different catalytic sites θ, τ and σ, respectively. Assume that adsorption/desorption steps are **not** rate-limiting and that the recombinatory trimolecular elementary reaction step over the catalytic surface is irreversible. Finally, assume that D only adsorbs on θ and that the reaction is operated at finite conversion.

a) Construct the minimum set of elementary reaction steps that describes the above overall reaction.

b) Derive an expression for the rate of formation of D.

c) Calculate the reaction orders in A, B, C, and D as function of the relevant surface coverages. What are the minimum and maximum reaction orders in A, B, C, and D?

d) Derive an expression for the apparent activation energy as function of the relevant surface coverages.

EXAM PRACTICE QUESTION Kinetics 7

Consider the oxidation of CO on a Pt surface. CO adsorbs molecularly and its adsorbed form is in equilibrium with gas-phase CO. O_2 adsorbs dissociatively. The oxygen atom reacts with adsorbed CO to form CO_2 that immediately desorbs from the catalytic surface. Assume that the rate of dissociative adsorption is equal to the rate of the surface reaction.

a) Rationalize why it is likely (or realistic) that CO_2 immediately desorbs from the catalytic surface after its formation.

b) Show by means of a mathematical proof that, under the conditions as described above, the reaction order in CO can be -2.

EXAM PRACTICE QUESTION Kinetics 8 ✿✿✿

CO oxidation can proceed over a Rh catalyst to produce CO_2. This reaction proceeds according to a Langmuir-Hinshelwood mechanism wherein O_2 adsorbs in a molecular fashion.

a) Construct the set of 5 elementary reaction steps that describe this chemo-kinetic network.

b) Assume that CO oxidation is the rate-determining step. Construct a rate expression for the rate of formation of CO_2 at arbitrary non-zero conversion. Clearly show which assumptions are used and to which steps in your derivation these pertain.

c) Show, on the basis of your rate expression in the previous subquestion, that the reaction rate is equal to zero at equilibrium.

d) Derive an expression for the reaction order in CO as function of the partial pressures of the reactants and/or products.

e) Derive an expression for the reaction order in O_2 as function of the partial pressures of the reactants and/or products. You are not expected to repeat parts of the derivation that are analogous with the previous subquestion as long as you properly refer to these steps.

f) Derive an expression for the apparent activation energy.

g) Motivate why the apparent activation energy is typically observed to be negative at very high temperature.

EXAM PRACTICE QUESTION Kinetics 9 ✿✿✿✿

Consider the reaction between hydrogen and chlorine gas that proceeds according to the following elementary reaction steps.[1]

1. $Cl_2 \rightarrow 2Cl\cdot$ (C.7)
2. $Cl\cdot + H_2 \rightarrow HCl + H\cdot$ (C.8)
3. $H\cdot + Cl_2 \rightarrow HCl + Cl\cdot$ (C.9)
4. $2Cl\cdot \rightarrow Cl_2$ (C.10)
5. $H\cdot + HCl \rightarrow H_2 + Cl\cdot$ (C.11)

(C.12)

a) Derive an expression for the rate of formation of HCl as function of the **partial pressures** of H_2 and Cl_2.

b) How does the rate expression as found in (a) change when an additional elementary reaction step (6) corresponding to a **parallel and identical pathway** of the elementary reaction step (5) is added to the chemokinetic network?

c) Derive the reaction orders in H_2 and Cl_2 for this chemokinetic network, including the additional elementary reaction step (6).

If you were not able to construct an answer in (b), try to answer this question without the additional elementary reaction step (6).

[1] Recall that in the notation X · the radical of X is meant.

d) Derive an expression for the apparent activation energy for this reaction, including the additional **elementary reaction step (6)**.

If you were not able to construct an answer in (b), try to answer this question without the additional elementary reaction step (6).

e) What is the effect on the apparent activation energy by inclusion of the additional elementary reaction step (6)? Provide a rationalization for your findings.

C.3 Statistical thermodynamics

EXAM PRACTICE QUESTION Statistical Thermodynamics 1 ✿✿✿

Consider the following reaction which is at equilibrium:

$$\mathrm{A} + \mathrm{B} \leftrightharpoons \mathrm{C} + \mathrm{D} \tag{C.13}$$

- Molecule A has three energetic states. The ground state of A lies ΔE higher than the ground state of molecule 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 molecule A.
- Finally, molecule D has three energetic states. Its ground state equals that of the ground state of molecule 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 $T \to 0$ and $T \to \infty$. Provide a physical interpretation of your results (i.e. rationalize the obtained values).

EXAM PRACTICE QUESTION Statistical Thermodynamics 2 ✿✿✿✿

Consider the following reaction which is at equilibrium:

$$\mathrm{A} + \mathrm{B} \leftrightharpoons \mathrm{C} + \mathrm{D} \tag{C.14}$$

- 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 B 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).

EXAM PRACTICE QUESTION Statistical Thermodynamics 3 ✪✪✪✪

Consider the hypothetical reaction:

$$\mathrm{A} + \mathrm{B} \to \mathrm{C} \tag{C.15}$$

- A and B both have a double-degenerate ground state which are all equal in energy with respect to each other.
- A has a single excited state at ΔE above the ground state of A.
- B has two excited states at $2\Delta E$ and $3\Delta E$ with respect to the ground state of B. Finally, C has a triple degenerate ground state and no excited states. The reaction is exothermic by ΔE.

a) Provide a schematic drawing of the energy levels of the system.

b) Construct the partition functions for A, B and C.

c) Calculate the average energy of A, B and C with respect to the lowest energetic quantum state available.

d) Calculate the molar reaction entropy $\Delta S_{R,m}$ in the limit that T$\to \infty$.

e) Provide a rationalization or interpretation for the sign (i.e. positive or negative) for the answer you have obtained for $\Delta S_{R,m}$.

EXAM PRACTICE QUESTION Statistical Thermodynamics 4

Consider the equilibrium:

$$A + B \leftrightharpoons C + D \tag{C.16}$$

- Molecule A has three energy levels separated by $\Delta E = \epsilon$
- Molecule B has two energy levels, separated by $\Delta E = \epsilon$ and the ground state at the same level as the ground state of molecule A.
- Molecules C and D both have a double-degenerate ground state located $\Delta E = 2\epsilon$ above the ground state of molecule A and no excited states.

a) Draw a schematic representation of the energy levels of all the molecules.

b) Derive the partition function for each of the molecules.

c) Derive the equilibrium constant for this system.

d) What is the value for the equilibrium constant at very low and very high temperature? Provide a chemical interpretation for your findings.

EXAM PRACTICE QUESTION Statistical Thermodynamics 5

Steam reforming is an industrially used process for the production of synthesis gas. In this process, water and methane is converted to carbon monoxide and hydrogen gas.

Consider the equilibrium:

$$CH_4 + H_2O \leftrightarrow CO + 3H_2 \tag{C.17}$$

Assume that:

- CH_4 has three energy levels, separated by Δ E = ϵ.
- H_2O has two energy levels, separated by Δ E = ϵ and the ground state at the same level as the ground state of CH_4.
- CO and H_2 both have only a double-degenerate ground state located at Δ E = 2ϵ above the ground state of CH_4.

a) Draw a schematic representation of the energy levels of the molecules.

b) Derive the partition function for each of the molecules.

c) Derive an expression for the equilibrium constant of the system.

d) What is the value of the equilibrium constant at very low and at very high temperature? Provide a clear interpretation of your findings in terms of the occupation of the energy levels.

EXAM PRACTICE QUESTION Statistical Thermodynamics 6 ✪✪✪✪

A metallic nanoparticle exhibits two types of surfaces, each with a unique topology, on which CO can adsorb. In this exercise, we will refer to these surfaces as surface A and surface B. From single crystal temperature programmed desorption experiments, it has been determined that CO adsorbs 40 kJ/mol stronger on surface A as compared to surface B. The number of active sites on both surfaces was determined using a titration experiment to be the same. The surface coverage of surface A is represented by the variable θ_A and the surface coverage of surface B is represented by θ_B.

a) Draw a schematic depiction of the situation described above.

b) Construct the partition function for both surfaces from the following fundamental expression

$$Q = W \cdot q^S \tag{C.18}$$

wherein S represent the number of occupied active sites and W a binomial weight factor representing the total number of possible configurations. This weight factor is given by

$$W = \frac{N!}{(N-S)!S!} \tag{C.19}$$

wherein N represents the total number of available sites. You are not expected in this exercise to derive the weight factor. Clearly distinguish between the different surfaces when using the above variables. For example, use subscripts to refer to surface A or B.

c) Construct an expression for the ratio between θ_A and θ_B. (hint: assume that the chemical potential of both surfaces is equal and solve for the ratio)

d) Calculate the ratio between θ_A and θ_B in the limit of very low and very high temperature.

EXAM PRACTICE QUESTION Statistical Thermodynamics 7 ✪✪✪✪

Consider a model system of a catalytic surface consisting of 2 x 2 active sites as depicted in Figure C.1a. In this model, we differentiate between two types of active sites, schematically depicted as *light* and *dark* tiles. In a similar fashion, adsorbates are represented as *black* and *white* pieces. A *black* piece on a *dark* tile or a *white* piece on a *light* tile has an energy of $E = -\epsilon$. In contrast, a *black* piece on a *light* tile or *vice versa* corresponds to an energy $E = 0$.

a) Show that there are six different configurations to place 2 black and 2 white tiles on the model catalytic surface. Confirm that the most stable configuration has an energy $E = -4\epsilon$ and the least stable configuration has an energy $E = 0$.

b) Categorize the six microstates you have found into three macrostates and construct the partition function for this system.

c) Derive the expression for the average energy $\langle E \rangle$ for this system. Determine the limits at $T \to 0$ and $T \to \infty$. Rationalize the values you have found for these expressions.

(a) *Empty surface.* **(b)** *Most stable configuration.*

Figure C.1: *Schematic depiction of the model catalytic surface. The surface consists of two dark and two light tiles in a checkerboard fashion.*

d) We introduce an occupancy factor η, which is the fraction of pieces on the most stable tiles. For example, $\eta = 1$ for the most stable configuration and $\eta = 0$ for the most unstable configuration. Derive an expression for the **expected** or **average** value for η as a function of temperature using the partition function. What are the limiting values for η at $T \to 0$ and $T \to \infty$? Rationalize the values you found at these limits.

e) Identify the correlation between $\langle \eta \rangle$ and $\langle E \rangle$ and rationalize this correlation.

EXAM PRACTICE QUESTION Statistical Thermodynamics 8

Consider the isomerization reaction

$$\mathrm{A} \leftrightarrows \mathrm{B} \tag{C.20}$$

- A has infinitely many quantum states separated by an energy ΔE.
- B also has infinitely many quantum states, but separated by an energy 2ΔE.
- The isomerization reaction is exothermic by 3ΔE.

a) Construct a closed-form expression for the partition functions for A and B.

Hint: The series solution corresponding to the infinitely many quantum states converges by which a closed-form expression is possible.

b) Calculate the average reaction energy for the isomerization reaction as function of the temperature T.

c) Determine the reaction energy in the limits $T \to 0$ and $T \to \infty$. Provide a rationalization of your findings.

d) Calculate the molar entropy of the reaction as function of the temperature T.

e) Construct an expression for the equilibrium constant K for this reaction and show that under a first-order approximation of the exponent (hint: perform a Taylor expansion and cut this off after the first term) that the temperature at which the concentrations of A and B are equal (i.e. when K = 1) is given by

$$T = \frac{6}{k_\mathrm{B} \Delta E} \tag{C.21}$$

EXAM PRACTICE QUESTION Statistical Thermodynamics 9 ✿✿✿✿

Consider a ensemble of **5 particles** among which you can distribute **6 units of energy**. There are a number of ways in which 6 units of energy can be distributed over these 5 particles. One way to distribute 6 units of energy among 5 particles is by placing all 6 units of energy 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.

In this procedure, we 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. This procedure is schematically shown in Figure C.2. Herein, three macrostates and their corresponding number of microstates are given.

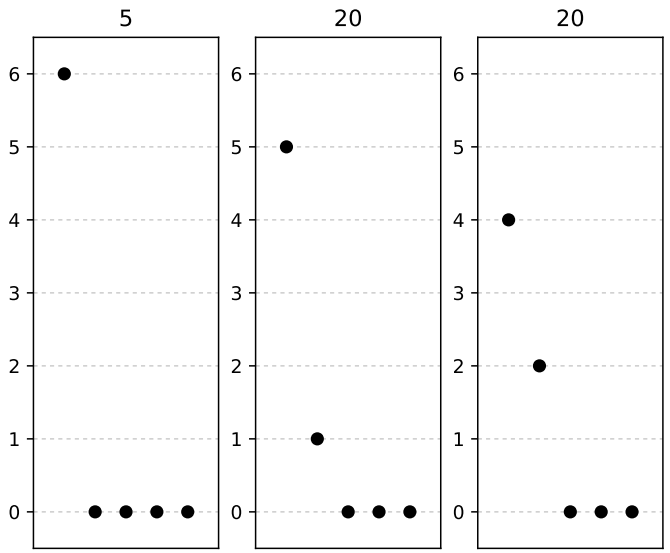


Figure C.2: *Schematic depiction of the first three macrostates for distributing 6 units of energy over 5 particles. Above each subfigure, the total number of microstates for that particular macrostate is given.*

Within a Maxwell-Boltzmann distribution, all particles are distinguishable from each other. Hence, for the first macrostate as shown in Figure C.2, 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

$$\Omega_i = \frac{N!}{\prod_i n_i!}, \tag{C.22}$$

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.

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 C.2, 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 always equals 6 (corresponding to the units of energy) and you can only use in total 5 digits (the number of particles). To exemplify this, the macrostates as shown in Figure C.2 correspond to 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

$$\Omega(N, q) = \binom{q + N - 1}{q} = \frac{(q + N - 1)!}{q!\,(N - 1)!}. \tag{C.23}$$

Again, you only have to show that equation C.23 is valid for this example.

d) Calculate the average number of particles in each energy level using the following formula

$$n_j = \sum_i \frac{\Omega_i}{\Omega} n_{i,j}, \tag{C.24}$$

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. Draw a graph wherein you show the average number of particles in each energy level as a function of the energy level i.

e) Show that the distribution complies with a Boltzmann-distribution as given by

$$n_i = A \exp\left(-\frac{i \cdot \Delta E}{RT}\right), \tag{C.25}$$

where A is a normalization constant and i corresponds to the energy level. What is the value for A?

f) Linearize the above Maxwell-Boltzmann equation and that it equals

$$y = a \cdot x + b \tag{C.26}$$

What are the values of a, b, x, and y? Match the following four terms with these variables:

(a) $\ln A$

(b) $\ln n_i$

(c) $i\Delta E$

(d) $\frac{1}{RT}$

g) Estimate the temperature T of the ensemble using the linearization. Use a value of 10 kJ/mol for ΔE.

⚠ Note: *I do not expect you to perform a linear regression. Simply using the first and last data point in the series and assuming that all other points lie on a straight line between these points suffices. This is not a very accurate method, but suffices here. If you seek a challenge, put the numbers in Excel and perform a true fit.*

C.4 Transition state theory

EXAM PRACTICE QUESTION 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 **in one dimension**. Because this rotation is unhindered, you are allowed to **approximate it using a one-dimensional translational partition function**. 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 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? Use these assumptions to construct the following equation:

$$k = \kappa K, \tag{C.27}$$

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:

$$k = \kappa \frac{1}{1 - \exp\left(\frac{-h\nu}{k_B T}\right)} \frac{Q^{\dagger}_{TS}}{Q_{IS}} \exp\left(\frac{-\Delta E_{act}}{k_B T}\right), \tag{C.28}$$

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 $Q^{\dagger}_{TS}$!**

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:

$$\exp x = 1 + x + \frac{x^2}{2!} + \frac{x^3}{3!} + \frac{x^4}{4!} \cdots \tag{C.29}$$

to show that the vibrational partition function can be simplified to

$$q_v = \frac{k_B T}{h\nu}, \tag{C.30}$$

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

$$k = \frac{k_B T}{h} \frac{Q^{\dagger}_{TS}}{Q_{IS}} \exp\left(\frac{-\Delta E_{act}}{k_B T}\right). \tag{C.31}$$

EXAM PRACTICE QUESTION Transition State Theory 3 ✪✪✪✪

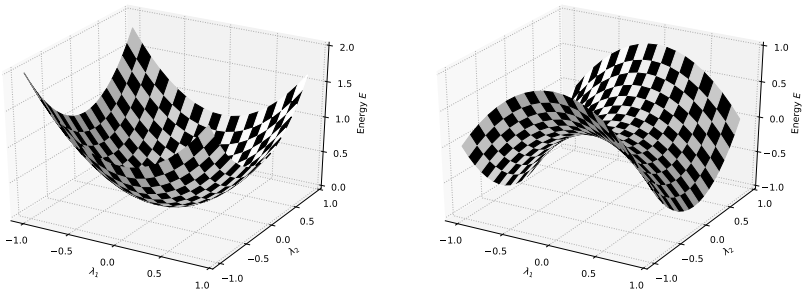
CO dissociation can proceed over a Co(111) surface, which is a hexagonal arrangement of Co atoms on a two-dimensional plane.[2] If we assume that the catalytic surface, i.e. the Co(111) surface, is completely static, then the potential energy E can be expressed as a six-dimensional function as given by

$$E = f\left(\vec{r_C}, \vec{r_O}\right), \tag{C.32}$$

where $\vec{r_C}$ and $\vec{r_O}$ are the positions of C and O, respectively. Note that

$$\vec{r} = \begin{pmatrix} x \\ y \\ z \end{pmatrix}. \tag{C.33}$$

Plotting a six-dimensional potential energy surface requires some kind of dimensionality reduction, hence we resort to providing a two-dimensional projection of E as shown in Figure C.3. In this Figure, the potential energy surface in the vicinity of the initial and transition state are given.



(a) *Initial state* **(b)** *Transition state*

Figure C.3: *Two-dimensional projection of the six-dimensional potential energy surface representing CO dissociation over a catalytic surface. λ_1 and λ_2 correspond to parameterized (orthonormal) directions. At $\lambda_1 = \lambda_2 = 0$, the initial state (left image) and the transition state (right image) are situated.*

[2] The exact topology of this surface is not relevant for answering this question.

a) Explain why the dimensionality of the potential energy surface for CO dissociation is six. Use the concept of degrees of freedom in your answering.

b) The two potential energy surfaces in Figure C.3 can each be further deconvoluted into two one-dimensional potential energy **curves**. These curves are parabola of E versus either λ_1 or λ_2. Draw these four one-dimensional potential energy curves (two for the initial state and two for the transition state). Copy the labels from the two-dimensional surfaces and indicate for each of the curves the nature of the parabola (i.e. mountain- or valley-type parabola).[3]

c) To which motion on the potential energy surface does the parameterized coordinate λ_1 correspond? What is the sign of the force constant k (i.e. the 2$^{\text{nd}}$ derivative) of this parabola? Provide a chemical interpretation of this result.

d) Detailed quantum chemical calculations were conducted for the initial and transition state of CO dissociation over Co(111). These calculations revealed that the wavenumbers $\overline{\nu_1}$ and $\overline{\nu_2}$ corresponding to a vibration in the direction of λ_1 and λ_2 were found to be

$$\overline{\nu_1} = 1200i \text{ cm}^{-1} \tag{C.34}$$

$$\overline{\nu_2} = 600 \text{ cm}^{-1}. \tag{C.35}$$

Why is the wavenumber $\overline{\nu_1}$ complex?

e) Calculate the average number of occupied vibrational states for the vibration in the direction corresponding to λ_2. Note that $\nu = 600 \text{ cm}^{-1}$ corresponds to $\omega = 18.0$ THz, where ω is the frequency.

f) Provide an expression for the reaction rate constant k at $T = 500$ K for CO dissociation over Co(111) using transition state theory. You may assume that $\overline{\nu_i} > 1500 \text{ cm}^{-1}$ for all vibrations, unless stated otherwise in this question. Explicitly calculate the numeric values for the pre-exponential factor as well as for the quotient of the total partition function corresponding to **motional** non-imaginary degrees of freedom of the transition state and the initial state as given by

$$K^\dagger = \frac{\prod_i q_i^{\text{TS}}}{\prod_j q_j^{\text{IS}}}. \tag{C.36}$$

g) Recast the expression of the reaction rate constant of the previous subquestion into Arrhenius form by calculating the activation energy and the pre-exponential factor.

[3] These types correspond to the shape of the parabola. In mathematical terms, a mountain parabola has a maximum, whereas a valley parabola has a minimum.

EXAM PRACTICE QUESTION Transition State Theory 4

In this question, we look into CO dissociation over a (flat) catalytic surface.

- In the initial state, CO has two translational degrees of freedom and otherwise only vibrational degrees of freedom.
- In the transition state, CO has only one translational degree of freedom and otherwise only vibrational degrees of freedom.
- In the final state, the separated C and O atoms have only vibrational degrees of freedom.

a) What is the total amount of degrees of freedom for CO in initial, transition and final state?

b) What is special about one of the vibrational degrees of freedom of CO in the transition state?

c) Construct the Eyring equation for the forward and backward reaction rate constant for CO dissociation. Explicitly show in your construction the nature and number of the partition functions in your expression.

For the remainder of this question, assume that all vibrational partition functions have a value of unity, as given by

$$q_{i,vib} = 1 \text{ for all } i. \tag{C.37}$$

d) What is the equilibrium constant for CO dissociation?

e) What is the activation energy and pre-exponential factor of the forward reaction rate constant in Arrhenius form?

EXAM PRACTICE QUESTION Transition State Theory 5

The Diels-Alder reaction between two cyclopentadiene (C_5H_6) molecules proceeds in the gas phase. In this question, you are tasked to obtain a reaction rate constant for this reaction.

a) How many translational, rotational and vibrational degrees of freedom does a **single** cyclopentadiene molecule have in the gas phase?

b) How many translational, rotational and vibrational degrees of freedom does this reaction have in the **initial state**? Note: the reaction proceeds between two cyclopentadiene molecules. Motivate your answer.

c) How many translational, rotational and vibrational degrees of freedom does this reaction have in the **transition state**? What is special about one of these vibrational degrees of freedom?

d) How many translational, rotational and vibrational degrees of freedom does this reaction have in the **final state**? Note that the final state corresponds to dicyclopentadiene, which is a single molecule.

e) Provide an expression for the reaction rate constant using transition state theory. Assume that all vibrational partition functions based on a frequency with a positive force constant are equal to unity for this subquestion and all following subquestions. Explicitly write out the partition functions in terms of their corresponding parameters (e.g. pressure, temperature, length, etc).

f) Compare your reaction rate constant to the one obtained using the Arrhenius equation. What is the (apparent) activation energy of the Arrhenius equation when describing the same reaction. What is the value of corresponding pre-exponential factor of the Arrhenius equation? Hint: remember that $k_{tst} = k_{arrhenius}$.

g) What is the fundamental difference between transition state theory and collision theory?

EXAM PRACTICE QUESTION Transition State Theory 6 ✿✿✿✿

Consider the the gas-phase Diels-Alder reaction of butadiene with ethylene to form cyclohexene. In this exercise, we aim to determine the entropy of activation of this reaction. We will guide you to the procedure in the form of the subquestions.

- The first three subquestions pertain to generating the mathematical expressions for the three types of configurational partition functions.
- Next, the Eyring equation for the reaction is constructed based on the given conditions.
- Finally, the entropy of activation, for this reaction, is derived.

a) Calculate the entropic contribution of a translational partition function.

b) Calculate the entropic contribution of a rotational partition function.

c) Calculate the entropic contribution of a vibrational partition function.

d) Construct the Eyring equation for the above reaction. Clearly indicate the nature and number of the partition functions in the initial and transition state. For the vibrational partition functions, construct the relevant product.

Hints:

- Recall that the initial state consists of two gas-phase molecules and the transition state of a single (weakly-bonded) complex.
- Ethylene is **not** a linear molecule!

e) The entropy of activation is defined as

$$\Delta S_{act} = S_{ts} - S_{is} \tag{C.38}$$

Determine the expression for the entropy of activation.

⚠ Note: If you were not able to construct the entropic contributions of the three types of partition functions or are in doubt whether you have the correct answer, please answer the following two questions instead:

(a) Why are we allowed to neglect the entropic contributions of the nuclear and electronic partition functions?

(b) Given the situation sketched, do you expect the entropy of activation to be positive or negative?

EXAM PRACTICE QUESTION Transition State Theory 7

Consider the following reaction

$$H_2 + Br_2 \rightarrow 2HBr \tag{C.39}$$

which occurs at $T = 450K$. Consider this reaction to be an elementary reaction step. The rate equation is hence given by

$$r = k_{\text{reaction}}[H_2][Br_2] \tag{C.40}$$

Collision theory can be utilized to calculate the collision frequency. The frequency is given by

$$k_{\text{collisions}} = \pi d^2 \left(\frac{8k_B T}{\pi \mu}\right)^{1/2} \tag{C.41}$$

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.

EXAM PRACTICE QUESTION Transition State Theory 8

Consider the dissociative adsorption of methane as given by

$$CH_4 + 2* \rightarrow CH_3 * + H* \tag{C.42}$$

Assume that in the transition state, all translational and rotational DOF are lost. Furthermore, assume that $q_{\text{vib}} \approx 1$. Use the variable $\Delta E_{\text{elec,act}}$ for the electronic activation energy and $\Delta E^{\dagger}_{\text{zpe}}$ for the difference in the zero-point energy between the transition and initial state.

a) Provide an expression for the reaction rate constant for dissociative adsorption of methane from transition state theory under the conditions as given above.

b) Provide an expression for the internal energy of activation. Use

$$\Delta U^{\dagger} = k_{\mathrm{B}} T^2 \frac{\partial \ln k}{\partial T} - k_{\mathrm{B}} T. \tag{C.43}$$

This expression is very similar to the Arrhenius activation energy, but by subtracting $k_{\mathrm{B}}T$, we exclude the frequency factor $\frac{k_{\mathrm{B}}T}{h}$.

c) Derive an expression for the entropy of activation using

$$\Delta S^{\dagger} = \frac{\partial}{\partial T}\left(k_{\mathrm{B}} T \left(\ln\left(k\right) - \ln\left(\frac{k_{\mathrm{B}}T}{h}\right)\right)\right). \tag{C.44}$$

Similar to the expression for the internal energy of activation, we exclude the frequency factor $\frac{k_{\mathrm{B}}T}{h}$ in the calculation of the entropy of activation.

d) Derive an expression for the Gibbs free energy of activation. Ignore the gas-expansion term by which

$$\Delta H^{\dagger} \approx \Delta U^{\dagger}, \tag{C.45}$$

and make use of

$$\Delta G^{\dagger} = \Delta H^{\dagger} - T\Delta S^{\dagger}. \tag{C.46}$$

e) Show that your expression for the Gibbs free energy of activation is consistent with

$$k = \frac{k_{\mathrm{B}}T}{h} \exp\left(-\frac{\Delta G^{\dagger}}{k_{\mathrm{B}}T}\right). \tag{C.47}$$

EXAM PRACTICE QUESTION Transition State Theory 9 ✪✪✪✪

Consider the hypothetical reaction between ethylene and hydrogen in the gas phase to produce ethane. It is assumed that this reaction can proceed in a single elementary reaction step.

a) Provide a listing of the number and nature of all motional partition functions of ethylene and hydrogen.

b) Provide a listing of the number of nature of all motional partition functions of the transition state complex of the reaction.

c) Construct a complete rate expression as function of the relevant partition functions for this reaction, based on transition state theory. Use a number-density based equilibrium constant in your derivation. Assume that the ideal gas law holds for all reactants and product.

You are **not** expected to provide a numerical value, but you are expected to write explicit expressions for the individual partition functions. You do **not** have to simplify the numerical expression obtained.

Clearly indicate to which molecules each of the partition functions pertain. For example, you can use subscripts for that (e for ethylene, h for hydrogen and ts for the transition state complex).

Hint 1: To save on writing a lot of expressions, feel free to use the product operator ($\prod_{i=1}^{N}$) or sum operator ($\sum_{i=1}^{N}$) when looping over multiple similar partition functions.

Hint 2: Do not forget about the zero-point energy.

Hint 3: Since the reaction pertains to a bimolecular reaction using number densities, do not forget about the volume correction.

d) Often, the rate expression is simplified by assuming the condition as shown mathematically by the formula below. Under which conditions is the assumption as given below valid?

$$\frac{1}{1 - exp(-\frac{-h\nu}{k_B T})} \approx 1 \tag{C.48}$$

EXAM PRACTICE QUESTION Transition State Theory 10 ✪✪✪✪

Consider the Diels-Alder reaction between butadiene and ethylene to form cyclohexene which can proceed via a single elementary reaction step as given by

$$C_2H_4 + C_4H_6 \rightarrow C_6H_{10} \tag{C.49}$$

To analyze the elementary reaction step, a potential energy surface is constructed as function of the distances between carbon atoms (1 and 6) and (4 and 5). The labeling of the carbon atoms is shown in Figure C.4.

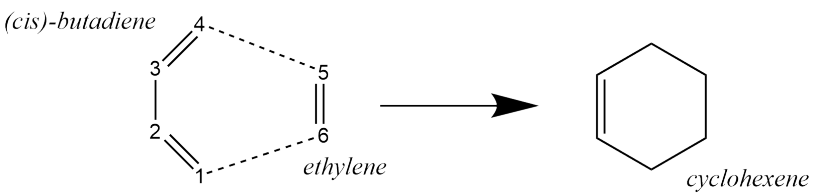


Figure C.4: *Figure showing labeling of the carbon atoms.*

The potential energy surface corresponding to this reaction is shown in the image below.

a) Provide a schematic drawing of the potential energy curve based on the heatmap. Clearly label the axes. Explain or draw how the potential energy curve can be extracted from the heatmap.

b) Identify the positions on the potential energy surface of the two stable states and the transition state using the energetic values as found from the heatmap. Provide the coordinates and a schematic drawing of the molecular complexes.

c) Determine the activation energy for the reaction in the forward and the backward direction.

d) Calculate the vibrational frequencies of the two vibrations in the parallel and perpendicular direction with respect to the reaction coordinate **at the stable state that is lowest in energy**. Clearly emphasize which assumptions you use in calculating these frequencies.

e) Calculate the vibrational frequency in the parallel and perpendicular direction with respect to the reaction coordinate **at the transition state**. What is the striking difference between the results found in this subquestion and the previous subquestion? Provide a rationalization of your findings.

APPENDIX D

EXAM EXERCISES SOLUTIONS

D.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.

D.2 Kinetics

EXAM SOLUTION Kinetics 1

a) The set of elementary reaction steps is given below. Herein, Equation D.3 is the rate-determining step.

$$1.\ CO + * \rightleftarrows CO* \tag{D.1}$$
$$2.\ O_2 + 2* \rightleftarrows 2O* \tag{D.2}$$
$$3.\ CO* + O* \rightarrow CO_2* + * \tag{D.3}$$
$$4.\ CO_2 + * \rightleftarrows CO_2* \tag{D.4}$$

Note: Microscopically speaking, equation D.3 is a reversible reaction but we consider it to be irreversible. A right arrow is used to describe the rate-determining step in order to emphasize this quasi-ideal assumption.

b) The required assumption to employ here is the quasi-equilibrium assumption. Based on this assumption, we need to find the Langmuir isotherms corresponding to all relevant coverages.

$$K_1 = \frac{\theta_{CO}}{p_{CO}\theta_*} \tag{D.5}$$

$$K_2 = \frac{\theta_O^2}{p_{O_2}\theta_*^2} \tag{D.6}$$

$$K_4 = \frac{\theta_{CO_2 *}}{\theta_* p_{CO_2}} \tag{D.7}$$

which leads to

$$\theta_{CO} = K_1 p_{CO}\theta_* \tag{D.8}$$

$$\theta_O = \sqrt{K_2 p_{O_2}}\theta_* \tag{D.9}$$

$$\theta_{CO_2} = K_4 p_{CO_2}\theta_* \tag{D.10}$$

The site balance for * is

$$\theta_* + \theta_{CO} + \theta_O + \theta_{CO_2} = 1 \tag{D.11}$$

leading to

$$\theta_{CO} = \frac{K_1 p_{CO}}{1 + K_1 p_{CO} + \sqrt{K_2 p_{O_2}} + K_4 p_{CO_2}} \tag{D.12}$$

$$\theta_O = \frac{\sqrt{K_2 p_{O_2}}}{1 + K_1 p_{CO} + \sqrt{K_2 p_{O_2}} + K_4 p_{CO_2}} \tag{D.13}$$

$$\theta_{CO_2} = \frac{K_4 p_{CO_2}}{1 + K_1 p_{CO} + \sqrt{K_2 p_{O_2}} + K_4 p_{CO_2}} \tag{D.14}$$

c) From the RDS (rate-determining step), the rate expression is as follows

$$r_{CO_2} = k_3 \theta_{CO}\theta_O \tag{D.15}$$

Combining all terms that have been derived in subquestion (a), we get

$$r_{CO_2} = \frac{k_3 K_1 \sqrt{K_2} p_{CO} \sqrt{p_{O_2}}}{(1 + K_1 p_{CO} + \sqrt{K_2 p_{O_2}} + K_4 p_{CO_2})^2} \tag{D.16}$$

d) The assumption that can be made is that CO is the Most Abundant Reaction Intermediate (MARI).

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 CO.

$$r_{CO_2} = \frac{k_3 K_1 \sqrt{K_2} p_{CO} \sqrt{p_{O_2}}}{(1 + K_1 p_{CO})^2} \tag{D.17}$$

$$\begin{aligned} n_{CO} &= p_{CO} \frac{\partial \ln r_{CO_2}}{\partial p_{CO}} && \text{(D.18)} \\ &= p_{CO} \left(\frac{\partial \ln p_{CO}}{\partial p_{CO}} - 2 \frac{\partial \ln (1 + K_1 p_{CO})}{\partial p_{CO}} \right) && \text{(D.19)} \\ &= 1 - 2 \frac{K_1 p_{CO}}{1 + K_1 p_{CO}} && \text{(D.20)} \\ &= 1 - 2\theta_{CO} && \text{(D.21)} \end{aligned}$$

The limits for the reaction order in CO are

$$n_{CO} \in [-1; 1] \tag{D.22}$$

f) The apparent activation energy is given by

$$\begin{aligned} \Delta E_{act}^{app} &= RT^2 \frac{\partial \ln r_{CO_2}}{\partial T} && \text{(D.23)} \\ &= RT^2 \left(\frac{\partial \ln k_3}{\partial T} + \frac{\partial \ln K_1}{\partial T} + \frac{\partial \ln \sqrt{K_2}}{\partial T} - 2 \frac{\partial \ln (1 + K_1 p_{CO})}{\partial T} \right) && \text{(D.24)} \\ &= RT^2 \left(\frac{\Delta E_{act}^{(3)}}{RT^2} + \frac{\Delta H_{ads}^{(1)}}{RT^2} + \frac{1}{2} \frac{\Delta H_{ads}^{(2)}}{RT^2} - 2 \frac{K_1 p_{CO}}{1 + K_1 p_{CO}} \frac{\Delta H_{ads}^{(1)}}{RT^2} \right) && \text{(D.25)} \\ &= \Delta E_{act}^{(3)} + (1 - 2\theta_{CO}) \Delta H_{ads}^{(1)} + \frac{1}{2} \Delta H_{ads}^{(2)} && \text{(D.26)} \end{aligned}$$

g) At very high temperature, the surface is nearly empty. Therefore, both CO and O_2 need to adsorb on the surface before reaction can take place. The adsorption enthalpy is always negative, which (in most of the cases) leads to a negative apparent activation energy at high temperatures.

EXAM SOLUTION Kinetics 2

a) The set of elementary reaction steps is given below. Herein, Equation D.30 is the rate-determining step.

1. $SO_3* \leftrightarrows SO_2 + O*$ (D.27)
2. $CH_4 + * \leftrightarrows CH_4*$ (D.28)
3. $SO_3 + * \leftrightarrows SO_3*$ (D.29)
4. $CH_4* + O* \rightarrow CH_3OH* + *$ (D.30)
5. $CH_3OH + * \leftrightarrows CH_3OH*$ (D.31)

Note: Microscopically speaking, equation D.30 is a reversible reaction but we consider it to be irreversible. A right arrow is used to describe the rate-determining step, emphasizing this quasi-ideal assumption.

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.

$$\theta_{CH_4} = \frac{K_2 p_{CH_4}}{1 + K_2 p_{CH_4} + K_3 p_{SO_3} + K_5 p_{CH_3OH} + \frac{K_1 K_3 p_{SO_3}}{p_{SO_2}}} \tag{D.32}$$

$$\theta_{SO_3} = \frac{K_3 p_{SO_3}}{1 + K_2 p_{CH_4} + K_3 p_{SO_3} + K_5 p_{CH_3OH} + \frac{K_1 K_3 p_{SO_3}}{p_{SO_2}}} \tag{D.33}$$

$$\theta_{CH_3OH} = \frac{K_5 p_{CH_3OH}}{1 + K_2 p_{CH_4} + K_3 p_{SO_3} + K_5 p_{CH_3OH} + \frac{K_1 K_3 p_{SO_3}}{p_{SO_2}}} \tag{D.34}$$

$$\theta_O = \frac{\frac{K_1 K_3 p_{SO_3}}{p_{SO_2}}}{1 + K_2 p_{CH_4} + K_3 p_{SO_3} + K_5 p_{CH_3OH} + \frac{K_1 K_3 p_{SO_3}}{p_{SO_2}}} \tag{D.35}$$

$$\tag{D.36}$$

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).

$$r_{CH_3OH} = k_4 \theta_{CH_4} \theta_O \tag{D.37}$$

$$= \frac{k_4 K_2 p_{CH_4} \frac{K_1 K_3 p_{SO_3}}{p_{SO_2}}}{\left(1 + K_2 p_{CH_4} + K_3 p_{SO_3} + K_5 p_{CH_3OH} + \frac{K_1 K_3 p_{SO_3}}{p_{SO_2}}\right)^2} \tag{D.38}$$

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.

$$r_{CH_3OH} = k_4 \theta_{CH_4} \theta_O = \frac{k_4 K_2 p_{CH_4} \frac{K_1 K_3 p_{SO_3}}{p_{SO_2}}}{\left(1 + K_5 p_{CH_3OH}\right)^2} \tag{D.39}$$

$$n_{CH_3OH} = p_{CH_3OH} \frac{\partial \ln r}{\partial p_{CH_3OH}} = -2\theta_{CH_3OH} \tag{D.40}$$

$$n_{CH_4} = p_{CH_4} \frac{\partial \ln r}{\partial p_{CH_4}} = 1 \tag{D.41}$$

f) The apparent activation energy is given by

$$\Delta E_{\text{act}}^{\text{app}} = RT^2 \frac{\partial \ln r}{\partial T} = \Delta E_{\text{act}}^{(4)} + \Delta H_1 + \Delta H_2 + \Delta H_3 - 2\theta_{\text{CH}_3\text{OH}} \Delta H_5 \tag{D.42}$$

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 Kinetics 3

a) The set of elementary reaction steps is given below. Herein, equations D.45 and D.46 are rate-determining for the formation of epoxide and oxygen, respectively.

$$1.\ \text{N}_2\text{O} + * \leftrightarrows \text{N}_2 + \text{O}* \tag{D.43}$$
$$2.\ \text{C}_2\text{H}_4 + * \leftrightarrows \text{C}_2\text{H}_4* \tag{D.44}$$
$$3.\ \text{C}_2\text{H}_4 * + \text{O}* \rightarrow \text{C}_2\text{H}_4\text{O} * + * \tag{D.45}$$
$$4.\ \text{O}_2 + 2* \rightarrow 2\text{O}* \tag{D.46}$$
$$5.\ \text{C}_2\text{H}_4\text{O} + * \leftrightarrows \text{C}_2\text{H}_4\text{O}* \tag{D.47}$$

Note: Microscopically speaking, equations D.45 and D.46 are reversible reactions but we consider them to be irreversible. A right arrow is used to describe the rate-determining steps, emphasizing this quasi-ideal assumption.

b) The the rate of formation of gas phase epoxide is:

$$r_{\text{C}_2\text{H}_4\text{O}} = k_3 \theta_{\text{C}_2\text{H}_4} \theta_{\text{O}} \tag{D.48}$$

The same procedure, as in exercise *Kinetics 1*, can be employed to derive the relevant Langmuir isotherms. Finally, one can plug in those to get the final expression for the rate of formation of the gas phase epoxide.

$$r_{\text{C}_2\text{H}_4\text{O}} = k_3 \frac{K_1 \frac{p_{\text{N}_2\text{O}}}{p_{\text{N}_2}} K_2 p_{\text{C}_2\text{H}_4}}{\left(1 + K_1 \frac{p_{\text{N}_2\text{O}}}{p_{\text{N}_2}} + K_2 p_{\text{C}_2\text{H}_4} + K_5 p_{\text{C}_2\text{H}_4\text{O}}\right)^2} \tag{D.49}$$

c) For deriving the rate of formation of molecular gas, one can repeat the same procedure as in the previous subquestion.

$$r_{O_2} = k_4 \theta_O^2 \tag{D.50}$$

$$= k_4 \frac{\left(K_1 \frac{p_{N_2O}}{p_{N_2}}\right)^2}{\left(1 + K_1 \frac{p_{N_2O}}{p_{N_2}} + K_2 p_{C_2H_4} + K_5 p_{C_2H_4O}\right)^2} \tag{D.51}$$

d) A table containing the upper and lower limit for the reaction orders in oxygen, nitrogen, nitrous oxide, ethylene and epoxide has been constructed for each one of the two rate expression.

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

(D.52)

e) Taking into consideration that ethylene and epoxide adsorb very weakly as compared to dissociative adsorption of nitrous oxide, the expressions for the rate formation of ethylene oxide and molecular oxygen simplify to:

$$r_{C_2H_4O} = k_3 \frac{K_1 \frac{p_{N_2O}}{p_{N_2}} K_2 p_{C_2H_4}}{\left(1 + K_1 \frac{p_{N_2O}}{p_{N_2}}\right)^2} \tag{D.53}$$

$$r_{O_2} = k_4 \frac{\left(K_1 \frac{p_{N_2O}}{p_{N_2}}\right)^2}{\left(1 + K_1 \frac{p_{N_2O}}{p_{N_2}}\right)^2}. \tag{D.54}$$

We obtain the the following reaction order for the epoxide

$$n_{O_2} = 0 \tag{D.55}$$

$$n_{N_2} = -1 + 2\theta_O \tag{D.56}$$

$$n_{N_2O} = 1 - 2\theta_O \tag{D.57}$$

$$n_{C_2H_4} = 1 \tag{D.58}$$

$$n_{C_2H_4O} = 0 \tag{D.59}$$

and for molecular oxygen

$$n_{O_2} = 0 \tag{D.60}$$

$$n_{N_2} = -2 + 2\theta_O \tag{D.61}$$

$$n_{N_2O} = 2 - 2\theta_O \tag{D.62}$$

$$n_{C_2H_4} = 0 \tag{D.63}$$

$$n_{C_2H_4O} = 0 \tag{D.64}$$

f) The apparent activation energy for epoxide formation is:

$$\Delta E_{\text{act}}^{\text{app}} = \Delta E_3 + \Delta H_1 \left(1 - 2\theta_{\text{O}}\right) + \Delta H_2, \tag{D.65}$$

and for the formation of molecular oxygen is:

$$\Delta E_{\text{act}}^{\text{app}} = \Delta E_4 + \Delta H_1 \left(2 - 2\theta_{\text{O}}\right). \tag{D.66}$$

EXAM SOLUTION Kinetics 4

a) The set of elementary reaction steps is given below. Herein, Equation D.71 is the irreversible rate-determining step.

$$1.\ \text{CO} + * \rightleftarrows \text{CO}* \tag{D.67}$$
$$2.\ \text{H}_2 + 2* \rightleftarrows 2\text{H}* \tag{D.68}$$
$$3.\ \text{H}_2 + 2\# \rightleftarrows 2\text{H}\# \tag{D.69}$$
$$4.\ \text{CO} * + \text{H}\# \rightleftarrows \text{CHO} * + \# \tag{D.70}$$
$$5.\ \text{CHO} * + \text{H}\# \rightarrow \text{CH}_2\text{O} * + \# \tag{D.71}$$
$$6.\ \text{CH}_2\text{O} * + \text{H}\# \rightleftarrows \text{CH}_3\text{O} * + \# \tag{D.72}$$
$$7.\ \text{CH}_3\text{O} * + \text{H}\# \rightleftarrows \text{CH}_3\text{OH} * + \# \tag{D.73}$$
$$8.\ \text{CH}_3\text{OH} + * \rightleftarrows \text{CH}_3\text{OH}* \tag{D.74}$$

Finally, note that H* does not directly react with any CH_xO* species, but it acts as an inhibiting term.

b) Equation D.69 represents the dissociative adsorption of hydrogen on the τ sites. From this, it follows that

$$K_3 = \frac{\tau_{\text{H}}^2}{p_{\text{H}_2} \tau_{\#}^2} \tag{D.75}$$
$$\tau_{\text{H}} = \tau_{\#} \sqrt{K_3 p_{\text{H}_2}} \tag{D.76}$$

The site-balance for site # is

$$\tau_{\#} + \tau_{\text{H}} = 1 \tag{D.77}$$

leading to

$$\tau_{\text{H}} = \frac{\sqrt{K_3 p_{\text{H}_2}}}{1 + \sqrt{K_3 p_{\text{H}_2}}} \tag{D.78}$$

c) From the RDS (rate-determining step), the rate expression is as follows

$$r = k_5 \theta_{\mathrm{CHO}} \tau_{\mathrm{H}}. \tag{D.79}$$

Next, we need to find the Langmuir isotherms corresponding to all relevant surface coverages. We start by assuming pseudo-equilibrium, which gives

$$K_1 = \frac{\theta_{\mathrm{CO}}}{p_{\mathrm{CO}} \theta_*} \tag{D.80}$$

$$K_2 = \frac{\theta_{\mathrm{H}}^2}{p_{\mathrm{H_2}} \theta_*^2} \tag{D.81}$$

$$K_4 = \frac{\theta_{\mathrm{CHO}} \tau_\#}{\theta_{\mathrm{CO}} \tau_{\mathrm{H}}} \tag{D.82}$$

which leads to

$$\theta_{\mathrm{CO}} = K_1 p_{\mathrm{CO}} \theta_* \tag{D.83}$$

$$\theta_{\mathrm{H}} = \sqrt{K_2 p_{\mathrm{H_2}}}\, \theta_* \tag{D.84}$$

$$\theta_{\mathrm{CHO}} = \frac{K_1 K_4 p_{\mathrm{CO}} \tau_{\mathrm{H}} \theta_*}{\tau_\#} = K_1 K_4 p_{\mathrm{CO}} \sqrt{K_3 p_{\mathrm{H_2}}}\, \theta_* \tag{D.85}$$

The site-balance for * is

$$\theta_{\mathrm{CO}} + \theta_{\mathrm{H}} + \theta_{\mathrm{CHO}} + \theta_* = 1 \tag{D.86}$$

leading to

$$\theta_{\mathrm{CO}} = \frac{K_1 p_{\mathrm{CO}}}{1 + K_1 p_{\mathrm{CO}} + \sqrt{K_2 p_{\mathrm{H_2}}} + K_1 K_4 p_{\mathrm{CO}} \sqrt{K_3 p_{\mathrm{H_2}}}} \tag{D.87}$$

$$\theta_{\mathrm{H}} = \frac{\sqrt{K_2 p_{\mathrm{H_2}}}}{1 + K_1 p_{\mathrm{CO}} + \sqrt{K_2 p_{\mathrm{H_2}}} + K_1 K_4 p_{\mathrm{CO}} \sqrt{K_3 p_{\mathrm{H_2}}}} \tag{D.88}$$

$$\theta_{\mathrm{CHO}} = \frac{K_1 K_4 p_{\mathrm{CO}} \sqrt{K_3 p_{\mathrm{H_2}}}}{1 + K_1 p_{\mathrm{CO}} + \sqrt{K_2 p_{\mathrm{H_2}}} + K_1 K_4 p_{\mathrm{CO}} \sqrt{K_3 p_{\mathrm{H_2}}}} \tag{D.89}$$

Finally, we can plug everything into our rate expression, by which we obtain

$$r = k_5 \frac{K_1 K_4 p_{\mathrm{CO}} K_3 p_{\mathrm{H_2}}}{\left(1 + K_1 p_{\mathrm{CO}} + \sqrt{K_2 p_{\mathrm{H_2}}} + K_1 K_4 p_{\mathrm{CO}} \sqrt{K_3 p_{\mathrm{H_2}}}\right)\left(1 + \sqrt{K_3 p_{\mathrm{H_2}}}\right)}. \tag{D.90}$$

⚠ Note: There are two different terms in the denominator corresponding to two different types of catalytic sites. Furthermore, the ($\sqrt{K_2 p_{\mathrm{H_2}}}$) term corresponds to H_2 coadsorption on the * sites which acts as an inhibiting term.

d) Determining the reaction order in H_2

$$n_{H_2} = p_{H_2} \frac{\partial \ln r}{\partial p_{H_2}} \tag{D.91}$$

$$= p_{H_2} \frac{\partial}{\partial p_{H_2}} (\ln p_{H_2} - \ln(1 + K_1 p_{CO} + \sqrt{K_2 p_{H_2}} \cdots$$

$$\cdots + K_1 K_4 p_{CO} \sqrt{K_3 p_{H_2}}) - \ln(1 + \sqrt{K_3 p_{H_2}})) \tag{D.92}$$

$$= 1 - \frac{1}{2} \frac{\sqrt{K_2 p_{H_2}}}{1 + K_1 p_{CO} + \sqrt{K_2 p_{H_2}} + K_1 K_4 p_{CO} \sqrt{K_3 p_{H_2}}} \cdots$$

$$\cdots - \frac{1}{2} \frac{K_1 K_4 p_{CO} \sqrt{K_3 p_{H_2}}}{1 + K_1 p_{CO} + \sqrt{K_2 p_{H_2}} + K_1 K_4 p_{CO} \sqrt{K_3 p_{H_2}}} \cdots$$

$$\cdots - \frac{1}{2} \frac{\sqrt{K_3 p_{H_2}}}{1 + \sqrt{K_3 p_{H_2}}} \tag{D.93}$$

$$= 1 - \frac{1}{2}\theta_H - \frac{1}{2}\theta_{CHO} - \frac{1}{2}\tau_H \tag{D.94}$$

⚠ Note: Because of the dual site mechanism, the reaction order in H_2 can never become negative.

Determining the reaction order in CO

$$n_{CO} = p_{CO} \frac{\partial \ln r}{\partial p_{CO}} \tag{D.95}$$

$$= p_{CO} \frac{\partial}{\partial p_{CO}} \left(\ln p_{CO} - \ln \left(1 + K_1 p_{CO} + \sqrt{K_2 p_{H_2}} + K_1 K_4 p_{CO} \sqrt{K_3 p_{H_2}} \right) \right) \tag{D.96}$$

$$= 1 - \frac{K_1 p_{CO}}{1 + K_1 p_{CO} + \sqrt{K_2 p_{H_2}} + K_1 K_4 p_{CO} \sqrt{K_3 p_{H_2}}} \cdots$$

$$\cdots - \frac{K_1 K_4 p_{CO} \sqrt{K_3 p_{H_2}}}{1 + K_1 p_{CO} + \sqrt{K_2 p_{H_2}} + K_1 K_4 p_{CO} \sqrt{K_3 p_{H_2}}} \tag{D.97}$$

$$= 1 - \theta_{CO} - \theta_{CHO} \tag{D.98}$$

e) Deriving the apparent activation energy

$$\Delta E_{\text{act}}^{\text{app}} = RT^2 \frac{\partial \ln r}{\partial T} \tag{D.99}$$

$$\begin{aligned} &= RT^2 \frac{\partial}{\partial T} \Bigg(\ln k_5 + \ln K_1 + \ln K_3 + \ln K_4 \cdots \\ &\cdots - \ln \left(1 + K_1 p_{\text{CO}} + \sqrt{K_2 p_{\text{H}_2}} + K_1 K_4 p_{\text{CO}} \sqrt{K_3 p_{\text{H}_2}} \right) \cdots \\ &\cdots - \ln \left(1 + \sqrt{K_3 p_{\text{H}_2}} \right) \Bigg) \end{aligned} \tag{D.100}$$

$$\begin{aligned} &= \Delta E_{\text{act}}^{(5)} + \Delta H_1 + \Delta H_3 + \Delta H_4 \cdots \\ &\cdots - \Delta H_1 \frac{K_1 p_{\text{CO}}}{1 + K_1 p_{\text{CO}} + \sqrt{K_2 p_{\text{H}_2}} + K_1 K_4 p_{\text{CO}} \sqrt{K_3 p_{\text{H}_2}}} \cdots \\ &\cdots - \frac{1}{2} \Delta H_2 \frac{\sqrt{K_2 p_{\text{H}_2}}}{1 + K_1 p_{\text{CO}} + \sqrt{K_2 p_{\text{H}_2}} + K_1 K_4 p_{\text{CO}} \sqrt{K_3 p_{\text{H}_2}}} \cdots \\ &\cdots - \left(\Delta H_1 + \Delta H_4 + \frac{1}{2} \Delta H_3 \right) \cdots \\ &\cdots \frac{K_1 K_4 p_{\text{CO}} \sqrt{K_3 p_{\text{H}_2}}}{1 + K_1 p_{\text{CO}} + \sqrt{K_2 p_{\text{H}_2}} + K_1 K_4 p_{\text{CO}} \sqrt{K_3 p_{\text{H}_2}}} \cdots \\ &\cdots - \frac{1}{2} \Delta H_3 \frac{\sqrt{K_3 p_{\text{H}_2}}}{1 + \sqrt{K_3 p_{\text{H}_2}}} \end{aligned} \tag{D.101}$$

$$\begin{aligned} &= \Delta E_{\text{act}}^{(5)} + \Delta H_1 \left(1 - \theta_{\text{CO}} - \theta_{\text{CHO}} \right) - \frac{1}{2} \Delta H_2 \theta_{\text{H}} \cdots \\ &\cdots + \Delta H_3 \left(1 - \frac{1}{2} \theta_{\text{CHO}} - \frac{1}{2} \tau_{\text{H}} \right) + \Delta H_4 \left(1 - \theta_{\text{CHO}} \right) \end{aligned} \tag{D.102}$$

EXAM SOLUTION Kinetics 5

a) The set of four elementary reaction steps that describe the catalytic oxidation of ethylene to ethylene epoxide is showed below.

$$1.\ \text{C}_2\text{H}_4 + * \rightleftarrows \text{C}_2\text{H}_4* \tag{D.103}$$

$$2.\ \text{O}_2 + 2* \rightleftarrows 2\text{O}* \tag{D.104}$$

$$3.\ \text{C}_2\text{H}_4 * + \text{O}* \rightarrow \text{C}_2\text{H}_4\text{O} * + * \tag{D.105}$$

$$4.\ \text{C}_2\text{H}_4\text{O} + * \rightleftarrows \text{C}_2\text{H}_4\text{O}* \tag{D.106}$$

Note: Microscopically speaking, equation D.105 is a reversible reaction but we consider it to be irreversible. A right arrow is used to describe the rate-determining step in order to emphasize this quasi-ideal assumption.

b) The expression describing the rate of formation of ethylene epoxide is

$$r = \frac{k_3^+ K_1 p_{C_2H_4} \sqrt{K_2 p_{O_2}}}{\left(1 + K_1 p_{C_2H_4} + \sqrt{K_2 p_{O_2}} + K_4 p_{C_2H_4O}\right)^2} \tag{D.107}$$

c) No products are formed, so the term corresponding to C_2H_4O will not be in the inhibiting term. The simplified version can be seen below.

$$r = \frac{k_3 K_1 p_{C_2H_4} \sqrt{K_2 p_{O_2}}}{\left(1 + K_1 p_{C_2H_4} + \sqrt{K_2 p_{O_2}}\right)^2} \tag{D.108}$$

d) C_2H_4 is the MARI. The corresponding final simplified version for the rate formation expression is

$$r = \frac{k_3 K_1 p_{C_2H_4} \sqrt{K_2 p_{O_2}}}{\left(1 + K_1 p_{C_2H_4}\right)^2} \tag{D.109}$$

e)

$$n_{C_2H_4} = 1 - 2\theta_{C_2H_4} \tag{D.110}$$

$$n_{O_2} = \frac{1}{2} \tag{D.111}$$

$$n_{C_2H_4O} = 0 \tag{D.112}$$

f)

$$\Delta E_{act} = \Delta E_{act,3} + \left(1 - 2\theta_{C_2H_4}\right) \Delta H_1 + \frac{1}{2} \Delta H_2 \tag{D.113}$$

g) At very high temperature, the surface is nearly empty. Therefore, both C_2H_4 and O_2 need to adsorb on the surface before reaction can take place. The adsorption enthalpy is always negative, which (in most of the cases) leads to a negative apparent activation energy at high temperatures.

h) From the two Langmuir-Hinshelwood isotherms it can be seen that this reaction takes place between two different types of active sites, each only adsorbing one of the reactants.

EXAM SOLUTION Kinetics 6

a) The set of five elementary reaction steps is given below.

1. $\mathrm{A} + * \rightleftarrows \mathrm{A}*$ (D.114)
2. $\mathrm{B} + \# \rightleftarrows \mathrm{B}\#$ (D.115)
3. $\mathrm{C} + s \rightleftarrows \mathrm{C}s$ (D.116)
4. $\mathrm{A} * + \mathrm{B}\# + \mathrm{C}s \rightarrow \mathrm{D} * + \# + s$ (D.117)
5. $\mathrm{D} + * \rightleftarrows \mathrm{D}*$ (D.118)

where * denotes a free sites of type θ, # denotes a free site of type τ and s denotes a free site of type σ.

b) Assume pseudo-equilibrium for all gas-solid reactions, we have the following equilibrium constants:

$$K_A = \frac{\theta_A}{p_A \theta_*} \tag{D.119}$$
$$K_B = \frac{\tau_B}{p_B \tau_\#} \tag{D.120}$$
$$K_C = \frac{\sigma_C}{p_C \sigma_s} \tag{D.121}$$
$$K_D = \frac{\theta_D}{p_D \theta_*} \tag{D.122}$$

There are 3 site-balances as given by

$$1 = \theta_* + \theta_A + \theta_D \tag{D.123}$$
$$1 = \tau_\# + \tau_B \tag{D.124}$$
$$1 = \sigma_s + \sigma_C \tag{D.125}$$

The general rate expression is given by

$$r = k_4 \theta_A \tau_B \sigma_C. \tag{D.126}$$

Combining the pseudo-equilibria with the site balances and plugging these into the fundamental rate expression gives

$$r = k_4 \frac{K_A p_A K_B p_B K_C p_C}{\left(1 + K_A p_A + K_D p_D\right)\left(1 + K_B p_B\right)\left(1 + K_C p_C\right)}. \tag{D.127}$$

c) The reaction order in A can be calculated as follows:

$$n_A = p_A \frac{\partial \ln r}{\partial p_A} \tag{D.128}$$
$$= p_A \frac{\partial}{\partial p_A} \ln \left(k_4 \frac{K_A p_A K_B p_B K_C p_C}{\left(1 + K_A p_A + K_D p_D\right)\left(1 + K_B p_B\right)\left(1 + K_C p_C\right)} \right) \tag{D.129}$$
$$= 1 - p_A \frac{\partial}{\partial p_A} \ln \left[\left(1 + K_A p_A + K_D p_D\right)\left(1 + K_B p_B\right)\left(1 + K_C p_C\right) \right] \tag{D.130}$$
$$= 1 - \theta_A \tag{D.131}$$

Using a similar strategy, the reaction orders in B, C and D are:

$$n_B = 1 - \tau_B \tag{D.132}$$

$$n_C = 1 - \sigma_C \tag{D.133}$$

$$n_D = -\theta_D \tag{D.134}$$

This gives the following limits on the orders:

$$n_A \in [0, 1] \tag{D.135}$$
$$n_B \in [0, 1] \tag{D.136}$$
$$n_C \in [0, 1] \tag{D.137}$$
$$n_D \in [-1, 0] \tag{D.138}$$

d) An expression for the apparent activation energy as function of the relevant surface coverages is given below.

$$\Delta E_{\text{act}}^{\text{app}} = RT^2 \frac{\partial \ln r}{\partial T} \tag{D.139}$$
$$= RT^2 \frac{\partial}{\partial T} k_4 \ln \left[\frac{K_A p_A K_B p_B K_C p_C}{\left(1 + K_A p_A + K_D p_D\right)\left(1 + K_B p_B\right)\left(1 + K_C p_C\right)} \right] \tag{D.140}$$
$$= E_{\text{act}}^{(4)} + \Delta H_A + \Delta H_B + \Delta H_C \cdots$$
$$\cdots - \frac{\partial}{\partial T} \ln \left[\left(1 + K_A p_A + K_D p_D\right)\left(1 + K_B p_B\right)\left(1 + K_C p_C\right) \right] \tag{D.141}$$
$$= E_{\text{act}}^{(4)} + \Delta H_A + \Delta H_B + \Delta H_C \cdots$$
$$\cdots - RT^2 \frac{\frac{\partial}{\partial T} K_A p_A + \frac{\partial}{\partial T} K_B p_B + \frac{\partial}{\partial T} K_C p_C + \frac{\partial}{\partial T} K_D p_D}{\left(1 + K_A p_A + K_D p_D\right)\left(1 + K_B p_B\right)\left(1 + K_C p_C\right)} \tag{D.142}$$
$$= E_{\text{act}}^{(4)} + \Delta H_A(1 - \theta_A) + \Delta H_B(1 - \tau_B) + \Delta H_C(1 - \sigma_C) - \Delta H_D \theta_D \tag{D.143}$$

EXAM SOLUTION Kinetics 7

a) CO_2 has a fulfilled octet configuration, hence it can be assumed to be coordinatively saturated. It can thus only weakly bond to the catalyst surface using a van der Waals interaction.

b) The set of elementary reaction steps is

$$\mathrm{CO} + * \rightleftarrows \mathrm{CO}* \tag{D.144}$$

$$\mathrm{O_2} + 2* \rightarrow 2\mathrm{O}* \tag{D.145}$$

$$\mathrm{CO}* + \mathrm{O}* \rightarrow \mathrm{CO_2} + 2* \tag{D.146}$$

Because the dissociative adsorption has the same rate as the CO recombination, we are not allowed to impose a rate-determining step approximation. Hence, we have to resort to employing a steady-state assumption. Because the question statement offers us the freedom to impose an irreversible-step approximation, we do this on the second and third elementary reaction step.

From this, we can obtain the following two expressions

$$\frac{d\theta_{\mathrm{O}}}{dt} = 2k_2^+ p_{\mathrm{O_2}} \theta_*^2 - k_3^+ \theta_{\mathrm{CO}} \theta_{\mathrm{O}} = 0 \tag{D.147}$$

$$\frac{d\left[\mathrm{CO_2}\right]}{dt} = \frac{N}{V} k_3^+ \theta_{\mathrm{CO}} \theta_{\mathrm{O}}, \tag{D.148}$$

where N is the total number of active sites on the catalyst surface in mol and V the volume wherein the catalyst resides.

By means of the steady-state approximation on the surface fraction of monoatomic oxygen, we get the following steady-state surface coverage

$$\theta_{\mathrm{O}} = \frac{2k_2^+ p_{\mathrm{O_2}} \theta_*^2}{k_3^+ \theta_{\mathrm{CO}}} \tag{D.149}$$

From the problem statement, we are allowed to use a quasi-equilibrium approximation for the surface coverage of CO, which yields

$$\theta_{CO} = K_1 p_{\mathrm{CO}} \theta_* \tag{D.150}$$

Insertion of equation D.150 into equation D.149 yields

$$\theta_{\mathrm{O}} = \frac{2k_2^+ p_{\mathrm{O_2}} \theta_*}{k_3^+ K_1 p_{\mathrm{CO}}} \tag{D.151}$$

By construction of a site balance, we can readily find the steady-state surface coverage for the free sites.

$$\theta_* = \frac{1}{1 + K_1 p_{\mathrm{CO}} + \frac{2k_2^+ p_{\mathrm{O_2}}}{k_3^+ K_1 p_{\mathrm{CO}}}} \tag{D.152}$$

Application of equation D.152 in conjunction with the other expressions for the surface expressions yields the following rate expression

$$r = \frac{N}{V} \frac{2k_2^+ p_{\mathrm{O_2}}}{\left(1 + K_1 p_{\mathrm{CO}} + \frac{2k_2^+ p_{\mathrm{O_2}}}{k_3^+ K_1 p_{\mathrm{CO}}}\right)^2} \tag{D.153}$$

To proof that the order in CO can be as low as -2, it makes sense to assume strongly poisoning conditions of CO. As such, we readily employ a MARI approximation on CO, by which the above rate expression can be simplified to

$$r = \frac{N}{V} \frac{2k_2^+ p_{O_2}}{(1 + K_1 p_{CO})^2}. \tag{D.154}$$

In a further straightforward manner, we can readily find an expression for the reaction order in CO as given by

$$n_{CO} = p_{CO} \frac{\partial \ln r^+}{\partial p_{CO}} = -2\theta_{CO} \tag{D.155}$$

In the situation wherein $\theta_{CO} = 1$, a reaction order of -2 is found. Q.E.D.

EXAM SOLUTION Kinetics 8

a) The set of elementary reaction steps is given below.

1. $CO + * \rightleftarrows CO*$ (D.156)
2. $O_2 + * \rightleftarrows O_2*$ (D.157)
3. $O_2 * + * \rightleftarrows 2O*$ (D.158)
4. $CO * + O* \rightleftarrows CO_2 * + *$ (D.159)
5. $CO_2 + * \rightleftarrows CO_2*$ (D.160)

b) Because we have non-zero conversion, the site-balance includes all surface intermediates

$$1 = \theta_* + \theta_{CO} + \theta_{CO_2} + \theta_O + \theta_{O_2} \tag{D.161}$$

We apply the quasi-equilibrium approximation to steps 1,2,3 and 5.

$$\theta_{CO} = K_1 P_{CO} \theta_* \tag{D.162}$$
$$\theta_{O_2} = K_2 P_{O_2} \theta_* \tag{D.163}$$
$$\theta_O^2 = K_3 \theta_{O_2} \theta_* \longrightarrow \theta_O = \sqrt{K_2 K_3 P_{O_2}} \theta_* \tag{D.164}$$
$$\theta_{CO_2} = K_5 P_{CO_2} \theta_* \tag{D.165}$$

The coverage of free sites can be obtained by substituting equation D.161

$$\theta_* = \frac{1}{1 + K_1 P_{CO} + K_2 P_{O_2} + \sqrt{K_2 K_3 P_{O_2}} + K_5 P_{CO_2}} \tag{D.166}$$

leading to

$$\theta_{CO} = \frac{K_1 P_{CO}}{1 + K_1 P_{CO} + K_2 P_{O_2} + \sqrt{K_2 K_3 P_{O_2}} + K_5 P_{CO_2}} \tag{D.167}$$

$$\theta_{O_2} = \frac{K_2 P_{O_2}}{1 + K_1 P_{CO} + K_2 P_{O_2} + \sqrt{K_2 K_3 P_{O_2}} + K_5 P_{CO_2}} \tag{D.168}$$

$$\theta_{O} = \frac{\sqrt{K_2 K_3 P_{O_2}}}{1 + K_1 P_{CO} + K_2 P_{O_2} + \sqrt{K_2 K_3 P_{O_2}} + K_5 P_{CO_2}} \tag{D.169}$$

$$\theta_{CO_2} = \frac{K_5 P_{CO_2}}{1 + K_1 P_{CO} + K_2 P_{O_2} + \sqrt{K_2 K_3 P_{O_2}} + K_5 P_{CO_2}} \tag{D.170}$$

CO oxidation (step 4) is the rate-determining step. The rate expression (including the backward reaction at non-zero conversion) is as follows

$$\begin{aligned} r &= k_4^+ \theta_{CO} \theta_O - k_4^- \theta_{CO_2} \theta_* \\ &= \frac{k_4^+ K_1 P_{CO} \sqrt{K_2 K_3 P_{O_2}} - k_4^- K_5 P_{CO_2}}{\left(1 + K_1 P_{CO} + K_2 P_{O_2} + \sqrt{K_2 K_3 P_{O_2}} + K_5 P_{CO_2}\right)^2} \end{aligned} \tag{D.171}$$

c) We can rewrite the rate expression

$$\begin{aligned} r &= \frac{k_4^+ K_1 P_{CO} \sqrt{K_2 K_3 P_{O_2}} \left(1 - \frac{K_5 P_{CO_2}}{K_4 K_1 P_{CO} \sqrt{K_2 K_3 P_{O_2}}}\right)}{\left(1 + K_1 P_{CO} + K_2 P_{O_2} + \sqrt{K_2 K_3 P_{O_2}} + K_5 P_{CO_2}\right)^2} \\ &= \frac{k_4^+ K_1 P_{CO} \sqrt{K_2 K_3 P_{O_2}} \left(1 - \frac{1}{K_{eq}} \frac{P_{CO_2}}{P_{CO} \sqrt{P_{O_2}}}\right)}{\left(1 + K_1 P_{CO} + K_2 P_{O_2} + \sqrt{K_2 K_3 P_{O_2}} + K_5 P_{CO_2}\right)^2} \end{aligned} \tag{D.172}$$

With K_{eq} the overall reaction equilibrium constant, obtained from the microkinetic network

$$K_{eq} = \frac{K_1 K_4 \sqrt{K_2 K_3}}{K_5} \tag{D.173}$$

The *thermodynamic* equilibrium constant gives us the reaction quotient at equilibrium

$$K_{eq} = \frac{P_{CO_2}}{P_{CO} \sqrt{P_{O_2}}} \tag{D.174}$$

Therefore, at equilibrium

$$r = \frac{k_4^+ K_1 P_{CO} \sqrt{K_2 K_3 P_{O_2}} \left(1 - \frac{1}{K_{eq}} Keq\right)}{\left(1 + K_1 P_{CO} + K_2 P_{O_2} + \sqrt{K_2 K_3 P_{O_2}} + K_5 P_{CO_2}\right)^2} = 0 \tag{D.175}$$

d) Recall that the reaction order is defined with respect to the forward reaction

$$r^+ = \frac{k_4^+ K_1 P_{CO} \sqrt{K_2 K_3 P_{O_2}}}{\left(1 + K_1 P_{CO} + K_2 P_{O_2} + \sqrt{K_2 K_3 P_{O_2}} + K_5 P_{CO_2}\right)^2} \tag{D.176}$$

$$n_{CO} = P_{CO} \frac{\partial \ln r^+}{\partial P_{CO}} \tag{D.177}$$

$$= P_{CO} \left(\frac{\partial \ln P_{CO}}{\partial P_{CO}} + 2 \frac{\partial \ln \theta_*}{\partial P_{CO}} + \frac{\partial \ln k_4^+ K_1 \sqrt{K_2 K_3 P_{O_2}}}{\partial P_{CO}} \right) \tag{D.178}$$

$$\frac{\partial \ln P_{CO}}{\partial P_{CO}} = \frac{1}{P_{CO}} \tag{D.179}$$

$$\frac{\partial \ln k_4^+ K_1 \sqrt{K_2 K_3 P_{O_2}}}{\partial P_{CO}} = 0 \tag{D.180}$$

$$\frac{\partial \ln \theta_*}{\partial P_{CO}} = -\frac{\partial \ln \left(\frac{1}{\theta_*}\right)}{\partial \frac{1}{\theta_*}} \frac{\partial \frac{1}{\theta_*}}{\partial P_{CO}} = -\theta_* \frac{\partial \frac{1}{\theta_*}}{\partial P_{CO}} \tag{D.181}$$

$$\frac{\partial \frac{1}{\theta_*}}{\partial P_{CO}} = \frac{\partial \left(1 + K_1 P_{CO} + K_2 P_{O_2} + \sqrt{K_2 K_3 P_{O_2}} + K_5 P_{CO_2}\right)}{\partial P_{CO}} = K_1 \tag{D.182}$$

$$n_{CO} = P_{CO} \left(\frac{1}{P_{CO}} - 2 K_1 \theta_* \right) = 1 - 2 K_1 P_{CO} \theta_* = 1 - 2\theta_{CO} \tag{D.183}$$

e)

$$n_{O_2} = P_{O_2} \frac{\partial \ln r^+}{\partial P_{O_2}} \tag{D.184}$$

$$= P_{O_2} \left(\frac{1}{2} \frac{\partial \ln P_{O_2}}{\partial P_{O_2}} + 2 \frac{\partial \ln \theta_*}{\partial P_{O_2}} + \frac{\partial \ln k_4^+ K_1 P_{CO} \sqrt{K_2 K_3}}{\partial P_{O_2}} \right)$$

$$\frac{\partial \frac{1}{\theta_*}}{\partial P_{O_2}} = \frac{\partial \left(K_2 P_{O_2} + \sqrt{K_2 K_3} \sqrt{P_{O_2}}\right)}{\partial P_{O_2}} = K_2 + \frac{1}{2} \sqrt{\frac{K_2 K_3}{P_{O_2}}} \tag{D.185}$$

$$n_{O_2} = \frac{1}{2} - 2 K_2 P_{O_2} \theta_* - \sqrt{K_2 K_3 P_{O_2}} \theta_* = \frac{1}{2} - 2\theta_{O_2} - \theta_O \tag{D.186}$$

f)

$$\Delta E_{\text{act}}^{\text{app}} = RT^2 \frac{\partial \ln r^+}{\partial T} \tag{D.187}$$

$$= RT^2 \frac{\partial}{\partial T}\left(\ln k_4^+ + \ln K_1 + \frac{1}{2}\ln K_2 + \frac{1}{2}\ln K_3 + 2\ln\theta_*\right)$$

$$= \Delta E_{\text{act}}^{(4)} + \Delta H_1 + \frac{1}{2}\Delta H_2 + \frac{1}{2}\Delta H_3 - 2\theta_*\Big(\Delta H_1 K_1 P_{\text{CO}} \cdots$$

$$\cdots + \Delta H_2 K_2 P_{\text{O}_2} + \frac{\Delta H_2 + \Delta H_3}{2}\sqrt{K_2 K_3 P_{O2}} + \Delta H_5 K_5 P_{\text{CO}_2}\Big) \tag{D.188}$$

$$= \Delta E_{\text{act}}^{(4)} + \Delta H_1\,(1 - 2\theta_{\text{CO}}) + \Delta H_2\left(\frac{1}{2} - 2\theta_{\text{O}_2} - \theta_{\text{O}}\right)\cdots$$

$$\cdots + \Delta H_3\left(\frac{1}{2} - \theta_{\text{O}}\right) - 2\Delta H_5\theta_{\text{CO}_2} \tag{D.189}$$

g) At high temperature, the surface will be almost empty. A single reaction event will then be a concerted process of adsorption, reaction and desorption. The adsorption step tends to be exothermic as bonds are formed between adsorbate and the surface. As a result, this energy directly benefits the activation of the adsorbed complex, lowering the apparent barrier.

$$\lim_{\theta_* \to 1} \Delta E_{\text{act}}^{\text{app}} = \Delta E_{\text{act}}^{(4)} + \Delta H_1 + \frac{1}{2}\Delta H_2 + \frac{1}{2}\Delta H_3 \tag{D.190}$$

EXAM SOLUTION Kinetics 9

a) Apply the steady-state approximation on the intermediates.[1]

$$[\text{H}\cdot] = k_2[\text{Cl}\cdot][\text{H}_2] - k_3[\text{H}\cdot][\text{Cl}_2] - k_5[\text{H}\cdot][\text{HCl}] = 0 \tag{D.191}$$

$$[\text{Cl}\cdot] = 2k_1[\text{Cl}_2] - k_2[\text{Cl}\cdot][\text{H}_2] + k_3[\text{H}\cdot][\text{Cl}_2] - 2k_4[\text{Cl}\cdot]^2 + k_5[\text{H}\cdot][\text{HCl}] = 0 \tag{D.192}$$

Combining equations D.191 and D.192 yields

$$[\text{Cl}\cdot] = \sqrt{\frac{k_1}{k_4}[\text{Cl}_2]}. \tag{D.193}$$

Inserting equation D.193 into equation D.191 then gives after some trivial rearrangement

$$[\text{H}\cdot] = \frac{k_2\sqrt{\frac{k_1}{k_4}[\text{Cl}_2]}[\text{H}_2]}{k_3[\text{Cl}_2] + k_5[\text{HCl}]} \tag{D.194}$$

[1] Recall that in the notation X· the radical of X is meant.

Using these two equations for the steady-state conccntration of the intermediates, we can readily derive the rate expression to be

$$r = k_2[\mathrm{Cl}\cdot][\mathrm{H_2}] + k_3[\mathrm{H}\cdot][\mathrm{Cl_2}] - k_5[\mathrm{H}\cdot][\mathrm{HCl}] \tag{D.195}$$

$$= k_2\sqrt{\frac{k_1}{k_4}[\mathrm{Cl_2}]}[\mathrm{H_2}] + k_3\frac{k_2\sqrt{\frac{k_1}{k_4}[\mathrm{Cl_2}]}[\mathrm{H_2}]}{k_3[\mathrm{Cl_2}] + k_5[\mathrm{HCl}]}[\mathrm{Cl_2}] - k_5\frac{k_2\sqrt{\frac{k_1}{k_4}[\mathrm{Cl_2}]}[\mathrm{H_2}]}{k_3[\mathrm{Cl_2}] + k_5[\mathrm{HCl}]}[\mathrm{HCl}] \tag{D.196}$$

$$= k_2\sqrt{\frac{k_1}{k_4}[\mathrm{Cl_2}]}[\mathrm{H_2}]\left(1 + \frac{k_3[\mathrm{Cl_2}] - k_5[\mathrm{HCl}]}{k_3[\mathrm{Cl_2}] + k_5[\mathrm{HCl}]}\right) \tag{D.197}$$

$$= k_2\sqrt{\frac{k_1}{k_4}[\mathrm{Cl_2}]}[\mathrm{H_2}]\left(\frac{2k_3[\mathrm{Cl_2}]}{k_3[\mathrm{Cl_2}] + k_5[\mathrm{HCl}]}\right) \tag{D.198}$$

$$= \frac{2k_2k_3\sqrt{\frac{k_1}{k_4}}[\mathrm{H_2}][\mathrm{Cl_2}]^{3/2}}{k_3[\mathrm{Cl_2}] + k_5[\mathrm{HCl}]} \tag{D.199}$$

b) Since the pathway is in parallel, one is allowed to lump the two rate constants k_5 and k_6 together. Replacing k_5 in the above derivation by $k_5 + k_6$ will result in the following answer

$$r = \frac{2k_2k_3\sqrt{\frac{k_1}{k_4}}[\mathrm{H_2}][\mathrm{Cl_2}]^{3/2}}{k_3[\mathrm{Cl_2}] + (k_5 + k_6)[\mathrm{HCl}]} \tag{D.200}$$

c) Determining the reaction orders is moderately straightforward and applying the fundamental formula readily results in

$$n_{\mathrm{Cl_2}} = [\mathrm{Cl_2}]\frac{\partial \ln r^+}{\partial[\mathrm{Cl_2}]} = \frac{3}{2} - \frac{k_3[\mathrm{Cl_2}]}{k_3[\mathrm{Cl_2}] + k\prime[\mathrm{HCl}]} \tag{D.201}$$

$$n_{\mathrm{H_2}} = [\mathrm{H_2}]\frac{\partial \ln r^+}{\partial[\mathrm{H_2}]} = 1 \tag{D.202}$$

d) Using the formal definition of the apparent activation energy gives

$$\Delta E_{\mathrm{act}}^{\mathrm{app}} = RT^2\frac{\partial \ln r^+}{\partial T} \tag{D.203}$$

$$= RT^2\frac{\partial}{\partial T}\left\{\ln k_2 + \frac{1}{2}\ln k_1 - \frac{1}{2}\ln k_4 + \ln k_3 - \cdots \right.$$
$$\left. \cdots - \ln\left(k_3[\mathrm{Cl_2}] + (k_5 + k_6)[\mathrm{HCl}]\right)\right\} \tag{D.204}$$

$$= \Delta E_{\mathrm{act}}^{(2)} + \frac{1}{2}\Delta E_{\mathrm{act}}^{(1)} - \frac{1}{2}\Delta E_{\mathrm{act}}^{(4)} + \Delta E_{\mathrm{act}}^{(3)} + \cdots$$
$$\cdots + \frac{\Delta E_{\mathrm{act}}^{(3)}k_3[\mathrm{Cl_2}] + (\Delta E_{\mathrm{act}}^{(5)}k_5 + \Delta E_{\mathrm{act}}^{(6)}k_6)[\mathrm{HCl}]}{k_3[\mathrm{Cl_2}] + (k_5 + k_6)[\mathrm{HCl}]} \tag{D.205}$$

e) By the inclusion of the additional pathway, an additional (positive) contribution to the apparent activation energy is found. This can be readily rationalized as the inclusion of a secondary parallel retardation path results in a decrease of the overall product of HCl.

D.3 Statistical thermodynamics

EXAM SOLUTION Statistical Thermodynamics 1

a) A schematic representation of the distribution of the energetic states over the four molecules is provided below

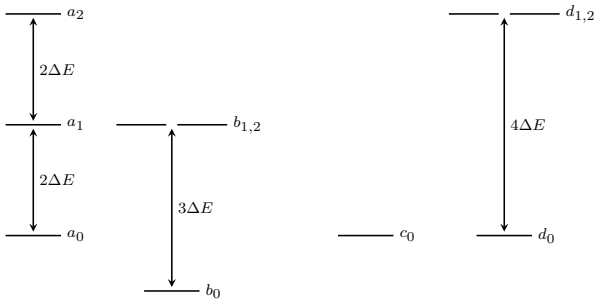


Figure D.1: *Energy level diagram of A, B, C, and D.*

b) The energy level of b_0 is set to the global ground state (i.e. zero). From this, the partition functions for each molecule are

$$q_A = \exp\left(\frac{-\Delta E}{k_\mathrm{B}T}\right) + \exp\left(\frac{-3\Delta E}{k_\mathrm{B}T}\right) + \exp\left(\frac{-5\Delta E}{k_\mathrm{B}T}\right) \tag{D.206}$$

$$q_B = 1 + 2\exp\left(\frac{-3\Delta E}{k_\mathrm{B}T}\right) \tag{D.207}$$

$$q_C = \exp\left(\frac{-\Delta E}{k_\mathrm{B}T}\right) \tag{D.208}$$

$$q_D = \exp\left(\frac{-\Delta E}{k_\mathrm{B}T}\right) + 2\exp\left(\frac{-5\Delta E}{k_\mathrm{B}T}\right) \tag{D.209}$$

c) The equilibrium constant K for the above reaction is

$$K = \frac{q_C q_D}{q_A q_B} \tag{D.210}$$

d) When $T \to 0$, all exponentials go to zero, whereas at $T \to \infty$, all exponentials go to unity. Thus the limits for the equilibrium constant are

$$K(T \to 0) = \lim \frac{0 \cdot 0}{1 \cdot 0} = 0 \tag{D.211}$$

$$K(T \to \infty) = \lim \frac{1 \cdot 3}{3 \cdot 3} = \frac{1}{3} \tag{D.212}$$

At $T \to 0$, only the lowest state, also known as ground 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 Statistical Thermodynamics 2

a) A schematic representation of the distribution of the energetic states over the four molecules is provided below

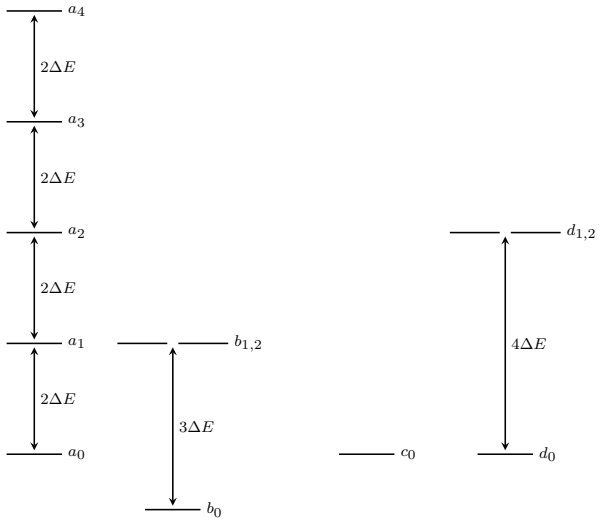


Figure D.2: *Energy level diagram of A, B, C, and D.*

b) Set the energy level of b_0 to the global ground state (i.e. zero)

$$q_A = \exp\left(-\frac{\Delta E}{k_\mathrm{B}T}\right) + \exp\left(-\frac{3\Delta E}{k_\mathrm{B}T}\right) + \exp\left(-\frac{5\Delta E}{k_\mathrm{B}T}\right)\cdots$$
$$\cdots + \exp\left(-\frac{7\Delta E}{k_\mathrm{B}T}\right) + \exp\left(-\frac{9\Delta E}{k_\mathrm{B}T}\right) \tag{D.213}$$

$$q_B = 1 + 2\exp\left(-\frac{3\Delta E}{k_\mathrm{B}T}\right) \tag{D.214}$$

$$q_C = \exp\left(-\frac{\Delta E}{k_\mathrm{B}T}\right) \tag{D.215}$$

$$q_D = \exp\left(-\frac{\Delta E}{k_\mathrm{B}T}\right) + 2\exp\left(-\frac{5\Delta E}{k_\mathrm{B}T}\right) \tag{D.216}$$

c) The average energy of molecule B is given by

$$\langle E_B\rangle = k_\mathrm{B}T^2\frac{\partial \ln q_B}{\partial T} \tag{D.217}$$

$$= \frac{2\cdot 3\Delta E\cdot \exp\left(-\frac{3\Delta E}{k_\mathrm{B}T}\right)}{1+2\exp\left(-\frac{3\Delta E}{k_\mathrm{B}T}\right)} \tag{D.218}$$

At $T\to 0$, $\langle E_B\rangle = 0$ as only the ground state is occupied which has an energy value of 0.
At $T\to\infty$, $\langle E_B\rangle = 2\Delta E$, as all its states are equally occupied. Hence, we get the arithmetic average of the energy values of all these states.

d) The equilibrium constant K for the above reaction is

$$K = \frac{q_C q_D}{q_A q_B} \tag{D.219}$$

e) When $T \to 0$, all exponentials go to zero, whereas at $T \to \infty$, all exponentials go to unity. Thus:

$$K(T \to 0) = \lim \frac{0 \cdot 0}{1 \cdot 0} = 0 \tag{D.220}$$

$$K(T \to \infty) = \lim \frac{1 \cdot 3}{5 \cdot 3} = \frac{1}{5} \tag{D.221}$$

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 Statistical Thermodynamics 3

a) The energy levels are given in Figure D.3, where we have set the energy of the ground state of molecule C as $E_0 = 0$.

b) We use a Boltzmann distribution to determine the occupation of the energy levels

$$q_A = 2\exp\left(\frac{-\Delta E}{k_B T}\right) + \exp\left(\frac{-2\Delta E}{k_B T}\right) \tag{D.222}$$

$$q_B = 2\exp\left(\frac{-\Delta E}{k_B T}\right) + \exp\left(\frac{-3\Delta E}{k_B T}\right) + \exp\left(\frac{-4\Delta E}{k_B T}\right) \tag{D.223}$$

$$q_C = 3 \tag{D.224}$$

⚠ Note: The energies here are given per molecule.

c) Considering isolated molecules

$$\langle E \rangle = \sum_i \frac{E_i P_i}{q} \tag{D.225}$$

$$\langle E_A \rangle = \frac{2\Delta E \exp\left(\frac{-\Delta E}{k_B T}\right) + 2\Delta E \exp\left(\frac{-2\Delta E}{k_B T}\right)}{2\exp\left(\frac{-\Delta E}{k_B T}\right) + \exp\left(\frac{-2\Delta E}{k_B T}\right)} \tag{D.226}$$

$$\langle E_B \rangle = \frac{2\Delta E \exp\left(\frac{-\Delta E}{k_B T}\right) + 3\Delta E \exp\left(\frac{-3\Delta E}{k_B T}\right) + 4\Delta E \exp\left(\frac{-4\Delta E}{k_B T}\right)}{2\exp\left(\frac{-\Delta E}{k_B T}\right) + \exp\left(\frac{-3\Delta E}{k_B T}\right) + \exp\left(\frac{-4\Delta E}{k_B T}\right)} \tag{D.227}$$

$$\langle E_C \rangle = \frac{0}{3} = 0 \tag{D.228}$$

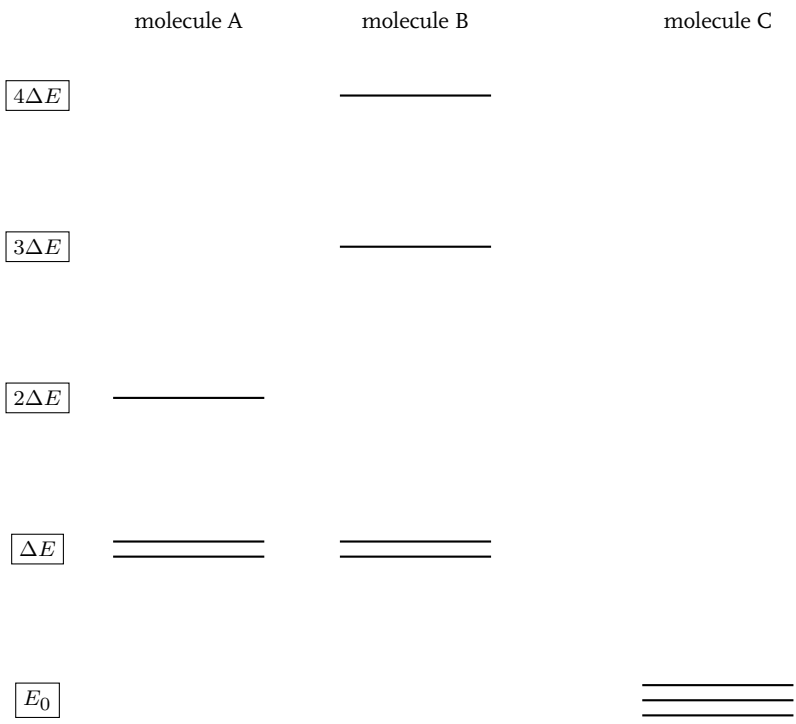


Figure D.3: *Energy levels for molecules A, B and C.*

d) We will consider here a reaction of 1 mole of A and 1 mole of B to yield 1 mole of C. We now need to account for the distinguishability of the particles in the ensemble. The partition functions for the initial and final state are given by

$$Q_{\text{FS}} = \frac{q_C^{N_C}}{N_C!} \tag{D.229}$$

$$Q_{\text{IS}} = \frac{q_A^{N_A} q_B^{N_B}}{N_A! \cdot N_B!} \tag{D.230}$$

Inserting the above two expressions into the definition for the entropy[2]

[2] Note that the $N_x!$ terms in the denominator disappears because we take the derivative towards T. The power in N_x becomes a multiplicative constant because of the natural logarithm. Since we are interested in the **molar entropy**, we divide the results by N by which the multiplicative constant N disappears.

$$S = \frac{\partial \left(k_\mathrm{B} T \ln Q\right)}{\partial T} = k_\mathrm{B} \ln Q + k_\mathrm{B} T \frac{\partial \ln Q}{\partial T} \tag{D.231}$$

$$\Delta S_{\mathrm{R,m}} = S_{\mathrm{FS}} - S_{\mathrm{IS}} \tag{D.232}$$

$$= R \ln\left(\frac{q_C}{q_A q_B}\right) + RT \frac{\partial \left(\ln \frac{q_C}{q_A q_B}\right)}{\partial T} \tag{D.233}$$

$$\frac{\partial \ln q_i}{\partial T} = \frac{1}{q_i} \frac{\partial q_i}{\partial T} \tag{D.234}$$

$$\frac{\partial q_A}{\partial T} = \frac{1}{k_\mathrm{B} T^2} \left(2\Delta E \exp\left(\frac{-\Delta E}{k_\mathrm{B} T}\right) + 2\Delta E \exp\left(\frac{-2\Delta E}{k_\mathrm{B} T}\right)\right) \tag{D.235}$$

$$\frac{\partial q_B}{\partial T} = \frac{1}{k_\mathrm{B} T^2} \left(2\Delta E \exp\left(\frac{-\Delta E}{k_\mathrm{B} T}\right) + 3\Delta E \exp\left(\frac{-3\Delta E}{k_\mathrm{B} T}\right) \cdots \right.$$
$$\left. \cdots + 4\Delta E \exp\left(\frac{-4\Delta E}{k_\mathrm{B} T}\right)\right) \tag{D.236}$$

$$\frac{\partial q_C}{\partial T} = 0 \tag{D.237}$$

$$\Delta S_{\mathrm{R,m}} = R \ln\left(\frac{q_C}{q_A q_B}\right) - \frac{1}{T} \left(\frac{2\Delta E}{q_A} \exp\left(\frac{-\Delta E}{k_\mathrm{B} T}\right) + \frac{2\Delta E}{q_A} \cdots \right.$$
$$\cdots \exp\left(\frac{-2\Delta E}{k_\mathrm{B} T}\right) + \frac{2\Delta E}{q_B} \exp\left(\frac{-\Delta E}{k_\mathrm{B} T}\right) + \frac{3\Delta E}{q_B} \cdots$$
$$\left. \cdots \exp\left(\frac{-3\Delta E}{k_\mathrm{B} T}\right) + \frac{4\Delta E}{q_B} \exp\left(\frac{-4\Delta E}{k_\mathrm{B} T}\right)\right) \tag{D.238}$$

Taking the limit of $T \to \infty$:

$$\lim_{T\to\infty} q_A = 3 \tag{D.239}$$

$$\lim_{T\to\infty} q_B = 4 \tag{D.240}$$

$$\lim_{T\to\infty} q_C = 3 \tag{D.241}$$

Gives for the reaction entropy

$$\lim_{T\to\infty} \Delta S_{\mathrm{R,m}} = R \ln\left(\frac{1}{4}\right) = -R \ln(4) \tag{D.242}$$

We see that the second term in eq. D.231 completely disappears. The same conclusion could be drawn if a different relation for the entropy was used

$$\lim_{T\to\infty} S = \lim_{T\to\infty} \frac{\langle E \rangle}{T} + k_\mathrm{B} \ln Q = k_\mathrm{B} \ln Q \tag{D.243}$$

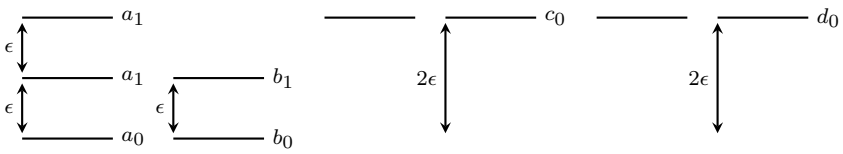
$$\lim_{T\to\infty} \Delta S_{\mathrm{R,m}} = R \ln\left(\frac{q_C}{q_A q_B}\right) = -R \ln(4) \tag{D.244}$$

e) If we go towards very high temperatures, we expect the energy levels of all particles to be occupied with equal probability. The number of permutations over the energy levels correlates directly to the number of microstates. In going from the initial to the final state, both the number of energy levels and the number of molecules decreases. The number of microstates therefore decreases, corresponding to a loss in entropy. This rationalizes the negative sign for the entropy difference.

If we were to consider the same situation at finite temperature, we would need to consider the occupation of each energy level, which is contained in the second term of eq. D.238.

EXAM SOLUTION Statistical Thermodynamics 4

a) A schematic representation of the distribution of the energy levels of all molecules is provided below



b) The energy levels of a_0 and b_0 are set to the global ground state (i.e. zero). From this, the partition functions for each molecule are

$$q_A = 1 + \exp\left(\frac{-\epsilon}{k_B T}\right) + \exp\left(\frac{-2\epsilon}{k_B T}\right) \tag{D.245}$$

$$q_B = 1 + \exp\left(\frac{-\epsilon}{k_B T}\right) \tag{D.246}$$

$$q_C = 2\exp\left(\frac{-2\epsilon}{k_B T}\right) \tag{D.247}$$

$$q_D = 2\exp\left(\frac{-2\epsilon}{k_B T}\right) \tag{D.248}$$

c) The equilibrium constant K for the above reaction is

$$K = \frac{q_C q_D}{q_A q_B} = \frac{\left(2\exp\left(\frac{-2\epsilon}{k_B T}\right)\right)\left(2\exp\left(\frac{-2\epsilon}{k_B T}\right)\right)}{\left(1 + \exp\left(\frac{-\epsilon}{k_B T}\right) + \exp\left(\frac{-2\epsilon}{k_B T}\right)\right)\left(1 + \exp\left(\frac{-\epsilon}{k_B T}\right)\right)} \tag{D.249}$$

d) When $T \to 0$, all exponentials go to zero, whereas at $T \to \infty$, all exponentials go to unity. Thus the limits for the equilibrium constant K are

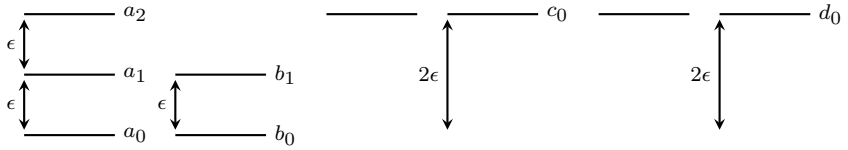
$$\lim_{T\to 0} K = \frac{0}{1} = 0 \tag{D.250}$$

$$\lim_{T\to\infty} K = \frac{2\cdot 2}{3\cdot 2} = \frac{2}{3} \tag{D.251}$$

Note: A similar approach was used in *Statistical Thermodynamics 1* to determine the limits of K. If in doubt, go back to to that question and check the explanation.

EXAM SOLUTION Statistical Thermodynamics 5

a) A schematic representation of the distribution of the energy levels of all molecules is provided below



⚠ Note: a is CH_4, b is H_2O, c is H_2 and d is CO.

b) The partition functions for each molecule are

$$q_A = 1 + \exp\left(\frac{-\epsilon}{k_B T}\right) + \exp\left(\frac{-2\epsilon}{k_B T}\right) \tag{D.252}$$

$$q_B = 1 + \exp\left(\frac{-\epsilon}{k_B T}\right) \tag{D.253}$$

$$q_C = 2\exp\left(\frac{-2\epsilon}{k_B T}\right) \tag{D.254}$$

$$q_D = 2\exp\left(\frac{-2\epsilon}{k_B T}\right) \tag{D.255}$$

c) The equilibrium constant K for the above reaction is

$$K = \frac{q_C^3 q_D}{q_A q_B} = \frac{\left(2\exp\left(\frac{-2\epsilon}{k_B T}\right)\right)^3 \left(2\exp\left(\frac{-2\epsilon}{k_B T}\right)\right)}{\left(1+\exp\left(\frac{-\epsilon}{k_B T}\right)+\exp\left(\frac{-2\epsilon}{k_B T}\right)\right)\left(1+\exp\left(\frac{-\epsilon}{k_B T}\right)\right)} \tag{D.256}$$

d)

$$\lim_{T\to 0} K = \frac{0}{1} = 0 \tag{D.257}$$

$$\lim_{T\to\infty} K = \frac{2^3\cdot 2}{3\cdot 2} = \frac{16}{6} = \frac{8}{3} \tag{D.258}$$

At $T = 0$, only the ground state is occupied, hence the system is in its ground state wherein only A and B exist. In this conditions, the equilibrium constant is zero. At $T \to \infty$, all states are equally likely and thus the equilibrium constants represents the arithmetic average of the product of the states of C and D over the states of A and B.

EXAM SOLUTION Statistical Thermodynamics 6

a) Many answer are valid here. Either draw a nanoparticle wherein two types of sites are highlighted or a checkerboard surface wherein two diferent types of cells are shown.

b) Straightforward implementation of the supplied formulas yields the following two expressions for the partition functions

$$Q_A = \frac{N_A!}{(N_A - S_A)!S_A!} q_A^{S_A} \tag{D.259}$$

$$Q_B = \frac{N_B!}{(N_B - S_B)!S_B!} q_B^{S_B} \tag{D.260}$$

In the above formulas, N corresponds to the total number of active sites of a particular site and S the number of occupied sites.

c) From the above formulas, we can readily calculate the chemical potential by application of the Stirling approximation

$$\mu_A = -k_B T \frac{\partial \ln Q_A}{\partial S_A} \tag{D.261}$$

$$= k_B T \frac{\partial}{\partial S_A} \Big[\left(N_A - S_A\right) \ln \left(N_A - S_A\right) - \left(N_A - S_A\right) \cdots$$

$$\cdots + S_A \ln S_A - S_A - S_A \ln q_A \Big] \tag{D.262}$$

$$= -k_B T \ln \left(\frac{N_A - S_A}{S_A} q_A \right) \tag{D.263}$$

We obtain a similar expression for μ_B as given by

$$\mu_B = -k_B T \ln \left(\frac{N_B - S_B}{S_B} q_B \right) \tag{D.264}$$

To calculate the ratio between the fractional coverage of A and B, we set the two chemical potential equal to each other, which gives

$$\mu_A = \mu_B \tag{D.265}$$

$$-k_B T \ln \left(\frac{N_A - S_A}{S_A} q_A \right) = -k_B T \ln \left(\frac{N_B - S_B}{S_B} q_B \right) \tag{D.266}$$

$$\frac{N_A - S_A}{S_A} q_A = \frac{N_B - S_B}{S_B} q_B \tag{D.267}$$

$$\frac{\left(\frac{\theta_B}{1-\theta_B}\right)}{\left(\frac{\theta_A}{1-\theta_A}\right)} = \frac{q_B}{q_A} \tag{D.268}$$

The right hand side of the above expression can be solved by noting that CO adsorbs 40 kJ/mol stronger on site A as compared to site B. Hence, we set the zero of energy to the adsorption energy of A, by which we can set

$$\frac{q_B}{q_A} = \exp\left(\frac{-\Delta E}{k_\mathrm{B}T}\right) = \exp\left(-\frac{40\mathrm{kJ\ /\ mol}}{k_\mathrm{B}T}\right) \tag{D.269}$$

d) For find the low and high temperature surface ratios, we need to evaluate the limiting conditions when $T \to 0$ and $T \to \infty$.

For very low temperature, the fraction

$$\frac{\left(\frac{\theta_B}{1-\theta_B}\right)}{\left(\frac{\theta_A}{1-\theta_A}\right)} \to 0 \tag{D.270}$$

By rearranging the above equation, the following limiting condition can be found

$$\frac{\theta_B/\theta_A - \theta_B}{1-\theta_B}. \tag{D.271}$$

Since θ_B lies on the interval [0,1], even in the case that $\theta_B \neq 0$, the limiting conditions is met when $\frac{\theta_B}{\theta_A} \to 0$ as a consequence of $\theta_B \to 0$. This answer makes sense as CO adsorbs stronger on site A than on site B, thus we would anticipate that CO prefers to reside exclusively on site A at very low temperature.

For very high temperature, the fraction

$$\frac{\left(\frac{\theta_B}{1-\theta_B}\right)}{\left(\frac{\theta_A}{1-\theta_A}\right)} \to 1 \tag{D.272}$$

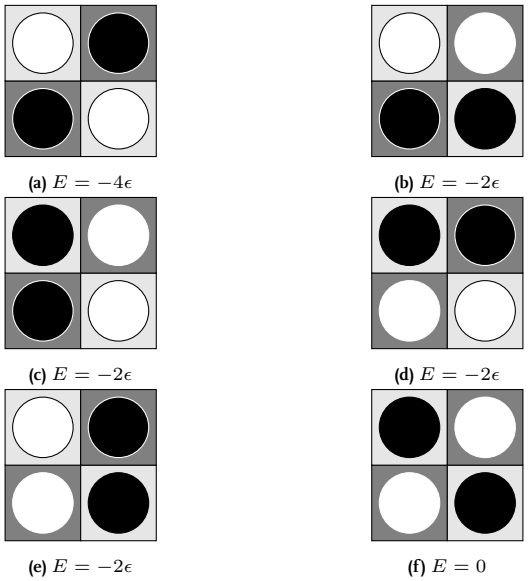
This condition is met when $\theta_A = \theta_B$, which corresponds to CO spreading to all possible surface sites to maximize its (mixing) entropy.

EXAM SOLUTION Statistical Thermodynamics 7

a) The different microstates are given in Figure D.4.

b) The three macrostates are those corresponding to $E = -4\epsilon$, $E = -2\epsilon$ and $E = 0$. We re-scale all energies in such a way that the ground state corresponds to $E = 0$. The partition function is thus as follows:

$$q = 1 + 4\exp\left(\frac{-2\epsilon}{k_\mathrm{B}T}\right) + \exp\left(\frac{-4\epsilon}{k_\mathrm{B}T}\right) \tag{D.273}$$



(a) $E = -4\epsilon$ **(b)** $E = -2\epsilon$ **(c)** $E = -2\epsilon$ **(d)** $E = -2\epsilon$ **(e)** $E = -2\epsilon$ **(f)** $E = 0$

Figure D.4: *The six different configurations (microstates) to place two black and two white tiles on the model catalytic surface.*

c) Expression for average energy $\langle E \rangle$ for this system is

$$\langle E \rangle = k_{\mathrm{B}} T^2 \frac{\partial \ln q}{\partial T} = \frac{8\epsilon \exp\left(\frac{-2\epsilon}{k_{\mathrm{B}} T}\right) + 4\epsilon \exp\left(\frac{-4\epsilon}{k_{\mathrm{B}} T}\right)}{1 + 4\exp\left(\frac{-2\epsilon}{k_{\mathrm{B}} T}\right) + \exp\left(\frac{-4\epsilon}{k_{\mathrm{B}} T}\right)} \tag{D.274}$$

The limit at very low temperature is from the above equation:

$$\lim_{T \to 0} \langle E \rangle = 0 \tag{D.275}$$

At $T = 0$, only the ground state is occupied which has an energy of 0.

And the limit at very high temperature is

$$\lim_{T \to \infty} \langle E \rangle = \frac{8\epsilon + 4\epsilon}{1 + 4 + 1} = 2\epsilon \tag{D.276}$$

This answer corresponds to all states being equally occupied, so we get the arithmetic average of the energies for all the states.

d) Expected or average value for $\langle \eta \rangle$ as a function of temperature

$$\langle \eta \rangle = \sum_{i=0}^{3} P_i \cdot \eta_i \tag{D.277}$$

$$= \frac{1}{1 + 4\exp\left(\frac{-2\epsilon}{k_B T}\right) + \exp\left(\frac{-4\epsilon}{k_B T}\right)} + \frac{\frac{1}{2} \cdot 4\exp\left(\frac{-2\epsilon}{k_B T}\right)}{1 + 4\exp\left(\frac{-2\epsilon}{k_B T}\right) + \exp\left(\frac{-4\epsilon}{k_B T}\right)} \cdots$$

$$\cdots + \frac{0}{1 + 4\exp\left(\frac{-2\epsilon}{k_B T}\right) + \exp\left(\frac{-4\epsilon}{k_B T}\right)} \tag{D.278}$$

$$= \frac{1 + 2\exp\left(\frac{-2\epsilon}{k_B T}\right)}{1 + 4\exp\left(\frac{-2\epsilon}{k_B T}\right) + \exp\left(\frac{-4\epsilon}{k_B T}\right)} \tag{D.279}$$

At very low temperature, the average occupancy becomes:

$$\lim_{T \to 0} \langle \eta \rangle = \frac{1}{1} = 1 \tag{D.280}$$

At very low temperature, only the ground state is occupied which has an occupancy factor of unity.

At very high temperature, the average occupancy becomes:

$$\lim_{T \to \infty} \langle \eta \rangle = \frac{1 + 2}{6} = \frac{1}{2} \tag{D.281}$$

At very high temperature, all states are equally likely and thus the expectation value for the occupancy corresponds to the arithmetic average of the occupancy of all states.

e) The lowest energy corresponds to the highest occupancy factor and *vice versa*. The correlation between occupancy can best be described by the following formula:

$$\langle E \rangle = \big(1 - \langle \eta \rangle\big) \cdot 4\epsilon \tag{D.282}$$

The correlation is of course evident as the expected occupancy describes how many tiles have a favorable piece and this in turn determines the overall energetic stability.

EXAM SOLUTION Statistical Thermodynamics 8

a) From the Boltzmann-equation, we can readily establish the following partition functions for A and B.

$$q_A = \exp\left(-\frac{3\Delta E}{k_\mathrm{B}T}\right)\sum_{i=0}^{\infty}\exp\left(-\frac{i\Delta E}{k_\mathrm{B}T}\right) \tag{D.283}$$

$$= \frac{\exp\left(-\frac{3\Delta E}{k_\mathrm{B}T}\right)}{1-\exp\left(-\frac{\Delta E}{k_\mathrm{B}T}\right)} \tag{D.284}$$

$$q_B = \sum_{i=0}^{\infty}\exp\left(-\frac{2i\Delta E}{k_\mathrm{B}T}\right) \tag{D.285}$$

$$= \frac{1}{1-\exp\left(-\frac{2\Delta E}{k_\mathrm{B}T}\right)} \tag{D.286}$$

Note that we herein applied the solution for a geometric series.[3]

b) The average energy of state A is given by

$$\langle E_A\rangle = k_\mathrm{B}T^2\frac{\partial}{\partial T}\ln q \tag{D.287}$$

$$= 3\Delta E - k_\mathrm{B}T^2\frac{\partial}{\partial T}\ln\left(1-\exp\left(-\frac{\Delta E}{k_\mathrm{B}T}\right)\right) \tag{D.288}$$

$$= \Delta E\left(3+\frac{\exp\left(-\frac{\Delta E}{k_\mathrm{B}T}\right)}{1-\exp\left(-\frac{\Delta E}{k_\mathrm{B}T}\right)}\right). \tag{D.289}$$

In a similar fashion, we find for B

$$\langle E_B\rangle = \Delta E\left(\frac{2\exp\left(-\frac{2\Delta E}{k_\mathrm{B}T}\right)}{1-\exp\left(-\frac{2\Delta E}{k_\mathrm{B}T}\right)}\right). \tag{D.290}$$

Thus, the average reaction energy is given by

$$\langle E_B\rangle - \langle E_A\rangle = \Delta E\left(\frac{2\exp\left(-\frac{2\Delta E}{k_\mathrm{B}T}\right)}{1-\exp\left(-\frac{2\Delta E}{k_\mathrm{B}T}\right)} - 3 - \frac{\exp\left(-\frac{\Delta E}{k_\mathrm{B}T}\right)}{1-\exp\left(-\frac{\Delta E}{k_\mathrm{B}T}\right)}\right) \tag{D.291}$$

c) Since the limit

$$\lim_{T\to 0}\frac{\exp\left(-\frac{\Delta E}{k_\mathrm{B}T}\right)}{1-\exp\left(-\frac{\Delta E}{k_\mathrm{B}T}\right)} = 0 \tag{D.292}$$

it follows that

$$\lim_{T\to 0}\left(\langle E_B\rangle - \langle E_A\rangle\right) = -3\Delta E. \tag{D.293}$$

[3] Have a look at Exercise 2.5 for a detailed derivation.

The limit for $T \to \infty$ is rather complex, but let me show you a nice trick to solve it.

$$\lim_{T\to\infty}\left[\Delta E\left(\frac{\exp\left(-2\frac{2\Delta E}{k_\mathrm{B}T}\right)}{1-\exp\left(-\frac{2\Delta E}{k_\mathrm{B}T}\right)}-3-\frac{\exp\left(-\frac{\Delta E}{k_\mathrm{B}T}\right)}{1-\exp\left(-\frac{\Delta E}{k_\mathrm{B}T}\right)}\right)\right] \tag{D.294}$$

Observe that we can rewrite the first term as

$$\frac{\exp\left(-\frac{2\Delta E}{k_\mathrm{B}T}\right)}{1-\exp\left(-\frac{2\Delta E}{k_\mathrm{B}T}\right)}=\frac{2}{\exp\left(\frac{2\Delta E}{k_\mathrm{B}T}\right)-1} \tag{D.295}$$

$$=\frac{2}{\left(\exp\left(\frac{\Delta E}{k_\mathrm{B}T}\right)-1\right)\left(\exp\left(\frac{\Delta E}{k_\mathrm{B}T}\right)+1\right)} \tag{D.296}$$

by which we can combine the first and third terms as given

$$\frac{2}{\left(\exp\left(\frac{\Delta E}{k_\mathrm{B}T}\right)-1\right)\left(\exp\left(\frac{\Delta E}{k_\mathrm{B}T}\right)+1\right)}-\frac{1}{\left(\exp\left(\frac{\Delta E}{k_\mathrm{B}T}\right)-1\right)} \tag{D.297}$$

$$=\frac{2}{\left(\exp\left(\frac{\Delta E}{k_\mathrm{B}T}\right)-1\right)\left(\exp\left(\frac{\Delta E}{k_\mathrm{B}T}\right)+1\right)}-\frac{\left(\exp\left(\frac{\Delta E}{k_\mathrm{B}T}\right)+1\right)}{\left(\exp\left(\frac{\Delta E}{k_\mathrm{B}T}\right)-1\right)\left(\exp\left(\frac{\Delta E}{k_\mathrm{B}T}\right)+1\right)} \tag{D.298}$$

$$=\frac{\left(1-\exp\left(\frac{\Delta E}{k_\mathrm{B}T}\right)\right)}{\left(\exp\left(\frac{\Delta E}{k_\mathrm{B}T}\right)-1\right)\left(\exp\left(\frac{\Delta E}{k_\mathrm{B}T}\right)+1\right)} \tag{D.299}$$

$$=-\frac{1}{\left(\exp\left(\frac{\Delta E}{k_\mathrm{B}T}\right)+1\right)} \tag{D.300}$$

whose limit can be readily established

$$\lim_{T\to\infty}\left[-\frac{1}{\left(\exp\left(\frac{\Delta E}{k_\mathrm{B}T}\right)+1\right)}\right]=-\frac{1}{2}. \tag{D.301}$$

Combining all terms then yields

$$\lim_{T\to\infty}\left[\Delta E\left(\frac{2\exp\left(-\frac{2\Delta E}{k_\mathrm{B}T}\right)}{1-\exp\left(-\frac{2\Delta E}{k_\mathrm{B}T}\right)}-3-\frac{\exp\left(-\frac{\Delta E}{k_\mathrm{B}T}\right)}{1-\exp\left(-\frac{\Delta E}{k_\mathrm{B}T}\right)}\right)\right]=-\frac{7}{2}\Delta E. \tag{D.302}$$

If you do not like the mathematical struggle, you can also deduce the answer by reasoning. This reasoning goes as follows.[4] The ground state of B is $3\Delta E$ lower than that of A. For every level of B, there will be two levels of A. On average, these two levels of A will be $\frac{1}{2}\Delta E$ higher than that of B. Thus, $\frac{1}{2}\Delta E$ need to be subtracted from $3\Delta E$ to obtain the final answer.

Interpretation / Rationalization:

- In the limit of $\lim_{T\to 0}$, only the ground state is occupied and hence the reaction energy correspond to the energetic difference between the ground states of A and B.
- In the limit of $\lim_{T\to \infty}$, all states are occupied. State B only has half the number of energetic levels as compared to state A, on top of A being $3\Delta E$ higher in energy. Hence, considering N states of B, there will be $2N$ states of A. On average, the additional excited states of B will thus be twice as high in energy as compared to those of A. As such, the excited states of B are **on average** $\frac{1}{2}\Delta E$ higher in energy than those of state A, by which the average reaction energy drops by an additional $\frac{1}{2}\Delta E$ on top of the $-3\Delta E$.

d) The molar entropy of A is given by

$$S_A = N\frac{\partial}{\partial T}\left(k_\mathrm{B}T\ln q_A\right) \tag{D.303}$$

$$= R\left[\frac{\frac{\Delta E}{k_\mathrm{B}T}}{\exp\left(\frac{\Delta E}{k_\mathrm{B}T}\right)-1} - \ln\left(1-\exp\left(-\frac{\Delta E}{k_\mathrm{B}T}\right)\right)\right] \tag{D.304}$$

and for B by

$$S_B = N\frac{\partial}{\partial T}\left(k_\mathrm{B}T\ln q_B\right) \tag{D.305}$$

$$= R\left[\frac{\frac{2\Delta E}{k_\mathrm{B}T}}{\exp\left(\frac{2\Delta E}{k_\mathrm{B}T}\right)-1} - \ln\left(1-\exp\left(-\frac{2\Delta E}{k_\mathrm{B}T}\right)\right)\right] \tag{D.306}$$

by which the molar reaction entropy can be found to be

$$S_R = S_B - S_A \tag{D.307}$$

$$= R\left[\frac{\frac{2\Delta E}{k_\mathrm{B}T}}{\exp\left(\frac{2\Delta E}{k_\mathrm{B}T}\right)-1} - \frac{\frac{\Delta E}{k_\mathrm{B}T}}{\exp\left(\frac{\Delta E}{k_\mathrm{B}T}\right)-1} + \ln\left(\frac{1-\exp\left(-\frac{\Delta E}{k_\mathrm{B}T}\right)}{1-\exp\left(-\frac{2\Delta E}{k_\mathrm{B}T}\right)}\right)\right] \tag{D.308}$$

e) The equilibrium constant is given by

$$K = \frac{q_B}{q_A} = \frac{\frac{1}{1-\exp\left(-\frac{2\Delta E}{k_\mathrm{B}T}\right)}}{\frac{\exp\left(-\frac{3\Delta E}{k_\mathrm{B}T}\right)}{1-\exp\left(-\frac{\Delta E}{k_\mathrm{B}T}\right)}}, \tag{D.309}$$

[4] It might help to make a drawing and identify the principal repetitive unit for the infinite system.

from which it can be found that the following equality should hold

$$\frac{\exp\left(-\frac{3\Delta E}{k_B T}\right)}{1-\exp\left(-\frac{\Delta E}{k_B T}\right)} = \frac{1}{1-\exp\left(-\frac{2\Delta E}{k_B T}\right)}. \tag{D.310}$$

The first-order Taylor approximation of the above equation is

$$K\prime = \frac{1-3\beta\Delta E}{\beta\Delta E} = \frac{1}{2\beta\Delta E}, \tag{D.311}$$

wherein we have introduced the thermodynamic temperature $\beta = \frac{1}{k_B T}$ as a means for short-hand notation.

Solving for β yields

$$\beta = 6\Delta E \tag{D.312}$$

by which we find that the equilibrium temperature T is given by

$$T = \frac{6\Delta E}{k_B}. \tag{D.313}$$

EXAM SOLUTION Statistical Thermodynamics 9

a) The number of microstate for the first three macrostates can be calculated as follows

$$\Omega_1 = \frac{5!}{4!\cdot 1!} = 5 \tag{D.314}$$

$$\Omega_2 = \frac{5!}{3!\cdot 1!\cdot 1!} = 5\cdot 4 = 20 \tag{D.315}$$

$$\Omega_3 = \frac{5!}{3!\cdot 1!\cdot 1!} = 5\cdot 4 = 20 \tag{D.316}$$

The values correspond to the expectations and thus equation C.22 is correct.

b) The complete set of possible configurations (microstates) is given in Figure D.5.

c) The total number of microstates is given by

$$\Omega_{5,6} = \frac{(5+6-1)!}{6!\cdot 4!} = 210 \tag{D.317}$$

d) The average number of particles is given in Table D.1.

e) A is the value for the lowest energy level, which corresponds to 2.

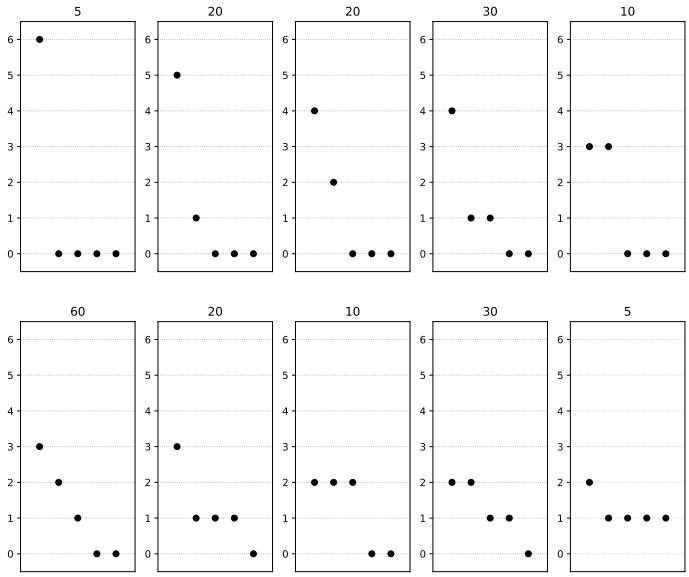


Figure D.5: *Set of possible macrostates (and corresponding number of microstates) for placing 6 units of energy among 5 particles.*

Table D.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	0.024

f) The correct answers are

$$b = \ln Ay \qquad = \ln n_i \tag{D.318}$$

$$a = 1/RT \tag{D.319}$$

$$x = i\Delta E \tag{D.320}$$

$$\tag{D.321}$$

g) The temperature of the ensemble can be approximated as follows. The slope a can be approximated using

$$a \approx \frac{\ln n_6 - \ln n_0}{6\Delta E - 0\Delta E} \tag{D.322}$$

$$= \frac{\ln\left(0.024/2.000\right)}{6\Delta E} \tag{D.323}$$

$$= -7.371 \cdot 10^{-5} \tag{D.324}$$

From the slope, we can readily establish the temperature by

$$T = -\frac{1}{R \cdot a} \tag{D.325}$$

$$= -\frac{1}{8.3145 \cdot -7.384 \cdot 10^{-5}} \tag{D.326}$$

$$= 1631.6 \text{ K}. \tag{D.327}$$

Note that this answer differs substantially from the fitted solution of 2463.42 K due to strong non-linearity of the trend.

D.4 Transition state theory

EXAM SOLUTION Transition State Theory 1

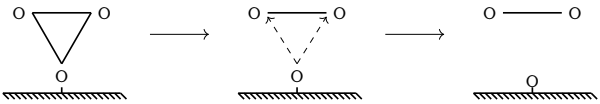


Figure D.6: *Schematic depiction of the initial, transition and final state of O_3 dissociation over a catalytic surface. Note that this is a side view, where the viewing direction is parallel to the catalytic surface. The reaction coordinate is shown as a dashed arrow in the image for the transition state.*

a) 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 $\frac{k_B T}{h}$. Another DOF is the rotational DOF and all other DOFs are vibrational. In the initial state, all DOFs are of a vibrational nature.

$$k = \frac{k_B T}{h} \frac{q_v^{(7)} q_r^{(1)}}{q_v^{(9)}} \exp\left(\frac{-\Delta E_{\text{act}}}{k_B T}\right) = \frac{k_B T}{h} q_{r,1D} \exp\left(\frac{-\Delta E_{\text{act}}}{k_B T}\right) \tag{D.328}$$

wherein we approximate

$$q_{r,1D} \to q_{t,1D}. \tag{D.329}$$

b) The Arrhenius-form activation energy is within this approximation given by:

$$\Delta E_{\text{act}}^{\text{arrhenius}} = k_B T^2 \frac{\partial \ln k}{\partial T} \tag{D.330}$$

Plugging the above rate expression into this formula yields for the activation energy

$$\Delta E_{\text{act}}^{\text{arrhenius}} = \Delta E_{\text{act}} + \frac{3}{2} k_B T. \tag{D.331}$$

If the two forms (Arrhenius and Eyring) are equal, this yields the following expression for the pre-exponential factor:

$$\nu_{\text{arrhenius}} = \frac{k_B T}{h} \cdot e^{3/2} \cdot q_r \tag{D.332}$$

c)

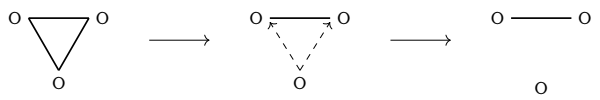


Figure D.7: *Schematic depiction of the initial, transition and final state of O_3 dissociation over a catalytic surface. Note that this is a top view, where the viewing direction is perpendicular to the catalytic surface. The reaction coordinate is shown as a dashed arrow in the image for the transition state.*

$$k = \frac{k_B T}{h} \frac{q_v^{(8)}}{q_v^{(9)}} \exp\left(\frac{-\Delta E_{\text{act}}}{k_B T}\right) = \frac{k_B T}{h} \exp\left(\frac{-\Delta E_{\text{act}}}{k_B T}\right) \tag{D.333}$$

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:

$$\Delta E_{\text{act}}^{\text{arrhenius}} = \Delta E_{\text{act}} + k_B T \tag{D.334}$$

And the corresponding pre-exponential factor becomes:

$$\nu_{\text{arrhenius}} = \frac{k_B T}{h} \cdot e \tag{D.335}$$

e) The important difference between situation (1) and (2) is that in situation (1) 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 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

$$K = \frac{Q_{\text{TS}}}{Q_{\text{IS}}} \tag{D.336}$$

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:

$$K = q_{v,\text{weak}} \cdot \frac{Q_{\text{TS}}^{\dagger}}{Q_{\text{IS}}} \cdot \frac{q_{\text{TS},e}}{q_{\text{IS},e}}, \tag{D.337}$$

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:

$$k = \kappa \frac{1}{1 - \exp\left(\frac{-h\nu}{k_B T}\right)} \frac{Q_{TS}^{\dagger}}{Q_{IS}} \exp\left(\frac{-\Delta E_{act}}{k_B T}\right). \tag{D.338}$$

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)

$$q_v = \frac{1}{1 - \exp\left(\frac{-h\nu}{k_B T}\right)} \tag{D.339}$$

$$\approx \frac{1}{1 - 1 + \left(\frac{-h\nu}{k_B T}\right)} \tag{D.340}$$

$$\approx \frac{k_B T}{h\nu} \tag{D.341}$$

f) To obtain the general expression for the Eyring equation, the identity $\nu = \kappa$ needs to be true in order to cancel out the κ in the equation.

EXAM SOLUTION Transition State Theory 3

a) The CO molecule consists of two atoms, which each have three independent degrees of freedom (i.e. x, y, and z direction). The dimensionality of the potential energy surface corresponds to these degrees of freedom and is thus a mapping from six-dimensional space to one-dimensional space:

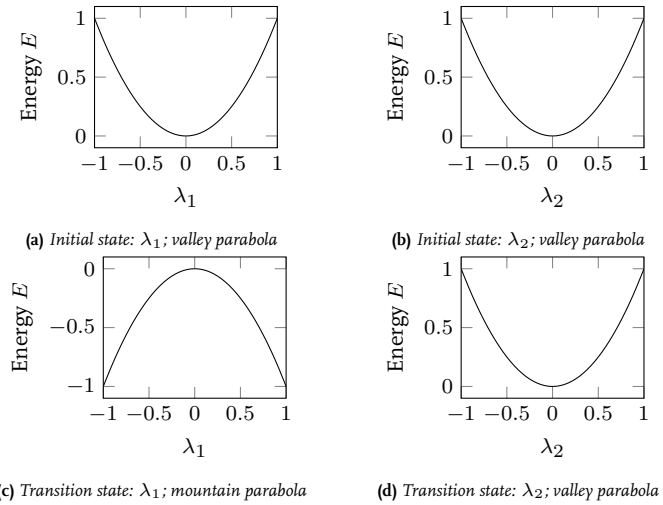
$$f : \mathbb{R}^6 \to \mathbb{R}. \tag{D.342}$$

b) The one-dimensional deconvoluted plots are provided in Figure D.8. There are three valley-parabola and one mountain-parabola.

c) Since the λ_1 direction corresponds to a mountain parabola, its force constant is negative. A negative force constant results in an imaginary frequency according to

$$\nu = \sqrt{\frac{k}{m}}. \tag{D.343}$$

The only motion in the transition state that has an imaginary frequency is the motion in the direction of the reaction coordinate. In fact, this is exactly the criterion that defines the transition



(a) *Initial state: λ_1; valley parabola*

(b) *Initial state: λ_2; valley parabola*

(c) *Transition state: λ_1; mountain parabola*

(d) *Transition state: λ_2; valley parabola*

Figure D.8: *One-dimensional deconvoluted potential energy curves.*

state. The chemical interpretation is thus as follows: the transition state corresponds to the highest point in energy in the direction of the reaction coordinate, while being a minimum in all other directions. Any perturbation in the direction of λ_1 in the transition state will result in a lowering of the energy, which is in line with the sign of the force constant.

d) In line with the reasoning of the previous subquestion: if the force constant is negative, this gives rise to an imaginary frequency. Thus that the wavenumber is complex because the imaginary part is nonzero.

e) For typical temperatures employed in catalysis ($T < 500$ K), typically only the ground state is occupied for the vibrational frequencies.

$$f = \frac{1}{1 - \exp\left(\frac{-h\omega}{k_B T}\right)} = 1.21 \approx 1, \tag{D.344}$$

with $\omega = 18 \cdot 10^{12}$ Hz and $T = 500$ K.

f) The initial state has six vibrational partition functions with $\nu_i = 1500\ \mathrm{cm}^{-1}$ and the transition state has five vibrational partition functions of which one has $\nu = 600\ \mathrm{cm}^{-1}$ and all the others $\nu_i = 1500\ \mathrm{cm}^{-1}$, thus

$$K^\dagger = \frac{\left(1 - \exp\left(\frac{-h\omega_1}{k_B T}\right)\right)^6}{\left(1 - \exp\left(\frac{-h\omega_1}{k_B T}\right)\right)^4 \left(1 - \exp\left(\frac{-h\omega_2}{k_B T}\right)\right)}, \tag{D.345}$$

where $\omega_1 = c \cdot \nu_1 = 1500 \cdot 10^2 \cdot c = 450$ THz and $\omega_2 = 18$ THz. Thus the equilibrium constant

between initial state and final state yields:

$$K^\dagger = \frac{\left(1 - \exp\left(\frac{-h\omega_1}{k_\mathrm{B}T}\right)\right)^2}{\left(1 - \exp\left(\frac{-h\omega_2}{k_\mathrm{B}T}\right)\right)} = \frac{1}{0.8223\ldots} \approx 1.21 \tag{D.346}$$

The pre-exponential factor is thus:

$$\nu_{\text{pre-exp}} = \frac{k_\mathrm{B}T}{h} K^\dagger \approx 1.04 \cdot 10^{13} \cdot 1.21 = 1.26 \cdot 10^{13}\ \mathrm{s}^{-1} \tag{D.347}$$

g) From transition state theory, the reaction rate constant is given by

$$k^{\text{tst}} = \frac{k_\mathrm{B}T}{h} K^\dagger \exp\left(\frac{-\Delta E_{\text{act}}}{k_\mathrm{B}T}\right) \tag{D.348}$$

$$= \nu_{\text{pre-exp}} \exp\left(\frac{-\Delta E_{\text{act}}}{k_\mathrm{B}T}\right). \tag{D.349}$$

The Arrhenius-form activation energy is given by

$$\Delta E_{\text{act}}^{\text{arr}} = k_\mathrm{B}T^2 \frac{\partial \ln k}{\partial T} \tag{D.350}$$

$$= k_\mathrm{B}T^2 \frac{\partial}{\partial T}\Big(\ln T + 2\ln\left(1 - \exp\left(\frac{-h\omega_1}{k_\mathrm{B}T}\right)\right)\cdots$$

$$\cdots - \ln\left(1 - \exp\left(\frac{-h\omega_2}{k_\mathrm{B}T}\right)\right) - \frac{\Delta E_{\text{act}}}{k_\mathrm{B}T}\Big) \tag{D.351}$$

$$= k_\mathrm{B}T + \Delta E_{\text{act}} - \frac{2h\omega_1 \exp\left(\frac{-h\omega_1}{k_\mathrm{B}T}\right)}{1 - \exp\left(\frac{-h\omega_1}{k_\mathrm{B}T}\right)} + \frac{h\omega_2 \exp\left(\frac{-h\omega_2}{k_\mathrm{B}T}\right)}{1 - \exp\left(\frac{-h\omega_2}{k_\mathrm{B}T}\right)} \tag{D.352}$$

$$\approx \Delta E_{\text{act}} + k_\mathrm{B}T \tag{D.353}$$

The reason we can neglect the last two terms is because they are much smaller than ΔE_{act} or $k_\mathrm{B}T$. This should not come as a surprise as we are basically calculating the energetic contribution of vibrational states above the ground state. We already found that under typical conditions only the ground state is occupied, thus these contributions should be negligible.

To calculate the Arrhenius-style pre-exponential factor, we simply use the principle that both versions of the reaction rate constant should (of course) be equal to each other

$$k^{\text{tst}} = k^{\text{arr}} \tag{D.354}$$

$$\frac{k_\mathrm{B}T}{h} K^\dagger \exp\left(\frac{-\Delta E_{\text{act}}}{k_\mathrm{B}T}\right) = \nu \exp\left(\frac{-\Delta E_{\text{act}} - k_\mathrm{B}T}{k_\mathrm{B}T}\right), \tag{D.355}$$

thus

$$\nu = \frac{k_\mathrm{B}T}{h} K^\dagger \exp(1) \tag{D.356}$$

EXAM SOLUTION Transition State Theory 4

a) CO has two atoms, hence $N_{DOF} = 3N = 6$.

b) In the transition state, one DOF in the direction of the reaction coordinate has a negative force constant and thus corresponds to an imaginary frequency.

c) The Eyring equations for the forward and backward reaction rate constants for CO dissociation are

$$k_f = \frac{k_B T}{h} \frac{q_v^{(4)} q_t}{q_v^{(4)} q_t^{(2)}} \exp\left(\frac{-\Delta E_{a,f}}{k_B T}\right), \tag{D.357}$$

$$k_b = \frac{k_B T}{h} \frac{q_v^{(4)} q_t}{q_v^{(6)}} \exp\left(\frac{-\Delta E_{a,b}}{k_B T}\right). \tag{D.358}$$

d) The equilibrium constant for CO dissociation is:

$$K = \frac{k_f}{k_b} \tag{D.359}$$

$$= \frac{1}{q_t^{(2)}} \exp\left(-\frac{\Delta E_{a,f} - \Delta E_{a,b}}{k_B T}\right) \tag{D.360}$$

$$= \frac{1}{q_t^{(2)}} \exp\left(\frac{-\Delta H_r}{k_B T}\right) \tag{D.361}$$

Note that you can also solve this question by starting from :

$$K = \prod_i q_i^{\nu_i} \tag{D.362}$$

$$= \frac{q_{FS}}{q_{IS}} \tag{D.363}$$

$$= \frac{1}{q_t^{(2)}} \frac{q_{e,FS}}{q_{e,IS}} \tag{D.364}$$

$$= \frac{1}{q_t^{(2)}} \exp\left(\frac{-\Delta H_r}{k_B T}\right) \tag{D.365}$$

e) Note that there is a single translational partition function in the numerator and two in the denominator, effectively giving one $q_t = L\frac{\sqrt{2\pi m k_B T}}{h}$ term.

$$\Delta E_a^{arr} = k_B T^2 \frac{\partial \ln k}{\partial T} \tag{D.366}$$

$$= k_B T^2 \frac{\partial}{\partial T} \ln \left(\frac{k_B T}{h} \frac{q_v^{(4)} q_t}{q_v^{(4)} q_t^{(2)}} \exp\left(\frac{-\Delta E_{a,f}}{k_B T} \right) \right) \tag{D.367}$$

$$= k_B T^2 \frac{\partial}{\partial T} \left(\ln T - \frac{1}{2} \ln T - \frac{\Delta E_{a,f}}{k_B T} \right) \tag{D.368}$$

$$= \frac{1}{2} k_B T + \Delta E_{a,f} \tag{D.369}$$

Arrhenius and Eyring theory should give the same rate constants, hence

$$k^{arr} = k^{tst}. \tag{D.370}$$

From the above expression, it follows that:

$$\nu^{arr} = \frac{k^{tst}}{\exp\left(-\frac{\frac{1}{2} k_B T + \Delta E_{a,f}}{k_B T} \right)} \tag{D.371}$$

$$= \frac{\frac{k_B T}{h} \frac{q_t}{q_t^{(2)}} \exp\left(\frac{-\Delta E_{a,f}}{k_B T} \right)}{\exp\left(-\frac{\frac{1}{2} k_B T + \Delta E_{a,f}}{k_B T} \right)} \tag{D.372}$$

$$= \frac{k_B T}{h} \frac{q_t \exp\left(\frac{1}{2}\right)}{q_t^{(2)}} \tag{D.373}$$

Note that it is **not** allowed to cancel out two of the translational partition functions as these are *a priori* not equal in magnitude.

EXAM SOLUTION Transition State Theory 5

a) C_5H_6 has 11 atoms, hence $N_{DOF} = 3N = 33$. Because C_5H_6 is in the gas phase, it has 3 translational, 3 rotational and 27 vibrational degrees of freedom.

b) The initial state corresponds to two molecules, hence 6 translational, 6 rotational and 54 vibrational degrees of freedom.

c) The transition state should be treated as a single gas phase molecule, hence 3 translational, 3 rotational and 60 vibrational degrees of freedom of which one DOF corresponds to the imaginary frequency. (alternatively, 59 real vibrational DOF and 1 imaginary vibrational DOF).

d) The final state is a single gas phase molecule, hence 3 translational, 3 rotational and 60 vibrational degrees of freedom.

e) Reaction rate constant can be written as:

$$k = \frac{k_\mathrm{B}T}{h} \frac{(2\pi m_{ts} k_\mathrm{B}T)^{3/2} \left(8\pi^2 k_\mathrm{B}T\right)^{3/2} \sqrt{I_{ts}} h^6}{\left[\left(2\pi m_{cpd} k_\mathrm{B}T\right)^{3/2} \left(8\pi^2 k_\mathrm{B}T\right)^{3/2}\right]^2 \sqrt{\pi} I_{cpd}} \exp\left(-\frac{\Delta E_{\text{act, elec}} + \Delta E_{\text{zpe}}}{k_\mathrm{B}T}\right), \quad \text{(D.374)}$$

where I_{cpd} corresponds to the product of the individual moments of inertia around the three rotational axes.

f)

$$\Delta E_{\text{act}}^{\text{arr}} = \Delta E_{\text{act}} - 2k_\mathrm{B}T \quad \text{(D.375)}$$

$$k_0 = \frac{k_\mathrm{B}T}{h} \frac{q_{\text{rot}}^{\ddagger,(3)} q_{\text{trans}}^{\ddagger,(3)}/V}{q_{\text{rot}}^{(6)} q_{\text{trans}}^{(6)}/V^2} \exp(-2) \quad \text{(D.376)}$$

g) Collision theory considers molecules to be rigid spheres by which they can only contain translational degrees of freedom. In contrast, in the transition state theory all configurational (i.e. including rotational and vibrational) degrees of freedom are taken into account.

EXAM SOLUTION Transition State Theory 6

a) The total translational partition function for an ensemble of N distinguishable[5] molecules is given by

$$Q_\mathrm{t} = q_\mathrm{t}^N \quad \text{(D.377)}$$

From this, the translational entropy is calculated by

$$\begin{aligned} S_t &= \frac{\partial}{\partial T}\left(k_\mathrm{B}T \ln Q_t\right) && \text{(D.378)} \\ &= \frac{\partial}{\partial T}\left(k_\mathrm{B}T \left(N \ln q_t\right)\right) && \text{(D.379)} \\ &= k_\mathrm{B}\left(N \ln q_t\right) + N k_\mathrm{B}T \frac{\partial}{\partial T} \ln q_t && \text{(D.380)} \\ &= N k_\mathrm{B} \ln\left(q_t \cdot \exp\left(\frac{3}{2}\right)\right) && \text{(D.381)} \end{aligned}$$

b) The total rotational partition function for an ensemble of N distinguishable[6] molecules is given by

$$Q_\mathrm{r} = q_\mathrm{r}^N \quad \text{(D.382)}$$

[5] We wait to introduce the correction factor $\frac{1}{N!}$ to account for the indistinguishability till subquestion e). So technically we are now deriving the expression for N **distinguishable** molecules.

[6] See note 1.

From this, the rotational entropy is calculated by

$$S_r = \frac{\partial}{\partial T}\left(k_\mathrm{B} T \ln Q_r\right) \tag{D.383}$$
$$= \frac{\partial}{\partial T}\left(k_\mathrm{B} T \left(N \ln q_r\right)\right) \tag{D.384}$$
$$= k_\mathrm{B}\left(N \ln q_r\right) + N k_\mathrm{B} T \frac{\partial}{\partial T} \ln q_r \tag{D.385}$$
$$= N k_\mathrm{B} \ln\left(q_r \cdot \exp\left(\frac{3}{2}\right)\right) \tag{D.386}$$

c) The total vibrational partition function corresponding to a single normal mode for an ensemble of N distinguishable[7] molecules is given by

$$Q_\mathrm{v} = q_\mathrm{v}^N \tag{D.387}$$

$$S_v = \frac{\partial}{\partial T}\left(k_\mathrm{B} T \ln Q_v\right) \tag{D.388}$$
$$= \frac{\partial}{\partial T}\left(k_\mathrm{B} T \left(N \ln q_v\right)\right) \tag{D.389}$$
$$= k_\mathrm{B}\left(N \ln q_v\right) + N k_\mathrm{B} T \frac{\partial}{\partial T} \ln q_v \tag{D.390}$$
$$= N k_\mathrm{B}\left(\frac{\frac{h\nu}{k_\mathrm{B}T}}{\exp\left(\frac{h\nu}{k_\mathrm{B}T}\right) - 1} - \ln\left(1 - \exp\left(-\frac{h\nu}{k_\mathrm{B}T}\right)\right)\right) \tag{D.391}$$
$$= N k_\mathrm{B}\left(\ln\left(q_v\right) + \frac{\frac{h\nu}{k_\mathrm{B}T}}{\exp\left(\frac{h\nu}{k_\mathrm{B}T}\right) - 1}\right) \tag{D.392}$$

d)
- Ethylene has 3 translational, 3 rotational and 12 vibrational degrees of freedom.
- Butadiene has 3 translational, 3 rotational and 24 vibrational degrees of freedom.
- The transition state complex has 3 translational, 3 rotational, 41 vibrational degrees of freedom and one imaginary frequency.

From this, the Eyring equation becomes

$$k = \frac{k_\mathrm{B} T}{h} \frac{q_{t,ts,3d} q_{r,ts,3d} \prod_i^{41} q_{i,v,ts}}{q_{t,e,3d} q_{r,e,3d} \prod_i^{12} q_{i,v,e} \times q_{t,b,3d} q_{r,b,3d} \prod_i^{24} q_{i,v,b}} \exp\left(-\frac{\Delta E^\ddagger}{k_\mathrm{B} T}\right), \tag{D.393}$$

wherein the subscript e and b and ts refer to ethylene, butadiene and the transition state, respectively and $\prod_i^N$ highlights the fact that the vibrational partition functions cannot *a priori* be assumed to be equal. Furthermore, $\Delta E^\ddagger$ corresponds to the ZPE-corrected electronic activation energy.

e) Let us first derive a formula for the entropy of a single state, so either for ethylene, butadiene or the transition state. Let us not forget that we still need to introduce the correction factor $1/N!$ to accomodate the fact that molecules of the same type are indistinguishable from a quantum mechanical perspective.

[7] See note 1.

$$\Delta S_{\text{state}} = \frac{\partial}{\partial T}\left(k_{\text{B}} T \ln Q_{\text{total}}\right) \tag{D.394}$$

$$= \frac{\partial}{\partial T}\left(k_{\text{B}} T \ln\left(\frac{1}{N!}\left[q_{t,3d} \times q_{r,3d} \times \prod_i q_{v,i}\right]^N\right)\right) \tag{D.395}$$

$$= \frac{\partial}{\partial T}\left(N k_{\text{B}} T\left(\ln q_{t,3d} + \ln q_{r,3d} + \sum_i \ln q_{v,i}\right) - N \ln N + N\right) \tag{D.396}$$

$$= S_t + S_r + \sum_i S_{v,i} - \ln N \tag{D.397}$$

The first three terms, i.e. S_t, S_r and S_v are those that correspond to the subquestions (a), (b) and (c) and we can thus readily calculate using our previous answer the total entropy for a single state.[8]

$$\frac{\Delta S}{N k_{\text{B}}} = \ln\left(q_t \frac{\exp\left(\frac{3}{2}\right)}{N}\right) + \ln\left(q_r \exp\left(\frac{3}{2}\right)\right) + \sum_i \left(\ln\left(q_{v,i}\right) + \frac{\frac{h\nu}{k_{\text{B}}T}}{\exp\left(\frac{h\nu}{k_{\text{B}}T}\right) - 1}\right) \tag{D.398}$$

This can be done for all three states (ethylene, butadiene and the transition state) by which the entropy of activation can be readily determined from

$$\Delta S^{\ddagger} = \Delta S_{\text{TS}} - \Delta S_{\text{ethylene}} - \Delta S_{\text{butadiene}}. \tag{D.399}$$

Alternatively, one can answer the following:

(a) The entropic contribution of the nuclear and electronic partition functions can be neglected as we can assume that the ground state configurations are non-degenerate. (recall that entropy measures the number of different configurations!)

(b) The entropy of activation can be guestimated to be negative as the configurational degrees of freedom will vastly decrease when two freely moving gas molecules have to meet to form a weakly bound transition state complex.

EXAM SOLUTION Transition State Theory 7

a) First, we calculate d^2,

$$d^2 = \left(\frac{1.5 \cdot 10^{-10} + 2.8 \cdot 10^{-10}}{2}\right)^2 = 4.6 \cdot 10^{-20}\ \text{m}^2 \tag{D.400}$$

[8] It is customary to insert the $-\ln N$ in the term corresponding to the translational partition function.

then the reduced mass.

$$\mu = \frac{1.008 \cdot 2 \cdot 79.904 \cdot 2}{1.008 \cdot 2 + 79.904 \cdot 2} \cdot 1.66 \cdot 10^{-27} = 3.30 \cdot 10^{-27} \text{ kg} \tag{D.401}$$

Finally, we plug in the values and we get the value for the collision frequency.

$$k = \pi \cdot 4.6 \cdot 10^{-20} \left(\frac{8k_b \cdot 450}{\pi \cdot 3.30 \cdot 10^{-27}} \right)^{1/2} = 3.16 \cdot 10^{-16} \text{ collisions} \cdot \text{m}^3 \cdot \text{s}^{-1} \tag{D.402}$$

b) The unit for $k_{collision}$ is collisions $\cdot$ m$^3 \cdot$ 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)

$$k_{\text{reaction}} = k_{\text{collision}} \cdot \exp\left(\frac{-\Delta E_a}{RT} \right) = 3.16 \cdot 10^{-16} \cdot \exp\left(\frac{-200 \cdot 10^3}{R \cdot 450} \right) \tag{D.403}$$

$$= 1.9206713 \cdot 10^{-39} \text{ m}^3 \cdot \text{s}^{-1} \tag{D.404}$$

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.)

EXAM SOLUTION Transition State Theory 8

a) According to transition state theory, the expression for the reaction rate constant for the dissociative adsorption of methane is:

$$k = \frac{k_\text{B}T}{h} \frac{q^\ddagger}{q_\text{is}} \exp\left(-\frac{\Delta E_{\text{elec,act}}}{k_\text{B}T} \right) \tag{D.405}$$

$$= \frac{k_\text{B}T}{h} \frac{1}{q_\text{t}^{(3)} q_\text{r}^{(3)}} \exp\left(-\frac{\Delta E_{\text{elec,act}} + \Delta E_{\text{zpe}}}{k_\text{B}T} \right) \tag{D.406}$$

$$= \frac{k_\text{B}T}{h} \left[\left(\frac{\sqrt{2\pi m k_\text{B}T}}{h} \right)^3 V \frac{\sqrt{\pi}}{\sigma} \sqrt{\frac{T^3}{\Theta_A \Theta_B \Theta_C}} \right]^{-1} \cdots$$

$$\cdots \exp\left(-\frac{\Delta E_{\text{elec,act}} + \Delta E_{\text{zpe}}}{k_\text{B}T} \right) \tag{D.407}$$

b) The internal energy of activation is:

$$\Delta U^\dagger = k_\mathrm{B}T^2 \frac{\partial}{\partial T} \ln \left\{ \frac{k_\mathrm{B}T}{h} \left[\left(\frac{\sqrt{2\pi m k_\mathrm{B}T}}{h} \right)^3 V \frac{\sqrt{\pi}}{\sigma} \sqrt{\frac{T^3}{\Theta_A \Theta_B \Theta_C}} \right]^{-1} \cdots \right.$$
$$\left. \cdots \exp\left(-\frac{\Delta E_\mathrm{elec,act} + \Delta E_\mathrm{zpe}}{k_\mathrm{B}T} \right) \right\} - k_\mathrm{B}T \tag{D.408}$$
$$= \Delta E_\mathrm{elec,act} + \Delta E_\mathrm{zpe} + k_\mathrm{B}T - \frac{3}{2}k_\mathrm{B}T - \frac{3}{2}k_\mathrm{B}T - k_\mathrm{B}T \tag{D.409}$$
$$= \Delta E_\mathrm{elec,act} + \Delta E_\mathrm{zpe} - 3k_\mathrm{B}T \tag{D.410}$$

c) The entropy of activation is:

$$\Delta S^\dagger = \frac{\partial}{\partial T} \left(k_\mathrm{B}T \ln \left\{ \left[\left(\frac{\sqrt{2\pi m k_\mathrm{B}T}}{h} \right)^3 V \frac{\sqrt{\pi}}{\sigma} \sqrt{\frac{T^3}{\Theta_A \Theta_B \Theta_C}} \right]^{-1} \cdots \right. \right.$$
$$\left. \left. \cdots \exp\left(-\frac{\Delta E_\mathrm{elec,act} + \Delta E_\mathrm{zpe}}{k_\mathrm{B}T} \right) \right\} \right) \tag{D.411}$$
$$= k_\mathrm{B} \ln \left\{ \left[\left(\frac{\sqrt{2\pi m k_\mathrm{B}T}}{h} \right)^3 V \frac{\sqrt{\pi}}{\sigma} \sqrt{\frac{T^3}{\Theta_A \Theta_B \Theta_C}} \right]^{-1} \right\} - 3k_\mathrm{B} \tag{D.412}$$

d) The Gibbs free energy of activation is:

$$\Delta G^\dagger = \Delta U^\dagger - T\Delta S^\dagger \tag{D.413}$$
$$= \Delta E_\mathrm{elec,act} + \Delta E_\mathrm{zpe} - k_\mathrm{B}T \ln \left\{ \left[\left(\frac{\sqrt{2\pi m k_\mathrm{B}T}}{h} \right)^3 \cdots \right. \right.$$
$$\left. \left. \cdots V \frac{\sqrt{\pi}}{\sigma} \sqrt{\frac{T^3}{\Theta_A \Theta_B \Theta_C}} \right]^{-1} \right\}. \tag{D.414}$$

e) According to definition

$$k = \frac{k_\mathrm{B}T}{h} \exp\left(-\frac{\Delta G^\dagger}{k_\mathrm{B}T} \right) \tag{D.415}$$
$$= \frac{k_\mathrm{B}T}{h} \exp\left(-\frac{1}{k_\mathrm{B}T} \left(\Delta E_\mathrm{elec,act} + \Delta E_\mathrm{zpe} \cdots \right. \right.$$
$$\left. \left. \cdots - k_\mathrm{B}T \ln \left\{ \left[\left(\frac{\sqrt{2\pi m k_\mathrm{B}T}}{h} \right)^3 V \frac{\sqrt{\pi}}{\sigma} \sqrt{\frac{T^3}{\Theta_A \Theta_B \Theta_C}} \right]^{-1} \right\} \right) \right) \tag{D.416}$$
$$= \frac{k_\mathrm{B}T}{h} \left[\left(\frac{\sqrt{2\pi m k_\mathrm{B}T}}{h} \right)^3 V \frac{\sqrt{\pi}}{\sigma} \sqrt{\frac{T^3}{\Theta_A \Theta_B \Theta_C}} \right]^{-1} \cdots$$
$$\cdots \exp\left(-\frac{\Delta E_\mathrm{elec,act} + \Delta E_\mathrm{zpe}}{k_\mathrm{B}T} \right), \tag{D.417}$$

which completely matches the result of subquestion (a).

EXAM SOLUTION Transition State Theory 9

a) The overall reaction is

$$C_2H_4 + H_2 \rightleftarrows C_2H_6 \tag{D.418}$$

H_2 is a homonuclear diatomic. The total number of motional degrees of freedom (DOF) is $3N = 6$. There are 3 translational DOF, 2 rotational DOF (because the molecule is invariant to rotation around the interatomic axis) and 1 vibrational DOF.

C_2H_4 has 6 atoms. The total number of motional DOF is $3N = 18$. There are 3 translational DOF, 3 rotational DOF and $18 - 6 = 12$ vibrational DOF.

b) The transition state complex will take the form of $[E{-}{-}H_2]$ with E denoting ethylene. This complex has 8 atoms, with $3N = 24$ motional DOF. There are 3 translational DOF, 2 rotational DOF and $24 - 6 = 18$ vibrational DOF. Of these 18 vibrational DOF, 17 will be real and 1 will be imaginary (corresponding to the reaction coordinate).

c) The rate constant in the forward direction[9] is given by

$$k^+ = \frac{k_B T}{h} \frac{Q_{TS}/V}{Q_E/V \times Q_{H2}/V} \exp\left(\frac{-\Delta E_{\text{act,elec}}}{k_B T}\right) \tag{D.419}$$

Here, Q_{TS} is the motional partition function of the transition state without the imaginary mode. $Q_{IS} = Q_E Q_H$ is the motional partition function of the initial state. Using the listing of the partition functions obtained in the previous questions, these take the following forms

$$Q_{TS} = \prod_{i=1}^{3} q_{r,i}^{TS} \prod_{j=1}^{3} q_{t,j}^{TS} \prod_{k=1}^{17} q_{v,k}^{TS} \tag{D.420}$$

$$Q_{\text{E}} = \prod_{i=1}^{3} q_{r,i}^{\text{E}} \prod_{j=1}^{3} q_{t,j}^{\text{E}} \prod_{k=1}^{12} q_{v,k}^{\text{E}} \tag{D.421}$$

$$Q_{\text{H}_2} = \prod_{i=1}^{2} q_{r,i}^{\text{H}_2} \prod_{j=1}^{3} q_{t,j}^{\text{H}_2} q_{v,1}^{\text{H}_2} \tag{D.422}$$

The translational modes depend on the mass of each molecule/complex:

$$\prod_{j=1}^{3} q_{t,j}^{(n)} = V \left(\frac{2\pi m^{(n)} k_B T}{h^2}\right)^{\frac{3}{2}} \tag{D.423}$$

The rotational modes depend on the moment of inertia of each molecule/complex, as well as their symmetry character. For ethylene and the TS-complex we have to use the asymmetrical form of the rotational partition function

$$\prod_{j=1}^{3} q_{r,j}^{(n)} = \frac{1}{\sigma} \sqrt{\frac{\pi T^3}{\Theta_A^{(n)} \Theta_B^{(n)} \Theta_C^{(n)}}} \tag{D.424}$$

[9] This rate constant is constructed using a number-density based equilibrium constant.

For hydrogen we use the expression for homonuclear diatomics

$$\prod_{i=1}^{2} q_{r,i}^{\mathrm{H_2}} = \frac{4\pi^2 I_{\mathrm{H_2}} k_{\mathrm{B}} T}{h^2} \tag{D.425}$$

The vibrational modes depend on the frequencies of the internal vibrations for each molecule

$$q_{v,k}^{(n)} = \frac{\exp\left(\frac{-h\nu_k^{(n)}}{2k_{\mathrm{B}}T}\right)}{1-\exp\left(\frac{-h\nu_k^{(n)}}{k_{\mathrm{B}}T}\right)} \tag{D.426}$$

Note here the inclusion of the ZPE term.

Assuming all gases to be ideal, the rate equation based on the partial pressures is then given by

$$r = \frac{\partial p_C}{\partial t} \tag{D.427}$$

$$= k^{+}\left(\frac{1}{k_{\mathrm{B}}T}\right) P_{\mathrm{E}} P_{\mathrm{H_2}} \tag{D.428}$$

$$= \frac{V}{h}\frac{Q_{TS}}{Q_E Q_{\mathrm{H_2}}} \exp\left(\frac{-\Delta E_{\mathrm{act,elec}}}{k_{\mathrm{B}}T}\right) P_{\mathrm{E}} P_{\mathrm{H_2}} \tag{D.429}$$

Alternatively, one could build the expression in terms of the number-density of the gas phase reactants.[10] In that case, the reaction would be

$$r = \frac{\partial \rho_C}{\partial t} \tag{D.430}$$

$$= \frac{k_{\mathrm{B}}TV}{h}\frac{Q_{TS}}{Q_E Q_{\mathrm{H_2}}} \exp\left(\frac{-\Delta E_{\mathrm{act,elec}}}{k_{\mathrm{B}}T}\right) \rho_{\mathrm{E}} \rho_{\mathrm{H_2}} \tag{D.431}$$

d) If the vibrational temperature is much larger than the (thermodynamic) temperature

$$\Theta_v = \frac{h\nu}{k_{\mathrm{B}}} >> T \tag{D.432}$$

This makes the term in the exponential become strongly negative, such that

$$\frac{1}{1-\exp\left(-\frac{\Theta_v}{T}\right)} \approx \frac{1}{1-0} = 1 \tag{D.433}$$

This can occur e.g. if the barrier for vibrational excitation is large with respect to the available thermal (kinetic) energy. Then, only the vibrational ground state will be occupied, corresponding to $q_{\mathrm{vib}} = 1$ (relative to the ZPE level).

[10] Both a number-based as well as a pressure-based reaction rate equation are valid.

EXAM SOLUTION Transition State Theory 10

a) The potential energy curve is by definition oriented from initial to final state alongside the reaction coordinate. This reaction coordinate lies alongside the diagonal of the contour plot. The potential energy curve should correspond to a quasi-parabolic profile wherein the bonded state (cyclohexene) is lower in energy as compared to the dissociated state (ethylene and butadiene). The transition state lies higher than both the initial and final state.

b)
- The initial state lies at (3.0, 3.0)
- The final state lies at (1.6, 1.6)
- The transition state lies at (2.2, 2.2) and corresponds to highest point on the reaction coordinate.

The molecular complexes can be easily drawn by considering the C-C bond lengths.

c)
- The activation energy in the forward direction is 52.53 kJ/mol.
- The activation energy in the backward direction is 256.2 kJ/mol.

d) Using a three-point finite difference stencil (see exercise 4.7) and assuming a harmonic potential close around the stable point on the PES, the force constants can be found to be

$$k_{\parallel}^{\mathrm{FS}} = \frac{E(r_0 - h) - 2E(r_0) + E(r_0 + h)}{h^2} \tag{D.434}$$
$$= \frac{27.68 - 2 \cdot 0 + 3.48}{0.1^2} \tag{D.435}$$
$$= 3116\mathrm{kJ/A}^2 \tag{D.436}$$

$$k_{\perp}^{\mathrm{FS}} = \frac{E(r_0 - h) - 2E(r_0) + E(r_0 + h)}{h^2} \tag{D.437}$$
$$= \frac{15.71 - 2 \cdot 0 + 15.71}{0.1^2} \tag{D.438}$$
$$= 3142\mathrm{kJ/A}^2 \tag{D.439}$$

From these, the frequencies can be calculated by[11]

$$\omega = \sqrt{\frac{k}{m}}. \tag{D.440}$$

e) Using the same strategy as in the previous subquestion, the force constants are found to be

$$k_{\parallel}^{\mathrm{TS}} = \frac{E(r_0 - h) - 2E(r_0) + E(r_0 + h)}{h^2} \tag{D.441}$$
$$= \frac{244.52 - 2 \cdot 256.20 + 254.71}{0.1^2} \tag{D.442}$$
$$= -1317\mathrm{kJ/A}^2 \tag{D.443}$$

[11] Within the scope of this question, it is undefined which mass to use, so depending on your choice of the mass, different answers are possible.

$$k_{\perp}^{\mathrm{TS}} = \frac{E(r_0 - h) - 2E(r_0) + E(r_0 + h)}{h^2} \tag{D.444}$$

$$= \frac{257.36 - 2 \cdot 256.20 + 257.36}{0.1^2} \tag{D.445}$$

$$= 232\mathrm{kJ/A}^2 \tag{D.446}$$

The result as found here is in line with the definition of a transition state. There is a single imaginary frequency in the direction of the reaction coordinate and all other frequencies are real-valued. The most striking difference between this result and the one from the previous subquestion thus relates to the observation of a single imaginary frequency.

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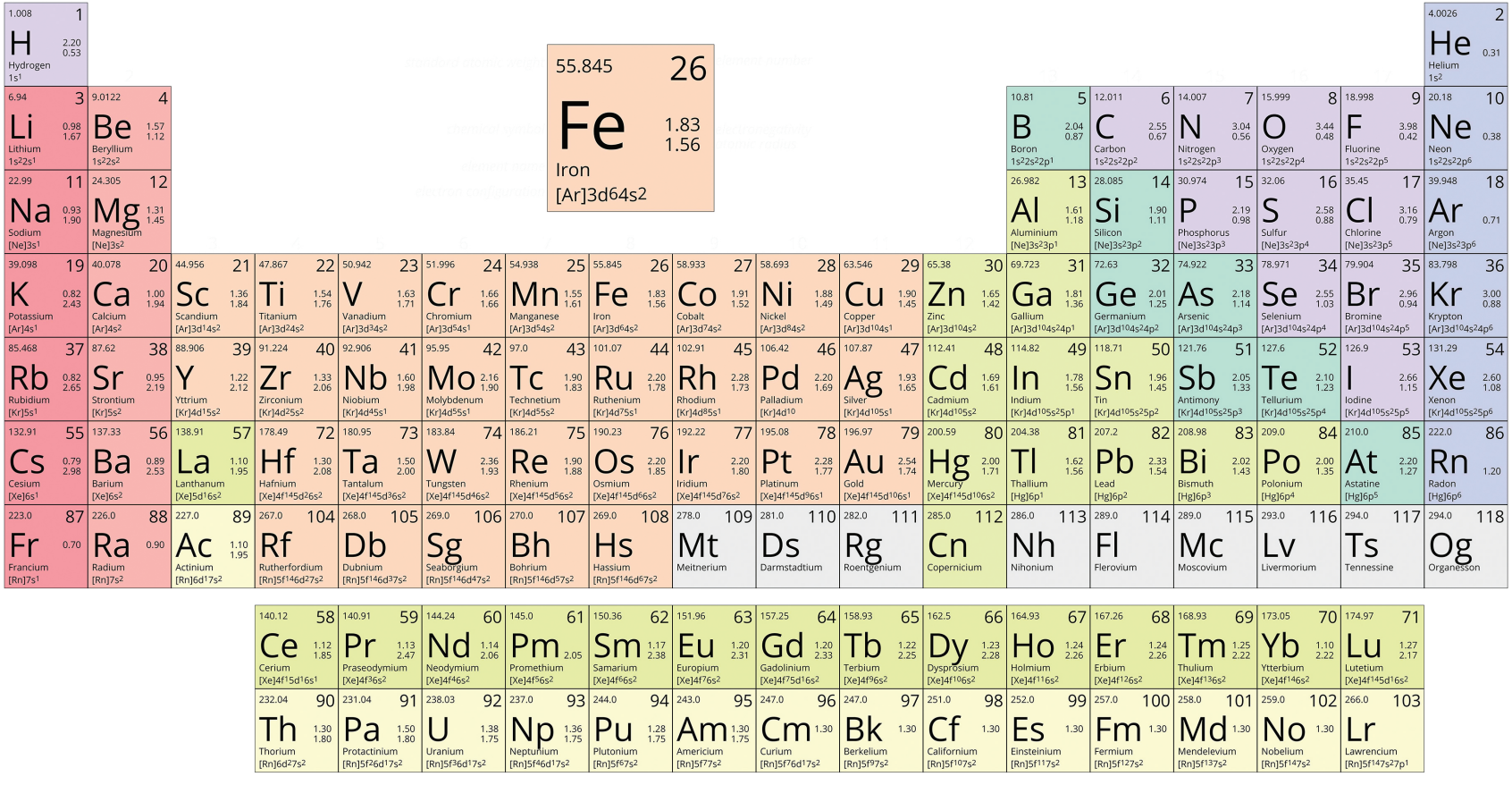
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