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 $p_A = X_A p$

Geoffrey M. Bowers Ruth A. Bowers

CHENSTANDING THROUGH CARS

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Preface

The journey to create this book began on a long walk to our office during graduate school in 2003. Walking from the stadium parking lot at Penn State to the chemistry buildings gave us plenty of time to think and talk, and one morning we were particularly excited about brainstorming ways that chemistry can be used to describe cars. Immediately upon arriving at work, we typed up our ideas, thinking that some day we would teach a summer camp or course with this theme. Occasionally, we would add to the list and daydream ways to present the material. Nine years later, while our eldest son was napping during a daylong drive to visit family for the holidays, we developed a draft table of contents and decided to write up our ideas as a book.

We put the time and effort into writing this book because we learned so much from one another simply while brainstorming the topics, and we were astounded that there was no such text already. Geoff's interdisciplinary chemistry and engineering background and enthusiasm for cars, combined with Ruth's interests in education and the chemistry of consumer products, gave us a unique perspective on marrying and marketing the "chemistry of cars." We both firmly believe in teaching chemistry by stressing practical applications, as we want our students to become informed consumers of everyday chemistry who can make educated decisions on personal, environmental, health, and political matters. The automobile is a great example of a consumer product with an abundance of chemistry hiding in plain sight, and personal transportation has an impact on a wide variety of socially important issues, including energy and the global carbon balance. There is almost nothing in an automobile that cannot be described from a chemical perspective, but for this book, we have chosen several major car systems and chemistry concepts to showcase the links between our passions.

As a reader, we expect that you picked up this book already having some level of interest in either chemistry or cars, with a desire to learn more about both. We have provided some basic chemical and automotive background in the appendices, so you can brush up on general chemistry topics or the basic systems in a car if you feel the need. Some of the chemistry topics presented in the book do build on one another, so the chapters are best read in order if you do not have a strong background in chemistry already. If you are using this book in a chemistry course or in conjunction with a general chemistry textbook, we hope you can skip around to meet your course goals. As you are reading, you may have a desire for information beyond what we feel is within the scope of this book. We have provided many references that guided us for specific topics, but you may find more information in sources as varied as patents, automotive technician manuals, chemistry textbooks, and handbooks on the chemistry of specific classes of compounds (such as pollutants or polymers). Additionally, there are many diagrams, animations, and videos available from various online resources that may help you better visualize concepts described in this text. We encourage you to look up a topic or phrase online and to use these preexisting visualization tools as often as possible. Finally, we love teaching and we are passionate about cars, so we are very interested in interacting with you if you are reading this book. To that end, we have made ourselves available to you the readers via a dedicated Twitter account (@CarChemProf) and an associated blog (http://www.thechemistryofcars.com/). Please visit these to ask us direct questions and see responses from us and other experts or to hear the latest news about car chemistry.

Despite our driving passions, this book would not be what it is without a great deal of support from many individuals. Many thanks go to several people at Taylor and Francis, including Lance Wobus for taking a chance on our idea, Barbara Glunn our editor, and to David Fausel for coordinating the project. Thanks also go to Dr. John D'Angelo for introducing us to Lance when we first decided to write this book. Several individuals also graciously reviewed the book draft one or even several times. We extend our thanks to Larry Bowers, Peter Wagoner, Arielle Polakos, and David Bish for helpful comments and suggestions that helped develop the book into what it is today. Thanks are also due to Geoff's parents, Larry and Janet Bowers, for providing us with a calm and peaceful working environment to bring the book draft near completion during the summer of 2013. Geoff would also like to thank Larry for instilling both his love of cars/ racing and his interests in chemistry-there would be no book without your influence over the years. In addition, we thank Ruth's parents, Bret and Peggy Rivers, who were probably surprised when we arrived at their home for a visit and immediately requested paper and pen to jot down our initial outline for this text. Peggy's visit, cooking, and grandson wrangling during a spring break from school were also essential in the final stages of revision.

This book is dedicated to Isaac and James. May our love of cars be passed down to you and give us all many years of joy and togetherness.

About the authors

Geoffrey M. Bowers is an interdisciplinary researcher and educator who has been teaching chemistry to undergraduates and supervising graduate and undergraduate research at small liberal arts colleges since 2008. Geoff holds a Bachelor of Science degree in chemical engineering and a Cooperative Education Certificate from Purdue University as well as a PhD in chemistry from The Pennsylvania State University. After earning his



PhD for studies of strontium binding in natural minerals using ⁸⁷Sr nuclear magnetic resonance (NMR) spectroscopy, Dr. Bowers spent several years as a postdoctoral research associate at the University of Illinois in the Department of Geology and Michigan State University in the Department of Chemistry, where he furthered his expertise in NMR by using the technique to study both structural and dynamical behavior at mineral-fluid interfaces. He completed one year of his post-doc while also serving as a visiting faculty member in the Chemistry Department at Gustavus Adolphus College teaching general and environmental chemistry. Geoff is currently an assistant professor of chemistry and an adjunct assistant professor of materials engineering at Alfred University, a regional university in southern New York focused on undergraduate education. Since arriving at Alfred, Bowers has taught a variety of courses including general chemistry, thermodynamics, kinetics, quantum mechanics, environmental chemistry, and several topics courses including "The Chemistry and History of the Manhattan Project" and "The Chemistry of Cars." Dr. Bowers's educational philosophy emphasizes the value of and advocates for student-faculty co-learning experiences (such as undergraduate research), employs a variety of student-centered techniques in the classroom, uses real-world examples whenever possible, and stresses authentic assessment and teamwork skills in his courses. To keep up

with educational best practices, Geoff is active in the Project Kaleidoscope Upstate New York Regional Network. He recently completed an 18-month term as a co-leader of the network steering committee, which he still serves on as a delegate. Over his career, Dr. Bowers has been the recipient of several teaching awards and an undergraduate research mentor award. In addition to his professional academic history, Dr. Bowers has two years of industrial R&D experience in the composite wet friction material industry, where he worked on engineering composite materials for heavy-duty and automotive clutch plates.

Ruth Bowers is a chemistry educator specializing in teaching chemistry at the high school/collegiate interface. She earned a BS in chemistry from Purdue University with an environmental chemistry specialization. During her time at Purdue, Ruth became interested in chemistry education while working as a tutor in the chemistry resource room and collaborating with the chemistry education faculty about curricular design. Ruth then attended graduate school at The Pennsylvania State University where she completed work in both the chemistry and education departments, ultimately earning her MEd in curriculum and instruction and a Pennsylvania state teaching certification. For her master's degree, she studied the impact of an "atoms first" approach to general chemistry (where the course begins with atomic structure and builds in size up to reactions steadily over the semester) on student comprehension of select chemistry topics. Ruth also received a teaching award from the Department of Chemistry for being an outstanding laboratory teaching assistant and served as a trainer and supervisor to both laboratory and recitation teaching assistants. Since then, Ruth has served as an adjunct instructor at Penn State University, Gustavus Adolphus College, Alfred State College, and Alfred University, teaching general chemistry laboratories and lecture courses. In her current position as adjunct instructor of chemistry at Alfred University, Ruth also developed and implemented curricula for teaching the chemistry of consumer products as an honors seminar course and a regularly occurring high school summer camp.

Geoff is an automotive enthusiast who loves working on cars, driving, and watching many types of racing. He has been to many major auto shows in the United States and several types of racing events including the Indianapolis 500, the United States Grand Prix (Formula 1), the NHRA US Nationals, Pikes Peak Hill Climb, Grand American Six Hours of Watkins Glen, and others. Ruth also has ties to automotive history, as she spent her childhood mere miles from the site of one of the first successful test drives of a gasoline-powered automobile in the United States. When not focused on racing or teaching, Geoff and Ruth both enjoy spending time with their sons Isaac and James and their basenji Cooper, gardening, skiing, playing hockey, fishing, and being outdoors with family, friends, and their camera.

Introduction: Cars and chemistry

The car

Cars have captured the imagination and stirred the passion of millions of men and women worldwide since the first car appeared in 1886. Iconic carmakers like Porsche, Ferrari, and BMW are now recognized across the globe, as are timeless iconic cars like the Corvette, Shelby Cobra, Porsche 911, and Ferrari F40. Whether you love luxury and refinement, raw muscle-car power, protecting the environment, or the ultimate blend of art, science, and engineering that is the exotic super car or race car—there is an automobile club, and network of supporters/suppliers out there that share your interests. Many men and women gladly volunteer their weekends to work as marshals at various types of local to international racing events that span the four seasons (SCCA, rally, drift, driving school, etc.); automotive enthusiasts can be found at car shows, car auctions, drag strips, and racetracks year-round; and every city and town in America seems to have at least one automobile dealer, tire dealer, auto parts store, and/or mechanic's shop. You would be hard pressed not to find several television shows about automobiles on the air every day, and cars at one point even spawned their own 24-hour network (Speed). Truly, there is a global subculture of people who dedicate their lives to learning about, maintaining, modifying, racing, and loving cars.

Why are people so fascinated with cars? We challenge you to attend a local SCCA, NHRA, IMSA/Sports Car, NASCAR, or Indy Car rally or other racing event and interact with the drivers, mechanics, and fans without taking away some level of passion about cars. The smooth and sharp lines of a race car are not only aesthetically pleasing, but all are placed with a great deal of care and precision to provide an engineering function and/or racing advantage. The car demands your wonder because it is a conundrum of the simple and astoundingly complex. For example, the beautifully straightforward yet intricate nature of an engine and the sound of it roaring to life can put smiles on faces of any age and education. You can almost feel the car itself anticipating its dance around the racetrack or down the drag strip as the engine growls and pops and all your senses respond to becoming immersed in the exhaust vapors, smells, and sounds of raw speed and excitement. Backyard mechanics get the satisfaction of doing something themselves—and doing it right—when they repair or modify a car. Young and old find a medium for expressing themselves by building the outrageous, the sleeper, the one-of-a-kind paint job, or even covering the windows and tailgate with loud stickers expressing their passions. Working on cars and appreciating cars with family is a great way to spend time together and pass on a legacy to the next generation, as well as saving or even making money. I find myself struggling to keep my heart rate down and not burst from excitement just writing this section of the book.

Yet with all the moving power of a car and the hundreds of millions who use them every day, we suspect many would have a hard time answering the question, "What is a car?" It is a machine clad in artwork harnessing the power of explosive chemistry. It is a network of interconnecting systems all working together to move thousands of pounds of man and machine toward a goal. A car is a collection of parts that are the brainchild of thousands of people and more than 100 years of innovation. It is a gateway to freedom, a means of expression, or just a way of getting from here to there. And it is also exceedingly dependent on chemistry—for the energy to move, the tires that hug the road, the polymers that form the interior, the variety of fluids that permeate the many systems, the colors in the paint, and the headlamps that light your way at night.

Chemistry

Chemistry is the study of matter and the changes it undergoes. More specifically, chemistry involves the study of matter with consideration of atoms and molecules, the interaction of different types of matter together, and the interaction of matter and energy. Chemists are interested in every-thing from reactions to physical properties and study materials from biomolecules to terrestrial and extraterrestrial rocks and soils. Today, chemistry is often called the *central science* because it provides a bridge between the physical, life, and earth sciences, as well as connecting these fields with health and engineering disciplines.

Chemistry has its ancient roots in alchemy, a study that blended early science with philosophy. While many goals of alchemy were unachievable, such as turning common metals into precious ones, the methodical study and documentation of the work by alchemists caused them to shape our ways of understanding the natural world. In addition to developing basic chemical methods such as ore extraction and distillation, alchemists created a framework to understand and organize matter.

Alchemy eventually gave way to the branches of science we know today because advances in mathematics and analytical methods permitted more in-depth study of the natural world. In the late seventeenth through early nineteenth centuries, work by Robert Boyle (characteristics of gases), Antoine LeVoisier (conservation of mass), and John Dalton (atomic theory) defined the new study of chemistry and set the stage for what chemistry has become today. These early chemists differed from alchemists in that their goals were to develop theories to describe the world, rather than creating or transforming substances.

With the development of atomic theory and a better understanding of the nature of matter came a need to organize the known elements and a search for commonality between chemical species. In the mid– to late– nineteenth century, Dmitri Mendeleev published a periodic table that not only systematically organized known elements, but predicted the existence of several others that would be discovered later in time, thereby securing its credibility. Since that time, the periodic table has undergone some minor organizational changes, but most chemistry students can still recognize the original pattern described by Mendeleev.

Modern chemistry has come a long way from the roots of alchemy, but there are still many exciting challenges in need of bright new chemists to resolve. A few notable discoveries in modern chemistry and chemical physics include the creation of synthetic elements via radiochemical methods, recognition, and implementation of catalytic methods for achieving chemical reactions, development of the quantum mechanical theory of the atom, the discovery and advancement of computational chemistry, and the astounding advances in analytical methods. Today, chemists play crucial roles in addressing many socially important questions, from developing methods to duplicate rare and valuable products available in nature, to improving sensitivity and developing new analytical techniques to improve animal or environmental health, to discovering more environmentally friendly methods for making existing and new chemical products, to inventing new methods for harvesting and storing energy, and to managing our global greenhouse gases. Chemists now work in one or more of the traditional subdisciplines (organic, inorganic, analytical, or physical) or combine their studies with another science to work in an interdisciplinary field. They are often part of large collaborations of scientists from varied disciplines and backgrounds working on a common problem from different approaches. Chemists are also involved in automotive pigments and coatings, the tire and rubber industry, the glass science community, and many other areas/groups whose work is integral to cars and their production.

Chemistry in cars

Whether you are an auto enthusiast wanting to know more about the science behind your favorite ride, a chemist wanting to know more about the parts under the hood of your transportation to work, or a student

interested in practical applications of science, we think that you will be able to find something of interest about both chemistry and cars in this book.

We start in Chapter 1 with a discussion of gases, one of the earliest interests in modern chemistry and one of the first ideas that prompted us to write this book. Gases are essential inputs and outputs of a combustion engine, and their properties make it possible for us to have comfortable suspensions, inflated tires, cushioning foams, air bags, and climate control. One of the great things about gases is that you probably already have a basic understanding of the fundamental behavior of gases developed through your own experiences. Knowing that a hot-air balloon rises because its air is less dense than the atmosphere translates into knowing that a cold-air intake on a car can increase the amount of oxygen available for combustion in your car's engine.

In Chapter 2, we delve into the fundamental reaction that occurs in every internal combustion engine: hydrocarbon combustion. Building on the gas laws, we can describe the physical and chemical processes that occur in four-stroke gasoline and diesel engines. Additionally, we discuss ways of describing the complex fuel mixture known as gasoline, the energy released during combustion, the ways to improve engine efficiency and power (such as turbochargers and superchargers), and alternatives to petroleum-derived fuels.

Chapter 3 continues our discussion of combustion and brings to light a series of other important automotive reactions called oxidationreduction (REDOX) reactions. Combustion itself is a REDOX reaction that is revisited here, and we explore other reactions, including the basis for the operation of a battery, catalytic converters, and the dreaded rusting of a classic car. Current hybrid electric vehicles would not be possible without past advances in battery chemistry, and research in the fields of battery improvement and hydrogen fuel cell technology are going strong today. Both require significant knowledge of REDOX and materials chemistry.

Intermolecular forces, the interactions that attract similar molecules together, are at the heart of Chapter 4. As in the case of gas laws, you probably have many prior experiences that prepare you for understanding this topic. Just as oil and vinegar (an aqueous organic acid) separate in salad dressing, wax and other organic coatings repel water from your car. Intermolecular forces are also essential to describe the behavior and value of such diverse products as engine oil, gasoline additives, and detergents.

In Chapter 5, we build upon the energetic concepts introduced in our discussion of combustion and discuss ways of managing the temperature of critical automobile components and systems, including you, the driver. This chapter combines ideas from previous chapters, such as energy, thermochemistry, solutions, and intermolecular forces.

Chapter 6 covers the materials chemistry of the car, which helps us understand various components such as plastics, rubbers, composites, and alloys. We discuss polymers and rubber chemistry that build upon the elements of organic chemistry presented earlier and present a more detailed look at the what and why of automotive alloys. We end this chapter with a discussion of hydrogen fuel cells and some of the chemistry roadblocks that must be overcome before vehicles powered by these devices can become a safe and reliable mode of transportation.

Chapter 7 deals with the ways that light interacts with your car. We discuss how light of various energies interacts with the molecules of your car, and we use these ideas to explore paints and the light-based degradation of plastics and other polymers. We also cover the light that your car generates in headlamps and taillights. You have probably seen advances in domestic light bulbs in recent years, and car headlights and taillights have benefited from this new technology to generate clearer, brighter, and longer lasting interior and exterior lighting.

Perhaps our greatest motivation for writing this book is that the car represents an ideal and untapped medium for engaging with, exploring, and building excitement about the science of chemistry to STEMfocused* high school, technical school, and college students of all ages. For example, cars can be used to tie together the material presented in a typical undergraduate chemistry curriculum, making car chemistry an ideal topic for a synthesis-type (as defined in Bloom's taxonomy) college capstone course. Faculty and students interested in this avenue are encouraged to use this book as a foundation for developing broader questions about car chemistry and/or to explore topics in this book independently and in greater detail, leading to more complex calculations, discussion of more intricate reactions and reaction mechanisms, etc. Ideas for helping make this book function in that setting can be found in Appendix E. At the same time, cars have great general appeal and can easily be used to teach chemistry to upper-level high-school students and beginning college students and inspire them/you to pursue chemistry or STEM-related goals. From these perspectives, the book is intended either as the core material for a collegiate outreach summer program, as a source of real-world examples for college faculty to use in the classroom, or as a topic of personal interest.

The checkered flag

Our primary objectives in this text are to help the novice car user understand cars through chemical principles, to help teach the novice chemist basic chemical principles and their value in the context of cars, and to help upper-level chemists synthesize the knowledge they have gained and examine one way it manifests in the real world. A secondary goal of

* Science, technology, engineering, and mathematics.

the book is to increase public interest in the chemical sciences, and a third is to introduce a deeper understanding of cars and a passion for them in our readers. We hope that when you finish the book, you will be able to describe and discuss a car in much more detail than you could before reading the text. At the same time, we expect that you will be able to intelligently discuss chemical issues related to the car, perhaps using cars as a means to engage others about the exciting science of chemistry. More specific learning outcomes have been provided at the beginning of each section to help you monitor your own learning progress. We also hope that when you finish the text, you will have developed a deeper appreciation for both chemistry and your car. Enjoy the book!

chapter one

The properties and behavior of gases

Gases and gas-phase chemistry play very important roles in the world around us and critical roles in several important systems in cars. Gases are often used in shock absorbers and struts, are released during combustion reactions, are the basis of power generation in internal combustion engines, and are critical to the efficient operation of these engines from several perspectives. In this chapter, we will introduce some of the basic concepts used to understand gas behavior and apply these concepts to gain a greater understanding of the automobile. Since gases are so pervasive in the structure, function, and operation of cars, many of these concepts will be revisited in subsequent chapters.

1.1 *Kinetic molecular theory (KMT)*

Chemistry Concepts: thermodynamics, statistics, gas laws *Expected Learning Outcomes*:

- Explain the basic principles of KMT
- Identify the inaccurate assumptions of KMT

Gases are the least dense and most compressible state of matter. Because their density is so low, we often consider gas behavior without worrying about interactions between molecules. These intermolecular interactions significantly complicate our understanding of chemistry in liquids and solids. However, the low density of gases and the subsequent minor role of intermolecular forces in gas behavior allow us to gain significant insight about gases with relatively simple and straightforward models like the ideal-gas equation or the van der Waals gas equation. These models, particularly the ideal-gas equation, are based upon a well-established theory about gas behavior known as kinetic molecular theory (KMT).

Kinetic molecular theory provides a physical rationale that explains the empirical relationships (those observed in the laboratory) between gas temperature, pressure, volume, number of molecules, etc. It also helps to explain one of the major reaction theories in chemistry known as collision theory, which says that reactions occur when molecules collide with the appropriate energy and in an appropriate orientation. Kinetic molecular theory is relatively simple, and it is actually quite remarkable that five basic statements involving several unrealistic assumptions about gas behavior can make sense of well-known relationships between gas properties. Kinetic molecular theory says:

- 1. A gas is composed of molecules separated by distances much greater than the size of the molecules themselves. Because of these large separations, the gas molecules can be considered as points in space that take up no volume.
- 2. Gas molecules are in constant motion in random directions.
- 3. Gas molecules frequently collide, and all collisions are elastic (kinetic energy is conserved).
- 4. Gas molecules exert neither attractive nor repulsive forces on one another.
- 5. The average kinetic energy of a collection of gas molecules is proportional to the temperature in Kelvin (K). Any two gases at the same temperature will have the same average kinetic energy.

Kinetic molecular theory leads directly to the derivation of the ideal-gas equation (see Section 1.5), which is useful for understanding many gas phenomena, including the roles of gases in several fundamental aspects of the automobile.

Let us examine several aspects of kinetic molecular theory in greater detail. Both the first and fourth points are related to our earlier discussion of gas density. In fact, the statement "separated by distances much greater than the size of the molecules themselves" is actually a fancy way of saying "a low-density phase." In KMT, the low density is manifested not only as point four, which states that intermolecular forces are ignored in this model, but also that the volume of the gas particles themselves is ignored, which is the second half of point one. If the distance between particles is many orders of magnitude larger than the size of the particles themselves, then the volume occupied by the gas particles is very small. As we approach an infinite separation between the particles, whatever volume they truly occupy becomes negligible. The "kinetic" part of KMT comes from the second, third, and fifth statements. It seems logical that the particles will be in constant motion, since they have a very low mass and they would be a solid or liquid if the molecules were moving more slowly. The elasticity of collisions, item three, simply means that kinetic energy is not transformed into potential energy or any other form during collisions between gas molecules. Two molecules in an arbitrary collision may have different speeds before and after the collision, but the sum of their kinetic energies before and after will be identical. This also relates to the key point hidden in statement number five, namely that there is a distribution of molecular speeds in a gas. In the room you are in, there is a likelihood that some gas molecule is barely moving and that some

molecule is moving so fast that it hits each boundary in the room several times while you read this sentence. But there are an enormous number of gas molecules in any room. In fact, the number is so large that it is impossible to measure the kinetic energy of any individual particle at any point in time (for reference, a 215/55R16 tire holds $\approx 3.5 \times 10^{24}$ gas molecules when filled to a typical internal pressure of 35 psi at 25°C).

So how do we estimate the kinetic energy of gas particles? It turns out that, for gases, temperature is actually a measure of the average kinetic energy. We can't measure the temperature or kinetic energy of an individual molecule, though. A thermometer placed in a room is struck by a large number of gas particles in any given interval of time, meaning that temperature always gives the average kinetic energy of the gas molecules in a space. In fact, some relatively simple calculations reveal that at 273 K $(0^{\circ}C)$ and a pressure equivalent to 1 atm, nitrogen gas molecules experience on average ≈10¹⁰ (10 billion) collisions per second. It is also important in kinetic molecular theory to remember the difference between velocity and kinetic energy. The distribution of molecular velocities will change as the mass of the gas particles varies (recall that kinetic energy of a moving body is proportional to the mass times the velocity squared), but the fifth point indicates that the total kinetic energy is always directly proportional to the temperature. Essentially, a heavy body and a light body at high temperature have the same high kinetic energy; however, the heavy body will be moving with lower velocity, since it possesses greater mass. This fifth point also illustrates one of the basic tenets of statistical mechanics, that the number of entities in a chemical system is always so large that we observe weighted averages when we measure physical properties.

As noted earlier, many of the statements in kinetic molecular theory involve assumptions that are physically unrealistic. For example, gas molecules do have a real size and take up some of the volume in a container, in contrast to statement one. It is also unlikely that every collision between gas molecules is elastic. Some energy may be converted to another form, such as molecular rotation or vibration rather than translational energy. Statement four is certainly not true in the case of large molecules or high gas densities. For example, large noble gas molecules can be observed to pair in molecular dynamics simulations of gas behavior, presumably due to strong dispersion forces, which are an intermolecular attraction that is directly proportional to the size of the molecule (see Chapter 4). However, removing many of the assumptions that seem unreasonable actually cause very small changes in the relationships predicted by the ideal-gas equation and kinetic molecular theory. For example, the van der Waals equation eliminates the assumption that the gas particles have no volume with a volume correction term and acknowledges molecular interactions in an interaction correction, both of which involve empirically determined constants. In both cases, these corrections produce significant variations

only for large gas molecules and high gas densities, meaning the ideal-gas equation is more than adequate under many conditions.

While kinetic molecular theory may seem to have little to do with a car, it actually explains the source of power in conventional internal combustion engines. As we will discuss in Chapter 2, burning a fossil fuel converts the chemical energy stored within the chemical structure to kinetic energy of the gas molecules and what is termed *work of expansion*. It is partly the kinetic energy of the gas-phase molecules that pushes on the piston, turning the crankshaft, and ultimately turning the wheels. The gas laws and KMT are the heart that drives the internal combustion engine.

1.2 Tires, pressure, and pressure units

Chemistry Concepts: dimensional analysis, kinetic molecular theory, statistical thermodynamics

Expected Learning Outcomes:

- Understand how gas pressure is related to the motion of gasphase molecules
- Define pressure and use dimensional analysis to convert between common units
- Use tire pressure to explain the difference between gauge and absolute pressure measurements
- Use the behavior of tires to prove that a relationship exists between temperature and pressure of gases

Have you ever wondered why you need to add air to your tires in the winter or release air in the summer to maintain ideal tire pressure? Or have you observed that the pressure in your tires is higher after you go for a drive than before you left? Or heard race drivers and teams talking over a pit radio about warming up tires on race day? All of these behaviors relate directly to the concept of pressure, specifically the relationship between temperature and pressure that is implied in kinetic molecular theory, which is the subject of this section.

To begin, we must define pressure, which is the amount of force exerted per unit area. You can experience pressure yourself simply by standing flat on your feet, then standing on your tiptoes. The pull on your body due to gravity hasn't changed, but you are concentrating that force over different areas. The smaller area supporting your body weight when on your tiptoes increases the pressure on your toes, and the pain signal sent by your nerves to your brain are a direct indicator of that change in pressure. In the case of gas-rich systems such as our atmosphere, the force generating pressure arises from collisions between the gas molecules and the boundaries of an object rather than the downward pull of gravity in our tiptoe example. One can easily observe that gas pressure does not have a direction. In fact, if it did and gravity were solely responsible for gas pressure, we would likely all be flat due to the weight of the atmosphere crushing down upon us. This nondirectionality of gas pressure relates back to kinetic molecular theory and the fact that particles are constantly in motion in random directions, meaning that the likelihood of being hit by a particle on the side of your foot is the same as being hit by a particle directly on top of your head. Statistical mechanics tells us that when there are a large number of particles, as there always are in macroscopic chemical systems, a large number of collisions occur at every point on a surface in any one observable interval of time, supporting the idea that pressure is relatively constant in all directions.

Kinetic molecular theory and the definition of pressure also tell us that there must be some sort of relationship between gas pressure and gas temperature. We know that force is mass times acceleration, and it is known that acceleration is the derivative of velocity. From Section 1.1, we know that kinetic energy is also proportional to mass and velocity (velocity squared, to be precise). Thus, pressure and kinetic energy both depend in some way on mass and velocity, and if KMT tells us that temperature is a measure of the average kinetic energy in a system of gas particles, there must be some link between gas pressure and temperature. This has been demonstrated in the laboratory and is known as Gay-Lussac's law, named for Joseph Gay-Lussac, who first observed the effect in 1809.

$$\frac{p_1}{T_1} = \frac{p_2}{T_2}$$

It is imperative that in Gay-Lussac's law (and all of the other gas laws involving temperature) that you use absolute temperature in Kelvin (K) when you perform a calculation. Gay-Lussac's law is the first of many "simple" gas laws we will explore in the rest of this chapter, and it explains quite a bit about tires and tire pressures. For example, "warming up" the tires in a race car is in part directly related to Gay-Lussac's law, as we will see in the following discussion.

There are many different units that can be used to discuss pressure, and the most appropriate unit is often determined by the specific situation under consideration. For example, if we are discussing pressures deep inside the Earth, the pressure is so high that it would not be very useful to use a pressure unit with a small increment such as pounds per square inch (psi). Use of psi in geological systems would necessitate the use of very large numbers that are difficult to interpret, and there is no need for that type of precision. Shallow geological pressures are often better considered in kilobars, or kbar (1 kbar is roughly 1000 atm, or equivalent to 1000 times the pressure exerted by our atmosphere at 273 K at sea level). In the case of cars, the pressures we are working with are rarely more than a few atmospheres, which make a pressure unit with a small increment like psi a reasonable choice due to the finer precision with which pressure can be measured. The common units of pressure and their equivalencies with respect to atmospheric pressure are listed in Table 1.1.

A discussion of pressure-measuring devices can easily be found on the Internet or in a general chemistry or general physics textbook. However, an issue related to pressure measurement that is less commonly discussed in chemistry is whether the pressure due to the atmosphere is included in the measurement or not (Figure 1.1). Clearly, if a tire indicates it is to be inflated to 35 psi, you need to know if this is 35 psi beyond atmospheric pressure or if it is a total of 35 psi in the tire, and you need to know whether your pressure gauge accounts for atmospheric pressure or not. If you make a mistake, you could end up

una Equivalencies				
Pressure unit	Symbol	Equivalence (with respect to 1 atm)		
Atmosphere	atm	1		
Torr	torr	760		
Millimeters of mercury	mm Hg	760		
Bar	bar	1.01		
Kilopascals	kPa	101.3		
Pounds per square inch	psi	14.7		

Table 1.1 Common Pressure Units, their Symbols, and Equivalencies



Figure 1.1 Difference between gauge (top) and absolute (bottom) pressure.

over- or underinflating your tire by about 50%! Underinflation reduces fuel economy and increases the chance that the tire will burst under normal driving conditions. In chemistry, physics, and engineering, abso*lute pressures* are those that include the pressure due to the atmosphere in their value. For example, to fill a tire to 35 psia (psi absolute), you will need to add 35 psi – 14.7 psi = 20.3 psi to the tire. Gauge pressures are those that exclude the contribution due to the atmosphere, and it is gauge pressure that we commonly find written on the side of tires. When you place a tire on a wheel, the tire already holds gas from the atmosphere. As we now know, those gas particles should have the same kinetic energy as those in the atmosphere and collide with the tire walls in all directions, i.e., the tire must have close to 14.7 psi of pressure already. However, that tire is considered "flat," and the gas inside the tire will not support much (if any) of the weight of the vehicle. If you fill that tire to 35 psig (psi gauge), it will really contain 14.7 psi + 35 psi = 49.7 psi of total pressure, and the gas inside the tire will nicely support the weight of the vehicle. Nearly all tire gauges read gauge pressure. You can verify that your pressure gauge reads gauge or absolute pressure by noting the pressure before placing it on the tire stem: If it reads zero, the device measures gauge pressure. If it reads a value between 14 and 15 psi, it displays absolute pressure. It is very important when using the simple and combined ideal-gas laws that you use absolute pressures in your calculations.

Car tires represent an ideal example of the pressure/temperature relationship revealed in Gay-Lussac's law. In racing, drivers often turn their cars violently back and forth across the track behind the pace car before a green flag is waived. They also allow gaps to build between the car they are pursuing before the green flag, then slam on the gas and spin the drive wheels. If you are a fan of drag racing, you know that spinning the drive wheels before a race occurs routinely, with Pro-Stock, Funny Cars, and Top Fuel Dragsters all beginning the race with a significant burnout at the starting line, frictionally heating the drive tires via significant wheel spin. Formula-1 cars can often be observed in the paddock before qualifying or before a race with electric tire-warmers wrapping the wheels. In all of these cases, the drivers/teams are warming up their tires. Part of the reason for these preracing actions is surely to optimize the level of grip, or the coefficient of friction between the tire itself and the road surface, which is related to the "tackiness" of the rubber and the rubber chemistry as well as mechanical properties of the tire rubber. But some of it is also related to tire pressure. Let's say that your team filled your tires to 40 psia the night before a race when the temperature was 15°C (288 K). They move the tires out to the pit box in the morning, where they sit in the hot sun until they go on your car during the race. Perhaps the tires warm to 30°C (303 K) in