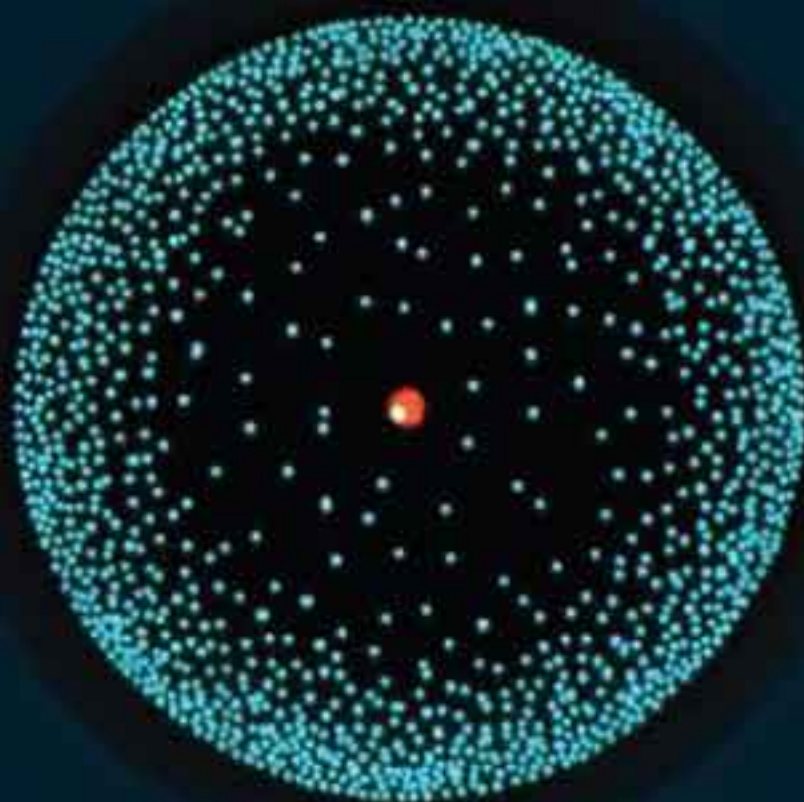


PHYSICAL CHEMISTRY

2E

DAVID W. BALL



Periodic Table of the Elements

1	MAIN GROUP METALS																TRANSITION METALS										METALLOIDS										NONMETALS																																																																																																																																																																																																																																																											
1	Hydrogen 1 H 1.0079																Uranium 92 U 238.0289										Atomic number										Symbol										Atomic weight																																																																																																																																																																																																																																																	
2	1A (1)																2A (2)																3A (13)																4A (14)																5A (15)																6A (16)																7A (17)																8A (18)																																																																																																																																																																															
2	Lithium 3 Li 6.941																Beryllium 4 Be 9.0122																Boron 5 B 10.811																Carbon 6 C 12.011																Nitrogen 7 N 14.0067																Oxygen 8 O 15.9994																Fluorine 9 F 18.9984																Neon 10 Ne 20.1797																																																																																																																																																																															
3	Sodium 11 Na 22.9898																Magnesium 12 Mg 24.3050																Aluminum 13 Al 26.9815																Silicon 14 Si 28.0855																Phosphorus 15 P 30.9738																Sulfur 16 S 32.066																Chlorine 17 Cl 35.4527																Argon 18 Ar 39.948																																																																																																																																																																															
4	Potassium 19 K 39.0983																Calcium 20 Ca 40.078																Scandium 21 Sc 44.9559																Titanium 22 Ti 47.867																Vanadium 23 V 50.9415																Chromium 24 Cr 51.9961																Manganese 25 Mn 54.9380																Iron 26 Fe 55.845																Cobalt 27 Co 58.9332																Nickel 28 Ni 58.6934																Copper 29 Cu 63.546																Zinc 30 Zn 65.38																Gallium 31 Ga 69.723																Germanium 32 Ge 72.61																Arsenic 33 As 74.9216																Selenium 34 Se 78.96																Bromine 35 Br 79.904																Krypton 36 Kr 83.80															
5	Rubidium 37 Rb 85.4678																Strontium 38 Sr 87.62																Yttrium 39 Y 88.9059																Zirconium 40 Zr 91.224																Niobium 41 Nb 92.9064																Molybdenum 42 Mo 95.96																Technetium 43 Tc (97.907)																Ruthenium 44 Ru 101.07																Rhodium 45 Rh 102.9055																Palladium 46 Pd 106.42																Silver 47 Ag 107.8682																Cadmium 48 Cd 112.411																Indium 49 In 114.818																Tin 50 Sn 118.710																Antimony 51 Sb 121.760																Tellurium 52 Te 127.60																Iodine 53 I 126.9045																Xenon 54 Xe 131.29															
6	Cesium 55 Cs 132.9055																Barium 56 Ba 137.327																Lanthanum 57 La 138.9055																Hafnium 72 Hf 178.49																Tantalum 73 Ta 180.9479																Tungsten 74 W 183.84																Rhenium 75 Re 186.207																Osmium 76 Os 190.23																Iridium 77 Ir 192.22																Platinum 78 Pt 195.084																Gold 79 Au 196.9666																Mercury 80 Hg 200.59																Thallium 81 Tl 204.3833																Lead 82 Pb 207.2																Bismuth 83 Bi 208.9804																Polonium 84 Po (208.98)																Astatine 85 At (209.99)																Radon 86 Rn (222.02)															
7	Francium 87 Fr (223.02)																Radium 88 Ra (226.0254)																Actinium 89 Ac (227.0278)																Rutherfordium 104 Rf (267)																Dubnium 105 Db (268)																Seaborgium 106 Sg (271)																Bohrium 107 Bh (272)																Hassium 108 Hs (270)																Meitnerium 109 Mt (276)																Darmstadtium 110 Ds (281)																Roentgenium 111 Rg (280)																Copernicium 112 Cn (285)																Ununtrium 113 Uut Discovered 2004																Ununquadium 114 Uuq Discovered 1999																Ununpentium 115 Uup Discovered 2004																Ununhexium 116 Uuh Discovered 1999																Ununseptium 117 Uus Discovered 2010																Ununoctium 118 Uuo Discovered 2002															

Note: Atomic masses are 2007 IUPAC values (up to four decimal places). Numbers in parentheses are atomic masses or mass numbers of the most stable isotope of an element.

Lanthanides
Actinides

Cerium 58 Ce 140.116	Praseodymium 59 Pr 140.9076	Neodymium 60 Nd 144.242	Promethium 61 Pm (144.91)	Samarium 62 Sm 150.36	Europium 63 Eu 151.964	Gadolinium 64 Gd 157.25	Terbium 65 Tb 158.9254	Dysprosium 66 Dy 162.50	Holmium 67 Ho 164.9303	Erbium 68 Er 167.26	Thulium 69 Tm 168.9342	Ytterbium 70 Yb 173.054	Lutetium 71 Lu 174.9668
Thorium 90 Th 232.0381	Protactinium 91 Pa 231.0359	Uranium 92 U 238.0289	Neptunium 93 Np (237.0482)	Plutonium 94 Pu (244.064)	Americium 95 Am (243.061)	Curium 96 Cm (247.07)	Berkelium 97 Bk (247.07)	Californium 98 Cf (251.08)	Einsteinium 99 Es (252.08)	Fermium 100 Fm (257.10)	Mendelevium 101 Md (258.10)	Nobelium 102 No (259.10)	Lawrencium 103 Lr (262.11)

Standard Colors for Atoms in Molecular Models

- carbon atoms
- hydrogen atoms
- oxygen atoms
- nitrogen atoms
- chlorine atoms

Physical Constants

Quantity	Symbol	Value	Unit
Speed of light in vacuum	c	2.99792458×10^8	m/s
Permittivity of free space	ϵ_0	$8.854187817 \times 10^{-12}$	C ² /J·m
Gravitation constant	G	6.673×10^{-11}	N·m ² /kg ²
Planck's constant	h	$6.62606876 \times 10^{-34}$	J·s
Elementary charge	e	$1.602176462 \times 10^{-19}$	C
Electron mass	m_e	$9.10938188 \times 10^{-31}$	kg
Proton mass	m_p	$1.67262158 \times 10^{-27}$	kg
Neutron mass	m_n	$1.67492735 \times 10^{-27}$	kg
Bohr radius	a_0	$5.291772083 \times 10^{-11}$	m
Rydberg constant	R	109737.31568	cm ⁻¹
Avogadro's constant	N_A	$6.02214199 \times 10^{23}$	mol ⁻¹
Faraday's constant	\mathcal{F}	96485.3415	C/mol
Ideal gas constant	R	8.314472	J/mol·K
		0.0820568	L·atm/mol·K
		0.08314472	L·bar/mol·K
		1.98719	cal/mol·K
Boltzmann's constant	k, k_B	$1.3806503 \times 10^{-23}$	J/K
Stefan-Boltzmann constant	σ	5.670400×10^{-8}	W/m ² ·K ⁴
Bohr magneton	μ_B	$9.27400899 \times 10^{-24}$	J/T
Nuclear magneton	μ_N	$5.05078317 \times 10^{-27}$	J/T

Source: Excerpted from Peter J. Mohr and Barry N. Taylor, CODATA Recommended Values of the Fundamental Physical Constants, *J. Phys. Chem. Ref. Data*, vol. 28, 1999.



PHYSICAL CHEMISTRY SECOND EDITION



PHYSICAL CHEMISTRY

SECOND EDITION

David W. Ball

Cleveland State University

With contributions by

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University of North Carolina, Chapel Hill



Australia • Brazil • Mexico • Singapore • United Kingdom • United States

Physical Chemistry, Second Edition

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IN MEMORY OF MY FATHER



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Preface

There is an old joke that the thing a first-term politician wants the most is a second term. Something similar can be said for authors of first-edition textbooks: What they want the most is a second edition. A second edition is, after all, a reaffirmation that the author's vision is worth another round of effort, time, and expense—not just by the author, but by editors and editorial assistants and reviewers and accuracy checkers and ancillary writers and more. It's also a reaffirmation that there are adopters in the community actually using the textbook, for no reputable company would put forth the effort, time, and expense if the first edition wasn't being used.

A second edition is also a chance for reflection on the overall philosophy of the textbook, and you know what? In this case it hasn't changed. Even though new textbooks have been published since the first edition of this book appeared, the market still cries out for a *textbook*, not an *encyclopedia*, of physical chemistry, one that speaks to undergraduate students at their level and not the level of graduate students studying for their cumulative exams.

There's evidence that the first edition did that. I've gotten dozens of emails from students with positive feedback about the text, complimenting it on its ability to communicate physical chemistry concepts to them, the ultimate users. Think of that: Students making positive comments about a physical chemistry text! It seems that the philosophy of the first edition struck a chord with those who are the primary beneficiaries of a textbook.

A second edition also provides a chance for improvement, for what first edition is perfect? Such was the case here. In the second edition, there are several new features:

- A significantly larger number of end-of-chapter exercises, providing additional practice on existing and new topics. Overall, chapter exercises have been expanded by more than 50%, giving instructors and students more flexibility in exercising their physical chemistry muscles.
- New emphasis on molecular-level phenomenological thermodynamics. Granted, classical thermodynamics is based on the behavior of bulk materials. But as chemists, we should never forget that matter is composed of atoms and molecules, and any opportunity to relate the behavior of matter to atoms and molecules reinforces the fundamentals of chemistry.
- Running commentaries in many of the worked example in each chapter. The commentaries, placed in the margin, give additional hints or insights to working out the examples as a way to improve student comprehension.
- A “Key Equations” section to summarize the important equations of the chapter and improve student learning.

Of course, the second edition also benefits from several years of my actually using the first edition in class, seeing what works and what doesn't, and ultimately benefiting from my own students' feedback as they learn the subject.

Acknowledgments

Thanks to Chris Simpson, acquiring editor at Cengage Learning's chemistry group, for his support of a second edition. Thanks also to Liz Woods, content developer for chemistry, who ultimately got into a daily exchange with me (via several media!) as the project progressed, keeping me on track, answering my questions, and providing all sorts of advice. Thanks to Janice Yi, photo research manager at QBS Learning, for her diligent efforts in finding new and replacement photos, as well as Jared Sterzer, senior project manager at PreMediaGlobal, for his production services. Finally, I'd be remiss if I didn't mention Shelly Tommasone. Shelly was the local sales representative who introduced this project to her editors years ago, ultimately becoming listed as Signing Representative for the first edition. Since that time, we've kept in touch regularly as our careers have evolved. She is no longer with Cengage, but she remains a recipient of regular email updates and is a partner in occasional dinner dates to celebrate the success of the text. Shelly, this textbook is all your fault, and I thank you for it!

Several colleagues made important contributions to the evolution of the content. Tom Baer of the Chemistry Department of the University of North Carolina contributed quite a bit of suggested text regarding the molecular basis of thermodynamics, especially in Chapters 1–4. His perspective on the topic greatly expanded the overall vision of the thermodynamics section of the book, and I am grateful for his point of view and his willingness to share it. Any misrepresentation of this topic is, however, my own. Mark Waner of John Carroll University provided an in-depth analysis of some of the spectroscopy chapters, allowing me to benefit from experiences other than my own. Again, any errors that exist are mine. Mark also looked over the page proofs, and I appreciate his double duty on this project. Thanks to Jorg Woehl of the University of Wisconsin – Milwaukee for constructing the Student Solutions Manual and to Mary Turner at Maryville College for writing the Instructor Solutions Manual, as these ancillaries can be a hugely useful tool in student learning (if used properly).

Thanks to everyone who gave me feedback about the first edition, both faculty and students (*especially* students!). Perhaps it was a mistake listing my email address in the first edition—it made it all too easy to contact me with comments about the book, both positive and negative. The positive comments are appreciated; I'm happy knowing that this book is making a useful contribution to your physical chemistry experience. The negative comments were divided into two categories: constructive comments and unconstructive ones. The constructive comments have, hopefully, been incorporated into the second edition to improve it, and I thank everyone for their comments. The unconstructive comments ... well, there's a reason there's a "trash" folder in most email clients.

Major revision of the first edition started when I was serving as a Distinguished Visiting Professor at the U.S. Air Force Academy in Colorado Springs, Colorado. Thanks to the CSU College of Sciences and Health Professions for supporting a leave of absence so I could spend a year at USAFA. Thanks also to the faculty and staff, both military and civilian, of the Chemistry Department at USAFA for their friendship, camaraderie, professionalism, and support. It was an experience that I remember fondly and will never forget.

Finally, thanks as always to my immediate family: wife Gail and sons Stuart and Alex. As time goes on, it gets harder and harder to express my appreciation for the support they've given me over the years. To paraphrase Isaac Asimov, gratitude is best when it doesn't evaporate itself in empty phrases, so: thanks, family, for everything.

David W. Ball
Cleveland, Ohio

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Gases and the Zeroth Law of Thermodynamics

Much of physical chemistry can be presented in a developmental manner: One can grasp the easy ideas first and then progress to the more challenging ideas, which is similar to how these ideas were developed in the first place. Two of the major topics of physical chemistry—thermodynamics and quantum mechanics—lend themselves naturally to this approach.

In this first chapter on physical chemistry, we revisit a simple idea from general chemistry: gas laws. Gas laws—straightforward mathematical expressions that relate the observable properties of gases—were among the first quantifications of chemistry, dating from the 1600s, a time when the ideas of alchemy ruled. Gas laws provided the first clue that quantity, *how much*, is important in understanding nature. Some gas laws like Boyle's, Charles's, Amontons's, and Avogadro's laws are simple mathematically. Others can be very complex.

Chemistry understands that matter is composed of atoms and molecules, so we will also need to understand how physical chemical ideas relate to these particles; that is, we can take a molecular approach to the topic. We will adopt this approach many times in the next few chapters.

In chemistry, the study of large, or macroscopic, systems involves thermodynamics; in small, or microscopic, systems, it can involve quantum mechanics. In systems that change their structures over time, the topic is kinetics. But they all have basic connections with thermodynamics. We will begin the study of physical chemistry with thermodynamics: the study of heat and work in chemistry.

1.1 Synopsis

This chapter starts with some definitions, an important one being the thermodynamic *system*, and the macroscopic variables that characterize it. If we are considering a gas in our system, we will find that various mathematical relationships are used to relate the physical variables that characterize this gas. Some of these relationships—"gas laws"—are simple but inaccurate. Other gas laws are more complicated but more accurate. Some of these more complicated gas laws have experimentally determined parameters that are tabulated to be looked up later, and they may or may not have physical justification. We develop some relationships (mathematical ones) using some simple calculus. These mathematical manipulations will be useful in later chapters as we get deeper into thermodynamics. Finally, we introduce thermodynamics from a molecular point of view, because an acceptable model of thermodynamics must connect to the atomic theory of matter.



- 1.1 Synopsis
- 1.2 System, Surroundings, and State
- 1.3 The Zeroth Law of Thermodynamics
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- 1.5 Partial Derivatives and Gas Laws
- 1.6 Nonideal Gases
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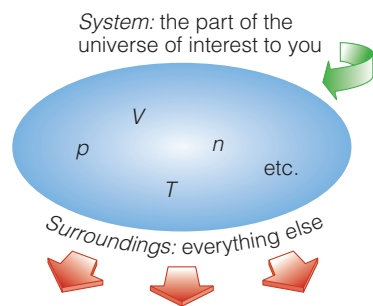


FIGURE 1.1 The system is the part of the universe of interest, and its state is described using macroscopic variables like pressure, volume, temperature, and moles. The surroundings are everything else. As an example, a system could be a refrigerator and the surroundings could be the rest of the house (and the surrounding space).

1.2 System, Surroundings, and State

Imagine you have a container holding some material of interest to you, as in Figure 1.1. The container does a good job of separating the material from everything else. Imagine, too, that you want to make measurements of the properties of that material, independent from the measurements of everything else around it. The material of interest is defined as the *system*. The “everything else” is defined as the *surroundings*. These definitions have an important function because they specify what part of the universe we are interested in: the system. Furthermore, using these definitions, we can immediately ask other questions: What interactions are there between the system and the surroundings? What is exchanged between the system and the surroundings?

For now, we consider the system itself. How do we describe it? That depends on the system. For example, a biological cell is described differently from the interior of a star. But for now, let us pick a simple system, chemically speaking.

Consider a system that consists of a pure gas. How can we describe this system? Well, the gas has a certain volume, a certain pressure, a certain temperature, a certain chemical composition, a certain number of atoms or molecules, a certain chemical reactivity, and so on. If we can measure, or even dictate, the values of those descriptors, then we know everything we need to know about the properties of our system. We say that we know the *state* of our system.

If the state of the system shows no tendency to change, we say that the system is *at equilibrium* with the surroundings.* The equilibrium condition is a fundamental consideration of thermodynamics. Although not all systems are at equilibrium, we almost always use equilibrium as a reference point for understanding the thermodynamics of a system.

There is one other characteristic of our system that we ought to know: its energy. The energy is related to all of the other measurables of our system (as the measurables are related to each other, as we will see shortly). The understanding of how the energy of a system relates to its other measurables is called *thermodynamics* (literally, “heat movement”). Although thermodynamics (“thermo”) ultimately deals with energy, it deals with other measurables too, and so the understanding of how those measurables relate to each other is an aspect of thermodynamics.

How do we define the state of our system? To begin, we focus on its physical description, as opposed to the chemical description. We find that we are able to describe the macroscopic properties of our gaseous system using only a few observables: They are the system’s pressure, temperature, volume, and amount of matter (see Table 1.1). These measurements are easily identifiable and have well-defined units. Volume has common units of liter, milliliter, or cubic centimeter. [The cubic meter is the *Système International* (SI) unit of volume but these other units are commonly used as a matter of convenience.] Pressure has common units of atmosphere, torr, pascal (1 pascal = 1 N/m² and is the SI unit for pressure), or bar. Volume and pressure also have obvious minimum values against which a scale can be based. Zero volume and zero pressure are both easily definable. Amount of material is similar. It is easy to specify an amount in a system, and having nothing in the system corresponds to an amount of zero.

The temperature of a system has not always been an obvious measurable of a system, and the concept of a “minimum temperature” is relatively recent. In 1603, Galileo was the first to try to quantify changes in temperature with a water thermometer. Gabriel Daniel Fahrenheit devised the first widely accepted numerical temperature scale after

*Equilibrium can be a difficult condition to define for a system. For example, a mixture of H₂ and O₂ gases may show no noticeable tendency to change, but it is not at equilibrium. It’s just that the reaction between these two gases is so slow at normal temperatures and in the absence of a catalyst that there is no perceptible change.

TABLE 1.1 Common state variables and their units

Variable	Symbol	Common units
Pressure	p	Atmosphere, atm (= 1.01325 bar)
		Torricelli, torr (= $\frac{1}{760}$ atm)
		Pascal (SI unit)
		Pascal, Pa (= $\frac{1}{100,000}$ bar)
		Millimeters of mercury, mmHg (= 1 torr)
Volume	V	Cubic meter, m ³ (SI unit)
		Liter, L (= $\frac{1}{1000}$ m ³)
		Milliliter, mL (= $\frac{1}{1000}$ L)
		Cubic centimeter, cm ³ (= 1 mL)
Temperature	T	Degrees Celsius, °C, or kelvins, K
		°C = K – 273.15
Amount	n	Moles (can be converted to grams using molecular weight)

developing a successful mercury thermometer in 1714, with zero set at the lowest temperature he could generate in his lab. Anders Celsius developed a different scale in 1742 in which the reference points were set at the freezing and boiling points of water.* These are *relative*, not *absolute*, temperatures. Warmer and colder objects have a temperature value in these relative scales that is decided with respect to these and other defined points in the scale. In both cases, temperatures lower than zero are possible and so the temperature of a system can sometimes be reported as a negative value. Volume, pressure, and amount cannot have a negative value, and later we define a temperature scale that cannot, either. Temperature is now considered a well-understood variable of a system.

1.3 The Zeroth Law of Thermodynamics

Thermodynamics is based on a few statements called *laws* that have broad application to physical and chemical systems. As simple as these laws are, it took many years of observation and experimentation before they were formulated and recognized as scientific laws. Three such statements that we will eventually discuss are the first, second, and third laws of thermodynamics.

However, there is an even more fundamental idea that is usually assumed but rarely stated because it is so obvious. Occasionally, this idea is referred to as the zeroth law of thermodynamics, because even the first law depends on it. It has to do with one of the variables that was introduced in the previous section, temperature.

What is temperature? *Temperature is a measure of how much kinetic energy the particles of a system have.* The higher the temperature, the more energy a system has, all other variables defining the state of the system (volume, pressure, and so on) being the same. Because thermodynamics is in part the study of energy, temperature is a particularly important variable of a system.

We must be careful when interpreting temperature, however. Temperature is *not* a form of energy. Instead, it is a parameter used to compare amounts of energy of different systems.

*Curiously, Celsius originally set his zero point at the boiling point of water, and 100 at the freezing point. The year after Celsius died, 1744, Swedish botanist Carolus Linneaus reversed it, so the higher temperature had the higher numerical value. Until 1948, the scale was preferentially called the centigrade scale, but “Celsius scale” is now considered the proper term.

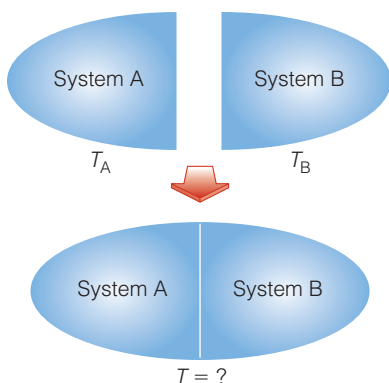


FIGURE 1.2 What happens to the temperature when two individual systems are brought together?

Consider two systems, A and B, in which the temperature of A is greater than the temperature of B (Figure 1.2). Each is a *closed system*, which means that matter cannot move in or out of each system but energy can. The state of each system is defined by quantities like pressure, volume, and temperature. The two systems are brought together and physically joined but kept separate from each other, as shown. For example, two pieces of metal can be brought into contact with each other, or two containers of gas can be connected by a closed stopcock. Despite the connection, matter will not be exchanged between the two systems or with the surroundings.

What about their temperatures, T_A and T_B ? What is always observed is that energy transfers from one system to another. As energy transfers between the two systems, the two temperatures change until the point where $T_A = T_B$. At that point, the two systems are said to be at *thermal equilibrium*. Energy may still transfer between the systems, but the *net* change in energy will be zero and the temperature will not change further. The establishment of thermal equilibrium is independent of the system size. It applies to large systems, small systems, and any combination of large and small systems.

The energy transferred from one system to another due to temperature differences is called *heat*. We say that heat has flowed from system A to system B. Further, if a third system C is in thermal equilibrium with system A, then $T_C = T_A$ and system C must be in thermal equilibrium with system B also. This idea can be expanded to include any number of systems, but the basic idea illustrated by three systems is summed up by a statement called the zeroth law of thermodynamics:

The zeroth law of thermodynamics: If two systems (of any size) are in thermal equilibrium with each other and a third system is in thermal equilibrium with one of them, then it is in thermal equilibrium with the other also.

This is obvious from personal experience, and fundamental to thermodynamics.

The zeroth law is based on our experience and at first glance may seem obvious. However, the consequences of this “obvious” statement can be—will be—quite profound. Scientific laws are not proven. We accept them as correct because they have never been observed to be violated.

EXAMPLE 1.1

Consider three systems at 37.0°C : a 1.0-L sample of H_2O , 100 L of neon gas at 1.00 bar pressure, and a small crystal of sodium chloride, NaCl . Comment on their thermal equilibrium status in terms of the varying sizes of the systems. Will there be any net transfer of energy if they are brought into contact?

SOLUTION

Thermal equilibrium is dictated by the temperature of the systems involved, not the sizes. Because all systems are at the same temperature [that is, $T(\text{H}_2\text{O}) = T(\text{Ne}) = T(\text{NaCl})$], they are all in thermal equilibrium with each other. To invoke the zeroth law, if the water is in thermal equilibrium with the neon and the neon is in thermal equilibrium with the sodium chloride, then the water is in thermal equilibrium with the sodium chloride. No matter what the relative sizes of the systems are, there should be no net transfer of energy between any of the three systems.

The zeroth law introduces a new idea. One of the variables that defines the state of our system (the *state variables*) changes its value. In this case, the temperature has changed. We are ultimately interested in how the state variables change and how these changes relate to the energy of our system.

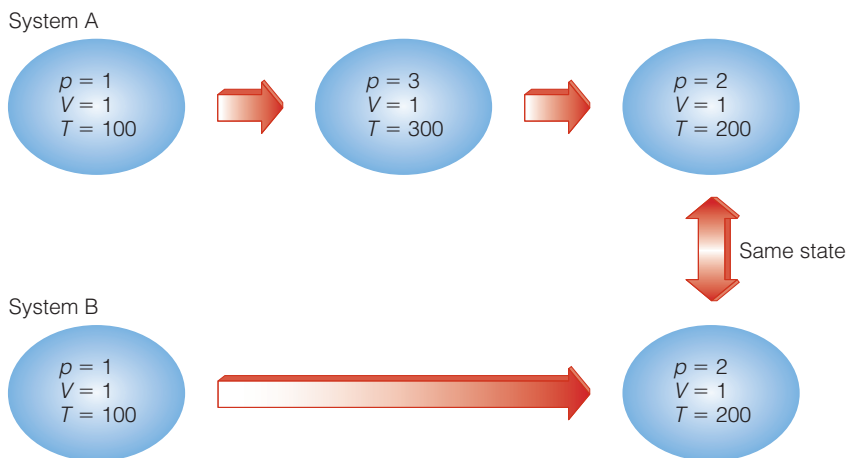


FIGURE 1.3 The state of a system is determined by what the state variables *are*, not how the system got there. In this example, the initial and final states of the two Systems (A) and (B) are the same, regardless of the fact that System (A) was higher in temperature and pressure in the interim.

The final point with respect to the system and its variables is the fact that the system does not remember its previous state. The state of the system is dictated by the values of the state variables, not their previous values or how they changed. Consider the two systems in Figure 1.3. System A goes to a higher temperature before settling on $T = 200$ temperature units. System B goes directly from the initial conditions to the final conditions. Therefore, the two states are the same. It does not matter that the first system was at a higher temperature; the state of the system is dictated by what the state variables are, not what they were, or how they got there.

1.4 Equations of State

Phenomenological thermodynamics is based on *experiment*, on measurements that you might make in a lab, garage, or kitchen. For example, for any fixed amount of a pure gas, two state variables are pressure, p ,* and volume, V . Each can be controlled independently of each other. The pressure can be varied while the volume is kept constant, or vice versa. Temperature, T , is another state variable that can be changed independently from p and V . However, experience has shown that if a certain pressure, volume, and temperature were specified for a particular sample of gas at equilibrium, then all measurable, macroscopic properties of that sample have certain specific values. That is, these three state variables determine the complete state of our gas sample. Notice that we are implying the existence of one other state variable: amount. The amount of material in the system, designated by n , is usually given in units of moles.

Further, arbitrary values for all four variables p , V , n , and T are not possible simultaneously. Again, experience (that is, experiment) shows this. It turns out that only two of the three state variables p , V , and T are truly independent for any given amount of a gas. Once two values are specified, then the third one must have a certain value. This means that there is a mathematical equation into which we can substitute for two of the variables and calculate what the remaining variable must be. Say such an equation requires that we know p and V and lets us calculate T . Mathematically, there exists some function F such that

$$F(p, V) = T \quad \text{at fixed } n \quad (1.1)$$

*The preferred IUPAC symbol for pressure is p , not P , which stands for power.

where the function is written as $F(p, V)$ to emphasize that the variables are pressure and volume, and that the outcome yields the value of the temperature T . Equations like equation 1.1 are called *equations of state*. One can also define equations of state that yield p or V instead of T . In fact, many equations of state can be algebraically rearranged to yield one of several possible state variables.

The earliest equations of state for gases were determined by Boyle, Charles, Amontons, Avogadro, Gay-Lussac, and others. We know these equations as the various *gas laws*. In the case of Boyle's gas law, the equation of state involves multiplying the pressure by the volume to get a number whose value depended on the temperature of the gas:

$$p \cdot V = F(T) \quad \text{at fixed } n \quad (1.2)$$

whereas Charles's gas law involves volume and temperature:

$$\frac{V}{T} = F(p) \quad \text{at fixed } n \quad (1.3)$$

Avogadro's law relates volume and amount, but at fixed temperature and pressure:

$$V = F(n) \quad \text{at fixed } T, p \quad (1.4)$$

In the above three equations, if the temperature, pressure, or amount were kept constant, then the respective functions $F(T)$, $F(p)$, and $F(n)$ would be constants. This means that if one of the state variables that can change does, the other must also change in order for the gas law to yield the same constant. This leads to the familiar predictive ability of the above gas laws using the forms

$$p_1 V_1 = F(T) = p_2 V_2 \quad \text{or} \quad p_1 V_1 = p_2 V_2 \quad (1.5)$$

Similarly, using equations 1.3 and 1.4, we can get

$$\frac{V_1}{T_1} = \frac{V_2}{T_2} \quad (1.6)$$

$$\frac{V_1}{n_1} = \frac{V_2}{n_2} \quad (1.7)$$

All three gas laws involve volume, and they can be rewritten as

$$V \propto \frac{1}{p}$$

$$V \propto T$$

$$V \propto n$$

where the symbol \propto means "is proportional to." We can combine the three proportionalities above into one:

$$V \propto \frac{nT}{p} \quad (1.8)$$

Because p , V , T , and n are the only four independent state variables for a gas, the proportionality form of equation 1.8 can be turned into an equality by using a proportionality constant:

$$V = R \cdot \frac{nT}{p} \quad (1.9)$$

where we use R to represent the proportionality constant. This equation of state relates the static (unchanging) values of p , V , T , and n , not changes in these values. It is usually rewritten as

$$pV = nRT \quad (1.10)$$

which is the familiar *ideal gas law*, with R being the *ideal gas law constant*.

At this point, we must return to a discussion of temperature units and introduce the proper thermodynamic temperature scale. It has already been mentioned that the Fahrenheit and Celsius temperature scales have arbitrary zero points. What is needed is a temperature scale that has an absolute zero point that is physically relevant. Values for temperature can then be scaled from that point. In 1848, the British scientist William Thomson (Figure 1.4), later made a baron and taking the title Lord Kelvin, considered the temperature–volume relationship of gases and other concerns (some of which we will address in future chapters) and proposed an absolute temperature scale where the minimum possible temperature is about -273°C , or 273 Celsius-sized degrees below the freezing point of water. [A modern value is -273.15°C , and is based on the triple point (discussed in Chapter 6) of H_2O , not the freezing point.] A scale was established by making the degree size for this absolute scale the same as the Celsius scale. In thermodynamics, gas temperatures are almost always expressed in this new scale, called the *absolute scale* or the *Kelvin scale*, and the letter K is used (without a degree sign) to indicate a temperature in kelvins. Because the degree sizes are the same, there is a simple conversion between a temperature in degrees Celsius and the same temperature in kelvins:

$$\text{K} = ^\circ\text{C} + 273.15 \quad (1.11)$$

Occasionally, the conversion is truncated to three significant figures and becomes simply $\text{K} = ^\circ\text{C} + 273$.

In all of the gas laws given above, *the temperature must be expressed in kelvins!* The absolute temperature scale is the only appropriate scale for thermodynamic temperatures. (For *changes* in temperature, the units can be kelvins or degrees Celsius, because the change in temperature will be the same. However, the absolute value of the temperature will be different.)

Having established the proper temperature scale for thermodynamics, we can return to the constant R . This value, the ideal gas law constant, is probably the most important physical constant for macroscopic systems. Its specific numerical value depends on the units used to express the pressure and volume. Table 1.2 lists various values of R . The ideal gas law is the best-known equation of state for a gaseous system. Gas systems whose state variables p , V , n , and T vary according to the ideal gas law satisfy one criterion of an *ideal gas* (the other criterion is presented in Chapter 2). *Nonideal* (or *real*) *gases*, which do not follow the ideal gas law exactly, can approximate ideal gases if they are kept at high temperature and low pressure.

It is useful to define a set of reference state variables for gases, because they can have a wide range of values that can in turn affect other state variables. The most common set of reference state variables for pressure and temperature is $p = 1.0$ bar and $T = 273.15$ K = 273.15°C . These conditions are called *standard temperature and pressure*,* abbreviated STP. Much of the thermodynamic data reported for gases are given for conditions of STP. SI also defines *standard ambient temperature and pressure*, SATP, as 298.15 K for temperature and 1 bar for pressure (1 bar = 0.987 atm).

*1 atm is commonly used as standard pressure, although technically it is incorrect. Because 1 bar = 0.987 atm, the error introduced is slight.

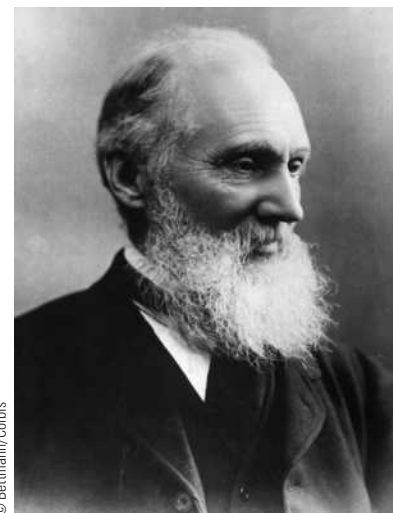


FIGURE 1.4 William Thomson, later Baron Kelvin (1824–1907), a Scottish physicist. Thomson established the necessity of a minimum absolute temperature, and proposed a temperature scale based on that absolute zero. He also performed valuable work on the first transatlantic cable. Thomson was made a baron in 1892 and borrowed the name of the Kelvin River. Because he left no heirs, there is no current Baron Kelvin.

TABLE 1.2 Values for R , the ideal gas law constant

$R = 0.08205 \text{ L}\cdot\text{atm}/\text{mol}\cdot\text{K}$
$0.08314 \text{ L}\cdot\text{bar}/\text{mol}\cdot\text{K}$
$1.987 \text{ cal}/\text{mol}\cdot\text{K}$
$8.314 \text{ J}/\text{mol}\cdot\text{K}$
$62.36 \text{ L}\cdot\text{torr}/\text{mol}\cdot\text{K}$

EXAMPLE 1.2

Calculate the volume of 1 mole of an ideal gas at SATP.

SOLUTION

Using the ideal gas law and the appropriate value for R :

$$V = \frac{nRT}{p} = \frac{(1 \text{ mol})(0.08314 \frac{\text{L}\cdot\text{bar}}{\text{mol}\cdot\text{K}})(298.15 \text{ K})}{1 \text{ bar}}$$

$$V = 24.79 \text{ L}$$

Here we use the value of R that has bar units.

This is slightly larger than the volume of 1 mole of ideal gas at STP because the temperature is slightly larger than at STP.

Liquids and solids can also be described by equations of state. However, unlike equations of state for gases, condensed-phase equations of state have constants that are unique to each substance. That is, there is no “ideal liquid law constant” or “ideal solid law constant” analogous to the ideal gas law constant. In much, but not all, of the cases to be considered here, we will be considering equations of state for a gas.

1.5 Partial Derivatives and Gas Laws

A major use of equations of state in thermodynamics is to determine how one state variable is affected when another state variable changes. In order to do this, we need the tools of calculus. For example, a straight line, as in Figure 1.5a, has a slope given by $\Delta y/\Delta x$, which in words is simply “the change in y as x changes.” For a straight line, the slope is the same everywhere on the line. For curved lines, as shown in Figure 1.5b, the slope is constantly changing. Instead of writing the slope of the curved line as $\Delta y/\Delta x$, we use the symbolism of calculus and write it as dy/dx , and we call this “the derivative of y with respect to x .”

Equations of state deal with many variables. The *total derivative* of a function of multiple variables, $F(x, y, z, \dots)$, is defined as

$$dF = \left(\frac{\partial F}{\partial x}\right)_{y,z,\dots} dx + \left(\frac{\partial F}{\partial y}\right)_{x,z,\dots} dy + \left(\frac{\partial F}{\partial z}\right)_{x,y,\dots} dz + \dots \quad (1.12)$$

In equation 1.12, we are taking the derivative of the function F with respect to one variable at a time. In each case, the other variables are held constant. Thus, in the first term, the derivative

$$\left(\frac{\partial F}{\partial x}\right)_{y,z,\dots} \quad (1.13)$$

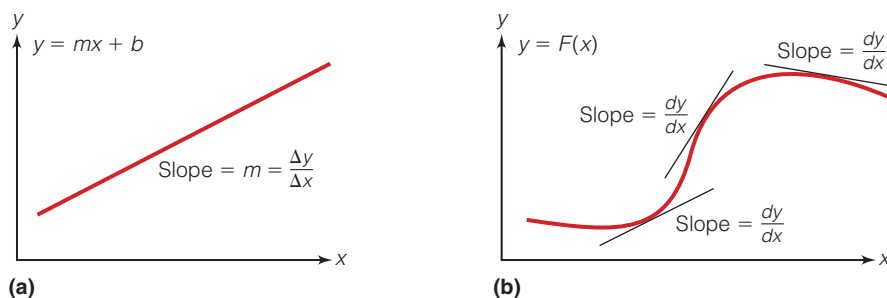


FIGURE 1.5 (a) Definition of slope for a straight line. The slope is the same at every point on the line. (b) A curved line also has a slope, but it changes from point to point. The slope of the line at any particular point is determined by the derivative of the equation for the line.

is the derivative of the function F with respect to x only, and the variables y , z , and so on are treated as constants. Such a derivative is a *partial derivative*. The total derivative of a multivariable function is the sum of all of its partial derivatives, each multiplied by the infinitesimal change in the appropriate variable (given as dx , dy , dz , and so on in equation 1.12).

Using equations of state, we can take derivatives and determine expressions for how one state variable changes with respect to another. Sometimes these derivatives lead to important conclusions about the relationships between the state variables, and this can be a powerful technique in working with thermodynamics.

For example, consider our ideal gas equation of state. Suppose we need to know how the pressure varies with respect to temperature, assuming the volume and number of moles in our gaseous system remain constant. The partial derivative of interest can be written as

$$\left(\frac{\partial p}{\partial T}\right)_{V,n}$$

Several partial derivatives relating the different state variables of an ideal gas can be constructed, some of which are more useful or understandable than others. However, any derivative of R is zero, because R is a constant.

Because we have an equation that relates p and T —the ideal gas law—we can evaluate this partial derivative analytically. The first step is to rewrite the ideal gas law so that pressure is all by itself on one side of the equation. The ideal gas law becomes

$$p = \frac{nRT}{V}$$

The next step is to take the derivative of both sides with respect to T , while treating everything else as a constant. The left side becomes

$$\left(\frac{\partial p}{\partial T}\right)_{V,n}$$

which is the partial derivative of interest. Taking the derivative of the right side:

$$\frac{\partial}{\partial T}\left(\frac{nRT}{V}\right) = \frac{nR}{V} \frac{\partial}{\partial T}T = \frac{nR}{V} \cdot 1 = \frac{nR}{V}$$

Combining the two sides:

$$\left(\frac{\partial p}{\partial T}\right)_{V,n} = \frac{nR}{V} \quad (1.14)$$

That is, from the ideal gas law, we are able to determine how one state variable varies with respect to another in an analytic fashion (that is, with a specific mathematical expression). A plot of pressure versus temperature is shown in Figure 1.6. Consider what equation 1.14 is telling you. A derivative is a *slope*. Equation 1.14 gives you the plot of pressure (y -axis) versus temperature (x -axis). If you took a sample of an ideal gas, measured its pressure at different temperatures but at constant volume, and plotted the data, you would get a straight line. The slope of that straight line should be equal to nR/V . The numerical value of this slope would depend on the volume and number of moles of the ideal gas.

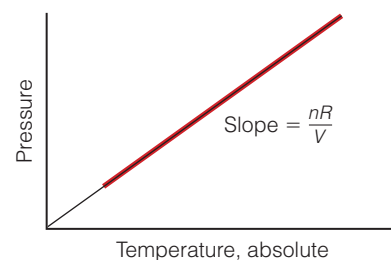


FIGURE 1.6 Plotting the pressure of a gas versus its absolute temperature, one gets a straight line whose slope equals nR/V . Algebraically, this is a plot of the equation $p = (nR/V) \cdot T$. In calculus terms, the slope of this line is $(\partial p/\partial T)_{V,n}$ and is constant.

EXAMPLE 1.3

Determine the change of pressure with respect to volume, all else remaining constant, for an ideal gas.