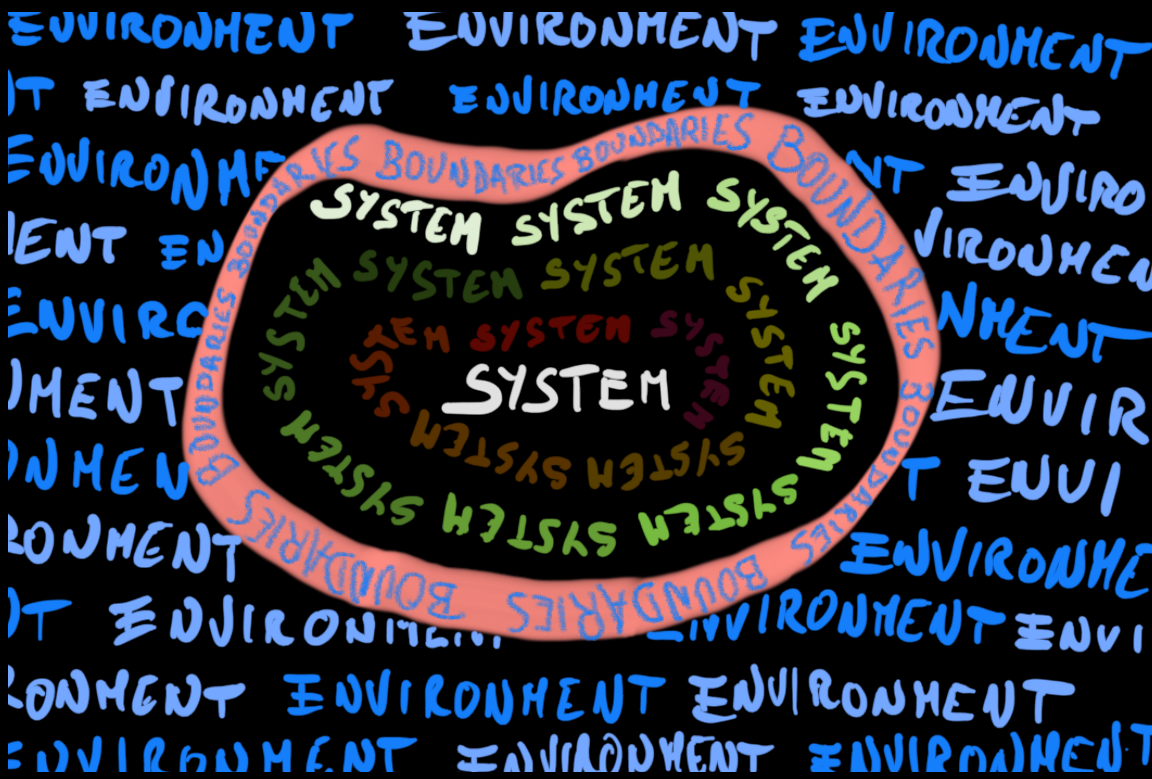
The Live Textbook of Physical Chemistry

Volume 1: Classical Thermodynamics and Chemical Kinetics



Roberto Peverati

$P^{\varepsilon}V^{\varepsilon} = R_a T_i$
research

The Live Textbook of Physical Chemistry, Volume 1

Which Way and How Fast

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Roberto Peverati

12 November 2026

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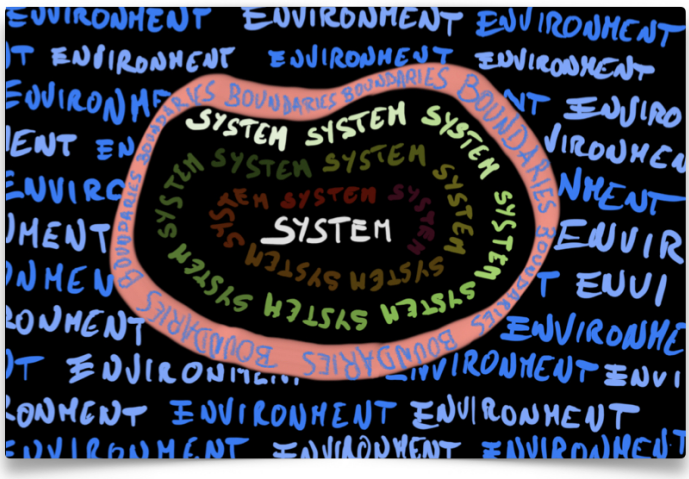
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Preface

Which Way and How Fast



This textbook is the official textbook for the Physical Chemistry 1 Course (CHM 3001) at Florida Institute of Technology.

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Author's Note to the August 2024 Edition

2024 marks the fifth year of existence for "The Live Textbook of Physical Chemistry." Faithful to my initial intent, the textbook has evolved substantially from its humble beginnings, and it continues to evolve to this day. Five years is a long time in education, and much has happened during this

period, including a pandemic that forced everyone to online teaching and learning, and the rise of generative AI in many fields, including education and Academia. I have big plans for the next phase of the book's evolution, but due to time constraints and the ever-increasing demands of academic duties, I had to postpone them for now. As such, the structure of the textbook has largely remained unchanged. If and when I will have time to restructure my entire courses, as well as the textbooks that go with them, I will present a true "Second Edition" of "The Live Textbook," but this is not it yet.

What I did have time to do, however, was to bring "The Live Textbook" up to the standards of a true academic textbook. Since its inception, I was well aware that there was a glaring omission: exercises. This summer, I finally had the opportunity to add new review sections at the end of every chapter, each containing practice problems and study questions. These new sections are designed to help readers verify their understanding of each chapter's content. More importantly, they are intended for my students to test their knowledge before exams. For this reason, they follow the same style as the questions I have used in my exams over the past five years. In fact, several of these questions and exercises are taken directly from previous exams. I can't promise that the same questions will be in future exams, but familiarizing with them will give a student the edge over students that decide to ignore them.

Finally, I am not pretending to have been unaware of the emergence of AI, generative models, and their impact on education, so I've tried to put them to a good use. In the past five years, I specifically used ChatGPT and Claude to rewrite some sections of this textbook, and I have made it clear when that was the case. These tools were especially valuable this summer for the new exercises and questions sections, where I abundantly used them to help supplement my existing materials with newly generated ones. I made sure the AI didn't hallucinate and to fix it when it did, so hopefully, everything is consistent. I must confess that I would not have met the deadline for the beginning of the semester without this new technology. Hopefully, this serves as a good example of how AI can be incorporated into the classroom.

Additionally, in the summer of 2026, I have reworked all of the pictures in the textbook to add alt-text descriptions. This is important for accessibility and it is (hopefully) compliant with the new Government directives on online accessibility for education.

As usual, if you spot any mistakes, I encourage you to reach out to me at the contacts listed above.

How to Use This Book

If you are a student in my course, please read this book carefully, since everything that will be in your exams is explained here! Since this book is specifically tailored for the CHM 3001 course at Florida Tech, there are no superfluous parts. In other words, everything in it might be subject to question in the quizzes and the final exam.

> Definitions and worked examples are numbered (e.g., Definition 1.1, Example 4.1) and are set apart from the rest of the text in boxes, blue for definitions and green for examples. Notes are highlighted in this format (indented, and following a grey vertical bar). Please study the definitions carefully since they are fundamental concepts that will be used several times in the remainder of the text, and they will be subject to quizzes and exams. Worked examples are essential for cementing the concepts, and you should attempt to solve them first without looking at the solution. Even if you were able to solve an example on your own, always read the solution after, since it might contain additional explanations expanding the main concepts in the text.

Navigating the book should be straightforward. On each page, there is a useful sidebar on the left that gives you an overview of all chapters, with a few important tools at its top. Arrows to move between chapters are at the bottom of each page. If you are old-school and prefer a pdf, you can download a printout by clicking on the corresponding icon at the top of the sidebar. If you are *really* old-school and prefer a printed book, the best solution is to download the pdf and print it yourself. It is a LaTeX book, and I can promise you it will look good on paper. However, I cannot provide physical copies to each student. In the sidebar, you will find a useful search box that is capable of searching the entire book. The most adventurous will find there a link to the raw GitHub source code. Feel free to head to the GitHub repository of this book and fork it.

For my students, each chapter of this book represents one week of work in the classroom and at home. The sidebar on the left will reflect your syllabus, as well as the main structure of the class on Canvas. The book is a live document, which means it will be updated throughout the semester with new material. While you are not required to check it every day, you might want to review each week's chapter before the lecture on Friday.

How This Book Is Organized

The book is divided into four parts:

- **Part I, The Laws of Thermodynamics** (chapters 1–6), builds the laws of thermodynamics with the simplest systems possible, mostly an ideal gas in a cylinder, and without chemical reactions. Along the way, we introduce heat, work, internal energy, enthalpy, and entropy, and the zeroth, first, second, and third laws. Part I ends with the definition of the standard state and with a first look at a chemical reaction.
- **Part II, Chemical Thermodynamics** (chapters 7–10), applies the laws to chemical reactions: the heat of reactions (thermochemistry), the thermodynamic potentials, the Gibbs energy, and chemical equilibrium.
- **Part III, Phase Equilibria and Solutions** (chapters 11–13), uses the same tools for real gases, for the phase transitions of pure substances, and for mixtures.
- **Part IV, Chemical Kinetics** (chapter 14), leaves equilibrium behind and asks how fast reactions go.

Many textbooks place thermochemistry right after the first law, since the heat of a reaction requires only the enthalpy. In this book, thermochemistry opens Part II instead, after the entropy. This way, all the laws are in place when we meet our first reactions, and we can ask the real chemical question from the start: not only how much heat a reaction releases, but whether it happens at all. Answering this question leads us directly to the thermodynamic potentials, which then appear as the tool that solves a concrete problem rather than as abstract definitions. The title of the book reflects the same structure: the first three parts tell us which way a process goes, and the last one tells us how fast.

A Note on Units

In general, we will use SI units or some of their multiples throughout the textbook, lectures, and exercises. For example, temperatures will be measured in kelvin (K), energetic terms will be measured in either joules (J) or kilojoules (kJ), while volumes will be measured in cubic meters, or more often in liters (L), where $1\,\mathrm{L} = 10^{-3}\,\mathrm{m}^3$. An important exception is made for pressures, which will be measured in bars (bar). This exception is not completely unjustified, since bar is still an (unconventional) multiple of the SI unit of pressure, pascal (Pa), where $1\,\mathrm{bar} = 10^5\,\mathrm{Pa}$. This choice is made to retain a reasonable similarity with the unit atmosphere (atm) which is extensively used in several other chemistry textbooks ($1\,\mathrm{atm} = 1.013\,\mathrm{bar}$) and in previous physical chemistry courses.

We will generally also try to avoid conversion between units, except for some trivial conversion between degrees Celsius (°C) and Kelvin, with the

conversion factor being an addition of 273.15 K. Other unconventional conversions might happen in some of the exercises, with the conversion factors always reported within the exercise itself. Additionally, we will avoid unnecessary conversion between the average atmospheric pressure and bars by setting $P_{\text{atm}} = 1\,\text{bar}$, rather than $P_{\text{atm}} = 1\,\text{atm} = 1.013\,\text{bar}$, an approximation that is mostly inconsequential, at least at the scale of the problems that we treat here.

A Note on the Use of AI

The November 2026 revision of this book was prepared with the help of Claude Code (Anthropic's Claude Opus 5.5), an AI assistant. The book, its structure, its scope, and its approach to teaching thermodynamics and kinetics are my own, developed over several years of teaching this course. In the revision, I used the AI as an assistant: to proofread the text, to rephrase passages, to draft new sections, figures, examples, and review questions following my outline and instructions, and to write the code for the computed figures. Every change was reviewed, corrected or rewritten, and approved by me, and I take full responsibility for the content of the book, including any remaining errors.

This live open textbook is distributed under the CC BY-NC-SA 4.0 License. The Python scripts that generate the figures are available under the MIT License. The first version of the book was funded in 2021 by the Florida Tech Open Educational Resources Grant Program, a collaboration of the Teaching Council, eEducation, and the Evans Library. That grant planted the seed; the current edition has since grown well beyond it, with a new structure, new chapters and sections, and new figures throughout.

Part I.

The Laws of Thermodynamics

1. Introduction to Thermodynamics

Why does a match burn once we strike it, while the ashes never turn back into a match? Why does salt dissolve in water but sand does not? How much heat do we get from burning a liter of gasoline, and how much of it can we actually turn into work? And when a reaction stops, why does it stop where it does, and not sooner or later? Every chemist faces questions like these, and thermodynamics is the part of physical chemistry that answers them. The remarkable thing is that thermodynamics answers them without knowing anything about molecules. It works only with quantities that we can measure in the lab, such as temperature, pressure, volume, and heat, and it builds a few simple laws on top of them. Because it does not depend on any particular model of matter, nothing that we will learn about atoms and molecules later will ever force us to change it.

Before we can use these laws, we need a few tools. In this chapter, we will introduce them: a gentle version of calculus, which is the language thermodynamics is written in; the idea of a thermodynamic system, which is the piece of the universe we decide to study; and the variables that describe it, with the important distinction between state and path functions. None of these tools is difficult on its own, but we will use all of them in every chapter that follows, so it is worth taking the time to get comfortable with them now.

1.1. Calculus for Physical Chemistry: Slicing and Gluing

Calculus is a powerful mathematical tool that helps us understand and analyze change. At its core, calculus involves two main procedures: differentiation and integration. These concepts are fundamental to the study of thermodynamics, as they enable us to examine how physical systems change. Undergraduate students often find calculus intimidating due to its rigorous presentation in mathematical courses. However, a strong mathematical foundation, while beneficial, is not always mandatory to study thermodynamics effectively.

If you are a student who lacks confidence in mathematics, I encourage you not to be deterred by the presence of calculus in this physical chemistry textbook. If you break this initial wall of fear for calculus, you might find this textbook quite rewarding. After all, we will finally explain where all those unmemorable formulas that you've been presented in introductory general chemistry courses are coming from. To facilitate your task, we will present in this chapter a simplified view of calculus. The starting point will be a basic question: how do we measure things in science? To answer this question, we will use calculus to measure the length of an object. At a first glance, this approach might seem pedantic. Why do we need to use calculus, with all of its mathematical complications, when we can just grab a ruler and stack it against our object to measure its length? However, we need to remind ourselves that our ultimate goal is physical chemistry, and calculus is the language of this field. By focusing on the straightforward task of measuring a simple length, we aim to make calculus more accessible and less daunting.[1] From this simple starting point, we will expand our horizon to introduce the central topic of this textbook: Thermodynamics. Our main focus will be on the relationship between chemistry and thermodynamics, but since this is an advanced undergraduate textbook, we will need to do that from a rigorous perspective. If we want to see it in simple terms, we either deal with the approach of not explaining where things are coming from that is abundantly used in freshman chemistry courses, or we make the effort of learning a bit of calculus so we can use it to understand the world.

1.1.1. Differentiation: Infinite Slicing

Differentiation can be thought of as "slicing an object into infinitely thin pieces" to understand how it changes at a specific point. Imagine you have a long stick and you want to measure how its length changes along a specific direction. To do this, you would cut the stick into infinitely thin slices. Each slice is so thin that its change in length is practically infinitesimal. By examining each of these tiny slices and how they change, you can understand the rate at which the stick's length changes at any given point. This process of infinite slicing is called differentiation, and it is the most powerful tool to understand things that change, that is, most of the things we are interested in science.

How so? Let's look at a simple example. If we start from a stick of length L, we can infinitely slice it into infinitesimally small pieces of length dL. These incredibly tiny pieces are called **differentials** of the original quantity, in this particular case, the length of our stick. The beauty of these

[1] I apologize in advance to the mathematicians that will read this book and cringe at the several unexplained approximations I have made. I am fully aware of the dangers of not introducing these concepts rigorously, but some compromises have to be made…

differentials, dL, is that they don't really depend on how long our object initially was: they will always be *infinitesimally small*. Imagine, for example, that you start with an object whose length is 1 m. After you slice it an infinite amount of times, each differential could be pictured as a length of 0.000[...]0001 m, where we have replaced an infinite amount of zeros with the notation [...]. If we start instead with a second object whose length is 1 km, we end up with differentials that are just as infinitesimally small. This picture with infinitely many zeros is only a way to visualize the idea: a differential is smaller than any number that we could write down, no matter how many zeros we use.

Now, through some mathematical magic, these strange numbers with an infinite amount of zeros, are essentially the closest thing you can get to 0, without practically being 0. For this reason, they can be used much more effectively than something that purely doesn't exist.[2] The key word here is *essentially*, because the differentials are as close to zero as we want, but they still contain some fundamental information related to the original objects. In the first place, they still have the dimension (and the units) of the original quantity: dL is an infinitesimal *length*, measured in meters, and it cannot be compared with, say, an infinitesimal time. Additionally, the differentials will also contain information on the rate of change (the "slope") of the length in the original objects. The question that remains is: How are we going to access this apparently hidden information? In other words, how are we going to reconstruct the length of the original object from the differentials? The answer is surprisingly simple: By comparing different differentials to each other. More specifically, despite their zeroness, we are allowed to calculate the ratio between differentials, such as $\frac{dL}{dx}$. In this specific case, we are calculating the ratio between the differential of the length of our stick, and the position, x, along an axis that is oriented the same way as our stick.[3] This special ratio is called the *derivative*, and it is fundamental to compare one differential to another. In simple terms, the derivative tells us how one quantity (the one at the top) changes, when we purposely change another (the one at the bottom). Going back to our simple example, the derivative $\frac{dL}{dx}$ tells us how the length of our stick changes when we change the position on the axis. For this case, the derivative is a simple number $\frac{dL}{dx} = 1$, but more complicated cases are possible. So, how can we use this information to measure the length of our stick? A second calculus procedure, integration, comes to our rescue.

[2] Yes, we are purposely skipping a lot of stuff here, see the note above.

[3] The axis doesn't have to have the same orientation of the stick, but it is easier if we do so, in the first place.

1.1.2. Integration: Gluing Together Differentials

Integration is the procedure that glues infinitely tiny slices back together to reconstruct the initial object. In simple terms, if you start with the infinitely thin slices of length that you cut earlier, you can add them all up to find the total length of the stick. Integration takes all these infinitesimally small pieces and combines them into a whole, helping you determine the accumulated total from the infinitesimal changes. Obviously this procedure is very complicated, and it involves gluing (summing over) an infinite amount of infinitesimally small things. If you can't wrap your head around this, that's OK, this concept puzzled humanity for thousands of years. The ancient Greeks were very concerned by this, but they failed to find a solution.[4] It took two 17^{th} century geniuses, Isaac Newton and Gottfried Wilhelm Leibniz, to figure out how to do so.

The solution came by first defining the mathematical operation that "undoes" the slicing:

$$L = \int dL. \tag{1.1}$$

This operation is called an integral, and is represented by the symbol $\int$. The integral is the inverse of d, as it reconstructs the original object by gluing together an infinite amount of infinitesimally small differentials. This operation is, in practice, just a sanity check for the differentiation procedure introduced in the previous section. What eq. 1.1 is telling us, is nothing other than: if you start from an object, L, and apply a certain operation to it (d), then there has to be another operation ($\int$) that undoes what the first operation did. This inverse procedure becomes really useful when we want to measure things in the real world. How so? Because we can compare differentials of an unknown quantity to differentials of known ones, and then use the latter to reconstruct the former. In our simple example, we can use the derivative, $\frac{dL}{dx} = 1$, to compare the length of the object (unknown) to the position along our axis (known, because we can manipulate it). This is the mathematical counterpart of taking an object with unknown length, and comparing it to the length of a standard stick (a meter, a kilometer, a mile, …). The formula that describes this operation is:

$$L = \int dL = \int_i^f 1dx = x_f - x_i = \Delta x, \tag{1.2}$$

where the length (L) of the original object is reconstructed by fixing the initial piece at position x_i on the x axis, the final piece at position x_f,

[4] Look up Zeno's paradoxes for an interesting account of the situation at Greece's times.

and then by gluing together the differentials dx in between these points, using the integral procedure. Switching from dL to dx has the noticeable advantage of going from something that we initially don't know anything about (the length of the stick) to something that we can manipulate as much as we want, because we specifically built it for this task (the position along the axis, x). This concept, of course, is not limited to length. If we differentiate an area, or a volume, or a pressure, or a temperature using eq. 1.1, we obtain the corresponding differentials. By comparing these differentials to specifically built ones that we are able to manipulate to our will, we can reconstruct the original quantity via integration, using eq. 1.2. Every differential will retain the *dimension* of the original quantity (dT still retains the dimension of a temperature, a.k.a. it *is* a temperature, despite the fact that it has a value of essentially zero). In addition, every differential will retain *hidden* information about the initial object, which we can reconstruct by comparing to something we know, and then by applying integration to the latter. Notice that it is the operation in eq. 1.2 that turns the infinitesimal pieces back into a finite, measurable quantity, by comparing an unknown differential to a known one. This is effectively the "measuring" procedure, written in mathematical terms.

When we wrote eq. 1.2, we glanced over the fact that $\int_i^f 1dx = x_f - x_i$. Where did that come from? And most importantly, how are we going to manage more complicated cases? At this point, you'll have to go fetch a mathematics textbook, as you need to know how to perform some of those integrals. For all intents and purposes, we can use those formulas as recipes that mathematicians have written in the past. Granted, we are well aware of the fact that if we want to understand where the formulas are coming from, it is possible to do so with a little effort.[5] Mathematicians have clear rules on how to compute many of these objects, and one of such rules tells us that $\int_i^f dx = x_f - x_i$. Other common integration rules that we'll need in this course are, for example: $\int_i^f x^n\, dx = \frac{x^{n+1}}{n+1}\Big|_i^f = \frac{1}{n+1}\left(x_f^{n+1} - x_i^{n+1}\right)$ for $n \neq -1$, and $\int_i^f x^{-1} dx = \ln|x_f| - \ln|x_i| = \ln\left|\frac{x_f}{x_i}\right|$.

This is indeed a good point to go fetch that old math textbook and refresh some of the simplest integration rules, as well as some of the simplest differentiation ones. Not that we will use all of them, but we might indeed use a few ones.

[5] Yes, this is to a degree analogous to the plug and chug approach of general chemistry that we are trying to avoid here. However, we'll let this one pass, otherwise we risk presenting a mathematics textbook, rather than a physical chemistry one.

1.1.3. Calculus for Thermodynamics

Now comes the interesting question: How are we going to practically perform these two important operations of differentiation and integration in thermodynamics? Well, imagine we need to study the behavior of a machine that prints out a number on a display. The first thing we need to do if we want to study this machine is to find something that makes the number change. Let's represent this something with a knob. We can then turn the knob voluntarily one way or another, and register how the number changes on the display. This is how you apply calculus in thermodynamics (and in most science, for that matter). Our machine might be the length of an object L, while our knob might be the position along an axis x. We can voluntarily change the position on the axis, and observe how the length changes on the display. Does that sound familiar? Can we use eq. 1.2 to do so? I believe so…

Now, obviously the example of length and position is the simplest we could imagine, and doesn't really pertain to physical chemistry. A more relevant example is that of a gas, whose pressure changes when we change the temperature at constant volume. In this case, the pressure, P, is the machine, and the temperature, T, is the knob. To understand the machine, we will need to know the derivative $\frac{dP}{dT}$. In many cases the derivative between our machine and our knob(s) might not be as simple as 1. In some of such cases, the derivative might be a different number, while in others it might be as complicated as a function itself. Some of the machines we will encounter might have more than just one knob, each with their own specific derivative, and each as complicated as it might be. In all cases, however, our analysis follows the same procedure: First, we identify all the knobs that affect the machine. Second, we use calculus to voluntarily change the position of the knobs and to register how the machine behaves. In mathematical terms, this procedure is to define and study the total differential:

$$d\mathcal{M} = \left(\frac{\partial \mathcal{M}}{\partial a}\right) da + \left(\frac{\partial \mathcal{M}}{\partial b}\right) db + \left(\frac{\partial \mathcal{M}}{\partial c}\right) dc + \cdots, \tag{1.3}$$

where $\mathcal{M}$ is our machine, $d\mathcal{M}$ is its total differential, $\{a, b, c, \cdots\}$ are the variables that affect the machine's behavior (i.e. the knobs), and $\frac{\partial \mathcal{M}}{\partial a}$ represents a partial derivative of the machine $\mathcal{M}$ with respect to the variable a obtained by keeping all other variables constant. Notice that the number of variables is left unidentified, as it is our goal to identify all of the variables that a machine depends on, and there are as many as necessary.

The final piece of the puzzle we need to apply calculus to thermodynamics is to know whether or not we can apply these two procedures to any quantity that enters the picture. The answer to this question, unfortunately, is a



Figure 1.1.: A machine $\mathcal{M}$ with three knobs, a, b, and c. Turning each knob by an infinitesimal amount (da, db, dc) changes the number on the display. The total change, $d\mathcal{M}$, is the sum of the three contributions in eq. 1.3, each obtained by multiplying how sensitive the machine is to that knob (the partial derivative) by how much we turned it.

resounding no. Differentiation and integration can be applied to many variables that are "well-behaved." Such variables are called **state variables** in thermodynamics. Unfortunately though, there are also a few variables that are not well-behaved at all. These are called **path variables** in thermodynamics. It turns out that some of the quantities that thermodynamics is mostly concerned about, such as heat and work, belong to this "ill-behaved" category. Before we delve deeper into state and path variables, however, we need to define what variables are in thermodynamics. And before we can do that, we need to take a whole step back and define what thermodynamics is concerned about, that is the thermodynamic system.

1.2. Thermodynamic Systems

A thermodynamic system—or just simply a system—is a portion of space with defined boundaries that separate it from its surroundings (see also the title picture of this book). The surroundings may include other thermodynamic systems or physical systems that are not thermodynamic systems. A boundary may be a real physical barrier or a purely notional one. Defining a system this way is itself a deliberate simplification that is common in science. This procedure is often jokingly referred to as the "spherical cow" analogy,[6] where a complex real-world object (a cow) is treated as a simple sphere to make the math tractable. Typical examples of systems are reported in Figure 1.2 below.

In the first case, a liquid is contained in a typical Erlenmeyer flask. The

[6]The "spherical cow" analogy is sometimes quoted in its extended, joking form as "a spherical cow in a vacuum." See Wikipedia's article on the spherical cow and the article *Higher multipoles of the cow*, American Journal of Physics 94, 264 (2026).

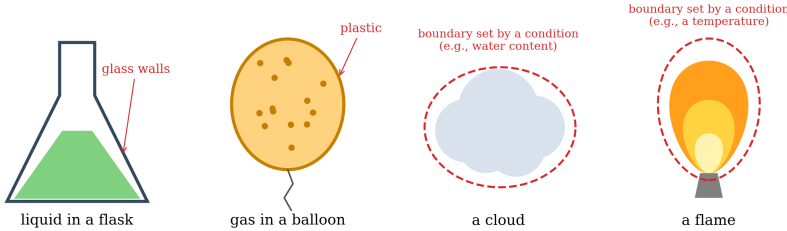


Figure 1.2.: Examples of Thermodynamic Systems and Their Boundaries. The Liquid in a Flask and the Gas in a Balloon Have Physical Boundaries, while the Boundaries of a Cloud and of a Flame (Dashed Red Lines) Are Defined by a Condition that We Choose.

boundaries of the system are the glass walls of the flask (and the surface of the liquid, which separates it from the air above). The second system is represented by the gas contained in a balloon. The boundary is a physical barrier also in this case, being the plastic of the balloon. The third case is that of a thundercloud. The boundary is not a well-defined physical barrier, but rather some condition of pressure and chemical composition at the interface between the cloud and the atmosphere. Finally, the fourth case is the case of an open flame. In this case, the boundary is again non-physical, and possibly even harder to define than for a cloud. For example, we can choose to define the flame based on some temperature threshold, color criterion, or even some chemical one. Despite the lack of physical boundaries, the cloud and the flame—as portions of space containing matter—can be defined as a thermodynamic system.

A system can exchange exclusively mass, exclusively energy, or both mass and energy with its surroundings. Depending on the boundaries' ability to transfer these quantities, a system is defined as open, closed, or isolated. An open system exchanges both mass and energy. A closed system exchanges only energy, but not mass. Finally, an isolated system exchanges neither mass nor energy.

When a system exchanges mass or energy with its surroundings, some of its parameters (variables) change. For example, if a system loses mass to the surroundings, the number of molecules (or moles) in the system will decrease. Similarly, if a system absorbs some energy, one or more of its variables (such as its temperature) increase. Mass and energy can flow into the system or out of the system. Let's consider mass exchange only. If some molecules of a substance leave the system, and then the same amount of molecules flow back into the system, the system will not be modified. We can count, for example, 100 molecules leaving a system and assign them the value of –100 in an outgoing process, and then observe the same 100

molecules going back into the system and assign them a value of +100. Regardless of the number of molecules present in the system in the first place, the overall balance will be –100 (from the outgoing process) +100 (from the ingoing process) = 0, which brings the system to its initial situation (mass has not changed). However, from a mathematical standpoint, we could have equally assigned the label +100 to the outgoing process and –100 to the ingoing one, and the overall total would have stayed the same: +100–100 = 0. Which of the two labels is best? For this case, it seems natural to define a mass going out of the system as negative (the system is losing it), and a mass going into the system as positive (the system is gaining it), but is it as straightforward for energy?

Type of System	**Mass**	**Energy** (either heat or work)
Open	Y	Y
Closed	N	Y
Isolated	N	N

Here is another example. Let's consider a system that is composed of your body. When you exercise, you lose mass in the form of water (sweat) and CO_2 (from respiration). This mass loss can be easily measured by stepping on a scale before and after exercise. The number you observe on the scale will go down. Hence you have lost weight. After exercise, you will reintegrate the lost mass by drinking and eating. If you have reinstated the same amount you have lost, your weight will be the same as before the exercise (no weight loss). Nevertheless, which label do you attach to the amounts that you have lost and gained? Let's say that you are running a 5 km race without drinking or eating, and you measure your weight dropping 2 kg after the race. After the race, you drink 1.5 kg of water and eat a 500 g energy bar. Overall you did not lose any weight, and it would seem reasonable to label the 2 kg that you've lost as negative (–2) and the 1.5 kg of water that you drank and the 500 g bar that you ate as positive (+1.5 +0.5 = +2). But is it the only way? After all, you didn't gain nor lose any weight, so why not calling the 2 kg due to exercise +2 and the 2 that you've ingested as –2? It might seem silly, but mathematically it would not make any difference, the total would still be zero. Now, let's consider energy instead of mass. To run the 5 km race, you have spent 500 kcal, which then you reintegrate precisely by eating the energy bar. Which sign would you put in front of the kilocalories that you "burned" during the race? In principle, you've lost them, so if you want to be consistent, you should use a negative sign. But if you think about it, you've put quite an

effort to "lose" those kilocalories, so it might not feel bad to assign them a positive sign instead. After all, it's perfectly OK to say, "I've done a 500 kcal run today", while it might sound quite awkward to say, "I've done a –500 kcal run today." Our previous exercise with mass demonstrates that it doesn't really matter which sign you put in front of the quantities. As long as you are consistent throughout the process, the signs will cancel out. If you've done a +500 kcal run, you've eaten a bar for –500 kcal, resulting in a total zero loss/gain. Alternatively, if you've done a –500 kcal run, you would have eaten a +500 kcal bar, for a total of again zero loss/gain.

These simple examples demonstrate that the sign that we assign to quantities that flow through a boundary is arbitrary (i.e., we can define it any way we want, as long as we are always consistent with ourselves). There is no best way to assign those signs. If you ask two different people, you might obtain two different answers. But we are scientists, and we must make sure to be rigorous. For this reason, chemists have established a convention for the signs that we will follow throughout this course. If we are consistent in following the convention, we are guaranteed to never make any mistake with the signs.

Definition 1.1. *The chemistry convention of the sign is system-centric:*[a]

- *If something (energy or mass) goes **into** the system it has a **positive** sign (the system is gaining)*
- *If something (energy or mass) goes **out of** the system it has a **negative** sign (the system is losing)*

[a] Notice that physicists use a different sign convention when it comes to thermodynamics. To eliminate confusion, I will not describe the physics convention here, but if you are reading thermodynamics on a physics textbook, or if you are browsing the web and stumble on thermodynamics formula (e.g., on Wikipedia), please be advised that some quantity, such as work, might have a different sign than the one that is used in this textbook. Obviously, the science will not change, but you need to be *always* consistent, so if you decide that you want to use the physics convention, make sure to *always* use the physics convention. In this course, on the other hand, we will *always* use the chemistry one, as defined here.

If you want a trick to remember the convention, use the weight loss/gain during the exercise example above. You are the system, if you lose weight, the kilograms will be negative (–2 kg), while if you gain weight, they will be positive (+2 kg). Similarly, if you eat an energy bar, you are the system, and you will have increased your energy by +500 kcal (positive). In contrast, if you burned energy during exercise, you are the system, and you will have

lost energy, hence –500 kcal (negative). If the system is a balloon filled with gas, and the balloon is losing mass, you are the balloon, and you are losing weight; hence the mass will be negative. If the balloon is absorbing heat (likely increasing its temperature and increasing its volume), you are the system, and you are gaining heat; hence heat will be positive.

1.3. Thermodynamic Variables

The system is defined and studied using parameters that are called variables. These variables are quantities that we can measure, such as pressure and temperature. However, don't be surprised if, on some occasions, you encounter variables that are a little harder to measure directly, such as entropy. If we know the values of all the "relevant variables" of a system, we know the state of the system. The relationships between all possible variables and the state of the system are called "state functions". Imagine state functions as the "machines" that we described in the previous section. The relevant variables are called natural variables, and you should imagine them as the "knobs" of the machines that we want to study. When we need to study a specific aspect of the system, then we need to know the total differential of the state function that is relevant for that aspect.

What are the "relevant variables" of a system? The answer to this question depends on the system, and it is not always straightforward. The simplest case is the case of an ideal gas, for which the natural variables are those that enter the ideal gas law and the corresponding equation:

$$PV = nRT \tag{1.4}$$

Therefore, the natural variables for an ideal gas are the pressure P, the volume V, the number of moles n, and the temperature T, with R being the ideal gas constant. Recalling from the general chemistry courses, R is a universal dimensional constant which has the value of $R = 8.31\,\mathrm{J\,mol^{-1}\,K^{-1}}$ in SI units. We will use the ideal gas equation and its variables as an example to discuss variables and functions in this chapter. We will analyze more complicated cases in the next chapters. Variables can be classified according to numerous criteria, each with its advantages and disadvantages. A typical classification is:

- **Physical variables** (P, V, T in the ideal gas law): independent of the chemical composition of the system.
- **Chemical variables** (n in the ideal gas law): dependent on the chemical composition of the system.

Alternatively, another useful classification is:

- **Intensive variables** (P, T in the ideal gas law): independent of the physical size (extension) of the system.
- **Extensive variables** (V, n in the ideal gas law): dependent on the physical size (extension) of the system.

When we deal with thermodynamic systems, it is more convenient to work with intensive variables. Luckily, it is relatively easy to convert extensive variables into intensive ones by just taking the ratio between the two of them. For an ideal gas, by taking the ratio between V and n, we obtain the intensive variable called molar volume:

$$\overline{V} = \frac{V}{n}. \tag{1.5}$$

We can then recast eq. 1.4 as:

$$P\overline{V} = RT, \tag{1.6}$$

which is the preferred equation that we will use for the remainder of this course. The ideal gas equation connects the 3 variables pressure, molar volume, and temperature, reducing the number of independent variables to just 2. In other words, once 2 of the 3 variables are known, the other one can be easily obtained using these simple relations:

$$P(T, \overline{V}) = \frac{RT}{\overline{V}}, \tag{1.7}$$

$$\overline{V}(T, P) = \frac{RT}{P}, \tag{1.8}$$

$$T(P, \overline{V}) = \frac{P\overline{V}}{R}. \tag{1.9}$$

These equations define three state functions, each one expressed in terms of two independent natural variables. For example, eq. 1.7 defines the state function called "pressure", expressed as a function of temperature and molar volume. Similarly, eq. 1.8 defines the "molar volume" as a function of temperature and pressure, and eq. 1.9 defines the "temperature" as a function of pressure and molar volume. As we mentioned above, when we know the natural variables that define a state function, we can express the function using its total differential, for example for the pressure $P(T, \overline{V})$, using the definition of total differential in eq. 1.3, we get:

$$dP = \left(\frac{\partial P}{\partial T}\right) dT + \left(\frac{\partial P}{\partial \overline{V}}\right) d\overline{V} \tag{1.10}$$

Recalling Schwarz's theorem, the mixed partial second derivatives that can be obtained from eq. 1.10 are the same:

$$\frac{\partial^2 P}{\partial T \partial \overline{V}} = \frac{\partial}{\partial \overline{V}} \frac{\partial P}{\partial T} = \frac{\partial}{\partial T} \frac{\partial P}{\partial \overline{V}} = \frac{\partial^2 P}{\partial \overline{V} \partial T} \tag{1.11}$$

Which can be easily verified considering that:

$$\frac{\partial}{\partial \overline{V}} \frac{\partial P}{\partial T} = \frac{\partial}{\partial \overline{V}} \left(\frac{R}{\overline{V}} \right) = -\frac{R}{\overline{V}^2} \tag{1.12}$$

and

$$\frac{\partial}{\partial T} \frac{\partial P}{\partial \overline{V}} = \frac{\partial}{\partial T} \left(\frac{-RT}{\overline{V}^2} \right) = -\frac{R}{\overline{V}^2} \tag{1.13}$$

While for the ideal gas law, all the variables are "well-behaved" and always satisfy Schwarz's theorem, we will encounter some variables for which Schwarz's theorem does not hold.

1.3.1. State and Path Functions

Before going further, we should clarify two words that we have been using somewhat loosely: *variable* and *function*. In mathematics, a variable is a quantity that we can choose freely (a knob), while a function is a quantity whose value is determined by the variables (the display). In thermodynamics, this distinction is not fixed, but depends on what we decide to control. For an ideal gas, we can choose P, V, and n and calculate $T = \frac{PV}{nR}$, or we can choose T, V, and n and calculate $P = \frac{nRT}{V}$: the temperature is a variable in the second case and a function in the first. What these quantities have in common is that, once the state of the system is fixed, their values are fixed too. For this reason, the terms *state variable* and *state function* are used interchangeably, and we will mostly use the latter.

Mathematically, if Schwarz's theorem is violated (i.e., if the mixed second derivatives are not equal), then the corresponding function cannot be integrated. Quantities of this kind do not describe a state at all, but they depend on the path that the system follows to go from one state to another. For this reason, they are never used as variables (there is no "heat knob" that sets the state of a system), and they are called **path functions** (sometimes also path variables). In contrast, the well-behaved quantities that can be used to define the state of the system are the **state functions** (or state variables).

Since path functions violate Schwarz's theorem, their differential cannot be defined exactly, therefore eq. 1.2 does not exist. The most typical examples of path functions that we will encounter in the next chapters are heat (Q) and work (W). For these functions, we can attempt to infinitely slice the initial variable by using the same calculus procedure introduced in section 1.1.1 and defined in eq. 1.1. The resulting infinitely small pieces, however, are different than regular "exact" differentials, and are called **inexact differentials**. To differentiate between exact and inexact differentials, we use the letter d for the former, and the letter for the latter. It is important to remember that inexact differentials are defined using eq. 1.1, but the procedure in eq. 1.2 does not exist for them. Summarizing for a case that we will use often in thermodynamics, we can define the following quantity for heat (Q):

$$Q = \int Q. \tag{1.14}$$

However, we cannot use the familiar formula given by eq. 1.2 to calculate it:

$$\int_i^f Q \neq Q_f - Q_i, \tag{1.15}$$

as the left hand side of this equation is not defined.[7] Work also behaves similarly.

> We will return to exact and inexact differentials when we discuss heat and work, but for this chapter, it is crucial to notice the difference between a state function and a path function. A typical example to understand the difference between state and path function is to consider the distance between two geographical locations. Let's, for example, consider the distance between New York City and Los Angeles. If we fly straight from one city to the other, there are roughly 4,000 km between them. This "air distance" depends exclusively on the geographical location of the two cities. It stays constant regardless of the method of transportation that I have access to travel between them. Since the cities' positions depend uniquely on their latitudes and longitudes, the "air distance" is a state function, i.e., it is uniquely defined from a simple relationship between measurable variables. However, the "air distance" is not the distance that I will practically have to drive when I go from NYC to LA. Such

[7] Technically, the integral itself does exist, but it takes different values when calculated along different paths, so it is not unique.

"travel distance" depends on the method of transportation that I decide to take (airplane vs. car vs. train vs. boat vs. …). It will depend on a plentiful amount of other factors such as the choice of the road to be traveled (if going by car), the atmospheric conditions (if flying), and so on. A typical "travel distance" by car is, for example, about 4,500 km, which is about 12% more than the "air distance." Indeed, we could even design a very inefficient road trip that avoids all highways and will result in a "travel distance" of 8,000 km or even more (200% of the "air distance"). The "travel distance" is a clear example of a path function because it depends on the specific path that I decide to travel to go from NYC to LA. See Figure 1.3.



Figure 1.3.: State Functions vs. Path Functions.

1.4. Chapter Review

1.4.1. Key Ideas

- **Calculus is slicing and gluing.** A differential, such as dL, is an infinitesimally small piece of a quantity; differentiation slices, and integration glues the pieces back together.
- **The total differential** of a function of several variables adds up the effect of each variable: $d\mathcal{M} = \left(\frac{\partial \mathcal{M}}{\partial a}\right) da + \left(\frac{\partial \mathcal{M}}{\partial b}\right) db + \cdots$.
- **A system** is the part of the universe we choose to study. Open systems exchange mass and energy, closed systems only energy, and isolated systems neither.
- **Sign convention:** in chemistry, energy that enters the system (heat absorbed, work done on it) is positive, and energy that leaves it is negative.
- **Variables are intensive or extensive.** Intensive ones (such as T and P) do not depend on the size of the system; extensive ones (such as V and n) do.

- **State and path functions.** State functions (also called state variables) depend only on the current state and have exact differentials; any of them can be chosen as a variable or calculated as a function of the others. Heat and work are path functions, with inexact differentials, Q and W.

1.4.2. Study Questions

1. What is a differential, such as dL?

a. The derivative of L with respect to position.
b. A small but finite change in L, such as 1 mm.
c. An infinitesimally small piece of L that keeps the dimension of a length.
d. The total length L of the object.
e. A pure number with no dimension.

---

2. What does integration do, in the language of this chapter?

a. It glues together infinitely many infinitesimal pieces to reconstruct the whole quantity.
b. It slices a quantity into infinitesimal pieces.
c. It calculates the slope of a function at a point.
d. It converts a quantity from one unit to another.
e. It removes the dimension from a quantity.

---

3. Which of the following does an isolated system exchange with its surroundings?

a. Mass only.
b. Energy only.
c. Both mass and energy.
d. Neither mass nor energy.
e. Heat, but not work.

---

4. According to the chemistry sign convention, what is the sign of the heat released by a system to its surroundings?

a. Positive, since heat is energy.
b. Negative, since the system is losing energy.
c. Zero, since energy is conserved.
d. Positive if the process is fast, negative if it is slow.
e. It depends on the temperature of the surroundings.

---

5. Which of the following is an intensive variable?

a. Volume.
b. Number of moles.
c. Mass.
d. Temperature.
e. Total energy.

---

6. What is the total differential of the pressure of an ideal gas, $P(T, \overline{V})$?

a. $dP = \frac{dT}{d\overline{V}}$.
b. $dP = PdT + Pd\overline{V}$.
c. $dP = \frac{\partial P}{\partial T} + \frac{\partial P}{\partial \overline{V}}$.
d. $dP = \left(\frac{\partial T}{\partial P}\right) dT + \left(\frac{\partial \overline{V}}{\partial P}\right) d\overline{V}$.
e. $dP = \left(\frac{\partial P}{\partial T}\right) dT + \left(\frac{\partial P}{\partial \overline{V}}\right) d\overline{V}$.

---

7. What does Schwarz's theorem state for a state function?

a. The mixed second partial derivatives are equal, regardless of the order of differentiation.
b. The first derivatives are always zero.
c. The function cannot be integrated.
d. The function depends on the path.
e. The second derivatives are always positive.

---

8. Which of the following is a path function?

a. Pressure.

b. Temperature.
c. Work.
d. Molar volume.
e. Internal energy.

---

9. What does the symbol indicate, as in Q?

a. An exact differential.
b. An inexact differential, whose integral depends on the path.
c. A partial derivative.
d. A state function.
e. A very large change.

---

10. In the example of the trip from New York to Los Angeles, why is the air distance a state function?

a. Because it depends on the means of transportation.
b. Because it changes with the weather.
c. Because it depends only on the positions of the two cities, not on the route.
d. Because it is always longer than the travel distance.
e. Because it is measured in kilometers.

Answers

1.c, 2.a, 3.d, 4.b, 5.d, 6.e, 7.a, 8.c, 9.b, 10.c

2. Temperature, Heat, and Work

In chapter 1, we introduced the tools that we need to study thermodynamics: a bit of calculus, the definition of a system, and the distinction between state and path functions. In this chapter, we will define the two ways in which a system can exchange energy with its surroundings, heat and work, and we will learn how to calculate them. Before we do that, however, we need a solid definition of temperature, which comes from the zeroth law of thermodynamics.

2.1. What Is Thermodynamics?

Thermodynamics is the branch of science that deals with heat and work, and their relation to energy. These are the two ways in which energy can be transferred between a system and its surroundings:

- **Work** is exchanged when the system changes one of its external, macroscopic parameters against a force. The typical example in chemistry is a gas that changes its volume by pushing a piston against an external pressure.
- **Heat** is exchanged because of a temperature difference between the system and its surroundings, without any change in the external parameters. Heat flows through the random collisions between the molecules at the boundary, from the hotter side to the colder one.

As we saw in chapter 1, heat and work are not "well-behaved" quantities because they are path functions. While it might be simple to measure the amount of heat and/or work experimentally, these measured quantities cannot be used to define the state of a system. Since heat and work are path functions, their values depend directly on the methods used to transfer them (their paths). Understanding and quantifying these energy transfers is the reason why thermodynamics was developed in the first place. The origins of thermodynamics date back to the eighteenth and nineteenth centuries, when steam engines started to be used to convert heat into work for technological applications. These early scientists needed a mathematical tool to understand how heat and work were related to each other, and how they were related to the other variables that they were able to measure, such as temperature and volume.

Before we even discuss the definition of energy and how it relates to heat and work, it is crucial to introduce the essential concept of temperature. Temperature is an intuitive concept that has a surprisingly complex definition at the microscopic level.[1] However, for all our purposes, it is not essential to have a microscopic definition of temperature, as long as we have the guarantee that this quantity can be measured unambiguously. In other words, we only need a mathematical definition of temperature that agrees with the physical existence of thermometers.

2.2. The Zeroth Law of Thermodynamics

We all know from experience that if we put a hot object in contact with a cold one, after some time they reach the same temperature, and heat stops flowing between them. When this happens, we say that the two objects are in *thermal equilibrium*. The zeroth law of thermodynamics states that if two thermodynamic systems are each in thermal equilibrium with a third one, then they are in thermal equilibrium with each other. The law might appear trivial and possibly redundant, but it is exactly what makes thermometers possible: the thermometer is the third system, and if it reads the same temperature when in contact with two different objects, we can conclude that the two objects are in thermal equilibrium with each other, even if they have never touched. For this reason, the zeroth law is a fundamental requirement for the mathematical formulation of thermodynamics, and it needs to be stated. The zeroth law can be summarized by the following simple mathematical relation:

Definition 2.1. *Zeroth Law of Thermodynamics:* If $T_A = T_B$, and $T_B = T_C$, then $T_A = T_C$.

Notice that when we state the zeroth law, it appears intuitive. However, this is not necessarily the case. Let's, for example, consider a pot of boiling water at $P = 1$ bar. Its temperature, T_{H_2O}, is about 373 K. Let's now submerge in this water a coin made of wood and another coin made of metal. After some sufficient time, the wood coin will be in thermal equilibrium with the water, and its temperature $T_W = T_{H_2O}$. Similarly, the metal coin will also be in thermal equilibrium with the water, hence $T_M = T_{H_2O}$. According to the zeroth law, the temperature of the wood coin and that of the metal coin are precisely the same $T_W = T_M = 373$ K, even if they are not in direct contact with each other. Now here's the catch: since wood and metal transmit heat in different manners, if I take the coins out of the water and put them immediately in your hands, one of them will feel just

[1] In fact, we will not even give a rigorous microscopic definition of temperature within this textbook.

warm, but the other will burn you. If you had to guess the temperature of the two coins without a thermometer, and without knowing that they were immersed in boiling water, would you suppose that they have the same temperature? Probably not.

The zeroth law tells us that temperature can be measured, but not which numbers to assign to it. The Celsius scale uses two arbitrary reference points, the freezing and boiling points of water, at 0 and 100 °C. A more natural choice comes from gases: at constant pressure, the volume of a gas decreases linearly as it cools, and, if we extrapolate, every gas reaches zero volume at the same temperature, −273.15 °C. Since a negative volume makes no sense, this temperature is the lowest possible one, called *absolute zero*. The Kelvin scale, which we use throughout this book, starts from it: $T\,[\mathrm{K}] = t\,[^\circ\mathrm{C}] + 273.15$, and absolute temperatures are never negative. We will see in chapter 4 that the second law gives this zero a meaning that does not depend on gases at all. We will then see in chapter 6 that absolute zero can never be reached, and in chapter 11 why all gases point to the same zero, and how real gases behave when they are cooled down.

2.3. Equilibrium, Stationary States, and Quasi-Static Processes

In the rest of this chapter, we will compare processes that happen "fast" with processes that happen "slowly." These words are vague on their own: is one second fast or slow? A second is an eternity for a molecule, and an instant for a galaxy. To use them with precision, we need to compare the speed of a process with something that belongs to the system itself. In other words, we need an internal property of the system that we can use as a yardstick to compare external stimuli to. That something is how quickly the system can return to equilibrium. Let's start by defining exactly what we mean by equilibrium.

Definition 2.2. *Equilibrium state:* A state in which the macroscopic variables of the system (such as T, P, V, and the composition) do not change with time, *and* there are no net flows of energy or matter, neither inside the system nor between the system and its surroundings.

The second part of the definition is important. A system can have variables that do not change with time, and still not be at equilibrium. Consider a metal rod with one end on a hot plate and the other end in a bucket of ice. After a while, the temperature at each point of the rod stops changing: it is high near the plate and low near the ice. Heat, however, flows continuously

through the rod, from the plate to the ice. A state like this is called a **stationary state** (or *steady state*):

Definition 2.3. *Stationary state:* A state in which the macroscopic variables of the system do not change with time, but which is maintained by a continuous flow of energy or matter through the system.

The rod in a stationary state does not have *a* temperature: it has a different temperature at every point. Only at equilibrium are the intensive variables, such as T and P, uniform throughout the system, so that a single value describes the whole system. This is why the thermodynamics in this book deals with equilibrium states: they are the only states that we can describe with a handful of variables, and the only ones that we can represent as points in a diagram such as the PV plots in this chapter. Stationary states are just as important in nature (a living cell is a stationary state, not an equilibrium one), but they are the subject of non-equilibrium thermodynamics, which is beyond the scope of this course.

When we disturb a system at equilibrium, for example by suddenly moving a piston, the system goes through a series of states that are not at equilibrium: for a short while, the gas near the piston has a different pressure than the gas far from it, and pressure waves bounce around the container. Eventually, these differences die out, and the system reaches a new equilibrium state. The time this takes is called **relaxation time**:

Definition 2.4. *Relaxation time:* The time, τ, that a system needs to return to equilibrium after a disturbance.

The relaxation time depends on the system *and* on the variable that is relaxing. Pressure differences in a gas travel at the speed of sound, so in a container that is a few centimeters wide, the pressure becomes uniform in a fraction of a millisecond. Temperature differences, instead, are smoothed out by heat conduction, which is much slower: a cold glass of water in a warm room takes tens of minutes to reach the temperature of the room. Some chemical reactions have relaxation times longer than the age of the universe: diamond is not at equilibrium with graphite, but nobody has ever seen a diamond turn into graphite at room temperature.

We now have the yardstick that we were looking for. A process is **fast** if the conditions of the system change on a time scale that is shorter than, or comparable to, its relaxation time, so that the system has no time to adjust and is driven away from equilibrium. A process is **slow** if the conditions change on a time scale much longer than the relaxation time, so that the system has always enough time to re-equilibrate. Notice that the same process can be slow for one variable and fast for another. Pushing a piston

in one second is slow for the pressure of the gas, which equalizes in less than a millisecond, but it is fast for the exchange of heat through the walls of the container, which takes minutes. In the limit of a process that is slow compared to all the relevant relaxation times, we have:

Definition 2.5. *Quasi-static process:* A process that happens slowly enough, compared to the relaxation time of the system, that the system passes through a continuous sequence of equilibrium states.

A few things to notice about this definition:

1. **A quasi-static process can be drawn as a line.** Since every intermediate state is an equilibrium state, it has well-defined values of P, V, and T, and the whole process is a continuous line in a PV diagram. A process that is not quasi-static, instead, has well-defined initial and final states only: in between, the gas does not have a single pressure, and the process cannot be drawn as a line. We will see an example of this in the one-step expansion below.
2. **A quasi-static process is an idealization.** Any real process takes a finite time, so it is never perfectly quasi-static. However, many real processes are slow enough to be treated as quasi-static to an excellent approximation, and, as we will see in this chapter, we can approach the quasi-static limit as closely as we want by splitting a process into more and more smaller steps.
3. **Quasi-static does not mean "at equilibrium with the surroundings."** The system is at equilibrium *internally* at every moment, but it may still exchange energy with the surroundings. In chapter 3, we will see that when the system is also balanced with its surroundings at every moment, the process becomes *reversible*.

2.4. Calculation of Heat

Heat (Q) is a property that gets transferred between substances. Similarly to work, the amount of heat that flows through a boundary can be measured, but its mathematical treatment is complicated because *heat is a path function*. As you probably recall from general chemistry, the ability of a substance to absorb heat is given by a coefficient called the heat capacity, which is measured in SI in $\frac{\text{J}}{\text{mol K}}$. However, since heat is a path function, these coefficients are not unique, and we have different ones depending on how the heat transfer happens.

2.4.1. Processes at Constant Volume (Isochoric)

The heat capacity at constant volume measures the ability of a substance to absorb heat at constant volume. Recalling from general chemistry, the molar heat capacity at constant volume has the following formal definition:

> The molar heat capacity at constant volume is the amount of heat required to increase the temperature of 1 mol of a substance by 1 K at constant volume.

This is a procedural definition that defines how we can measure C_V in practice. While this procedure is useful in laboratory settings and in introductory chemistry courses, we need to go beyond it to understand its origin and its meaning. Have you ever wondered why you need to increase the temperature by 1 K? What if you want to increase it by 2? Or 1/2, or 1/1000? Also, the definition is highly imprecise, as there certainly has to be a difference when we increase the temperature of a substance from 1 K to 2 K, to when we increase it from 1001 K to 1002 K. Those situations certainly cannot lead to the same results. How are we going to circumvent this poor definition? We need to apply calculus to remove those arbitrary units and arbitrary increments (remember that differentials are all the same size, and unitless):

$$C_V = \frac{Q_V}{ndT} \Rightarrow Q_V = nC_V dT. \tag{2.1}$$

This new differential definition of C_V is independent of the unit we use to measure it, and does not require a procedural definition. Given a known value of C_V, the amount of heat that gets transferred can be easily calculated by measuring the changes in temperature, after integration of eq. 2.1:

$$Q_V = nC_V dT \rightarrow \int Q_V = n\int_{T_i}^{T_f} C_V dT \rightarrow Q_V = nC_V \int_{T_i}^{T_f} dT, \tag{2.2}$$

which, assuming C_V independent of temperature, simply becomes:

$$Q_V \cong nC_V \Delta T. \tag{2.3}$$

2.4.2. Processes at Constant Pressure (Isobaric)

Similarly to the previous case, the heat capacity at constant pressure measures the ability of a substance to absorb heat at constant pressure. Recalling again from general chemistry:

> The molar heat capacity at constant pressure is the amount of heat required to increase the temperature of 1 mol of a substance by 1 K at constant pressure.

And once again, applying calculus to obtain a differential definition of C_P, we get:

$$C_P = \frac{Q_P}{ndT} \Rightarrow Q_P = nC_P dT \rightarrow \int Q_P = n\int_{T_i}^{T_f} C_P dT, \tag{2.4}$$

which results in the simple formula:

$$Q_P \cong nC_P \Delta T. \tag{2.5}$$

2.5. Calculation of Work

In thermodynamics, work (W) is the ability of a system to transfer energy by exerting a force on its surroundings. Work can be measured simply by evaluating its effects, such as displacing a massive object by some amount of space. The mathematical treatment of work, however, is complicated because *work is a path function.* In the following sections, we will analyze how work is calculated in some prototypical situations commonly encountered in the thermodynamical treatment of systems.

Let's consider the situation in Figure 2.1, where a special beaker with a piston that is free to move is filled with an ideal gas. The beaker sits on a desk, so the piston is not subject to any external forces other than the external pressure, P_{ext}, and the internal pressure of the gas, P.[2] The piston is initially compressed to a position that is not in equilibrium (i). After the process, the piston reaches a final equilibrium position (f). How do we calculate the work (W) performed by the system?

From basic physics, we recall that the infinitesimal amount of work associated with an object moving in space is given by the force acting on the object (F) multiplied by the infinitesimal amount it gets displaced (dh):

[2] For this simple thought experiment, we will ignore any external force that is not significant. In other words, we will not consider the friction of the piston on the beaker walls or any other foreign influence.

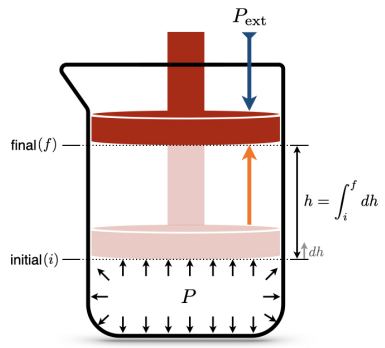


Figure 2.1.: Isothermal Expansion of an Ideal Gas Against a Constant External Pressure.

$$W = -Fdh, \tag{2.6}$$

where the negative sign comes from the chemistry sign convention, Definition 1.1, since the work in Figure 2.1 is *performed* by the system (expansion). Which force should we use? When the gas expands, the work it performs is the energy needed to push back the surroundings, so the relevant force is the one that the surroundings exert on the piston. Relying upon another definition from physics, the pressure is the ratio between the force (F) and the area (A) that such force acts upon, so the force exerted by the surroundings is related to the external pressure, P_{ext}, by:

$$P_{\text{ext}} = F/A. \tag{2.7}$$

Obtaining F from eq. 2.7 and replacing it in eq. 2.6, we obtain:

$$W = -P_{\text{ext}} \underbrace{Adh}_{dV}, \tag{2.8}$$

and considering that Adh (area times infinitesimal height) is the definition of an infinitesimal volume dV, we obtain:

$$W = -P_{\text{ext}} dV. \tag{2.9}$$

The external pressure is not necessarily the same as the pressure of the gas, P. In an expansion that is fast compared to the relaxation time of the gas, the gas inside the beaker does not even have a single pressure, and the part near the piston can be at a very different pressure than the surroundings.

However, if the expansion is quasi-static (definition 2.5) and the piston is always balanced, $P_{\text{ext}} = P$ at every moment, and the work can be written using the pressure of the gas:

$$W = -PdV \qquad (\text{when } P_{\text{ext}} = P). \tag{2.10}$$

If we want to calculate the amount of work performed by a system, W, from eq. 2.9, we need to recall that W is an inexact differential. As such, we cannot integrate it from initial to final as for the (exact) differential of a state function, because:

$$\int_i^f W \neq W_f - W_i, \tag{2.11}$$

but rather:

$$\int_{\text{path}} W = W, \tag{2.12}$$

where the integration is performed along the *path*. Using eq. 2.12, we can integrate eq. 2.9 as:

$$\int W = W = -\int_i^f P_{\text{ext}} dV, \tag{2.13}$$

where the integral on the left-hand side is taken along the path,[3] while the integral on the right-hand side can be taken between the initial and final states, since V is a state function. How do we solve the integral in eq. 2.13? It turns out that there are many different ways to solve this integral (perhaps not surprisingly, since the left-hand side depends on the path), which we will explore in the next section.

2.5.1. $|W_{\text{max}}|$ and $|W_{\text{min}}|$ in Processes at Constant Temperature (Isothermal)

At constant temperature, the piston in Figure 2.1 moves along the isotherm in figure 2.2, obtained for 1 mol of an ideal gas at $T = 298$ K.

[3] from here on we will replace the notation $\int_{\text{path}}$ with the more convenient $\int$ and we will keep in mind that the integral of an inexact differential must be taken along the path.

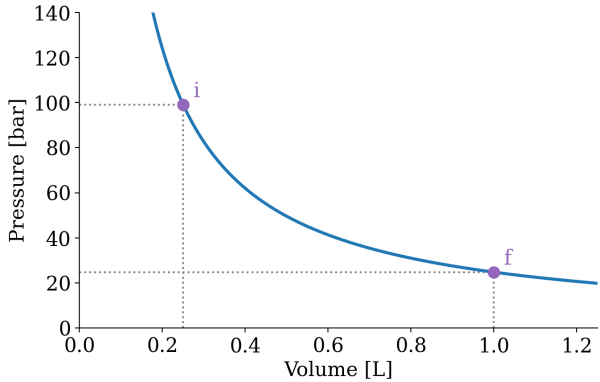


Figure 2.2.: Isotherm of 1 mol of an ideal gas at 298 K, with the initial (i) and final (f) states of an expansion.

An expansion of the gas will happen between P_i and P_f. If the expansion happens in one step, for example by suddenly releasing the piston against the external atmospheric pressure, the process is not quasi-static: only the initial and final states are equilibrium states, and the gas in between has no single pressure. The external pressure, however, is well defined and constant, and we can use it (for example $P_f = P_{\text{ext}} = 1$ bar), and solve the integral as:

$$W_{\text{1-step}} = -\int_i^f P_{\text{ext}} dV = -P_{\text{ext}} \int_i^f dV = -P_{\text{ext}}(V_f - V_i). \tag{2.14}$$

Notice how the work is negative, since during an expansion the work is performed by the system (recall the chemistry sign convention). The absolute value of the work[4] represents the red area in figure 2.3:

$$|W_{\text{1-step}}| = P_{\text{ext}}(V_f - V_i) \tag{2.15}$$

If the process happens in two steps by pausing at an intermediate position (1) until equilibrium is reached, then we should calculate the work by dividing it into two separate processes, A and B, and solve each one as we did in the previous case. The first process is an expansion between P_i and P_1, with P_1 constant. The absolute value of the work, W_A, is represented by the blue area in figure 2.4:

$$|W_A| = P_1(V_1 - V_i) \tag{2.16}$$

[4] we use the absolute value to avoid confusions due to the fact that the expansion work is negative according to Definition 1.1.

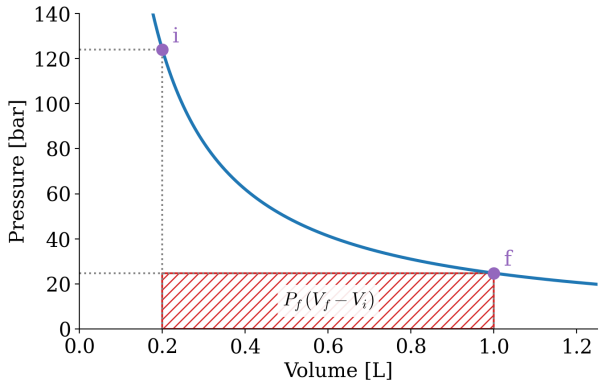


Figure 2.3.: Work for a one-step expansion against a constant external pressure: the red rectangle under the final pressure.

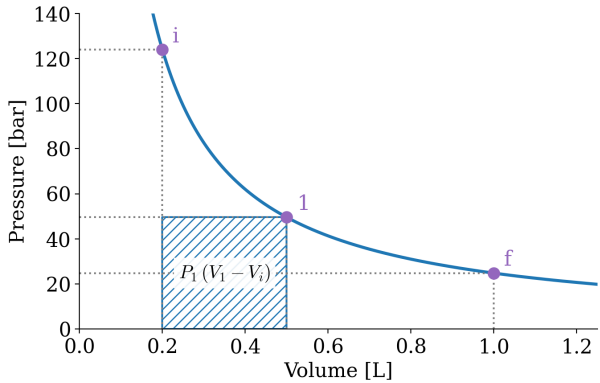


Figure 2.4.: Work for the first step of a two-step expansion: the blue rectangle under the intermediate pressure.

The second process is an expansion between P_1 and P_f, with $P_f = P_{\text{ext}}$ constant. The absolute value of the work for this second process is represented by the green area in figure 2.5:

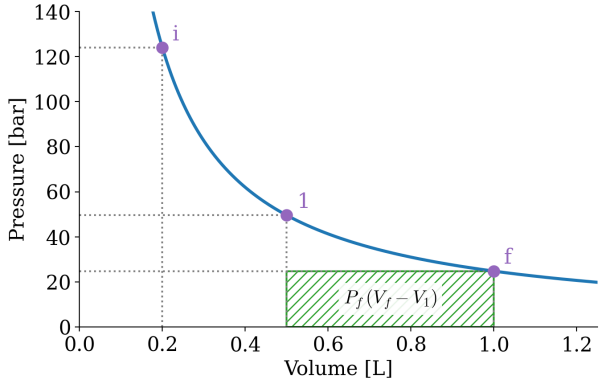


Figure 2.5.: Work for the second step of a two-step expansion: the green rectangle under the final pressure.

$$|W_B| = P_f(V_f - V_1) \tag{2.17}$$

The total absolute value of the work for the 2-step process is given by the sum of the two areas, as in figure 2.6:

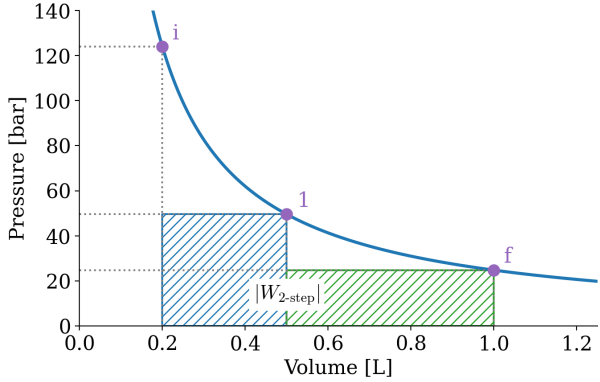


Figure 2.6.: Total work for the two-step expansion: the sum of the blue and green rectangles.

$$\left|W_{2\text{-step}}\right| = |W_A| + |W_B| = P_1(V_1 - V_i) + P_f(V_f - V_1). \tag{2.18}$$

As can be easily verified by comparing the shaded areas in the plots, $|W_{\text{2-step}}| > |W_{\text{1-step}}|$.

We can easily extend this procedure to consider processes that happen in 3, 4, 5, ..., n steps. What is the limit of this procedure? In other words, what happens when $n \to \infty$? A simple answer is given by figure 2.7, which clearly demonstrates that the maximum value of the area underneath the curve $|W_{\text{max}}|$ is achieved in an ∞-step process. In this limit, each step is infinitesimally small, the external pressure is always equal to the pressure of the gas, and we can use eq. 2.10 to calculate the work as:

$$|W_{\infty\text{-step}}| = |W_{\text{max}}| = \sum_{n}^{\infty} P_n(V_n - V_{n-1}) = \int_i^f P dV. \tag{2.19}$$

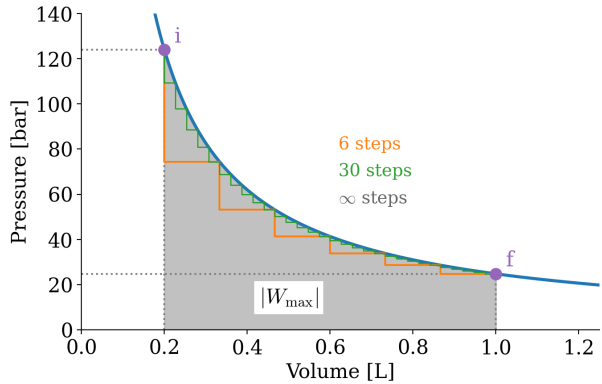


Figure 2.7.: Maximum work for the isothermal expansion: the whole area under the isotherm, which is the limit of an expansion performed in more and more steps (6 steps in orange, 30 steps in green, ∞ steps in gray).

The integral on the right hand side of eq. 2.19 can be solved for an ideal gas by calculating the pressure using the ideal gas law $P = \frac{nRT}{V}$, and solving the integral since n, R, and T are constant:

$$|W_{\text{max}}| = nRT \int_i^f \frac{dV}{V} = nRT \ln \frac{V_f}{V_i}. \tag{2.20}$$

This example demonstrates why work is a path function. If we perform the expansion in a single step, which is not quasi-static, the system performs an amount of work that is much smaller than the amount of work it can perform if the expansion between the same points happens in an ∞-step process. Each step of the ∞-step process is infinitesimally small, so the gas

is always at equilibrium: the ∞-step process is quasi-static, and it is the only one that follows the isotherm as a line.

The same considerations that we made up to this point for expansion processes apply in reverse to compression ones. The only difference is that the work associated with compressions will have a positive sign since it must be performed onto the system. As such, the amount of work for a transformation that happens in a finite number of steps will be an upper bound to the minimum amount of work required to compress the system.[5] $|W_{\text{min}}|$ for compressions is calculated as the area underneath the PV curve, exactly as $|W_{\text{max}}|$ for expansions in eq. 2.19.

2.6. Chapter Review

2.6.1. Key Ideas

- **The zeroth law:** two systems in thermal equilibrium with a third one are in thermal equilibrium with each other. This is what makes thermometers possible.
- **Heat** is exchanged because of a temperature difference. At constant volume or pressure, it is calculated from the heat capacities: $Q_V = n\int C_V\,dT$ and $Q_P = n\int C_P\,dT$.
- **Work** of expansion is $W = -\int P_{\text{ext}}\,dV$, negative for an expansion (the system does work) and positive for a compression.
- **Equilibrium vs. stationary states:** at equilibrium, the variables do not change *and* nothing flows; a stationary state has constant variables maintained by a steady flow. "Fast" and "slow" are measured against the relaxation time, τ, and a **quasi-static** process is slow enough to pass only through equilibrium states.
- **Work depends on the path.** Between the same two states, a one-step, a two-step, and an infinitely-many-step expansion give different amounts of work.
- **Maximum work:** for an isothermal ideal gas expansion, the most work is extracted in infinitely many steps, $|W_{\text{max}}| = nRT\ln\frac{V_f}{V_i}$, and the least work is needed for a compression performed in the same way.

2.6.2. Study Questions

1. What does the zeroth law of thermodynamics state?

[5] In contrast to a lower bound for expansion processes.

a. If two systems are each in thermal equilibrium with a third one, then they are in thermal equilibrium with each other.
b. The energy of the universe is conserved.
c. The entropy of the universe increases.
d. Heat always flows from hot to cold objects.
e. The entropy of a perfect crystal is zero at 0 K.

---

2. What is a quasi-static process?

a. A process that happens in less than one second.
b. A process in which the system is always in a stationary state, with a steady flow of heat through it.
c. A process in which the temperature of the system does not change.
d. A process slow enough, compared to the relaxation time of the system, that the system passes only through equilibrium states.
e. A process in which no work is exchanged.

---

3. What is the differential definition of the molar heat capacity at constant volume?

a. $C_V = \frac{Q_V}{\Delta T}$.
b. $C_V = \frac{Q_V}{n\,dT}$.
c. $C_V = n\,Q_V\,dT$.
d. $C_V = \frac{dT}{Q_V}$.
e. $C_V = \frac{Q_P}{n\,dT}$.

---

4. How is the heat exchanged at constant pressure calculated, assuming C_P independent of temperature?

a. $Q_P = nC_V\Delta T$.
b. $Q_P = P\Delta V$.
c. $Q_P = nRT\ln\frac{V_f}{V_i}$.
d. $Q_P = 0$.
e. $Q_P = nC_P\Delta T$.

---

5. Why is the work of an expansion negative in the chemistry sign convention?

a. Because the volume decreases.
b. Because the pressure is negative.
c. Because the work is performed by the system, which loses energy.
d. Because the temperature decreases.
e. Because work is a path function.

---

6. What is the work for a one-step expansion against a constant external pressure?

a. $W = -P_{\text{ext}}(V_f - V_i)$.
b. $W = P_{\text{ext}}(V_f - V_i)$.
c. $W = -nRT \ln \frac{V_f}{V_i}$.
d. $W = 0$.
e. $W = nC_V \Delta T$.

---

7. A gas expands isothermally between the same initial and final states in one step, in two steps, or in infinitely many steps. In which case is the absolute value of the work the largest?

a. One step.
b. Two steps.
c. It is the same in all cases.
d. Infinitely many steps.
e. It depends on the gas.

---

8. What is the absolute value of the maximum work for the isothermal expansion of an ideal gas?

a. $|W_{\text{max}}| = P_{\text{ext}} \Delta V$.
b. $|W_{\text{max}}| = nRT \ln \frac{V_f}{V_i}$.
c. $|W_{\text{max}}| = nR\Delta T$.
d. $|W_{\text{max}}| = nC_V \Delta T$.
e. $|W_{\text{max}}| = nRT \frac{V_f}{V_i}$.

---

9. What do the one-step, two-step, and infinitely-many-step expansions demonstrate?

a. That work is a state function.
b. That the temperature changes during an isothermal process.
c. That heat and work are the same thing.
d. That the ideal gas law is not valid.
e. That work depends on how the process is carried out between the same initial and final states.

---

10. How must a compression be performed to require the minimum amount of work?

a. As fast as possible, in one step.
b. In two steps.
c. Quasi-statically, in infinitely many steps.
d. At constant volume.
e. Against zero external pressure.

Answers

1.a, 2.d, 3.b, 4.e, 5.c, 6.a, 7.d, 8.b, 9.e, 10.c

3. First Law of Thermodynamics

In chapter 2, we learned how to calculate heat and work, and we saw that both of them are path functions: their values depend on how a process is carried out. In this chapter, we will connect heat and work to a state function, the internal energy, and we will see how this connection becomes one of the most fundamental laws of nature, the first law of thermodynamics. Along the way, we will introduce a second state function, the enthalpy, which will become the protagonist when we study the heat of chemical reactions in chapter 7.

3.1. Calculation of Internal Energy Changes

Energy is a property of a system that can be either transferred or converted. The internal energy (U) of a system is a thermodynamic state function defined as:

Definition 3.1. *Internal Energy:* The energy contained within the system, excluding kinetic energy and potential energy of motion and position of the system as a whole.

In the absence of chemical transformations, heat and work are the only two forms of energy that thermodynamics is concerned with. Keeping in mind Definition 1.1, which gives the convention for the signs of heat and work, the change in internal energy of a system can be written as:

$$\Delta U = Q + W, \tag{3.1}$$

which we can write in differential form by considering that the internal energy is a state function, as:

$$dU = Q + W, \tag{3.2}$$

which, for processes where the pressure of the system equals the external pressure (as in the quasi-static processes with a balanced piston that we discussed in section 2.5, and in processes at constant pressure, where the

system is in mechanical equilibrium with the atmosphere), using eq. 2.10 becomes:

$$dU = Q - PdV. \tag{3.3}$$

3.1.1. Internal Energy in Isothermal Processes

To study the behavior of the internal energy in a process at constant temperature ($dT = 0$), James Prescott Joule (1818–1889) created the apparatus depicted in Figure 3.1.

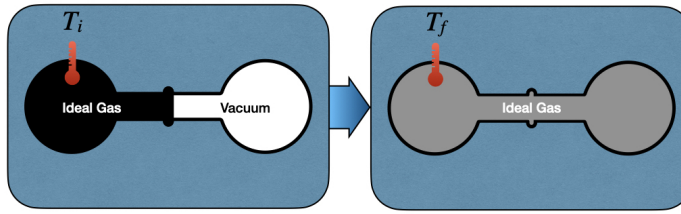


Figure 3.1.: The Joule Expansion Experiment.

The left side of the Joule apparatus's inner chamber is filled with an ideal gas, while a vacuum is created in the right chamber. Both chambers are immersed in a water bath, whose temperature is monitored with a thermometer: if the gas absorbed or released any heat during the experiment, the temperature of the water would change. When the valve between the chambers is opened, the gas expands into the empty chamber and equilibrates. The work associated with the transformation is:

$$W = -P_{\text{ext}}dV = 0, \tag{3.4}$$

since the gas expands into a vacuum, there is nothing for it to push against, and $P_{\text{ext}} = 0$. Thus, any change in internal energy must be due to heat, which can be detected by monitoring the temperature at the beginning, T_i, and at the end of the experiment, T_f. Joule observed that, for a gas behaving ideally, the temperature does not change, $T_i = T_f$. Since the temperature doesn't change, no heat is exchanged, and therefore the internal energy stays constant:

$$dU = Q = 0. \tag{3.5}$$

> Notice that Joule's conclusion is valid only for an ideal gas. If we expand a real gas, we do notice a change in temperature associated with the expansion. A typical example of this behavior is when you use a pressurized spray bottle and release its content for an extended time in the air. The container will typically get colder. We will discuss this behavior in chapter 11 when we will study non-ideal gases.

From this simple experiment, we can conclude that the internal energy of an ideal gas depends only on its temperature.

3.1.2. Internal Energy in Adiabatic Processes

An adiabatic process is defined as a process that happens without the exchange of heat. As such, $Q = 0$, and the work associated with an adiabatic process is equal to the change in internal energy:

$$dU = W = -PdV, \tag{3.6}$$

which can then be calculated using the formulas that we derived in section 2.5. Notice that the work is still a path function: in general, its value depends on the path. However, *along adiabatic paths*, the work is fixed by the change of a state function, so all adiabatic paths connecting the same two states require the same amount of work. Notice also that isothermal and adiabatic are two very different processes. While an adiabatic process happens without the exchange of heat across the system's boundaries, this does not mean that the system's temperature does not change. Isothermal processes are usually associated with a heat transfer across the boundaries to maintain the temperature of the system constant. For adiabatic processes, it is quite the opposite since they are usually associated with a change in temperature.

3.1.3. Internal Energy in Isochoric Processes

An isochoric process is a process in which the volume does not change. Therefore, $W = 0$, and $dU = Q_V$, which using eq. 2.1, becomes:

$$dU = Q_V = nC_V dT. \tag{3.7}$$

Since no work is performed at these conditions, the heat exchanged is equal to the change of a state function, ΔU. Once again, heat is still a path function in general, but *along constant-volume paths* its value is fixed by the initial and final states only. Eq. 3.7 also gives a mathematical justification of

the concept of heat capacity at constant volume. C_V can now be interpreted as the partial derivative (a coefficient) of a state function (the internal energy):

$$C_V = \left(\frac{\partial U}{\partial T}\right)_{V,n=1}, \tag{3.8}$$

where we have replaced the total derivative d with a partial one ∂, and we have specified that the differentiation happens at constant volume and number of moles. Eq. 3.8 brings a rigorous definition of heat capacity at constant volume for 1 mol of substance:

Definition 3.2. *The heat capacity of a substance, C_V, represents its ability to absorb **energy** at constant **volume**.*

3.1.4. Internal Energy in Isobaric Processes

In an isobaric process, the pressure does not change, hence $dP = 0$. Unfortunately, eq. 3.2 for this case does not simplify further, as happened in the two previous cases. However, in section 2.4.2, we have introduced the useful concept of heat capacity at constant P. C_P was used in an isobaric process in the same manner as C_V was used in the isochoric case. That is, as a coefficient to measure the amount of heat absorbed at constant pressure. Eq. 3.8 gave a mathematical definition of C_V as the partial derivative of a state function (the internal energy). But if heat capacities are coefficients, and coefficients are partial derivatives of state functions, how do we explain C_P? In order to do so, we can introduce a new state function, called the enthalpy (H), as:

$$H = U + PV, \tag{3.9}$$

and its differential, calculated as:

$$dH = dU + d(PV) = dU + PdV + \overbrace{VdP}^{0}, \tag{3.10}$$

which can be rearranged as:

$$dU = dH - PdV. \tag{3.11}$$

Replacing eq. 3.11 into eq. 3.3:

$$dH - PdV = Q_P - PdV, \tag{3.12}$$

which simplifies to:

$$dH = Q_P = nC_P dT. \tag{3.13}$$

Eq. 3.13 establishes that the heat exchanged at constant pressure is equal to a new state function called the enthalpy, defined by eq. 3.9. It also establishes a mathematical justification of the concept of heat capacity at constant pressure. Similarly to C_V, C_P can now be interpreted as the partial derivative (a coefficient) of the new state function (the enthalpy):

$$C_P = \left(\frac{\partial H}{\partial T}\right)_{P,n=1}, \tag{3.14}$$

Eq. 3.14 brings also a rigorous definition of heat capacity at constant pressure for 1 mol of substance:

Definition 3.3. *The heat capacity of a substance, C_P, represents its ability to absorb* ***enthalpy*** *at constant* ***pressure****.*

3.2. The First Law of Thermodynamics

We finally come to a working definition of the first law. If we take an isolated system—i.e., a system that exchanges neither energy nor mass with its surroundings—its internal energy is conserved. If the internal energy is conserved, $dU = 0$. Therefore, for an isolated system:

$$Q = -W, \tag{3.15}$$

and heat and work can be easily calculated using any of the appropriate formulas introduced in either section 2.5 or section 2.4.

The first law is a conservation law. It is intuitive since it comes directly from Lavoisier's principle of "nothing is lost, nothing is created, everything is transformed." Considering that the only system that is truly isolated is the universe, we can condense the first law in one simple sentence:

Definition 3.4. *First Law of Thermodynamics:* The energy of the universe is conserved.

3.3. Reversible and Irreversible Processes

Let's now consider the cycle in Figure 3.2. The process in this case starts from state 1 (system at P_1V_1), expands to state 2 (system at P_2V_2), and compresses back to state 1 (system back to P_1V_1).

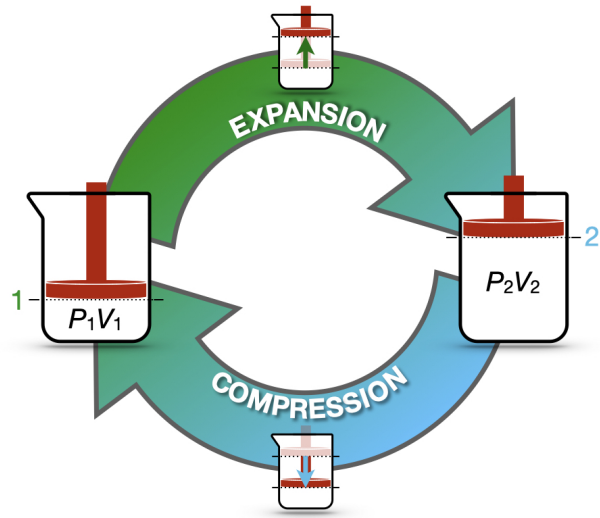


Figure 3.2.: Expansion/Compression Cycle of an Ideal Gas.

Since the process starts and finishes at the same state, the value of the internal energy at the end of the process will be the same as its value at the beginning, regardless of the path:[1]

$$\oint dU = 0, \tag{3.16}$$

where the symbol $\oint$ indicates an integral around a cycle. Considering the work associated with the cycle, however, the situation is radically different because it depends on the path that the system is taking, and in general

$$\oint_{\text{path}} W \neq 0. \tag{3.17}$$

For instance, if we perform the expansion in one step, the work associated with it will be (using eq. 2.14):[2]

[1] recall that the internal energy is a state function, so its value depends exclusively on the conditions at the beginning and at the end. In a cycle, we're going back to the same point, so the conditions at the beginning and at the end are equal by definition.

[2] notice that the work for the expansion is negative, as it should be.

$$W_{\text{1-step}}^{\text{expansion}} = -P_2(\underbrace{V_2 - V_1}_{>0}) < 0, \tag{3.18}$$

and if we also perform the compression in 1-step:[3]

$$W_{\text{1-step}}^{\text{compression}} = -P_1(\underbrace{V_1 - V_2}_{<0}) > 0. \tag{3.19}$$

With a little bit of math, it is easy to prove that the total work for the entire cycle is:

$$\begin{aligned} W_{\text{1-step}}^{\text{cycle}} &= W_{\text{1-step}}^{\text{expansion}} + W_{\text{1-step}}^{\text{compression}} \\ &= -P_2(V_2 - V_1) - P_1(V_1 - V_2) \\ &= -P_2(V_2 - V_1) + P_1(V_2 - V_1) \\ &= (\underbrace{V_2 - V_1}_{>0})(\underbrace{P_1 - P_2}_{>0}) > 0, \end{aligned} \tag{3.20}$$

or, in other words, the surroundings have to put more work into the compression than they get back from the expansion. Since the gas returns to its initial state, $\oint dU = 0$, and this extra work must leave the system as heat. The energy is not destroyed, but part of the work has been degraded into heat.

> In practice, if we want to manually perform this cycle by pushing on the piston by hand, we will notice that it requires more energy to push down than the amount it gives back when we release it, and it moves back up.

In contrast, if both the expansion and the compression happen in a quasi-static ∞-step manner, the work associated with them will be W_{max} and W_{min}, respectively, which are calculated using eq. 2.20. The total work related to the cycle will be in this case:

$$\begin{aligned} W_{\infty\text{-step}}^{\text{cycle}} &= W_{\text{max}}^{\text{expansion}} + W_{\text{min}}^{\text{compression}} \\ &= -nRT \ln \frac{V_f}{V_i} - nRT \ln \frac{V_i}{V_f} \\ &= -nRT \underbrace{\left(\ln \frac{V_f}{V_i} - \ln \frac{V_f}{V_i} \right)}_{=0} = 0, \end{aligned} \tag{3.21}$$

[3] notice that the work for the compression is positive, as it should be.

which means that, in this case, the work obtained from the expansion is exactly the work needed for the compression, and no work is degraded into heat.

> In practice, if we were able to perform this cycle manually by pushing the piston down by hand, we would notice that it requires the same amount of energy to push down as the amount it gives back when it moves up.

This process can happen both ways without losses, and is called *reversible*:

Definition 3.5. *Reversible process:* A process whose direction can be inverted at any moment by an infinitesimally small change in the conditions of the surroundings (for example, an infinitesimally small increase of the external pressure), so that the system goes back through exactly the same states.[a]

[a] Adapted from: Sears, F.W. and Salinger, G.L. (1986), Thermodynamics, Kinetic Theory, and Statistical Thermodynamics, 3rd edition (Addison-Wesley).

What does Definition 3.5 imply in practice? Three things:

1. **A reversible process is quasi-static, and more.** It happens in an infinite number of infinitesimal steps, so the system passes through equilibrium states only (definition 2.5). In addition, at each step the system is balanced with its surroundings (for example, $P = P_{\text{ext}}$ at every moment), and there is no friction or other dissipation. Every reversible process is quasi-static, but a quasi-static process is not necessarily reversible: a piston that moves very slowly but with friction converts part of the work into heat at every step, and the process cannot be undone without leaving a trace. We will see a second example, a slow flow of heat between two bodies at different temperatures, in section 5.3.
2. **A reversible process is the most efficient one.** A reversible expansion gives the maximum work, W_{max}, and a reversible compression requires the minimum work, W_{min}. Running a reversible process forward and then backward leaves no trace, neither in the system nor in the surroundings.
3. **All real processes are irreversible.** Reversible processes are idealizations, like the ideal gas. We can approach them by carrying out a process slowly compared to the relaxation time of the system, and with as little friction as possible, but never reach them. Despite this, they are extremely useful, since they set the limits that real processes can only approach.

3.4. Chapter Review

3.4.1. Key Ideas

- **Internal energy, U,** is a state function: the energy contained in the system.
- **The first law:** energy is conserved, $dU = Q + W$. Heat and work are path functions, but their sum is not.
- **Ideal gas:** U depends only on the temperature (Joule's experiment), so $\Delta U = 0$ for any isothermal process.
- **Special processes:** $\Delta U = W$ in an adiabatic process, and $\Delta U = Q_V$ in an isochoric one, with $C_V = \frac{1}{n}\left(\frac{\partial U}{\partial T}\right)_V$.
- **Enthalpy,** $H = U + PV$, is the state function whose change equals the heat at constant pressure, $\Delta H = Q_P$.
- **Reversible processes** happen in infinitely many steps, always at equilibrium; an expansion followed by the reverse compression leaves no net work only if both are reversible.

3.4.2. Study Questions

1. What is the internal energy of a system?

a. The kinetic energy of the system as a whole.
b. The energy contained within the system, excluding the kinetic and potential energy of the system as a whole.
c. The heat stored in the system.
d. The work that the system can perform.
e. The potential energy of the system in a gravitational field.

---

2. What is the first law of thermodynamics in differential form for a closed system?

a. $dU = Q + W$.
b. $dU = Q - W$.
c. $dU = TdS$.
d. $dU = 0$ always.
e. $dU = PdV$.

---

3. What did Joule conclude from the expansion of an ideal gas into a vacuum?

a. The gas cools down during the expansion.
b. The gas performs work on the surroundings.
c. Heat flows into the gas.
d. The internal energy of an ideal gas depends only on its temperature.
e. The internal energy of an ideal gas depends on its volume.

---

4. What characterizes an adiabatic process?

a. The temperature is constant.
b. The volume is constant.
c. The pressure is constant.
d. The internal energy is constant.
e. No heat is exchanged, so $dU = W$.

---

5. How does the internal energy change in an isochoric process?

a. $dU = -PdV$.
b. $dU = 0$.
c. $dU = nC_V dT$.
d. $dU = nC_P dT$.
e. $dU = W$.

---

6. How can the heat capacity at constant volume be written as a derivative of a state function?

a. $C_V = \left(\frac{\partial U}{\partial T}\right)_V$ (for 1 mol).
b. $C_V = \left(\frac{\partial H}{\partial T}\right)_P$ (for 1 mol).
c. $C_V = \left(\frac{\partial U}{\partial V}\right)_T$.
d. $C_V = \left(\frac{\partial T}{\partial U}\right)_V$.
e. $C_V = \left(\frac{\partial P}{\partial T}\right)_V$.

---

7. What is the definition of enthalpy?

a. $H = U - PV$.
b. $H = U + TS$.
c. $H = Q + W$.
d. $H = U + PV$.
e. $H = U - TS$.

---

8. To which quantity is the heat exchanged at constant pressure equal?

a. The change in internal energy, ΔU.
b. The change in enthalpy, ΔH.
c. The work, W.
d. Zero.
e. The change in temperature, ΔT.

---

9. An ideal gas is expanded in one step and then compressed back in one step. What is the total work of this cycle?

a. Zero, since the gas returns to its initial state.
b. Negative, since net work is performed by the gas.
c. It is equal to the change in internal energy.
d. It cannot be calculated.
e. Positive, since more work is spent compressing the gas than is obtained from the expansion.

---

10. What is the total work of an expansion–compression cycle of an ideal gas performed reversibly, in infinitely many steps, at constant temperature?

a. Positive.
b. Negative.
c. Zero.
d. Infinite.
e. Equal to nRT.

Answers

1.b, 2.a, 3.d, 4.e, 5.c, 6.a, 7.d, 8.b, 9.e, 10.c

4. Thermodynamic Cycles

The first law of thermodynamics places no restrictions on the conversion of energy from one form to another. For example, let's consider once again the Joule experiment (Figure 3.1). If we design a cycle that goes from the gas on the left chamber only to the gas equilibrated in both chambers and backward, as in Figure 4.1, there are no restrictions imposed on this hypothetical cycle by the first law.

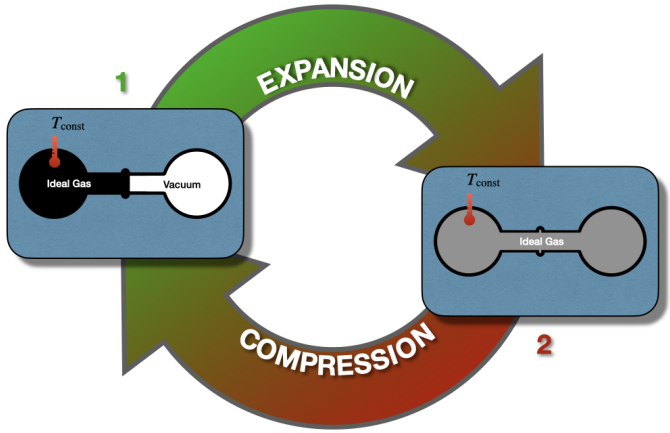


Figure 4.1.: Closing the Cycle in The Joule Expansion Experiment.

As we saw in section 3.1.1, states 1 and 2 have exactly the same energy at constant temperature. Restricting the analysis to the information contained in the first law, the ideal gas could hypothetically go from state 1 (all gas in the left chamber) to state 2 (gas in both chambers), as well as spontaneously close the cycle back from state 2 to state 1, without external intervention. While the transformation from $1 \rightarrow 2$ is intuitively spontaneous (it's the same transformation that we considered in section 3.1.1), the backward transformation from $2 \rightarrow 1$ is clearly not as intuitive. In this case, the gas should spontaneously compress back to the left side, leaving a vacuum on the right chamber, without interventions from the outside. This transformation is clearly never observed. A gas just does not spontaneously

concentrate on one side of a room, leaving a vacuum on the other side. In fact, when we need to create a vacuum, a lot of energy must be spent. Suppose we use exclusively information contained in the first law. In this case, there is nothing that might suggest a system's preference to perform the transformation $1 \to 2$, while preventing the $2 \to 1$ from happening spontaneously. Both states have the same energy, and

$$\oint dU = 0. \tag{4.1}$$

James Joule himself was indeed convinced that this must be the case and that we don't observe the backward transformation in practice only because we cannot build ideal machines.[1] Another scientist of that era was not convinced. William Thomson, the 1st Baron Kelvin (1824–1907), was unsure about this idea, and invested substantial resources to try to prove Joule wrong.[2]

The key to resolving the controversy, in favor of Kelvin, came from an unexpected source: the theoretical work of the French military engineer Nicolas Léonard Sadi Carnot (1796–1832), published years before Joule and Kelvin started working on this problem, and largely forgotten until Kelvin and Rudolf Clausius built on it in the late 1840s and 1850s.[3] At that time, the importance of steam engines was growing for industrial applications, but a theoretical perspective was lacking. Carnot was convinced that a scientific understanding of heat engines was necessary to improve their efficiency.

4.1. Carnot Cycle

The main contribution of Carnot to thermodynamics is his abstraction of the steam engine's essential features into a more general and idealized heat engine. The definition of Carnot's idealized cycle is as follows:

Definition 4.1. A *Carnot cycle* is an idealized process composed of two isothermal and two adiabatic transformations. Each transformation is either an expansion or a compression of an *ideal gas*. All transformations are assumed to be *reversible*, and no energy is lost

[1] Either because we don't really have ideal gases, or because we are unable to construct mechanical devices without loss, or in general because of other experimental factors.

[2] Interestingly enough, both Joule and Lord Kelvin are now recognized as key figures in the development of thermodynamics and science in general. So much so, that the energy unit and the temperature unit in the SI system are named after them.

[3] Carnot's lone book, the *Réflexions sur la Puissance Motrice du Feu* ("Reflections on the Motive Power of Fire") was published in France in 1824, the same year Kelvin was born and just 6 years after Joule's birth.

to mechanical friction.

A Carnot cycle connects two "heat reservoirs" at temperatures T_h (hot) and T_l (low), respectively. The reservoirs have a large thermal capacity so that their temperatures are unaffected by the cycle. The system is composed exclusively of the ideal gas, which is the only substance that changes temperature throughout the cycle. If we report the four transformations of a Carnot cycle on a PV diagram, we obtain the following plot:

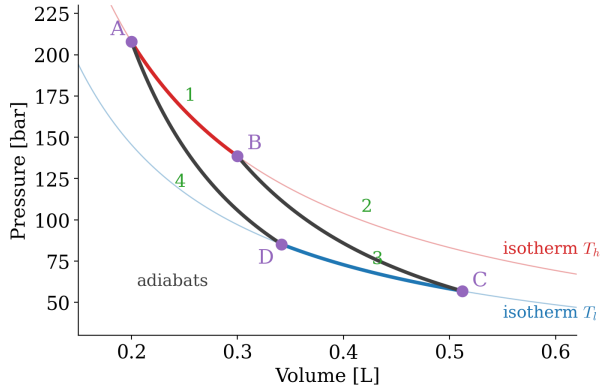


Figure 4.2.: PV-Diagram of a Carnot Cycle (computed for 1 mol of a monatomic ideal gas between $T_h = 600$ K and $T_l = 300$ K).

4.1.1. Stage 1: Isothermal Expansion $A \to B$

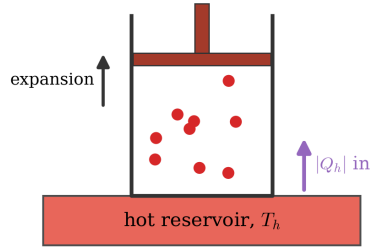


Figure 4.3.: Stage 1 of a Carnot cycle: isothermal expansion. The cylinder is in contact with the hot reservoir, from which the gas absorbs the heat $|Q_h|$.

Starting the analysis of the cycle from point A in Figure 4.2, the first

transformation we encounter is an isothermal expansion at T_h (figure 4.3). Since the transformation is isothermal:

$$\Delta U_1 = \overset{<0}{\widetilde{W_1}} + \overset{>0}{\widetilde{Q_1}} = 0 \Rightarrow Q_1 = -W_1, \tag{4.2}$$

and heat and work can be calculated for this stage using eq. 2.20:

$$\begin{aligned} Q_1 = |Q_h| &= nRT_h \overset{>0 \text{ since } V_B > V_A}{\widetilde{\ln \frac{V_B}{V_A}}} > 0, \\ W_1 = -Q_1 &= -nRT_h \ln \frac{V_B}{V_A} < 0, \end{aligned} \tag{4.3}$$

where we denoted $|Q_h|$ the absolute value of the heat that gets **into** the system from the hot reservoir.

4.1.2. Stage 2: Adiabatic Expansion $B \to C$

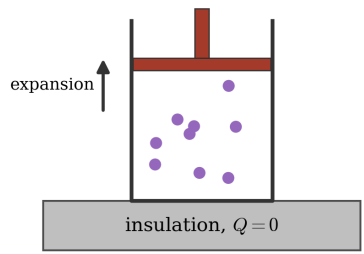


Figure 4.4.: Stage 2 of a Carnot cycle: adiabatic expansion. The cylinder is insulated, no heat is exchanged, and the gas cools down while it keeps expanding.

The second transformation is an adiabatic expansion between T_h and T_l (figure 4.4). Since we are at adiabatic conditions:

$$Q_2 = 0 \Rightarrow \Delta U_2 = W_2, \tag{4.4}$$

and the negative energy (expansion work) can be calculated using:

$$\Delta U_2 = W_2 = n \underbrace{\int_{T_h}^{T_l} C_V dT}_{<0 \text{ since } T_l<T_h} < 0. \tag{4.5}$$

4.1.3. Stage 3: Isothermal Compression $C \to D$

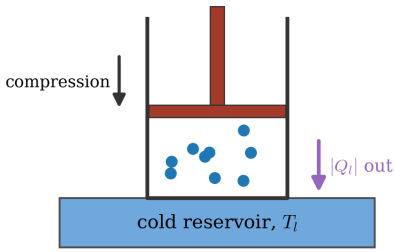


Figure 4.5.: Stage 3 of a Carnot cycle: isothermal compression. The cylinder is in contact with the cold reservoir, to which the gas releases the heat $|Q_l|$.

The third transformation is an isothermal compression at T_l (figure 4.5). The formulas are the same as those used for stage 1, but they will result in heat and work with reversed signs (since this is a compression):

$$\Delta U_3 = \overset{>0}{\widetilde{W_3}} + \overset{<0}{\widetilde{Q_3}} = 0 \Rightarrow Q_3 = -W_3, \tag{4.6}$$

and:

$$\begin{aligned} Q_3 &= -|Q_l| = nRT_l \overbrace{\ln \frac{V_D}{V_C}}^{<0 \text{ since } V_D<V_C} < 0, \\ W_3 &= -Q_3 = -nRT_l \ln \frac{V_D}{V_C} > 0, \end{aligned} \tag{4.7}$$

where $|Q_l|$ is the absolute value of the heat that gets **out of** the system to the cold reservoir ($Q_3 = -|Q_l|$ being the heat entering the system).

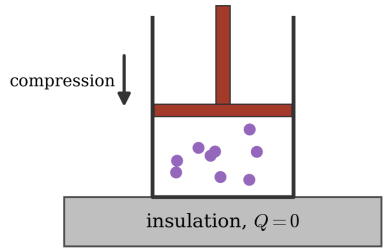


Figure 4.6.: Stage 4 of a Carnot cycle: adiabatic compression. The cylinder is insulated again, and the compression warms the gas back to its initial temperature.

4.1.4. Stage 4: Adiabatic Compression $D \to A$

The fourth and final transformation is an adiabatic compression that restores the system to point A, bringing it from T_l to T_h (figure 4.6). Similarly to stage 2:

$$Q_4 = 0 \Rightarrow \Delta U_4 = W_4, \tag{4.8}$$

since we are at adiabatic conditions. The energy associated with this process is now positive (compression work), and can be calculated using:

$$\Delta U_4 = W_4 = n \underbrace{\int_{T_l}^{T_h} C_V dT}_{>0 \text{ since } T_h > T_l} > 0. \tag{4.9}$$

Notice how $\Delta U_4 = -\Delta U_2$ because $\int_x^y = -\int_y^x$.

4.2. Energy, Heat, and Work in the Carnot Cycle

Summarizing the results of the previous sections, the total amount of energy for a Carnot cycle is:

$$\begin{aligned}\Delta U_{\mathrm{TOT}} &= \Delta U_1 + \Delta U_2 + \Delta U_3 + \Delta U_4 \\ &= 0 + n\int_{T_h}^{T_l} C_V dT + 0 + n\int_{T_l}^{T_h} C_V dT \\ &= n\int_{T_h}^{T_l} C_V dT - n\int_{T_h}^{T_l} C_V dT = 0\end{aligned} \tag{4.10}$$

which is zero, as it must be for any cycle, since $\oint dU = 0$. Notice how the result comes about: the two isothermal stages do not change the energy of an ideal gas, while the energy lost by the gas in the adiabatic expansion (from T_h to T_l) is exactly regained in the adiabatic compression (from T_l back to T_h). The amounts of work and heat, however, are not zero, since Q and W are path functions. Adding up the work of the four stages, the two adiabatic terms cancel out for the same reason, and we obtain:

$$\begin{aligned}W_{TOT} &= W_1 + W_2 + W_3 + W_4 \\ &= -nRT_h \ln\frac{V_B}{V_A} + n\int_{T_h}^{T_l} C_V dT - nRT_l \ln\frac{V_D}{V_C} + n\int_{T_l}^{T_h} C_V dT \\ &= -nRT_h \ln\frac{V_B}{V_A} - nRT_l \ln\frac{V_D}{V_C},\end{aligned} \tag{4.11}$$

The two volume ratios are not independent. Since the two adiabats connect the same two temperatures, it can be shown that $V_C/V_D = V_B/V_A$.[4] Therefore, $\ln\frac{V_D}{V_C} = -\ln\frac{V_B}{V_A}$, and eq. 4.11 reduces to:

$$W_{TOT} = -nR\,(T_h - T_l)\ln\frac{V_B}{V_A} < 0, \tag{4.12}$$

which is negative, because $T_h > T_l$ and $V_B > V_A$. Negative work means that the work is done by the system. In other words, the system is performing PV-work by transferring heat from a hot reservoir to a cold one via a Carnot cycle. On the other hand, for the heat:

[4] This relation follows from the equation of an adiabatic transformation of an ideal gas, which we do not derive in this book. We will take it as given.

$$\begin{aligned} Q_{\text{TOT}} &= Q_1 + Q_2 + Q_3 + Q_4 \\ &= |Q_h| + 0 - |Q_l| + 0 \\ &= nRT_h \ln \frac{V_B}{V_A} + nRT_l \ln \frac{V_D}{V_C} \\ &= nR\left(T_h - T_l\right) \ln \frac{V_B}{V_A} = -W_{TOT}, \end{aligned} \tag{4.13}$$

which is exactly what we should expect from the first law: since $\Delta U_{\text{TOT}} = 0$, all the net heat absorbed by the gas in a cycle must leave it as work. Since the heat is exchanged only in the two isothermal stages, this can be written as:

$$W_{TOT} = -(Q_1 + Q_3), \tag{4.14}$$

and, replacing Q_1 and Q_3 with the absolute values of the heats drawn from the hot and cold reservoirs, $|Q_h|$, and $|Q_l|$ respectively:

$$|W_{TOT}| = |Q_h| - |Q_l|\,, \tag{4.15}$$

or, in other words, more heat is extracted from the hot reservoir than it is put into the cold one. The difference between the absolute value of these amounts of heat gives the total work of the cycle. This process is depicted in Figure 4.7.

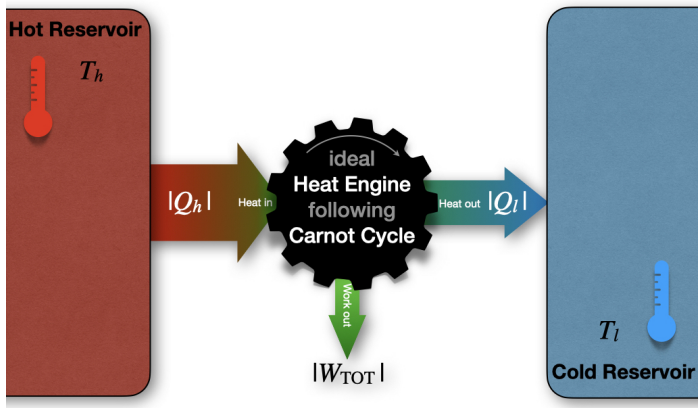


Figure 4.7.: Carnot Cycle Diagram.

Example 4.1 (A Carnot Cycle Run in Reverse)**.** Up to this point, we have discussed Carnot cycles working in the hot → cold direction (*A*

$\rightarrow B \rightarrow C \rightarrow D \rightarrow A$), since this is the primary mode of operation of heat engines that produce work. However, a heat engine could also—in principle—work in the reversed cold $\rightarrow$ hot direction ($A \rightarrow D \rightarrow C \rightarrow B \rightarrow A$). Write the equations for heat, work, and energy of each stage of a Carnot cycle going the opposite direction than the one discussed in section 4.1 and section 4.2.
Solution: When the heat engine works in reverse order, the formulas remain the same, but all the signs in front of Q, W, and U will be reversed. In this case, the total work would get **into** the system, and heat would be transferred from the cold reservoir to the hot one. Figure 4.7 would be modified as in figure 4.8.

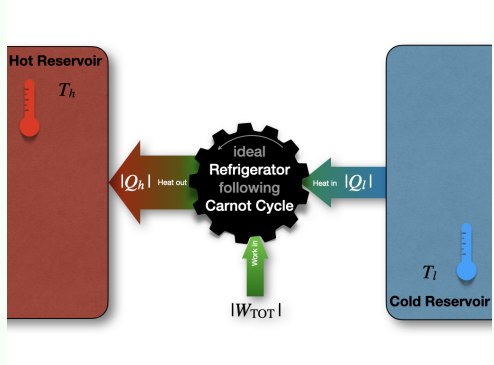


Figure 4.8.: A Carnot cycle run in reverse works as a refrigerator: the work $|W_{TOT}|$ is used to move the heat $|Q_l|$ from the cold reservoir to the hot one.

This reversed mode of operation is the basic principle behind refrigerators and air conditioning.

4.3. Efficiency of a Carnot Cycle

The efficiency (ε) of a cycle is defined as the ratio between the absolute value of the work extracted from the cycle ($|W_{TOT}|$) and the heat that gets into the system ($|Q_h|$):

$$\varepsilon = \frac{|W_{TOT}|}{|Q_h|} = \frac{-W_{TOT}}{Q_1} \tag{4.16}$$

where the minus sign in front of the work is necessary because the efficiency is defined as a positive number. Replacing eq. 4.14 into eq. 4.16, we

obtain:

$$\varepsilon = \frac{Q_3 + Q_1}{Q_1} = 1 + \frac{Q_3}{Q_1}. \tag{4.17}$$

If we go back to eq. 4.16 and we replace eq. 4.12 for W_{TOT} and eq. 4.3 for Q_1, we obtain:

$$\varepsilon = \frac{nR\,(T_h - T_l)\ln V_B/V_A}{nRT_h \ln V_B/V_A} = \frac{T_h - T_l}{T_h} = 1 - \frac{T_l}{T_h} < 1, \tag{4.18}$$

which proves that the efficiency of a Carnot cycle is strictly smaller than 1.[5] In other words, no cycle can convert 100% of the heat into work it extracts from a hot reservoir. Eq. 4.18 also has a deeper meaning. Since the efficiency of a Carnot cycle does not depend on the substance inside it, the ratio $\frac{|Q_l|}{|Q_h|} = \frac{T_l}{T_h}$ defines temperature without any reference to a particular thermometer. This is the *thermodynamic temperature scale*, introduced by Kelvin in 1848, and it coincides with the scale of the gas thermometer of chapter 2. In this scale, absolute zero is the temperature of a cold reservoir that would receive no heat at all, so that the engine could turn all the heat into work, which is exactly what the second law forbids. This finding had remarkable consequences on the entire thermodynamics field and set the foundation for the introduction of entropy. We will use eq. 4.16 and eq. 4.18 for this purpose in the next chapter, but we conclude the discussion on Carnot cycles by returning to Lord Kelvin. In 1851 he used this finding to formulate his statement "It is impossible for a self-acting machine, unaided by any external agency, to convey heat from one body to another at a higher temperature. It is impossible, by means of inanimate material agency, to derive mechanical effect from any portion of matter by cooling it below the temperature of the coldest of the surrounding objects."[6] This statement conclusively disproved Joule's original theories and demonstrated that there is some fundamental principle to govern the flow of heat beyond the first law of thermodynamics.

4.3.1. Refrigerators and Heat Pumps

For a cycle run in reverse, as in figure 4.8, the efficiency is replaced by the *coefficient of performance* (COP), the ratio between what we want and the work that we pay for it. A refrigerator is meant to extract the heat $|Q_l|$ from the cold reservoir (the inside of the fridge), while a heat pump is

[5] Eq. 4.18 can be equal to 1 only if $T_l = 0$ K or $T_h = \infty$, two conditions that are both equally impossible.

[6] Thomson W. Transactions of the Royal Society of Edinburgh. 1851 XX 261–268, 289–298..

meant to deliver the heat $|Q_h|$ to the hot reservoir (the inside of a house in winter). Following the same steps as for eq. 4.18, for a Carnot cycle:

$$\mathrm{COP}_{\text{refrigerator}} = \frac{|Q_l|}{|W_{TOT}|} = \frac{T_l}{T_h - T_l}, \qquad \mathrm{COP}_{\text{heat pump}} = \frac{|Q_h|}{|W_{TOT}|} = \frac{T_h}{T_h - T_l}. \tag{4.19}$$

Unlike the efficiency, the COP can be (and usually is) larger than 1, since the work is used only to *move* heat, not to create it. For example, a heat pump that keeps a house at 20 °C (293 K) when it is 0 °C outside (273 K) has a Carnot COP of $\frac{293}{20} \approx 15$: in the ideal case, every joule of electricity delivers 15 joules of heat to the house. Real heat pumps reach COPs of about 3–4, which still makes them much more efficient than electric heaters, whose COP is 1. The COP decreases as the temperature difference grows, which is why heat pumps work less well in very cold climates.

4.4. Chapter Review

4.4.1. Key Ideas

- **The first law is not enough:** it allows processes that never happen, such as a gas spontaneously compressing into half of its container.
- **The Carnot cycle** is made of two reversible isotherms and two reversible adiabats, between a hot reservoir at T_h and a cold one at T_l.
- **Over a full cycle,** $\Delta U = 0$, so the total work equals minus the total heat exchanged.
- **Efficiency** is the work produced divided by the heat absorbed from the hot reservoir. For a Carnot cycle, $\varepsilon = 1 - \frac{T_l}{T_h} < 1$.
- **No engine converts all of its heat into work,** because some heat must always be released to the cold reservoir.
- **Refrigerators and heat pumps** are reversed cycles, rated by their coefficient of performance: $\frac{T_l}{T_h - T_l}$ and $\frac{T_h}{T_h - T_l}$ for Carnot cycles. The COP is usually larger than 1.
- **Run in reverse,** a Carnot cycle uses work to move heat from the cold to the hot reservoir: it works as a refrigerator.

4.4.2. Study Questions

1. What does the first law of thermodynamics say about a gas that spontaneously compresses back into one side of the Joule apparatus?

a. It forbids it, since energy would not be conserved.
b. It requires work to be done on the gas.
c. It requires heat to flow out of the gas.
d. Nothing: the process would conserve energy, so the first law does not forbid it.
e. It shows that the process is spontaneous.

---

2. What transformations make up a Carnot cycle?

a. Two isochoric and two isobaric transformations.
b. Two isothermal and two adiabatic reversible transformations.
c. Four isothermal transformations.
d. Four adiabatic transformations.
e. One isothermal, one adiabatic, one isochoric, and one isobaric transformation.

---

3. What happens during the isothermal expansion at T_h in a Carnot cycle?

a. $\Delta U = 0$, heat is absorbed from the hot reservoir, and the same amount of energy leaves as work.
b. No heat is exchanged.
c. The temperature drops from T_h to T_l.
d. Heat is released to the cold reservoir.
e. Work is done on the gas.

---

4. What happens during the adiabatic expansion in a Carnot cycle?

a. Heat is absorbed from the hot reservoir.
b. The internal energy stays constant.
c. Heat is released to the cold reservoir.
d. The volume decreases.
e. No heat is exchanged, the gas performs work, and its temperature drops from T_h to T_l.

---

5. What is the total change in internal energy for a complete Carnot cycle?

a. $nR(T_h - T_l)\ln\frac{V_B}{V_A}$.
b. $nC_V(T_h - T_l)$.
c. Zero, since the internal energy is a state function.
d. Equal to the total work.
e. Equal to the heat absorbed from the hot reservoir.

---

6. What is the total work of a Carnot cycle?

a. $W_{TOT} = nR(T_h - T_l)\ln\frac{V_B}{V_A}$.
b. $W_{TOT} = -nR(T_h - T_l)\ln\frac{V_B}{V_A}$.
c. $W_{TOT} = 0$.
d. $W_{TOT} = nRT_h\ln\frac{V_B}{V_A}$.
e. $W_{TOT} = nC_V(T_h - T_l)$.

---

7. How is the efficiency of a heat engine defined?

a. $\varepsilon = \frac{|Q_h|}{|W_{TOT}|}$.
b. $\varepsilon = \frac{|Q_l|}{|Q_h|}$.
c. $\varepsilon = \frac{|W_{TOT}|}{|Q_l|}$.
d. $\varepsilon = \frac{|W_{TOT}|}{|Q_h|}$.
e. $\varepsilon = \frac{T_h}{T_l}$.

---

8. What is the efficiency of a Carnot cycle in terms of the reservoir temperatures?

a. $\varepsilon = 1 - \frac{T_l}{T_h}$.
b. $\varepsilon = 1 - \frac{T_h}{T_l}$.
c. $\varepsilon = \frac{T_h}{T_l}$.
d. $\varepsilon = \frac{T_h - T_l}{T_l}$.
e. $\varepsilon = 1$.

---

9. Why is the efficiency of a Carnot cycle always smaller than 1?

a. Because of friction in the engine.
b. Because the gas is not ideal.
c. Because heat is a state function.
d. Because the cycle is irreversible.
e. Because it would be 1 only if $T_l = 0$ K or $T_h = \infty$, which are impossible.

---

10. What happens when a Carnot cycle is run in reverse?

a. It produces more work than the forward cycle.
b. It reaches 100% efficiency.
c. Work is put into the system, and heat is moved from the cold reservoir to the hot one, as in a refrigerator.
d. Heat flows from the hot reservoir to the cold one without work.
e. It violates the first law.

Answers

1.d, 2.b, 3.a, 4.e, 5.c, 6.b, 7.d, 8.a, 9.e, 10.c

5. Entropy and the Second Law of Thermodynamics

In chapter 4, we used heat engines to understand why some processes are spontaneous while others are not, and we found that no engine can convert all the heat it absorbs into work. Carnot's findings did not just inspire Lord Kelvin on this subject, but they also motivated Rudolf Clausius (1822–1888) to introduce a new state function, the *entropy*. In this chapter, we will follow Clausius' reasoning to define the entropy, we will use it to write the second law of thermodynamics, and we will then look at the same quantity from the microscopic point of view of Boltzmann, to understand what entropy really measures.

5.1. Entropy

Let's return to the efficiency of a Carnot cycle, and bring together the two expressions that we found in eq. 4.17 and eq. 4.18:

$$\varepsilon = 1 + \frac{Q_3}{Q_1} = 1 - \frac{T_l}{T_h}. \tag{5.1}$$

Subtracting 1 from both sides, we obtain $\frac{Q_3}{Q_1} = -\frac{T_l}{T_h}$. We can then multiply both sides by $\frac{Q_1}{T_l}$, which separates the quantities related to the cold reservoir from the ones related to the hot reservoir:

$$\frac{Q_3}{T_l} = -\frac{Q_1}{T_h}, \tag{5.2}$$

or, moving everything to the left-hand side:

$$\frac{Q_3}{T_l} + \frac{Q_1}{T_h} = 0. \tag{5.3}$$

The left-hand side of eq. 5.3 is a sum of two terms, one for each isothermal stage of the Carnot cycle. Each term is the heat exchanged during that

stage, divided by the temperature at which it is exchanged. Since, according to Definition 4.1, each transformation in a Carnot cycle is reversible, these are heats exchanged at reversible conditions, Q_{REV}. The two adiabatic stages do not contribute, since no heat is exchanged during them.

Is this result special to the Carnot cycle? To find out, let's look at the heat exchanged by an ideal gas along *any* reversible path, not just along isotherms and adiabats. From the first law, the reversible heat is $Q_{\text{REV}} = dU - W_{\text{REV}}$. Since the internal energy of an ideal gas depends only on its temperature (section 3.1.1), $dU = nC_V\,dT$ for any process, and the reversible work is $W_{\text{REV}} = -P\,dV = -\frac{nRT}{V}dV$. Therefore:

$$Q_{\text{REV}} = nC_V\,dT + \frac{nRT}{V}\,dV. \tag{5.4}$$

This looks like a total differential, eq. 1.3, but it is not one. If we apply the Schwarz test of chapter 1 to the two coefficients, the derivative of nC_V with respect to V is zero, while the derivative of $\frac{nRT}{V}$ with respect to T is $\frac{nR}{V}$. The two mixed derivatives are different, as we expect for the heat, which is a path function. Now let's divide both sides of eq. 5.4 by the temperature:

$$\frac{Q_{\text{REV}}}{T} = \frac{nC_V}{T}\,dT + \frac{nR}{V}\,dV. \tag{5.5}$$

This time, the derivative of $\frac{nC_V}{T}$ with respect to V is zero, and the derivative of $\frac{nR}{V}$ with respect to T is also zero. The test is passed: eq. 5.5 is an exact differential.[1] Dividing by T removed the T from the coefficient of dV, which was the only thing that made the heat path-dependent. And since the integral of an exact differential around a closed path is always zero, for *any* reversible cycle of an ideal gas we have:

$$\oint \frac{Q_{\text{REV}}}{T} = 0. \tag{5.6}$$

The Carnot result, eq. 5.3, is just a special case: along the two isotherms we add $\frac{Q}{T}$, and along the two adiabats we add nothing.

We have proved eq. 5.6 only for the ideal gas, but the result is general. Carnot showed that every reversible engine working between the same two temperatures has the same efficiency, whatever substance it contains (otherwise, coupling two different engines would let us move heat from a cold body to a hot one with no other effect, which, as we will see in this chapter, never happens). Since the efficiency fixes $\frac{Q_3}{Q_1}$, eq. 5.3 holds for the Carnot

[1] In fact, we can integrate it directly: if C_V is constant, $\frac{Q_{\text{REV}}}{T} = d\left(nC_V \ln T + nR \ln V\right)$.

cycles of every substance, and from there one can show that eq. 5.6 holds for any reversible cycle of any substance. We will not go through this general proof, which requires more work than it is worth here; the ideal-gas calculation already shows the essential point.

Eq. 5.6 is a remarkable result. The heat, Q, is a path function, and its integral around a cycle is in general *not* zero. However, if we take the heat exchanged reversibly and divide it by the temperature, we obtain a quantity whose integral around *any* reversible cycle is zero. As we saw for the energy in eq. 3.16, this is precisely the property that defines a state function: when we go back to the starting point, we always find the same value. Clausius realized this in 1865, and he decided to call the new state function *entropy*, and to indicate it with the letter S:

Definition 5.1. *Entropy:* The state function S whose infinitesimal change is equal to the heat exchanged at reversible conditions, divided by the temperature at which it is exchanged:

$$dS = \frac{Q_{\text{REV}}}{T}. \tag{5.7}$$

For a transformation between an initial and a final state, the change in entropy is obtained by integration along any reversible path that connects the two states:

$$\Delta S = S_f - S_i = \int_i^f \frac{Q_{\text{REV}}}{T}. \tag{5.8}$$

Let's unpack Definition 5.1:

1. **Dividing by T turns a path function into a state function.** In chapter 1, we introduced inexact differentials, such as Q, which cannot be integrated as differences between final and initial values. Eq. 5.7 tells us that, for reversible processes, dividing Q_{REV} by the temperature turns it into the exact differential of a state function, dS. Mathematicians call $1/T$ an *integrating factor*.
2. **Only the reversible heat works.** The heat exchanged along an irreversible path is different, and dividing it by T does *not* give dS. To calculate the entropy change of an irreversible process, we must find a reversible path between the same initial and final states and calculate ΔS along that path. Since the entropy is a state function, the result is valid for the irreversible process as well.
3. **The same heat matters more at low temperature.** The entropy change produced by a given amount of heat is larger when the heat is exchanged at a low temperature than at a high temperature.

Intuitively, giving 1 kJ of heat to a cold object changes it more than giving the same 1 kJ to a hot one.

4. **The units of entropy are energy divided by temperature**, J/K in SI. The entropy is an extensive property, and its molar version, $\overline{S}$, is measured in $\mathrm{J\,mol^{-1}\,K^{-1}}$.
5. **Only changes in entropy are defined, for now.** Eq. 5.8 gives us differences in entropy, but not absolute values. We will see in chapter 6 that the third law of thermodynamics fixes the zero of the entropy scale.

5.2. Irreversible Cycles

Up to this point, we have discussed *reversible* cycles only. What happens when the cycle is irreversible? In chapter 4, we saw that the efficiency of a Carnot cycle, eq. 4.18, is the maximum efficiency that any cycle working between two temperatures can reach. Any real (irreversible) cycle loses some energy along the way, for example to friction, and its efficiency is always smaller than the Carnot one. Therefore, eq. 5.1 does not hold anymore for an *irreversible* cycle, and it must be replaced by an inequality:

$$\overbrace{1+\frac{Q_3^{\mathrm{IRR}}}{Q_1^{\mathrm{IRR}}}}^{\varepsilon_{\mathrm{IRR}}} < \overbrace{1-\frac{T_l}{T_h}}^{\varepsilon_{\mathrm{REV}}}. \tag{5.9}$$

Following exactly the same steps used in section 5.1 (subtracting 1 from both sides and multiplying by $\frac{Q_1^{\mathrm{IRR}}}{T_l}$, which is positive, so the direction of the inequality does not change), we obtain:

$$\frac{Q_3^{\mathrm{IRR}}}{Q_1^{\mathrm{IRR}}} < -\frac{T_l}{T_h} \longrightarrow \frac{Q_3^{\mathrm{IRR}}}{T_l} + \frac{Q_1^{\mathrm{IRR}}}{T_h} < 0 \longrightarrow \sum_i \frac{Q_{\mathrm{IRR},i}}{T_i} < 0, \tag{5.10}$$

which, using the same calculus procedure as before, becomes:

$$\oint \frac{Q_{\mathrm{IRR}}}{T} < 0. \tag{5.11}$$

Putting eq. 5.6 and eq. 5.11 together, we obtain:

$$\oint \frac{Q}{T} \leq 0, \tag{5.12}$$

where the equal sign holds for reversible cycles exclusively, while the inequality sign holds for irreversible ones. Eq. 5.12 is known as the **Clausius inequality**. In words, it tells us that around an irreversible cycle, the system always gives away more "heat divided by temperature" than it absorbs. This is the mathematical version of the fact that some of the energy that goes through a real engine is always wasted.

5.3. The Second Law of Thermodynamics

We are now ready to use the Clausius inequality to understand spontaneity. Let's consider an isolated system that undergoes an irreversible transformation from state 1 to state 2, and then let's bring it back from state 2 to state 1 along a reversible path, as in Figure 5.1.

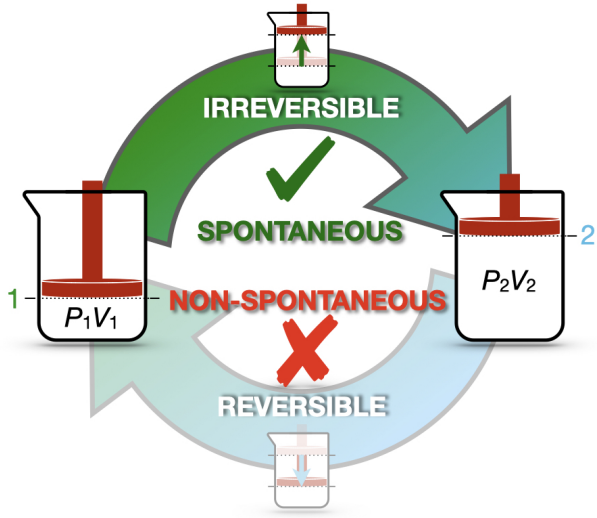


Figure 5.1.: Spontaneous and Non-Spontaneous Transformations in a Cycle.

This cycle is similar to the one in Figure 4.1 for the Joule expansion experiment: the gas expands spontaneously into the vacuum ($1 \to 2$), but it never goes back on its own ($2 \to 1$). To bring it back, we must compress it from the outside.[2] Since the cycle contains an irreversible step, it is irreversible

[2]Strictly speaking, during the reversible compression the system cannot be isolated, since a reversible return to state 1 requires exchanging heat and work with the surroundings. This does not affect our argument: we use the reversible path only as a tool to calculate the entropy change between states 1 and 2, and since the entropy is a state function, the result does not depend on how we actually bring the system back. This is therefore a plausibility argument rather than a rigorous proof, but it

overall, and the Clausius inequality, eq. 5.12, gives:

$$\int_1^2 \frac{Q_{\text{IRR}}}{T} + \int_2^1 \frac{Q_{\text{REV}}}{T} < 0. \tag{5.13}$$

The second integral is taken along a reversible path, so, according to eq. 5.8, it is the entropy change from state 2 to state 1, which is $-\Delta S$, where $\Delta S = S_2 - S_1$ is the entropy change of the forward process. Moving it to the right-hand side, we obtain:

$$\underbrace{\int_1^2 \frac{Q_{\text{REV}}}{T}}_{\Delta S} > \underbrace{\int_1^2 \frac{Q_{\text{IRR}}}{T}}_{=0}, \tag{5.14}$$

where the right-hand side is zero because the system is isolated during the forward process, and therefore $Q_{\text{IRR}} = 0$. Eq. 5.14 simply becomes:

$$\Delta S > 0. \tag{5.15}$$

What does eq. 5.15 tell us?

1. **In an isolated system, spontaneous processes increase the entropy.** Every irreversible process that happens on its own in an isolated system has $\Delta S > 0$. Spontaneous processes are always irreversible, since reversible processes are idealizations that require infinitely slow, controlled changes.
2. **The entropy changes even if no heat is exchanged.** In the Joule expansion, $Q = 0$, and yet $\Delta S > 0$. This is not a contradiction: the entropy change must be calculated along a reversible path between the same states, and along that path heat *is* exchanged. We will calculate this value in chapter 6.
3. **The reverse process would decrease the entropy**, and it never happens on its own in an isolated system. This is why the gas never goes back to one side of the box.

Since the only system that is truly isolated is the universe, we can write a concise statement for a new fundamental law of thermodynamics:

Definition 5.2. *Second Law of Thermodynamics:* For any spontaneous process, the entropy of the universe increases.

Historically, the second law was first stated in terms of heat and engines, in two classical forms that we can now derive from the entropy:

leads to the correct result.

- **Clausius statement:** heat cannot flow spontaneously from a colder body to a hotter one. If the heat $Q > 0$ moved on its own from a reservoir at T_l to one at $T_h > T_l$, the entropy of the universe would change by $-\frac{Q}{T_l} + \frac{Q}{T_h} < 0$.
- **Kelvin statement:** no cyclic process can absorb heat from a single reservoir and convert it entirely into work. After a full cycle, the entropy of the engine is unchanged, while the reservoir loses the entropy $\frac{Q}{T}$, so the entropy of the universe would decrease.

The two statements are equivalent: a device that violated one of them could be combined with an ordinary engine or refrigerator to violate the other. Both are contained in Kelvin's 1851 words that we quoted at the end of chapter 4.

The entropy also lets us complete the distinction between quasi-static and reversible processes that we started in chapter 3. Consider two large reservoirs, at T_h and T_l, connected by a thin rod that conducts heat very poorly. Heat flows so slowly that both reservoirs pass only through equilibrium states, and the process is quasi-static. Yet, when the heat Q moves from the hot reservoir to the cold one, the entropy of the universe changes by $\frac{Q}{T_l} - \frac{Q}{T_h} > 0$, and the process is irreversible: the heat will never flow back on its own. A slow process is reversible only if, in addition, there are no finite differences of temperature (or pressure) between the system and its surroundings, and no friction.

5.4. Boltzmann Entropy

Up to this point, we have treated entropy as a macroscopic quantity, defined through heat and temperature. This definition is powerful, but it does not tell us what entropy *is* at the level of molecules, which is where chemistry happens. The microscopic meaning of entropy was found by Ludwig Eduard Boltzmann (1844–1906), who connected it to the number of ways in which the molecules of a system can be arranged.

To understand Boltzmann's idea, we need to distinguish between two ways of describing a system:

- A **macrostate** is described by the macroscopic variables that we can measure, such as pressure, volume, and temperature.
- A **microstate** is a complete specification of where every single molecule is and how it moves.[3]

[3] Positions and velocities are continuous quantities, so to count microstates we have to divide space into small cells, and only ask which cell each molecule is in. Quantum mechanics, which we will study in P-Chem 2, makes this counting exact, since the energy levels of molecules are discrete.

Many different microstates correspond to the same macrostate, since we can swap molecules around without changing the pressure or the temperature. The number of microstates that correspond to a given macrostate is called its **multiplicity**, and is indicated with Ω.

5.4.1. Counting Microstates

Let's see how this works with a simple example. Consider a box divided into two halves, left and right, containing just four molecules, which we label a, b, c, and d. Each molecule can be in either half, and we consider as a macrostate the number of molecules in the left half. The microstates are all the possible ways of assigning each molecule to one of the two halves:

Table 5.1.: Microstates of four molecules in a box divided into two halves.

Molecules on the left	Microstates (molecules on the left)	Ω
4	$abcd$	1
3	abc, abd, acd, bcd	4
2	ab, ac, ad, bc, bd, cd	6
1	a, b, c, d	4
0	none	1

The same microstates are drawn in figure 5.2, where each box is one microstate, and each row collects the microstates that belong to the same macrostate.

There are $2^4 = 16$ microstates in total. If the molecules move around randomly, each microstate is equally likely, and the probability of each macrostate is proportional to its multiplicity. Notice three things in table 5.1:

1. **The evenly distributed macrostate is the most probable.** Two molecules on each side has $\Omega = 6$, which corresponds to a probability of 6/16, almost 40%.
2. **The macrostate with all molecules on one side is the least probable.** It has $\Omega = 1$, so its probability is only 1/16.
3. **The effect becomes overwhelming for many molecules.** With N molecules, the probability of finding all of them on the left is $1/2^N$. For $N = 100$ molecules, this is about 10^{-30}. For a mole of gas, with $N \approx 6 \times 10^{23}$, it is so small that it will never be observed. This is why the gas in the Joule experiment never goes back to one side of

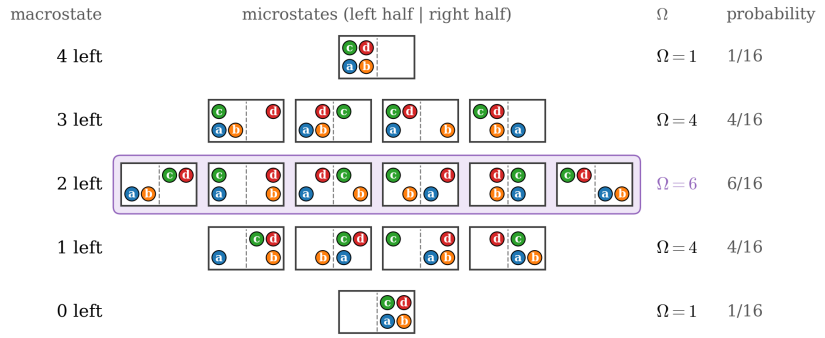


Figure 5.2.: The 16 Microstates of Four Molecules in a Box Divided into Two Halves, Grouped by Macrostate (Number of Molecules in the Left Half). The Evenly Distributed Macrostate (Highlighted) Has the Most Microstates.

the box: not because it is forbidden, but because it is overwhelmingly improbable.

5.4.2. The Boltzmann Equation

Boltzmann connected the multiplicity to the thermodynamic entropy through the formula that became famous as the **Boltzmann equation**:

$$S = k_B \ln \Omega, \tag{5.16}$$

where k_B is the Boltzmann constant, $k_B = R/N_A = 1.380649 \times 10^{-23}\,\mathrm{J/K}$, with R being the ideal gas constant and N_A Avogadro's constant. The Boltzmann constant is the ideal gas constant "per molecule", and it is the conversion factor between the microscopic counting of Ω and the macroscopic entropy measured in J/K.

Why the logarithm? If we put together two independent systems, the number of microstates of the combined system is the *product* of the two multiplicities, $\Omega = \Omega_1 \Omega_2$, since every microstate of the first can be combined with every microstate of the second. However, the entropy is extensive, so the entropy of the combined system must be the *sum* of the two entropies. The logarithm is the function that turns products into sums: $k_B \ln(\Omega_1 \Omega_2) = k_B \ln \Omega_1 + k_B \ln \Omega_2$.

Let's now check that Boltzmann's entropy agrees with Clausius' one, using the expansion of an ideal gas into twice its initial volume. Each molecule now has twice as many positions available, so, for each microstate of the

initial state, there are 2^N microstates of the final state, where N is the number of molecules. Using eq. 5.16:

$$\Delta S = k_B \ln \Omega_f - k_B \ln \Omega_i = k_B \ln \frac{\Omega_f}{\Omega_i} = k_B \ln 2^N = N k_B \ln 2 = nR \ln 2, \tag{5.17}$$

where in the last step we used $N k_B = n N_A \frac{R}{N_A} = nR$. In chapter 6, we will calculate the same entropy change from Clausius' definition, obtaining $\Delta S = nR \ln \frac{V_f}{V_i}$, which for $V_f = 2V_i$ is exactly the same result. The two definitions of entropy describe the same quantity.

5.4.3. Why "Disorder" Can Be Misleading

Entropy is often described as a measure of "disorder." This description is not completely wrong, but it can be misleading. A more accurate description is that the entropy measures the *number of microscopic arrangements* compatible with what we observe macroscopically. For example, when ice melts, the entropy increases because the water molecules in the liquid can move around and take many more positions and orientations than in the rigid crystal. Calling the liquid "more disordered" is a shortcut for "has many more microstates," and it is the number of microstates that we should keep in mind.

The shortcut becomes a misconception when we apply it to everyday objects. A messy room does not have a higher thermodynamic entropy than a tidy one. The thermodynamic entropy counts the arrangements of about 10^{23} molecules, and the arrangement of a few dozen books and socks does not contribute to it in any measurable way. Moreover, a messy room and a tidy room are each just *one* specific arrangement of the objects. If we really want to count arrangements of objects, we need many identical copies of the same room.[4]

[4] A better version of the analogy is that of a hotel with many identical rooms containing the same objects. The collection of all the unmade rooms in the morning has a higher entropy than the collection of the same rooms after the housekeepers have arranged all the objects in every room in exactly the same way.

5.5. Chapter Review

5.5.1. Key Ideas

- **Clausius entropy:** $dS = \frac{Q_{\text{REV}}}{T}$. The entropy is a state function, measured in J/K.
- **Why dividing by T works:** for an ideal gas, $Q_{\text{REV}} = nC_V\,dT + \frac{nRT}{V}dV$ fails the Schwarz test, but $\frac{Q_{\text{REV}}}{T}$ passes it. Its integral around any reversible cycle is zero, which makes S a state function ($1/T$ is an integrating factor).
- **Irreversible processes:** to calculate ΔS, we use a reversible path between the same two states, since S is a state function.
- **Clausius inequality:** $\oint \frac{Q}{T} \leq 0$ around any cycle, with the equal sign only for reversible cycles.
- **The second law:** the entropy of the universe increases in every spontaneous process, and stays constant only in reversible ones.
- **Classical statements:** heat does not flow spontaneously from cold to hot (Clausius), and no cycle turns the heat of a single reservoir entirely into work (Kelvin). Both follow from the increase of the entropy of the universe.
- **Boltzmann entropy:** $S = k_B \ln \Omega$, where Ω counts the microstates compatible with the macroscopic state. Spontaneous processes move toward the macrostates with the most microstates.

5.5.2. Study Questions

1. Which quantity has a sum (or integral) equal to zero around any reversible cycle?

a. The heat, Q_{REV}.
b. The heat divided by the temperature, $\frac{Q_{\text{REV}}}{T}$.
c. The work, W.
d. The temperature, T.
e. The heat multiplied by the temperature, $Q_{\text{REV}}T$.

---

2. Which formula defines the entropy according to Clausius?

a. $dS = \frac{Q_{\text{REV}}}{T}$.
b. $dS = \frac{Q_{\text{IRR}}}{T}$.
c. $dS = Q_{\text{REV}}\,T$.
d. $S = \frac{T}{Q}$.

e. $dS = \frac{W}{T}$.

---

3. How can we calculate the entropy change of an irreversible process?

a. By integrating the irreversible heat divided by the temperature.
b. It cannot be calculated.
c. By using the work instead of the heat.
d. By calculating it along a reversible path between the same initial and final states.
e. By assuming it is always zero.

---

4. What are the units of entropy in the SI?

a. J.
b. K/J.
c. J · K.
d. J/mol.
e. J/K.

---

5. What is the Clausius inequality?

a. $\oint \frac{Q}{T} \geq 0$.
b. $\oint \frac{Q}{T} = 0$ always.
c. $\oint \frac{Q}{T} \leq 0$.
d. $\oint Q \leq 0$.
e. $\oint dS > 0$.

---

6. How does the efficiency of an irreversible cycle compare with that of a Carnot cycle between the same temperatures?

a. It is smaller.
b. It is larger.
c. It is the same.
d. It is always zero.
e. It can be larger than 1.

---

7. What does the second law of thermodynamics state?

a. The energy of the universe is conserved.
b. The entropy of the universe is constant.
c. The entropy of a system always increases.
d. For any spontaneous process, the entropy of the universe increases.
e. Heat can be completely converted into work.

---

8. A gas expands into a vacuum inside an insulated container (the Joule expansion). What are the heat exchanged and the entropy change of the gas?

a. $Q > 0$ and $\Delta S > 0$.
b. $Q = 0$ and $\Delta S > 0$.
c. $Q = 0$ and $\Delta S = 0$.
d. $Q < 0$ and $\Delta S < 0$.
e. $Q = 0$ and $\Delta S < 0$.

---

9. Which formula is the Boltzmann equation for the entropy?

a. $S = k_B \Omega$.
b. $S = R \ln T$.
c. $S = \frac{\Omega}{k_B}$.
d. $S = k_B T$.
e. $S = k_B \ln \Omega$.

---

10. Four molecules move randomly in a box divided into two halves. Which macrostate is the most probable?

a. All four molecules on the left.
b. Three molecules on the left and one on the right.
c. Two molecules on each side.
d. All four molecules on the right.
e. All macrostates are equally probable.

Answers

1.b, 2.a, 3.d, 4.e, 5.c, 6.a, 7.d, 8.b, 9.e, 10.c

6. Calculation of Entropy and the Third Law of Thermodynamics

In chapter 5, we defined the entropy as a state function, and we found that the entropy of the universe increases in every spontaneous process. A definition, however, is not very useful until we know how to calculate it. In this chapter, we will learn how to calculate the entropy changes of the most common transformations: heating and cooling, expansions and compressions, and phase changes. We will then see how to account for the surroundings, and we will introduce the third law of thermodynamics, which fixes the zero of the entropy scale and allows us to tabulate absolute entropies. Finally, we will define the standard state, the common reference for all thermodynamic tables, and we will use it to look at our first chemical reaction.

The Second Law can be used to infer the spontaneity of a process, as long as the entropy of the universe is considered. To do so, we need to remind ourselves that the universe can be divided into a system and its surroundings (environment). When we calculate the entropy of the universe as an indicator of the spontaneity of a process, we need to *always* consider changes in entropy in *both* the system (sys) and its surroundings (surr):

$$\Delta S^{\text{universe}} = \Delta S^{\text{sys}} + \Delta S^{\text{surr}}, \tag{6.1}$$

or, in differential form:

$$dS^{\text{universe}} = dS^{\text{sys}} + dS^{\text{surr}}. \tag{6.2}$$

6.1. Calculation of ΔS^{sys}

In general ΔS^{sys} can be calculated from its definition, definition 5.1, integrated along a reversible path, eq. 5.8. In practice, it is always convenient to keep in mind that entropy is a state function, and as such it does not depend on the path. For this reason, we can break every transformation into elementary steps, and calculate the entropy on any path that goes from the initial state to the final state, such as, for example:

$$\begin{array}{ccc} P_i, T_i & \xrightarrow{\Delta_{\mathrm{TOT}} S^{\mathrm{sys}}} & P_f, T_f \\ {\scriptstyle \Delta_1 S^{\mathrm{sys}}} \searrow & & \nearrow {\scriptstyle \Delta_2 S^{\mathrm{sys}}} \\ & P_i, T_f & \end{array} \tag{6.3}$$

$$\Delta_{\mathrm{TOT}} S^{\mathrm{sys}} = \Delta_1 S^{\mathrm{sys}} + \Delta_2 S^{\mathrm{sys}},$$

with $\Delta_1 S^{\mathrm{sys}}$ calculated at constant P, and $\Delta_2 S^{\mathrm{sys}}$ at constant T. The most important elementary steps from which we can calculate the entropy resemble the prototypical processes for which we calculated the energy in section 3.1.

6.1.1. Entropy in Isothermal Processes

- For an ideal gas at constant temperature $\Delta U = 0$, and $Q_{\mathrm{REV}} = -W_{\mathrm{REV}}$. Using the formula for W_{REV} in eq. 2.19 (or its analogue for P), we obtain:

$$\Delta S^{\mathrm{sys}} = \int_i^f \frac{Q_{\mathrm{REV}}}{T} = \frac{-W_{\mathrm{REV}}}{T} = \frac{nRT \ln \frac{V_f}{V_i}}{T} = nR \ln \frac{V_f}{V_i}, \tag{6.4}$$

  or, similarly:

$$\Delta S^{\mathrm{sys}} = nR \ln \frac{P_i}{P_f}. \tag{6.5}$$

- A phase change is a particular case of an isothermal process that does not follow the formulas introduced above since an ideal gas never liquefies. The entropy associated with a phase change at constant pressure can be calculated from its definition, remembering that $Q_{\mathrm{REV}} = \Delta H$. For example for vaporizations:

$$\Delta_{\mathrm{vap}} S = \frac{\Delta_{\mathrm{vap}} H}{T_B}, \tag{6.6}$$

with $\Delta_{\mathrm{vap}} H$ being the enthalpy of vaporization of a substance, and T_B its boiling temperature.

It is experimentally observed that the entropies of vaporization of many liquids have almost the same value of:

$$\Delta_{\mathrm{vap}} S \approx 10.5R, \tag{6.7}$$

which corresponds in SI to the range of about 85–88 J/(mol K). This simple rule is named **Trouton's rule**, after the Irish physicist who discovered it, Frederick Thomas Trouton (1863–1922).

Example 6.1 (Entropy of vaporization of water)**.** Calculate the standard entropy of vaporization of water knowing $\Delta_{\text{vap}}H^{\ominus}_{\text{H}_2\text{O}} = 44$ kJ/mol.[a]
Solution: Using eq. 6.6—and knowing that at standard conditions of $P^{\ominus} = 1$ bar the boiling temperature of water is 373 K—we calculate:

$$\Delta_{\text{vap}}S^{\ominus}_{\text{H}_2\text{O}} = \frac{44 \times 10^3 \text{J/mol}}{373 \text{ K}} = 118 \text{ J mol}^{-1} \text{ K}^{-1}. \tag{6.8}$$

The entropy of vaporization of water is far from Trouton's rule range of 85–88 J/(mol K) because of the hydrogen bond interactions between its molecules. Other similar exceptions are ethanol, formic acid, and hydrogen fluoride.

[a] The symbol $^{\ominus}$ indicates a quantity at the standard pressure of 1 bar. We will define standard states precisely in section 6.5.

6.1.2. Entropy in Adiabatic Processes

Since adiabatic processes happen without the exchange of heat, $Q = 0$, it would be tempting to think that $\Delta S^{\text{sys}} = 0$ for every one of them. A transformation at constant entropy (isentropic) is always, in fact, a reversible adiabatic process. However, the opposite case is not always true, and an irreversible adiabatic transformation is usually associated with a change in entropy. To explain this fact, we need to recall that the definition of entropy includes the heat exchanged at reversible conditions only. Therefore, for irreversible adiabatic processes $\Delta S^{\text{sys}} \neq 0$. The calculation of the entropy change for an irreversible adiabatic transformation requires a substantial effort, and we will not cover it at this stage. The situation for adiabatic processes can be summarized as follows:

$$\begin{aligned} &\text{reversible:} && \frac{Q_{\text{REV}}}{T} = 0 \longrightarrow \Delta S^{\text{sys}} = 0 \quad \text{(isentropic)}, \\ &\text{irreversible:} && \frac{Q_{\text{IRR}}}{T} = 0 \longrightarrow \Delta S^{\text{sys}} \neq 0. \end{aligned} \tag{6.9}$$

6.1.3. Entropy in Isochoric Processes

We can calculate the heat exchanged in a process that happens at constant volume, Q_V, using eq. 2.2. Since the heat exchanged at those conditions equals the energy (eq. 3.7), and the energy is a state function, we can use Q_V regardless of the path (reversible or irreversible). The entropy associated with the process will then be:

$$\Delta S^{\text{sys}} = \int_i^f \frac{Q_{\text{REV}}}{T} = \int_i^f nC_V \frac{dT}{T}, \tag{6.10}$$

which, assuming C_V independent of temperature and solving the integral on the right-hand side, becomes:

$$\Delta S^{\text{sys}} \approx nC_V \ln \frac{T_f}{T_i}. \tag{6.11}$$

6.1.4. Entropy in Isobaric Processes

Similarly to the constant volume case, we can calculate the heat exchanged in a process that happens at constant pressure, Q_P, using eq. 2.4. Again, similarly to the previous case, Q_P equals a state function (the enthalpy), and we can use it regardless of the path to calculate the entropy as:

$$\Delta S^{\text{sys}} = \int_i^f \frac{Q_{\text{REV}}}{T} = \int_i^f nC_P \frac{dT}{T}, \tag{6.12}$$

which, assuming C_P independent of temperature and solving the integral on the right-hand side, becomes:

$$\Delta S^{\text{sys}} \approx nC_P \ln \frac{T_f}{T_i}. \tag{6.13}$$

6.2. Calculation of ΔS^{surr}

While the entropy of the system can be broken down into simple cases and calculated using the formulas introduced above, the entropy of the surroundings does not require such a complicated treatment, and it can always be calculated as:

$$\Delta S^{\text{surr}} = \frac{Q_{\text{surr}}}{T_{\text{surr}}} = \frac{-Q_{\text{sys}}}{T_{\text{surr}}}, \tag{6.14}$$

or, in differential form:

$$dS^{\text{surr}} = \frac{Q_{\text{surr}}}{T_{\text{surr}}} = \frac{-Q_{\text{sys}}}{T_{\text{surr}}}, \tag{6.15}$$

where the substitution $Q_{\text{surr}} = -Q_{\text{sys}}$ can be performed regardless of whether the transformation is reversible or not. In other words, the surroundings always absorb heat reversibly. To justify this statement, we need to restrict the analysis of the interaction between the system and the surroundings to just the vicinity of the system itself. Outside of a generally restricted region, the rest of the universe is so vast that it remains untouched by anything happening inside the system.[1] To facilitate our comprehension, we might consider a system composed of a beaker on a workbench. We can then consider the room that the beaker is in as the immediate surroundings. To all effects, the beaker+room combination behaves as a system isolated from the rest of the universe. The room is obviously much larger than the beaker itself, and therefore every energy production that happens in the system will have minimal effect on the parameters of the room. For example, an exothermic chemical reaction occurring in the beaker will not affect the overall temperature of the room substantially. When we study our reaction, T_{surr} will be constant, and the transfer of heat from the reaction to the surroundings will happen at reversible conditions.

Example 6.2 (Freezing of supercooled water)**.** Calculate the changes in entropy of the universe for the process of 1 mol of supercooled water, freezing at –10°C, knowing the following data: $\Delta_{\text{fus}}H = 6$ kJ/mol, $C_P^{\text{H}_2\text{O}_{(l)}} = 76\ \text{J mol}^{-1}\,\text{K}^{-1}$, $C_P^{\text{H}_2\text{O}_{(s)}} = 38\ \text{J mol}^{-1}\,\text{K}^{-1}$, and assuming both C_P to be independent of temperature.
Solution: ΔS^{sys} for the process under consideration can be calculated using the following cycle:

[1] Even if we think of the most energetic event that we could imagine happening here on earth—such as the explosion of an atomic bomb or the hit of a meteorite from outer space—such an event will not modify the average temperature of the universe by the slightest degree.

$$\begin{array}{ccccc} \mathrm{H_2O}_{(l)} & \xrightarrow{\Delta S_{\text{sys}}} & \mathrm{H_2O}_{(s)} & & T = 263\ \mathrm{K} \\ \Delta S_1 \big\downarrow & & \big\uparrow \Delta S_3 & & \\ \mathrm{H_2O}_{(l)} & \xrightarrow{\Delta S_2} & \mathrm{H_2O}_{(s)} & & T = 273\ \mathrm{K} \end{array} \tag{6.16}$$

$$\Delta S^{\text{sys}} = \Delta S_1 + \Delta S_2 + \Delta S_3$$

ΔS_1 and ΔS_3 are the isobaric heating and cooling processes of liquid and solid water, respectively, and can be calculated by filling the given data into eq. 6.12. ΔS_2 is a phase change (isothermal process) and can be calculated translating eq. 6.6 to the freezing transformation. Overall:

$$\begin{aligned} \Delta S^{\text{sys}} &= \int_{263}^{273} \frac{C_P^{\mathrm{H_2O}_{(l)}}}{T} dT + \frac{-\Delta_{\text{fus}} H}{273} + \int_{273}^{263} \frac{C_P^{\mathrm{H_2O}_{(s)}}}{T} dT \\ &= 76 \ln \frac{273}{263} - \frac{6 \times 10^3}{273} + 38 \ln \frac{263}{273} = -20.6\ \mathrm{J/K}. \end{aligned} \tag{6.17}$$

Don't be confused by the fact that ΔS^{sys} is negative. This is ***not*** the entropy of the universe! Hence it tells ***nothing*** about spontaneity! We can now calculate ΔS^{surr} from Q_{sys}, noting that we can calculate the enthalpy around the same cycle in eq. 6.16. To do that, we already have $\Delta_{\text{fus}} H$ from the given data, and we can calculate ΔH_1 and ΔH_3 using eq. 2.4.

$$\begin{aligned} Q^{\text{sys}} = \Delta H &= \int_{263}^{273} C_P^{\mathrm{H_2O}_{(l)}} dT + (-\Delta_{\text{fus}} H) + \int_{273}^{263} C_P^{\mathrm{H_2O}_{(s)}} dT \\ &= 76 \times 10^{-3}(273 - 263) - 6 + 38 \times 10^{-3}(263 - 273) \\ &= -5.6\ \mathrm{kJ}. \end{aligned}$$

$$\Delta S^{\text{surr}} = \frac{-Q_{\text{sys}}}{T} = \frac{5.6 \times 10^3}{263} = +21.3\ \mathrm{J/K}. \tag{6.18}$$

Bringing eq. 6.16 and eq. 6.18 results together, we obtain:

$$\Delta S^{\text{universe}} = \Delta S^{\text{sys}} + \Delta S^{\text{surr}} = -20.6 + 21.3 = +0.7\ \mathrm{J/K}. \tag{6.19}$$

Since the entropy changes in the universe are positive, the process is spontaneous, as expected.

6.3. Clausius Theorem

By replacing eq. 6.15 into eq. 6.2 we can write the differential change in the entropy of the system as:

$$dS^{\text{sys}} = dS^{\text{universe}} - dS^{\text{surr}} = dS^{\text{universe}} + \frac{Q_{\text{sys}}}{T}. \tag{6.20}$$

According to the second law, for any spontaneous process $dS^{\text{universe}} \geq 0$, and therefore, replacing it into eq. 6.20:

$$dS^{\text{sys}} \geq \frac{Q_{\text{sys}}}{T}, \tag{6.21}$$

which is the mathematical expression of the so-called **Clausius theorem**. Eq. 6.21 distinguishes between three conditions:

$$\begin{aligned} dS^{\text{sys}} &> \frac{Q_{\text{sys}}}{T} && \text{spontaneous, irreversible transformation} \\ dS^{\text{sys}} &= \frac{Q_{\text{sys}}}{T} && \text{reversible transformation} \\ dS^{\text{sys}} &< \frac{Q_{\text{sys}}}{T} && \text{non-spontaneous, irreversible transformation.} \end{aligned} \tag{6.22}$$

Clausius theorem provides a useful criterion to infer the spontaneity of a process, especially in cases where it's hard to calculate $\Delta S^{\text{universe}}$. Eq. 6.21 requires knowledge of quantities that are dependent on the system exclusively, such as the difference in entropy, the amount of heat that crosses the boundaries, and the temperature at which the process happens.[2] If a process produces more entropy than the amount of heat that crosses the boundaries divided by the absolute temperature, it will be spontaneous. Vice versa, if the entropy produced is smaller than the amount of heat crossing the boundaries divided by the absolute temperature, the process will be non-spontaneous. The equality holds for systems in equilibrium with their surroundings, or for reversible processes since they happen through a series of equilibrium states. Measuring or calculating these quantities might not always be the simplest of calculations. We will return to the Clausius theorem in chapter 8, when we seek more convenient indicators of spontaneity.

[2] In cases where the temperature of the system changes throughout the process, T is just the (constant) temperature of its immediate surroundings, T_{surr}, as explained in section 6.2.

6.4. The Third Law of Thermodynamics

So far, we have calculated only *changes* of the entropy, ΔS, in the same way that we calculated only changes of the internal energy and of the enthalpy in chapter 3. Thermodynamics, in general, gives us only differences, and we never need, nor know, the absolute value of the energy of a system. For the entropy, however, nature gives us a zero that is not arbitrary at all, thanks to the third law of thermodynamics.

The third law has an interesting history. At the beginning of the twentieth century, Walther Hermann Nernst (1864–1941) was measuring ΔG and ΔH of reactions between solids at lower and lower temperatures.[3] He noticed that the two quantities became closer and closer as the temperature decreased, and that their curves approached each other with the same slope. Since $\Delta G = \Delta H - T\Delta S$, this meant that $\Delta_{\text{rxn}} S \to 0$ as $T \to 0$. In 1906, he proposed that this is always true, and the statement became known as **Nernst's heat theorem**: the entropy change of any reaction between pure crystalline solids goes to zero at absolute zero. If all reactions have $\Delta S = 0$ at $T = 0$, then all substances must have the same entropy at $T = 0$, and we can choose this common value as the zero of the scale. A few years later, Max Planck (1858–1947) made this choice explicit, and the statement took the form that we use today:

Definition 6.1. *Third Law of Thermodynamics:* The entropy of a perfectly ordered, pure, crystalline substance is zero at $T = 0$ K.

Why zero, and why only for a *perfect* crystal? The Boltzmann equation, eq. 5.16, gives us the answer. In a perfect crystal at absolute zero, every atom is at its place in the lattice, and the crystal is in its lowest energy state. There is only one way to arrange it, so $\Omega = 1$ and $S = k_B \ln 1 = 0$.

If a crystal can freeze in more than one arrangement with the same energy, it keeps some entropy even at 0 K, which is called **residual entropy**. A classic example is carbon monoxide. The CO molecule is almost symmetric, so in the crystal each molecule can point either way, CO or OC, with almost the same energy. If each of the N_A molecules in one mole has 2 orientations, $\Omega = 2^{N_A}$, and:

$$S_{\text{residual}} = k_B \ln 2^{N_A} = N_A k_B \ln 2 = R \ln 2 = 5.76 \ \frac{\text{J}}{\text{mol K}}, \tag{6.23}$$

which is close to the residual entropy measured for solid carbon monoxide. Ice has a residual entropy too, because the hydrogen atoms in the

[3] Walther Nernst was awarded the 1920 Nobel Prize in Chemistry for his work in thermochemistry.

crystal can be arranged in many equivalent ways. This is why the definition specifies a *perfectly ordered* crystal: the residual entropy could be removed, at least in principle, by forcing the substance into a single perfect arrangement, a procedure that in practice can be extremely difficult.

The third law sets an unambiguous zero of the entropy scale, similar to what happens with absolute zero in the temperature scale (chapter 2 and chapter 4). The absolute value of the entropy of every substance can then be calculated in reference to this zero, and absolute entropies are always positive. This is in stark contrast to the internal energy and the enthalpy, for which we cannot measure absolute values, and we must always resort to differences.

How are absolute entropies measured? Putting together the third law with the entropy changes that we calculated in section 6.1, we can follow the absolute entropy of a substance from 0 K up to any temperature, as in figure 6.1 for water. The entropy starts from zero, increases smoothly while the substance is heated, as $\int \frac{C_P}{T} dT$, and jumps up at each phase transition, by $\frac{\Delta H}{T}$. The jump at boiling is by far the largest, since the gas has much more room for its molecules than the liquid. In the lab, the absolute entropy is obtained exactly this way, by measuring the heat capacity from temperatures as low as possible, together with the enthalpies of the phase transitions.

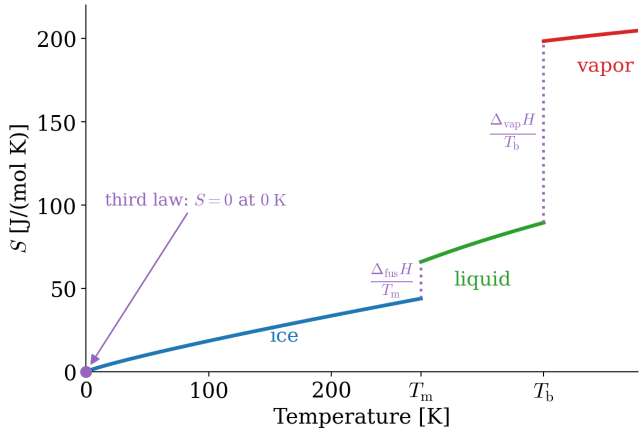


Figure 6.1.: Absolute Entropy of Water at 1 bar as a Function of Temperature, Computed from Approximate Heat Capacities of Ice, Liquid Water, and Vapor, and from the Enthalpies of Fusion and Vaporization.

The third law has two important consequences at low temperatures:

1. **Heat capacities vanish at absolute zero.** The entropy at temperature T is $S(T) = \int_0^T \frac{C_P}{T}\,dT$ (plus the jumps at the phase transitions). For this integral to give a finite value, C_P must go to zero as $T \to 0$; otherwise, the $\frac{1}{T}$ in the integrand would make it infinite. Experiments confirm this: the heat capacity of crystals drops to zero at low temperatures, typically as T^3, as you can see from the way the curve of ice starts in figure 6.1.[4] This is very different from the ideal gas, whose $C_V = \frac{3}{2}R$ does not depend on temperature. The ideal gas, however, is not a good model near absolute zero, where every substance is a solid.
2. **Absolute zero cannot be reached.** This consequence, also due to Nernst, is often called the *unattainability principle*. Let's see why it follows from the third law.

How do we cool something to very low temperatures? Many cooling methods work by alternating two steps, as in figure 6.2. First, at constant temperature, we change a parameter X that affects the entropy of the substance, such as the pressure of a gas or the magnetic field applied to a magnetic salt, and we let the heat flow out into a cold reservoir. This lowers the entropy of the substance from the blue curve to the red curve. Then, we isolate the substance and change the parameter back adiabatically, so that the entropy stays constant. To keep the same entropy on the blue curve, the substance must move to a lower temperature. Repeating the two steps, we go down a staircase toward absolute zero.

Here is where the third law comes in. Since both curves must reach $S = 0$ at $T = 0$, they get closer and closer to each other as the temperature decreases. Each isothermal step lowers the entropy by less, and each adiabatic step lowers the temperature by less. The staircase gets finer and finer, and it would take an infinite number of steps to reach $T = 0$. If the two curves ended at different entropies at $T = 0$, a single adiabatic step from the lower curve could bring the substance all the way to absolute zero. The third law forbids this.

This is a true limit of nature, not of our technology. Physicists have cooled small samples to below a billionth of a kelvin, but never to absolute zero, and the third law tells us that they never will. Notice the parallel with the second law: the second law says that no engine can convert all its heat into work, and the third law says that no refrigerator can extract all the heat from a system.

[4] The T^3 behavior was explained by Peter Debye in 1912, using quantum mechanics.

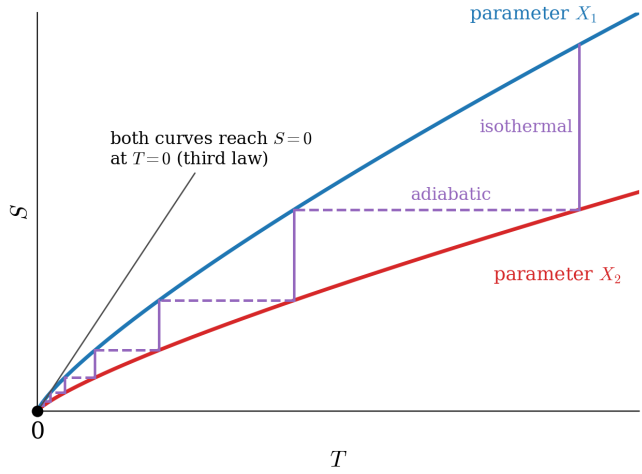


Figure 6.2.: Cooling by Alternating Isothermal and Adiabatic Steps Between Two Values of a Parameter X (Schematic). Since the Third Law Requires Both Entropy Curves to Reach $S = 0$ at $T = 0$, Each Step Is Smaller than the Previous One, and Absolute Zero Is Approached but Never Reached.

6.5. Standard States and a First Chemical Reaction

Since we can measure the absolute entropy of every substance, we can collect the values in tables and use them for any process that we like. To make such tables useful, however, everybody must agree on the conditions at which the values are reported. The entropy of a substance depends on its temperature, as in figure 6.1, and, for a gas, it also depends strongly on the pressure, as we saw in eq. 6.5. For this reason, thermodynamic tables report the properties of each substance in a common reference state, called the *standard state*:

Definition 6.2. *Standard State:* The standard state of a substance is its pure form at the standard pressure, $P^{\ominus} = 1$ bar. For a gas, it is the pure gas at $P^{\ominus}$, assuming ideal gas behavior. For a liquid or a solid, it is the pure liquid or the pure solid at $P^{\ominus}$.

Quantities that refer to the standard state are marked with the symbol $^{\ominus}$, as in $S^{\ominus}$. The standard pressure is $P^{\ominus} = 100$ kPa $= 1$ bar.[5] Notice that

[5] Prior to 1982, the value $P^{\ominus} = 1$ atm was used. The two values are within 1% of each other, since 1 atm = 101.325 kPa.

the definition does not include a temperature. A standard state can be defined at any temperature, but most tables report their values at room temperature, $T = 298.15$ K, which we will often round to 298 K. Do not confuse the standard state with the "standard temperature and pressure" (STP, 0 °C and 1 atm) that you might have used for gases in general chemistry. For example, the standard molar entropy of liquid water at 298 K is $S^{\ominus}_{\mathrm{H_2O}_{(l)}} = 70.0\ \frac{\mathrm{J}}{\mathrm{mol\ K}}$, close to the value that we can read on the curve in figure 6.1 at that temperature. A comprehensive list of standard entropies of inorganic and organic compounds is reported in Appendix A.

We now have everything that we need to look at our first chemical reaction. A chemical reaction transforms some substances, the *reactants*, into other substances, the *products*. We can write a general reaction as:

$$a\mathrm{A} + b\mathrm{B} \rightarrow c\mathrm{C} + d\mathrm{D}, \tag{6.24}$$

where a, b, c, d are the stoichiometric coefficients of species $\mathrm{A}, \mathrm{B}, \mathrm{C}, \mathrm{D}$. The change of a state function during a reaction is the value for the products minus the value for the reactants, each multiplied by its stoichiometric coefficient. To write this in a compact form, we give a sign to each coefficient, and we call the result the *stoichiometric number*, ν_i:

Definition 6.3. *Signs of the stoichiometric numbers:*

- ν_i is **positive** if i is a **product**.
- ν_i is **negative** if i is a **reactant**.

For the general reaction in eq. 6.24, $\nu_{\mathrm{A}} = -a$, $\nu_{\mathrm{B}} = -b$, $\nu_{\mathrm{C}} = +c$, and $\nu_{\mathrm{D}} = +d$. With this convention, the standard entropy of a reaction is calculated from the tabulated standard entropies as:

$$\Delta_{\mathrm{rxn}} S^{\ominus} = \sum_i \nu_i S^{\ominus}_i = \underbrace{(cS^{\ominus}_{\mathrm{C}} + dS^{\ominus}_{\mathrm{D}})}_{\text{products}} - \underbrace{(aS^{\ominus}_{\mathrm{A}} + bS^{\ominus}_{\mathrm{B}})}_{\text{reactants}}, \tag{6.25}$$

where the sum runs over all reactants and products. Notice how equation eq. 6.25 extends beyond reactions with two reactants and two products, and it can generally account for any reactions with any numbers of reactants and products.

Example 6.3 (Entropy of the synthesis of ammonia)**.** Calculate the standard entropy of reaction at 298 K for the synthesis of ammonia:

$$\mathrm{N}_{2(g)} + 3\mathrm{H}_{2(g)} \rightarrow 2\mathrm{NH}_{3(g)},$$

knowing the following standard entropies: $S^{\ominus}_{\mathrm{N}_{2(g)}} = 191.6\ \frac{\mathrm{J}}{\mathrm{mol\ K}}$, $S^{\ominus}_{\mathrm{H}_{2(g)}} = 130.7\ \frac{\mathrm{J}}{\mathrm{mol\ K}}$, and $S^{\ominus}_{\mathrm{NH}_{3(g)}} = 192.8\ \frac{\mathrm{J}}{\mathrm{mol\ K}}$.
Solution: The stoichiometric numbers are $\nu_{\mathrm{N}_2} = -1$, $\nu_{\mathrm{H}_2} = -3$, and $\nu_{\mathrm{NH}_3} = +2$. Using eq. 6.25:

$$\begin{aligned}\Delta_{\mathrm{rxn}} S^{\ominus} &= 2\, S^{\ominus}_{\mathrm{NH}_{3(g)}} - S^{\ominus}_{\mathrm{N}_{2(g)}} - 3\, S^{\ominus}_{\mathrm{H}_{2(g)}} \\ &= 2(192.8) - 191.6 - 3(130.7) = -198.1\ \frac{\mathrm{J}}{\mathrm{mol\ K}}.\end{aligned}$$

The entropy of the system decreases. This makes sense, since four molecules of gas become two, and fewer molecules have fewer ways to arrange themselves in the same volume.

Does this negative result mean that nitrogen and hydrogen cannot form ammonia? Not at all. As we learned in section 6.2, and as we saw for supercooled water in example 6.2, the entropy of the system alone tells us *nothing* about spontaneity: we must also account for the surroundings. When the reaction happens at constant temperature and pressure, it exchanges heat with its surroundings, and their entropy changes by $\Delta S^{\mathrm{surr}} = -Q_{\mathrm{sys}}/T$. To decide whether ammonia forms, we need to know how much heat the reaction releases or absorbs. Calculating the heat of chemical reactions is the job of *thermochemistry*, the topic of the next chapter, where we will finally apply the laws of thermodynamics to chemistry. And even then, thermodynamics will tell us only *which way* the reaction goes, not *how fast*. These are two separate questions, and we will need both to understand chemistry.

6.6. Chapter Review

6.6.1. Key Ideas

- **Spontaneity** requires the entropy of the whole universe: $\Delta S^{\mathrm{universe}} = \Delta S^{\mathrm{sys}} + \Delta S^{\mathrm{surr}}$.
- **System:** $\Delta S^{\mathrm{sys}} = nR \ln \frac{V_f}{V_i}$ (isothermal ideal gas), 0 (reversible adiabatic), $nC_P \ln \frac{T_f}{T_i}$ (isobaric heating), and $\frac{\Delta H}{T}$ (phase change at the transition temperature).
- **Surroundings:** $\Delta S^{\mathrm{surr}} = -\frac{Q_{\mathrm{sys}}}{T_{\mathrm{surr}}}$, since the surroundings behave as a large reservoir.
- **Trouton's rule:** many liquids have $\Delta_{\mathrm{vap}} S \approx 85$–$88$ J/(mol K); liquids with hydrogen bonds, such as water, have more.
- **A process can be spontaneous** even if the entropy of the system decreases, as long as the surroundings gain more entropy (as when supercooled water freezes).

- **The third law:** the entropy of a perfect crystal is zero at 0 K (Nernst and Planck), since a perfect crystal has a single microstate. It allows us to tabulate absolute entropies, $S^{\ominus}$; crystals that freeze in many arrangements keep a residual entropy.
- **Consequences:** heat capacities vanish as $T \to 0$, and absolute zero cannot be reached in a finite number of steps.
- **Standard state:** the pure substance at $P^{\ominus} = 1$ bar (an ideal gas, for gases), at any temperature, usually 298.15 K. Thermodynamic tables report standard values, marked with $^{\ominus}$.
- **Reaction entropies:** $\Delta_{\text{rxn}}S^{\ominus} = \sum_i \nu_i S_i^{\ominus}$, with stoichiometric numbers ν_i positive for products and negative for reactants. A negative $\Delta_{\text{rxn}}S^{\ominus}$, as for the synthesis of ammonia, does not mean that a reaction cannot happen: we also need the entropy of the surroundings.

6.6.2. Study Questions

1. How is the entropy change of the universe calculated?

a. $\Delta S^{\text{universe}} = \Delta S^{\text{sys}} + \Delta S^{\text{surr}}$.
b. $\Delta S^{\text{universe}} = \Delta S^{\text{sys}} - \Delta S^{\text{surr}}$.
c. $\Delta S^{\text{universe}} = \Delta S^{\text{sys}}$.
d. $\Delta S^{\text{universe}} = \Delta S^{\text{sys}} \cdot \Delta S^{\text{surr}}$.
e. $\Delta S^{\text{universe}} = 0$ always.

---

2. What is the entropy change of an ideal gas in an isothermal expansion?

a. $\Delta S = 0$.
b. $\Delta S = nC_V \ln \frac{T_f}{T_i}$.
c. $\Delta S = nR \ln \frac{V_f}{V_i}$.
d. $\Delta S = nR(V_f - V_i)$.
e. $\Delta S = \frac{W}{T}$.

---

3. How is the entropy of vaporization of a liquid calculated at its boiling point?

a. $\Delta_{\text{vap}}S = \Delta_{\text{vap}}H \cdot T_B$.
b. $\Delta_{\text{vap}}S = nR \ln T_B$.
c. $\Delta_{\text{vap}}S = 0$.

d. $\Delta_{\text{vap}}S = \Delta_{\text{vap}}H - T_B$.
e. $\Delta_{\text{vap}}S = \frac{\Delta_{\text{vap}}H}{T_B}$.

---

4. Why does water deviate from Trouton's rule?

a. Because it boils at 100 °C.
b. Because of the hydrogen bonds between its molecules.
c. Because its molar mass is small.
d. Because it is an ideal liquid.
e. Because its enthalpy of vaporization is negative.

---

5. What is the entropy change of the system in a reversible adiabatic process?

a. Always positive.
b. Always negative.
c. Equal to $\frac{Q}{T}$ with $Q > 0$.
d. Zero, since the process is isentropic.
e. Infinite.

---

6. What is the standard state of a gas?

a. The pure gas, behaving ideally, at $P^{\ominus} = 1$ bar, at any temperature.
b. The gas at 0 °C and 1 atm.
c. The gas at 0 K, where its entropy is zero.
d. The gas mixed with air at 1 bar and 298.15 K.
e. The gas at the pressure where it liquefies.

---

7. How is the entropy change of the surroundings calculated?

a. $\Delta S^{\text{surr}} = \frac{Q_{\text{sys}}}{T_{\text{sys}}}$.
b. $\Delta S^{\text{surr}} = -\Delta S^{\text{sys}}$.
c. $\Delta S^{\text{surr}} = \frac{-Q_{\text{sys}}}{T_{\text{surr}}}$.
d. $\Delta S^{\text{surr}} = 0$.
e. $\Delta S^{\text{surr}} = nR \ln \frac{V_f}{V_i}$.

---

8. Supercooled water freezes spontaneously at –10 °C, even though the entropy of the water decreases. How is this possible?

a. The entropy of the universe decreases, which is allowed for freezing.
b. The second law does not apply to phase changes.
c. The process is reversible.
d. The entropy of the water actually increases.
e. The heat released to the surroundings increases their entropy by more than the water loses.

---

9. What does the Clausius theorem state?

a. $dS^{\text{sys}} = \frac{Q}{T}$ always.
b. $dS^{\text{sys}} \geq \frac{Q}{T}$, with the equality for reversible processes.
c. $dS^{\text{sys}} \leq \frac{Q}{T}$ for spontaneous processes.
d. $dS^{\text{sys}} = 0$ for all processes.
e. $dS^{\text{universe}} < 0$ for spontaneous processes.

---

10. What does the third law of thermodynamics make possible for the entropy that is not possible for the enthalpy?

a. Calculating changes at constant pressure.
b. Measuring it with a calorimeter.
c. Using it for chemical reactions.
d. Tabulating absolute values, since it fixes the zero of the entropy scale.
e. Making it independent of temperature.

Answers

1.a, 2.c, 3.e, 4.b, 5.d, 6.a, 7.c, 8.e, 9.b, 10.d

Part II.

Chemical Thermodynamics

7. Thermochemistry

With this chapter, we begin the second part of the book, where we apply the laws of thermodynamics to chemistry. So far, we have studied changes in energy and entropy in the absence of chemical reactions, with one exception: at the end of chapter 6, we found that the synthesis of ammonia decreases the entropy of the system (example 6.3), and we left open the question of whether the reaction happens at all. To answer it, we need to know the heat that the reaction exchanges with its surroundings. When a chemical reaction takes place, some bonds break and some new ones form. Breaking a bond always requires energy, while forming a bond always releases energy. The balance between the energy spent to break the bonds of the reactants and the energy released when the bonds of the products form determines whether the reaction, overall, absorbs or releases energy.[1] For a proper thermodynamic treatment of the system, this extra energy must be included in the net balance. In this chapter, we will learn how to calculate it from tabulated data, and we will then use it to answer our question about ammonia.

7.1. Reaction Enthalpies

Since most chemical reactions happen at constant atmospheric pressure (isobaric conditions) in the lab, we can use eq. 3.13 to replace the inexact differential of the heat with the exact differential of the state function called enthalpy. The advantage of this transformation is that it allows us to study the heat associated with chemical reactions at constant pressure independently of their path. Using the same notation that we introduced for reaction entropies in section 6.5, the heat associated with the reaction (rxn) is defined as:

$$\Delta_{\text{rxn}} H = H_{\text{products}} - H_{\text{reactants}} \, . \tag{7.1}$$

[1] A common misconception is that energy is "stored" in chemical bonds and released when they break. It is the opposite: a bond is a more stable (lower-energy) arrangement than the separated atoms, so breaking it always costs energy. Fuels release energy when they burn because the bonds that form in the products (for example, in CO_2 and H_2O) are, overall, stronger than the ones broken in the reactants.

For the general reaction in eq. 6.24, the heat at constant pressure is equal to the enthalpy of reaction, which is calculated as:

$$Q_P = \Delta_{\text{rxn}}H = \underbrace{(cH_{\text{C}} + dH_{\text{D}})}_{\text{products}} - \underbrace{(aH_{\text{A}} + bH_{\text{B}})}_{\text{reactants}}. \tag{7.2}$$

Using the stoichiometric numbers, we can write it in compact form as:

$$\Delta_{\text{rxn}}H = \sum_i \nu_i H_i, \tag{7.3}$$

where ν_i is the stoichiometric number of species i, positive for products and negative for reactants, as in definition 6.3. Eq. 7.3 has exactly the same form as the one that we used for reaction entropies, eq. 6.25.

Using the chemistry sign convention, Definition 1.1, reactions are classified in terms of the sign of their reaction enthalpies as follows:

Definition 7.1.

- $\Delta_{\text{rxn}}H > 0 \Rightarrow$ *Endothermic reaction* (heat is gained by the system).
- $\Delta_{\text{rxn}}H < 0 \Rightarrow$ *Exothermic reaction* (heat is lost by the system).

7.2. Calorimetry

Reaction enthalpies are measured with a *calorimeter*, an insulated container in which the reaction takes place. Since the calorimeter does not exchange heat with the rest of the lab, the heat released or absorbed by the reaction stays inside it and changes its temperature. If the calorimeter (including everything inside it) has a total heat capacity C_{cal}, a temperature change ΔT corresponds to the heat of reaction:

$$Q_{\text{rxn}} = -C_{\text{cal}}\,\Delta T, \tag{7.4}$$

where the negative sign follows the chemistry sign convention: an exothermic reaction ($Q_{\text{rxn}} < 0$) warms the calorimeter ($\Delta T > 0$). The heat capacity of the calorimeter is determined beforehand by calibration, either with an electrical heater that supplies a known amount of energy, or with a reaction whose heat is accurately known, such as the combustion of benzoic acid.

There are two main kinds of calorimeters, and they measure two different state functions:

- **Constant-pressure calorimeters** are open to the atmosphere. The simplest example is the "coffee-cup" calorimeter of general chemistry labs, used for reactions in solution. At constant pressure, eq. 3.13 tells us that the heat equals the enthalpy change, $Q_P = \Delta_{\text{rxn}}H$.
- **Constant-volume (bomb) calorimeters** are sealed steel containers, called *bombs*, immersed in a water bath. They are used for combustions, where the sample burns in an excess of oxygen under pressure. At constant volume, no work is done, and the heat equals the energy change, $Q_V = \Delta_{\text{rxn}}U$, as in eq. 3.7.

Since tables report enthalpies, the energies measured in bomb calorimeters must be converted. Using the definition of enthalpy, eq. 3.9:

$$\Delta_{\text{rxn}}H = \Delta_{\text{rxn}}U + \Delta(PV).$$

The volumes of liquids and solids are so small that their contribution to $\Delta(PV)$ is negligible. For the gases, we can use the ideal gas law, $PV = nRT$, and at constant temperature $\Delta(PV) = \Delta n_{\text{gas}}RT$, which gives:

$$\Delta_{\text{rxn}}H = \Delta_{\text{rxn}}U + \Delta n_{\text{gas}}RT, \tag{7.5}$$

where Δn_{gas} is the number of moles of gaseous products minus the number of moles of gaseous reactants, per mole of reaction. If the number of moles of gas does not change, or if no gases are involved, $\Delta_{\text{rxn}}H \approx \Delta_{\text{rxn}}U$.

Example 7.1 (Combustion of methane in a bomb calorimeter)**.** A sample of 0.0200 mol of methane is burned in a bomb calorimeter with $C_{\text{cal}} = 10.00$ kJ/K, and the temperature of the calorimeter increases by 1.772 K. Calculate $\Delta_{\text{rxn}}U$ and $\Delta_{\text{rxn}}H$ at 298 K for the reaction:

$$\text{CH}_{4(g)} + 2\text{O}_{2(g)} \rightarrow \text{CO}_{2(g)} + 2\text{H}_2\text{O}_{(l)}.$$

Solution: Using eq. 7.4, the heat released by the sample is:

$$Q_V = -C_{\text{cal}}\,\Delta T = -10.00 \times 1.772 = -17.72 \text{ kJ}.$$

Since the bomb has a constant volume, this heat is the energy change of the reaction, and per mole of methane:

$$\Delta_{\text{rxn}}U = \frac{Q_V}{n} = \frac{-17.72 \text{ kJ}}{0.0200 \text{ mol}} = -886 \text{ kJ/mol}.$$

In the reaction, 3 moles of gas (1 of methane and 2 of oxygen) become 1

mole of gas (carbon dioxide), while water is liquid, so $\Delta n_{\text{gas}} = 1 - 3 = -2$. Using eq. 7.5:

$$\Delta_{\text{rxn}}H = -886 + (-2)(8.314 \times 10^{-3})(298) = -886 - 5 = -891 \text{ kJ/mol}.$$

The difference between $\Delta_{\text{rxn}}H$ and $\Delta_{\text{rxn}}U$ is only about 0.5%. The reaction enthalpy is more negative than the energy because the gas contracts, and at constant pressure the atmosphere does work on the system as it shrinks. We will obtain the same value of $\Delta_{\text{rxn}}H$ from tabulated data in example 7.2.

Experiments like this one, repeated for many substances, are the source of the tabulated enthalpies of formation that we introduce next.

7.3. Standard Enthalpies of Formation

In principle, we could use eq. 7.3 to calculate the reaction enthalpy associated with any reaction. However, to do so, the absolute enthalpies H_i of reactants and products would be required. Unfortunately, absolute enthalpies are not known—and theoretically unknowable, since this would require an absolute zero for the enthalpy scale, which does not exist. This is the key difference with the entropy, for which the third law provides a natural zero (section 6.4), so that we could use the absolute values $S_i^\ominus$ directly in eq. 6.25. For the enthalpy, we must instead choose a zero, and use enthalpies relative to this reference. The reference is defined as the constituent elements in their standard state, and the enthalpies of 1 mol of substance relative to this reference are called **standard enthalpies of formation**.

Definition 7.2. The *standard enthalpy of formation* of compound i, $\Delta_{\text{f}}H_i^\ominus$, is the change of enthalpy during the formation of 1 mol of i from its constituent elements, with all substances in their standard states.

The standard states are the ones that we defined in definition 6.2, at the standard pressure $P^\ominus = 1$ bar. As for the entropies, there is no standard temperature, but standard enthalpies of formation are usually reported at room temperature, $T = 298.15$ K. For the elements, the reference is the form in which each element is most stable at standard pressure (for example, for hydrogen, carbon, and oxygen the reference forms are $\text{H}_{2(g)}$, $\text{C}_{(s,\text{graphite})}$, and $\text{O}_{2(g)}$, respectively). Since forming an element from

itself requires no change at all, the standard enthalpy of formation of an element in its reference form is zero.[2]

For example, the standard enthalpies of formation of some common compounds at $T = 298.15$ K are calculated from the following reactions:

$$\begin{aligned} \mathrm{C}_{(s,\text{graphite})} + \mathrm{O}_{2(g)} &\rightarrow \mathrm{CO}_{2(g)} \qquad & \Delta_\mathrm{f}H^\ominus_{\mathrm{CO}_{2(g)}} &= -394 \text{ kJ/mol} \\ \mathrm{C}_{(s,\text{graphite})} + 2\mathrm{H}_{2(g)} &\rightarrow \mathrm{CH}_{4(g)} \qquad & \Delta_\mathrm{f}H^\ominus_{\mathrm{CH}_{4(g)}} &= -75 \text{ kJ/mol} \\ \mathrm{H}_{2(g)} + \frac{1}{2}\mathrm{O}_{2(g)} &\rightarrow \mathrm{H_2O}_{(l)} \qquad & \Delta_\mathrm{f}H^\ominus_{\mathrm{H_2O}_{(l)}} &= -286 \text{ kJ/mol} \end{aligned} \tag{7.6}$$

A comprehensive list of standard enthalpies of formation of inorganic and organic compounds is also reported in Appendix A.

7.4. Hess's Law

The calculation of a standard reaction enthalpy can be performed using the following cycle:

$$\begin{array}{ccc} \text{reactants} & \xrightarrow{\Delta_\text{rxn}H^\ominus} & \text{products} \\ {\scriptstyle -\Delta_\mathrm{f}H^\ominus_\text{reactants}}\ \big\downarrow & & \big\uparrow\ {\scriptstyle \Delta_\mathrm{f}H^\ominus_\text{products}} \\ \multicolumn{3}{c}{\text{"elements in their standard reference state"}} \end{array} \tag{7.7}$$

This process is summarized by the simple formula:

$$\Delta_\text{rxn}H^\ominus = \Delta_\mathrm{f}H^\ominus_\text{products} - \Delta_\mathrm{f}H^\ominus_\text{reactants}. \tag{7.8}$$

Notice how there is a negative sign in front of the enthalpy of formation of the reactants because they are normally defined for the reactions that go from the elements to the reactants and not vice-versa. To close the cycle in eq. 7.7, however, we should go from the reactants to the elements, and therefore we must invert the sign in front of the formation enthalpies of the reactants. Similarly to eq. 7.3, Eq. 7.8 can be generalized to any reaction, resulting in:

[2] There are some exceptions, such as phosphorus, for which the most stable form at 1 bar is black phosphorus, but white phosphorus is chosen as the standard reference state for zero enthalpy of formation. For the purposes of this course, however, we can safely ignore them.

$$\Delta_{\text{rxn}}H^{\ominus} = \sum_i \nu_i \Delta_{\text{f}}H_i^{\ominus}, \tag{7.9}$$

which is a mathematical expression of the law that is known as **Hess's Law**. Hess's law is valid at constant pressure because, at those conditions, the heat of reaction—a path function—is equal to the enthalpy of reaction—a state function. Therefore, the enthalpy of a reaction depends exclusively on the initial and final state, and it can be obtained via the pathway that passes through the elements in their standard state (the formation pathway).

Example 7.2 (Combustion enthalpy of methane from Hess's law)**.** Calculate the standard enthalpy of combustion at 298 K of 1 mol of methane, using the data in eq. 7.6.
Solution: The reaction that is under consideration is:

$$\text{CH}_{4(g)} + 2\text{O}_{2(g)} \rightarrow \text{CO}_{2(g)} + 2\text{H}_2\text{O}_{(l)} \qquad \Delta_{\text{rxn}}H^{\ominus} = ?$$

Using Hess's Law, eq. 7.9, the enthalpy of combustion of methane is:

$$\Delta_{\text{rxn}}H^{\ominus} = \Delta_{\text{f}}H^{\ominus}_{\text{CO}_{2(g)}} + 2\Delta_{\text{f}}H^{\ominus}_{\text{H}_2\text{O}_{(l)}} - \Delta_{\text{f}}H^{\ominus}_{\text{CH}_{4(g)}} - 2\underbrace{\Delta_{\text{f}}H^{\ominus}_{\text{O}_{2(g)}}}_{=0}$$

whose values are reported in eq. 7.6. Notice that the formation enthalpy of $\text{O}_{2(g)}$ is zero, since it is an element in its standard state. The final result is:

$$\Delta_{\text{rxn}}H^{\ominus} = \overbrace{-394}^{\Delta_{\text{f}}H^{\ominus}_{\text{CO}_{2(g)}}} + 2\overbrace{(-286)}^{\Delta_{\text{f}}H^{\ominus}_{\text{H}_2\text{O}_{(l)}}} - \overbrace{(-75)}^{\Delta_{\text{f}}H^{\ominus}_{\text{CH}_{4(g)}}} = -891 \text{ kJ/mol}.$$

where the negative sign indicates that the reaction is exothermic (see definition 7.1), as we should expect. This is the same value that we obtained from the bomb calorimeter in example 7.1. The cycle that we used to solve this exercise can be summarized as:

$$\begin{array}{ccc} \text{CH}_{4(g)} + 2\text{O}_{2(g)} & \xrightarrow{\Delta_{\text{rxn}}H^{\ominus}} & \text{CO}_{2(g)} + 2\text{H}_2\text{O}_{(l)} \\ {\scriptstyle -\Delta_{\text{f}}H^{\ominus}_{\text{CH}_{4(g)},\text{O}_{2(g)}}} \searrow & & \nearrow {\scriptstyle \Delta_{\text{f}}H^{\ominus}_{\text{CO}_{2(g)},\text{H}_2\text{O}_{(l)}}} \\ & \text{H}_{2(g)}, \text{C}_{(s,\text{graphite})}, \text{O}_{2(g)} & \end{array}$$

Notice that at standard pressure and $T = 298$ K water is in liquid form. However, when we burn methane, the heat associated with the exothermic reaction immediately vaporizes the water. Substances in different states of matter have different formation enthalpies, and $\Delta_{\text{f}}H^{\ominus}_{\text{H}_2\text{O}_{(g)}} = -242$ kJ/mol. The difference between the formation enthalpies of the same substance in different states represents the latent heat that separates them. For example, for water:

$$\begin{aligned}\Delta_{\text{vap}}H^{\ominus}_{\text{H}_2\text{O}} &= \Delta_{\text{f}}H^{\ominus}_{\text{H}_2\text{O}_{(g)}} - \Delta_{\text{f}}H^{\ominus}_{\text{H}_2\text{O}_{(l)}} \\ &= (-242) - (-286) = +44\ \text{kJ/mol}\end{aligned}$$

which is the latent heat of vaporization for water, $\Delta_{\text{vap}}H^{\ominus}_{\text{H}_2\text{O}}$, the same value that we used in example 6.1. The latent heat is positive to indicate that the system absorbs energy in going from the liquid to the gaseous state (and it will release energy when going the opposite direction from gas to liquid).

The same cycle can be drawn as an enthalpy diagram, figure 7.1, where each species sits at its enthalpy relative to the elements. Since the enthalpy is a state function, the two paths from the reactants to the products, directly or through the elements, must give the same enthalpy change.

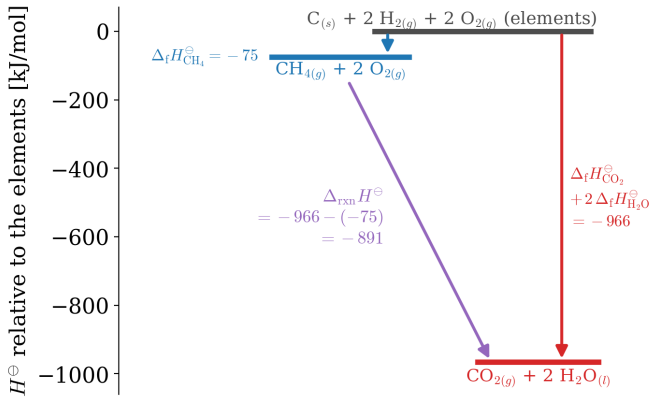


Figure 7.1.: Enthalpy Diagram of the Hess Cycle for the Combustion of Methane at 298 K, with the Data of eq. 7.6. The Reaction Enthalpy (Purple) Is the Difference Between the Formation Enthalpies of the Products (Red) and of the Reactants (Blue). All Values Are in kJ/mol.

7.5. Bond Enthalpies

When the formation enthalpies of a compound are not available, we can still estimate a reaction enthalpy from the bonds that break and form, as we described at the beginning of this chapter. The *bond enthalpy* is the enthalpy needed to break 1 mol of a given bond in the gas phase. Since the same bond has slightly different strengths in different molecules, tables report average values, such as those in table 7.1.

Table 7.1.: Average Bond Enthalpies.

Bond	Bond enthalpy [kJ/mol]	Bond	Bond enthalpy [kJ/mol]
H–H	436	N–H	391
C–H	413	N N	945
O–H	463	O=O	498
C–C	348	C=O (in CO_2)	799

Breaking a bond always requires energy, and forming a bond always releases it, so:

$$\Delta_{\text{rxn}}H \approx \sum_{\text{broken}} (\text{bond enthalpies}) - \sum_{\text{formed}} (\text{bond enthalpies}). \tag{7.10}$$

Notice that the order is the opposite of Hess's law: the bonds of the *reactants* come first, with a positive sign. For example, in the synthesis of ammonia we break one N N bond and three H–H bonds, and we form six N–H bonds:

$$\Delta_{\text{rxn}}H \approx [945 + 3(436)] - 6(391) = 2253 - 2346 = -93 \text{ kJ/mol},$$

very close to the value of −91.8 kJ/mol obtained from the formation enthalpies. The agreement is not always this good, since bond enthalpies are averages, and eq. 7.10 is valid only when all reactants and products are gases. Formation enthalpies, when available, should always be preferred.

7.6. Calculations of Enthalpies of Reaction at $T \neq 298$ K

Standard enthalpies of formation are usually reported at room temperature (T = 298 K), but enthalpies of formation at any temperature T' can be calculated from the values at 298 K using eq. 2.4 and eq. 3.13:

$$\begin{aligned} dH = C_P dT \rightarrow \int_{H^\ominus_{298}}^{H^\ominus_{T'}} dH &= \int_{298}^{T'} C_P dT \\ H^\ominus_{T'} - H^\ominus_{298} &= \int_{298}^{T'} C_P dT \\ H^\ominus_{T'} &= H^\ominus_{298} + \int_{298}^{T'} C_P dT, \end{aligned} \tag{7.11}$$

which, in conjunction with Hess's Law, eq. 7.9, results in:

$$\Delta_{\text{rxn}}H^{\ominus}_{T'} = \Delta_{\text{rxn}}H^{\ominus}_{298} + \int_{298}^{T'} \Delta C_P dT, \tag{7.12}$$

with $\Delta C_P = \sum_i \nu_i C_{P,i}$. Eq. 7.12 is known as **Kirchhoff's law**, after the German physicist Gustav Robert Kirchhoff (1824–1887).

Example 7.3 (Reaction enthalpy at 398 K)**.** Calculate $\Delta_{\text{rxn}}H^{\ominus}_{398}$ of the following reaction at 398 K, knowing that $\Delta_{\text{rxn}}H^{\ominus}_{298}$ is -283.0 kJ/mol, and the following C_P values: $CO_{(g)}$ = 29 J/(mol K), $O_{2(g)}$ = 30 J/(mol K), $CO_{2(g)}$ = 38 J/(mol K):

$$CO_{(g)} + \frac{1}{2}O_{2(g)} \rightarrow CO_{2(g)},$$

Solution: Using eq. 7.12 we obtain:

$$\Delta_{\text{rxn}}H^{\ominus}_{398} = \overbrace{-283.0}^{\Delta_{\text{rxn}}H^{\ominus}_{298}} + \int_{298}^{398} (\overbrace{38}^{C_P^{CO_2}} - \overbrace{29}^{C_P^{CO}} - \frac{1}{2}\overbrace{30}^{C_P^{O_2}}) \times 10^{-3} dT,$$

which, assuming that the heat capacities do not depend on the temperature, becomes:

$$\begin{aligned}\Delta_{\text{rxn}}H^{\ominus}_{398} &= -283.0 + \left(38 - 29 - \frac{1}{2}30\right) \times 10^{-3}(398 - 298) \\ &= -283.6 \text{ kJ/mol.}\end{aligned}$$

As we notice from this result, a difference in temperature of 100 K translates into a change in $\Delta_{\text{rxn}}H^{\ominus}$ of this reaction of only 0.6 kJ/mol. This is a trend that is often observed, and values of $\Delta_{\text{rxn}}H$ are very weakly dependent on changes in temperature for most chemical reactions. This numerical result can also be compared with the amount that is experimentally measured for $\Delta_{\text{rxn}}H^{\ominus}_{398}$ of this reaction, which is –283.67 kJ/mol. This comparison strongly supports the assumption that we used to solve the integral in eq. 7.12, confirming that the heat capacities are mostly independent of temperature.

7.7. Spontaneity of Chemical Reactions

We can now go back to the question that we left open at the end of chapter 6: does the synthesis of ammonia happen? To decide whether a process is spontaneous, we need the entropy of the universe, eq. 6.1. For a reaction at

constant temperature and pressure, both of its pieces come from tabulated data:

- The entropy of the system is the reaction entropy, which we calculate from the standard entropies with eq. 6.25.
- The entropy of the surroundings comes from the heat that the reaction exchanges with them, eq. 6.14. At constant pressure, this heat is the reaction enthalpy, $Q_{\text{sys}} = \Delta_{\text{rxn}}H$, and therefore:

$$\Delta S^{\text{surr}} = -\frac{\Delta_{\text{rxn}}H}{T}. \tag{7.13}$$

An exothermic reaction releases heat and increases the entropy of the surroundings, while an endothermic reaction absorbs heat and decreases it.

Example 7.4 (Is the synthesis of ammonia spontaneous?)**.** Using the result of example 6.3, $\Delta_{\text{rxn}}S^{\ominus} = -198.1\ \frac{\text{J}}{\text{mol K}}$, and knowing that $\Delta_{\text{f}}H^{\ominus}_{\text{NH}_{3(g)}} = -45.9$ kJ/mol, decide whether the synthesis of ammonia at standard conditions and 298 K is spontaneous:

$$\text{N}_{2(g)} + 3\text{H}_{2(g)} \rightarrow 2\text{NH}_{3(g)}.$$

Solution: Using Hess's law, eq. 7.9, and remembering that the formation enthalpies of $\text{N}_{2(g)}$ and $\text{H}_{2(g)}$ are zero, since they are elements in their reference form:

$$\Delta_{\text{rxn}}H^{\ominus} = 2\Delta_{\text{f}}H^{\ominus}_{\text{NH}_{3(g)}} - \underbrace{\Delta_{\text{f}}H^{\ominus}_{\text{N}_{2(g)}}}_{=0} - 3\underbrace{\Delta_{\text{f}}H^{\ominus}_{\text{H}_{2(g)}}}_{=0} = 2(-45.9) = -91.8\ \text{kJ/mol}.$$

The reaction is exothermic, and the heat that it releases increases the entropy of the surroundings, eq. 7.13:

$$\Delta S^{\text{surr}} = -\frac{\Delta_{\text{rxn}}H^{\ominus}}{T} = -\frac{-91.8\times10^3}{298} = +308.1\ \frac{\text{J}}{\text{mol K}}.$$

The entropy of the universe is therefore:

$$\Delta S^{\text{universe}} = \Delta_{\text{rxn}}S^{\ominus} + \Delta S^{\text{surr}} = -198.1 + 308.1 = +110.0\ \frac{\text{J}}{\text{mol K}},$$

and the reaction is spontaneous. Just as for the freezing of supercooled water in example 6.2, the system loses entropy, but the heat that it releases increases the entropy of the surroundings by more.

This result should not make us think that a bottle of nitrogen and hydrogen turns into ammonia on its own. At room temperature, the reaction is so slow that nothing measurable happens, even over years. In industry, ammonia is produced with the Haber–Bosch process, which uses a catalyst and high temperatures to make the reaction fast enough. Thermodynamics tells us which way a reaction goes; how fast it goes is the subject of chemical kinetics, which we will introduce in chapter 14.

The calculation in example 7.4 works, but it requires two separate pieces, one for the system and one for the surroundings. We can combine them in a single expression by multiplying the entropy of the universe by $-T$:

$$-T\Delta S^{\text{universe}} = -T\Delta_{\text{rxn}}S + \Delta_{\text{rxn}}H = \Delta_{\text{rxn}}H - T\Delta_{\text{rxn}}S. \tag{7.14}$$

Since T is positive, a reaction is spontaneous ($\Delta S^{\text{universe}} > 0$) when the right-hand side of eq. 7.14 is negative. For the synthesis of ammonia, it is $-91.8 - 298 \times (-0.1981) = -32.8$ kJ/mol. Notice that the right-hand side contains only properties of the system, and no reference to the surroundings. This combination of enthalpy and entropy is so useful that it deserves its own name. In the next chapter, we will see that it is the change of a new state function, the Gibbs energy, and we will discover the general family of functions to which it belongs, called the thermodynamic potentials.

7.8. Chapter Review

7.8.1. Key Ideas

- **Reaction enthalpy** is the heat exchanged by a reaction at constant pressure: negative for exothermic reactions, positive for endothermic ones.
- **Reaction enthalpies** are calculated with the same stoichiometric numbers, ν_i, that we used for reaction entropies: negative for reactants and positive for products.
- **Calorimetry:** $Q_{\text{rxn}} = -C_{\text{cal}}\Delta T$. A constant-pressure calorimeter measures $\Delta_{\text{rxn}}H$, a bomb calorimeter measures $\Delta_{\text{rxn}}U$, and the two are related by $\Delta_{\text{rxn}}H = \Delta_{\text{rxn}}U + \Delta n_{\text{gas}}RT$.
- **Standard enthalpies of formation,** $\Delta_{\text{f}}H^{\ominus}$, refer to the standard state at $P^{\ominus} = 1$ bar, and they are zero for elements in their most stable form. Unlike entropies, enthalpies have no natural zero, so only these relative values can be tabulated.
- **Hess's law:** since H is a state function, $\Delta_{\text{rxn}}H^{\ominus} = \sum_i \nu_i \Delta_{\text{f}}H_i^{\ominus}$, whatever the path of the reaction.

- **Bond enthalpies** give quick estimates for gas-phase reactions: bonds broken minus bonds formed.
- **Other temperatures (Kirchhoff's law):** $\Delta_{\text{rxn}}H^{\ominus}_{T'} = \Delta_{\text{rxn}}H^{\ominus}_{298} + \int_{298}^{T'} \Delta C_P \, dT$, and the correction is usually small.
- **Spontaneity of a reaction:** $\Delta S^{\text{universe}} = \Delta_{\text{rxn}}S - \frac{\Delta_{\text{rxn}}H}{T}$. A reaction that lowers the entropy of the system, such as the synthesis of ammonia, can still be spontaneous if it releases enough heat. The combination $\Delta_{\text{rxn}}H - T\Delta_{\text{rxn}}S = -T\Delta S^{\text{universe}}$ depends only on the system, and it is negative for spontaneous reactions.
- **Which way, not how fast:** thermodynamics tells us whether a reaction is spontaneous, but not how fast it goes.

7.8.2. Study Questions

1. What characterizes an endothermic reaction?

a. $\Delta_{\text{rxn}}H < 0$, and heat is released by the system.
b. $\Delta_{\text{rxn}}H = 0$.
c. $\Delta_{\text{rxn}}H > 0$, and heat is gained by the system.
d. The reaction is always spontaneous.
e. The reaction happens at constant volume.

---

2. What is the sign convention for the stoichiometric coefficients ν_i?

a. Positive for products and negative for reactants.
b. Positive for reactants and negative for products.
c. Always positive.
d. Positive for gases and negative for liquids.
e. Positive for elements and negative for compounds.

---

3. What is the standard enthalpy of formation of a compound?

a. The enthalpy of the compound at 0 K.
b. The enthalpy change when 1 mol of the compound is decomposed into atoms.
c. The heat released when the compound burns in oxygen.
d. The absolute enthalpy of the compound at 298 K.

e. The enthalpy change when 1 mol of the compound is formed from its elements, with all substances in their standard states.

---

4. What is the standard pressure used in thermodynamic tables?

a. 0 bar.
b. 1 bar.
c. 1 atm exactly.
d. 10 bar.
e. It depends on the substance.

---

5. What is the standard enthalpy of formation of $\mathrm{O}_{2(g)}$?

a. −286 kJ/mol.
b. −394 kJ/mol.
c. +498 kJ/mol.
d. 0 kJ/mol, since it is an element in its standard state.
e. It cannot be measured.

---

6. Which formula expresses Hess's law?

a. $\Delta_{\mathrm{rxn}}H^{\ominus} = \sum_i \nu_i \Delta_{\mathrm{f}}H_i^{\ominus}$.
b. $\Delta_{\mathrm{rxn}}H^{\ominus} = \sum_i \Delta_{\mathrm{f}}H_i^{\ominus}$.
c. $\Delta_{\mathrm{rxn}}H^{\ominus} = \prod_i \nu_i \Delta_{\mathrm{f}}H_i^{\ominus}$.
d. $\Delta_{\mathrm{rxn}}H^{\ominus} = Q_V$.
e. $\Delta_{\mathrm{rxn}}H^{\ominus} = \sum_i \nu_i S_i^{\ominus}$.

---

7. Why can Hess's law be used to calculate reaction enthalpies?

a. Because all reactions are exothermic.
b. Because heat is a state function.
c. Because the enthalpy is a state function, so its change does not depend on the path.
d. Because all reactions happen at standard conditions.
e. Because enthalpies of formation are always negative.

---

8. What does the difference between the enthalpies of formation of $H_2O_{(g)}$ and $H_2O_{(l)}$ represent?

a. The enthalpy of formation of water.
b. The heat capacity of water.
c. The enthalpy of combustion of hydrogen.
d. Zero, since they are the same substance.
e. The enthalpy (latent heat) of vaporization of water.

---

9. How can a reaction enthalpy at a temperature T' be calculated from its value at 298 K?

a. $\Delta_{\text{rxn}}H_{T'} = \Delta_{\text{rxn}}H_{298} \cdot \frac{T'}{298}$.
b. $\Delta_{\text{rxn}}H_{T'} = \Delta_{\text{rxn}}H_{298} + \int_{298}^{T'} \Delta C_P \, dT$.
c. $\Delta_{\text{rxn}}H_{T'} = \Delta_{\text{rxn}}H_{298}$ always.
d. $\Delta_{\text{rxn}}H_{T'} = \Delta_{\text{rxn}}H_{298} - T'\Delta S$.
e. $\Delta_{\text{rxn}}H_{T'} = \int_{298}^{T'} C_P \, dT$.

---

10. The synthesis of ammonia has $\Delta_{\text{rxn}}S^{\ominus} < 0$. Why is it spontaneous at 298 K?

a. Because the entropy of the system does not matter for spontaneity.
b. Because the reaction is endothermic.
c. Because every reaction between gases is spontaneous.
d. Because the heat that it releases increases the entropy of the surroundings by more than the system loses.
e. Because the reaction is fast at room temperature.

---

11. A bomb calorimeter measures the heat of a reaction at constant volume. Which quantity does it give?

a. $\Delta_{\text{rxn}}H$.
b. $\Delta_{\text{rxn}}U$, which can be converted to $\Delta_{\text{rxn}}H$ with $\Delta_{\text{rxn}}H = \Delta_{\text{rxn}}U + \Delta n_{\text{gas}}RT$.
c. $\Delta_{\text{rxn}}S$.
d. The work done by the reaction.

e. The heat capacity of the products.

---

12. How is a reaction enthalpy estimated from bond enthalpies?

a. Bonds formed minus bonds broken.
b. Bonds broken plus bonds formed.
c. Bonds broken minus bonds formed.
d. The sum of the bond enthalpies of the products.
e. It cannot be estimated from bond enthalpies.

Answers

1.c, 2.a, 3.e, 4.b, 5.d, 6.a, 7.c, 8.e, 9.b, 10.d, 11.b, 12.c

8. Thermodynamic Potentials

In chapter 5 and chapter 6, we learned that the entropy of the universe tells us whether a process is spontaneous, and in section 7.7 we used it to show that the synthesis of ammonia is spontaneous. This criterion is general, but it is not very practical: to use it, we always need to calculate what happens to the surroundings, in addition to what happens to the system. Chemists would much rather have a criterion that depends only on the system, and that works at the conditions that we can easily control in a lab, such as constant temperature and constant pressure. At the end of chapter 7, we already found a hint: for a reaction at constant T and P, the combination $\Delta H - T\Delta S$ of the system alone tells us whether the reaction is spontaneous (eq. 7.14). In this chapter, we will build such criteria. We will start by combining the first and second laws into a single equation, and we will then use a simple mathematical trick to define new state functions, called *thermodynamic potentials*, each tailored to a specific set of experimental conditions. One of them, the Gibbs energy, will be the protagonist of the rest of this book.

8.1. Fundamental Equation of Thermodynamics

Let's summarize some of the results from the first and second law of thermodynamics that we have seen so far. For reversible processes in closed systems, the first law gives us the change in internal energy, and the definition of entropy gives us the reversible heat:

$$\begin{aligned} \text{From } 1^{\text{st}} \text{ Law:} \qquad & dU = Q_{\text{REV}} - PdV \\ \text{From The Definition of Entropy:} \qquad & dS = \frac{Q_{\text{REV}}}{T} \rightarrow Q_{\text{REV}} = TdS \\ \Rightarrow \quad & dU = TdS - PdV. \end{aligned} \tag{8.1}$$

Eq. 8.1 is called the **fundamental equation of thermodynamics** since it combines the first and the second laws. Even though we started the derivation above by restricting to reversible transformations only, if we

look carefully at eq. 8.1, we notice that it exclusively involves state functions (U, T, S, P, and V). Since state functions do not care about the path, the relation between their changes must be the same for any path, and it applies to both reversible and irreversible processes. The fundamental equation, however, remains constrained to closed systems. This fact restricts its utility for chemistry, since when a chemical reaction happens, the amounts of the chemical species change.

At the end of the 19$^{\text{th}}$ century, Josiah Willard Gibbs (1839–1903) proposed an important addition to the fundamental equation to account for changes in composition. Gibbs was able to do so by introducing a new quantity that he called the chemical potential:

Definition 8.1. The *chemical potential* is the amount of energy absorbed or released due to a change of the particle number of a given chemical species.

The chemical potential of species i is usually abbreviated as μ_i, and it enters the fundamental equation of thermodynamics as:

$$dU = TdS - PdV + \sum_i \mu_i dn_i, \tag{8.2}$$

where dn_i is the differential change in the number of moles of substance i, and the summation extends over all chemical species in the system. In words, μ_i tells us by how much the energy of the system changes when we add a tiny amount of species i, while keeping everything else fixed. As we will see in the next chapters, it measures the "escaping tendency" of a species: matter spontaneously moves from where its chemical potential is high to where it is low, just like heat moves from high to low temperature.

According to the fundamental equation, the internal energy of a system is a function of the three variables entropy, S, volume, V, and the numbers of moles $\{n_i\}$.[1] To emphasize this connection, we can use the notation $U(S, V, \{n_i\})$, and we call S, V, and $\{n_i\}$ the **natural variables** of the energy. Using the language of chapter 1, the natural variables are the "knobs" that control the "machine" U: if we know how to turn them, we know everything about how U changes.

[1] In the case of the numbers of moles we include them in curly brackets to indicate that there might be more than one, depending on how many species are present.

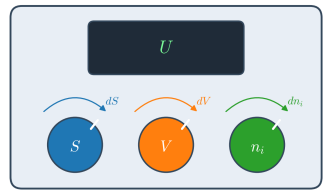


Figure 8.1.: The internal energy as a machine. Its natural variables, the knobs that control it, are the entropy S, the volume V, and the numbers of moles $\{n_i\}$, as in eq. 8.2.

8.2. Thermodynamic Potentials

The natural variables of the internal energy have a practical problem. While the volume and the number of moles are easy to control, nobody has ever built an "entropy-meter," and we have no knob to set the entropy of a system in the lab. The knobs that we *can* easily turn are the temperature (with a thermostat or a water bath) and the pressure (by leaving the beaker open to the atmosphere). We would like, therefore, to define new state functions whose natural variables include T and P instead of S and V.

There is a simple trick to do this, called a **Legendre transformation**. Look at eq. 8.2: the variables appear in pairs, multiplied together, as T and S in TdS, and $-P$ and V in $-PdV$. These pairs are called *conjugate variables*. In each pair, one variable is intensive (T and $-P$), the other one is extensive (S and V), and their product has the units of an energy.[2] Now, let's subtract the product TS from U and take the differential. Using the product rule, $d(TS) = TdS + SdT$, and therefore:

$$d(U - TS) = \underbrace{TdS - PdV + \sum_i \mu_i dn_i}_{dU} - TdS - SdT = -SdT - PdV + \sum_i \mu_i dn_i. \tag{8.3}$$

The term TdS has disappeared, and it has been replaced by $-SdT$. The new function, $U - TS$, has T as a natural variable instead of S: we have swapped a knob that we cannot turn for one that we can. This is all there is to a Legendre transformation: to replace a natural variable with its conjugate partner, we subtract the product of the two from the original

[2] The intensive variable can be thought of as a thermodynamic "force," and the extensive one as the corresponding "displacement," similarly to how a force times a displacement gives a work in classical mechanics.

function. In the language of our machines, a Legendre transformation swaps one knob for its partner, as summarized in figure 8.2. The new functions obtained this way are called **thermodynamic potentials**.[3]

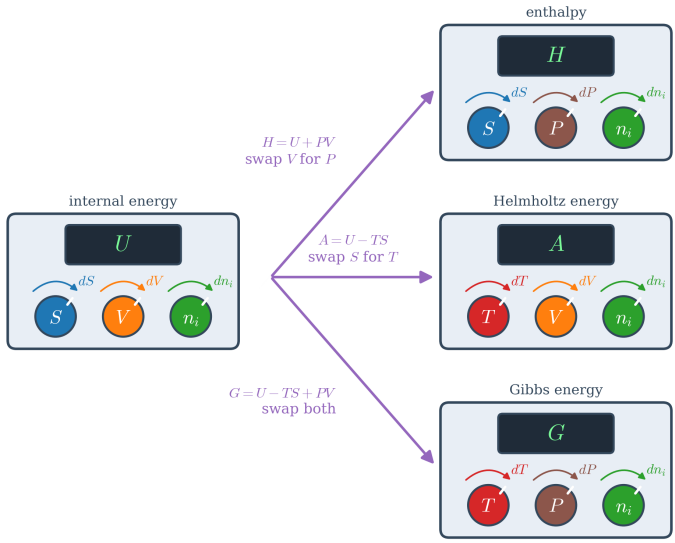


Figure 8.2.: The Legendre transformations as knob swaps. Starting from the internal energy, whose knobs are S, V, and $\{n_i\}$, we obtain the enthalpy by swapping the volume knob for the pressure knob, the Helmholtz energy by swapping the entropy knob for the temperature knob, and the Gibbs energy by swapping both. The knob of each variable has the same color in all the figures of this chapter.

We have already used this trick, without saying it, when we defined the enthalpy in section 3.1.4. If we take the internal energy and subtract the product of the conjugate variables $-P$ and V, we obtain $U - (-P)V = U + PV = H$, as in eq. 3.9. Taking the differential of this definition, we obtain:

$$dH = dU + VdP + PdV, \tag{8.4}$$

and using the fundamental equation, eq. 8.2, to replace dU, we obtain:

[3]Even if we introduced both concepts in the same chapter, it is important to never confuse the *thermodynamic potentials*—which are energy functions such as H, A, and G—with the *chemical potential*—which describes how the energy changes with the composition.

$$\begin{aligned} dH &= TdS - PdV + \sum_i \mu_i dn_i + VdP + PdV \\ &= TdS + VdP + \sum_i \mu_i dn_i, \end{aligned} \tag{8.5}$$

which is the fundamental equation for enthalpy. The natural variables of the enthalpy are S, P, and $\{n_i\}$. The Legendre transformation has allowed us to go from $U(S, V, \{n_i\})$ to $H(S, P, \{n_i\})$ by replacing the dependence on the extensive variable, V, with an intensive one, P.

The function that we have obtained in eq. 8.3, where we replaced the entropy with the temperature, is called the Helmholtz energy, A:

$$A = U - TS, \tag{8.6}$$

and its fundamental equation is:

$$\begin{aligned} dA = dU - SdT - TdS &= TdS - PdV + \sum_i \mu_i dn_i - SdT - TdS \\ &= -SdT - PdV + \sum_i \mu_i dn_i. \end{aligned} \tag{8.7}$$

The Helmholtz energy is named after Hermann Ludwig Ferdinand von Helmholtz (1821–1894), and its natural variables are temperature, volume, and the number of moles.

Finally, we can perform both Legendre transformations at once, to replace both the entropy and the volume with their intensive partners. In that case, we define a new function called the Gibbs energy, G, as:

$$G = U - TS + PV = H - TS, \tag{8.8}$$

which, taking again the differential and using eq. 8.2 becomes:

$$\begin{aligned} dG = dU - SdT - TdS + VdP + PdV &= dH - SdT - TdS \\ &= TdS - PdV + \sum_i \mu_i dn_i - SdT - TdS + VdP + PdV \\ &= VdP - SdT + \sum_i \mu_i dn_i. \end{aligned} \tag{8.9}$$

The Gibbs energy is named after Willard Gibbs himself, and its natural variables are temperature, pressure, and number of moles: exactly the knobs that we control when we run a reaction in an open beaker.

A summary of the four thermodynamic potentials is given in table 8.1.

Table 8.1.: Summary of the Four Thermodynamic Potentials.

Potential	Symbol	Fundamental Equation	Natural Var.
Energy	U	$dU = TdS - PdV + \sum_i \mu_i dn_i$	$S, V, \{n_i\}$
Enthalpy	H	$dH = TdS + VdP + \sum_i \mu_i dn_i$	$S, P, \{n_i\}$
Helmholtz	A	$dA = -SdT - PdV + \sum_i \mu_i dn_i$	$T, V, \{n_i\}$
Gibbs	G	$dG = -SdT + VdP + \sum_i \mu_i dn_i$	$T, P, \{n_i\}$

Let's look at what this table tells us:

1. **Each potential is suited to different conditions.** We should use the potential whose natural variables are the ones that we keep constant in our experiment. The internal energy is natural for an isolated, rigid container. The enthalpy is natural for heat exchanged at constant pressure, as we saw in chapter 7. The Helmholtz energy is natural for processes at constant temperature and volume, such as reactions in a sealed rigid vessel. The Gibbs energy is natural for processes at constant temperature and pressure, which is the case for most chemical reactions in the lab and for all the processes in living organisms.
2. **No information is lost.** A Legendre transformation does not throw away anything: the four potentials contain exactly the same information, written in terms of different variables.
3. **The thermodynamic potentials are the analog of the potential energy in classical mechanics.** A ball rolls downhill, and it stops at the bottom, where its potential energy is at a minimum. As we will show in the next section, a system at constant T and V evolves spontaneously towards the minimum of A, and a system at constant T and P evolves towards the minimum of G.[4]

8.3. Gibbs and Helmholtz Energies

The Legendre transformation procedure translates all information contained in the original function to the new one. Therefore, $H(S, P, \{n_i\})$, $A(T, V, \{n_i\})$, and $G(T, P, \{n_i\})$ all contain the same information that is in $U(S, V, \{n_i\})$. However, the new functions depend on different natural variables, and they are useful at different conditions. For example, when we want to study chemical changes, we are interested in studying the term

[4] For the mathematically inclined, an entertaining method to summarize the same thermodynamic potentials is the thermodynamic square.

$\sum_i \mu_i dn_i$ that appears in each thermodynamic potential. To do so, we need to isolate the chemical term by keeping all other natural variables constant. For example, changes in the chemical term will correspond to changes in the internal energy at constant S and constant V:

$$dU(S,V,\{n_i\}) = \sum_i \mu_i dn_i \quad \text{if} \quad dS = dV = 0. \tag{8.10}$$

Similarly:

$$\begin{aligned} dH(S,P,\{n_i\}) &= \sum_i \mu_i dn_i \quad \text{if} \quad dS = dP = 0, \\ dA(T,V,\{n_i\}) &= \sum_i \mu_i dn_i \quad \text{if} \quad dT = dV = 0, \\ dG(T,P,\{n_i\}) &= \sum_i \mu_i dn_i \quad \text{if} \quad dT = dP = 0. \end{aligned} \tag{8.11}$$

The latter two cases are particularly interesting, since most of chemistry happens at constant temperature and either constant volume,[5] or constant pressure.[6] Neither of them requires the entropy to be constant, which we could not control anyway. We will now show that A and G also give us what we were looking for at the beginning of this chapter: criteria for spontaneity that depend only on the system. The starting point is the Clausius theorem, eq. 6.21, which contains the second law written in terms of the system only:

$$dS^{\text{sys}} \geq \frac{Q}{T_{\text{surr}}} \quad \longrightarrow \quad TdS \geq Q, \tag{8.12}$$

where in the second step we multiplied both sides by T, the temperature of the system and of its surroundings, which we keep constant. We can now consider two cases, side by side: constant V (left), where no work is done and the heat is $Q_V = dU$, and constant P (right), where the heat is $Q_P = dH$:

constant V :	constant P :
$TdS \geq dU$	$TdS \geq dH$
$TdS - dU \geq 0$	$TdS - dH \geq 0$

(8.13)

[5] For example, several industrial processes in sealed reactors.
[6] For example, most processes in a chemistry lab.

On the other hand, at constant temperature, $SdT = 0$, and the differentials of the definitions of A and G, eq. 8.6 and eq. 8.8, simplify to:

$$\begin{aligned} &\text{constant } T, V: && \text{constant } T, P: \\ &(dA)_{T,V} = dU - TdS && (dG)_{T,P} = dH - TdS \\ &dU = (dA)_{T,V} + TdS && dH = (dG)_{T,P} + TdS \end{aligned} \tag{8.14}$$

Replacing dU and dH from the last line of eq. 8.14 into eq. 8.13, the terms TdS cancel out, and we obtain:

$$\begin{aligned} TdS - (dA)_{T,V} - TdS \geq 0 \qquad & TdS - (dG)_{T,P} - TdS \geq 0 \\ (dA)_{T,V} \leq 0 \qquad & (dG)_{T,P} \leq 0. \end{aligned} \tag{8.15}$$

These are the conditions on dA and dG for inferring the spontaneity of a process. Notice how they contain only properties of the system: the entropy change of the surroundings is hidden inside them, through the heat that the system exchanges. They can be summarized as follows:

Definition 8.2.

- During a spontaneous process at constant *temperature* and *volume*, the *Helmholtz energy* will decrease ($dA < 0$), until it reaches a stationary point at which the system will be at equilibrium ($dA = 0$).
- During a spontaneous process at constant *temperature* and *pressure*, the *Gibbs energy* will decrease ($dG < 0$), until it reaches a stationary point at which the system will be at equilibrium ($dG = 0$).

8.4. Maxwell Relations

Let's consider the fundamental equations for the thermodynamic potentials that we have derived in section 8.2:

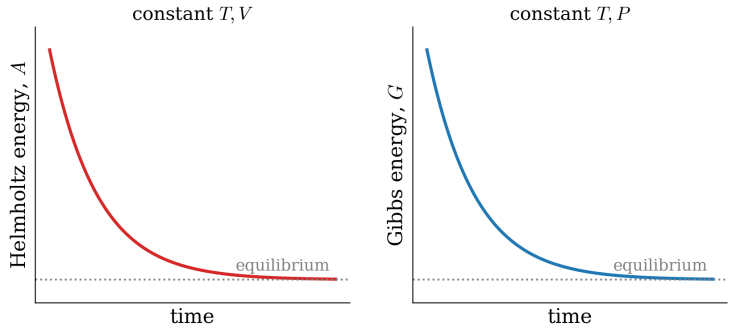


Figure 8.3.: Behavior of Helmholtz (red) and Gibbs (blue) Energies for Spontaneous Processes at Constant T, V (left) and Constant T, P (right).

$$\begin{aligned} dU(S,V,\{n_i\}) &= \;\; TdS - PdV + \sum_i \mu_i dn_i \\ dH(S,P,\{n_i\}) &= \;\; TdS + VdP + \sum_i \mu_i dn_i \\ dA(T,V,\{n_i\}) &= -SdT - PdV + \sum_i \mu_i dn_i \\ dG(T,P,\{n_i\}) &= -SdT + VdP + \sum_i \mu_i dn_i \; . \end{aligned} \tag{8.16}$$

Since we know the natural variables of each potential, we can also write the same differentials using the general formula for the total differential, eq. 1.3. Each coefficient in front of dS, dV, dT, dP, or dn_i is a partial derivative of the potential:

$$
\begin{aligned}
dU &= \underbrace{\left(\frac{\partial U}{\partial S}\right)_{V,\{n_i\}}}_{T} dS + \underbrace{\left(\frac{\partial U}{\partial V}\right)_{S,\{n_i\}}}_{-P} dV + \sum_i \underbrace{\left(\frac{\partial U}{\partial n_i}\right)_{S,V,\{n_{j\neq i}\}}}_{\mu_i} dn_i \\
dH &= \underbrace{\left(\frac{\partial H}{\partial S}\right)_{P,\{n_i\}}}_{T} dS + \underbrace{\left(\frac{\partial H}{\partial P}\right)_{S,\{n_i\}}}_{V} dP + \sum_i \underbrace{\left(\frac{\partial H}{\partial n_i}\right)_{S,P,\{n_{j\neq i}\}}}_{\mu_i} dn_i \\
dA &= \underbrace{\left(\frac{\partial A}{\partial T}\right)_{V,\{n_i\}}}_{-S} dT + \underbrace{\left(\frac{\partial A}{\partial V}\right)_{T,\{n_i\}}}_{-P} dV + \sum_i \underbrace{\left(\frac{\partial A}{\partial n_i}\right)_{T,V,\{n_{j\neq i}\}}}_{\mu_i} dn_i \\
dG &= \underbrace{\left(\frac{\partial G}{\partial T}\right)_{P,\{n_i\}}}_{-S} dT + \underbrace{\left(\frac{\partial G}{\partial P}\right)_{T,\{n_i\}}}_{V} dP + \sum_i \underbrace{\left(\frac{\partial G}{\partial n_i}\right)_{T,P,\{n_{j\neq i}\}}}_{\mu_i} dn_i \ ,
\end{aligned}
\tag{8.17}
$$

Comparing eq. 8.16 and eq. 8.17 term by term, we can read off what each partial derivative is equal to. For example, the coefficient of dS in dU is T in the first equation and $\left(\frac{\partial U}{\partial S}\right)_{V,\{n_i\}}$ in the second one, so these two quantities must be equal. In this way, we obtain the following new definitions:

$$
\begin{aligned}
T &= \left(\frac{\partial U}{\partial S}\right)_{V,\{n_i\}} = \left(\frac{\partial H}{\partial S}\right)_{P,\{n_i\}} \\
-P &= \left(\frac{\partial U}{\partial V}\right)_{S,\{n_i\}} = \left(\frac{\partial A}{\partial V}\right)_{T,\{n_i\}} \\
V &= \left(\frac{\partial H}{\partial P}\right)_{S,\{n_i\}} = \left(\frac{\partial G}{\partial P}\right)_{T,\{n_i\}} \\
-S &= \left(\frac{\partial A}{\partial T}\right)_{V,\{n_i\}} = \left(\frac{\partial G}{\partial T}\right)_{P,\{n_i\}}
\end{aligned}
\tag{8.18}
$$

and:

$$
\begin{aligned}
\mu_i &= \left(\frac{\partial U}{\partial n_i}\right)_{S,V,\{n_{j\neq i}\}} = \left(\frac{\partial H}{\partial n_i}\right)_{S,P,\{n_{j\neq i}\}} \\
&= \left(\frac{\partial A}{\partial n_i}\right)_{T,V,\{n_{j\neq i}\}} = \left(\frac{\partial G}{\partial n_i}\right)_{T,P,\{n_{j\neq i}\}} \ .
\end{aligned}
$$

Since T, P, V, and S are now defined as first partial derivatives of a thermodynamic potential, we can take a second partial derivative with respect to the other natural variable. As we saw in chapter 1, Schwarz's theorem guarantees that, for a state function, the order in which we take the two

derivatives does not matter. Therefore, the two mixed second derivatives of each potential must be equal, which gives the following relations:

$$\begin{aligned}
\frac{\partial^2 U}{\partial S \partial V} &= +\left(\frac{\partial T}{\partial V}\right)_{S,n_i} = -\left(\frac{\partial P}{\partial S}\right)_{V,n_i} \\
\frac{\partial^2 H}{\partial S \partial P} &= +\left(\frac{\partial T}{\partial P}\right)_{S,n_i} = +\left(\frac{\partial V}{\partial S}\right)_{P,n_i} \\
-\frac{\partial^2 A}{\partial T \partial V} &= +\left(\frac{\partial S}{\partial V}\right)_{T,n_i} = +\left(\frac{\partial P}{\partial T}\right)_{V,n_i} \\
\frac{\partial^2 G}{\partial T \partial P} &= -\left(\frac{\partial S}{\partial P}\right)_{T,n_i} = +\left(\frac{\partial V}{\partial T}\right)_{P,n_i}
\end{aligned} \tag{8.19}$$

The relations in eq. 8.19 are called **Maxwell relations**,[7] and are useful in experimental settings to relate quantities that are hard to measure with others that are more intuitive. Their real power is that they let us calculate how the entropy changes with pressure or volume, which we cannot measure directly, from how P, V, and T are related, which we can measure easily.

Let's see an example. The third Maxwell relation tells us that $\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V$. For an ideal gas, $P = \frac{nRT}{V}$, and the right-hand side is easy to calculate: $\left(\frac{\partial P}{\partial T}\right)_V = \frac{nR}{V}$. Therefore, $dS = \frac{nR}{V} dV$ at constant temperature, and integrating between V_i and V_f:

$$\Delta S = nR \ln \frac{V_f}{V_i} \qquad \text{(constant } T\text{)}, \tag{8.20}$$

which is exactly the result that we obtained in eq. 6.4, using the heat exchanged along a reversible path. With the Maxwell relation, we obtained it without ever thinking about heat, starting only from the ideal gas law.

Example 8.1 (Deriving a Maxwell relation)**.** Derive the last Maxwell relation in eq. 8.19.
Solution: We can start our derivation from the definitions of V and S as partial derivatives of G:

$$V = \left(\frac{\partial G}{\partial P}\right)_{T,\{n_i\}} \qquad \text{and:} \qquad -S = \left(\frac{\partial G}{\partial T}\right)_{P,\{n_i\}},$$

and then take a second partial derivative of each quantity with respect to the second variable:

[7] Maxwell relations should not be confused with the Maxwell equations of electromagnetism.

$$\left(\frac{\partial V}{\partial T}\right)_{P,\{n_i\}} = \frac{\partial}{\partial T}\left[\left(\frac{\partial G}{\partial P}\right)_{T,\{n_i\}}\right]_{P,\{n_i\}}$$

$$-\left(\frac{\partial S}{\partial P}\right)_{T,\{n_i\}} = \frac{\partial}{\partial P}\left[\left(\frac{\partial G}{\partial T}\right)_{P,\{n_i\}}\right]_{T,\{n_i\}}.$$

These two derivatives are mixed partial second derivatives of G with respect to T and P, and therefore, according to Schwarz's theorem, they are equal to each other:

$$\frac{\partial}{\partial T}\left[\left(\frac{\partial G}{\partial P}\right)_{T,\{n_i\}}\right]_{P,\{n_i\}} = \frac{\partial}{\partial P}\left[\left(\frac{\partial G}{\partial T}\right)_{P,\{n_i\}}\right]_{T,\{n_i\}},$$

hence:

$$\left(\frac{\partial V}{\partial T}\right)_{P,\{n_i\}} = -\left(\frac{\partial S}{\partial P}\right)_{T,\{n_i\}},$$

which is the last of Maxwell relations, as defined in eq. 8.19. This relation is particularly useful because it connects the quantity $\left(\frac{\partial S}{\partial P}\right)_{T,\{n_i\}}$—which is impossible to measure in a lab—with the quantity $\left(\frac{\partial V}{\partial T}\right)_{P,\{n_i\}}$—which is easier to measure from an experiment that determines isobaric volumetric thermal expansion coefficients.

8.5. Chapter Review

8.5.1. Key Ideas

- **Fundamental equation:** $dU = T\,dS - P\,dV + \sum_i \mu_i\,dn_i$. It contains only state functions, so it applies to reversible and irreversible processes alike.
- **Chemical potential:** μ_i measures how the energy changes when moles of species i are added.
- **Legendre transformations** swap a variable with its conjugate, giving $H = U + PV$, $A = U - TS$, and $G = U - TS + PV$, each with its own natural variables.
- **Spontaneity criteria:** at constant T and V, the Helmholtz energy decreases ($dA < 0$); at constant T and P, the Gibbs energy decreases

($dG < 0$).
- **Maxwell relations** follow from the equality of mixed second derivatives, and they turn hard-to-measure derivatives of S into easy-to-measure ones of P, V, and T.

8.5.2. Study Questions

1. What is the fundamental equation of thermodynamics for a closed system?

a. $dU = TdS + PdV$.
b. $dU = Q - PdV$ only for reversible processes.
c. $dU = TdS - PdV$.
d. $dU = SdT - VdP$.
e. $dU = TdS - VdP$.

---

2. Why does the fundamental equation apply to irreversible processes too, even if it was derived for reversible ones?

a. Because it contains only state functions.
b. Because irreversible processes do not exist.
c. Because heat is a state function.
d. Because it contains the entropy.
e. Because it is an approximation.

---

3. What is the chemical potential?

a. The energy stored in chemical bonds.
b. The potential energy of a molecule.
c. The pressure of a chemical species.
d. The energy needed to break a molecule into atoms.
e. The amount of energy absorbed or released due to a change in the number of particles of a chemical species.

---

4. What are the natural variables of the internal energy?

a. T, P, $\{n_i\}$.
b. S, V, $\{n_i\}$.

c. T, V, $\{n_i\}$.
d. S, P, $\{n_i\}$.
e. U, V, T.

---

5. What does a Legendre transformation do?

a. It adds heat to the system.
b. It removes all information from the original function.
c. It converts a path function into a state function.
d. It defines a new function by subtracting a product of conjugate variables, replacing one natural variable with its conjugate.
e. It changes the units of the energy.

---

6. What are the natural variables of the Gibbs energy?

a. T, P, $\{n_i\}$.
b. S, V, $\{n_i\}$.
c. T, V, $\{n_i\}$.
d. S, P, $\{n_i\}$.
e. G, H, S.

---

7. What is the fundamental equation for the Helmholtz energy?

a. $dA = TdS - PdV + \sum_i \mu_i dn_i$.
b. $dA = -SdT + VdP + \sum_i \mu_i dn_i$.
c. $dA = -SdT - PdV + \sum_i \mu_i dn_i$.
d. $dA = TdS + VdP + \sum_i \mu_i dn_i$.
e. $dA = SdT + PdV$.

---

8. What is the condition for a spontaneous process at constant temperature and pressure?

a. $dA < 0$.
b. $dS = 0$.
c. $dH > 0$.
d. $dG > 0$.

e. $dG < 0$, until $dG = 0$ at equilibrium.

---

9. From which mathematical property do the Maxwell relations follow?

a. The first law of thermodynamics.
b. The equality of the mixed second derivatives of a state function (Schwarz's theorem).
c. The ideal gas law.
d. The definition of the chemical potential.
e. The Clausius inequality.

---

10. Why is the Maxwell relation $\left(\frac{\partial V}{\partial T}\right)_P = -\left(\frac{\partial S}{\partial P}\right)_T$ useful?

a. Because it shows that the entropy is constant.
b. Because it defines the temperature.
c. Because it is valid only for ideal gases.
d. Because it relates a quantity that is hard to measure (how S changes with P) to one that is easy to measure (thermal expansion).
e. Because it gives the value of the Gibbs energy.

Answers

1.c, 2.a, 3.e, 4.b, 5.d, 6.a, 7.c, 8.e, 9.b, 10.d

9. Gibbs Energy

In chapter 8, we found that, at constant temperature and pressure, a process is spontaneous if it decreases the Gibbs energy of the system. In this chapter, we will concentrate on chemical processes that happen at these conditions.[1] We will learn how to calculate the Gibbs energy of a reaction from tabulated data, and how the Gibbs energy changes with temperature, pressure, and composition. These three dependencies will be the foundations of the next chapters on chemical equilibrium, phase equilibrium, and solutions.

9.1. Gibbs Equation

Recalling from chapter 8, the definition of G is:

$$G = U - TS + PV = H - TS, \tag{9.1}$$

which, taking the differential at constant T and P, becomes:

$$dG = dH \overbrace{- SdT}^{=0} - TdS = dH - TdS. \tag{9.2}$$

Integrating eq. 9.2 between the initial and final states of a process results in:

$$\begin{gathered} \int_i^f dG = \int_i^f dH - T \int_i^f dS \\ \Delta G = \Delta H - T\Delta S \end{gathered} \tag{9.3}$$

which is the famous **Gibbs equation** for ΔG. Using Definition 8.2, we can use ΔG to infer the spontaneity of a chemical process that happens at constant T and P using $\Delta G \leq 0$. If we set ourselves at standard conditions,

[1] The majority of chemical reactions in a lab happen at those conditions, and all biological functions happen at those conditions as well.

we can calculate the standard Gibbs energy of reaction, $\Delta_{\text{rxn}}G^{\ominus}$, for any reaction as:

$$\begin{aligned}\Delta_{\text{rxn}}G^{\ominus} &= \Delta_{\text{rxn}}H^{\ominus} - T\Delta_{\text{rxn}}S^{\ominus} \\ &= \sum_i \nu_i \Delta_{\text{f}}H_i^{\ominus} - T\sum_i \nu_i S_i^{\ominus},\end{aligned} \tag{9.4}$$

where $\Delta_{\text{f}}H_i^{\ominus}$ are the standard enthalpies of formation, $S_i^{\ominus}$ are the standard entropies, and ν_i are the stoichiometric coefficients for every species i involved in the reaction. All these quantities are commonly available, and we have already discussed their usage in chapter 7 and chapter 6, respectively.[2]

The following four options are possible for $\Delta G^{\ominus}$ of a chemical reaction:

$\Delta G^{\ominus}$		$\Delta H^{\ominus}$	$\Delta S^{\ominus}$	Spontaneous?
$-$	*if*	$-$	$+$	*Always*
$+$	*if*	$+$	$-$	*Never*
$-/+$	*if*	$-$	$-$	*Depends on T:* spontaneous at low T
$+/-$	*if*	$+$	$+$	*Depends on T:* spontaneous at high T

Or, in other words:

- Exothermic reactions that increase the entropy are always spontaneous.
- Endothermic reactions that reduce the entropy are always non-spontaneous.
- For the other two cases, the spontaneity of the reaction depends on the temperature:
  - Exothermic reactions that reduce the entropy are spontaneous at low T.
  - Endothermic reactions that increase the entropy are spontaneous at high T.

[2] It is not uncommon to see values of $\Delta_{\text{f}}G^{\ominus}$ tabulated alongside $\Delta_{\text{f}}H^{\ominus}$ and $S_i^{\ominus}$, which simplifies even further the calculation. In fact, a comprehensive list of standard Gibbs energy of formation of inorganic and organic compounds is reported in the appendix of this book (Appendix A). For cases where $\Delta_{\text{f}}G^{\ominus}$ are not reported, they can always be calculated from their constituents.

The synthesis of ammonia is an example of the third case. Its standard Gibbs energy of reaction at 298 K is $\Delta_{\text{rxn}}G^{\ominus} = -91.8 - 298 \times (-0.1981) = -32.8$ kJ/mol, the same number that we obtained from the entropy of the universe in section 7.7, and the same that we get from the tabulated Gibbs energy of formation of ammonia, $2\Delta_{\text{f}}G^{\ominus}_{\text{NH}_{3(g)}} = 2(-16.4)$ kJ/mol. The reaction is spontaneous at room temperature, but it becomes non-spontaneous at high temperature, where the $-T\Delta_{\text{rxn}}S^{\ominus}$ term wins. If we assume that $\Delta_{\text{rxn}}H^{\ominus}$ and $\Delta_{\text{rxn}}S^{\ominus}$ do not depend on temperature, the switch happens where $\Delta_{\text{rxn}}G^{\ominus} = 0$, at $T = \frac{91.8\times10^3}{198.1} \approx 463$ K.

figure 9.1 shows the four cases as lines, since, if ΔH and ΔS do not depend much on the temperature, $\Delta G = \Delta H - T\Delta S$ is a straight line with intercept ΔH and slope $-\Delta S$. In the two cases where the spontaneity depends on the temperature, the line crosses $\Delta G = 0$ at $T = \frac{\Delta H}{\Delta S}$, the temperature at which the reaction changes direction.

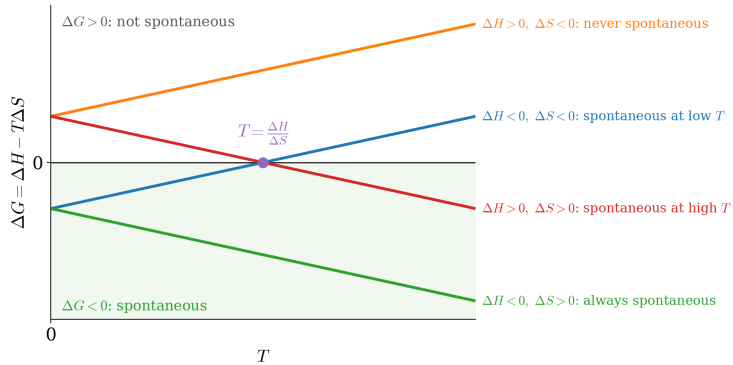


Figure 9.1.: Gibbs Energy of Reaction as a Function of Temperature for the Four Combinations of the Signs of ΔH and ΔS (Schematic). Reactions Are Spontaneous Where $\Delta G < 0$ (Shaded Region).

A simple criterion to estimate the sign of the entropy change of a reaction is to count the moles of *gas* among the reactants and the products. Gases have much larger entropies than liquids and solids, since their molecules can occupy a much larger volume. Therefore, if the reaction produces more moles of gas than it consumes, it will most likely increase the entropy. Vice versa, if the number of moles of gas decreases, the entropy will most likely decrease. For example, the combustion of methane, $\text{CH}_{4(g)} + 2\text{O}_{2(g)} \rightarrow \text{CO}_{2(g)} + 2\text{H}_2\text{O}_{(l)}$, goes from 3 moles of gas to 1, and its entropy change is indeed negative. This criterion is only a rule of thumb: when the number of moles of gas does not change, we need the tabulated entropies to decide.

As we saw in section 8.2, the natural variables of the Gibbs energy are the temperature, T, the pressure, P, and chemical composition, as the number

of moles $\{n_i\}$. The Gibbs energy can therefore be expressed using the total differential as (see also the last formula in eq. 8.17):

$$dG(T,P,\{n_i\}) = \underbrace{\left(\frac{\partial G}{\partial T}\right)_{P,\{n_i\}}}_{\text{temperature dependence}} dT + \underbrace{\left(\frac{\partial G}{\partial P}\right)_{T,\{n_i\}}}_{\text{pressure dependence}} dP + \sum_i \underbrace{\left(\frac{\partial G}{\partial n_i}\right)_{T,P,\{n_{j\neq i}\}}}_{\text{composition dependence}} dn_i. \tag{9.5}$$

If we know the behavior of G as we vary each of the three natural variables independently of the other two, we can reconstruct the total differential dG. Each of these terms represents a coefficient in eq. 9.5, which are given in eq. 8.18.

9.2. Temperature Dependence of ΔG

$$\left(\frac{\partial G}{\partial T}\right)_{P,\{n_i\}} = -S$$

Let's analyze the first coefficient that gives the dependence of the Gibbs energy on temperature. Since this coefficient is equal to $-S$ and the entropy is always positive, G must decrease when T increases at constant P and $\{n_i\}$, and vice versa.

If we replace this coefficient for $-S$ in the Gibbs equation, eq. 9.3, we obtain:

$$\Delta G = \Delta H + T\left(\frac{\partial \Delta G}{\partial T}\right)_{P,\{n_i\}}, \tag{9.6}$$

and since eq. 9.6 includes both ΔG and its partial derivative with respect to temperature $\left(\frac{\partial \Delta G}{\partial T}\right)_{P,\{n_i\}}$ we need to rearrange it to include the temperature derivative only. To do so, we can start by evaluating the partial derivative of $\left(\frac{\Delta G}{T}\right)$ using the product rule:

$$\left[\frac{\partial\left(\frac{\Delta G}{T}\right)}{\partial T}\right]_{P,\{n_i\}} = \frac{1}{T}\left(\frac{\partial \Delta G}{\partial T}\right)_{P,\{n_i\}} - \frac{1}{T^2}\Delta G, \tag{9.7}$$

which, replacing ΔG from eq. 9.6 into eq. 9.7, becomes:

$$\left[\frac{\partial\left(\frac{\Delta G}{T}\right)}{\partial T}\right]_{P,\{n_i\}} = \frac{1}{T}\left(\frac{\partial \Delta G}{\partial T}\right)_{P,\{n_i\}} - \frac{1}{T^2}\left[\Delta H + T\left(\frac{\partial \Delta G}{\partial T}\right)_{P,\{n_i\}}\right]$$
$$= \frac{1}{T}\left(\frac{\partial \Delta G}{\partial T}\right)_{P,\{n_i\}} - \frac{\Delta H}{T^2} - \frac{1}{T}\left(\frac{\partial \Delta G}{\partial T}\right)_{P,\{n_i\}}, \tag{9.8}$$

which simplifies to:

$$\left[\frac{\partial\left(\frac{\Delta G}{T}\right)}{\partial T}\right]_{P,\{n_i\}} = -\frac{\Delta H}{T^2}. \tag{9.9}$$

Eq. 9.9 is known as the **Gibbs–Helmholtz equation**, and is useful in its integrated form to calculate the Gibbs energy for a chemical reaction at any temperature T by knowing just the standard Gibbs energy of formation and the standard enthalpy of formation for the individual species, which are usually reported at $T = 298$ K. The integration is performed as follows:

$$\int_{T_i=298\text{ K}}^{T_f=T} \frac{\partial\left(\frac{\Delta_{\text{rxn}} G}{T}\right)}{\partial T} = -\int_{T_i=298\text{ K}}^{T_f=T} \frac{\Delta_{\text{rxn}} H}{T^2}$$
$$\frac{\Delta_{\text{rxn}} G^{\ominus}(T)}{T} = \frac{\Delta_{\text{rxn}} G^{\ominus}}{298\text{ K}} + \Delta_{\text{rxn}} H^{\ominus}\left(\frac{1}{T} - \frac{1}{298\text{ K}}\right), \tag{9.10}$$

giving the integrated Gibbs–Helmholtz equation:

$$\frac{\Delta_{\text{rxn}} G^{\ominus}(T)}{T} = \frac{\sum_i \nu_i \Delta_{\text{f}} G_i^{\ominus}}{298\text{ K}} + \sum_i \nu_i \Delta_{\text{f}} H_i^{\ominus}\left(\frac{1}{T} - \frac{1}{298\text{ K}}\right) \tag{9.11}$$

9.3. Pressure Dependence of ΔG

$$\left(\frac{\partial G}{\partial P}\right)_{T,\{n_i\}} = V$$

We can now turn our attention to the second coefficient that gives how the Gibbs energy changes when the pressure changes. To do this, we put the system at constant T and $\{n_i\}$, and then we consider infinitesimal variations of G. From eq. 8.9:

$$dG = VdP - SdT + \sum_i \mu_i dn_i \quad \xrightarrow{\text{constant } T,\{n_i\}} \quad dG = VdP, \tag{9.12}$$

which is the differential equation that we were looking for. To study changes of G for macroscopic changes in P, we can integrate eq. 9.12 between initial and final pressures, and considering an ideal gas, we obtain:

$$\begin{aligned} \int_i^f dG &= \int_i^f VdP \\ \Delta G &= nRT \int_i^f \frac{dP}{P} = nRT \ln \frac{P_f}{P_i}. \end{aligned} \tag{9.13}$$

If we take $P_i = P^\ominus = 1\,\text{bar}$, we can rewrite eq. 9.13 as:

$$G = G^\ominus + nRT \ln \frac{P_f}{P^\ominus}, \tag{9.14}$$

which is useful to convert standard Gibbs energies of formation to pressures different from standard pressure, using:

$$\Delta_\text{f} G = \Delta_\text{f} G^\ominus + nRT \ln \frac{P_f}{\underbrace{P^\ominus}_{=1\text{ bar}}} = \Delta_\text{f} G^\ominus + nRT \ln P_f \tag{9.15}$$

For liquids and solids, V is essentially independent of P (liquids and solids are incompressible), and eq. 9.12 can be integrated as:

$$\Delta G = \int_i^f VdP = V \int_i^f dP = V\Delta P. \tag{9.16}$$

The plots in Figure 9.2 show the remarkable difference in the behaviors of $\Delta_\text{f} G$ for a gas and for a liquid, as obtained from eq. 9.13 and eq. 9.16.

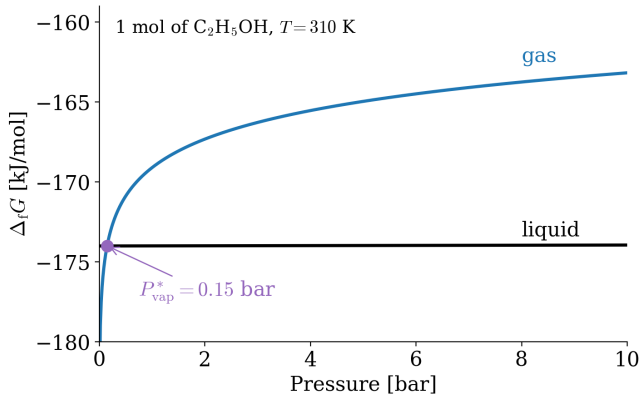


Figure 9.2.: Pressure Dependence of the Gibbs Energy of Formation of Liquid and Gaseous Ethanol at T = 310 K. The Curves Cross at the Vapor Pressure of Liquid Ethanol at this Temperature, which is 0.15 bar.

9.4. Composition Dependence of ΔG

$$\left(\frac{\partial G}{\partial n_i}\right)_{T,P} = \mu_i$$

The third and final coefficient gives the chemical potential as the dependence of G on the chemical composition at constant T and P. To understand what the chemical potential means, let's consider a pure substance, and let's imagine building a sample of it by adding small amounts, dn, one after the other, at constant T and P. Each small amount that we add is identical to what is already in the sample. Therefore, each of them changes the Gibbs energy by the same amount, $dG = \mu^* dn$, where μ^* indicates the chemical potential of the pure substance. In other words, μ^* is an intensive property: it depends on T and P, but not on how much substance we have. Since the Gibbs energy is extensive, when there is no substance there is also no Gibbs energy. We can then integrate from an empty sample ($n = 0$, $G = 0$) to a sample with n moles and Gibbs energy G:

$$\int_0^G dG = \int_0^n \mu^* dn, \tag{9.17}$$

and since μ^* does not depend on the number of moles, we can take it out of the integral:

$$\int_0^G dG = \mu^* \int_0^n dn \quad \rightarrow \quad G = \mu^* n \quad \rightarrow \quad \mu^* = \frac{G}{n}, \tag{9.18}$$

which gives a straightforward interpretation of the chemical potential of a pure substance as the molar Gibbs energy.

In a mixture, the chemical potential of a component is no longer simply G/n, since its molecules are surrounded by molecules of other kinds. The derivative $\mu_i = \left(\frac{\partial G}{\partial n_i}\right)_{T,P,n_{j\neq i}}$ is an example of a *partial molar quantity*:

Definition 9.1. The *partial molar quantity* of component i, $\overline{X}_i = \left(\frac{\partial X}{\partial n_i}\right)_{T,P,n_{j\neq i}}$, is the change in the extensive property X per mole of i added to a mixture, at constant temperature, pressure, and amounts of all the other components.

The most intuitive example is the volume. Adding 1 mol of water (18 cm^3) to a large amount of pure water increases the volume by 18 cm^3, but adding it to a large amount of ethanol increases the volume by only about 14 cm^3, because the water molecules pack tightly around the ethanol molecules. Partial molar quantities depend on the composition of the mixture. The chemical potential is the partial molar Gibbs energy, $\mu_i = \overline{G}_i$.

Repeating the argument of eq. 9.17 for a mixture built by adding all the components at once, at constant composition, gives:

$$G = \sum_i n_i \mu_i. \tag{9.19}$$

Differentiating eq. 9.19 gives $dG = \sum_i \mu_i dn_i + \sum_i n_i d\mu_i$, and at constant T and P, eq. 8.17 gives $dG = \sum_i \mu_i dn_i$. The two expressions agree only if:

$$\sum_i n_i d\mu_i = 0 \qquad \text{(constant } T, P\text{)}, \tag{9.20}$$

which is the **Gibbs–Duhem equation**. It tells us that the chemical potentials of the components of a mixture cannot change independently. For a binary mixture, $d\mu_\text{B} = -\frac{n_\text{A}}{n_\text{B}} d\mu_\text{A}$: if the chemical potential of one component increases, the other one must decrease.

We can start from eq. 9.14 and write for a pure substance that is brought from $P_i = P^\ominus$ to $P_f = P$ at constant T:

$$G - G^{\ominus} = nRT \ln \frac{P}{P^{\ominus}}, \tag{9.21}$$

dividing both sides by n, we obtain:

$$\frac{G}{n} - \frac{G^{\ominus}}{n} = RT \ln \frac{P}{P^{\ominus}}, \tag{9.22}$$

which, for a pure substance at $P^{\ominus} = 1$ bar, becomes:

$$\mu^* - \mu^{\ominus} = RT \ln P. \tag{9.23}$$

Notice that, while we use the pressure of the gas inside the logarithm in eq. 9.23, the quantity is formally divided by the standard pressure $P^{\ominus} = 1$ bar, and therefore it is a dimensionless quantity, as it should be. For simplicity of notation, however, we will omit the division by $P^{\ominus}$ in the remainder of this textbook, especially wherever it does not create confusion. Let's now consider a mixture of ideal gases, and let's try to find out whether the chemical potential of a pure gas inside the mixture, μ_i^{mixture}, is the same as its chemical potential outside the mixture, μ^*. To do so, we can use eq. 9.23 and replace the pressure P with the partial pressure P_i:

$$\mu_i^{\text{mixture}} = \mu_i^{\ominus} + RT \ln P_i, \tag{9.24}$$

where the partial pressure P_i can be obtained from the simple relation that is known as **Dalton's Law**:

$$P_i = y_i P, \tag{9.25}$$

with y_i being the concentration of gas i measured as a mole fraction in the gas phase $y_i = \frac{n_i}{n_{\text{TOT}}} < 1$. Replacing eq. 9.25 into eq. 9.24, we obtain:

$$\begin{aligned} \mu_i^{\text{mixture}} &= \mu_i^{\ominus} + RT \ln(y_i P) \\ &= \underbrace{\mu_i^{\ominus} + RT \ln P}_{\mu_i^*} + RT \ln y_i, \end{aligned} \tag{9.26}$$

which then reduces to the following equation:

$$\mu_i^{\text{mixture}} = \mu_i^* + RT \ln y_i. \tag{9.27}$$

Analyzing eq. 9.27, we can immediately see that, since $y_i < 1$:

$$\mu_i^{\text{mixture}} < \mu_i^*, \tag{9.28}$$

or, in other words, the chemical potential of a substance in the mixture is always lower than the chemical potential of the pure substance. If we consider a process where we start from two separate pure ideal gases and finish with a mixture of the two, we can calculate the change in Gibbs energy due to the mixing process with:

$$\Delta_{\text{mixing}} G = \sum n_i \left(\mu_i^{\text{mixture}} - \mu_i^*\right) < 0, \tag{9.29}$$

or, in other words, the process is spontaneous under all circumstances, and pure ideal gases will always mix.

9.5. Chapter Review

9.5.1. Key Ideas

- **Gibbs equation:** at constant T and P, $\Delta G = \Delta H - T\Delta S$, which balances enthalpy and entropy.
- **Temperature dependence:** $\left(\frac{\partial G}{\partial T}\right)_P = -S$, and the Gibbs–Helmholtz equation gives ΔG at other temperatures from ΔH.
- **Pressure dependence:** $\left(\frac{\partial G}{\partial P}\right)_T = V$. For an ideal gas, $G = G^{\ominus} + nRT \ln \frac{P}{P^{\ominus}}$; for liquids and solids, G barely changes with P.
- **Chemical potential:** for a pure substance, $\mu^* = G/n$; for an ideal gas in a mixture, $\mu_i = \mu_i^{\ominus} + RT \ln P_i$.
- **Partial molar quantities:** in a mixture, $\mu_i = \left(\frac{\partial G}{\partial n_i}\right)_{T,P,n_{j\neq i}}$ is the partial molar Gibbs energy, $G = \sum_i n_i \mu_i$, and the Gibbs–Duhem equation, $\sum_i n_i \, d\mu_i = 0$, links the changes of the chemical potentials.
- **Mixing:** ideal gases always mix spontaneously, since $\Delta_{\text{mixing}} G < 0$.

9.5.2. Study Questions

1. Which equation gives the Gibbs energy change of a process at constant T and P?

a. $\Delta G = \Delta H + T\Delta S$.
b. $\Delta G = \Delta H - T\Delta S$.
c. $\Delta G = \Delta U - T\Delta S$.
d. $\Delta G = T\Delta S - \Delta H$.
e. $\Delta G = \Delta H \cdot \Delta S$.

---

2. An exothermic reaction decreases the entropy of the system. When is it spontaneous?

a. Always.
b. Never.
c. Only at high temperature.
d. Only at low temperature.
e. Only at high pressure.

---

3. An endothermic reaction increases the entropy of the system. When is it spontaneous?

a. Only at high temperature.
b. Only at low temperature.
c. Always.
d. Never.
e. Only at low pressure.

---

4. Since $\left(\frac{\partial G}{\partial T}\right)_{P,\{n_i\}} = -S$, how does the Gibbs energy of a substance change when the temperature increases?

a. It increases, since the entropy is positive.
b. It stays constant.
c. It increases linearly with the volume.
d. It oscillates.
e. It decreases, since the entropy is positive.

---

5. What is the Gibbs–Helmholtz equation?

a. $\left(\frac{\partial G}{\partial P}\right)_T = V$.
b. $\Delta G = \Delta H - T\Delta S$.
c. $\left[\frac{\partial(\Delta G/T)}{\partial T}\right]_P = -\frac{\Delta H}{T^2}$.
d. $\left[\frac{\partial(\Delta G/T)}{\partial T}\right]_P = \frac{\Delta S}{T^2}$.
e. $\Delta G = -RT \ln K$.

---

6. What is the pressure dependence coefficient of the Gibbs energy?

a. $\left(\frac{\partial G}{\partial P}\right)_{T,\{n_i\}} = -V.$
b. $\left(\frac{\partial G}{\partial P}\right)_{T,\{n_i\}} = V.$
c. $\left(\frac{\partial G}{\partial P}\right)_{T,\{n_i\}} = -S.$
d. $\left(\frac{\partial G}{\partial P}\right)_{T,\{n_i\}} = H.$
e. $\left(\frac{\partial G}{\partial P}\right)_{T,\{n_i\}} = 0.$

---

7. How does the Gibbs energy of an ideal gas depend on the pressure at constant temperature?

a. $G = G^{\ominus} - nRT \ln \frac{P}{P^{\ominus}}$
b. $G = G^{\ominus} + nRT \frac{P}{P^{\ominus}}$
c. $G = G^{\ominus} + V\Delta P.$
d. $G = G^{\ominus} + nRT \ln \frac{P}{P^{\ominus}}$
e. G does not depend on P.

---

8. Why does the Gibbs energy of a liquid change much less with pressure than that of a gas?

a. Because the molar volume of a liquid is small and almost independent of pressure.
b. Because liquids have zero entropy.
c. Because liquids are always at standard pressure.
d. Because the Gibbs energy of a liquid is zero.
e. Because liquids do not have a chemical potential.

---

9. What is the chemical potential of a pure substance?

a. Its enthalpy.
b. Its entropy per mole.
c. Its pressure divided by RT.
d. Zero at standard conditions.
e. Its molar Gibbs energy, $\mu^* = G/n$.

---

10. Two pure ideal gases are allowed to mix at constant T and P. What is the sign of $\Delta_{\text{mixing}}G$?

a. Positive, so the gases do not mix.
b. Zero, since ideal gases do not interact.
c. Negative, so the gases always mix spontaneously.
d. It depends on the gases.
e. It depends on the temperature.

Answers

1.b, 2.d, 3.a, 4.e, 5.c, 6.b, 7.d, 8.a, 9.e, 10.c

10. Chemical Equilibrium

In chapter 9, we learned that the Gibbs energy decreases during a spontaneous process at constant temperature and pressure, and we found how it depends on the composition of a mixture. In this chapter, we will apply these results to chemical reactions. Most reactions do not go all the way to products: they stop at a mixture of reactants and products, the chemical equilibrium. We will see that the composition of this mixture is set by the minimum of the Gibbs energy, which leads us to the equilibrium constant that you know from general chemistry. We will then study how the equilibrium constant changes with temperature and pressure, which gives a mathematical form to Le Chatelier's principle.

10.1. Reaction Quotient and Equilibrium Constant

Let's consider a prototypical reaction at constant T, P:

$$a\mathrm{A} + b\mathrm{B} \rightarrow c\mathrm{C} + d\mathrm{D} \tag{10.1}$$

The Gibbs energy of the reaction is defined as:

$$\Delta_{\mathrm{rxn}} G = G_{\mathrm{products}} - G_{\mathrm{reactants}} = G^{\mathrm{C}} + G^{\mathrm{D}} - G^{\mathrm{A}} - G^{\mathrm{B}}, \tag{10.2}$$

and replacing the absolute Gibbs energies with the chemical potentials μ_i, we obtain:

$$\Delta_{\mathrm{rxn}} G = c\mu_{\mathrm{C}} + d\mu_{\mathrm{D}} - a\mu_{\mathrm{A}} - b\mu_{\mathrm{B}}. \tag{10.3}$$

Assuming the reaction is happening in the gas phase, we can then use eq. 9.24 to replace the chemical potentials with their value in the reaction mixture, as:

$$\begin{aligned}\Delta_{\text{rxn}}G &= c(\mu_{\text{C}}^{\ominus} + RT\ln P_{\text{C}}) + d(\mu_{\text{D}}^{\ominus} + RT\ln P_{\text{D}}) + \\ &\quad - a(\mu_{\text{A}}^{\ominus} + RT\ln P_{\text{A}}) - b(\mu_{\text{B}}^{\ominus} + RT\ln P_{\text{B}}) \\ &= \underbrace{c\mu_{\text{C}}^{\ominus} + d\mu_{\text{D}}^{\ominus} - a\mu_{\text{A}}^{\ominus} - b\mu_{\text{B}}^{\ominus}}_{\Delta_{\text{rxn}}G^{\ominus}} + RT\ln\frac{P_{\text{C}}^{c}\cdot P_{\text{D}}^{d}}{P_{\text{A}}^{a}\cdot P_{\text{B}}^{b}}.\end{aligned} \tag{10.4}$$

We can define a new quantity called the *reaction quotient* as a function of the partial pressures of each substance:[1]

$$Q_P = \frac{P_{\text{C}}^{c}\cdot P_{\text{D}}^{d}}{P_{\text{A}}^{a}\cdot P_{\text{B}}^{b}}, \tag{10.5}$$

and we can then simply rewrite eq. 10.4 using eq. 10.5 as:

$$\Delta_{\text{rxn}}G = \Delta_{\text{rxn}}G^{\ominus} + RT\ln Q_P. \tag{10.6}$$

This equation tells us that the sign of $\Delta_{\text{rxn}}G$ is influenced by the reaction quotient Q_P. For a spontaneous reaction at the beginning, the partial pressures of the reactants are much higher than the partial pressures of the products, therefore $Q_P \ll 1$ and $\Delta_{\text{rxn}}G < 0$, as we expect. As the reaction proceeds, the partial pressures of the products will increase, while the partial pressures of the reactants will decrease. Consequently, both Q_P and $\Delta_{\text{rxn}}G$ will increase. The reaction will completely stop when $\Delta_{\text{rxn}}G = 0$, which is the chemical equilibrium point. At the reaction equilibrium:

$$\Delta_{\text{rxn}}G = 0 = \Delta_{\text{rxn}}G^{\ominus} + RT\ln K_P, \tag{10.7}$$

where we have defined a new quantity called **equilibrium constant**, as the value the reaction quotient assumes when the reaction reaches equilibrium, and we have denoted it with the symbol K_P.[2] From eq. 10.7 we can derive the following fundamental equation on the standard Gibbs energy of reaction:

$$\Delta_{\text{rxn}}G^{\ominus} = -RT\ln K_P. \tag{10.8}$$

To extend the concept of K_P beyond the four species in the prototypical reaction eq. 10.1, we can use the product of a series symbol $\left(\prod_i\right)$, and write:

[1] Notice that since we used eq. 9.23 to derive the reaction quotient, the partial pressures inside it are always dimensionless since they are divided by $P^{\ominus}$.

[2] The subscript P refers to the fact that the equilibrium constant is measured in terms of partial pressures.

$$K_P = \prod_i P_{i,\text{eq}}^{\nu_i}, \tag{10.9}$$

where $P_{i,\text{eq}}$ are the partial pressures of each species at equilibrium. Eq. 10.9 is in principle valid for ideal gases only. However, reactions involving ideal gases are pretty rare. As such, we can further extend the concept of equilibrium constant and write:

$$K_{\text{eq}} = \prod_i a_{i,\text{eq}}^{\nu_i}, \tag{10.10}$$

where we have replaced the partial pressure at equilibrium, $P_{i,\text{eq}}$, with a new concept introduced initially by Gilbert Newton Lewis (1875–1946),[3] that he termed **activity**, and represented by the letter a. The activity is a dimensionless "effective concentration" that tells us how much each species contributes to the equilibrium. Its expression depends on the state of the species:

- **Ideal gases:** the activity is the partial pressure divided by the standard pressure, $a_i = P_i/P^{\ominus}$, as in eq. 10.9.
- **Non-ideal gases:** the pressure is replaced by an "effective pressure," the fugacity, $a_i = f_i/P^{\ominus}$, which we will introduce in chapter 11.
- **Pure liquids and solids:** the activity is simply $a_i = 1$. This is why pure solids and liquids do not appear in the equilibrium constants that you wrote in general chemistry.
- **Solutions:** for dilute solutions, the activity is approximately equal to a measured concentration, such as the mole fraction, or the molar concentration divided by the standard one, $[i]/[i]^{\ominus}$ with $[i]^{\ominus} = 1$ mol/L. For concentrated solutions, a correction factor is needed. We will derive the activity of solutions in chapter 13.

For now, it is interesting to use the activity to write the definition of the following two constants:

$$K_y = \prod_i \left(y_{i,\text{eq}}\right)^{\nu_i} \qquad\qquad K_C = \prod_i \left([i]_{\text{eq}}/[i]^{\ominus}\right)^{\nu_i}, \tag{10.11}$$

which can then be related with K_P for a mixture of ideal gases using:

$$P_i = y_i P \qquad\qquad P_i = \frac{n_i}{V} RT = [i]RT, \tag{10.12}$$

which then results in:

[3] Gilbert Lewis is the same scientist who invented the concept of Lewis Structures.

$$K_P = K_y \cdot \left(\frac{P}{P^\ominus}\right)^{\Delta\nu} \qquad K_P = K_C \left(\frac{[i]^\ominus RT}{P^\ominus}\right)^{\Delta\nu}, \tag{10.13}$$

with $\Delta\nu = \sum_i \nu_i$.

Using the general equilibrium constant, K_{eq}, we can also rewrite the fundamental equation on $\Delta_{\text{rxn}}G^\ominus$ that we derived in eq. 10.8 to be applicable at most conditions, as:

$$\Delta_{\text{rxn}}G^\ominus = -RT \ln K_{\text{eq}}, \tag{10.14}$$

and since $\Delta_{\text{rxn}}G^\ominus$ depends on T, P and $\{n_i\}$, it is useful to explore how K_{eq} depends on those variables as well.

10.2. Extent of Reaction and the Minimum of the Gibbs Energy

We said that a reaction stops when $\Delta_{\text{rxn}}G = 0$. But what exactly is $\Delta_{\text{rxn}}G$ while a reaction is still going? It is not the difference between two finished states, as the Δ symbol might suggest. To see what it really is, we need a variable that tells us how far a reaction has gone.

Let's go back to our prototypical reaction, eq. 10.1. Every time the reaction proceeds, the amounts of all species change together, in the ratios set by the stoichiometric coefficients: if a moles of A disappear, c moles of C must appear. We can capture all these changes with a single variable, the **extent of reaction**, ξ (the Greek letter "xi"), defined by:

$$dn_i = \nu_i \, d\xi \qquad \text{or, after integration,} \qquad n_i = n_{i,0} + \nu_i \, \xi, \tag{10.15}$$

where $n_{i,0}$ is the amount of species i at the start, and ν_i is its stoichiometric number (negative for reactants, positive for products, as in definition 6.3). The extent of reaction is measured in moles, and it is the same number for every species: $\xi = 0$ at the start, and $\xi = 1$ mol when the reaction has gone "once" as written, with a moles of A and b moles of B turned into c moles of C and d moles of D.

At constant T and P, the change in Gibbs energy of the reacting mixture is given by the last line of eq. 8.16 with $dT = dP = 0$. Replacing dn_i with eq. 10.15, we get:

$$dG = \sum_i \mu_i \, dn_i = \left(\sum_i \nu_i \mu_i \right) d\xi \quad \longrightarrow \quad \left(\frac{\partial G}{\partial \xi} \right)_{T,P} = \sum_i \nu_i \mu_i = \Delta_{\text{rxn}} G, \tag{10.16}$$

where in the last step we recognized the same combination of chemical potentials that appears in eq. 10.3. This is the meaning of $\Delta_{\text{rxn}} G$: it is the **slope** of the Gibbs energy of the mixture as a function of the extent of reaction. Its value changes as the reaction proceeds, because the chemical potentials depend on the composition.

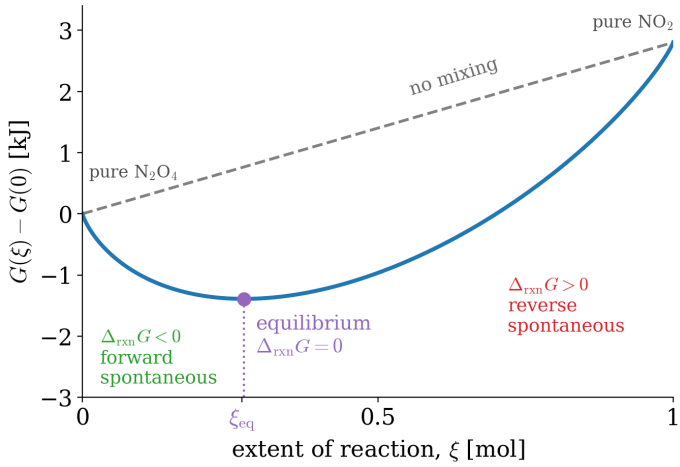


Figure 10.1.: Gibbs energy of the mixture as a function of the extent of reaction for $N_2O_{4(g)} \rightleftarrows 2\,NO_{2(g)}$ at 298 K and 1 bar, starting from 1 mol of N_2O_4, computed from the standard Gibbs energies of formation in the appendix. The dashed line is the Gibbs energy if reactants and products were kept separate. Mixing lowers the Gibbs energy and creates a minimum, at the equilibrium extent of reaction.

Let's look at what figure 10.1 tells us about the dissociation of dinitrogen tetroxide into nitrogen dioxide:

1. **The slope decides the direction.** To the left of the minimum, the slope is negative, $\Delta_{\text{rxn}} G < 0$, and the Gibbs energy decreases if the reaction moves forward. To the right of the minimum, the slope is positive, and the reaction runs spontaneously in reverse. Either way, the mixture slides downhill toward the bottom of the curve.
2. **Equilibrium is the bottom of the curve.** At the minimum, the slope is zero, $\Delta_{\text{rxn}} G = 0$, and the reaction has no reason to go in

either direction. This is the chemical equilibrium of eq. 10.7, and its position, ξ_{eq}, gives the equilibrium composition.

3. **Mixing is what makes a minimum.** If reactants and products stayed separate, the Gibbs energy would follow the dashed straight line, and the reaction would go either all the way or not at all, depending on the sign of $\Delta_{\text{rxn}}G^{\ominus}$. Because the gases mix, the Gibbs energy drops below this line by the Gibbs energy of mixing, which is always negative (eq. 9.29). This is why some products always form, even when $\Delta_{\text{rxn}}G^{\ominus} > 0$, as in this case, and why most reactions stop at a mixture instead of going to completion.
4. $\boldsymbol{\Delta_{\text{rxn}}G^{\ominus}}$ **is the slope of the dashed line,** that is, the Gibbs energy difference between the pure products and the pure reactants, each at standard pressure. It decides *where* the minimum falls, through K_{eq}, but it is not the quantity that drives the reaction at a given moment: that is $\Delta_{\text{rxn}}G$.

Example 10.1 (Equilibrium composition of dinitrogen tetroxide)**.** One mole of $N_2O_{4(g)}$ is kept at 298 K and a total pressure of 1 bar, where it partially dissociates into $NO_{2(g)}$. Using $\Delta_f G^{\ominus} = 99.8$ kJ/mol for $N_2O_{4(g)}$ and 51.3 kJ/mol for $NO_{2(g)}$, find the extent of reaction and the composition at equilibrium.
Solution: The standard Gibbs energy of reaction is:

$$\Delta_{\text{rxn}}G^{\ominus} = 2(51.3) - 99.8 = 2.8 \text{ kJ/mol},$$

and from eq. 10.8:

$$K_P = \exp\left(-\frac{\Delta_{\text{rxn}}G^{\ominus}}{RT}\right) = \exp\left(-\frac{2\,800}{8.314 \times 298}\right) = 0.323.$$

Using eq. 10.15 with $n_{N_2O_4,0} = 1$ mol and $n_{NO_2,0} = 0$, at a generic extent of reaction we have $n_{N_2O_4} = 1 - \xi$, $n_{NO_2} = 2\xi$, and a total of $1 + \xi$ moles of gas. With a total pressure of 1 bar, the partial pressures are equal to the mole fractions, and the equilibrium constant becomes:

$$K_P = \frac{P_{NO_2}^2}{P_{N_2O_4}} = \frac{\left(\frac{2\xi}{1+\xi}\right)^2}{\frac{1-\xi}{1+\xi}} = \frac{4\xi^2}{1-\xi^2}.$$

Solving for ξ gives:

$$\xi_{\text{eq}} = \sqrt{\frac{K_P}{4 + K_P}} = \sqrt{\frac{0.323}{4.323}} = 0.273 \text{ mol}.$$

At equilibrium, we have 0.727 mol of N_2O_4 and 0.546 mol of NO_2, with mole fractions $y_{N_2O_4} = 0.571$ and $y_{NO_2} = 0.429$. This is exactly

the position of the minimum in figure 10.1. Even though $\Delta_{\text{rxn}}G^{\ominus}$ is positive, more than a quarter of the N_2O_4 dissociates, thanks to the Gibbs energy of mixing.

10.3. Temperature Dependence of K_{eq}

To study the temperature dependence of K_{eq} we can use eq. 10.14 for the general equilibrium constant and write:

$$\ln K_{\text{eq}} = -\frac{\Delta G^{\ominus}}{RT}, \tag{10.17}$$

which we can then differentiate with respect to temperature at constant $P, \{n_i\}$ on both sides:

$$\left(\frac{\partial \ln K_{\text{eq}}}{\partial T}\right)_{P,\{n_i\}} = -\frac{1}{R}\left[\frac{\partial\left(\frac{\Delta G^{\ominus}}{T}\right)}{\partial T}\right]_{P,\{n_i\}}, \tag{10.18}$$

and, using the Gibbs–Helmholtz equation (eq. 9.9) to simplify the right-hand side, becomes:

$$\left(\frac{\partial \ln K_{\text{eq}}}{\partial T}\right)_{P,\{n_i\}} = -\frac{1}{R}\left(-\frac{\Delta H^{\ominus}}{T^2}\right) = \frac{\Delta H^{\ominus}}{RT^2}, \tag{10.19}$$

which gives the dependence of $\ln K_{\text{eq}}$ on T that we were looking for. Eq. 10.19 is also called **van 't Hoff equation**,[4] and it is the mathematical expression of Le Chatelier's principle. The simplest interpretation is as follows:

- For an exothermic reaction ($\Delta H^{\ominus} < 0$): K_{eq} will decrease as the temperature increases.
- For an endothermic reaction ($\Delta H^{\ominus} > 0$): K_{eq} will increase as the temperature increases.

If we integrate the van 't Hoff equation between two arbitrary points at constant P, and assuming constant $\Delta H^{\ominus}$, we obtain the following:

$$\int_1^2 d\ln K_{\text{eq}} = \frac{\Delta H^{\ominus}}{R}\int_1^2 \frac{dT}{T^2}, \tag{10.20}$$

[4] named after Jacobus Henricus "Henry" van 't Hoff Jr. (1852–1911).

which leads to the linear equation:

$$\ln K_{\text{eq}}(2) = \ln K_{\text{eq}}(1) - \frac{\Delta H^{\ominus}}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right), \tag{10.21}$$

which is the equation that produces the so-called **van 't Hoff plots**, from which $\Delta H^{\ominus}$ can be experimentally determined:

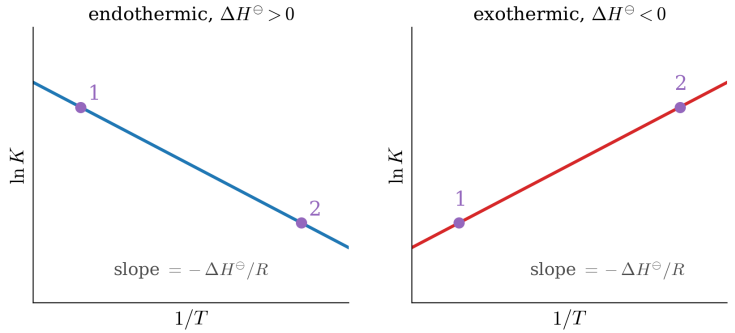


Figure 10.2.: Van 't Hoff Plots for an Endothermic (Left, Blue) and an Exothermic (Right, Red) Reaction at Constant P.

10.4. Pressure and Composition Dependence of K_{eq}

While K_P is independent of both total pressure and number of moles for an ideal gas, the same is not necessarily true for the other equilibrium constants.

$$\left(\frac{\partial K_P}{\partial P}\right)_{T,\{n_i\}} = 0 \qquad \left(\frac{\partial K_P}{\partial n_i}\right)_{T,P} = 0. \tag{10.22}$$

For example, it is easy to look at eq. 10.13 and determine that K_y usually depends on P.[5] Using Dalton's Law, eq. 9.25, we can also notice that the equilibrium partial pressures of the reactants and products in a gas-phase reaction can be expressed in terms of their equilibrium mole fractions y_i and

[5] K_y becomes independent of P in the particular case where $\Delta\nu = 0$, i.e., for reactions where the total number of moles of reactants is the same as the total number of moles of the products.

the total pressure P. As such, we can use K_y to demonstrate that the equilibrium mole fractions will change when P changes,[6] as it is demonstrated by the following exercise.

Example 10.2 (Dissociation of chlorine under pressure)**.** Calculate the mole fraction change for the dissociation of $\mathrm{Cl}_{2(g)}$ when the pressure is increased from $P^\ominus$ to $P_f = 2.5$ bar at constant $T = 2\,298$ K, knowing that $\Delta_\mathrm{f}G^\ominus_{\mathrm{Cl}_{(g)}} = 105.3$ kJ/mol and $\Delta_\mathrm{f}H^\ominus_{\mathrm{Cl}_{(g)}} = 121.3$ kJ/mol, and remembering that both of these values are tabulated at $T = 298$ K.
Solution: Let's consider the reaction:

$$\mathrm{Cl}_{2(g)} \rightleftarrows 2\mathrm{Cl}_{(g)}$$

We can divide the exercise into two parts. In the first one, we will deal with calculating the equilibrium constant at $T = 2\,298$ K from the data at $T = 298$ K. In the second one, we will calculate the change in mole fraction when the pressure is increased from $P^\ominus = 1$ bar to $P_f = 2.5$ bar.

- Let's begin the first part by calculating $\Delta_\mathrm{rxn}G^\ominus$ and $\Delta_\mathrm{rxn}H^\ominus$ from:

$$\Delta_\mathrm{rxn}G^\ominus = 2\Delta_\mathrm{f}G^\ominus_{\mathrm{Cl}_{(g)}} - \Delta_\mathrm{f}G^\ominus_{\mathrm{Cl}_{2(g)}}$$
$$\Delta_\mathrm{rxn}H^\ominus = 2\Delta_\mathrm{f}H^\ominus_{\mathrm{Cl}_{(g)}} - \Delta_\mathrm{f}H^\ominus_{\mathrm{Cl}_{2(g)}},$$

  and since $\mathrm{Cl}_{2(g)}$ is an element in its most stable form at $T = 298$ K, its standard enthalpy and Gibbs energy of formation are $\Delta_\mathrm{f}H^\ominus_{\mathrm{Cl}_{2(g)}} = \Delta_\mathrm{f}G^\ominus_{\mathrm{Cl}_{2(g)}} = 0$. Therefore:[a]

$$\Delta_\mathrm{rxn}G^\ominus = 2 \cdot 105.3 - 0 = 210.6 \text{ kJ/mol}$$
$$\Delta_\mathrm{rxn}H^\ominus = 2 \cdot 121.3 - 0 = 242.6 \text{ kJ/mol}.$$

  Using eq. 10.8 to calculate $K_P(P^\ominus, 298\text{ K})$, we obtain:[b]

$$\ln[K_P(P^\ominus, 298\text{ K})] = \frac{-\Delta_\mathrm{rxn}G^\ominus}{RT} = \frac{-210.6 \times 10^3}{8.31 \cdot 298} = -85.0.$$

  We can now use the integrated van 't Hoff equation, eq. 10.21, to calculate K_P at $T = 2\,298$ K:

$$\ln[K_P(P^\ominus, 2\,298\text{ K})] = \ln[K_P(P^\ominus, 298\text{ K})] + \\ - \frac{\Delta_\mathrm{rxn}H^\ominus}{R}\left(\frac{1}{2\,298} - \frac{1}{298}\right),$$

[6] Keep in mind that K_P will *not* change.

which becomes:

$$\ln[K_P(P^\ominus,2\,298\text{ K})] = -85.0 + \\ - \frac{242.6\times10^3}{8.31}\left(\frac{1}{2\,298}-\frac{1}{298}\right) = 0.262\,,$$

which corresponds to:

$$K_P(P^\ominus, 2\,298\text{ K}) = \exp(0.262) = 1.30.$$

- Let's now move to the second part of the exercise, where we increase the pressure from 1 bar to 2.5 bar at constant $T = 2\,298$ K. We start by writing the definition of K_P and K_y:

$$K_P = \frac{P^2_{\mathrm{Cl}_{(g)}}}{P_{\mathrm{Cl}_{2(g)}}} \qquad\qquad K_y = \frac{y^2_{\mathrm{Cl}_{(g)}}}{y_{\mathrm{Cl}_{2(g)}}},$$

and using eq. 10.13:

$$\Delta\nu = 2-1 = 1$$
$$K_P = K_y\cdot\frac{P}{P^\ominus} \quad\longrightarrow K_y = K_P\left(\frac{P}{P^\ominus}\right)^{-1},$$

we can calculate the initial K_y at $P_i = P^\ominus$, using:

$$K_y(P^\ominus, 2\,298\text{ K}) = 1.30 = \frac{1.30}{1}.$$

and calculate the initial concentration of $\mathrm{Cl}_{2(g)}$ and $\mathrm{Cl}_{(g)}$ at $P^\ominus$, recalling that $y_{\mathrm{Cl}_{2(g)}} = 1 - y_{\mathrm{Cl}_{(g)}}$:

$$K_y(P_i, 2\,298\text{ K}) = \frac{\left(y^i_{\mathrm{Cl}_{(g)}}\right)^2}{1-y^i_{\mathrm{Cl}_{(g)}}} = 1.30.$$

Solving the quadratic equation, we obtain one negative answer—which is unphysical—,[c] and:

$$y^i_{\mathrm{Cl}_{(g)}} = 0.662 \quad\longrightarrow y^i_{\mathrm{Cl}_{2(g)}} = 1-0.662 = 0.338.$$

At the end of the process, $P_f = 2.5$ bar, and we obtain:

$$K_y(P_f, 2\,298\text{ K}) = 0.520 = K_P\frac{P^\ominus}{P_f} = \frac{1.30}{2.5},$$

and, using the same technique used before to solve the quadratic equation:

$$K_y(P_f, 2\,298\text{ K}) = \frac{\left(y^f_{\text{Cl}_{(g)}}\right)^2}{1 - y^f_{\text{Cl}_{(g)}}} = 0.520,$$

gives:

$$y^f_{\text{Cl}_{(g)}} = 0.507 \quad \longrightarrow y^f_{\text{Cl}_{2(g)}} = 1 - 0.507 = 0.493.$$

To summarize, when we increase the pressure from 1 bar to 2.5 bar at $T = 2\,298$ K, the equilibrium constant in terms of the mole fraction decreases from $K_y(P^\ominus, 2\,298\text{ K}) = 1.30$ to $K_y(P_f = 2.5\text{ bar}, 2\,298\text{ K}) = 0.520$. This reduction is causing a shift of the equilibrium towards the reactants, with the concentration of $\text{Cl}_{2(g)}$ increasing from $y^i_{\text{Cl}_{2(g)}} = 0.338$ to $y^f_{\text{Cl}_{2(g)}} = 0.493$ and the concentration of $\text{Cl}_{(g)}$ decreasing from $y^i_{\text{Cl}_{(g)}} = 0.662$ to $y^f_{\text{Cl}_{(g)}} = 0.507$.

[a] Notice how a positive $\Delta_{\text{rxn}}G^\ominus$ indicates that the dissociation of $\text{Cl}_{2(g)}$ is non-spontaneous at $T = 298$ K and $P = 1$ bar. As such, we should expect a very small value for K_P.

[b] The result corresponds to $K_P = 1.2 \times 10^{-37}$, an incredibly minuscule number, as we should expect given the data of $\Delta_{\text{rxn}}G^\ominus$.

[c] Concentration cannot be negative.

The dependence of K_{eq} on P highlighted above is another mathematical expression of Le Chatelier's principle, on this occasion, for changes in pressure. The interpretation for a reaction happening in the gas phase is as follows:

- If the total pressure increases, the equilibrium will shift towards the side of the chemical equation that contains the smallest total number of moles of gas (the equilibrium in example 10.2 shifts toward the reactant).

10.5. Chapter Review

10.5.1. Key Ideas

- **Reaction Gibbs energy:** $\Delta_{\text{rxn}}G = \Delta_{\text{rxn}}G^\ominus + RT\ln Q$, which changes as the reaction proceeds.

- **Extent of reaction:** $\Delta_{\text{rxn}}G = \left(\frac{\partial G}{\partial \xi}\right)_{T,P}$ is the slope of the Gibbs energy of the mixture; equilibrium is the minimum, where $\Delta_{\text{rxn}}G = 0$. Mixing is what creates the minimum.
- **Equilibrium constant:** $\Delta_{\text{rxn}}G^{\ominus} = -RT\ln K_{\text{eq}}$, with $K_{\text{eq}} = \prod_i a_{i,\text{eq}}^{\nu_i}$; pure liquids and solids have $a = 1$.
- **Temperature:** the van 't Hoff equation, $\frac{d\ln K_{\text{eq}}}{dT} = \frac{\Delta_{\text{rxn}}H^{\ominus}}{RT^2}$, says that K increases with T for endothermic reactions and decreases for exothermic ones.
- **Pressure:** K_P does not depend on the pressure, but the composition does, through $K_P = K_y\,(P/P^{\ominus})^{\Delta\nu}$. This is Le Chatelier's principle in mathematical form.

10.5.2. Study Questions

1. How is the Gibbs energy of a reaction related to the reaction quotient?

a. $\Delta_{\text{rxn}}G = \Delta_{\text{rxn}}G^{\ominus} + RT\ln Q$.
b. $\Delta_{\text{rxn}}G = \Delta_{\text{rxn}}G^{\ominus} - RT\ln Q$.
c. $\Delta_{\text{rxn}}G = RTQ$.
d. $\Delta_{\text{rxn}}G = \Delta_{\text{rxn}}G^{\ominus}Q$.
e. $\Delta_{\text{rxn}}G = -RT\ln K$.

---

2. What is true at chemical equilibrium?

a. $\Delta_{\text{rxn}}G^{\ominus} = 0$.
b. $Q = 1$.
c. $\Delta_{\text{rxn}}G = 0$, and the reaction quotient equals the equilibrium constant.
d. The reaction stops because the reactants are used up.
e. $K = 0$.

---

3. How is the standard Gibbs energy of reaction related to the equilibrium constant?

a. $\Delta_{\text{rxn}}G^{\ominus} = RT\ln K_{\text{eq}}$.
b. $\Delta_{\text{rxn}}G^{\ominus} = K_{\text{eq}}/RT$.
c. $\Delta_{\text{rxn}}G^{\ominus} = RTK_{\text{eq}}$.
d. $\Delta_{\text{rxn}}G^{\ominus} = 0$ at equilibrium.
e. $\Delta_{\text{rxn}}G^{\ominus} = -RT\ln K_{\text{eq}}$.

---

4. The dissociation of $\mathrm{Cl}_{2(g)}$ has a large positive $\Delta_{\mathbf{rxn}}G^{\ominus}$ at 298 K. What does this tell us about its equilibrium constant?

a. It is very large.
b. It is very small.
c. It is equal to 1.
d. It is negative.
e. It cannot be defined.

---

5. What is the activity of a pure liquid or solid?

a. Its mole fraction.
b. Its molar concentration.
c. Its vapor pressure.
d. 1.
e. 0.

---

6. What is the meaning of $\Delta_{\mathbf{rxn}}G$ in terms of the extent of reaction, ξ?

a. It is the slope of the Gibbs energy of the reacting mixture, $\left(\frac{\partial G}{\partial \xi}\right)_{T,P}$, which is zero at equilibrium.
b. It is the difference between the Gibbs energies of the pure products and the pure reactants, which never changes during the reaction.
c. It is the total Gibbs energy of the mixture at the end of the reaction.
d. It is equal to ξ multiplied by RT.
e. It is the Gibbs energy of mixing, which is always positive.

---

7. What is the van 't Hoff equation?

a. $\left(\frac{\partial \ln K_{\mathrm{eq}}}{\partial T}\right)_P = -\frac{\Delta H^{\ominus}}{RT^2}$.
b. $\left(\frac{\partial \ln K_{\mathrm{eq}}}{\partial T}\right)_P = \frac{\Delta S^{\ominus}}{R}$.
c. $\left(\frac{\partial \ln K_{\mathrm{eq}}}{\partial T}\right)_P = \frac{\Delta H^{\ominus}}{RT^2}$.

d. $\left(\frac{\partial K_{\text{eq}}}{\partial P}\right)_T = 0$.
e. $\ln K_{\text{eq}} = -\frac{\Delta G^\ominus}{R}$.

---

8. How does the equilibrium constant of an exothermic reaction change when the temperature increases?

a. It increases.
b. It stays constant.
c. It becomes negative.
d. It first increases, then decreases.
e. It decreases.

---

9. In a van 't Hoff plot of $\ln K$ versus $1/T$, what is the slope of the line?

a. $\frac{\Delta H^\ominus}{R}$.
b. $-\frac{\Delta H^\ominus}{R}$.
c. $\frac{\Delta S^\ominus}{R}$.
d. $-\Delta G^\ominus$.
e. RT.

---

10. What happens when the total pressure of a gas-phase reaction at equilibrium is increased, if the number of moles of gas changes in the reaction?

a. K_P increases, and the equilibrium shifts towards the products.
b. K_P decreases, and the equilibrium shifts towards the reactants.
c. Nothing changes.
d. K_P does not change, but the equilibrium shifts towards the side with fewer moles of gas.
e. The equilibrium shifts towards the side with more moles of gas.

Answers

1.a, 2.c, 3.e, 4.b, 5.d, 6.a, 7.c, 8.e, 9.b, 10.d

Part III.

Phase Equilibria and Solutions

11. Ideal and Non-Ideal Gases

Up to this point, we have used the ideal gas as our main example, and in chapter 10 we wrote equilibrium constants in terms of the partial pressures of ideal gases. Real gases, however, are not ideal: their molecules occupy some space, and they attract each other. In this chapter, we will first look back at how the ideal gas law was discovered, and then we will study what happens when its assumptions break down. We will see that non-ideal behavior is responsible for some very useful phenomena, such as the cooling of a gas when it expands and the liquefaction of gases, and we will introduce the fugacity, a quantity that allows us to keep using our thermodynamic formulas for non-ideal gases.

11.1. The Ideal Gas Equation

The concept of an ideal gas is a theoretical construct that allows for straightforward treatment and interpretation of gases' behavior. As such, the ideal gas is a simplified *model* that we use to understand nature, and it does not correspond to any real system. In typical "spherical cow" spirit, the ideal gas model strips away many real-world complications so we can focus on the core relationships between pressure, volume, temperature, and amount of gas. The following two assumptions define the ideal gas model:

Definition 11.1.

- The particles that compose an ideal gas do not occupy any volume.
- The particles that compose an ideal gas do not interact with each other.

Because of its simplicity, the ideal gas model has been the historical foundation of thermodynamics and of science in general. The first studies of the ideal gas behavior date back to the seventeenth century, and the scientists that performed them are among the founders of modern science.

11.1.1. Boyle's Law

In 1662 Robert Boyle (1627–1691) found that the pressure and the volume of an ideal gas are inversely related at constant temperature. Boyle's Law has the following mathematical description:

$$P \propto \frac{1}{V} \quad \text{at const. } T, \tag{11.1}$$

or, in other terms:

$$PV = k_1 \quad \text{at const. } T, \tag{11.2}$$

which results in the familiar PV plots of Figure 11.1. As we already discussed in chapter 2, each of the curves in Figure 11.1 is obtained at constant temperature, and it is therefore called *"isotherm."*

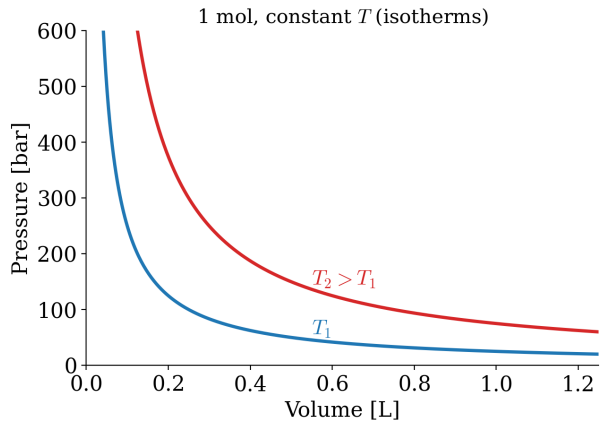


Figure 11.1.: PV-Diagram of 1 mol of an Ideal Gas.

11.1.2. Charles's and Gay-Lussac's Laws

It took scientists more than a century to expand Boyle's work and study the relationship between volume and temperature. In 1787 Jacques Alexandre César Charles (1746–1823) wrote the relationship known as Charles's Law:

$$V \propto T \quad \text{at const. } P, \tag{11.3}$$

or, in other terms:

$$V = k_2 T \quad \text{at const. } P, \tag{11.4}$$

which results in the plots of Figure 11.2. Each of the curves is obtained at constant pressure, and it is termed *"isobar."*

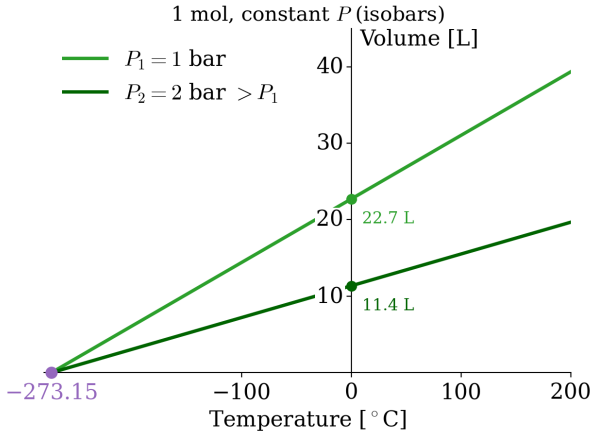


Figure 11.2.: VT-Diagram of 1 mol of an Ideal Gas.

The interesting thing about isobars is that each line seems to converge to a specific point along the temperature line when we extrapolate them to $V \to 0$. As we anticipated in chapter 2, this observation led to the introduction of the absolute temperature scale, suggesting that the temperature will never get smaller than $-273.15°C$. Charles's law in the form of eq. 11.4 holds only if T is measured from this point, in kelvin.

Why do all gases point to the same temperature? Because all of them approach the ideal gas at low pressure, and the ideal gas is made of point-like molecules that occupy no volume. Its volume, $V = \frac{nRT}{P}$, can therefore shrink all the way to zero, and it does so only at $T = 0$, whatever the gas and whatever the pressure. A real gas never gets there: its molecules have a finite size and attract each other, and it liquefies and then solidifies long before absolute zero, as we will see later in this chapter. The point at $-273.15°C$ is therefore an extrapolation of ideal behavior, not a measurement. That it coincides with the zero of the thermodynamic scale, which does not depend on any substance (chapter 4), is what makes the ideal gas such a good thermometer.

It took an additional 21 years to write a formal relationship between pressure and temperature. The following relationships were proposed by Joseph Louis Gay-Lussac (1778–1850) in 1808:

$$P \propto T \quad \text{at const. } V, \tag{11.5}$$

or, in other terms:

$$P = k_3 T \quad \text{at const. } V, \tag{11.6}$$

which results in the plots of Figure 11.3. Each of the curves is obtained at constant volume, and it is termed *"isochor."*

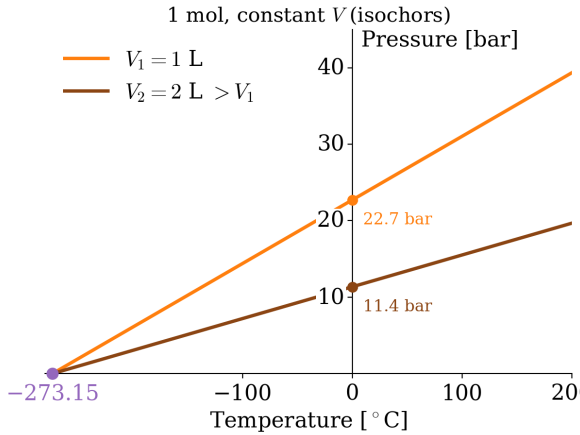


Figure 11.3.: PT-Diagram of 1 mol of an Ideal Gas.

11.1.3. Avogadro's Law

Three years later, in 1811, Amedeo Avogadro (1776–1856) discovered a seemingly unrelated principle by studying the composition of matter. His Avogadro's Law encodes the relationship between the number of moles in an ideal gas and its volume as:

$$V \propto n \quad \text{at const. } P, T, \tag{11.7}$$

or in other terms:

$$V = k_4 n \quad \text{at const. } P, T, \tag{11.8}$$

which results in the straight lines of Figure 11.4.

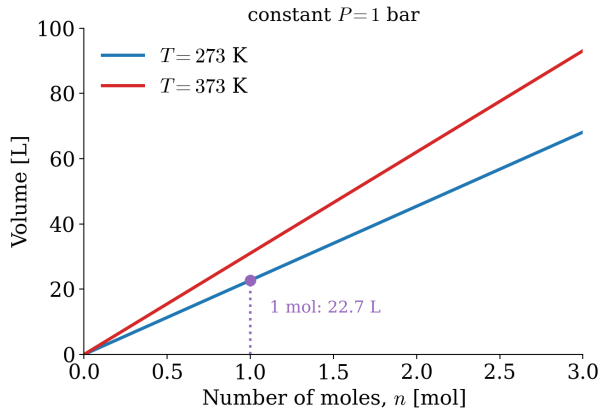


Figure 11.4.: Vn-Diagram of an Ideal Gas at Constant Pressure (1 bar).

11.1.4. The Ideal Gas Law

Despite all of the ingredients being available for more than 20 years, it's only in 1834 that Benoît Paul Émile Clapeyron (1799–1864) was finally able to combine them into what is now known as the **ideal gas Law**. Using the same formulas obtained above, we can write:

$$PV = \underbrace{k_3 T}_{\text{from Gay-Lussac's}} \cdot \underbrace{k_4 n}_{\text{from Avogadro's}}, \tag{11.9}$$

which by renaming the product of the two constants k_3 and k_4 as R, becomes:

$$PV = nRT \tag{11.10}$$

The value of the constant R can be determined experimentally by measuring the volume that 1 mol of an ideal gas occupies at a constant temperature (e.g., at $T = 0°\text{C}$) and a constant pressure (e.g., atmospheric pressure $P = 1$ atm). At those conditions, the volume is measured at 22.4 L, resulting in the following value of R:

$$R = \frac{VP}{nT} = \frac{22.4 \cdot 1}{1 \cdot 273} = 0.082 \ \frac{\text{L atm}}{\text{mol K}}, \tag{11.11}$$

which a simple conversion to SI units transforms into:

$$R = 8.31 \ \frac{\text{J}}{\text{mol K}}. \tag{11.12}$$

11.2. Behaviors of Non-Ideal Gases

Non-ideal gases (sometimes also referred to as "real gases"), do not behave as ideal gases because at least one of the assumptions in definition 11.1 is violated. What characterizes non-ideal gases is that there is no unique equation that we can use to describe their behavior. For this reason, we have a plethora of several experimental models, none of which is superior to the other. The van der Waals (vdW) equation is the only model that we will analyze in detail because of its simple interpretation. However, it is far from universal, and for several non-ideal gases, it is severely inaccurate. Other popular non-ideal gas equations are the Clausius equation, the virial equation, the Redlich–Kwong equation and several others.[1]

11.2.1. The van der Waals Equation

One of the simplest empirical equations that describe non-ideal gases was obtained in 1873 by Johannes Diderik van der Waals (1837–1923). The vdW equation includes two empirical parameters (a and b) with different values for different non-ideal gases. Each of the parameters corresponds to a correction for the breaking of one of the two conditions that define the ideal gas behavior (definition 11.1). The vdW equation is obtained from the ideal gas equation performing the following simple substitutions:

$$\begin{aligned} P &\rightarrow \left(P + \frac{a}{\overline{V}^2}\right) \\ \overline{V} &\rightarrow \left(\overline{V} - b\right), \end{aligned} \tag{11.13}$$

which results in:

$$\begin{aligned} P\overline{V} = RT &\rightarrow \left(P + \frac{a}{\overline{V}^2}\right)\left(\overline{V} - b\right) = RT \\ P &= \frac{RT}{\overline{V} - b} - \frac{a}{\overline{V}^2}. \end{aligned} \tag{11.14}$$

The parameter a accounts for the presence of intermolecular interactions, while the parameter b accounts for the non-negligible volume of the gas molecules. Despite the parameters having simple interpretations, their values for each gas must be determined experimentally. Values for these parameters for some significant non-ideal gases are reported below:

[1] For more information on empirical equations for non-ideal gases see Wikipedia's article on real gases.

	$a\left[\frac{\mathrm{L}^2\mathrm{bar}}{\mathrm{mol}^2}\right]$	$b\left[\frac{\mathrm{L}}{\mathrm{mol}}\right]$
Ammonia	4.225	0.0371
Argon	1.355	0.03201
Carbon dioxide	3.640	0.04267
Carbon monoxide	1.505	0.03985
Chlorine	6.579	0.05622
Freon	10.78	0.0998
Helium	0.0346	0.0238
Hydrogen	0.2476	0.02661
Mercury	8.200	0.01696
Methane	2.283	0.04278
Neon	0.2135	0.01709
Nitrogen	1.370	0.0387
Oxygen	1.382	0.03186
Radon	6.601	0.06239
Xenon	4.250	0.05105

11.2.2. Joule–Thomson Effect

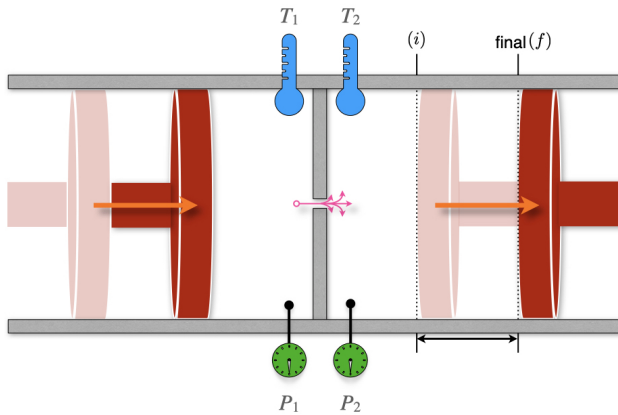


Figure 11.5.: The Joule–Thomson Experiment.

We have already met William Thomson, also known as Lord Kelvin, and his seminal work on the second law of thermodynamics. In conjunction with that work, Thomson is famous for developing a sensitive method for measuring the temperature changes related to the expansion of a gas. These experiments improved on the earlier work by James Joule, and Lord Kelvin's improved instrument depicted in Figure 11.5 is named the Joule–Thomson apparatus. The apparatus is composed of two chambers, each with its own mobile piston. The chambers are connected via a valve or a porous plug. The entire equipment is also thermally isolated from the surroundings. This instrument is a more sensitive version of the Joule expansion apparatus that we already described in chapter 3 (compare with Figure 3.1).

Thomson realized that a gas flowing through an obstruction experiences a drop in pressure. If the entire apparatus is insulated, it will not exchange heat with its surroundings ($Q = 0$), and each transformation will happen at adiabatic conditions. Let's consider an initial condition with 1 mol of gas in the left chamber, occupying a volume V_l, and a completely closed right chamber, for which $V_r^i = 0$. After the process completes, the volume of the left chamber will reduce to ${V_l}^f = 0$, while the volume of the right chamber will be V_r. Using the first law of thermodynamics, we can write:

$$\Delta U = U_r - U_l = \underbrace{Q}_{=0} + W = W_l + W_r, \tag{11.15}$$

with:

$$\begin{aligned} W_l &= -\int_{V_l}^{0} P_l dV = P_l V_l \\ W_r &= -\int_{0}^{V_r} P_r dV = -P_r V_r. \end{aligned} \tag{11.16}$$

Replacing eq. 11.16 into eq. 11.15, results in:

$$\begin{aligned} U_r - U_l &= P_l V_l - P_r V_r \\ \underbrace{U_r + P_r V_r}_{H_r} &= \underbrace{U_l + P_l V_l}_{H_l}, \end{aligned} \tag{11.17}$$

which, replacing the definition of enthalpy $H = U + PV$, we obtain:

$$\begin{aligned} H_r &= H_l \\ \Delta H &= 0, \end{aligned} \tag{11.18}$$

or, in other words, the process is **isenthalpic**. Using the total differential of H:

$$dH = \left(\frac{\partial H}{\partial T}\right)_P dT + \left(\frac{\partial H}{\partial P}\right)_T dP = C_P dT + \left(\frac{\partial H}{\partial P}\right)_T dP, \tag{11.19}$$

we obtain:

$$\Delta H = \int dH = \int C_P dT + \int \left(\frac{\partial H}{\partial P}\right)_T dP = 0, \tag{11.20}$$

or, in purely differential form:

$$dH = C_P dT + \left(\frac{\partial H}{\partial P}\right)_T dP = 0. \tag{11.21}$$

From eq. 11.21 we can define a new coefficient, called the *Joule–Thomson coefficient*, μ_{JT}, that measures the rate of change of temperature of a gas with respect to pressure in the Joule–Thomson process:

$$\mu_{\mathrm{JT}} = \left(\frac{\partial T}{\partial P}\right)_H = -\frac{1}{C_P}\left(\frac{\partial H}{\partial P}\right)_T. \tag{11.22}$$

The value of μ_{JT} depends on the type of gas, the temperature and pressure before expansion, and the heat capacity at constant pressure of the gas. The temperature at which μ_{JT} changes sign is called the "Joule–Thomson inversion temperature." Since the pressure decreases during an expansion, ∂P is negative by definition, and the following possibilities are available for μ_{JT}:

Gas temperature:	∂P	μ_{JT}	∂T	The gas will:
Below the inversion temperature	–	+	–	cool
Above the inversion temperature	–	–	+	warm

For example, helium has a very low Joule–Thomson inversion temperature at standard pressure ($T = 45$ K), and it warms when expanded at constant enthalpy at typical room temperatures. The only other gases that have standard inversion temperature lower than room temperature are hydrogen and neon. On the other hand, nitrogen and oxygen have high inversion temperatures ($T = 621$ K and $T = 764$ K, respectively), and they both cool when expanded at room temperature. Therefore, it is possible to use the Joule–Thomson effect in refrigeration processes such as air conditioning.[2] As we already discussed in chapter 3, the temperature of an ideal gas stays constant in an adiabatic expansion, therefore its Joule–Thomson coefficient is always equal to zero.

[2]Nitrogen and oxygen are the two most abundant gases in the air. A sequence of Joule–Thomson expansions is also used for the industrial liquefaction of air.

11.3. Critical Phenomena

11.3.1. Compressibility Factors

The compressibility factor is a correction coefficient that describes the deviation of a real gas from ideal gas behavior. It is usually represented with the symbol z, and is calculated as:

$$z = \frac{\overline{V}}{\overline{V}_{\text{ideal}}} = \frac{P\overline{V}}{RT}. \tag{11.23}$$

It is evident from eq. 11.23 that the compressibility factor is dependent on the pressure, and for an ideal gas $z = 1$ always. For a non-ideal gas at any given pressure, z can be higher or lower than one, separating the behavior of non-ideal gases into two possibilities. The dependence of the compressibility factor against pressure is represented for H_2 and CO_2 in Figure 11.6.

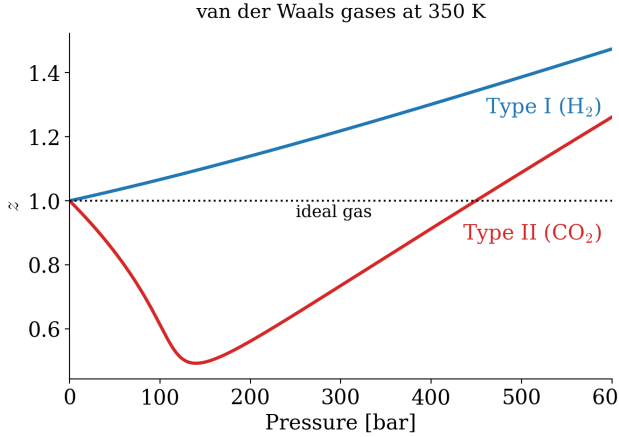


Figure 11.6.: Compressibility Factor of Hydrogen (Type I) and Carbon Dioxide (Type II) at 350 K, Computed with the van der Waals Equation.

The two types of possible behaviors are differentiated based on the compressibility factor at $P \to 0$. To analyze these situations we can use the vdW equation to calculate the compressibility factor as:

$$z = \frac{\overline{V}}{RT}\left(\frac{RT}{\overline{V} - b} - \frac{a}{\overline{V}^2}\right), \tag{11.24}$$

which can be simplified as $z = \frac{\overline{V}}{\overline{V}-b} - \frac{a}{RT\overline{V}}$. We are interested in what happens at low pressure, where the molar volume is very large compared to b. In this case, we can use the approximation $\frac{\overline{V}}{\overline{V}-b} = \frac{1}{1-b/\overline{V}} \approx 1 + \frac{b}{\overline{V}}$, which gives:

$$z \approx 1 + \frac{1}{\overline{V}}\left(b - \frac{a}{RT}\right) \approx 1 + \frac{P}{RT}\left(b - \frac{a}{RT}\right), \tag{11.25}$$

where in the last step we used the ideal gas law, $\frac{1}{\overline{V}} \approx \frac{P}{RT}$, which is a good approximation at low pressure. Eq. 11.25 is a straight line in P, and its slope gives the behavior of the compressibility factor near $P = 0$:

$$\left(\frac{\partial z}{\partial P}\right)_T\Bigg|_{P=0} = \frac{1}{RT}\left(b - \frac{a}{RT}\right), \tag{11.26}$$

which is then interpreted as follows:

- **Type I gases**: $b > \frac{a}{RT} \Rightarrow \frac{\partial z}{\partial P} > 0$ *molecular size* dominates (H_2−like behavior).
- **Type II gases**: $b < \frac{a}{RT} \Rightarrow \frac{\partial z}{\partial P} < 0$ *attractive forces* dominate (CO_2−like behavior).

The dependence of the compressibility factor as a function of temperature (Figure 11.7) results in different plots for each of the two types of behavior.

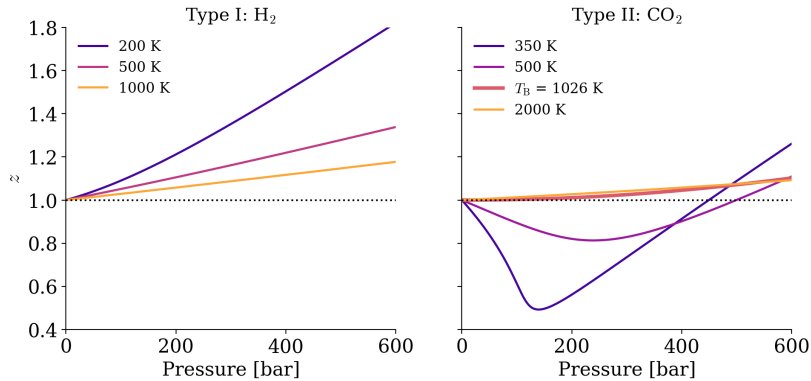


Figure 11.7.: Temperature Dependence of the Compressibility Factor, Computed with the van der Waals Equation. The van der Waals Boyle temperature of CO_2 (about 1030 K) is higher than the experimental value of 713 K, since the van der Waals equation is only an approximate model.

Both type I and type II non-ideal gases will approach the ideal gas behavior as $T \to \infty$, because $\frac{1}{RT} \to 0$ as $T \to \infty$. For type II gases, there are three interesting situations:

- At low T: $b < \frac{a}{RT} \Rightarrow \frac{\partial z}{\partial P} < 0$, which is the behavior described above.
- At high T: $b > \frac{a}{RT} \Rightarrow \frac{\partial z}{\partial P} > 0$, which is the same behavior of type I gases.
- At a very specific temperature, inversion will occur (i.e., at $T = 713$ K for CO_2). This temperature is called the **Boyle temperature**, T_B, and is the temperature at which the attractive and repulsive forces balance out. It can be calculated from the vdW equation, since $b - \frac{a}{RT_B} = 0 \Rightarrow T_B = \frac{a}{bR}$. At the Boyle temperature a type II gas shows ideal gas behavior over a large range of pressure.

11.3.2. Phase Diagram of a Non-Ideal Gas

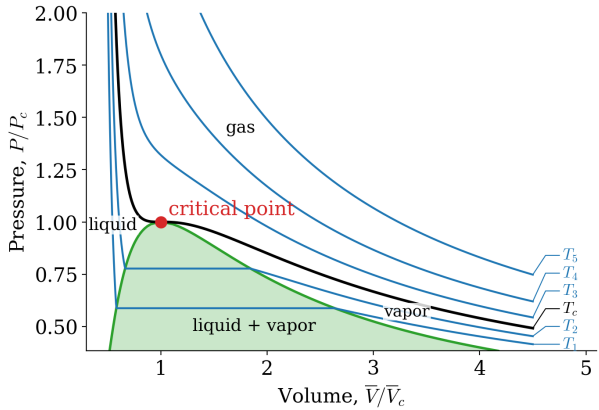


Figure 11.8.: The Pressure–Volume Diagram of a Non-Ideal Gas, Computed with the van der Waals Equation in Reduced Units (P/P_c and $\overline{V}/\overline{V}_c$). Below the Critical Temperature, the Flat Segments Inside the Green Region Mark the Coexistence of Liquid and Vapor.

Let's now turn our attention to the PV phase diagram of a non-ideal gas, reported in Figure 11.8. We can start the analysis from an isotherm at a high temperature. Since every gas will behave as an ideal gas at those conditions, the corresponding isotherms will look similar to those of an ideal gas (T_5 and T_4 in Figure 11.8). Lowering the temperature, we start to see the deviation from ideality getting more prominent (T_3 in Figure 11.8) until we reach a particular temperature called the critical temperature, T_c.

Definition 11.2. *Critical Temperature:* The temperature above which no appearance of a second phase is observed, regardless of how high the pressure becomes.

At the critical temperature and below, the gas liquefies when the pressure is increased. For this reason, the liquefaction of a gas is called a *critical phenomenon*.

The critical temperature is the coordinate of a unique point, called the **critical point**, that can be visualized in the three-dimensional T, P, V diagram of each gas (a surface whose slices at constant temperature are the isotherms of Figure 11.8).

The critical point has coordinates $\{T_c, P_c, \overline{V}_c\}$. These critical coordinates can be determined from the vdW equation at T_c, as:

$$T_c = \frac{8a}{27Rb} \qquad P_c = \frac{a}{27b^2} \qquad \overline{V}_c = 3b. \tag{11.27}$$

These relations are used, in practice, to determine the vdW constants a, b from the experimentally measured critical isotherms.

The critical compressibility factor, z_c, is predicted from the vdW equation at:

$$z_c = \frac{P_c \overline{V}_c}{RT_c} = \left(\frac{a}{27b^2}\right)\left(\frac{3b}{R}\right)\left(\frac{27Rb}{8a}\right) = \frac{3}{8} = 0.375, \tag{11.28}$$

a value that is independent of the gas. Experimentally measured values of z_c for different non-ideal gases are in the range of 0.2–0.3. These values can be used to infer the accuracy of the vdW equation for each non-ideal gas. Since the experimental z_c is usually lower than the one calculated from the vdW equation, we can deduce that the vdW equation overestimates the critical molar volume.

Notice how slicing the $PT\overline{V}$ diagram at constant T results in the PV diagram that we reported in Figure 11.8. On the other hand, slicing the $PT\overline{V}$ diagram at constant $\overline{V}$ results in a PT diagram, similar to the one that we will examine in detail in the next chapter.

11.4. Fugacity

The chemical potential of a pure ideal gas can be calculated using eq. 9.23. Since we are not interested in a mixture, we can drop the asterisk in μ^*, and rewrite eq. 9.23 as:

$$\mu_{\text{ideal}} = \mu^{\ominus} + RT \ln \frac{P}{P^{\ominus}}. \tag{11.29}$$

For a non-ideal gas, the pressure cannot be used in eq. 11.29 because the response of each gas to changes in pressure is not universal. We can, however, define a new variable to replace the pressure in eq. 11.29 and call it fugacity (f).

Definition 11.3. *Fugacity:* The effective pressure of a non-ideal gas that corresponds to the pressure of an ideal gas with the same temperature and chemical potential of the non-ideal one.

Eq. 11.29 then becomes:

$$\mu_{\text{non-ideal}} = \mu^{\ominus} + RT \ln \frac{f}{P^{\ominus}}. \tag{11.30}$$

To complete the definition of the fugacity, we need to decide how it relates to the pressure. At very low pressure, the molecules of any gas are so far apart that their volume and their interactions become negligible, and every gas behaves ideally. In this limit, the chemical potential of the non-ideal gas, eq. 11.30, must become equal to that of the ideal gas, eq. 11.29, which is possible only if the fugacity becomes equal to the pressure:

$$\lim_{P \to 0} \frac{f}{P} = 1, \tag{11.31}$$

in other words, the fugacity is defined so that any non-ideal gas approaches the ideal gas behavior as $P \to 0$. This condition, in conjunction with the $T \to \infty$ behavior obtained in the previous section, results in the following statement:

> The highest chances for any gas to behave ideally happen at high temperature and low pressure.

We can now return our attention to the definition of fugacity. Remembering that the chemical potential is the molar Gibbs energy of a substance, we can write:

$$d\mu_{\text{ideal}} = \overline{V}_{\text{ideal}} dP, \tag{11.32}$$

and:

$$d\mu_{\text{non-ideal}} = \overline{V}_{\text{non-ideal}} dP. \tag{11.33}$$

Subtracting eq. 11.32 from eq. 11.33, we obtain:

$$d\mu_{\text{non-ideal}} - d\mu_{\text{ideal}} = \left(\overline{V}_{\text{non-ideal}} - \overline{V}_{\text{ideal}}\right) dP, \tag{11.34}$$

which we can then integrate between 0 and P:

$$\mu_{\text{non-ideal}} - \mu_{\text{ideal}} = \int_0^P \left(\overline{V}_{\text{non-ideal}} - \overline{V}_{\text{ideal}}\right) dP. \tag{11.35}$$

Using eq. 11.29 and eq. 11.30 we can then replace the definition of chemical potentials, resulting in:

$$\ln f - \ln P = \frac{1}{RT} \int_0^P \left(\overline{V}_{\text{non-ideal}} - \overline{V}_{\text{ideal}}\right) dP, \tag{11.36}$$

which gives us a mathematical definition of the fugacity, as:

$$f = P \cdot \underbrace{\exp\left[\frac{1}{RT} \int_0^P \left(\overline{V}_{\text{non-ideal}} - \overline{V}_{\text{ideal}}\right) dP\right]}_{\text{fugacity coefficient, } \phi(T,P)}. \tag{11.37}$$

The exponential term in eq. 11.37 is complicated to write, but it can be interpreted as a coefficient—unique to each non-ideal gas—that can be measured experimentally. Such coefficients are dependent on pressure and temperature and are called the *fugacity coefficients*. Using letter ϕ to represent the fugacity coefficient, we can rewrite eq. 11.37 as:

$$f = \phi P, \tag{11.38}$$

which gives us a straightforward interpretation of the fugacity as an effective pressure. As such, the fugacity will have the same unit as the pressure, while the fugacity coefficients will be dimensionless.

As we already saw in chapter 10, the fugacity can be used to replace the pressure in the definition of the equilibrium constant for reactions that

involve non-ideal gases. The new constant is usually called K_f, and is obtained from:

$$K_f = \prod_i f_{i,\mathrm{eq}}^{\nu_i} = K_P \prod_i \phi_i^{\nu_i}. \tag{11.39}$$

11.5. Chapter Review

11.5.1. Key Ideas

- **Ideal gas:** molecules with no volume and no interactions, $PV = nRT$, combining Boyle's, Charles's, Gay-Lussac's, and Avogadro's laws.
- **Absolute zero:** all isobars extrapolate to zero volume at $-273.15\ ^\circ\mathrm{C}$, the origin of the Kelvin scale.
- **Van der Waals equation:** $\left(P + a\frac{n^2}{V^2}\right)(V - nb) = nRT$, where a accounts for attractions and b for the volume of the molecules.
- **Compressibility factor:** $z = \frac{PV}{RT}$ measures deviations from ideality, and $z = 1$ for an ideal gas.
- **Joule–Thomson effect:** an expansion at constant enthalpy cools a real gas below its inversion temperature.
- **Critical point:** above T_c, a gas cannot be liquefied by pressure alone.
- **Fugacity:** the effective pressure of a real gas, $f = \phi P$, with $\phi \to 1$ as $P \to 0$.

11.5.2. Study Questions

1. Which two assumptions define the ideal gas model?

a. The particles are spheres, and they move slowly.
b. The particles have the same mass, and they collide elastically.
c. The particles do not occupy any volume, and they do not interact with each other.
d. The particles are at rest, and they attract each other.
e. The gas is at low temperature and high pressure.

---

2. How did Charles's isobars lead to the idea of an absolute temperature scale?

a. When extrapolated to zero volume, all isobars meet at the same temperature, $-273.15\ ^\circ\mathrm{C}$.

b. They show that the volume is constant.
c. They are horizontal lines.
d. They meet at 0 °C.
e. They show that the pressure can be negative.

---

3. What does the parameter a in the van der Waals equation account for?

a. The volume of the gas molecules.
b. The temperature of the gas.
c. The number of moles.
d. The molar mass of the gas.
e. The attractive interactions between the gas molecules.

---

4. What quantity stays constant in a Joule–Thomson expansion?

a. The temperature.
b. The enthalpy.
c. The pressure.
d. The volume.
e. The internal energy.

---

5. When does a gas cool down in a Joule–Thomson expansion?

a. Always.
b. Never.
c. Only if it is an ideal gas.
d. When its temperature is below its inversion temperature ($\mu_{\mathrm{JT}} > 0$).
e. When its temperature is above its inversion temperature.

---

6. What is the compressibility factor of an ideal gas?

a. $z = 1$ at all conditions.
b. $z = 0$.
c. $z > 1$ at high pressure.

d. $z < 1$ at low temperature.
e. $z = 3/8$.

---

7. How is the Boyle temperature obtained from the van der Waals parameters?

a. $T_{\mathrm{B}} = \frac{8a}{27Rb}$.
b. $T_{\mathrm{B}} = \frac{bR}{a}$.
c. $T_{\mathrm{B}} = \frac{a}{bR}$.
d. $T_{\mathrm{B}} = \frac{a}{27b^2}$.
e. $T_{\mathrm{B}} = 3b$.

---

8. What is the critical temperature of a gas?

a. The temperature at which the gas freezes.
b. The temperature at which the gas behaves ideally.
c. The boiling temperature at 1 bar.
d. The temperature at which the compressibility factor is zero.
e. The temperature above which the gas cannot be liquefied, no matter how high the pressure.

---

9. The van der Waals equation predicts a critical compressibility factor $z_c = 3/8 = 0.375$, while experiments give 0.2–0.3. What does this tell us?

a. That the experiments are wrong.
b. That the van der Waals equation is only an approximate model.
c. That all gases are ideal at the critical point.
d. That the van der Waals equation is exact.
e. That the critical point does not exist.

---

10. What is the value of the fugacity coefficient, $\phi = f/P$, of any gas as $P \to 0$?

a. 0.
b. Infinity.

c. 3/8.
d. 1.
e. It depends on the gas.

Answers

1.c, 2.a, 3.e, 4.b, 5.d, 6.a, 7.c, 8.e, 9.b, 10.d

12. Phase Equilibrium

In chapter 11, we saw that a non-ideal gas can be liquefied, and that the liquid and the gas can coexist under certain conditions. In chapter 9, we introduced the chemical potential, the molar Gibbs energy of a substance, and we learned how it changes with temperature and pressure. In this chapter, we will put these two ideas together to understand when a pure substance is solid, liquid, or gas, and what happens at the boundaries between these phases. We will build the phase diagrams that chemists use every day, and we will derive the equations that tell us how melting and boiling points change with pressure.

12.1. Phase Stability

We have already encountered the gas, liquid, and solid phases and already discussed some of their properties. These terms are intuitive since these are the three most common states of matter.[1] For this reason, we have previously used the terms without the necessity of formally defining their meaning. However, a formal definition of "phase" is necessary to discuss several concepts in this chapter and the following ones:

Definition 12.1. *Phase:* A region of the system with homogeneous chemical composition and physical state.

Let's now use the total differential of the chemical potential and the definition of molar Gibbs energy for one component:

$$\begin{aligned} d\mu &= \left(\frac{\partial \mu}{\partial T}\right)_P dT + \left(\frac{\partial \mu}{\partial P}\right)_T dP \\ d\mu &= -S dT + \overline{V} dP, \end{aligned} \tag{12.1}$$

to write:

[1] Other states of matter—such as plasma—are possible, but they are not usually observed at the values of temperature and pressure that classical thermodynamics is usually applied to. Discussion of these extreme cases is beyond the scope of this textbook.

$$\left(\frac{\partial \mu}{\partial T}\right)_P = -S \qquad \left(\frac{\partial \mu}{\partial P}\right)_T = \overline{V}. \tag{12.2}$$

We can use these definitions to study the dependence of the chemical potential with respect to changes in pressure and temperature. If we plot μ as a function of T using the first coefficient in eq. 12.2, we obtain the diagram in Figure 12.1. The diagram presents three curves, each corresponding to one of the three most common states of matter – solid, liquid, and gas. As we saw in several previous chapters, the entropy of a phase is almost constant with respect to temperature,[2] and therefore the three curves are essentially straight, with negative slopes equal to $-S$. Since the solid has the smallest entropy of the three phases, its line is the least steep.[3] The difference between the slopes of the three lines is explained by the fact that each of these states has a different value of entropy:

$$\left(\frac{\partial \mu_{\text{solid}}}{\partial T}\right)_P = -S_{\text{s}} \qquad \left(\frac{\partial \mu_{\text{liquid}}}{\partial T}\right)_P = -S_{\text{l}} \qquad \left(\frac{\partial \mu_{\text{gas}}}{\partial T}\right)_P = -S_{\text{g}}, \tag{12.3}$$

and since the entropy of a gas is always bigger than the entropy of a liquid, which in turn, is yet bigger than the entropy of a solid ($S_{\text{g}} \gg S_{\text{l}} > S_{\text{s}}$), we obtain three lines with different slopes that intersect each other, as in Figure 12.1. What can we read from this diagram?

1. **The most stable phase has the lowest chemical potential.** At each temperature, the phase whose line is the lowest is the stable one (red segments in Figure 12.1). Just as a ball rolls downhill, matter moves spontaneously towards the phase with the lowest chemical potential, since this lowers the Gibbs energy at constant T and P.
2. **Phase changes happen where two lines cross.** At each intersection, the two phases have the same chemical potential, and they coexist. At the crossing between the solid and the liquid lines, the fusion (fus) process occurs, at the melting point T_{m}. At the crossing between the liquid and the gas lines, the vaporization (vap) process occurs, at the boiling point T_{b}.

[2] Think, for example, of the integral $\int S dT$, for which we can assume S independent of temperature to obtain $S\Delta T$. In practice, the entropy increases slightly with the temperature. Therefore the curves in Figure 12.1 are slightly concave downwards (remember that they are obtained from values of $-S$, so if S increases with T, the curves bend downwards.)

[3] The solid line would become perfectly flat only as $T \to 0$, where, according to the third law, the entropy of a perfect crystal goes to zero. At any temperature at which a substance melts, the entropy of the solid is positive, and its line slopes downward.

3. **Heating favors the phases with higher entropy.** Since the gas line is the steepest, the gas always wins at high enough temperature, while the solid always wins at low enough temperature.
4. **The liquid can be skipped.** Depending on the substance and on the pressure, the solid line might intersect the gas line before the liquid line. When that occurs, the liquid phase is never observed, and the solid turns directly into gas, at the sublimation (subl) point T_{subl}.

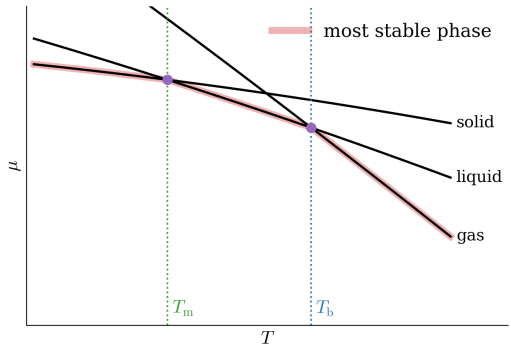


Figure 12.1.: Dependence of the Chemical Potentials of Solid, Liquid, and Gas Phases on Temperature at Constant Pressure.

The effects of pressure on this diagram can be studied using the second coefficient in eq. 12.2. For the majority of substances, $\overline{V}_{\text{g}} \gg \overline{V}_{\text{l}} > \overline{V}_{\text{s}}$, hence the curves will shift to lower values when the pressure is reduced, as in Figure 12.2. Notice also that since $\overline{V}_{\text{l}} \cong \overline{V}_{\text{s}}$, the shifts for both the solid and liquid lines are much smaller than the shift for the gas line. These shifts also translate to different values of the junctions, which means the phase changes will occur at different temperatures. Therefore both the melting point and the boiling point in general increase when pressure is increased (and vice versa). Notice how the change for the melting point is always much smaller than the change for the boiling point. Water is a noticeable exception to this trend because $\overline{V}_{\text{H}_2\text{O,l}} < \overline{V}_{\text{ice}}$. This explains the experimental observation that increasing the pressure on ice lowers its melting point.[4]

Considering the intersections between two lines, two phases are in equilibrium with each other at each of these points. For two or more phases to be in equilibrium, their chemical potentials must be equal:

[4] You might have heard that this is why we can skate on ice. The effect is real, but far too small to explain skating: the pressure under the blade of a skate lowers the melting point of ice by less than one degree, while we can skate on ice at –20 °C. Ice is slippery mostly because of a very thin, liquid-like layer that is always present on its surface, and because of the heat produced by friction.

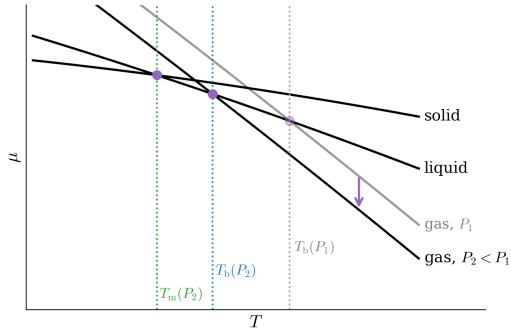


Figure 12.2.: Effect of Pressure on the Chemical Potential Diagram.

$$\mu_\alpha = \mu_\beta. \tag{12.4}$$

If we now change either the temperature or the pressure, the location of the intersection will be shifted (see again Figure 12.2 and the discussion above). For infinitesimal changes in variables, the new location will be:

$$\mu_\alpha + d\mu_\alpha = \mu_\beta + d\mu_\beta, \tag{12.5}$$

which using eq. 12.4, simply becomes:

$$d\mu_\alpha = d\mu_\beta. \tag{12.6}$$

Replacing the differential with the definition of chemical potential in eq. 12.1, we obtain:

$$\begin{aligned} -S_\alpha dT + \overline{V}_\alpha dP &= -S_\beta dT + \overline{V}_\beta dP \\ \underbrace{\left(S_\beta - S_\alpha\right)}_{\Delta S} dT &= \underbrace{\left(\overline{V}_\beta - \overline{V}_\alpha\right)}_{\Delta \overline{V}} dP, \end{aligned} \tag{12.7}$$

which can be rearranged into:

$$\frac{dP}{dT} = \frac{\Delta S}{\Delta \overline{V}}. \tag{12.8}$$

This equation is known as the **Clapeyron equation**, and it is the mathematical relation at the basis of the pressure-temperature phase diagrams. Plotting the results of eq. 12.8 on a PT phase diagram for common substances results in three lines representing the equilibrium between two different phases. Let's see what eq. 12.8 tells us about each line:

1. **The slope of a phase boundary is the ratio between two differences.** It depends only on how much the entropy and the molar volume change when we go from one phase to the other.
2. **The sign of the slope is decided by the volume change.** Going from a lower-temperature phase to a higher-temperature one, the entropy always increases ($\Delta S > 0$). Therefore, the line slopes up if the volume increases ($\Delta\overline{V} > 0$), and down if it decreases.
3. **Small volume changes give steep lines.** When the two phases have almost the same molar volume, as for a solid and a liquid, $\Delta\overline{V}$ is small, and the line is almost vertical. When one of the phases is a gas, $\Delta\overline{V}$ is large, and the line is much flatter.

12.2. Gibbs Phase Rule

In chapter 1, we have already seen that the number of independent variables required to describe an ideal gas is two. This number was derived by counting the total number of variables ($3 : P, \overline{V}, T$), and reducing it by one because the ideal gas law constrains the value of one of them, once the other two are fixed. For a generic system potentially containing more than one chemical substance in several different phases, however, the number of independent variables can be different than two. For a system composed of c components (chemical substances) and p phases, the number of independent variables, f, is given by the Gibbs phase rule:

$$f = c - p + 2. \tag{12.9}$$

The Gibbs phase rule derives from the fact that different phases are in equilibrium with each other at some conditions, resulting in the reduction of the number of independent variables at those conditions. More rigorously, when two phases are in thermodynamic equilibrium, their chemical potentials are equal (see eq. 12.4). For each equality, the number of independent variables—also called the number of *degrees of freedom*—is reduced by one. For example, the chemical potentials of the liquid and its vapor depend on both T and P. But when these phases are in equilibrium with each other, their chemical potentials must be equal. If either the pressure or the temperature is fixed, the other variable will be uniquely determined by the equality relation. In other terms, when a liquid is in equilibrium with its vapor at a given pressure, the temperature is determined by the fact that the chemical potentials of the two phases are the same, and is denoted as the boiling temperature T_b. Similarly, at a given temperature, the pressure of the vapor is uniquely determined by the same equality relation and is denoted as the vapor pressure, P^*.

The Gibbs phase rule is obtained considering that the number of independent variables is given by the total number of variables minus the constraints. The total number of variables is given by temperature, pressure, plus all the variables required to describe each of the phases. The composition of each phase is determined by $(c-1)$ variables.[5] The number of constraints is determined by the number of possible equilibrium relations, which is $c(p-1)$ since the chemical potential of each component must be equal in all phases. The number of degrees of freedom f is then given by $f = (c-1)p + 2 - c(p-1) = c - p + 2$, which is the Gibbs phase rule, as in eq. 12.9.

For a pure substance ($c = 1$, so $f = 3 - p$), eq. 12.9 gives:

1. **One phase, $f = 2$.** We can change both T and P independently, and the substance stays in the same phase. In a PT diagram, single phases are *areas*.
2. **Two phases, $f = 1$.** If we choose the temperature, the pressure at which the two phases coexist is fixed, and vice versa. Two-phase equilibria are *lines*.
3. **Three phases, $f = 0$.** Nothing can be chosen: three phases can coexist only at a single temperature and pressure. Three-phase equilibria are *points*.

12.3. PT Phase Diagrams

Let's now discuss the pressure–temperature diagram of a typical substance, as reported in Figure 12.3. Each of the lines reported in the diagram represents an equilibrium between two phases, and therefore it represents a condition that reduces the number of degrees of freedom to one. The lines can be determined using the Clapeyron equation, eq. 12.8. The interpretation of each line is as follows:

12.3.1. Liquid $\rightleftarrows$ Gas Equilibrium

For this equilibrium we can use Trouton's rule, eq. 6.7, and write:

$$\Delta_{\text{vap}} S = S_{\text{g}} - S_{\text{l}} \cong 88 \, \frac{\text{J}}{\text{mol K}} > 0 \quad \text{always}, \tag{12.10}$$

[5] For a 1-component system $c - 1 = 1 - 1 = 0$, and no additional variable is required to determine the composition of each phase. For a 2-component system, however, each phase will contain both components, hence $c - 1 = 2 - 1 = 1$ additional variable will be required to describe it–the mole fraction.

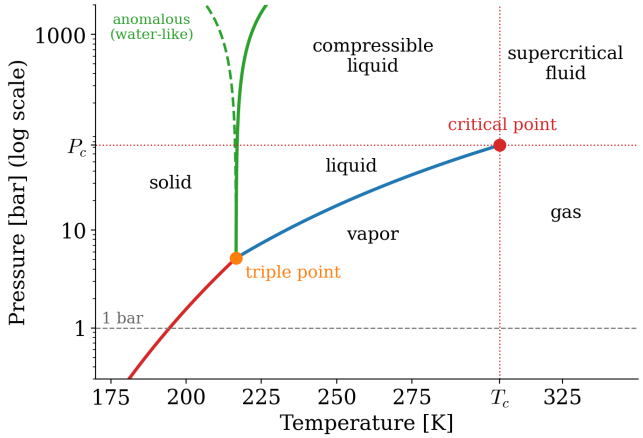


Figure 12.3.: The Pressure–Temperature Phase Diagram of Carbon Dioxide, Computed with the Clausius–Clapeyron Equation (the Pressure Axis Is Logarithmic). The Dashed Green Line Shows, for Comparison, an Anomalous Solid–Liquid Line with a Negative Slope, as for Water.

where the entropy of vaporization is always positive, even for cases where the Trouton's rule is violated. The difference in molar volumes is easily obtained, since the volume of the gas is always much greater than the volume of the liquid:

$$\overline{V}_{\mathrm{g}} - \overline{V}_{\mathrm{l}} \cong \overline{V}_{\mathrm{g}} = 22.4 \, \frac{\mathrm{L}}{\mathrm{mol}} > 0 \quad \text{always.} \tag{12.11}$$

Replacing these values in the Clapeyron equation, we obtain:

$$\frac{dP}{dT} = \frac{88}{22.4} \left(\frac{0.0831}{8.31} \right) = 0.04 \text{ bar/K} > 0 \quad \text{always,} \tag{12.12}$$

which is always positive, regardless of violations to Trouton's rule. Notice how small this value is: the liquid–gas line in Figure 12.3 is much flatter than the solid–liquid one.

12.3.2. Solid ⇄ Gas Equilibrium

If we look at the signs of each quantity, this case is similar to the previous one:

$$\begin{aligned} \Delta_{\text{subl}} S &> 0 \quad \text{always} \\ \Delta_{\text{subl}} \overline{V} &> 0 \quad \text{always} \end{aligned} \tag{12.13}$$

$$\frac{dP}{dT} > 0 \quad \text{always.}$$

However, the entropy of sublimation is larger than the entropy of vaporization, since going from solid to gas is equivalent to melting and then vaporizing ($\Delta_{\text{subl}} S = \Delta_{\text{fus}} S + \Delta_{\text{vap}} S$). Near the triple point, where the two lines meet, the solid–gas line is therefore steeper than the liquid–gas one.

12.3.3. Solid ⇄ Liquid Equilibrium

The final curve is for the solid-liquid equilibrium, for which we have:

$$\Delta_{\text{fus}} S = \frac{\Delta_{\text{fus}} H}{T_{\text{m}}} > 0 \quad \text{always,} \tag{12.14}$$

since fusion is always an endothermic process, ($\Delta_{\text{fus}} H > 0$). On the other side:

$$\Delta_{\text{fus}} \overline{V} = \overline{V}_{\text{l}} - \overline{V}_{\text{s}} > 0 \quad \text{generally.}$$

In other words, the difference of the molar volume of the liquid and that of the solid is positive for most substances, but it might be negative (for example for H_2O). As such:

$$\frac{dP}{dT} > 0 \quad \text{generally.} \tag{12.15}$$

For H_2O and a few other substances, $\frac{dP}{dT} < 0$, an anomalous behavior that has crucial consequences for the existence of life on earth.[6] Because of its

[6] As is well explained by Wikipedia's article on the properties of water: "The unusual density curve and lower density of ice than of water is vital to life—if water were most dense at the freezing point, then in winter the very cold water at the surface of lakes and other water bodies would sink, lakes could freeze from the bottom up, and all life in them would be killed. Furthermore, given that water is a good thermal insulator (due to its heat capacity), some frozen lakes might not completely thaw in summer. The layer of ice that floats on top insulates the water below. Water at about 4 °C (39 °F) also sinks to the bottom, thus keeping the temperature of the water at the bottom constant."

importance, this behavior is also depicted in Figure 12.3 using a dashed green line.

Since the differences in molar volumes between the solid and the liquid phases are usually small (changes are generally of the order of 10^{-3} L), $\frac{dP}{dT}$ is always much larger than for the previous two cases. The resulting lines for the solid–liquid equilibria are therefore almost vertical, regardless of the signs of their slopes.

12.3.4. The Triple Point and the Critical Point

The only point in the PT diagram where all the three phases coexist is called the triple point. The number of degrees of freedom at the triple point for every 1-component diagram is $f = 1 - 3 + 2 = 0$. The fact that the triple point has zero degrees of freedom means that its coordinates, $\{T_{\text{tp}}, P_{\text{tp}}, \overline{V}_{\text{tp}}\}$, are uniquely determined for each chemical substance. For this reason, the value of the triple point of water was fixed by definition—rather than measured—until 2019. This definition was necessary to establish the base unit of the thermodynamic temperature scale in the SI (the kelvin).[7]

In addition to the triple point where the solid, liquid, and gas phases meet, a triple point may involve more than one condensed phase. Triple points are common for substances with multiple solid phases (polymorphs), involving either two solid phases and a liquid one or three solid phases. Helium is a special case that presents a triple point involving two different fluid phases, called the lambda point. Since the number of degrees of freedom cannot be negative, the Gibbs phase rule for a 1-component diagram sets the limit to how many phases can coexist to just three. Therefore, quadruple points (or higher coexistence points) are not possible for pure substances, even for polymorphs.[8]

Another point with a fixed position in the PT diagram is the critical point, $\{T_{\text{c}}, P_{\text{c}}, \overline{V}_{\text{c}}\}$. We have already given the definition of the critical temperature in definition 11.2. This point represents the end of the liquid–gas equilibrium curve. This point is also semantically important to define different regions of the phase diagram, as in Figure 12.3. A gas whose temperature is below the critical temperature is called a *vapor*, since it can be liquefied by compression. A gas whose temperature and pressure are above the critical ones is called a *supercritical fluid*. Finally, a liquid whose pressure is above the critical point is called a *compressible liquid*.[9]

[7] For more information on the 2019 redefinition of the SI units, see Wikipedia's article on the 2019 redefinition of the SI base units.

[8] Notice that quadruple points are possible for 2-component diagrams.

[9] Notice that the temperature of a liquid must be below the critical point, otherwise it is no longer a liquid but rather a supercritical fluid.

12.4. The Clausius–Clapeyron Equation

Let's now take a closer look at the equilibrium between a condensed phase and the gas phase. For both the vaporization and sublimation processes, Clausius showed that the Clapeyron equation can be simplified by using:

$$\Delta_{\text{vap}}S = \frac{\Delta_{\text{vap}}H}{T} \qquad \Delta\overline{V} = \overline{V}_{\text{g}} - \overline{V}_{\text{l}} \cong \overline{V}_{\text{g}}, \tag{12.16}$$

resulting in:

$$\frac{dP}{dT} = \frac{\Delta_{\text{vap}}S}{\Delta\overline{V}} \cong \frac{\Delta_{\text{vap}}H}{T\overline{V}_{\text{g}}}. \tag{12.17}$$

Using the ideal gas law to replace the molar volume of the gas, we obtain:

$$\frac{dP}{dT} = \frac{P\Delta_{\text{vap}}H}{RT^2}, \tag{12.18}$$

which can be rearranged as:

$$\frac{dP}{P} = \frac{\Delta_{\text{vap}}H}{R}\frac{dT}{T^2}. \tag{12.19}$$

Eq. 12.19 is known as the **Clausius–Clapeyron equation**, and it measures the dependence of the vapor pressure of a substance as a function of the temperature. The Clausius–Clapeyron equation can be integrated to obtain:

$$\begin{aligned} \int_{P_i}^{P_f}\frac{dP}{P} &= \frac{\Delta_{\text{vap}}H}{R}\int_{T_i}^{T_f}\frac{dT}{T^2} \\ \ln\frac{P_f}{P_i} &= -\frac{\Delta_{\text{vap}}H}{R}\left(\frac{1}{T_f} - \frac{1}{T_i}\right). \end{aligned} \tag{12.20}$$

The integrated Clausius–Clapeyron equation shows that the vapor pressure depends exponentially on the temperature. Thus, even a small change in the temperature will result in a significant change in the vapor pressure. In fact, we daily use the fact that the vapor pressure of water changes drastically when we increase its temperature for cooking most of our food. For example, at an external pressure of 1 bar, it rapidly grows from $P^* = 0.02$ bar to $P^* = 1$ bar when the temperature is increased from $T = 293$ K (around room temperature) to $T = 373$ K (boiling point). The integrated Clausius–Clapeyron equation is also often used to determine the

enthalpy of vaporization from measurements of vapor pressure at different temperatures.

12.5. Chapter Review

12.5.1. Key Ideas

- **Phase stability:** at each T and P, the most stable phase is the one with the lowest chemical potential. Since $\left(\frac{\partial \mu}{\partial T}\right)_P = -\overline{S}$, the gas line is the steepest.
- **Phase equilibrium:** two phases coexist when their chemical potentials are equal.
- **Clapeyron equation:** $\frac{dP}{dT} = \frac{\Delta H}{T\Delta \overline{V}}$ gives the slope of each line in the PT diagram; the solid–liquid line of water has a negative slope because ice is less dense than liquid water.
- **Clausius–Clapeyron equation:** $\ln \frac{P_f}{P_i} = -\frac{\Delta_{\text{vap}} H}{R}\left(\frac{1}{T_f} - \frac{1}{T_i}\right)$, so the vapor pressure grows exponentially with T.
- **Gibbs phase rule:** $F = C - P + 2$. At the triple point of a pure substance, $F = 0$.
- **Critical point:** the end of the liquid–gas line, above which liquid and gas cannot be distinguished.

12.5.2. Study Questions

1. What is a phase?

a. A region of the system at constant temperature.
b. A region of the system with homogeneous chemical composition and physical state.
c. Any pure substance.
d. A region of the system with constant volume.
e. A mixture of solid and liquid.

---

2. In a plot of the chemical potential versus temperature, which phase has the steepest (most negative) slope, and why?

a. The solid, because it is the densest.
b. The liquid, because it can flow.
c. All phases have the same slope.
d. The gas, because it has the highest entropy.

e. The solid, because it has the highest entropy.

---

3. At a given temperature and pressure, which phase of a substance is the most stable?

a. The one with the lowest chemical potential.
b. The one with the highest chemical potential.
c. The one with the lowest entropy.
d. The one with the largest volume.
e. Always the liquid.

---

4. What condition must be satisfied for two phases to be in equilibrium?

a. Their entropies must be equal.
b. Their volumes must be equal.
c. Their enthalpies must be equal.
d. Their densities must be equal.
e. Their chemical potentials must be equal.

---

5. What is the Clapeyron equation?

a. $\frac{dP}{dT} = \frac{\Delta V}{\Delta S}$.
b. $\frac{dP}{dT} = \Delta S\, \Delta \overline{V}$.
c. $\frac{dP}{dT} = \frac{\Delta S}{\Delta \overline{V}}$.
d. $\frac{dP}{dT} = \frac{\Delta G}{\Delta \overline{V}}$.
e. $\frac{dP}{dT} = \frac{R}{\Delta \overline{V}}$.

---

6. Why does the solid–liquid line of water have a negative slope in the PT phase diagram?

a. Because ice has a higher entropy than liquid water.
b. Because the molar volume of ice is larger than that of liquid water.
c. Because water has hydrogen bonds.
d. Because the enthalpy of fusion of water is negative.
e. Because water boils at 100 °C.

---

7. What is the Gibbs phase rule?

a. $f = c + p + 2$.
b. $f = c - p$.
c. $f = p - c + 2$.
d. $f = c - p + 2$.
e. $f = 2 - p$.

---

8. How many degrees of freedom are there at the triple point of a pure substance?

a. 0.
b. 1.
c. 2.
d. 3.
e. It depends on the substance.

---

9. What does the critical point represent in a PT phase diagram?

a. The point where solid, liquid, and gas coexist.
b. The end of the solid–liquid line.
c. The normal boiling point.
d. The point where the solid sublimates.
e. The end of the liquid–gas equilibrium line.

---

10. According to the integrated Clausius–Clapeyron equation, how does the vapor pressure of a liquid depend on the temperature?

a. It decreases linearly.
b. It is independent of temperature.
c. It increases exponentially.
d. It increases linearly.
e. It is proportional to $1/T$.

Answers

1.b, 2.d, 3.a, 4.e, 5.c, 6.b, 7.d, 8.a, 9.e, 10.c

13. Multi-Component Phase Diagrams and Solutions

In chapter 12, we studied what happens when a single substance is split between two or more phases, and we used the chemical potential to understand when, for example, a liquid boils or a solid melts. Most of the chemistry we do in the lab, however, does not involve pure substances, but mixtures: we dissolve salts in water, we mix solvents, we bubble gases through liquids. In this chapter, we will extend the ideas of the previous chapter to systems that contain two or more chemical species. As we will see, the presence of a second component opens up a whole new set of phenomena that are extremely useful in practice, from the separation of liquids by distillation to the reason why we spread salt on icy roads in winter.

Systems that include two or more chemical species in the same phase are usually called *solutions*. The species present in the largest amount is usually called the *solvent*, and the others are called *solutes*. Solutions are possible for all three states of matter:

Type:	Solvent	Solute	Examples:
Solid solutions	Solid	Solid	Alloys: brass, bronze
	Solid	Liquid	Dental amalgam
	Solid	Gas	Hydrogen stored in palladium
Liquid solutions	Liquid	Solid	Saltwater, bleach
	Liquid	Liquid	Alcoholic beverages, vinegar
	Liquid	Gas	Carbonated drinks
Gaseous solutions	Gas	Solid	Smoke, smog
	Gas	Liquid	Aerosols and perfumes
	Gas	Gas	Air

13.1. Describing a Two-Component System

Let's start by counting how many variables we need to describe a solution of two components (a *binary* solution). Recalling the Gibbs phase rule from chapter 12, the number of degrees of freedom for $c = 2$ components is:

$$f = 2 - p + 2 = 4 - p. \tag{13.1}$$

What does eq. 13.1 mean?

1. **One phase needs three variables.** When the solution is in a single phase (e.g., a liquid), we need $4 - 1 = 3$ variables to describe it. These are usually the temperature, T, the pressure, P, and the composition. For two components, the composition is given by a single mole fraction, since the other one is obtained from $x_\mathrm{A} + x_\mathrm{B} = 1$. We will use x_i for the mole fractions in the liquid phase and y_i for those in the gas phase.
2. **Three variables would require a 3D plot.** To represent all states of a single-phase binary system, we would need a three-dimensional T, P, x diagram. Since 3D plots are hard to draw and to read, we will always keep one of the variables constant: either the temperature (obtaining a Px diagram) or the pressure (obtaining a Tx diagram).
3. **Two phases leave two variables.** When a liquid and its vapor coexist, $f = 4{-}2 = 2$. If we also fix the temperature, only one variable remains free. In other words, at a given temperature, once we choose the composition of the liquid, the pressure and the composition of the vapor are fixed by nature. This is what makes the diagrams in this chapter so useful: they tell us exactly what vapor will form above a given liquid.

13.2. Ideal Solutions and Raoult's Law

In chapter 11, we simplified the treatment of gases by introducing the ideal gas, a model where molecules do not interact with each other. For liquids, this assumption is simply impossible, since the interactions between molecules are what keeps a liquid together in the first place. We need, therefore, a different kind of simplification:

Definition 13.1. *Ideal solution:* A solution where the interactions between molecules of different species (A–B) are, on average, the same as the interactions between molecules of the same species (A–A and B–B).

In an ideal solution, a molecule of A does not "notice" whether its neighbors are molecules of A or B. This has two immediate consequences: mixing the two liquids releases or absorbs no heat ($\Delta_\mathrm{mix} H = 0$), and the volume of the mixture is the sum of the volumes of the two liquids ($\Delta_\mathrm{mix} V = 0$). The only thing that changes upon mixing is the number of ways in which we can arrange the molecules, which increases. As we saw in chapter 5, this means that the entropy increases, and that mixing in an ideal solution is a spontaneous process driven entirely by entropy. Mixtures of chemically similar molecules, such as benzene and toluene, or hexane and heptane, behave as ideal solutions to a very good approximation. We will also assume

that the vapor above the solution behaves as a mixture of ideal gases, which is reasonable at the low pressures that we usually deal with.

What is the vapor pressure of an ideal solution? Let's think about a molecule of A at the surface of the liquid. Its tendency to escape into the gas phase depends on how strongly it is held by its neighbors. In an ideal solution, the neighbors hold it exactly as strongly as in the pure liquid, so each molecule of A at the surface escapes as easily as it would from pure A. However, only a fraction x_{A} of the molecules at the surface are molecules of A. It is then reasonable to expect that the partial pressure of A above the solution is the vapor pressure of pure A, reduced by this fraction. This plausibility argument is confirmed experimentally, and it was formulated by François-Marie Raoult (1830–1901) in what is known as **Raoult's law**:

$$P_i = x_i P_i^*, \tag{13.2}$$

where P_i is the partial pressure of component i above the solution, x_i is its mole fraction in the liquid, and P_i^* is the vapor pressure of pure i at the same temperature. Raoult's law can also be used as an alternative definition of an ideal solution: a solution is ideal if all of its components follow eq. 13.2 at all compositions.

13.2.1. One Volatile Component

Let's first consider a solution where only one of the two components, A, is volatile. This is the case, for example, of a solution of sugar in water, since sugar has no measurable vapor pressure. In this case, the pressure above the solution is entirely due to A, and Raoult's law describes a straight line in the Px_{B} diagram, going from P_{A}^* for pure A ($x_{\mathrm{B}} = 0$) to zero for pure B ($x_{\mathrm{B}} = 1$), as in Figure 13.1.

Notice three things in Figure 13.1:

1. **The line separates two regions.** Above the line, the pressure is higher than the vapor pressure of the solution, and only the liquid is stable. Below the line, the pressure is lower, the liquid evaporates, and only the vapor is stable. Each region has $f = 3$ degrees of freedom, but only two of them are visible in the diagram, since the temperature is kept constant.
2. **Along the line, liquid and vapor coexist.** Raoult's law acts as an additional constraint for the points on the line, which have only two degrees of freedom. Since the temperature is fixed, choosing the composition of the liquid determines the pressure, and vice versa.

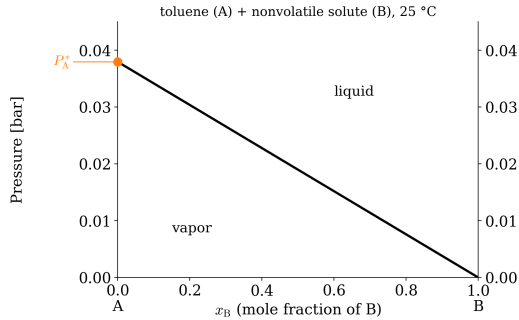


Figure 13.1.: The Pressure–Composition Phase Diagram of a Solution of Toluene (A) with a Nonvolatile Solute (B) at 25 °C.

3. **Adding a nonvolatile solute lowers the vapor pressure.** Moving from left to right along the line, the vapor pressure decreases. This is the first example of a *colligative property*, which we will discuss in detail at the end of this chapter.

13.2.2. Two Volatile Components

When both components are volatile, each of them follows Raoult's law, and both contribute to the vapor. Since we are treating the vapor as a mixture of ideal gases, the total pressure is simply the sum of the two partial pressures, according to Dalton's law, eq. 9.25:

$$P_{\mathrm{TOT}} = P_{\mathrm{A}} + P_{\mathrm{B}} = x_{\mathrm{A}} P_{\mathrm{A}}^* + x_{\mathrm{B}} P_{\mathrm{B}}^* = P_{\mathrm{A}}^* + x_{\mathrm{B}} \left(P_{\mathrm{B}}^* - P_{\mathrm{A}}^* \right), \qquad (13.3)$$

where in the last step we used $x_{\mathrm{A}} = 1 - x_{\mathrm{B}}$. Eq. 13.3 is the equation of a straight line that goes from P_{A}^* to P_{B}^*, as reported in red in Figure 13.2. The partial pressures of each of the two components are also reported, using black dotted lines.

Example 13.1 (Vapor composition above a toluene–benzene solution)**.** Calculate the mole fraction in the vapor phase of a liquid solution composed of 67% of toluene (A) and 33% of benzene (B) (in moles), given the vapor pressures of the pure substances: $P_{\mathrm{A}}^* = 0.03$ bar, and $P_{\mathrm{B}}^* = 0.10$ bar.

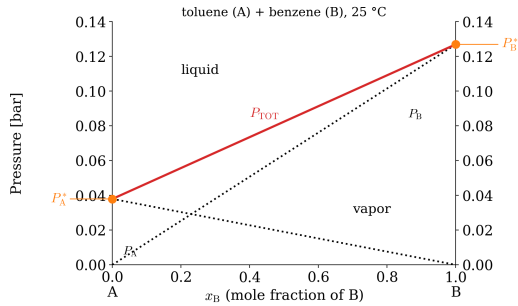


Figure 13.2.: The Pressure–Composition Phase Diagram of an Ideal Solution of toluene (A) and benzene (B) at 25 °C, Computed with Raoult's Law.

Solution: The data available for the system are summarized as follows:

$$\begin{aligned} x_A &= 0.67 & x_B &= 0.33 \\ P_A^* &= 0.03 \text{ bar} & P_B^* &= 0.10 \text{ bar} \\ & & P_{TOT} &= ? \\ y_A &= ? & y_B &= ? \end{aligned} \tag{13.4}$$

The partial pressures and the total pressure of the vapors can be calculated combining Raoult's and Dalton's laws:

$$\begin{aligned} P_A &= x_A P_A^* = 0.67 \cdot 0.03 = 0.020 \text{ bar} \\ P_B &= x_B P_B^* = 0.33 \cdot 0.10 = 0.033 \text{ bar} \\ P_{TOT} &= P_A + P_B = 0.053 \text{ bar}. \end{aligned} \tag{13.5}$$

Since each partial pressure is proportional to the number of moles of that component in the vapor, we can calculate the mole fractions in the vapor phase as:

$$\begin{aligned} y_A &= \frac{P_A}{P_{TOT}} & y_B &= \frac{P_B}{P_{TOT}} \\ y_A &= \frac{0.020}{0.053} = 0.38 & y_B &= \frac{0.033}{0.053} = 0.62. \end{aligned} \tag{13.6}$$

Notice how the vapor is much richer in benzene ($y_B = 0.62$) than the liquid ($x_B = 0.33$). Benzene has the higher vapor pressure (it is more *volatile*), so its molecules escape more easily into the gas phase.

The result of Example 13.1 is completely general: *the vapor above an ideal solution is always richer in the more volatile component than the liquid*

it comes from. Since the compositions of the liquid and of the vapor are different, we can report both of them in the same diagram, as in Figure 13.3. The line that gives the composition of the liquid, x_B, is called the *liquidus line* (or bubble point line), while the line that gives the composition of the vapor, y_B, is called the *dew point line.*

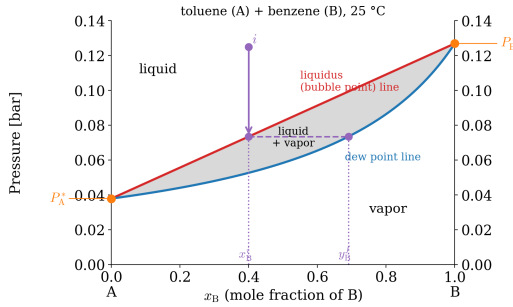


Figure 13.3.: The Pressure–Composition Phase Diagram of an Ideal Solution of toluene (A) and benzene (B) at 25 °C, with Both the Liquidus and the Dew Point Lines.

The liquidus and dew point lines enclose a new region of the diagram, where the liquid and the vapor coexist. Let's follow the arrow in Figure 13.3 to understand how to read this diagram:

1. **We start from a liquid** with composition x_B^i at high pressure (point i). Here only the liquid is stable.
2. **We lower the pressure** at constant temperature and composition, moving straight down, until we hit the liquidus line. At this pressure, the liquid starts to boil.
3. **The first bubble of vapor** that forms does not have the same composition as the liquid. Its composition is found by moving horizontally (at the same pressure) until we hit the dew point line, which gives y_B^f. As expected, the vapor is richer in the more volatile component, B.
4. **Inside the coexistence region**, any horizontal line (called a *tie line*) connects a liquid and a vapor in equilibrium with each other. Since there are only two degrees of freedom inside this region, and the temperature is fixed, once we fix the pressure, the compositions of both phases are determined.

A tie line tells us *what* the two phases are, but not *how much* of each we have. To find the amounts, we can use a simple bookkeeping argument. Let's call z_B the overall mole fraction of B in the whole system (the composition we started with), n_l and n_v the total moles of liquid and vapor, and x_B and y_B their compositions, read at the two ends of the tie line. The

total amount of B does not change when the system splits into two phases, so:

$$(n_\mathrm{l} + n_\mathrm{v})\, z_\mathrm{B} = n_\mathrm{l}\, x_\mathrm{B} + n_\mathrm{v}\, y_\mathrm{B} \quad \longrightarrow \quad n_\mathrm{l}\,(z_\mathrm{B} - x_\mathrm{B}) = n_\mathrm{v}\,(y_\mathrm{B} - z_\mathrm{B})\,. \tag{13.7}$$

Eq. 13.7 is called the **lever rule**, because it has the same form as the balance of a lever: if we think of the tie line as a seesaw resting on a pivot at z_B, the amount of each phase times its distance from the pivot is the same on both sides. The phase whose end of the tie line is *closer* to the overall composition is the more abundant one. The lever rule is valid on any tie line, in any two-component phase diagram, including the Tx_B diagrams that we will see next.

Example 13.2 (How much liquid and how much vapor?)**.** A solution with $z_\mathrm{B} = 0.40$ of the same two components as in example 13.1 ($P^*_\mathrm{A} = 0.03$ bar, $P^*_\mathrm{B} = 0.10$ bar) is brought to a pressure of 0.05 bar at constant temperature. What fraction of the moles is in the liquid?
Solution: At 0.05 bar, the liquid at the left end of the tie line has a total pressure equal to 0.05 bar. Using Raoult's law for both components:

$$P_\mathrm{TOT} = (1-x_\mathrm{B})P^*_\mathrm{A} + x_\mathrm{B}P^*_\mathrm{B} \quad \rightarrow \quad x_\mathrm{B} = \frac{P_\mathrm{TOT} - P^*_\mathrm{A}}{P^*_\mathrm{B} - P^*_\mathrm{A}} = \frac{0.05 - 0.03}{0.10 - 0.03} = 0.286,$$

and the vapor at the right end of the tie line has, from Dalton's law:

$$y_\mathrm{B} = \frac{x_\mathrm{B} P^*_\mathrm{B}}{P_\mathrm{TOT}} = \frac{0.286 \times 0.10}{0.05} = 0.571.$$

The overall composition, $z_\mathrm{B} = 0.40$, falls between the two, so the system is indeed split into two phases. Using the lever rule, eq. 13.7:

$$\frac{n_\mathrm{l}}{n_\mathrm{v}} = \frac{y_\mathrm{B} - z_\mathrm{B}}{z_\mathrm{B} - x_\mathrm{B}} = \frac{0.571 - 0.40}{0.40 - 0.286} = 1.50,$$

which means that 60% of the moles are in the liquid, and 40% in the vapor. The liquid is the more abundant phase, because its end of the tie line is closer to the overall composition.

13.2.3. Tx_B Phase Diagrams and Fractional Distillation

In the lab, we usually boil liquids at constant (atmospheric) pressure by increasing the temperature, rather than by reducing the pressure. It is therefore more useful to look at the phase diagram of a 2-component ideal

solution as a function of temperature at constant pressure. The Tx_B diagram for two volatile components is reported in Figure 13.4. As in the previous diagrams, the more volatile component is B (benzene), which has the lower boiling point, T_b^B.

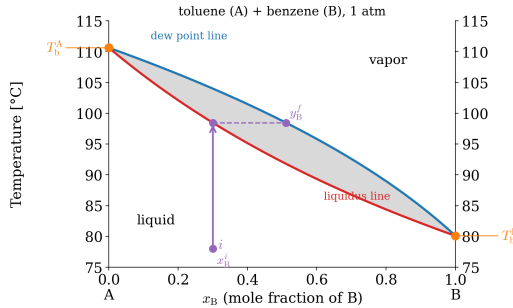


Figure 13.4.: The Temperature–Composition Phase Diagram of an Ideal Solution of toluene (A) and benzene (B) at 1 atm.

Let's compare Figure 13.4 with the pressure diagram:

1. **The phases are in reversed order.** Compared to the Px_B diagram of Figure 13.3, the liquid is now at the bottom (low temperature), and the vapor is on top (high temperature).
2. **The two lines form a lens.** The liquidus and dew point lines are curved, and they enclose a lens-shaped region where liquid and vapor coexist. Inside the lens there are only two degrees of freedom, and since the pressure is kept constant, only one of them is visible in the plot: if we choose the temperature, the compositions of both phases are fixed, and vice versa.
3. **A mixture boils over a range of temperatures.** If we heat a liquid of composition x_B^i, it starts boiling when it hits the liquidus line. The first vapor that forms has composition y_B^f, which is richer in the more volatile component B. As the vapor leaves, the remaining liquid becomes richer in A, and its boiling temperature increases. Unlike a pure substance, a mixture does not have a single boiling point.

The difference in composition between the liquid and the vapor can be exploited to separate the two components. If we collect the vapor and condense it, we obtain a liquid that is richer in B than the one we started from. If we boil this new liquid again, its vapor will be even richer in B. Each evaporation and condensation step corresponds to a horizontal line (from the liquidus line to the dew point line) followed by a vertical line (from the dew point line down to the liquidus line), as in the staircase of Figure 13.5. Each of these steps is called a *theoretical plate*, and by

repeating it enough times we can obtain almost pure B. This is the principle of *fractional distillation*.

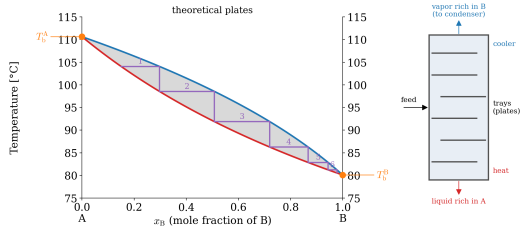


Figure 13.5.: The Fractional Distillation Process: Theoretical Plates Drawn on the Temperature–Composition Phase Diagram of Toluene and Benzene (Left), and a Schematic Distillation Column (Right).

In practice, the evaporations and condensations do not happen in separate flasks, but along a tall column filled with trays, as schematically depicted on the right of Figure 13.5. The mixture is heated at the bottom, and the temperature decreases with the height of the column. On each tray, the rising vapor partially condenses and the liquid partially evaporates, so that each tray works as one theoretical plate. The vapor collected at the top is rich in the most volatile component, while the liquid collected at the bottom is rich in the least volatile one. Counting the theoretical plates on the Tx_B diagram tells chemical engineers how many trays a column needs to reach the desired purity, which is how industrial distillation columns are sized.

13.3. Phase Diagrams of Non-Ideal Solutions

In most real solutions, the A–B interactions are not the same as the A–A and B–B ones, and Raoult's law is followed only over a small range of compositions. Let's start again from a solution with a single volatile component, A, whose typical behavior is reported in the Px_B plot of Figure 13.6.

What does Figure 13.6 tell us?

1. **When A is abundant ($x_B \to 0$), Raoult's law holds.** In this region, A is the solvent, and almost every molecule of A is surrounded by other molecules of A, as in the pure liquid. Its escaping tendency is therefore the same as in pure A, as Raoult's law assumes.
2. **When A is dilute ($x_B \to 1$), Henry's law holds.** In this region, A is the solute, and each molecule of A is surrounded almost exclusively by molecules of B. Its escaping tendency is now determined by the

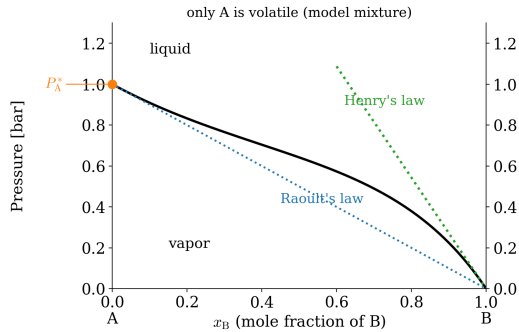


Figure 13.6.: The Pressure–Composition Phase Diagram of a Non-Ideal Solution Where Only A Is Volatile (Model Mixture with a Positive Deviation).

A–B interactions, which are different from the A–A ones. The partial pressure is still proportional to the mole fraction, but with a different proportionality constant, as shown by the green dotted line.

3. **In between, neither law holds**, and the curve must be measured experimentally.

The law that describes the dilute region was found by William Henry (1774–1836), who extensively studied the behavior of gases dissolved in liquids. **Henry's law** states that the partial pressure of a dilute solute i is proportional to its mole fraction in the solution:

$$P_i = k_{\mathrm{H},i}\, x_i \qquad (\text{for } x_i \to 0), \tag{13.8}$$

where the *Henry's law constant*, $k_{\mathrm{H},i}$, depends on the chemical nature of both the solute and the solvent, and on the temperature. Henry's law is commonly used for gases dissolved in liquids. For example, the amount of CO_2 dissolved in a carbonated drink is proportional to the pressure of CO_2 above it, which is why the drink goes flat when we open the bottle and the pressure drops. In a dilute solution, the solvent follows Raoult's law, while the solute follows Henry's law.

When both components are volatile, the total pressure is once again the sum of the two partial pressures. Two different behaviors are possible, depending on the strength of the A–B interactions, as reported in Figure 13.7:

- **Positive deviation** (left panel): the A–B interactions are weaker than the A–A and B–B ones. The molecules are held less strongly in the mixture than in the pure liquids, they escape more easily, and the vapor pressure is higher than the one predicted by Raoult's law.

Mixing these liquids typically absorbs heat ($\Delta_{\text{mix}}H > 0$). An example is the acetone/carbon disulfide mixture.

- **Negative deviation** (right panel): the A–B interactions are stronger than the A–A and B–B ones (for example, because A and B form hydrogen bonds with each other). The molecules are held more strongly, and the vapor pressure is lower than the one predicted by Raoult's law. Mixing these liquids typically releases heat ($\Delta_{\text{mix}}H < 0$). Examples are the acetone/chloroform and the hydrochloric acid/water mixtures. Negative deviations are slightly less common than positive ones.

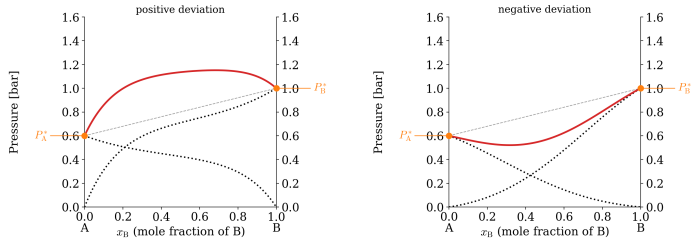


Figure 13.7.: The Pressure–Composition Phase Diagrams of Non-Ideal Solutions Containing Two Volatile Components at Constant Temperature (Model Mixtures).

If we move from the Px_B diagram to the Tx_B diagram, the behaviors observed in Figure 13.7 correspond to the diagrams in Figure 13.8. Since a higher vapor pressure means that the mixture boils at a lower temperature, a maximum in the Px_B diagram becomes a minimum in the Tx_B diagram, and vice versa.

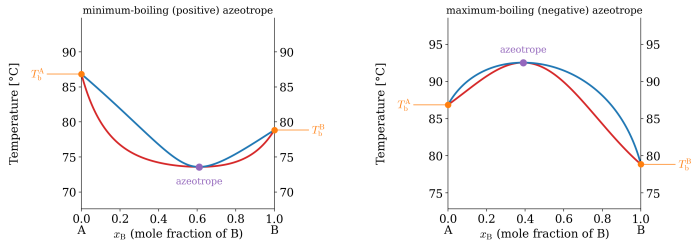


Figure 13.8.: The Temperature–Composition Phase Diagrams of Non-Ideal Solutions Containing Two Volatile Components at Constant Pressure (Model Mixtures).

The minimum (left plot) and maximum (right plot) points in Figure 13.8 are called *azeotropes*. At an azeotrope, the liquidus and dew point lines touch, so the liquid and the vapor have the same composition. If we boil a mixture

with the azeotropic composition, the vapor has the same composition as the liquid, and distillation cannot change it. The mixture boils at a single temperature, as if it was a pure substance. In practice, distillation can bring us *to* the azeotrope, but not past it. Two types of azeotropes exist, corresponding to the two types of deviation:

- **Positive (minimum-boiling) azeotrope** (left plot in Figure 13.8). A well-known example is the ethanol/water mixture at atmospheric pressure, with composition 95.6% ethanol by mass. This azeotrope boils at $T = 78.2$ °C, a temperature that is lower than the boiling points of both pure constituents (ethanol boils at $T = 78.4$ °C and water at $T = 100$ °C). This is why we cannot obtain pure ethanol from fermented mixtures by simple distillation.
- **Negative (maximum-boiling) azeotrope** (right plot in Figure 13.8). An example is the hydrochloric acid/water mixture at atmospheric pressure, with composition 20.2% hydrochloric acid by mass. This azeotrope boils at about $T = 110$ °C, a temperature that is higher than the boiling points of both pure constituents (hydrochloric acid boils at $T = -84$ °C and water at $T = 100$ °C).

13.4. Activity

To treat non-ideal solutions quantitatively, we need a quantity that plays the same role that the mole fraction plays in Raoult's law. We did something very similar for non-ideal gases in chapter 11, where we replaced the pressure with the fugacity, an *effective pressure*. For solutions, we will replace the mole fraction with an *effective mole fraction*, called the **activity**. Let's derive it step by step, using the vapor above the solution as a "probe" of what happens in the liquid.

1. **The vapor.** Assuming that the vapor behaves as an ideal gas, the chemical potential of component i in the vapor is given by eq. 11.29:

$$\mu_i^{\text{vapor}} = \mu_i^{\ominus} + RT \ln \frac{P_i}{P^{\ominus}}. \tag{13.9}$$

2. **Equilibrium with the solution.** If the vapor is in equilibrium with the solution, the chemical potential of i must be the same in both phases (eq. 12.4):

$$\mu_i^{\text{solution}} = \mu_i^{\text{vapor}} = \mu_i^{\ominus} + RT \ln \frac{P_i}{P^{\ominus}}. \tag{13.10}$$

3. **The pure liquid as a reference.** The same reasoning applies to the pure liquid i, which is in equilibrium with its vapor at the pressure

P_i^*. Its chemical potential, μ_i^*, is therefore:

$$\mu_i^* = \mu_i^{\ominus} + RT \ln \frac{P_i^*}{P^{\ominus}}. \tag{13.11}$$

4. **Subtracting** eq. 13.11 from eq. 13.10, the standard chemical potential of the gas and the standard pressure cancel out, and we obtain:

$$\mu_i^{\text{solution}} = \mu_i^* + RT \ln \frac{P_i}{P_i^*}. \tag{13.12}$$

Eq. 13.12 tells us that the ratio P_i/P_i^* measures how much the chemical potential of i in the solution differs from that of the pure liquid. We call this ratio the **activity** of component i:

$$a_i = \frac{P_i}{P_i^*} \qquad \Rightarrow \qquad \mu_i^{\text{solution}} = \mu_i^* + RT \ln a_i. \tag{13.13}$$

Let's look at what eq. 13.13 means:

1. **For an ideal solution, the activity is the mole fraction.** Using Raoult's law, eq. 13.2, $a_i = x_i$, and eq. 13.13 becomes:

$$\mu_i^{\text{solution}} = \mu_i^* + RT \ln x_i. \tag{13.14}$$

   Since $x_i < 1$, the logarithm is negative, and the chemical potential of a component in an ideal solution is always lower than that of the pure liquid. This is the same result we found for mixtures of ideal gases in chapter 9, and it is the reason why ideal solutions form spontaneously.
2. **For a non-ideal solution, the activity is an effective mole fraction.** We can write it as the mole fraction multiplied by a correction factor, called the *activity coefficient*, γ_i:

$$a_i = \gamma_i x_i \qquad \Rightarrow \qquad \mu_i^{\text{solution}} = \mu_i^* + RT \ln (\gamma_i x_i). \tag{13.15}$$

3. **The activity coefficient is measured from the vapor pressure.** Combining eq. 13.13 and eq. 13.15:

$$\gamma_i = \frac{P_i}{x_i P_i^*} = \frac{P_i}{P_i^{\text{R}}}, \tag{13.16}$$

   where $P_i^{\text{R}} = x_i P_i^*$ is the partial pressure predicted by Raoult's law. For a positive deviation, the measured pressure is higher than the Raoult one, and $\gamma_i > 1$. For a negative deviation, it is lower, and $0 < \gamma_i < 1$. For an ideal solution, $\gamma_i = 1$. This procedure is illustrated in Figure 13.9.

4. **The activity is a relative quantity.** It measures the "escaping tendency" of a component *relative* to a reference state, which in this case is the pure liquid at the same temperature and pressure, for which $a_i = 1$. This choice of reference (*standard state*) is a convention. We could choose a different one, and the values of the activities would change accordingly, but the physics would not. For gases, the standard state is the ideal gas at $P^{\ominus} = 1$ bar, and the activity is $f/P^{\ominus}$.

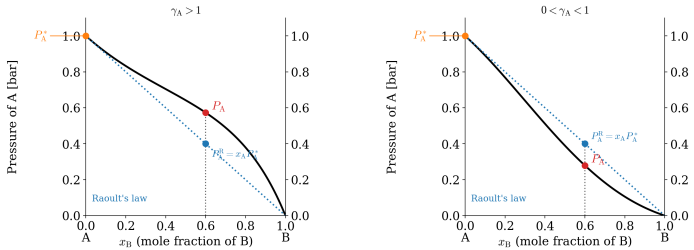


Figure 13.9.: Activity Coefficients from the Vapor Pressure: Positive (Left) and Negative (Right) Deviation from Raoult's Law (Model Mixtures).

As we already discussed in chapter 10, the activity is the most general quantity that we can use to define the equilibrium constant of a reaction (or the reaction quotient). The advantage of using the activity is that it's defined for ideal and non-ideal gases and mixtures of gases, as well as for ideal and non-ideal solutions in both the liquid and the solid phase.[1]

13.5. Colligative Properties

Colligative properties are properties of solutions that depend on the *number* of solute particles in the solution, and not on their chemical nature. They usually appear when we dissolve a nonvolatile solute (such as sugar or salt) in a volatile liquid solvent (such as water), and they are properties of the solvent, modified by the presence of the solute. We will discuss four of them: the lowering of the vapor pressure, the elevation of the boiling point, the depression of the melting point, and the osmotic pressure.

[1] Notice that, since the activity is a relative measure, the equilibrium constant expressed in terms of the activities is also a relative concept. In other words, it measures equilibrium relative to a standard state. This fact, however, should not surprise us, since the equilibrium constant is also related to $\Delta_{rxn}G^{\ominus}$ using Gibbs' relation. This is why the definition of a universally agreed-upon standard state is such an essential concept in chemistry, and why it is defined by the International Union of Pure and Applied Chemistry (IUPAC) and followed systematically by chemists around the globe.

All four of them have the same origin, which we have already found in eq. 13.14. In an ideal solution, the chemical potential of the solvent is:

$$\mu_{\text{solvent}}^{\text{solution}} = \mu_{\text{solvent}}^{*} + RT \ln x_{\text{solvent}} < \mu_{\text{solvent}}^{*}. \tag{13.17}$$

In other words, *dissolving a solute always lowers the chemical potential of the solvent.* This lowering is not due to any special interaction between solute and solvent. In an ideal solution there is none: it is a purely entropic effect, due to the increased number of ways in which the molecules can be arranged in the mixture. This is also why the result depends only on the mole fraction, and not on what the solute is. At the same time, the phases that contain only pure solvent (the vapor above the solution, since the solute is nonvolatile, and the solid, since the solute usually does not dissolve in the solid solvent) are not affected at all. The liquid is therefore stabilized with respect to both the vapor and the solid, as shown in Figure 13.10. For non-ideal solutions, the formulas that we will derive below are only valid approximately, but they work well for dilute solutions.

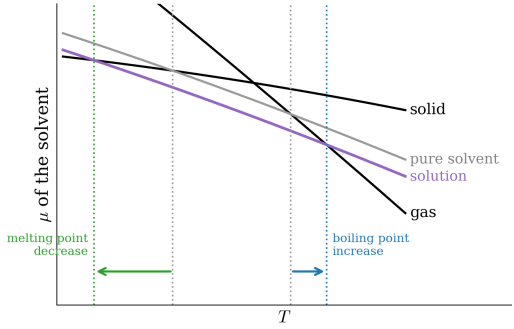


Figure 13.10.: Reduction of the Chemical Potential of the Liquid Phase Due to the Addition of a Solute.

For dilute solutions, the most useful measure of concentration is the molality, m, defined as the number of moles of solute divided by the mass of the solvent in kilograms:[2]

$$m = \frac{n_{\text{solute}}}{m_{\text{solvent}}}. \tag{13.18}$$

For a dilute solution, the mole fraction of the solute is related to the molality by a simple approximation. Since $n_{\text{solute}} \ll n_{\text{solvent}}$:

[2]Molality is preferred over molarity because it does not depend on the temperature, since masses, unlike volumes, do not change when the solution is heated or cooled.

$$x_{\text{solute}} = \frac{n_{\text{solute}}}{n_{\text{solute}} + n_{\text{solvent}}} \approx \frac{n_{\text{solute}}}{n_{\text{solvent}}} = \frac{n_{\text{solute}}}{m_{\text{solvent}}/M} = mM, \qquad (13.19)$$

where M is the molar mass of the solvent, in kg/mol.

13.5.1. Vapor Pressure Lowering

As we have already seen in Figure 13.1, the vapor pressure above a solution of a nonvolatile solute follows Raoult's law. Its difference with respect to the vapor pressure of the pure solvent is:

$$\begin{aligned} P^*_{\text{solvent}} - P_{\text{solution}} &= P^*_{\text{solvent}} - x_{\text{solvent}} P^*_{\text{solvent}} \\ &= (1 - x_{\text{solvent}})\, P^*_{\text{solvent}} = x_{\text{solute}} P^*_{\text{solvent}}, \end{aligned} \qquad (13.20)$$

which shows that the vapor pressure lowering depends only on the mole fraction of the solute, and not on its nature. As such, it is a colligative property.

13.5.2. Boiling Point Elevation and Melting Point Depression

Let's now look at Figure 13.10 again. Since the chemical potential of the liquid is lowered, its line crosses the line of the gas at a higher temperature, and the line of the solid at a lower temperature. Therefore, the boiling point increases, and the melting point decreases. To find out by how much, let's follow the boiling point step by step.[3]

1. **The equilibrium condition.** At the boiling point of the solution, T_{b}, the chemical potential of the pure vapor equals that of the solvent in the solution, eq. 13.17:

   $$\mu^*_{\text{gas}}(T_{\text{b}}) = \mu^*_{\text{liquid}}(T_{\text{b}}) + RT_{\text{b}} \ln x_{\text{solvent}} \quad \Rightarrow \quad \ln x_{\text{solvent}} = \frac{\mu^*_{\text{gas}} - \mu^*_{\text{liquid}}}{RT_{\text{b}}} = \frac{\Delta_{\text{vap}}G}{R} \qquad (13.21)$$

   where $\Delta_{\text{vap}}G$ is the molar Gibbs energy of vaporization of the *pure* solvent.

[3] This is a plausibility argument rather than a rigorous proof, since we will use two approximations that are valid only for dilute solutions.

2. **The Gibbs–Helmholtz equation.** We know that $\Delta_{\text{vap}}G = 0$ at the boiling point of the pure solvent, T_{b}^*. We can find its value at T_{b} by integrating the Gibbs–Helmholtz equation, eq. 9.9, between T_{b}^* and T_{b}, assuming that $\Delta_{\text{vap}}H$ is constant:

$$\frac{\Delta_{\text{vap}}G(T_{\text{b}})}{T_{\text{b}}} = \Delta_{\text{vap}}H\left(\frac{1}{T_{\text{b}}} - \frac{1}{T_{\text{b}}^*}\right) \quad \Rightarrow \quad \ln x_{\text{solvent}} = \frac{\Delta_{\text{vap}}H}{R}\left(\frac{1}{T_{\text{b}}} - \frac{1}{T_{\text{b}}^*}\right). \tag{13.22}$$

3. **The dilute-solution approximations.** For a dilute solution, $\ln x_{\text{solvent}} = \ln(1 - x_{\text{solute}}) \approx -x_{\text{solute}}$, and since T_{b} and T_{b}^* are very close to each other, $\frac{1}{T_{\text{b}}} - \frac{1}{T_{\text{b}}^*} = \frac{T_{\text{b}}^* - T_{\text{b}}}{T_{\text{b}}T_{\text{b}}^*} \approx -\frac{\Delta T_{\text{b}}}{(T_{\text{b}}^*)^2}$. Replacing both into eq. 13.22, and using eq. 13.19 for the mole fraction of the solute:

$$\Delta T_{\text{b}} = \frac{R\,(T_{\text{b}}^*)^2}{\Delta_{\text{vap}}H}\,x_{\text{solute}} = \underbrace{\frac{RM\,(T_{\text{b}}^*)^2}{\Delta_{\text{vap}}H}}_{K_{\text{b}}}\,m. \tag{13.23}$$

The constant K_{b} is called the *ebullioscopic constant* of the solvent, and it depends only on the properties of the pure solvent. For example, for water, using $M = 0.018$ kg/mol, $T_{\text{b}}^* = 373$ K, and $\Delta_{\text{vap}}H = 40.7$ kJ/mol, we obtain $K_{\text{b}} = 0.51\ \frac{\text{K kg}}{\text{mol}}$, in excellent agreement with the experimental value of $0.512\ \frac{\text{K kg}}{\text{mol}}$.

So far, we have assumed that each unit of solute produces one particle in solution. Since colligative properties depend on the *number* of particles, if a solute dissociates into ions, its effect is multiplied. We account for this with the *van 't Hoff factor*, i, which counts the number of particles produced by each formula unit of solute. The final formula for the boiling point elevation is:

$$\Delta T_{\text{b}} = T_{\text{b}}^{\text{solution}} - T_{\text{b}}^{\text{solvent}} = iK_{\text{b}}m. \tag{13.24}$$

For a solute that does not dissociate in solution, such as sugar, $i = 1$. For example, the strong electrolyte $CaCl_2$ completely dissociates into three particles in solution, one Ca^{2+} and two Cl^-, and $i = 3$. For cases of partial dissociation, such as weak acids, weak bases, and their salts, i can assume non-integer values.

The depression of the melting point is obtained with exactly the same procedure, using the equilibrium between the pure solid and the solution instead of the one between the pure vapor and the solution. The result is:

$$\Delta T_{\rm m} = T_{\rm m}^{\rm solution} - T_{\rm m}^{\rm solvent} = -iK_{\rm m}m, \qquad \text{with} \qquad K_{\rm m} = \frac{RM\,(T_{\rm m}^*)^2}{\Delta_{\rm fus}H}, \tag{13.25}$$

where $K_{\rm m}$ is the *cryoscopic constant* of the solvent, and the minus sign accounts for the fact that the melting temperature decreases ($\Delta T_{\rm m}$ is negative, while i, $K_{\rm m}$, and m are all positive). For water, $K_{\rm m} = 1.86\ \frac{\rm K\ kg}{\rm mol}$. This is why we spread salt on icy roads: a salt solution freezes at a lower temperature than pure water.

Notice from Figure 13.10 how the depression of the melting point is much larger than the elevation of the boiling point. To understand why, we can recall that the slope of each line in Figure 13.10 is $-S$ (eq. 12.2). When we lower the liquid line, the new crossing point moves more if the two crossing lines have similar slopes, and less if their slopes are very different. The slopes of the liquid and the solid lines differ by the entropy of fusion, which is small, while the slopes of the liquid and gas lines differ by the entropy of vaporization, which is large. Mathematically, since $\Delta H = T\Delta S$ at the transition, we can rewrite the two constants as $K = RMT^*/\Delta S$, where ΔS is the entropy of the corresponding transition. For water, $\Delta_{\rm fus}S = 22\ {\rm J\,mol^{-1}\,K^{-1}}$ and $\Delta_{\rm vap}S = 109\ {\rm J\,mol^{-1}\,K^{-1}}$, which explains why $K_{\rm m}$ is almost four times larger than $K_{\rm b}$.

13.5.3. Osmotic Pressure

The osmotic pressure is probably the most important colligative property for biology and medicine. Consider the apparatus in Figure 13.11, where a solution and the pure solvent are separated by a *semi-permeable* (osmotic) membrane. This membrane is made of a material that lets the solvent molecules through, but blocks the solute ones.

Since the chemical potential of the solvent in the solution is lower than that of the pure solvent, eq. 13.17, the solvent spontaneously flows from the pure side into the solution, across the membrane. As a consequence, the level of the solution rises, and its pressure increases. The flow stops when the extra pressure on the solution side raises the chemical potential of its solvent back to that of the pure solvent. This extra pressure, π, is called the **osmotic pressure**. We can calculate it step by step:

1. **The equilibrium condition.** At equilibrium, the chemical potential of the pure solvent at pressure P equals that of the solvent in the solution at pressure $P + \pi$:

$$\mu^*_{\rm solvent}(P) = \mu^*_{\rm solvent}(P + \pi) + RT \ln x_{\rm solvent}. \tag{13.26}$$

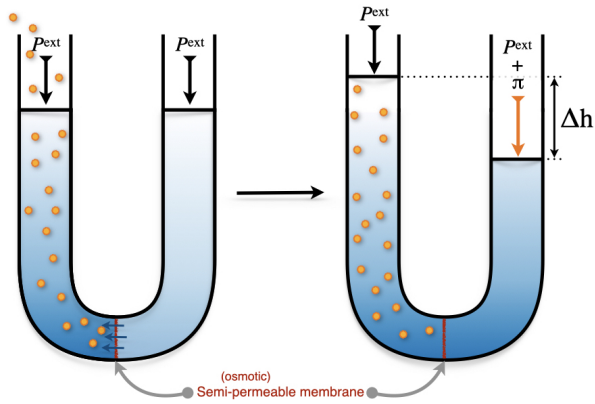


Figure 13.11.: Osmotic Pressure of a Solution.

2. **The effect of pressure.** As we saw in chapter 9, the chemical potential of a liquid increases with pressure as $d\mu = \overline{V}dP$, and, since liquids are essentially incompressible, $\mu^*_{\text{solvent}}(P+\pi) - \mu^*_{\text{solvent}}(P) = \overline{V}\pi$, where $\overline{V}$ is the molar volume of the solvent. Replacing into eq. 13.26:

$$\overline{V}\pi = -RT \ln x_{\text{solvent}}. \tag{13.27}$$

3. **The dilute-solution approximation.** Using again $-\ln x_{\text{solvent}} \approx x_{\text{solute}} \approx n_{\text{solute}}/n_{\text{solvent}}$, and noticing that $n_{\text{solvent}}\overline{V}$ is essentially the volume of the solution, V:

$$\pi = \frac{n_{\text{solute}}}{V} RT = i\, cRT, \tag{13.28}$$

where c is the molar concentration of the solute, and we have introduced again the van 't Hoff factor, i, to account for dissociation.

Eq. 13.28 was proposed by van 't Hoff, and it is remarkably similar to the ideal gas law. Morse later refined it by using the molality instead of the molar concentration, which gives better results at higher concentrations.[4] Osmotic pressures can be surprisingly large: a solution with $c = 0.10$ mol/L of sugar at room temperature has $\pi \approx 2.5$ bar, enough to push a column of water up by about 25 m. This is why intravenous fluids must have the same osmotic pressure as blood: if the solution were too dilute, water would flow into the red blood cells, making them swell and burst. If we apply to the solution side a pressure higher than π, we can reverse the flow and push pure solvent out of the solution. This process, called *reverse osmosis*, is widely used to obtain drinkable water from seawater.

[4] The Morse equation reads $\pi = imRT$. For dilute aqueous solutions, molality and molarity are nearly equal, since 1 kg of water occupies about 1 L.

13.6. Solid–Liquid Phase Diagrams

So far, we have looked at the equilibrium between a liquid solution and its vapor. The same ideas apply to the equilibrium between a liquid solution and a solid. The simplest, and very common, case is that of two substances that mix completely as liquids, but do not mix at all as solids: when the liquid freezes, each solid that forms is pure A or pure B. An example is the mixture of naphthalene (A, the molecule of mothballs) and benzene (B), whose Tx_B diagram is reported in figure 13.12.

The two curves in this diagram are something we already know: they are melting point depression curves. Starting from pure A, adding B lowers the temperature at which solid A forms, exactly as a solute lowers the melting point of a solvent in the colligative properties section above. Starting from pure B, adding A does the same to the melting point of B. For an ideal solution, each curve is given by the same procedure that we used for the boiling point elevation, eq. 13.22, with the enthalpy of fusion in place of the enthalpy of vaporization, and without the dilute-solution approximations:

$$\ln x_\mathrm{A} = \frac{\Delta_\mathrm{fus}H_\mathrm{A}}{R}\left(\frac{1}{T_\mathrm{m}^\mathrm{A}} - \frac{1}{T}\right) \qquad \ln x_\mathrm{B} = \frac{\Delta_\mathrm{fus}H_\mathrm{B}}{R}\left(\frac{1}{T_\mathrm{m}^\mathrm{B}} - \frac{1}{T}\right), \tag{13.29}$$

where each equation gives the composition of the liquid that is in equilibrium with the pure solid at temperature T.[5]

Let's follow the purple arrow in figure 13.12, cooling a liquid with $x_\mathrm{B} = 0.5$:

1. **The first crystals.** Nothing happens until the liquid reaches the red curve, at about 46 °C. At this temperature, crystals of *pure* naphthalene start to form. Notice that this is well below the melting point of pure naphthalene, 80 °C: the benzene acts as a solute and depresses its melting point.
2. **The liquid changes composition.** As naphthalene crystallizes, the remaining liquid becomes richer in benzene, and its freezing point drops further. The liquid slides down the red curve, while more and more solid naphthalene forms. At any temperature, the tie line connects pure solid A (on the left axis) to the liquid on the red curve, and the lever rule, eq. 13.7, tells us how much of each we have.

[5] Eq. 13.29 is also called the *ideal solubility* equation, since it gives the maximum mole fraction of a solid that can dissolve in a liquid at temperature T, if the solution is ideal.

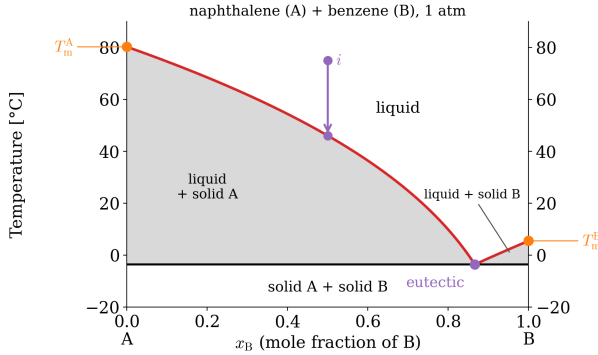


Figure 13.12.: The Temperature–Composition Phase Diagram of Naphthalene (A) and Benzene (B) at 1 atm, Computed with the Ideal Solubility Equation. The Two Solids Do Not Mix, and the Two Melting Point Curves Meet at the Eutectic Point.

3. **The eutectic point.** The liquid reaches the point where the two curves meet, called the **eutectic point**, at about $-3.6\ ^\circ\text{C}$ and $x_B = 0.87$. Here the liquid is in equilibrium with *both* solids. With three phases and two components, the phase rule leaves only one degree of freedom, which is used by the fixed pressure, so the temperature cannot change until all the liquid has frozen into a fine mixture of the two solids.
4. **Below the eutectic temperature**, no liquid can exist at any composition.

The eutectic temperature is the lowest temperature at which a liquid can exist in the mixture, lower than the melting points of both pure components. The word comes from the Greek for "easily melted," and eutectic mixtures are used exactly for this reason. Tin–lead solders melt at about 183 °C, well below the melting points of tin and lead, and salt melts ice on roads because the water–sodium chloride mixture has a eutectic at about −21 °C: as long as the temperature is above it, salt and ice in contact turn into a liquid brine.

13.7. Chapter Review

13.7.1. Key Ideas

- **Raoult's law:** in an ideal solution, $P_i = x_i P_i^*$, and the vapor is richer in the more volatile component.

- **Phase diagrams** (Px_B and Tx_B) show the liquidus and dew point lines; tie lines connect phases in equilibrium, and the **lever rule**, $n_\mathrm{l}(z_\mathrm{B} - x_\mathrm{B}) = n_\mathrm{v}(y_\mathrm{B} - z_\mathrm{B})$, gives how much of each.
- **Fractional distillation** repeats evaporation and condensation to separate the components, but it cannot go past an azeotrope.
- **Non-ideal solutions:** dilute solutes follow Henry's law, $P_i = k_{\mathrm{H},i}x_i$; deviations from Raoult's law are described by the activity, $a_i = \gamma_i x_i$.
- **Colligative properties** (vapor pressure lowering, boiling point elevation, melting point depression, osmotic pressure) depend only on the number of solute particles, because the solute lowers the chemical potential of the solvent.
- **Eutectics:** when two solids do not mix, their melting point curves meet at the eutectic point, the lowest temperature at which a liquid can exist.

13.7.2. Study Questions

1. What is an ideal solution?

a. A solution where the interactions between different molecules (A–B) are, on average, the same as those between equal molecules (A–A and B–B).
b. A solution where the molecules do not interact at all.
c. A solution whose vapor is an ideal gas.
d. A solution of a single component.
e. A solution that cannot be distilled.

---

2. What does Raoult's law state?

a. $P_i = y_i P_\mathrm{TOT}$.
b. $P_i = k_{\mathrm{H},i}x_i$.
c. $P_i = x_i P_i^*$.
d. $P_i = \frac{x_i}{P_i^*}$.
e. $P_i = x_i RT$.

---

3. What is the composition of the vapor above an ideal solution of two volatile components?

a. The same as the liquid.
b. Pure solvent.

c. Richer in the less volatile component.
d. Always 50% of each component.
e. Richer in the more volatile component.

---

4. A two-component system with overall composition $z_{\mathbf{B}}$ splits into a liquid ($x_{\mathbf{B}}$) and a vapor ($y_{\mathbf{B}}$). What does the lever rule state?

a. $n_{\mathrm{l}}\, x_{\mathrm{B}} = n_{\mathrm{v}}\, y_{\mathrm{B}}$.
b. $n_{\mathrm{l}}\,(z_{\mathrm{B}} - x_{\mathrm{B}}) = n_{\mathrm{v}}\,(y_{\mathrm{B}} - z_{\mathrm{B}})$, so the phase whose composition is closer to z_{B} is the more abundant.
c. The amounts of liquid and vapor are always equal.
d. $n_{\mathrm{l}} + n_{\mathrm{v}} = z_{\mathrm{B}}$.
e. The phase whose composition is farther from z_{B} is the more abundant.

---

5. Two substances mix completely as liquids but not at all as solids. What is their eutectic point?

a. The temperature at which both pure substances melt.
b. The point where the liquid and the vapor have the same composition.
c. The critical point of the mixture.
d. The point where the two melting point curves meet: the lowest temperature at which a liquid can exist, in equilibrium with both pure solids.
e. The temperature at which the mixture boils.

---

6. When does a component of a solution follow Henry's law?

a. When it is dilute (its mole fraction is close to zero).
b. When it is the solvent.
c. When it is pure.
d. When the solution is ideal.
e. When it is not volatile.

---

7. What is the molecular origin of a positive deviation from Raoult's law?

a. The A–B interactions are stronger than the A–A and B–B ones.
b. The solution is ideal.
c. The A–B interactions are weaker than the A–A and B–B ones.
d. The solute is nonvolatile.
e. The vapor is not an ideal gas.

---

8. Why can an azeotrope not be separated by simple distillation?

a. Because it does not boil.
b. Because it boils at 100 °C.
c. Because it contains only one component.
d. Because its components react with each other.
e. Because the liquid and the vapor have the same composition.

---

9. What is the activity coefficient of a component that shows a positive deviation from Raoult's law?

a. $\gamma_i = 0$.
b. $\gamma_i > 1$.
c. $\gamma_i = 1$.
d. $0 < \gamma_i < 1$.
e. $\gamma_i < 0$.

---

10. What is the common origin of all colligative properties?

a. The solute reacts with the solvent.
b. The solute increases the vapor pressure of the solvent.
c. The solute increases the chemical potential of the solvent.
d. The solute lowers the chemical potential of the solvent, an entropic effect that depends only on the mole fraction.
e. The solute changes the molar mass of the solvent.

Answers

1.a, 2.c, 3.e, 4.b, 5.d, 6.a, 7.c, 8.e, 9.b, 10.d

Part IV.

Chemical Kinetics

14. Chemical Kinetics

From thermodynamics, we can determine the spontaneity of a reaction and its extent, using ΔG and K_{eq}, respectively. However, thermodynamics does not provide any information on how *fast* the reaction is going to happen. For example, while the reaction that converts solid carbon from its diamond allotropic form into hexagonal graphite is thermodynamically spontaneous, it is so slow as to be virtually non-existent. Diamond is effectively a metastable phase. The speed of a chemical reaction is the subject of a branch of physical chemistry called chemical kinetics.

A chemical kinetics study aims to find the *rate* of a reaction and to find the microscopic steps that compose it, determining its *mechanism*. In this last chapter, we will therefore leave equilibrium behind and look at how concentrations change with time, how we can measure the rate of a reaction, and why reactions speed up when we heat them.

14.1. Differential and Integrated Rate Laws

The rate law of a chemical reaction is an equation that links the initial rate with the concentrations (or pressures) of the reactants. Rate laws usually include a constant parameter, k, called the *rate coefficient*, and several parameters found at the exponent of the concentrations of the reactants, and are called *reaction orders*. The rate coefficient depends on several conditions, including the reaction type, the temperature, the surface area of an adsorbent, light irradiation, and others. The rate coefficient is usually represented with the lowercase letter k, and it should not be confused with the thermodynamic equilibrium constant that is generally designated with the uppercase letter K. Another useful concept in kinetics is the half-life, usually abbreviated with $t_{1/2}$. The half-life is defined as the time required to reach half of the initial reactant concentration.

A reaction that happens in one single microscopic step is called elementary. Elementary reactions have reaction orders equal to the (integer) stoichiometric coefficients for each reactant. As such, only a limited number of elementary reactions are possible (four types are commonly observed), and they are classified according to their overall reaction order. The global

reaction order of a reaction is calculated as the sum of each reactant's individual orders and is, at most, equal to three. The number of molecules that take part in an elementary step is called its *molecularity*: an elementary step involving one molecule is *unimolecular*, one involving two molecules is *bimolecular*, and one involving three molecules is *termolecular*. Keep in mind that the order is an experimental property of the rate law, while the molecularity describes a single microscopic step: the two coincide only for elementary reactions. We examine in detail the four most common reaction orders below.

14.1.1. Zeroth-Order Reaction

For a zeroth-order reaction, the reaction rate is independent of the concentration of a reactant. In other words, if we have a reaction of the type:

$$\mathrm{A} \longrightarrow \text{products}$$

the differential rate law can be written:

$$-\frac{d[\mathrm{A}]}{dt} = k_0[\mathrm{A}]^0 = k_0, \tag{14.1}$$

which shows that any change in the concentration of A will have no effect on the speed of the reaction. The minus sign on the left-hand side is required because the rate is always defined as a positive quantity, while the derivative is negative because the concentration of the reactant is diminishing with time. Separating the variables [A] and t of eq. 14.1 and integrating both sides, we obtain the integrated rate law for a zeroth-order reaction as:

$$\begin{aligned} \int_{[\mathrm{A}]_0}^{[A]} d[\mathrm{A}] &= -k_0 \int_{t=0}^{t} dt \\ [\mathrm{A}] - [\mathrm{A}]_0 &= -k_0 t \end{aligned} \tag{14.2}$$

$$[\mathrm{A}] = [\mathrm{A}]_0 - k_0 t.$$

Using the integrated rate law, we notice that the concentration of the reactant diminishes linearly with respect to time. A plot of [A] as a function of t, therefore, will result in a straight line with a slope equal to $-k_0$, as in the plot of Figure 14.1.

Eq. 14.2 also suggests that the units of the rate coefficient for a zeroth-order reaction are of concentration divided by time, typically $\frac{\mathrm{M}}{\mathrm{s}}$, with M being

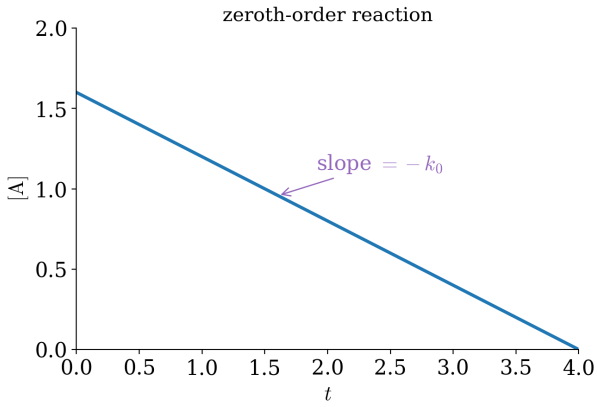


Figure 14.1.: Reaction Rate Plot for a Zeroth-Order Reaction.

the molar concentration in $\frac{\text{mol}}{\text{L}}$ and s the time in seconds. The half-life of a zero order reaction can be calculated from eq. 14.2, by replacing [A] with $\frac{1}{2}[\text{A}]_0$:

$$\begin{aligned} \frac{1}{2}[\text{A}]_0 &= [\text{A}]_0 - k_0 t_{1/2} \\ t_{1/2} &= \frac{[\text{A}]_0}{2k_0}. \end{aligned} \tag{14.3}$$

Zeroth-order reactions are common in several biochemical processes catalyzed by enzymes, such as the oxidation of ethanol to acetaldehyde in the liver by the alcohol dehydrogenase enzyme, which is zero-order in ethanol.

14.1.2. First-Order Reaction

In a first-order reaction, the rate is proportional to the concentration of a single reactant. If a first-order reaction is elementary, it involves a single molecule, and it is unimolecular (for example, an isomerization or a radioactive decay). However, many first-order reactions are not elementary, so we should not use the two words as synonyms. As for the previous case, if we consider a reaction of the type:

$$\text{A} \rightarrow \text{products}$$

the differential rate law for a first-order reaction is:

$$-\frac{d[\mathrm{A}]}{dt} = k_1[\mathrm{A}]. \tag{14.4}$$

Following the usual blueprint of separating the variables, and integrating both sides, we obtain the integrated rate law as:

$$\begin{aligned} \int_{[\mathrm{A}]_0}^{[A]} \frac{d[\mathrm{A}]}{[\mathrm{A}]} &= -k_1 \int_{t=0}^{t} dt \\ \ln \frac{[\mathrm{A}]}{[\mathrm{A}]_0} &= -k_1 t \end{aligned} \tag{14.5}$$

$$[\mathrm{A}] = [\mathrm{A}]_0 \exp(-k_1 t).$$

Using the integrated rate law to plot the concentration of the reactant, [A], as a function of time, t, we obtain an exponential decay, as in Figure 14.2.

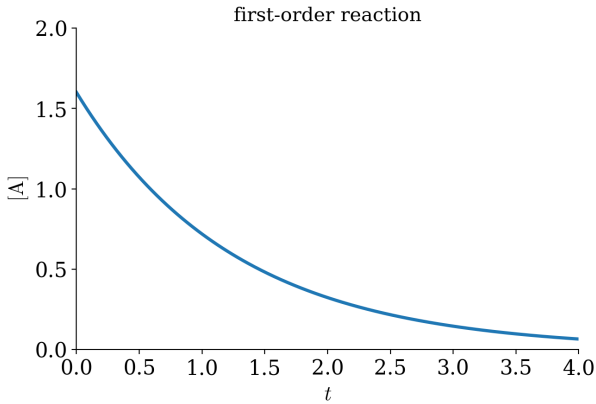


Figure 14.2.: Reaction Rate Plot for a First-Order Reaction.

However, if we plot the logarithm of the concentration, ln[A], as a function of time, we obtain a line with slope $-k_1$, as in the plot of Figure 14.3. From eq. 14.5, we can also obtain the units for the rate coefficient for a first-order reaction, which typically is $\frac{1}{\mathrm{s}}$, independent of concentration. Since the rate coefficient for first-order reactions has units of inverse time, it is sometimes called the frequency rate.

The half-life of a first-order reaction is:

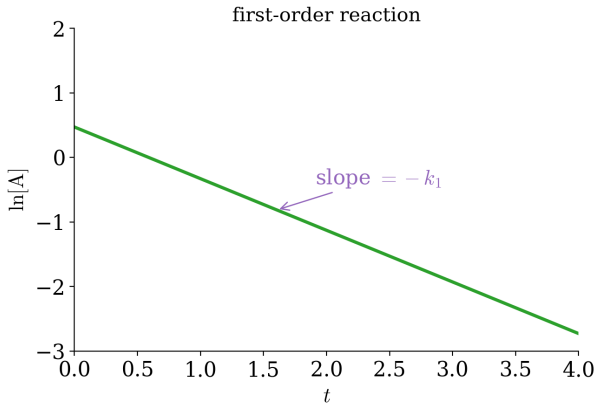


Figure 14.3.: Linear Plot for a First-Order Reaction. Notice that the Quantity on the y Axis is ln[A].

$$\ln \frac{\frac{1}{2}[\mathrm{A}]_0}{[\mathrm{A}]_0} = -k_1 t_{1/2}$$
$$t_{1/2} = \frac{\ln 2}{k_1}. \tag{14.6}$$

The half-life of a first-order reaction is independent of the initial concentration of the reactant. Therefore, the half-life can be used in place of the rate coefficient to describe the reaction rate. Typical examples of first-order reactions are radioactive decays. For radioactive isotopes, it is common to report their rate of decay in terms of their half-life. For example, the most stable uranium isotope, ^{238}U, has a half-life of 4.468×10^9 years, while the most common fissile isotope of uranium, ^{235}U, has a half-life of 7.038×10^8 years.[1] Other examples of first-order reactions in chemistry are the class of S_N1 nucleophilic substitution reactions in organic chemistry.

14.1.3. Second-Order Reaction

A reaction is second-order when the sum of the reaction orders is two. Elementary second-order reactions are also called *bimolecular reactions*. There are two possibilities, a simple one, where the reaction order of one reagent is two, or a more complicated one, with two reagents having each a reaction order of one.

[1] Notice how large these numbers are for uranium. To put these numbers in perspective, we can compare them with the half-life of a common isotope of plutonium, ^{241}Pu, which is $t_{1/2} = 14.3$ years.

- For the simple case, we can write the reaction as:

$$2\text{A} \rightarrow \text{products}$$

the differential rate law for a second-order reaction is:

$$-\frac{d[\text{A}]}{dt} = k_2[\text{A}]^2. \tag{14.7}$$

Following the same procedure used for the two previous cases, we can obtain the integrated rate law as:

$$\begin{aligned} \int_{[\text{A}]_0}^{[A]} \frac{d[\text{A}]}{[\text{A}]^2} &= -k_2 \int_{t=0}^{t} dt \\ \frac{1}{[\text{A}]} - \frac{1}{[\text{A}]_0} &= k_2 t \end{aligned} \tag{14.8}$$

$$\frac{1}{[\text{A}]} = \frac{1}{[\text{A}]_0} + k_2 t.$$

As for first-order reactions, the plot of the concentration as a function of time shows a non-linear decay. However, if we plot the inverse of the concentration, $\frac{1}{[\text{A}]}$, as a function of time, t, we obtain a line with slope $+k_2$, as in the plot of Figure 14.4.

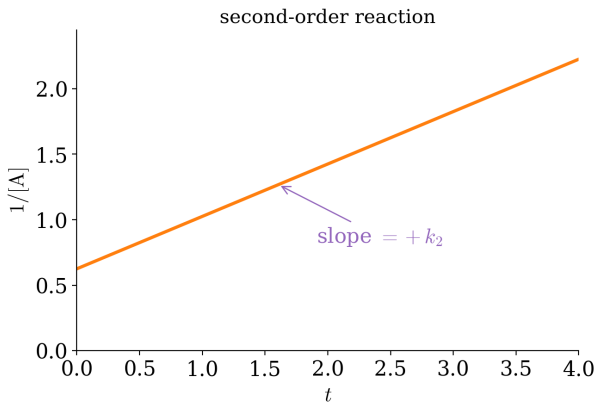


Figure 14.4.: Linear Plot for a Second-Order Reaction. Notice that the Quantity on the y Axis is 1/[A].

Notice that the line has a *positive* slope, in contrast with the previous two cases, for which the slopes were negative. The units of k for a simple second order reaction are calculated from eq. 14.8 and typically are $\frac{1}{\text{M}\cdot\text{s}}$.

The half-life of a simple second-order reaction is:

$$\begin{aligned} \frac{1}{\frac{1}{2}[\mathrm{A}]_0} - \frac{1}{[\mathrm{A}]_0} &= k_2 t_{1/2} \\ t_{1/2} &= \frac{1}{k_2[\mathrm{A}]_0}, \end{aligned} \tag{14.9}$$

which, perhaps not surprisingly, depends on the initial concentration of the reactant, $[\mathrm{A}]_0$. Therefore, if we start with a higher concentration of the reactant, the half-life will be shorter, and the reaction will be faster. An example of simple second-order behavior is the reaction $\mathrm{NO_2} + \mathrm{CO} \rightarrow \mathrm{NO} + \mathrm{CO_2}$, which is second-order in $\mathrm{NO_2}$ and zeroth-order in CO.

- For the complex second-order case, the reaction is:

  $$\mathrm{A} + \mathrm{B} \rightarrow \text{products}$$

  and the differential rate law is:

  $$-\frac{d[\mathrm{A}]}{dt} = k_2'[\mathrm{A}][\mathrm{B}]. \tag{14.10}$$

  The differential equation in eq. 14.10 has two variables, and cannot be solved exactly unless an additional relationship is specified. If we assume that the initial concentrations of the two reactants are equal, then $[\mathrm{A}] = [\mathrm{B}]$ at any time t, and eq. 14.10 reduces to eq. 14.7. If the concentrations of the reactants are different, then the integrated rate law will assume the following shape:

  $$\frac{[\mathrm{A}]}{[\mathrm{B}]} = \frac{[\mathrm{A}]_0}{[\mathrm{B}]_0} \exp\left\{\left([\mathrm{A}]_0 - [\mathrm{B}]_0\right) k_2' t\right\}. \tag{14.11}$$

  The units of k for a complex second order reaction can be calculated from eq. 14.11, and are the same as those for the simple case, $\frac{1}{\mathrm{M \cdot s}}$. The half-life of a complex second-order reaction cannot be easily written since two different half-lives could, in principle, be defined for each of the corresponding reactants.

14.1.4. Third- and Higher-Order Reactions

Although elementary reactions with order higher than two are possible, they are in practice infrequent, and only very few experimental third-order reactions are observed. Fourth-order or higher have never been observed because the probabilities for a simultaneous interaction between four molecules are essentially zero. Third-order elementary reactions are also called *termolecular reactions*. While termolecular reactions with three

identical reactants are possible in principle, there is no known experimental example. Some complex third-order reactions are known, such as:

$$2\mathrm{NO}_{(g)} + \mathrm{O}_{2(g)} \longrightarrow 2\mathrm{NO}_{2(g)}$$

for which the differential rate law can be written as:

$$-\frac{dP_{\mathrm{O}_2}}{dt} = k_3 P_{\mathrm{NO}}^2 P_{\mathrm{O}_2}. \tag{14.12}$$

14.2. Complex Rate Laws

It is essential to specify that the order of a reaction and its molecularity are equal only for elementary reactions. Reactions that follow complex laws are composed of several elementary steps, and they usually have non-integer reaction orders, for at least one of the reactants.

14.2.1. Consecutive Reactions

A reaction that happens following a sequence of two elementary steps can be written as follows:

$$\mathrm{A} \xrightarrow{k_1} \mathrm{B} \xrightarrow{k_2} \mathrm{C}$$

Assuming that each of the steps follows a first order kinetic law, and that only the reagent A is present at the beginning of the reaction, we can write the differential change in concentration of each species with respect to infinitesimal time dt, using the following formulas:

$$\begin{aligned} -\frac{d[\mathrm{A}]}{dt} &= k_1[\mathrm{A}] \Rightarrow [\mathrm{A}] = [\mathrm{A}]_0 \exp(-k_1 t) \\ \frac{d[\mathrm{B}]}{dt} &= k_1[\mathrm{A}] - k_2[\mathrm{B}] \\ \frac{d[\mathrm{C}]}{dt} &= k_2[\mathrm{B}]. \end{aligned} \tag{14.13}$$

These three equations represent a system of differential equations with three unknown variables. Unfortunately, these equations are linearly dependent on each other, and they are not sufficient to solve the system for each variable. To do so, we need to include a fourth equation, coming from the conservation of mass:

$$[\mathrm{A}]_0 = [\mathrm{A}] + [\mathrm{B}] + [\mathrm{C}]. \tag{14.14}$$

Using the first equation in eq. 14.13, we can now replace the concentration [A] in the second equation and solve for [B]:

$$\frac{d[\mathrm{B}]}{dt} + k_2[\mathrm{B}] = k_1[\mathrm{A}]_0 \exp(-k_1 t), \tag{14.15}$$

which can be simplified by multiplying both sides by $\exp(k_2 t)$:

$$\begin{aligned} \left(\frac{d[\mathrm{B}]}{dt} + k_2[\mathrm{B}]\right)\exp(k_2 t) &= k_1[\mathrm{A}]_0 \exp[(k_2 - k_1)t] \\ \Rightarrow \frac{d\left\{[\mathrm{B}]\exp(k_2 t)\right\}}{dt} &= k_1[\mathrm{A}]_0 \exp[(k_2 - k_1)t], \end{aligned} \tag{14.16}$$

which can then be integrated remembering that $[B]_0 = 0$, and $\int \exp(kx) = \frac{1}{k}\exp(kx)$:

$$[\mathrm{B}] = \frac{k_1}{k_2 - k_1}[\mathrm{A}]_0[\exp(-k_1 t) - \exp(-k_2 t)]. \tag{14.17}$$

We can then use both [A], from eq. 14.13, and [B], from eq. 14.17, in eq. 14.14 to solve for [C]:

$$\begin{aligned} [\mathrm{C}] &= [\mathrm{A}]_0 - [\mathrm{A}] - [\mathrm{B}] \\ &= [\mathrm{A}]_0 - [\mathrm{A}]_0 \exp(-k_1 t) - \frac{k_1}{k_2 - k_1}[\mathrm{A}]_0[\exp(-k_1 t) - \exp(-k_2 t)] \\ &= [\mathrm{A}]_0 \left\{1 + \frac{-k_2 \exp(-k_1 t) + k_1 \exp(-k_2 t)}{k_2 - k_1}\right\}. \end{aligned} \tag{14.18}$$

From these results, we can distinguish two typical behaviors, depending on which of the two steps is the slowest. The slowest step in a sequence is called the *rate-determining step*, since, just like the narrowest point of a funnel, it limits how fast the whole process can go.

The first behavior is observed when the second step is slower than, or comparable to, the first one. For example, Figure 14.5 reports the concentrations with respect to time for $k_1 = 2k_2$. In this case, the rate-determining step is the second reaction. A is converted into B faster than B can be converted into C, so the intermediate accumulates: its concentration grows, reaches a maximum, and then decreases as A runs out. The product C

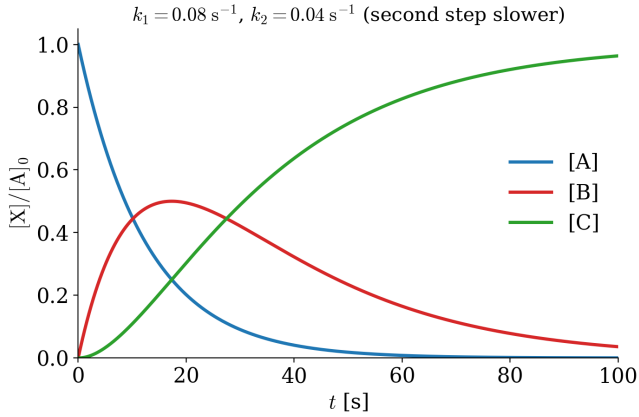


Figure 14.5.: Concentration Plot for a Process with Two Consecutive Reactions with the Second One Being the Rate-Determining Step.

forms slowly at the beginning (notice the S shape of its curve), since it has to wait for B to build up.

The second behavior is observed when the first step is much slower than the second one, $k_1 \ll k_2$, as in the plot of Figure 14.6. In this case, the rate-determining step is the first reaction. Every molecule of B is converted into C almost as soon as it is formed, so the concentration of the intermediate stays very small at all times, and C appears as fast as A disappears. As such, the process has the same rate law as an elementary reaction going directly from A to C.

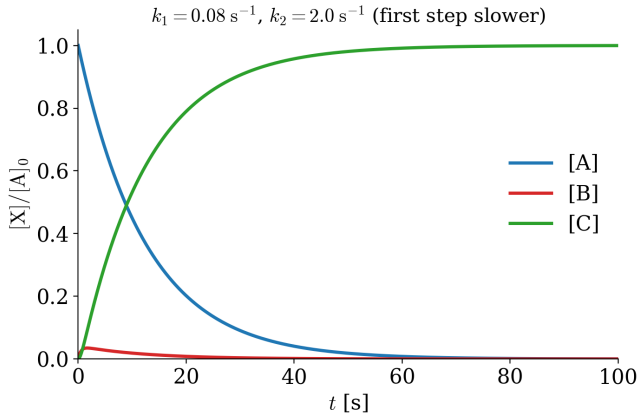


Figure 14.6.: Concentration Plot for a Process with Two Consecutive Reactions with the First One Being the Rate-Determining Step.

Since, in this second case, the concentration of B is small and almost constant throughout the process, we can approximate its derivative to zero. This simplification is known as the *steady-state approximation*, and it allows us to eliminate the intermediate from the treatment. Using the second line of eq. 14.13:

$$\frac{d[\mathrm{B}]}{dt} = k_1[\mathrm{A}] - k_2[\mathrm{B}] \approx 0 \quad \Rightarrow \quad [\mathrm{B}] \approx \frac{k_1}{k_2}[\mathrm{A}], \tag{14.19}$$

which is indeed very small, since $k_1 \ll k_2$. Replacing eq. 14.19 into the third line of eq. 14.13, the rate of formation of the product becomes:

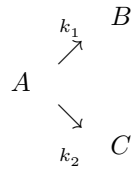
$$\frac{d[\mathrm{C}]}{dt} = k_2[\mathrm{B}] \approx k_1[\mathrm{A}], \tag{14.20}$$

which is exactly the rate law of an elementary first-order reaction going directly from A to C, with the rate coefficient of the slow step. The steady-state approximation is widely used to study processes that go through a series of very reactive intermediates, whose concentrations stay small and almost constant throughout the entire process:

$$\begin{aligned} &\mathrm{A} \xrightarrow{k_1} \mathrm{I}_1 \xrightarrow{k_2} \mathrm{I}_2 \longrightarrow \cdots \xrightarrow{k_n} \text{products} \\ &\quad \text{Steady State Approximation:} \\ &\mathrm{A} \longrightarrow \text{products} \end{aligned} \tag{14.21}$$

14.2.2. Competitive Reactions

A process where two elementary reactions happen in parallel, competing with each other, can be written as follows:



Assuming that each step follows first-order kinetics, we can write:

$$
\begin{aligned}
-\frac{d[\mathrm{A}]}{dt} &= k_1[\mathrm{A}] + k_2[\mathrm{A}] \Rightarrow [\mathrm{A}] = [\mathrm{A}]_0 \exp\left[-(k_1 + k_2)t\right] \\
\frac{d[\mathrm{B}]}{dt} &= k_1[\mathrm{A}] \Rightarrow [\mathrm{B}] = \frac{k_1}{k_1 + k_2}[\mathrm{A}]_0 \left\{1 - \exp\left[-(k_1 + k_2)t\right]\right\} \\
\frac{d[\mathrm{C}]}{dt} &= k_2[\mathrm{A}] \Rightarrow [\mathrm{C}] = \frac{k_2}{k_1 + k_2}[\mathrm{A}]_0 \left\{1 - \exp\left[-(k_1 + k_2)t\right]\right\}.
\end{aligned}
\tag{14.22}
$$

The concentration of each of the species can then be plotted against time, obtaining the diagram reported in Figure 14.7. The final concentrations of the products, $[\mathrm{B}]_f$ and $[\mathrm{C}]_f$, will depend on the values of the two rate coefficients. For example, if $k_1 > k_2$, $[\mathrm{B}]_f > [\mathrm{C}]_f$, as in Figure 14.7, but if $k_1 < k_2$, $[\mathrm{B}]_f < [\mathrm{C}]_f$.

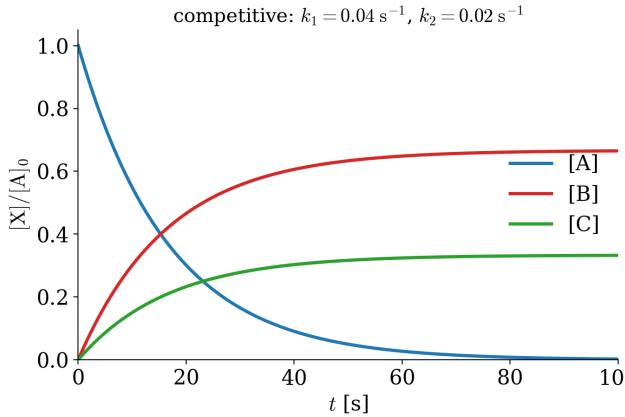


Figure 14.7.: Concentration Plot for a Process with Two Competitive Reactions.

An important relationship that can be derived from eq. 14.22 is that:

$$
\frac{[\mathrm{B}]}{[\mathrm{C}]} = \frac{k_1}{k_2}. \tag{14.23}
$$

14.2.3. Opposed Reactions

Another case of complex kinetic law happens when a pair of forward and reverse reactions occur simultaneously:

$$
\mathrm{A} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \mathrm{B}
$$

where the rate coefficients for the forward and backwards reaction, k_1 and k_{-1}, respectively, are not necessarily equal to each other, but comparable in magnitude. We can write the rate laws for each of these elementary steps as:

$$\begin{aligned} -\frac{d[\mathrm{A}]}{dt} &= k_1[\mathrm{A}] - k_{-1}[\mathrm{B}] = k_1[\mathrm{A}] - k_{-1}\left([\mathrm{A}]_0 - [\mathrm{A}]\right) \\ \frac{d[\mathrm{A}]}{dt} &= -(k_1 + k_{-1})[\mathrm{A}] + k_{-1}[\mathrm{A}]_0, \end{aligned} \tag{14.24}$$

which can then be integrated to:

$$\begin{aligned} [\mathrm{A}] &= [\mathrm{A}]_0 \frac{k_{-1} + k_1 \exp[-(k_1 + k_{-1})t]}{k_1 + k_{-1}} \\ [\mathrm{B}] &= [\mathrm{A}]_0 \left\{ 1 - \frac{k_{-1} + k_1 \exp[-(k_1 + k_{-1})t]}{k_1 + k_{-1}} \right\}. \end{aligned} \tag{14.25}$$

These formulas can then be used to obtain the plots in Figure 14.8.

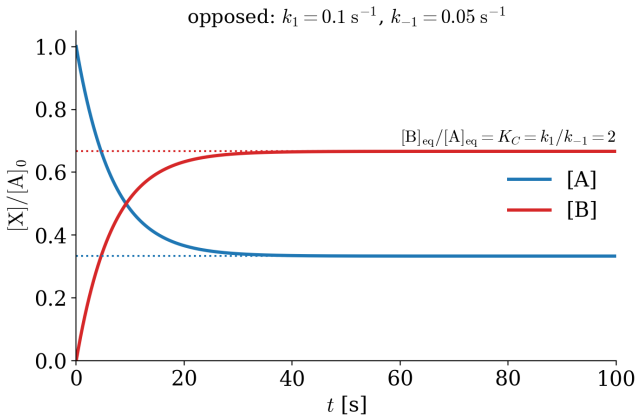


Figure 14.8.: Concentration Plot for a Process with Two Opposed Reactions.

As can be seen from the plots in Figure 14.8, after a sufficiently long time, the system reaches a dynamic equilibrium, where the concentrations of A and B don't change. These equilibrium concentrations can be calculated replacing $t = \infty$ in eq. 14.25:

$$\begin{aligned}[\mathrm{A}]_{\mathrm{eq}} &= [\mathrm{A}]_0 \frac{k_{-1}}{k_1 + k_{-1}} \\ [\mathrm{B}]_{\mathrm{eq}} &= [\mathrm{A}]_0 \frac{k_1}{k_1 + k_{-1}}.\end{aligned} \tag{14.26}$$

Considering that the concentrations of the species don't change at equilibrium:

$$\begin{aligned} -\frac{d[\mathrm{A}]_{\mathrm{eq}}}{dt} &= \frac{d[\mathrm{B}]_{\mathrm{eq}}}{dt} = 0 \\ &\Rightarrow\ k_1[\mathrm{A}]_{\mathrm{eq}} = k_{-1}[\mathrm{B}]_{\mathrm{eq}} \\ &\Rightarrow\ \frac{k_1}{k_{-1}} = \frac{[\mathrm{B}]_{\mathrm{eq}}}{[\mathrm{A}]_{\mathrm{eq}}} = K_C, \end{aligned} \tag{14.27}$$

where K_C is the equilibrium constant as defined in chapter 10. This is a rare link between kinetics and thermodynamics and appears only for opposed reactions after sufficient time has passed so that the system can reach the dynamic equilibrium.

14.3. Experimental Methods for Determination of Reaction Orders

To experimentally measure the reaction rate, we need a method to measure concentration changes with respect to time. The simplest way to determine the reaction rate is to monitor the entire reaction as it proceeds and then plot the resulting data differently until a linear plot is found. A summary of the results obtained in section 14.1 and that is useful for this task is reported in the following table:

	Zeroth-Order	*First-Order*	*Simple Second-Order*	*Complex Second-Order*
Differential Rate Law	$-\frac{d[\mathrm{A}]}{dt} = k_0[\mathrm{A}]^0 = k_0$	$-\frac{d[\mathrm{A}]}{dt} = k_1[\mathrm{A}]$	$-\frac{d[\mathrm{A}]}{dt} = k_2[\mathrm{A}]^2$	$-\frac{d[\mathrm{A}]}{dt} = k_2'[\mathrm{A}][\mathrm{B}]$
Integrated Rate Law	$[\mathrm{A}] = [\mathrm{A}]_0 - k_0 t$	$[\mathrm{A}] = [\mathrm{A}]_0 e^{-k_1 t}$	$\frac{1}{[\mathrm{A}]} = \frac{1}{[\mathrm{A}]_0} + k_2 t$	$\frac{[\mathrm{A}]}{[\mathrm{B}]} = \frac{[\mathrm{A}]_0}{[\mathrm{B}]_0} e^{([\mathrm{A}]_0 - [\mathrm{B}]_0)k_2' t}$
Units of k	$\frac{\mathrm{M}}{\mathrm{s}}$	$\frac{1}{\mathrm{s}}$	$\frac{1}{\mathrm{M}\cdot\mathrm{s}}$	$\frac{1}{\mathrm{M}\cdot\mathrm{s}}$
Linear Plot vs. t	$[\mathrm{A}]$	$\ln[\mathrm{A}]$	$\frac{1}{[\mathrm{A}]}$	$\ln\frac{[\mathrm{A}]_0[\mathrm{B}]}{[\mathrm{B}]_0[\mathrm{A}]}$
Half-life	$t_{1/2} = \frac{[\mathrm{A}]_0}{2k_0}$	$t_{1/2} = \frac{\ln 2}{k_1}$	$t_{1/2} = \frac{1}{k_2[\mathrm{A}]_0}$	not easily defined

However, this method works only if the reaction has few reactants, and it requires several measurements, each of which might be complicated to make. More useful methods to determine the reaction rate are the *initial rate* and the *isolation* methods that we describe below.

14.3.1. Initial Rates Method

The *initial rates method* involves measuring the rate of a reaction as soon as it starts before any significant change in the concentrations of the reactants occurs. The initial rate method is practical only if the reaction is reasonably slow, but it can measure the rate unambiguously when more than one reactant is involved. For example, if we have a reaction with the following stoichiometry:

$$\alpha\mathrm{A} + \beta\mathrm{B} \xrightarrow{k} \text{products}$$

the initial rate method can be used to determine the coefficients of the rate law:

$$\text{Rate} = k[\mathrm{A}]^{\alpha}[\mathrm{B}]^{\beta} \tag{14.28}$$

by designing three experiments, where the initial concentrations of A and B are appropriately changed. For example, let's consider the following experimental data from three different experiments:

	$[\mathrm{A}]_0$ (M)	$[\mathrm{B}]_0$ (M)	initial rate $\left(\frac{M}{s}\right)$
Experiment 1:	0.10	0.10	4.32
Experiment 2:	0.15	0.10	9.70
Experiment 3:	0.10	0.20	4.29

we can calculate α by taking the ratio of the rates measured in experiment 1 and 2:

$$\begin{aligned} \frac{\text{Rate}(1)}{\text{Rate}(2)} &= \frac{k(0.10\ \mathrm{M})^{\alpha}(0.10\ \mathrm{M})^{\beta}}{k(0.15\ \mathrm{M})^{\alpha}(0.10\ \mathrm{M})^{\beta}} \\ \frac{4.32}{9.70} &= \frac{(0.10\ \mathrm{M})^{\alpha}}{(0.15\ \mathrm{M})^{\alpha}} \\ 0.445 &= 0.667^{\alpha} \ \rightarrow\ \ln 0.445 = \alpha \ln 0.667 \\ \alpha &= \frac{-0.81}{-0.405} = 2. \end{aligned} \tag{14.29}$$

β can be calculated similarly by taking the ratio between experiments 1 and 3. Alternatively, we can also notice that the reaction rate does not change when the initial concentration $[\mathrm{B}]_0$ is doubled, therefore $\beta = 0$.

14.3.2. Isolation Method

Another method that is widely used to determine reaction orders is the *isolation method*. This method is performed by using large excess concentrations of all reactants but one. For example, if we have the following reaction with three reagents and unknown rate law:

$$\alpha\mathrm{A} + \beta\mathrm{B} + \gamma\mathrm{C} \xrightarrow{k} \text{products}$$

we can perform three different experiments, in each of which we use an excess amount of all reagents but one, such as:

- Experiment 1: $[\mathrm{A}]_0 = 1$ M, $[\mathrm{B}]_0 = 1000$ M, $[\mathrm{C}]_0 = 1000$ M, in which the reaction order with respect to A is measured.
- Experiment 2: $[\mathrm{A}]_0 = 1000$ M, $[\mathrm{B}]_0 = 1$ M, $[\mathrm{C}]_0 = 1000$ M, in which the reaction order with respect to B is measured.
- Experiment 3: $[\mathrm{A}]_0 = 1000$ M, $[\mathrm{B}]_0 = 1000$ M, $[\mathrm{C}]_0 = 1$ M, in which the reaction order with respect to C is measured.

From each experiment we can determine the *pseudo-order* of the reaction with respect to the reagent that is in minority concentration. For example, for the reaction above, we can write the rate law as:

$$\text{Rate} = k[\mathrm{A}]^{\alpha}[\mathrm{B}]^{\beta}[\mathrm{C}]^{\gamma} \tag{14.30}$$

and we can write the initial concentrations, $[X]_0$, and the final concentrations, $[X]_f$, of each of the species in experiment 1, as:

$$\begin{aligned}
[\mathrm{A}]_0 = 1\ \mathrm{M} &\longrightarrow [\mathrm{A}]_f = 0\ \mathrm{M} && (100\%\ \text{change})\\
[\mathrm{B}]_0 = 1000\ \mathrm{M} &\longrightarrow [\mathrm{B}]_f = 1000 - 1 = 999\ \mathrm{M} \cong [\mathrm{B}]_0 && (0.1\%\ \text{change})\\
[\mathrm{C}]_0 = 1000\ \mathrm{M} &\longrightarrow [\mathrm{C}]_f = 1000 - 1 = 999\ \mathrm{M} \cong [\mathrm{C}]_0\,. && (0.1\%\ \text{change})
\end{aligned}$$

The coefficient α can then be determined by incorporating the concentration of the reactants in excess into the rate constant as:

$$\begin{aligned} \text{rate} &= k[\text{A}]^{\alpha} \underbrace{[\text{B}]^{\beta}[\text{C}]^{\gamma}}_{\text{constant}} \\ &= k'[\text{A}]^{\alpha} \end{aligned}$$

and then determine α by verifying which order the data collected for [A] at various times fits. This can be simply achieved by using the zero-, first-, and second-order kinetic plots, as reported in the table above. We can determine β and γ by repeating the same procedure for the data from the other two experiments. For example, if we find for a specific reaction that $\alpha = 1$, $\beta = 2$, and $\gamma = 0$, we can then say that the reaction is pseudo-order one in A, pseudo-order two in B, and pseudo-order zero in C, with an overall reaction order of three.

14.4. Temperature Dependence of the Rate Coefficients

The dependence of the rate coefficient, k, on the temperature is given by the **Arrhenius equation**. This formula was derived by Svante August Arrhenius (1859–1927) in 1889 and is based on the simple experimental observation that almost every chemical process gets faster when the temperature is increased. Working on data from equilibrium reactions previously reported by van 't Hoff, Arrhenius proposed the following simple exponential formula to explain the increase of k when T is increased:

$$k = A \exp\left(-\frac{E_a}{RT}\right), \tag{14.31}$$

where A is the so-called Arrhenius pre-exponential factor, and E_a is the activation energy. Both of these terms are independent of temperature,[2] and they represent experimental quantities that are unique to each individual reaction. Since the vast majority of reactions speed up when the temperature increases, both A and E_a are positive.[3] The pre-exponential factor units are the same as the rate constant and will vary depending on the order of the reaction. As suggested by its name, the activation energy has units of energy per mole of substance, $\frac{\text{J}}{\text{mol}}$ in SI.

What does eq. 14.31 tell us?

[2] In theory, both A and E_a show a weak temperature dependence. However, they can be considered constants at most experimental conditions, since kinetic studies are usually performed in a small temperature range.

[3] A few reactions, such as some recombinations of radicals, slow down when the temperature increases, and they show a negative *apparent* activation energy. These reactions are not elementary: their mechanism involves more than one step, and the measured E_a is a combination of the activation energies of the individual steps.

1. **The rate coefficient grows exponentially with temperature.** For a typical activation energy of 50 kJ/mol, increasing the temperature from 298 K to 308 K almost doubles k. This is the origin of the rule of thumb that reactions near room temperature roughly double their rate for every 10 °C.
2. **Reactions with larger activation energies are more sensitive to temperature.** The larger E_a, the more a change in T affects the exponential.
3. **The exponential is the fraction of molecules that can react.** As we will see below, E_a is the height of an energy barrier, and $\exp\left(-\frac{E_a}{RT}\right)$ is related to the fraction of collisions that have enough energy to overcome it, while A is related to how often the molecules attempt to react.

The Arrhenius equation is experimentally useful in its linearized form. Taking the logarithm of both sides of eq. 14.31, we obtain $\ln k = \ln A - \frac{E_a}{R}\frac{1}{T}$, which is a straight line in a plot of $\ln k$ versus $1/T$. Applying eq. 14.31 to two experiments taken at different temperatures, and taking the ratio between the results, we obtain:

$$\ln \frac{k_{T_2}}{k_{T_1}} = -\frac{E_a}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right), \tag{14.32}$$

which gives the plot of Figure 14.9, from which E_a can be determined.

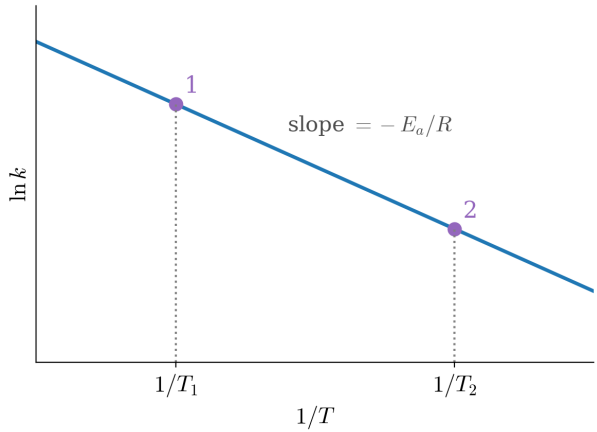


Figure 14.9.: Arrhenius Plot Obtained Using Experimental Data at Two Different Temperatures.

From empirical arguments, Arrhenius proposed the idea that reactants must acquire a minimum amount of energy before they can form any product.

He called this amount of minimum energy the activation energy. We can motivate this assumption by plotting energy of a reaction along the reaction coordinate, as in Figure 14.10. The reaction coordinate is defined as the minimum energy path that connects the reactants with the products. Along this path, the energy rises to a maximum, the *transition state*, before decreasing towards the products. The activation energy corresponds to the height of this barrier: only the molecules that collide with enough energy to reach the top of the barrier can turn into products. Notice that the barrier does not depend on whether the reaction is exothermic or endothermic: a reaction can be strongly spontaneous and still be extremely slow if its barrier is high, as in the diamond-to-graphite example at the beginning of this chapter.

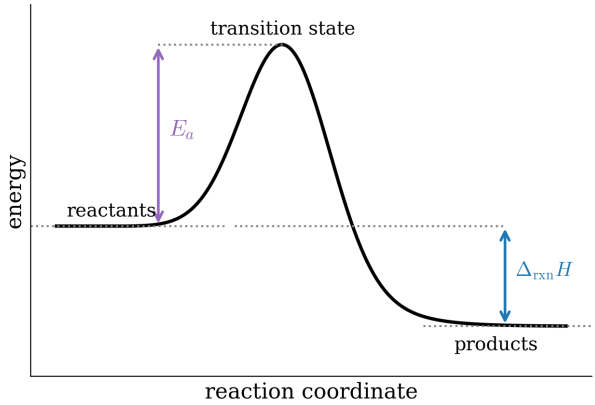


Figure 14.10.: Energy Profile of a Reaction along the Reaction Coordinate (Schematic).

14.5. Chapter Review

14.5.1. Key Ideas

- **Rate laws** relate the rate of a reaction to the concentrations; the order must be determined experimentally, and it equals the molecularity only for elementary reactions.
- **Integrated rate laws:** [A] vs t is linear for zeroth order, ln[A] vs t for first order, and $1/[\mathrm{A}]$ vs t for second order.
- **Half-life:** for a first-order reaction, $t_{1/2} = \frac{\ln 2}{k}$, independent of the initial concentration.
- **Complex reactions:** in consecutive reactions, the slowest step controls the rate, and a short-lived intermediate can be treated with

the steady-state approximation; competitive reactions give products in the ratio k_1/k_2; opposed reactions reach equilibrium with $K = k_1/k_{-1}$.

- **Experimental methods:** the initial rates and isolation methods determine the order with respect to each reactant.
- **Arrhenius equation:** $k = A\,e^{-E_a/RT}$, so a plot of $\ln k$ vs $1/T$ has slope $-E_a/R$.

14.5.2. Study Questions

1. How does the rate of a zeroth-order reaction depend on the concentration of the reactant?

a. It is proportional to the concentration.
b. It is proportional to the square of the concentration.
c. It is independent of the concentration.
d. It decreases exponentially with the concentration.
e. It is inversely proportional to the concentration.

---

2. Which plot gives a straight line for a first-order reaction?

a. ln[A] versus t, with slope $-k_1$.
b. [A] versus t, with slope $-k_1$.
c. $\frac{1}{[\mathrm{A}]}$ versus t, with slope k_1.
d. $[\mathrm{A}]^2$ versus t.
e. ln[A] versus $\frac{1}{T}$.

---

3. What is special about the half-life of a first-order reaction?

a. It is proportional to the initial concentration.
b. It is inversely proportional to the initial concentration.
c. It increases as the reaction proceeds.
d. It is always 1 second.
e. It does not depend on the initial concentration, since $t_{1/2} = \frac{\ln 2}{k_1}$.

---

4. Which plot gives a straight line for a simple second-order reaction?

a. [A] versus t.
b. $\frac{1}{[\mathrm{A}]}$ versus t.
c. $\ln[\mathrm{A}]$ versus t.
d. $\sqrt{[\mathrm{A}]}$ versus t.
e. $[\mathrm{A}]^2$ versus t.

---

5. When are the order of a reaction and its molecularity equal?

a. Always.
b. Never.
c. Only for first-order reactions.
d. Only for elementary reactions.
e. Only for reactions in the gas phase.

---

6. In the consecutive reactions $\mathrm{A} \to \mathrm{B} \to \mathrm{C}$ **with** $k_1 \ll k_2$**, what happens to the intermediate** B**?**

a. Its concentration stays small and almost constant, which justifies the steady-state approximation.
b. It accumulates and becomes the main product.
c. It is never formed.
d. Its concentration equals that of A.
e. It reacts back to A.

---

7. For two competitive first-order reactions, $\mathrm{A} \to \mathrm{B}$ (k_1) **and** $\mathrm{A} \to \mathrm{C}$ (k_2)**, what is the ratio of the products?**

a. $\frac{[\mathrm{B}]}{[\mathrm{C}]} = 1$.
b. $\frac{[\mathrm{B}]}{[\mathrm{C}]} = \frac{k_2}{k_1}$.
c. $\frac{[\mathrm{B}]}{[\mathrm{C}]} = \frac{k_1}{k_2}$.
d. $\frac{[\mathrm{B}]}{[\mathrm{C}]} = k_1 k_2$.
e. It changes with time.

---

8. For opposed reactions, $\mathrm{A} \rightleftharpoons \mathrm{B}$**, how is the equilibrium constant related to the rate coefficients?**

a. $K_C = \frac{k_{-1}}{k_1}$.
b. $K_C = k_1 + k_{-1}$.
c. $K_C = k_1 k_{-1}$.
d. $K_C = k_1 - k_{-1}$.
e. $K_C = \frac{k_1}{k_{-1}}$.

---

9. How is the isolation method performed?

a. By measuring only the initial rate.
b. By using a large excess of all reactants but one.
c. By separating the products as they form.
d. By running the reaction at very low temperature.
e. By using equal concentrations of all reactants.

---

10. How can the activation energy be obtained from the Arrhenius equation?

a. From the intercept of a plot of k versus T.
b. From the half-life of the reaction.
c. From the equilibrium constant.
d. From the slope of a plot of $\ln k$ versus $\frac{1}{T}$, which is $-\frac{E_a}{R}$.
e. From the reaction enthalpy.

Answers

1.c, 2.a, 3.e, 4.b, 5.d, 6.a, 7.c, 8.e, 9.b, 10.d

A. Appendix

A.1. Thermodynamic Data of Inorganic Substances at 298 K

Substance:	$\Delta_f \hat{H}^\circ$[kJ/mol]	$\Delta_f \hat{G}^\circ$[kJ/mol]	$\hat{S}^\circ$[J/(mol K)]	C_P [J/(mol K)]
Ag(g)	284.9	246	173	20.8
Ag(s)	0	0	42.6	25.4
Ag^+(aq)	105.8	77.1	73.5	
AgCN(s)	146	156.9	107.2	66.7
Ag_2CO_3(s)	−505.8	−436.8	167.4	112.3
$AgNO_3$(s)	−124.4	−33.4	140.9	93.1
Ag_2O(s)	−31.1	−11.2	121.3	65.9
Ag_2S(s)	−32.6	−40.7	144	76.5
AgBr(s)	−100.4	−96.9	107.1	52.4
AgCl(s)	−127.0	−109.8	96.3	50.8
AgF(s)	−204.6	−187	84	
AgI(s)	−61.8	−66.2	115.5	56.8
Al(g)	330	289.4	164.6	21.4
Al(s)	0	0	28.3	24.2
Al_2O_3(s)	−1675.7	−1582.3	50.9	79.0
AlF_3(s)	−1510.4	−1431.1	66.5	75.1
AlI_3(s)	−302.9		195.9	
$AlBr_3$(s)	−527.2		180.2	100.6
$AlCl_3$(s)	−704.5	−628.11	112.3	91.1
$Al(OH)_3$(s)	−1277			
$Al(OH)_4^-$(aq)	−1490	−1297	117	
$AlPO_4$(s)	−1733.8	−1617.9	90.8	93.2
Ar(g)	0		154.9	20.8
B(s)	0	0	5.9	11.1
B(g)	565	521.0	153.4	20.8
BH(g)	442.7	412.7	171.8	29.2
BH_3(g)	89.2	93.3	188.2	36.0
B_2S_3(s)	−240.6		100.0	111.7
Ba(g)	180	146	170.2	
Ba(s)	0	0	62.5	28.1
$BaCO_3$(s)	−1213.0	−1134.4	112.1	86.0
BaH_2(s)	−177	−138.2	63.0	
$BaBr_2$(s)	−757.3	−736.8	146.0	
$BaCl_2$(s)	−855	−806.7	123.7	75.1
BaF_2(s)	−1207.1	−1156.8	96.4	71.2
BaI_2(s)	−602.1	−597	167.0	
BaO(s)	−548.0	−520.3	72.1	47.3
$BaSO_4$(s)	−1473.2	−1362.2	132.2	101.8
Be(g)	324	286.6	136.3	20.8
Be(s)	0	0	9.5	13.4
$BeBr_2$(s)	−353.5		108	69.4
$BeCl_2$(s)	−490.4	−445.6	75.8	62.4
BeF_2(s)	−1026.8	−979.4	53.4	51.8
BeI_2(s)	−192.5		121	71.1
BeO(s)	−609.4	−580.1	13.8	25.6
$Be(OH)_2$(s)	−902.5	−815.0	45.5	62.1
$BeSO_4$(s)	−1205.2	−1093.8	77.9	85.7
Bi(g)	207.1	168.2	187	20.8
Bi(s)	0	0	56.7	25.5
Bi_2O_3(s)	−573.9	−493.7	151.5	113.5
$BiCl_3$(s)	−379.1	−315.0	177.0	105.0
Br^-(aq)	−121.4	−104.0	82.6	
Br(g)	111.9	82.4	175	20.8
Br_2(g)	30.9	3.1	245.5	36.0
Br_2(l)	0	0	152.2	75.7
BrCl(g)	14.6	−1	240.1	35.0
BrF(g)	−93.8	−109.2	229	33.0
BrF_3(g)	−1136	1119.4	254.4	66.6
C(g)	716.7	671.3	158.1	0.8
C(s,diamond)	1.9	2.9	2.4	6.1

Substance:	$\Delta_f H^\circ$ [kJ/mol]	$\Delta_f G^\circ$ [kJ/mol]	S° [J/(mol K)]	C_P [J/(mol K)]
C(s,graphite)	0	0	5.7	8.5
CBr_4(g)	83.9	67	358.1	
CBr_4(s)	29.4	47.7	212.5	
CCl_2F_2(g)	−477.4	−439.4	300.8	
CCl_2O(g)	−219.1	−204.9	283.5	
CCl_4(g)	−95.7	−53.6	309.9	
CCl_4(l)	−128.2	−62.6	216.2	
CF_4(g)	−933.6	−888.3	261.6	
CS_2(g)	116.7	67.1	237.8	45.4
CS_2(l)	89	64.6	151.3	76.4
CO(g)	−110.5	−137.2	197.7	29.1
CO_2(g)	−393.5	−394.4	213.8	37.1
Ca(g)	177.8	144	154.9	20.8
Ca(s)	0	0	41.6	25.9
$Ca(OH)_2$(s)	−985.2	−897.5	83.4	87.5
$CaBr_2$(s)	−682.8	−663.6	130	
$CaCl_2$(s)	−795.4	−748.8	108.4	72.9
CaCN(s)	−184.5			
$CaCO_3$(s,arag.)	−1207.8	−1128.2	88	82.3
$CaCO_3$(s,calc.)	−1207.6	−1129.1	91.7	83.5
CaF_2(s)	−1228.0	−1175.6	68.5	67.0
CaH_2(s)	−181.5	−142.5	41.4	41.0
CaI_2(s)	−533.5	−528.9	142	
CaO(s)	−634.9	−603.3	38.1	42.0
$CaSO_4$(s)	−1434.5	−1322.0	106.5	99.7
Cd(g)	111.8		167.7	20.8
Cd(s)	0	0	51.8	26.0
$CdBr_2$(s)	−316.2	−296.3	137.2	76.7
$CdCl_2$(s)	−391.5	−343.9	115.3	74.7
$CdCO_3$(s)	−750.6	−669.4	92.5	
CdF_2(s)	−700.4	−647.7	77.4	
CdS(s)	−161.9	−156.5	64.9	
$CdSO_4$(s)	−933.3	−822.7	123.0	99.6
Cl^-(aq)	−167.1	−131.2	56.6	
Cl(g)	121.3	105.3	165.2	21.8
Cl_2(g)	0	0	223.1	33.9
ClF(g)	−50.3	−51.8	217.9	32.1
ClF_3(g)	−163.2	−123.0	281.6	63.9
ClO_2(g)	89.1	105	263.7	46.0
Cl_2O(g)	80.3	97.9	266.2	45.4
Co(g)	424.7	380.3	179.5	23.0
Co(s)	0	0	30	24.8
$CoCl_2$(s)	−312.5	−269.8	109.2	78.5
Cr(g)	396.6	351.8	174.5	20.8
Cr(s)	0	0	23.8	23.4
Cr_2O_3(s)	−1139.7	−1058.1	81.2	118.7
$CrCl_2$(s)	−395.4	−356	115.3	71.2
$CrCl_3$(s)	−556.5	−486.1	123	91.8
CrO_2(g)	−598			
CrO_3(g)	−292.9		266.2	56.0
Cs(g)	76.5	49.6	175.6	20.8
Cs(s)	0	0	85.2	32.2
CsCl(s)	−443.0	−414.5	101.2	52.5
Cu(g)	337.4	297.7	166.4	20.8
Cu(s)	0	0	33.2	24.2
Cu_2O(s)	−168.6	−146.0	93.1	63.6
CuO(s)	−157.3	−129.7	42.6	
Cu_2S(s)	−79.5	−86.2	120.9	76.3
CuS(s)	−53.1	−53.6	66.5	47.8
$CuSO_4$(s)	−771.4	−662.2	109.2	
CuBr(s)	−104.6	−100.8	96.1	54.7
$CuBr_2$(s)	−141.8			
CuCl(s)	−137.2	−119.9	86.2	48.5
$CuCl_2$(s)	−220.1	−175.7	108.1	71.9
CuCN(s)	96.2	111.3	84.5	
F^-(aq)	−335.4	−278.8	−13.8 | |	
F(g)	79.4	62.3	158.8	22.7
F_2(g)	0	0	202.8	32.3
F_2O(g)	24.5	41.8	247.5	43.3
FO(g)	109	105.3	216.4	32.0
FB(g)	−122.2	−149.8	200.5	58.6
Fe(g)	416.3	370.7	180.5	25.7
Fe(s)	0	0	27.3	25.1
FeO(s)	−272.0	−251.4	60.7	
Fe^{2+}(aq)	−89.1	−78.9	−137.7 | |	
Fe_2O_3(s)	−824.2	−742.2	87.4	103.9
Fe^{3+}(aq)	−48.5	−4.7	−315.9 | |	
Fe_3O_4(s)	−1118.4	−1015.4	146.4	143.4
$FeCO_3$(s)	−740.6	−666.7	92.9	82.1
FeS_2(s)	−178.2	−166.9	52.9	62.2
$FeCl_2$(s)	−341.8	−302.3	118	75.7
$FeCl_3$(s)	−399.5	−334.0	142.3	96.7
$FeBr_2$(s)	−249.8	−238.1	140.6	
$FeBr_3$(s)	−268.2			
Fe_3C(s)	25.1	20.1	104.6	105.9
H(g)	218.0	203.3	114.7	20.8

Substance:	$\Delta_f H^\circ$[kJ/mol]	$\Delta_f G^\circ$[kJ/mol]	S°[J/(mol K)]	C_P [J/(mol K)]
H^+(aq)	0	0	0	
H_2(g)	0	0	130.7	28.8
H_2O(g)	−241.8	−228.6	188.8	33.6
H_2O(l)	−285.8	−237.1	70.0	75.3
H_2O_2(g)	−136.3	−105.6	232.7	43.1
H_2O_2(l)	−187.8	−120.4	109.6	89.1
H_2S(g)	−20.6	−33.4	205.8	34.2
H_2Se(g)	29.7	15.9	219	34.7
H_2SO_4(aq)	−909.3	−744.5	20.1	
H_2SO_4(l)	−814.0	−690.0	156.9	138.9
H_3PO_4(l)	−1271.7	−1123.6	150.8	145.0
H_3PO_4(s)	−1284.4	−1124.3	110.5	106.1
HBr(aq)	−121.6	−104.0	82.4	
HBr(g)	−36.3	−53.4	198.7	29.1
HCl(aq)	−167.2	−131.2	56.5	
HCl(g)	−92.3	−95.3	186.9	29.1
HCN(g)	135.1	124.7	201.8	35.9
HCN(l)	108.9	125	112.8	70.6
HF(aq)	−332.6	−278.8	−13.8 | |	
HF(g)	−273.3	−275.4	173.8	
HI(aq)	−55.2	−51.6	111.3	
HI(g)	26.5	1.7	206.6	29.2
HNO_2(g)	−79.5	−46.0	254.1	
HNO_3(aq)	−207.4	−111.3	146.4	
HNO_3(g)	−133.9	−73.5	266.9	54.1
HNO_3(l)	−174.1	−80.7	155.6	109.9
He(g)	0	0	126.2	20.8
Hg(g)	61.4	31.8	175	
Hg(l)	0	0	75.9	28.0
Hg_2(g)	108.8	68.2	288.1	
HgO(s)	−90.8	−58.5	70.3	44.1
HgS(s,red)	−58.2	−50.6	82.4	48.4
Hg_2SO_4(s)	−743.1	−625.8	200.7	132.0
$HgSO_4$(s)	−707.5			
Hg_2Cl_2(s)	−265.4	−210.7	191.6	191.6
$HgCl_2$(s)	−224.3	−178.6	146.0	146.0
Hg_2Br_2(s)	−206.9	−181.1	218.0	218.0
$HgBr_2$(s)	−170.7	−153.1	172.0	172.0
Hg_2I_2(s)	−121.3	−111	233.5	233.5
HgI_2(s)	−105.4	−101.7	180.0	180.0
I^-(aq)	−56.8	−51.6	106.5	
I(g)	106.8	70.2	180.8	20.8
I_2(g)	62.4	19.3	260.7	36.9
I_2(s)	0	0	116.1	54.4
HIO_3(s)	−230.1			
IBr(g)	40.8	3.7	258.8	36.4
ICl(g)	17.8	−5.5	247.6	35.6
IF(g)	−95.7	−118.5	236.2	33.4
K(g)	89.0	60.5	160.3	20.8
K(s)	0	0	64.7	29.6
K_2CO_3(s)	−1151.0	−1063.5	155.5	114.4
K_2O(s)	−361.5	−322.1	94.1	
K_2O_2(s)	−494.1	−425.1	102.1	
K_2SO_4(s)	−1437.8	−1321.4	175.6	131.5
KBr(s)	−393.8	−380.7	95.9	52.3
KCl(s)	−436.5	−408.5	82.6	51.3
KF(s)	−567.3	−537.8	66.6	49.0
KI(s)	−327.9	−324.9	106.3	52.9
$KClO_3$(s)	−397.7	−296.3	143.1	100.3
$KMnO_4$(s)	−837.2	−737.6	171.7	117.6
KNO_2(s)	−369.8	−306.6	152.1	107.4
KNO_3(s)	−494.6	−394.9	133.1	96.4
KSCN(s)	−200.2	−178.3	124.3	88.5
Kr(g)	0	0	164.1	20.8
Li(g)	159.3	126.6	138.8	20.8
Li(s)	0	0	29.1	24.9
Li^+(aq)	−278.5	−293.3	12.4	
Li_2O(s)	−597.9	−561.2	37.6	54.1
LiOH(s)	−487.5	−441.5	42.8	49.6
$LiNO_3$(s)	−483.1	−381.1	90.0	
LiBr(s)	−351.2	−342	74.3	
LiCl(s)	−408.6	−384.4	59.3	48.0
LiF(s)	−616	−587.7	35.7	41.6
LiI(s)	−270.4	−270.3	86.8	51.0
Mg(g)	147.1	112.5	148.6	20.8
Mg(s)	0	0	32.7	24.9
MgO(s)	−601.6	−569.3	27.0	37.2
$Mg(OH)_2$(s)	−924.5	−833.5	63.2	77.0
MgS(s)	−346.0	−341.8	50.3	45.6
$MgSO_4$(s)	−1284.9	−1170.6	91.6	96.5
$MgBr_2$(s)	−524.3	−503.8	117.2	
$MgCl_2$(s)	−641.3	−591.8	89.6	71.4
MgF_2(s)	−1124.2	−1071.1	57.2	61.6
Mn(g)	280.7	238.5	173.7	20.8
Mn(s)	0	0	32	26.3
MnO(s)	−385.2	−362.9	59.7	45.4

Substance:	$\Delta_f H^\circ$[kJ/mol]	$\Delta_f G^\circ$[kJ/mol]	S°[J/(mol K)]	C_P [J/(mol K)]
MnO_2(s)	−520.0	−465.1	53.1	54.1
MnO_4^-(aq)	−541.4	−447.2	191.2	
$MnBr_2$(s)	−384.9			
$MnCl_2$(s)	−481.3	−440.5	118.2	72.9
Mo(g)	658.1	612.5	182	20.8
Mo(s)	0	0	28.7	24.1
MoO_2(s)	−588.9	−533.0	46.3	56.0
MoO_3(s)	−745.1	−668.0	77.7	75.0
MoS_2(s)	−235.1	−225.9	62.6	63.6
MoS_3(s)	−364	−354	119	
N(g)	472.7	455.5	153.3	20.8
N_2(g)	0	0	191.6	29.1
NF_3(g)	−132.1	−90.6	260.8	53.4
NH_3(g)	−45.9	−16.4	192.8	35.1
NH_4^+(aq)	−133.3	−79.3	111.2	
NH_4Cl(s)	−314.4	−202.9	94.6	84.1
NH_4NO_3(s)	−365.6	−183.9	151.1	139.3
NH_4OH(l)	−361.2	−254.0	165.6	154.9
$(NH_4)_2SO_4$(s)	−1180.9	−901.7	220.1	187.5
N_2H_4(g)	95.4	159.4	238.5	
N_2H_4(l)	50.6	149.3	121.2	
NO_2(g)	33.2	51.3	240.1	37.2
N_2O(g)	81.6	103.7	220	38.6
NO(g)	91.3	87.6	210.8	
N_2O_4(g)	11.1	99.8	304.4	79.2
N_2O_4(l)	−19.5	97.5	209.2	142.7
Na(g)	107.5	77	153.7	20.8
Na(s)	0	0	51.3	28.2
Na^+(aq)	−240.2	−261.9	58.5	
Na_2CO_3(s)	−1130.7	−1044.4	135	112.3
Na_2O(s)	−414.2	−375.5	75.1	69.1
Na_2O_2(s)	−510.9	−447.7	95	89.2
Na_2SO_4(s)	−1387.1	−1270.2	149.6	128.2
NaBr(aq)	−361.7	−365.8	141.4	
NaBr(g)	−143.1	−177.1	241.2	36.3
NaBr(s)	−361.1	−349.0	86.8	51.4
NaCl(aq)	−407.3	−393.1	115.5	
NaCl(s)	−411.2	−384.1	72.1	50.5
NaCN(s)	−87.5	−76.4	115.6	70.4
NaF(aq)	−572.8	−540.7	45.2	
NaF(s)	−576.6	−546.3	51.1	46.9
NaN_3(s)	21.7	93.8	96.9	76.6
$NaNO_3$(aq)	−447.5	−373.2	205.4	
$NaNO_3$(s)	−467.9	−367.0	116.5	92.9
NaO_2(s)	−260.2	−218.4	115.9	72.1
NaOH(s)	−425.8	−379.7	64.4	59.5
NaH(s)	−56.3	−33.6	40	36.4
Ne(g)	0	0	146.3	20.8
Ni(g)	429.7	384.5	182.2	23.4
Ni(s)	0	0	29.9	26.1
Ni_2O_3(s)	−489.5			
$Ni(OH)_2$(s)	−529.7	−447.2	88	
$NiBr_2$(s)	−212.1			
$NiCl_2$(s)	−305.3	−259.0	97.7	71.7
NiF_2(s)	−651.4	−604.1	73.6	64.1
O(g)	249.2	231.7	161.1	21.9
O_2(g)	0	0	205.2	29.4
O_3(g)	142.7	163.2	238.9	39.2
OH^-(aq)	−230.0	−157.2	−10.9 | |	
Os(g)	791	745	192.6	20.8
Os(s)	0	0	32.6	24.7
OsO_4(g)	−337.2	−292.8	293.8	74.1
OsO_4(s)	−394.1	−304.9	143.9	
P(g,white)	316.5	280.1	163.2	20.8
P(s,black)	−39.3			
P(s,red)	−17.6	−12.5	22.8	21.2
P(s,white)	0	0	41.1	23.8
P_2(g)	144.0	103.5	218.1	
P_4(g)	58.9	24.4	280.0	
PCl_3(g)	−287.0	−267.8	311.8	71.8
PCl_3(l)	−319.7	−272.3	217.1	
PCl_5(g)	−374.9	−305.0	364.6	112.8
PH_3(g)	5.4	13.5	210.2	37.1
$POCl_3$(g)	−558.5	−512.9	325.5	
$POCl_3$(l)	−597.1	−520.8	222.5	
Pb(g)	195.2	162.2	175.4	20.8
Pb(s)	0	0	64.8	26.8
$PbCl_2$(s)	−359.4	−314.1	136	
$PbCO_3$(s)	−699.1	−625.5	131	87.4
PbO(s,litharge)	−219.0	−188.9	66.5	45.8
PbO(s,massic.)	−217.3	−187.9	68.7	45.8
PbO_2(s)	−277.4	−217.3	68.6	64.6
$Pb(NO_3)_2$(aq)	−416.3	−246.9	303.3	
$Pb(NO_3)_2$(s)	−451.9			
PbS(s)	−100.4	−98.7	91.2	49.5

Substance:	$\Delta_f H^\ominus$[kJ/mol]	$\Delta_f G^\ominus$[kJ/mol]	$S^\ominus$[J/(mol K)]	C_P [J/(mol K)]
$PbSO_4$(s)	−920.0	−813.0	148.5	103.2
Rb(g)	80.9	53.1	170.1	20.8
Rb(s)	0	0	76.8	31.1
RbCl(s)	−435.4	−407.8	95.9	52.4
S(g,rhombic)	277.2	236.7	167.8	23.7
S(s,rhombic)	0	0	32.1	22.6
SO_2(g)	−296.8	−300.1	248.2	39.9
SO_3(g)	−395.7	−371.1	256.8	50.7
SO_4^{2-}(aq)	−909.3	−744.5	18.5	
$SOCl_2$(g)	−212.5	−198.3	309.8	
Se(g,gray)	227.1	187	176.7	
Se(s,gray)	0	0	42.4	25.4
Si(g)	450	405.5	168.0	22.3
Si(s)	0	0	18.8	20.0
SiC(s,cubic)	−65.3	−62.8	16.6	26.9
SiC(s,hexag.)	−62.8	−60.2	16.5	26.7
$SiCl_4$(g)	−657.0	−617.0	330.7	
$SiCl_4$(l)	−687.0	−619.8	239.7	
SiH_4(g)	34.3	56.9	204.6	42.8
Sn(g,white)	301	266.2	168.5	21.3
Sn(s,gray)	−2.1	0.1	44.1	25.8
Sn(s,white)	0	0	51.2	27.0
$SnCl_4$(g)	−471.5	−432.2	365.8	98.3
$SnCl_4$(l)	−511.3	−440.1	258.6	165.3
SnO_2(s)	−557.6	−515.8	49	52.6
Ti(g)	473	428.4	180.3	24.4
Ti(s)	0	0	30.7	25.1
$TiCl_2$(s)	−513.8	−464.4	87.4	69.8
$TiCl_3$(s)	−720.9	−653.5	139.7	97.2
$TiCl_4$(g)	−763	−726.3	353	95.4
$TiCl_4$(l)	−804.2	−737.2	252.3	145.2
TiO_2(s)	−944.0	−888.8	50.6	55.0
U(g)	533	488.4	199.8	23.7
U(s)	0	0	50.2	27.7
UF_4(g)	−1598.7	−1572.7	368	91.2
UF_4(s)	−1914.2	−1823.3	151.7	116.0
UF_6(g)	−2147.4	−2063.7	377.9	129.6
UF_6(s)	−2197.0	−2068.5	227.6	166.8
UO_2(g)	−465.7	−471.5	274.6	51.4
UO_2(s)	−1085.0	−1031.8	77.0	63.6
V(g)	514.2	754.4	182.3	26.0
V(s)	0	0	28.9	24.9
V_2O_5(s)	−1550.6	−1419.5	131.0	127.7
VCl_3(s)	−580.7	−511.2	131.0	93.2
VCl_4(g)	−525.5	−492.0	362.4	96.2
VCl_4(l)	−569.4	−503.7	255.0	
Xe(g)	0	0	169.7	20.8
Zn(g)	130.4	94.8	161.0	20.8
Zn(s)	0	0	41.6	25.4
$ZnBr_2$(s)	−328.7	−312.1	138.5	
$ZnCl_2$(s)	−415.1	−369.4	111.5	71.3
ZnF_2(s)	−764.4	−713.3	73.7	65.7
ZnI_2(s)	−208.0	−209.0	161.1	
$Zn(NO_3)_2$(s)	−483.7			
ZnS(s,sphaler.)	−206.0	−201.3	57.7	46.0
$ZnSO_4$(s)	−982.8	−871.5	110.5	99.2
Zr(g)	608.8	566.5	181.4	26.7
Zr(s)	0	0	39	25.4
$ZrCl_2$(s)	−502.0	−386	110	
$ZrCl_4$(s)	−980.5	−889.9	181.6	119.8

A.2. Thermodynamic Data of Organic Substances at 298 K

Formula:	Name:	$\Delta_f H^\ominus$[kJ/mol]	$\Delta_f G^\ominus$[kJ/mol]	$S^\ominus$[J/(mol K)]	C_P [J/(mol K)]
$CHBr_3$	Bromoform(g)	25	16	331	71
$CHCl_3$	Chloroform(l)	−134.1	−73.7	201.7	114.2
$CHCl_3$	Chloroform(g)	−102.7	6.0	295.7	65.7
CH_2O_2	Formic acid(l)	−425	−361.4	129	99
CH_2O_2	Formic acid(g)	−378.7			
CH_3	Methyl(g)	145.7	47.9	194.2	38.7
CH_3Br	Bromomethane(l)	−59.8			
CH_3Br	Bromomethane(g)	−35.4	−26.3	246.4	42.4

Formula:	Name:	$\Delta_f H^\circ$[kJ/mol]	$\Delta_f G^\circ$[kJ/mol]	S°[J/(mol K)]	C_P [J/(mol K)]
CH_3Cl	Chloromethane(g)	−81.9	−63	234.6	40.8
CH_3F	Fluoromethane(g)	−234	−210	222.9	37.5
CH_3I	Iodomethane(l)	−13.6		136.2	126
CH_3I	Iodomethane(g)	14.4	16	254.1	44.1
CH_3NO_2	Nitromethane(l)	−112.6	−14.4	171.8	106.6
CH_3NO2	Nitromethane(g)	−80.8	−7	282.9	55.5
CH_4	Methane(g)	−74.6	−50.5	186.3	35.7
CH_4O	Methanol(l)	−239.2	−166.6	126.8	81.1
CH_4O	Methanol(g)	−201	−162.3	239.9	44.1
CH_5N	Methylamine(l)	−47.3	35.7	150.2	102.1
CH_5N	Methylamine(g)	−22.5	32.7	242.9	50.1
C_2H_2	Ethyne (acetylene)(g)	226.9	209	201	44
C_2H_4	Ethene(g)	52.5	68.4	219.3	42.9
C_2H4O_2	Acetic acid(l)	−484.3	−389.9	159.8	123.3
C_2H4O_2	Acetic acid(g)	−432.2	−374.2	283.5	63.4
C_2H_5Br	Bromoethane(l)	−90.5	−25.8	198.7	100.8
C_2H_5Br	Bromoethane(g)	−61.9	−23.9	286.7	64.5
C_2H_5Cl	Chloroethane(l)	−136.8	−59.3	190.8	104.3
C_2H_5Cl	Chloroethane(g)	−112.1	−60.4	276	62.8
$C2H_5NO_2$	Nitroethane(l)	−143.9			134.4
$C2H_5NO_2$	Nitroethane(g)	−103.8	−5	320.5	79
C_2H_6	Ethane(g)	−84	−32	229.2	52.5
C_2H_6O	Ethanol(l)	−277.6	−174.8	160.7	112.3
C_2H_6O	Ethanol(g)	−234.8	−167.9	281.6	65.6
C_2H_6O	Methoxymethane(l)	−203,3			
C_2H_6O	Methoxymethane(g)	−184.1	−112.6	266.4	
C_2H_7N	Ethylamine(l)	−74.1			130
C_2H_7N	Ethylamine(g)	−47.5	36.3	283.8	71.5
C_3H_4	Cyclopropene(g)	277.1	286	244	53
C_3H_4	Propyne(g)	185	194	248	61
C_3H_6	Cyclopropane(l)	35.2			
C_3H_6	Cyclopropane(g)	53.3	104.5	237.5	55.6
C_3H_6	Propene(g)	20	62	267	64
C_3H_6O	Acetone(l)	−248.4		199.8	126.3
C_3H_6O	Acetone(g)	−217.1	−152.7	295.3	74.5
$C_3H_6O_2$	Propanoic acid(l)	−510.7		191	152.8
$C_3H_6O_2$	Propanoic acid(g)	−455.7			
C_3H_8	Propane(l)	−120.9			
C_3H_8	Propane(g)	−103.8	−23.4	270.3	73.6
C_3H_8O	1-Propanol(l)	−302.6		193.6	143.9
C_3H_8O	1-Propanol(g)	−255.1		322.6	85.6
C_3H_8O	2-Propanol(l)	−318.1		181.1	156.5
C_3H_8O	2-Propanol(g)	−272.6		309.2	89.3
C_3H_9N	1-Propanamine(g)	−72	40	324	
C_4H_6	1-Butyne(l)	141.4			
C_4H_6	1-Butyne(g)	165.2	202	291	81
C_4H_6	2-Butyne(l)	119.1			
C_4H_6	2-Butyne(g)	145.7	185	283	78
C_4H_6	Cyclobutene(g)	156.7	175	64	64
C_4H_8	2-Methyl-1-propene(g)	−17	58	294	89
C_4H_8	1-Butene(l)	−20.8		227	118
C_4H_8	1-Butene(g)	0.1	71	306	86
C_4H_8	Cyclobutane(l)	3.7			
C_4H_8	Cyclobutane(g)	27.7	110	265	
$C_4H_8O_2$	Butanoic acid(l)	−533.8		222.2	178.6
$C_4H_8O_2$	Butanoic acid(g)	−475.9			
C_4H_{10}	2-Methylpropane(g)	−135	−21	295	97
C_4H_{10}	Butane(l)	−147.3			140.9
C_4H_{10}	Butane(g)	−125.7	−17	310	98
$C_4H_{10}O$	1-Butanol(l)	−327.3		225.8	177.2
$C_4H_{10}O$	1-Butanol(g)	−274.9			
$C_4H_{10}O$	2-Butanol(l)	−342.6		214.9	196.9
$C_4H_{10}O$	2-Butanol(g)	−292.8		359.5	112.7
C_5H_8	1-Pentyne(g)	144	210	330	105
C_5H_8	2-Pentyne(g)	129	194	332	99
C_5H_8	Cyclopentene(l)	4.3		201.2	122.4
C_5H_8	Cyclopentene(g)	34	111	290	75
C_5H_{10}	1-Pentene(l)	−46.9		262.6	154
C_5H_{10}	1-Pentene(g)	−21.1	79	346	110
C_5H_{10}	2-Methyl-1-butene(g)	−35.2	66	340	112
C_5H_{10}	2-Methyl-1-butene(l)	−61.1		254	157.2
C_5H_{10}	Cyclopentane(l)	−105.1		204.5	128.8
C_5H_{10}	Cyclopentane(g)	−76.4	39	293	83
$C_5H_{10}O_2$	Pentanoic acid(l)	−559.4		259.8	210.3
$C_5H_{10}O_2$	Pentanoic acid(g)	−491.9			
C_5H_{12}	2,2-Dimethylpropane(g)	−166	−15	306	122
C_5H_{12}	2-Methylbutane(g)	−155	−15	344	119
C_5H_{12}	Pentane(l)	−173.5			167.2
C_5H_{12}	Pentane(g)	−146.9	−8	349	120
$C_5H_{12}O$	1-Pentanol(l)	−351.6			208.1

Formula:	Name:	$\Delta_f H^\circ$[kJ/mol]	$\Delta_f G^\circ$[kJ/mol]	S°[J/(mol K)]	C_P [J/(mol K)]
$C_5H_{12}O$	1-Pentanol(g)	–294.6			
$C_5H_{12}O$	2-Pentanol(l)	–365.2			
$C_5H_{12}O$	2-Pentanol(g)	–311			
$C_5H_{12}O$	3-Pentanol(l)	–368.9			239.7
$C_5H_{12}O$	3-Pentanol(g)	–314.9			
$C_5H_{12}O$	Methyl tert-butyl ether(l)	–313.6		265.3	187.5
$C_5H_{12}O$	Methyl tert-butyl ether(g)	–283.7			
C_6H_6	Benzene(l)	49.1	124.5	173.4	136
C_6H_6	Benzene(g)	82.9	129.7	269.2	82.4
C_6H_7N	Aniline(l)				191.9
C_6H_7N	Aniline(g)	87.5	–7	317.9	107.9
C_6H_{10}	1-Hexyne(g)	124	219	369	128
C_6H_{10}	Cyclohexene(l)	–28.5		214.6	148.3
C_6H_{10}	Cyclohexene(g)	–5	107	311	105
C_6H_{12}	1-Hexene(l)	–74.2		295.2	183.3
C_6H_{12}	1-Hexene(g)	–43.5	87	385	132
C_6H_{12}	2-Methyl-1-pentene(g)	–59.4			
C_6H_{12}	2-Methyl-1-pentene(l)	–90			
C_6H_{12}	Cyclohexane(l)	–156.4			154.9
C_6H_{12}	Cyclohexane(g)	–123.4	32	298	106
C_6H_{12}	Methylcyclopentane(g)	–106.2			
C_6H_{12}	Methylcyclopentane(l)	–137.9			
$C_6H_{12}O_2$	Hexanoic acid(l)	–583.8			
$C_6H_{12}O_2$	Hexanoic acid(g)	–511.9			
C_6H_{14}	2,2-Dimethylbutane(g)	–185.9	–10	358	142
C_6H_{14}	2,2-Dimethylbutane(l)	–213.8		272.5	191.9
C_6H_{14}	2-Methylpentane(g)	–174.6	–5	381	144
C_6H_{14}	2-Methylpentane(l)	–204.6		290.6	193.7
C_6H_{14}	3-Methylpentane(g)	–171.9	–2	380	143
C_6H_{14}	3-Methylpentane(l)	–202.4		292.5	190.7
C_6H_{14}	Hexane(l)	–198.7			195.6
C_6H_{14}	Hexane(g)	–166.9	–0.3	388	143
$C_6H_{14}O$	1-Hexanol(l)	–377.5		287.4	240.4
$C_6H_{14}O$	1-Hexanol(g)	315.9			
$C_6H_{14}O$	2-Hexanol(l)	–392			
$C_6H_{14}O$	2-Hexanol(g)	–333.5			
C_7H_6O	Phenol(s)	–165.1		144	127.4
C_7H_6O	Phenol(g)	–96.4	–33	316	104
C_7H_8	Methylbenzene(l)	12.0		220	156
C_7H_8	Methylbenzene(g)	50.0	122	321	104
C_7H_{14}	1-Heptene(l)	–97.9		327.6	211.8
C_7H_{14}	1-Heptene(g)	–62.3	96	424	15
C_7H_{14}	Cycloheptane(l)	–156.6			
C_7H_{14}	Cycloheptane(g)	–118.1			
C_7H_{14}	Ethylcyclopentane(l)	–163.4		279.9	
C_7H_{14}	Ethylcyclopentane(g)	–126.9			
C_7H_{14}	Methylcyclohexane(g)	–154.7			
C_7H_{14}	Methylcyclohexane(l)	–190.1			184.8
$C_7H_{14}O_2$	Heptanoic acid(l)	–610.2			265.4
$C_7H_{14}O_2$	Heptanoic acid(g)	–536.2			
C_7H_{16}	2,2-Dimethylpentane(g)	–205.7			
C_7H_{16}	2,2-Dimethylpentane(l)	–238.3		300.3	221.1
C_7H_{16}	2-Methylhexane(g)	–194.5			
C_7H_{16}	2-Methylhexane(l)	–229.5		323.3	222.9
C_7H_{16}	3-Methylhexane(g)	–191.3			
C_7H_{16}	3-Methylhexane(l)	–226.4			
C_7H_{16}	Heptane(l)	–224.2			224.7
C_7H_{16}	Heptane(g)	–187.6	8	428	166
$C_7H_{16}O$	1-Heptanol(l)	–403.3			272.1
$C_7H_{16}O$	1-Heptanol(g)	–336.5			
C_8H_{10}	Ethylbenzene(l)	–12.3			183.2
C_8H_{10}	Ethylbenzene(g)	29.9	131	361	128
C_8H_{16}	1-Octene(l)	–124.5			241
C_8H_{16}	1-Octene(g)	–81.3	104	463	178
C_8H_{16}	Cyclooctane(l)	–167.7			

Formula:	Name:	$\Delta_f H^\circ$[kJ/mol]	$\Delta_f G^\circ$[kJ/mol]	S°[J/(mol K)]	C_P [J/(mol K)]
C_8H_{16}	Cyclooctane(g)	−124.4			
C_8H_{16}	Ethylcyclohexane(l)	−212.1		280.9	211.8
C_8H_{16}	Ethylcyclohexane(g)	−171.5			
$C_8H_{16}O_2$	Octanoic acid(l)	−636			297.9
$C_8H_{16}O_2$	Octanoic acid(g)	−554.3			
C_8H_{18}	2-Methylheptane(g)	−215.3			
C_8H_{18}	2-Methylheptane(l)	−255		356.4	252
C_8H_{18}	3-Methylheptane(g)	−212.5			
C_8H_{18}	3-Methylheptane(l)	−252.3		362.6	250.2
C_8H_{18}	Octane(l)	−250.1			254.6
C_8H_{18}	Octane(g)	−208.5	16	467	189
$C_8H_{18}O$	1-Octanol(l)	−426.5			305.2
$C_8H_{18}O$	1-Octanol(g)	−355.6			
C_8H_{19}	2,2-Dimethylhexane(g)	−224.5			
C_8H_{19}	2,2-Dimethylhexane(l)	−261.9			
C_9H_{18}	Propylcyclohexane(g)	−192		420	242
C_9H_{12}	Propylbenzene(g)	8	137	401	154
C_9H_{16}	1-Nonyne(l)	16.3			
C_9H_{16}	1-Nonyne(g)	62.3			
$C_9H_{18}O_2$	Nonanoic acid(l)	−659.7			362.4
$C_9H_{18}O_2$	Nonanoic acid(g)	−577.3			
C_9H_{20}	2,2-Dimethylheptane(g)	−246			
C_9H_{20}	2,2-Dimethylheptane(l)	−288.1			
C_9H_{20}	Nonane(l)	−274.7			284.4
C_9H_{20}	Nonane(g)	−228.2	25	506	212
$C_9H_{20}O$	1-Nonanol(l)	−453.4			
$C_9H_{20}O$	1-Nonanol(g)	−376.5			
$C_{10}H_8$	Naphthalene(g)	151	224	336	
$C_{10}H_{14}$	Butylbenzene(l)	−63.2		321.2	243.4
$C_{10}H_{14}$	Butylbenzene(g)	−11.8			
$C_{10}H_{20}$	1-Decene(l)	−173.8		425	300.8
$C_{10}H_{20}$	1-Decene(g)	−123.3			301
$C_{10}H_{20}$	Butylcyclohexane(l)	−263.1		345	271
$C_{10}H_{20}$	Butylcyclohexane(g)	−213.7			
$C_{10}H_{20}O_2$	Decanoic acid(s)	−713.7			
$C_{10}H_{20}O_2$	Decanoic acid(l)	−684.3			
$C_{10}H_{20}O_2$	Decanoic acid(g)	−594.9			
$C_{10}H_{22}$	2-Methylnonane(g)	−260.2			
$C_{10}H_{22}$	2-Methylnonane(l)	−309.8		420.1	313.3
$C_{10}H_{22}$	Decane(l)	−300.9			314.4
$C_{10}H_{22}$	Decane(g)	−249.5	33	545	235
$C_{10}H_{22}O$	1-Decanol(l)	−478.1			370.6
$C_{10}H_{22}O$	1-Decanol(g)	−396.6			
$C_{11}H_{10}$	1-Methylnaphthalene(l)	56.3		254.8	224.4
$C_{11}H_{10}$	2-Methylnaphthalene(s)	44.9		220	196
$C_{11}H_{10}$	2-Methylnaphthalene(g)	106.7			
$C_{11}H_{22}$	1-Undecene(g)				344.9
$C_{11}H_{24}$	Undecane(l)	−327.2			344.9
$C_{11}H_{24}$	Undecane(g)	−270.8	42	584	257
$C_{11}H_{24}O$	1-Undecanol(l)	−504.8			
$C_{12}H_{24}$	1-Dodecene(l)	−226.2		484.8	360.7
$C_{12}H_{24}$	1-Dodecene(g)	−165.4			
$C_{12}H_{24}O_2$	Dodecanoic acid(s)	−774.6			404.3
$C_{12}H_{24}O_2$	Dodecanoic acid(l)	−737.9			
$C_{12}H_{24}O_2$	Dodecanoic acid(g)	642			
$C_{12}H_{26}$	Dodecane(l)	−350.9			375.8
$C_{12}H_{26}$	Dodecane(g)	−289.4	50	623	280
$C_{12}H_{26}O$	1-Dodecanol(l)	−528.5			438.1
$C_{12}H_{26}O$	1-Dodecanol(g)	−436.6			
$C_{14}H_{10}$	Anthracene(g)	231			
$C_{14}H_{10}$	Phenanthrene(g)	207			
$C_{15}H_{30}$	Decylcyclopentane(l)	−367.3			
$C_{16}H_{26}$	Decylbenzene(l)	−218.3			
$C_{16}H_{26}$	Decylbenzene(g)	−138.6			
$C_{16}H_{32}$	1-Hexadecene(l)	−328.7		587.9	488.9

Formula:	Name:	$\Delta_f H^\circ$[kJ/mol]	$\Delta_f G^\circ$[kJ/mol]	S°[J/(mol K)]	C_P [J/(mol K)]
$C_{16}H_{32}$	1-Hexadecene(g)	−248.4			
$C_{16}H_{32}O_2$	Hexadecanoic acid(s)	−891.5		452.4	460.7
$C_{16}H_{32}O_2$	Hexadecanoic acid(l)	−838.1			
$C_{16}H_{32}O_2$	Hexadecanoic acid(g)	−737.1			
$C_{16}H_{34}$	Hexadecane(l)	−456.1			501.6
$C_{16}H_{34}$	Hexadecane(g)	−374.8			
$C_{18}H_{12}$	Chrysene(s)	145.3			
$C_{18}H_{12}$	Chrysene(g)	269.8			