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Quantum Chemistry and Spectroscopy 4e

Thomas Engel

PHYSICAL CHEMISTRY

Quantum Chemistry and Spectroscopy

FOURTH EDITION

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University of Washington

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To Walter and Juliane,
my first teachers,
and to Gloria,
Alex,
Gabrielle, and Amelie.

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About the Author



THOMAS ENGEL taught chemistry at the University of Washington for more than 20 years, where he is currently professor emeritus of chemistry. Professor Engel received his bachelor's and master's degrees in chemistry from the Johns Hopkins University and his Ph.D. in chemistry from the University of Chicago. He then spent 11 years as a researcher in Germany and Switzerland, during which time he received the Dr. rer. nat. habil. degree from the Ludwig Maximilians University in Munich. In 1980, he left the IBM research laboratory in Zurich to become a faculty member at the University of Washington.

Professor Engel has published more than 80 articles and book chapters in the area of surface chemistry. He has received the Surface Chemistry or Colloids Award from the American Chemical Society and a Senior Humboldt Research Award from the Alexander von Humboldt Foundation. Other than this textbook, his current primary science interests are in energy policy and energy conservation. He serves on the citizen's advisory board of his local electrical utility, and his energy-efficient house could be heated in winter using only a hand-held hair dryer. He currently drives a hybrid vehicle and plans to transition to an electric vehicle soon to further reduce his carbon footprint.

Preface

The fourth edition of *Quantum Chemistry and Spectroscopy* includes many changes to the presentation and content at both a global and chapter level. These updates have been made to enhance the student learning experience and update the discussion of research areas. At the global level, changes that readers will see throughout the textbook include:

- **Review of relevant mathematics skills.** One of the primary reasons that students experience physical chemistry as a challenging course is that they find it difficult to transfer skills previously acquired in a mathematics course to their physical chemistry course. To address this issue, contents of the third edition Math Supplement have been expanded and split into 11 two- to five-page Math Essentials, which are inserted at appropriate places throughout this book, as well as in the companion volume *Thermodynamics, Statistical Thermodynamics, and Kinetics*, just before the math skills are required. Our intent in doing so is to provide "just-in-time" math help and to enable students to refresh math skills specifically needed in the following chapter.
- **Concept and Connection.** A new Concept and Connection feature has been added to each chapter to present students with a quick visual summary of the most important ideas within the chapter. In each chapter, approximately 10–15 of the most important concepts and/or connections are highlighted in the margins.
- **End-of-Chapter Problems.** Numerical Problems are now organized by section number within chapters to make it easier for instructors to create assignments for specific parts of each chapter. Furthermore, a number of new Conceptual Questions and Numerical Problems have been added to the book. Numerical Problems from the previous edition have been revised.
- **Introductory chapter materials.** Introductory paragraphs of all chapters have been replaced by a set of three questions plus responses to those questions. This new feature makes the importance of the chapter clear to students at the outset.
- **Figures.** All figures have been revised to improve clarity. Also, for many figures additional annotation has been included to help tie concepts to the visual program.
- **Key Equations.** An end-of-chapter table that summarizes Key Equations has been added to allow students to focus on the most important of the many equations in each chapter. Equations in this table are set in red type where they appear in the body of the chapter.
- **Further Reading.** A section on Further Reading has been added to each chapter to provide references for students and instructors who would like a deeper understanding of various aspects of the chapter material.
- **Guided Practice and Interactivity**
  - **Mastering™ Chemistry,** with a new enhanced eBook, has been significantly expanded to include a wealth of new end-of-chapter problems from the fourth edition, new self-guided, adaptive Dynamic Study Modules with wrong answer feedback and remediation, and the new Pearson eBook, which is mobile friendly. Students who solve homework problems using Mastering™ Chemistry obtain immediate feedback, which greatly enhances learning associated with solving homework problems. This platform can also be used for pre-class reading quizzes linked directly to the eText that are useful in ensuring students remain current in their studies and in flipping the classroom.
  - **NEW! Pearson eText, optimized for mobile** gives students access to their textbook anytime, anywhere.
    - Pearson eText mobile app offers offline access and can be downloaded for most iOS and Android phones/tablets from the Apple App Store or Google Play
    - Configurable reading settings, including resizable type and night-reading mode
    - Instructor and student note-taking, highlighting, bookmarking, and search functionalities

- **NEW! 66 Dynamic Study Modules** help students study effectively on their own by continuously assessing their activity and performance in real time.
- Students complete a set of questions with a unique answer format that also asks them to indicate their confidence level. Questions repeat until the student can answer them all correctly and confidently. These are available as graded assignments prior to class and are accessible on smartphones, tablets, and computers.
- **Topics** include key math skills, as well as a refresher of general chemistry concepts such as understanding matter, chemical reactions, and the periodic table and atomic structure. Topics can be added or removed to match your coverage.

In terms of chapter and section content, many changes were made. The most significant of these changes are:

- Chapter 17, on nuclear magnetic resonance (NMR), has been completely rewritten and expanded with the significant contribution of co-author Alex Angerhofer. This chapter now covers the nuclear Overhauser effect and dynamic nuclear polarization, and presents an extensive discussion of how two-dimensional NMR techniques are used to determine the structure of macromolecules in solution.
- Section 5.4 has been revised and expanded to better explain conduction in solids.
- Section 6.6 has been extensively revised to take advances in quantum computing into account.
- Section 8.4, on the origin of selection rules, has been revised and expanded to enhance student learning.
- Sections 14.5, 14.7, and 14.10 have been extensively revised and reformulated to relate electronic transitions to molecular orbitals of the initial and final states.
- Section 14.12 has been revised to reflect advances in the application of FRET to problems of chemical interest.

For those not familiar with the third edition of *Quantum Chemistry and Spectroscopy*, our approach to teaching physical chemistry begins with our target audience, undergraduate students majoring in chemistry, biochemistry, and chemical engineering, as well as many students majoring in the atmospheric sciences and the biological sciences. The following objectives outline our approach to teaching physical chemistry.

- **Focus on teaching core concepts.** The central principles of physical chemistry are explored by focusing on core ideas and then extending these ideas to a variety of problems. The goal is to build a solid foundation of student understanding in a limited number of areas rather than to provide a condensed encyclopedia of physical chemistry. We believe this approach teaches students how to learn and enables them to apply their newly acquired skills to master related fields.
- **Illustrate the relevance of physical chemistry to the world around us.** Physical chemistry becomes more relevant to a student if it is connected to the world around us. Therefore, example problems and specific topics are tied together to help the student develop this connection. For example, topics such as scanning tunneling microscopy, quantum dots, and quantum computing are discussed and illustrated with examples from the recent chemistry literature. Every attempt is made to connect fundamental ideas to applications that could be of interest to the student.
- **Link the macroscopic and atomic-level worlds.** The manifestation of quantum mechanics in the macroscopic world is illustrated by discussions of the band structure of solids, atomic force microscopy, quantum mechanical calculations of thermodynamic state functions, and NMR imaging.
- **Present exciting new science in the field of physical chemistry.** Physical chemistry lies at the forefront of many emerging areas of modern chemical research. Heterogeneous catalysis has benefited greatly from mechanistic studies carried out using the techniques of modern surface science. Quantum computing, using the principles of superposition and entanglement, is on the verge of being a viable technology. The role of physical chemistry in these and other emerging areas is highlighted throughout the text.

- **Provide a versatile online homework program with tutorials.** Students who submit homework problems using Mastering™ Chemistry obtain immediate feedback, a feature that greatly enhances learning. Also, tutorials with wrong answer feedback offer students a self-paced learning environment.
- **Use web-based simulations to illustrate the concepts being explored and avoid math overload.** Mathematics is central to physical chemistry; however, the mathematics can distract the student from "seeing" the underlying concepts. To circumvent this problem, web-based simulations have been incorporated as end-of-chapter problems in several chapters so that the student can focus on the science and avoid a math overload. These web-based simulations can also be used by instructors during lecture. An important feature of the simulations is that each problem has been designed as an assignable exercise with a printable answer sheet that the student can submit to the instructor. Simulations, animations, and homework problem worksheets can be accessed at www.pearsonhighered.com/advchemistry.

Effective use of *Quantum Chemistry and Spectroscopy* does not require proceeding sequentially through the chapters or including all sections. Some topics are discussed in supplemental sections, which can be omitted if they are not viewed as essential to the course. Also, many sections are sufficiently self-contained that they can be readily omitted if they do not serve the needs of the instructor and students. This textbook is constructed to be flexible to your needs. I welcome the comments of both students and instructors on how the material was used and how the presentation can be improved.

Thomas Engel
University of Washington

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Many individuals have helped me to bring the text into its current form. Students have provided me with feedback directly and through the questions they have asked, which has helped me to understand how they learn. Many colleagues, including Peter Armentrout, Doug Doren, Gary Drobny, Alex Engel, Graeme Henkelman, Lewis Johnson, Tom Pratum, Bill Reinhardt, Peter Rosky, George Schatz, Michael Schick, Gabrielle Varani, and especially Wes Borden and Bruce Robinson, have been invaluable in advising me. I am also fortunate to have access to some end-of-chapter problems that were originally presented in *Physical Chemistry,* 3rd edition, by Joseph H. Noggle and in *Physical Chemistry,* 3rd edition, by Gilbert W. Castellan. The reviewers, who are listed separately, have made many suggestions for improvement, for which I am very grateful. All those involved in the production process have helped to make this book a reality through their efforts. Special thanks are due to Jim Smith, who guided the first edition, to the current editor Jeanne Zalesky, to the developmental editor Spencer Cotkin, and to Jennifer Hart and Beth Sweeten at Pearson, who have led the production process.

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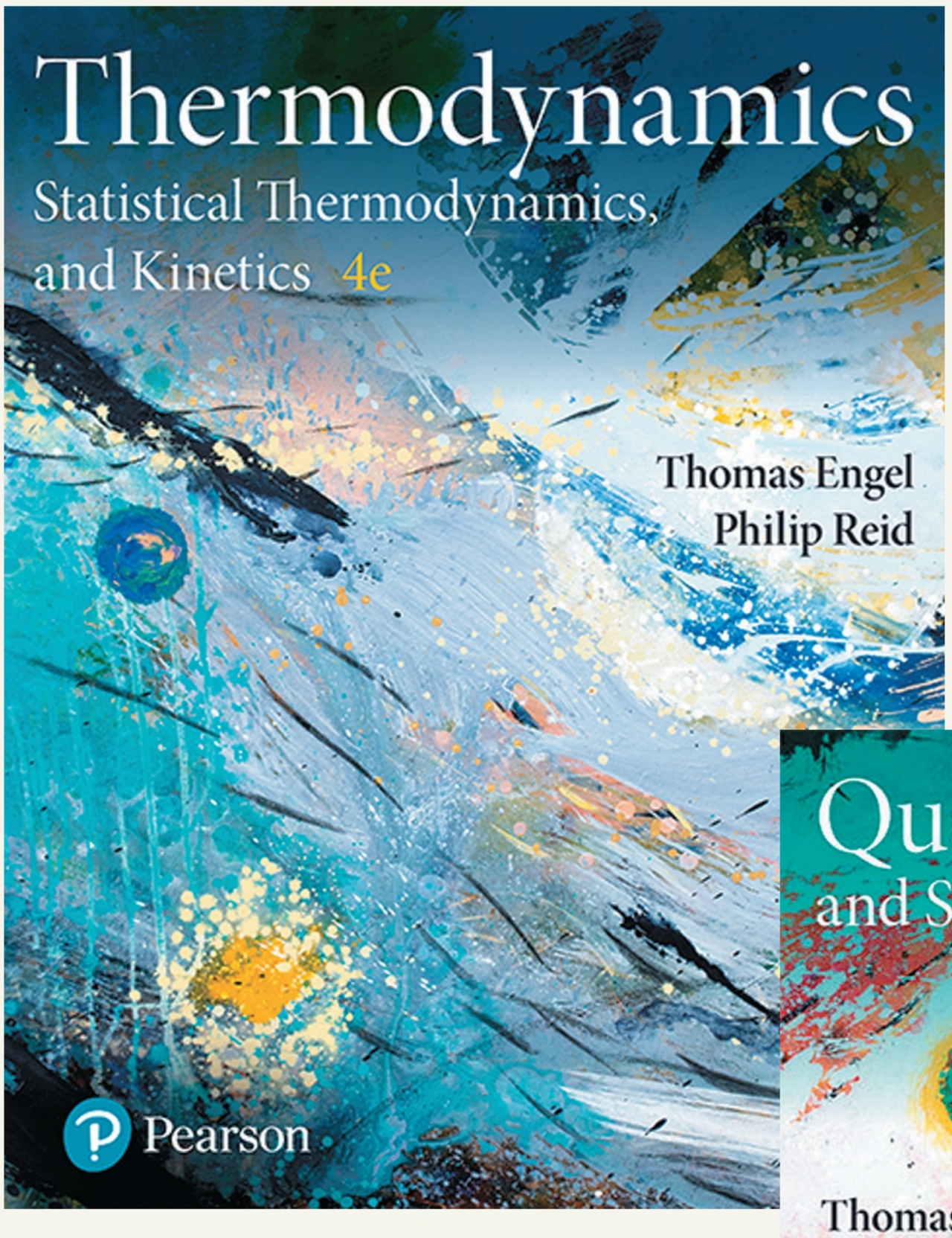
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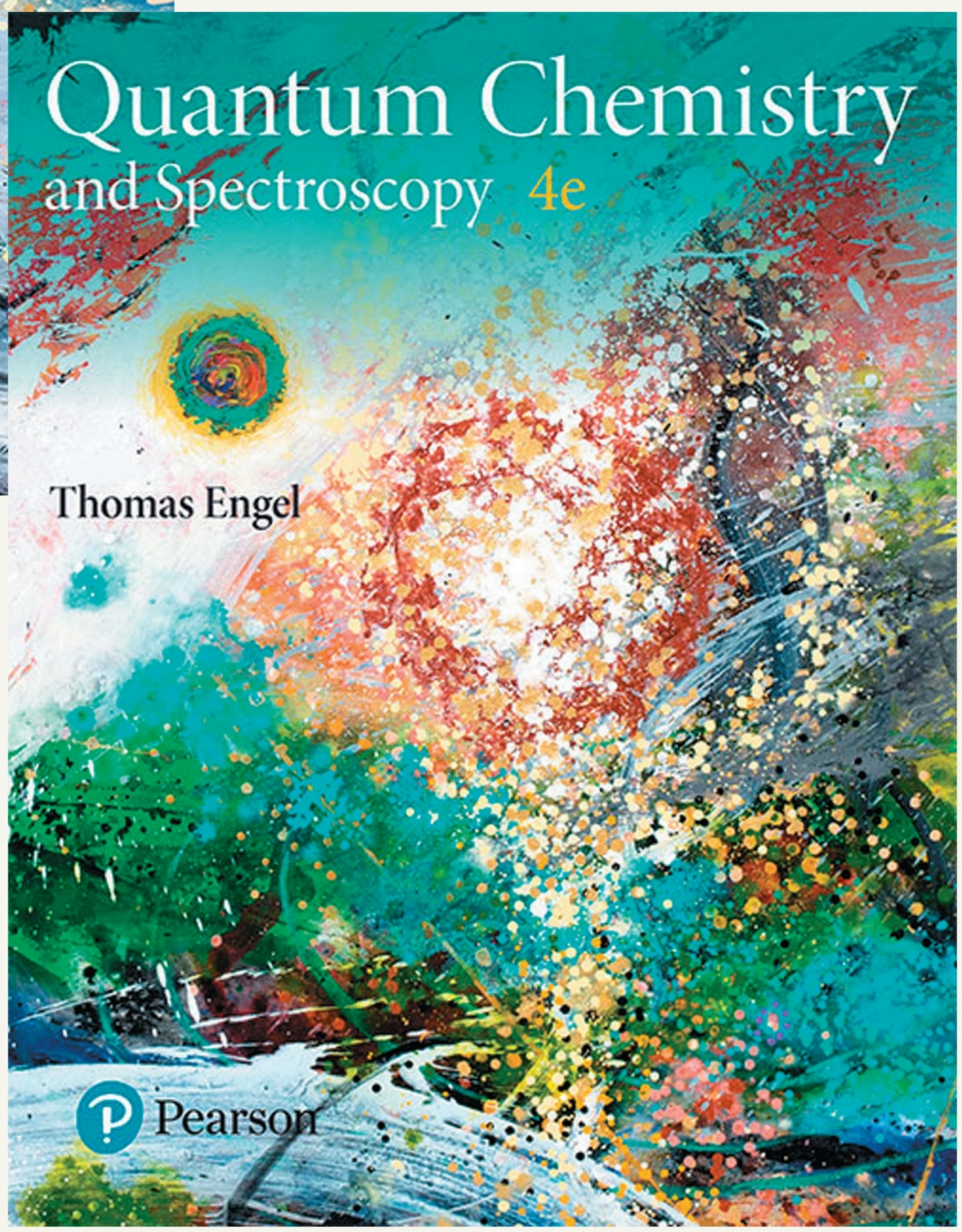
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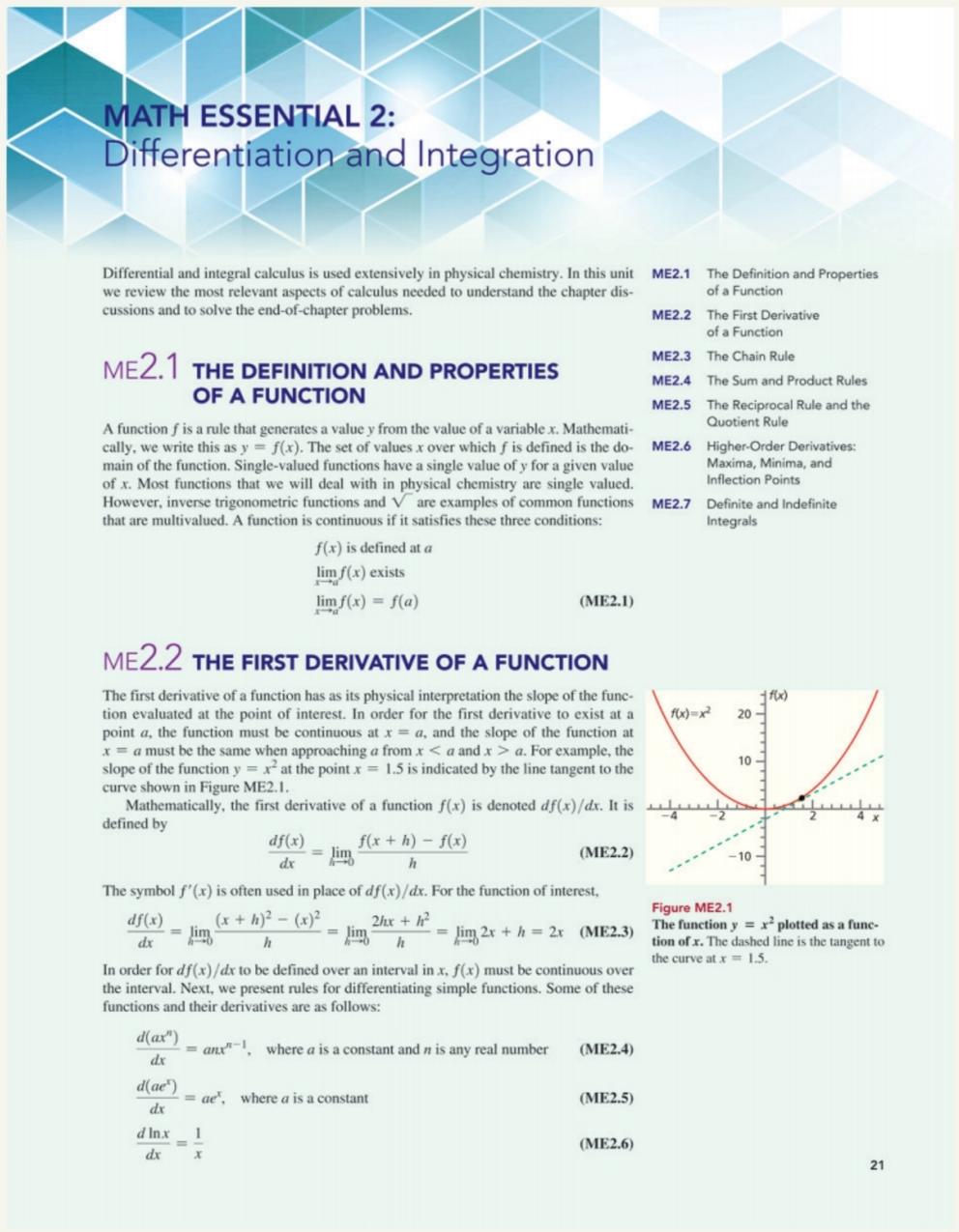
A Visual, Conceptual, and Contemporary Approach to Physical Chemistry





A Visual, Conceptual, and Contemporary Approach to Physical Chemistry

NEW! Math Essentials provide a review of relevant math skills, offer "just in time" math help, and enable students to refresh math skills specifically needed in the chapter that follows.



MATH ESSENTIAL 2:
Differentiation and Integration

Differential and integral calculus is used extensively in physical chemistry. In this unit we review the most relevant aspects of calculus needed to understand the chapter discussions and to solve the end-of-chapter problems.

ME2.1 The Definition and Properties of a Function
ME2.2 The First Derivative of a Function
ME2.3 The Chain Rule
ME2.4 The Sum and Product Rules
ME2.5 The Reciprocal Rule and the Quotient Rule
ME2.6 Higher-Order Derivatives: Maxima, Minima, and Inflection Points
ME2.7 Definite and Indefinite Integrals

ME2.1 THE DEFINITION AND PROPERTIES OF A FUNCTION

A function f is a rule that generates a value y from the value of a variable x. Mathematically, we write this as $y = f(x)$. The set of values x over which f is defined is the domain of the function. Single-valued functions have a single value of y for a given value of x. Most functions that we will deal with in physical chemistry are single valued. However, inverse trigonometric functions and $\sqrt{}$ are examples of common functions that are multivalued. A function is continuous if it satisfies these three conditions:

$f(x)$ is defined at a

$\lim_{x \to a} f(x)$ exists

$\lim_{x \to a} f(x) = f(a)$ **(ME2.1)**

ME2.2 THE FIRST DERIVATIVE OF A FUNCTION

The first derivative of a function has as its physical interpretation the slope of the function evaluated at the point of interest. In order for the first derivative to exist at a point a, the function must be continuous at $x = a$, and the slope of the function at $x = a$ must be the same when approaching a from $x < a$ and $x > a$. For example, the slope of the function $y = x^2$ at the point $x = 1.5$ is indicated by the line tangent to the curve shown in Figure ME2.1.

Figure ME2.1
The function $y = x^2$ plotted as a function of x. The dashed line is the tangent to the curve at $x = 1.5$.

Mathematically, the first derivative of a function $f(x)$ is denoted $df(x)/dx$. It is defined by

$$\frac{df(x)}{dx} = \lim_{h \to 0} \frac{f(x+h) - f(x)}{h} \quad \textbf{(ME2.2)}$$

The symbol $f'(x)$ is often used in place of $df(x)/dx$. For the function of interest,

$$\frac{df(x)}{dx} = \lim_{h \to 0} \frac{(x+h)^2 - (x)^2}{h} = \lim_{h \to 0} \frac{2hx + h^2}{h} = \lim_{h \to 0} 2x + h = 2x \quad \textbf{(ME2.3)}$$

In order for $df(x)/dx$ to be defined over an interval in x, $f(x)$ must be continuous over the interval. Next, we present rules for differentiating simple functions. Some of these functions and their derivatives are as follows:

$$\frac{d(ax^n)}{dx} = anx^{n-1}, \quad \text{where } a \text{ is a constant and } n \text{ is any real number} \quad \textbf{(ME2.4)}$$

$$\frac{d(ae^x)}{dx} = ae^x, \quad \text{where } a \text{ is a constant} \quad \textbf{(ME2.5)}$$

$$\frac{d \ln x}{dx} = \frac{1}{x} \quad \textbf{(ME2.6)}$$

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CHAPTER 6

Commuting and Noncommuting Operators and the Surprising Consequences of Entanglement

6.1 Commutation Relations
6.2 The Stern–Gerlach Experiment
6.3 The Heisenberg Uncertainty Principle
6.4 (Supplemental Section) The Heisenberg Uncertainty Principle Expressed in Terms of Standard Deviations
6.5 (Supplemental Section) A Thought Experiment Using a Particle in a Three-Dimensional Box
6.6 (Supplemental Section) Entangled States, Teleportation, and Quantum Computers

WHY is this material important?

The measurement process is different for a quantum-mechanical system than for a classical system. For a classical system, all observables can be measured simultaneously, and the precision and accuracy of the measurement is limited only by the instruments used to make the measurement. For a quantum-mechanical system, some observables can be measured simultaneously and exactly, whereas an uncertainty relation limits the degree to which other observables can be known simultaneously and exactly.

WHAT are the most important concepts and results?

Measurements carried out on a system in a superposition state change the state of the system. Two observables can be measured simultaneously and exactly only if their corresponding operators commute. Two particles can be entangled, after which their properties are no longer independent of one another. Entanglement is the basis of both teleportation and quantum computing.

WHAT would be helpful for you to review for this chapter?

It would be helpful to review the material on operators in Chapter 2.

6.1 COMMUTATION RELATIONS

In classical mechanics, a system can in principle be described completely. For instance, the position, momentum, kinetic energy, and potential energy of a mass falling in a gravitational field can be determined simultaneously at any point on its trajectory. The uncertainty in the measurements is only limited by the capabilities of the measurement technique. The values of all of these observables (and many more) can be known simultaneously. This is not generally true for a quantum-mechanical system. In the quantum world, in some cases two observables can be known simultaneously with high accuracy. However, in other cases, two observables have a fundamental uncertainty that cannot be eliminated through any measurement techniques. Nevertheless, as will be shown later,

Concept

For a quantum mechanical system, it is not generally the case that the values of all observables can be known simultaneously.

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NEW! Concept and Connection features in each chapter present students with quick visual summaries of the core concepts within the chapter, highlighting key take aways and providing students with an easy way to review the material.

UPDATED! Introductory paragraphs of all chapters have been replaced by a set of three questions plus responses to those questions making the relevance of the chapter clear at the outset.

UPDATED! All figures have been revised to improve clarity and for many figures, additional annotation has been included to help tie concepts to the visual program.

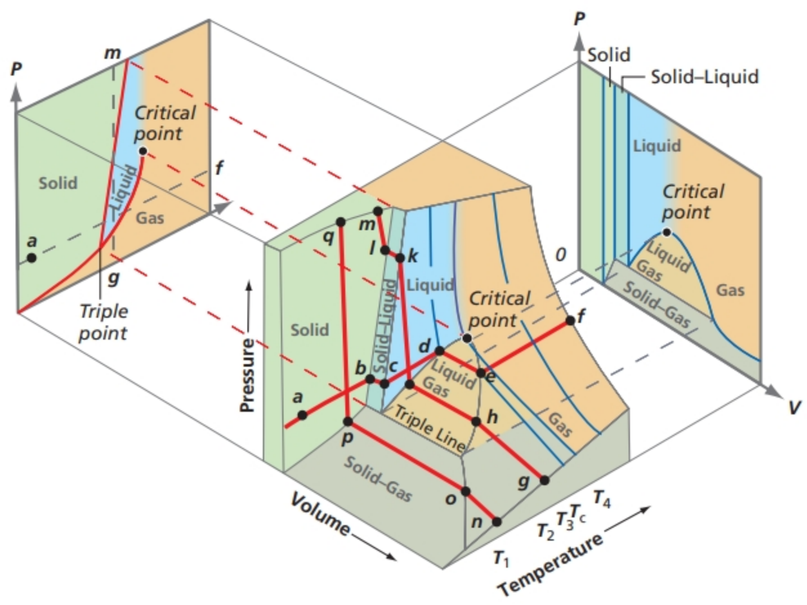
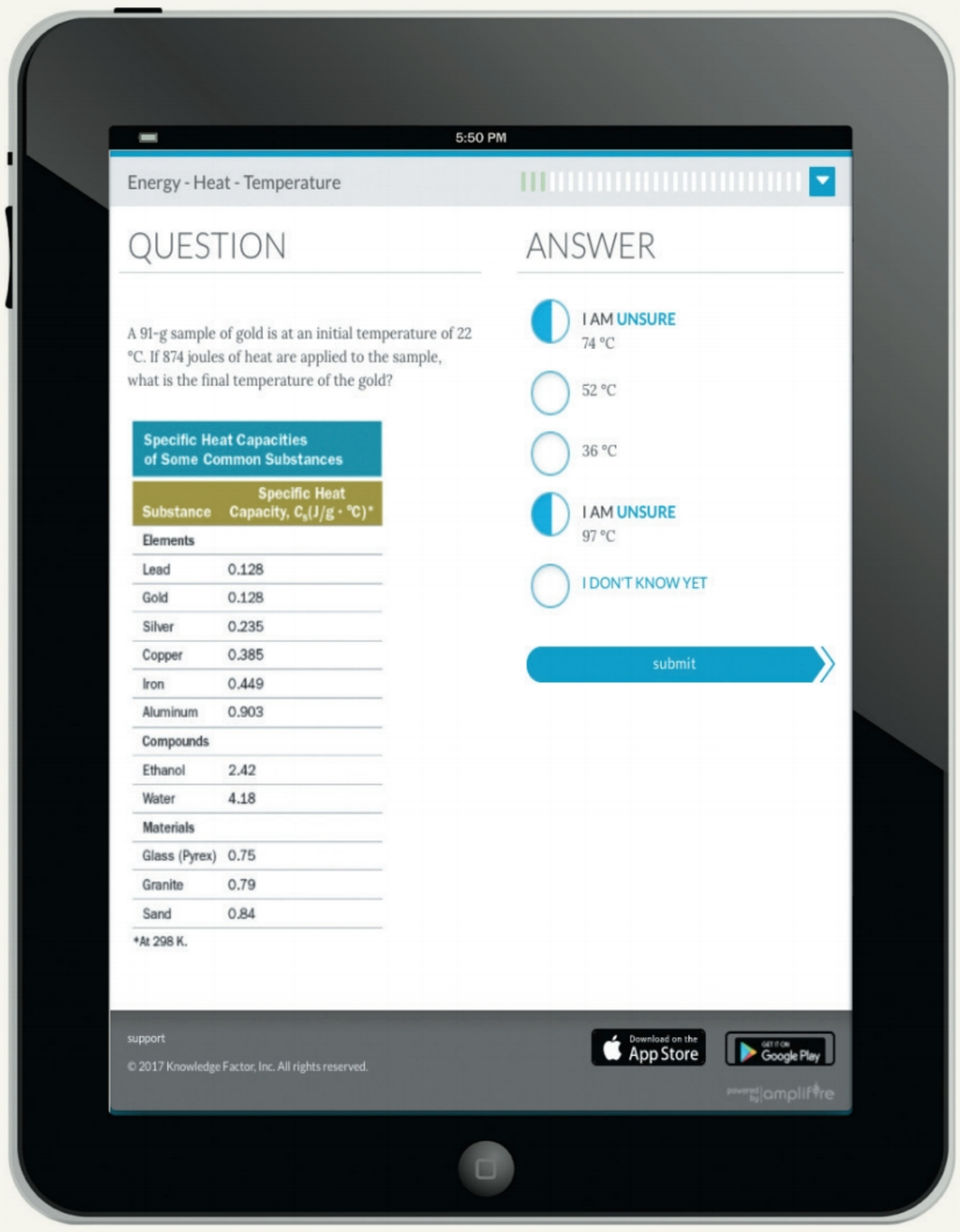


Figure 8.15
A *P–V–T* phase diagram for a substance that expands upon melting. The indicated processes are discussed in the text.

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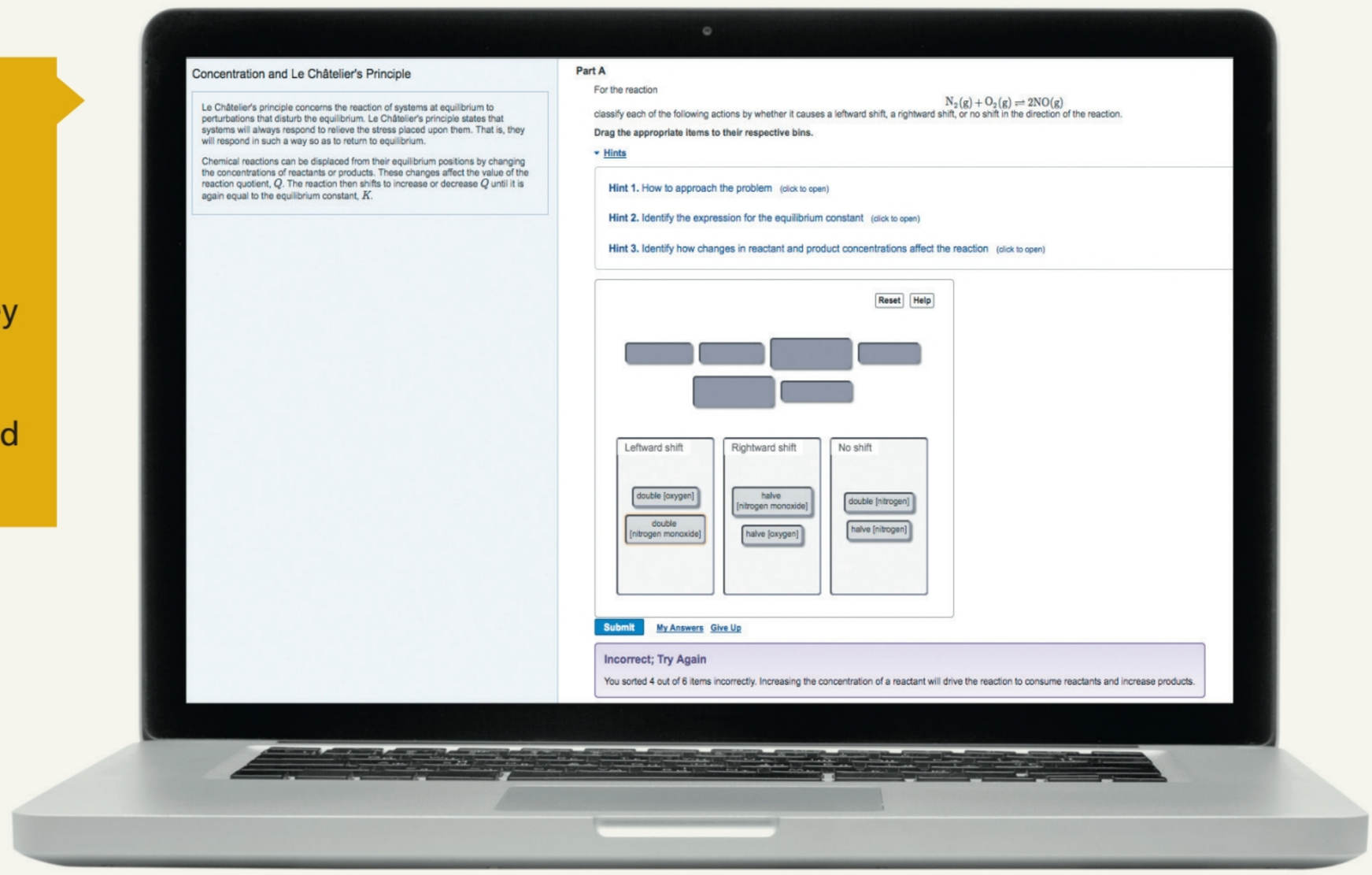
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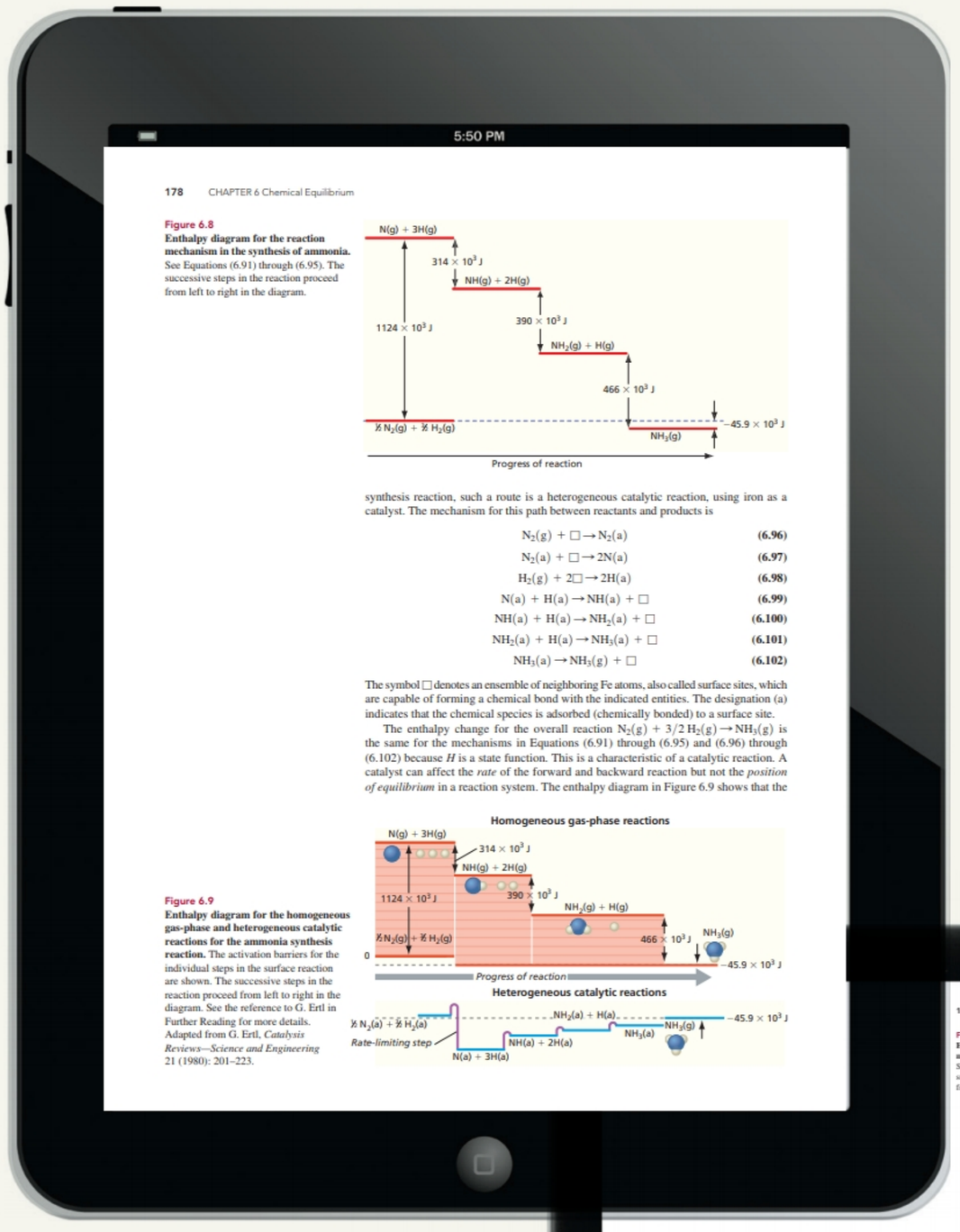


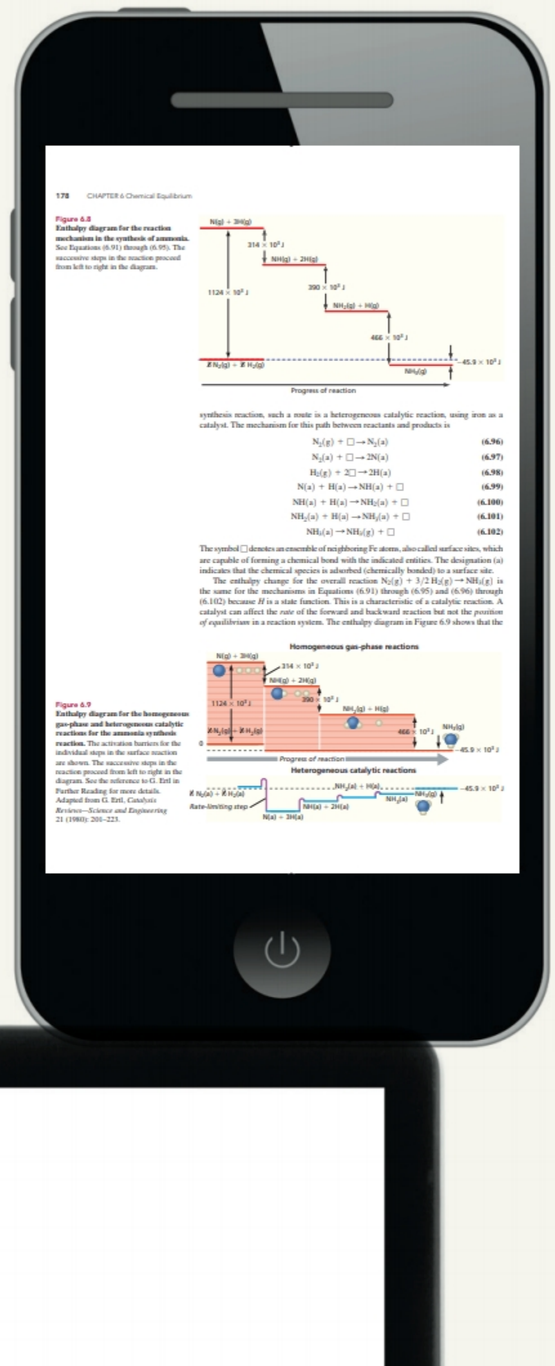
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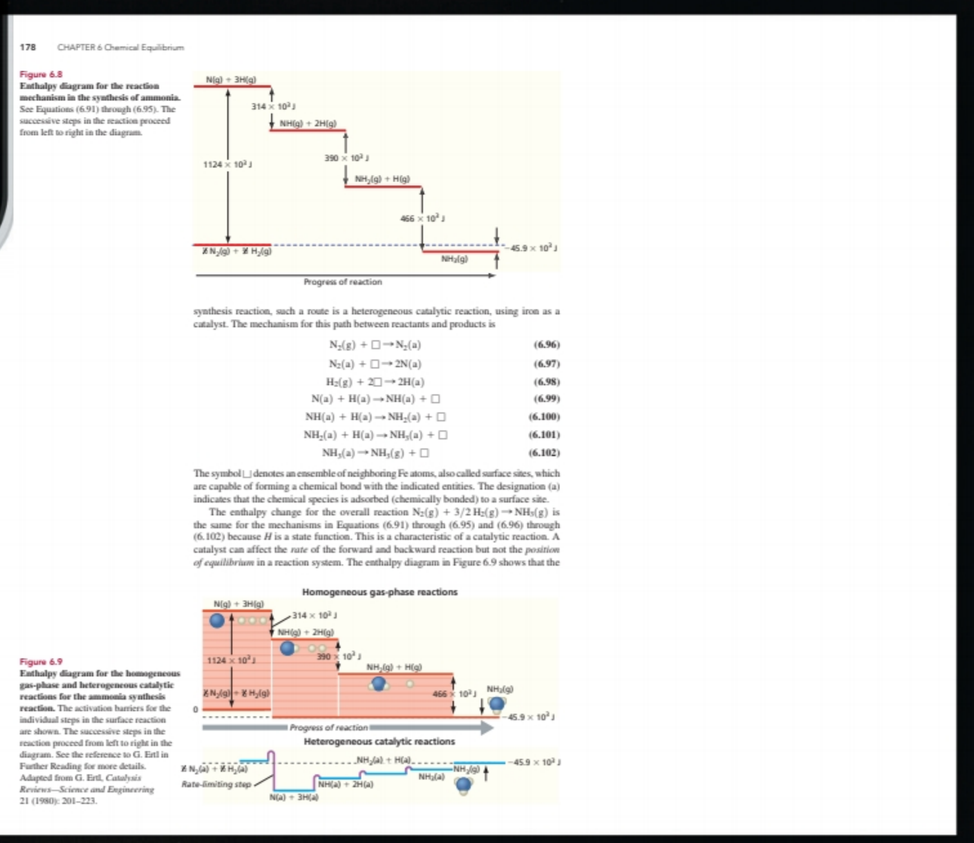
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MATH ESSENTIAL 1:
Units, Significant Figures, and Solving End of Chapter Problems

ME1.1 Units

ME1.2 Uncertainty and Significant Figures

ME1.3 Solving End-of-Chapter Problems

ME1.1 UNITS

Quantities of interest in physical chemistry such as pressure, volume, or temperature are characterized by their magnitude and their units. In this textbook, we use the SI (from the French *Le Système international d'unités*) system of units. All physical quantities can be defined in terms of the seven base units listed in Table ME1.1. For more details, see http://physics.nist.gov/cuu/Units/units.html. The definition of temperature is based on the coexistence of the solid, gaseous, and liquid phases of water at a pressure of 1 bar.

TABLE ME1.1 Base SI Units

Base Unit	Unit	Definition of Unit
Unit of length	meter (m)	The meter is the length of the path traveled by light in vacuum during a time interval of 1/299,792,458 of a second.
Unit of mass	kilogram (kg)	The kilogram is the unit of mass; it is equal to the mass of the platinum iridium international prototype of the kilogram kept at the International Bureau of Weights and Measures.
Unit of time	second (s)	The second is the duration of 9,192,631,770 periods of the radiation corresponding to the transition between the two hyperfine levels of the ground state of the cesium 133 atom.
Unit of electric current	ampere (A)	The ampere is the constant current that, if maintained in two straight parallel conductors of infinite length, is of negligible circular cross section, and if placed 1 meter apart in a vacuum would produce between these conductors a force equal to 2×10^{-7} kg m s^{-2} per meter of length. In this definition, 2 is an exact number.
Unit of thermodynamic temperature	kelvin (K)	The Kelvin is the unit of thermodynamic temperature. It is the fraction 1/273.16 of the thermodynamic temperature of the triple point of water.
Unit of amount of substance	mole (mol)	The mole is the amount of substance of a system that contains as many elementary entities as there are atoms in 0.012 kilogram of carbon 12 where 0.012 is an exact number. When the mole is used, the elementary entities must be specified and may be atoms, molecules, ions, electrons, other particles, or specified groups of such particles.
Unit of luminous intensity	candela (cd)	The candela is the luminous intensity, in a given direction, of a source that emits monochromatic radiation of frequency 540. $\times 10^{12}$ hertz and that has a radiant intensity in that direction of 1/683 watt per steradian.

Quantities of interest other than the seven base quantities can be expressed in terms of the units meter, kilogram, second, ampere, kelvin, mole, and candela. The most important of these derived units, some of which have special names as indicated, are listed in Table ME1.2. A more inclusive list of derived units can be found at http://physics.nist.gov/cuu/Units/units.html.

TABLE ME1.2 Derived Units

Unit	Definition	Relation to Base Units	Special Name	Abbreviation
Area	Size of a surface	m^2		m^2
Volume	Amount of three-dimensional space an object occupies	m^3		m^3
Velocity	Measure of the rate of motion	$m\ s^{-1}$		$m\ s^{-1}$
Acceleration	Rate of change of velocity	$m\ s^{-2}$		$m\ s^{-2}$
Linear momentum	Product of mass and linear velocity of an object	$kg\ m\ s^{-1}$		$kg\ m\ s^{-1}$
Angular momentum	Product of the moment of inertia of a body about an axis and its *angular* velocity with respect to the same axis	$kg\ m^2\ s^{-1}$		$kg\ m^2\ s^{-1}$
Force	Any interaction that, when unopposed, will change the motion of an object	$kg\ m\ s^{-2}$	newton	N
Pressure	Force acting per unit area	$kg\ m^{-1}\ s^{-2}$ $N\ m^{-2}$	pascal	Pa
Work	Product of force on an object and movement along the direction of the force	$kg\ m^2\ s^{-2}$	joule	J
Kinetic energy	Energy an object possesses because of its motion	$kg\ m^2\ s^{-2}$	joule	J
Potential energy	Energy an object possesses because of its position or condition	$kg\ m^2\ s^{-2}$	joule	J
Power	Rate at which energy is produced or consumed	$kg\ m^2\ s^{-3}$	watt	W
Mass density	Mass per unit volume	$kg\ m^{-3}$		$kg\ m^{-3}$
Radian	Angle at the center of a circle whose arc is equal in length to the radius	$m/m = 1$		$m/m = 1$
Steradian	Angle at the center of a sphere subtended by a part of the surface equal in area to the square of the radius	$m^2/m^2 = 1$		$m^2/m^2 = 1$
Frequency	Number of repeat units of a wave per unit time	s^{-1}	hertz	Hz
Electrical charge	Physical property of matter that causes it to experience an electrostatic force	A s	coulomb	C
Electrical potential	Work done in moving a unit positive charge from infinity to that point	$kg\ m^2\ s^{-3}/A$ W/A	volt	V
Electrical resistance	Ratio of the voltage to the electric current that flows through a conductive material	$kg\ m^2\ s^{-3}/A^2$ W/A^2	ohm	Ω

If SI units are used throughout the calculation of a quantity, the result will have SI units. For example, consider a unit analysis of the electrostatic force between two charges:

$$F = \frac{q_1 q_2}{8\pi\varepsilon_0 r^2} = \frac{C^2}{8\pi \times kg^{-1}s^4A^2m^{-3} \times m^2} = \frac{A^2s^2}{8\pi \times kg^{-1}s^4A^2m^{-3} \times m^2}$$

$$= \frac{1}{8\pi} kg\ m\ s^{-2} = \frac{1}{8\pi} N$$

Therefore, in carrying out a calculation, it is only necessary to make sure that all quantities are expressed in SI units rather than carrying out a detailed unit analysis of the entire calculation.

ME1.2 UNCERTAINTY AND SIGNIFICANT FIGURES

In carrying out a calculation, it is important to take into account the uncertainty of the individual quantities that go into the calculation. The uncertainty is indicated by the number of significant figures. For example, the mass 1.356 g has four significant figures. The mass 0.003 g has one significant figure, and the mass 0.01200 g has four significant figures. By convention, the uncertainty of a number is ± 1 in the rightmost digit. A zero at the end of a number that is not to the right of a decimal point is not significant. For example, 150 has two significant figures, but 150. has three significant figures. Some numbers are exact and have no uncertainty. For example, 1.00×10^6 has three significant figures because the 10 and 6 are exact numbers. By definition, the mass of one atom of ^{12}C is exactly 12 atomic mass units.

If a calculation involves quantities with a different number of significant figures, the following rules regarding the number of significant figures in the result apply:

- In addition and subtraction, the result has the number of digits to the right of the decimal point corresponding to the number that has the smallest number of digits to the right of the decimal point. For example $101 + 24.56 = 126$ and $0.523 + 0.10 = 0.62$.
- In multiplication or division, the result has the number of significant figures corresponding to the number with the smallest number of significant figures. For example, $3.0 \times 16.00 = 48$ and $0.05 \times 100. = 5$.

It is good practice to carry forward a sufficiently large number of significant figures in different parts of the calculation and to round off to the appropriate number of significant figures at the end.

ME1.3 SOLVING END-OF-CHAPTER PROBLEMS

Because calculations in physical chemistry often involve multiple inputs, it is useful to carry out calculations in a manner that they can be reviewed and easily corrected. For example, the input and output for the calculation of the pressure exerted by gaseous benzene with a molar volume of 2.00 L at a temperature of 595 K using the Redlich–Kwong equation of state $P = \dfrac{RT}{V_m - b} - \dfrac{a}{\sqrt{T}} \dfrac{1}{V_m(V_m + b)}$ in Mathematica is shown below. The statement in the first line clears the previous values of all listed quantities, and the semicolon after each input value suppresses its appearance in the output.

```
In[36]:=   Clear[r, t, vm, a, b, prk]
           r = 8.314 × 10^-2;
           t = 595;
           vm = 2.00;
           a = 452;
           b = .08271;
           prk = rt/(vm − b) − a/√t 1/(vm(vm + b))
out[42]=   21.3526
```

Invoking the rules for significant figures, the final answer is $P = 21.4$ bar.

The same problem can be solved using Microsoft Excel as shown in the following table.

	A	B	C	D	E	F
1	R	T	V_m	a	b	=((A2*B2)/(C2-E2))-(D2/SQRT(B2))*(1/(C2*(C2+E2)))
2	0.08314	595	2	452	0.08271	21.35257941

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MATH ESSENTIAL 2:
Differentiation and Integration

Differential and integral calculus is used extensively in physical chemistry. In this unit we review the most relevant aspects of calculus needed to understand the chapter discussions and to solve the end-of-chapter problems.

ME2.1 The Definition and Properties of a Function

ME2.2 The First Derivative of a Function

ME2.3 The Chain Rule

ME2.4 The Sum and Product Rules

ME2.5 The Reciprocal Rule and the Quotient Rule

ME2.6 Higher-Order Derivatives: Maxima, Minima, and Inflection Points

ME2.7 Definite and Indefinite Integrals

ME2.1 THE DEFINITION AND PROPERTIES OF A FUNCTION

A function f is a rule that generates a value y from the value of a variable x. Mathematically, we write this as $y = f(x)$. The set of values x over which f is defined is the domain of the function. Single-valued functions have a single value of y for a given value of x. Most functions that we will deal with in physical chemistry are single valued. However, inverse trigonometric functions and $\sqrt{}$ are examples of common functions that are multivalued. A function is continuous if it satisfies these three conditions:

$$f(x) \text{ is defined at } a$$
$$\lim_{x \to a} f(x) \text{ exists}$$
$$\lim_{x \to a} f(x) = f(a) \qquad \textbf{(ME2.1)}$$

ME2.2 THE FIRST DERIVATIVE OF A FUNCTION

The first derivative of a function has as its physical interpretation the slope of the function evaluated at the point of interest. In order for the first derivative to exist at a point a, the function must be continuous at $x = a$, and the slope of the function at $x = a$ must be the same when approaching a from $x < a$ and $x > a$. For example, the slope of the function $y = x^2$ at the point $x = 1.5$ is indicated by the line tangent to the curve shown in Figure ME2.1.

Mathematically, the first derivative of a function $f(x)$ is denoted $df(x)/dx$. It is defined by

$$\frac{df(x)}{dx} = \lim_{h \to 0} \frac{f(x + h) - f(x)}{h} \qquad \textbf{(ME2.2)}$$

The symbol $f'(x)$ is often used in place of $df(x)/dx$. For the function of interest,

$$\frac{df(x)}{dx} = \lim_{h \to 0} \frac{(x + h)^2 - (x)^2}{h} = \lim_{h \to 0} \frac{2hx + h^2}{h} = \lim_{h \to 0} 2x + h = 2x \qquad \textbf{(ME2.3)}$$

In order for $df(x)/dx$ to be defined over an interval in x, $f(x)$ must be continuous over the interval. Next, we present rules for differentiating simple functions. Some of these functions and their derivatives are as follows:

$$\frac{d(ax^n)}{dx} = anx^{n-1}, \quad \text{where } a \text{ is a constant and } n \text{ is any real number} \qquad \textbf{(ME2.4)}$$

$$\frac{d(ae^x)}{dx} = ae^x, \quad \text{where } a \text{ is a constant} \qquad \textbf{(ME2.5)}$$

$$\frac{d \ln x}{dx} = \frac{1}{x} \qquad \textbf{(ME2.6)}$$

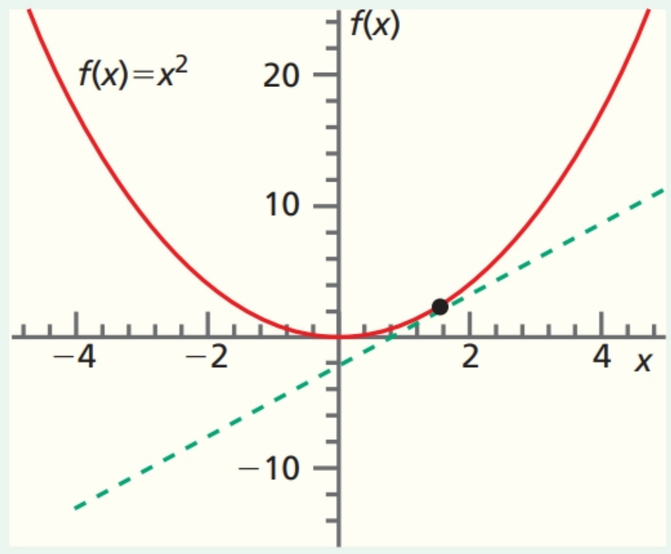


Figure ME2.1
The function $y = x^2$ plotted as a function of x. The dashed line is the tangent to the curve at $x = 1.5$.

$$\frac{d(a\sin x)}{dx} = a\cos x, \quad \text{where } a \text{ is a constant} \tag{ME2.7}$$

$$\frac{d(a\cos x)}{dx} = -a\sin x, \quad \text{where } a \text{ is a constant} \tag{ME2.8}$$

ME2.3 THE CHAIN RULE

In this section, we deal with the differentiation of more complicated functions. Suppose that $y = f(u)$ and $u = g(x)$. From the previous section, we know how to calculate $df(u)/du$. But how do we calculate $df(u)/dx$? The answer to this question is stated as the chain rule:

$$\frac{df(u)}{dx} = \frac{df(u)}{du}\frac{du}{dx} \tag{ME2.9}$$

Several examples illustrating the chain rule follow:

$$\frac{d\sin(3x)}{dx} = \frac{d\sin(3x)}{d(3x)}\frac{d(3x)}{dx} = 3\cos(3x) \tag{ME2.10}$$

$$\frac{d\ln(x^2)}{dx} = \frac{d\ln(x^2)}{d(x^2)}\frac{d(x^2)}{dx} = \frac{2x}{x^2} = \frac{2}{x} \tag{ME2.11}$$

$$\frac{d\left(x+\frac{1}{x}\right)^{-4}}{dx} = \frac{d\left(x+\frac{1}{x}\right)^{-4}}{d\left(x+\frac{1}{x}\right)}\frac{d\left(x+\frac{1}{x}\right)}{dx} = -4\left(x+\frac{1}{x}\right)^{-5}\left(1-\frac{1}{x^2}\right) \tag{ME2.12}$$

$$\frac{d\exp(ax^2)}{dx} = \frac{d\exp(ax^2)}{d(ax^2)}\frac{d(ax^2)}{dx} = 2ax\exp(ax^2), \quad \text{where } a \text{ is a constant} \tag{ME2.13}$$

Additional examples of use of the chain rule include:

$$d\left(\sqrt{3}x^{4/3}\right)/dx = (4/3)\sqrt{3}x^{1/3} \tag{ME2.14}$$

$$d\left(5e^{3\sqrt{2}x}\right)/dx = 15\sqrt{2}e^{3\sqrt{2}x} \tag{ME2.15}$$

$$\frac{d(4\sin kx)}{dx} = 4k\cos x, \quad \text{where } k \text{ is a constant}$$

$$\frac{d\left(\sqrt{3}\cos 2\pi x\right)}{dx} = -2\sqrt{3}\pi\sin 2\pi x \tag{ME2.16}$$

ME2.4 THE SUM AND PRODUCT RULES

Two useful rules in evaluating the derivative of a function that is itself the sum or product of two functions are as follows:

$$\frac{d[f(x)+g(x)]}{dx} = \frac{df(x)}{dx} + \frac{dg(x)}{dx} \tag{ME2.17}$$

For example,

$$\frac{d(x^3+\sin x)}{dx} = \frac{dx^3}{dx} + \frac{d\sin x}{dx} = 3x^2 + \cos x \tag{ME2.18}$$

$$\frac{d[\,f(x)g(x)\,]}{dx} = g(x)\frac{df(x)}{dx} + f(x)\frac{dg(x)}{dx} \qquad \textbf{(ME2.19)}$$

For example,

$$\frac{d[\,\sin(x)\,\cos(x)\,]}{dx} = \cos(x)\frac{d\,\sin(x)}{dx} + \sin(x)\frac{d\,\cos(x)}{dx}$$
$$= \cos^2 x - \sin^2 x \qquad \textbf{(ME2.20)}$$

ME2.5 THE RECIPROCAL RULE AND THE QUOTIENT RULE

How is the first derivative calculated if the function to be differentiated does not have a simple form such as those listed in the preceding section? In many cases, the derivative is found by using the product rule and the quotient rule given by

$$\frac{d\left(\dfrac{1}{f(x)}\right)}{dx} = -\frac{1}{[\,f(x)\,]^2}\frac{df(x)}{dx} \qquad \textbf{(ME2.21)}$$

For example,

$$\frac{d\left(\dfrac{1}{\sin x}\right)}{dx} = -\frac{1}{\sin^2 x}\frac{d\,\sin x}{dx} = \frac{-\cos x}{\sin^2 x} \qquad \textbf{(ME2.22)}$$

$$\frac{d\left[\dfrac{f(x)}{g(x)}\right]}{dx} = \frac{g(x)\dfrac{df(x)}{dx} - f(x)\dfrac{dg(x)}{dx}}{[\,g(x)\,]^2} \qquad \textbf{(ME2.23)}$$

For example,

$$\frac{d\left(\dfrac{x^2}{\sin x}\right)}{dx} = \frac{2x\,\sin x - x^2\cos x}{\sin^2 x} \qquad \textbf{(ME2.24)}$$

ME2.6 HIGHER-ORDER DERIVATIVES: MAXIMA, MINIMA, AND INFLECTION POINTS

A function $f(x)$ can have higher-order derivatives in addition to the first derivative. The second derivative of a function is the slope of a graph of the slope of the function versus the variable. In order for the second derivative to exist, the first derivative must be continuous at the point of interest. Mathematically,

$$\frac{d^2 f(x)}{dx^2} = \frac{d}{dx}\left(\frac{df(x)}{dx}\right) \qquad \textbf{(ME2.25)}$$

For example,

$$\frac{d^2\,\exp(ax^2)}{dx^2} = \frac{d}{dx}\left[\frac{d\,\exp(ax^2)}{dx}\right] = \frac{d[\,2ax\,\exp(ax^2)\,]}{dx}$$
$$= 2a\,\exp(ax^2) + 4a^2x^2\,\exp(ax^2), \quad \text{where } a \text{ is a constant} \qquad \textbf{(ME2.26)}$$

The symbol $f''(x)$ is often used in place of $d^2f(x)/dx^2$. If a function $f(x)$ has a concave upward shape $(\cup)$ at the point of interest, its first derivative is increasing with x and therefore $f''(x) > 0$. If a function $f(x)$ has a concave downward shape $(\cap)$ at the point of interest, $f''(x) < 0$.

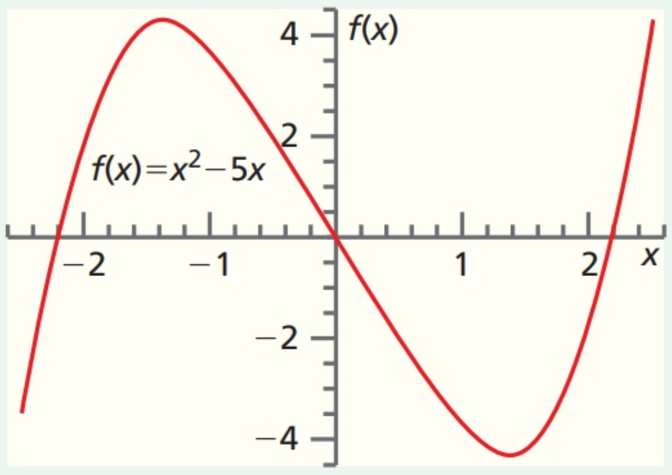


Figure ME2.2
$f(x) = x^3 - 5x$ plotted as a function of x. Note that it has a maximum and a minimum in the range shown.

The second derivative is useful in identifying where a function has its minimum or maximum value within a range of the variable, as shown next. Because the first derivative is zero at a local maximum or minimum, $df(x)/dx = 0$ at the values x_{max} and x_{min}. Consider the function $f(x) = x^3 - 5x$ shown in Figure ME2.2 over the range $-2.5 \le x \le 2.5$.

By taking the derivative of this function and setting it equal to zero, we find the minima and maxima of this function in the range

$$\frac{d(x^3 - 5x)}{dx} = 3x^2 - 5 = 0, \quad \text{which has the solutions } x = \pm\sqrt{\frac{5}{3}} = 1.291$$

The maxima and minima can also be determined by graphing the derivative and finding the zero crossings, as shown in Figure ME2.3.

Graphing the function clearly shows that the function has one maximum and one minimum in the range specified. Which criterion can be used to distinguish between these extrema if the function is not graphed? The sign of the second derivative, evaluated at the point for which the first derivative is zero, can be used to distinguish between a maximum and a minimum:

$$\frac{d^2f(x)}{dx^2} = \frac{d}{dx}\left[\frac{df(x)}{dx}\right] < 0 \quad \text{for a maximum}$$

$$\frac{d^2f(x)}{dx^2} = \frac{d}{dx}\left[\frac{df(x)}{dx}\right] > 0 \quad \text{for a minimum} \qquad \textbf{(ME2.27)}$$

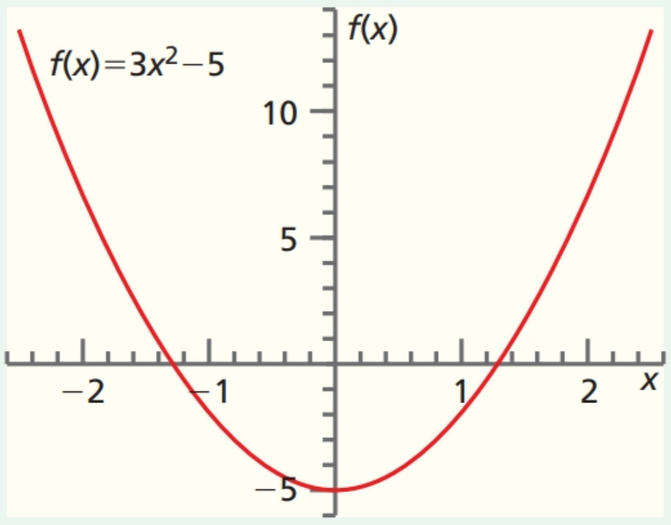


Figure ME2.3
The first derivative of the function shown in the previous figure as a function of x.

We return to the function graphed earlier and calculate the second derivative:

$$\frac{d^2(x^3 - 5x)}{dx^2} = \frac{d}{dx}\left[\frac{d(x^3 - 5x)}{dx}\right] = \frac{d(3x^2 - 5)}{dx} = 6x \qquad \textbf{(ME2.28)}$$

By evaluating

$$\frac{d^2f(x)}{dx^2} \quad \text{at } x = \pm\sqrt{\frac{5}{3}} = \pm 1.291 \qquad \textbf{(ME2.29)}$$

we see that $x = 1.291$ corresponds to the minimum, and $x = -1.291$ corresponds to the maximum.

If a function has an inflection point in the interval of interest, then

$$\frac{df(x)}{dx} = 0 \quad \text{and} \quad \frac{d^2f(x)}{dx^2} = 0 \qquad \textbf{(ME2.30)}$$

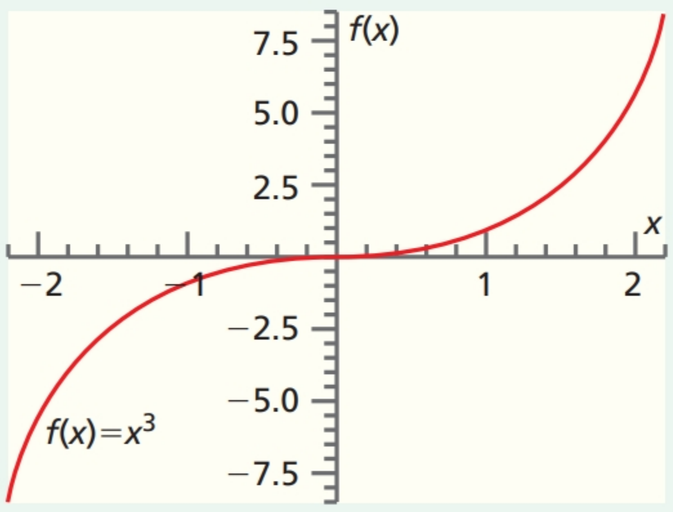


Figure ME2.4
$f(x) = x^3$ plotted as a function of x. The value of x at which the tangent to the curve is horizontal is called an inflection point.

An example for an inflection point is $x = 0$ for $f(x) = x^3$. A graph of this function in the interval $-2 \le x \le 2$ is shown in Figure ME2.4. In this case,

$$\frac{dx^3}{dx} = 3x^2 = 0 \quad \text{at } x = 0 \quad \text{and} \quad \frac{d^2(x^3)}{dx^2} = 6x = 0 \quad \text{at } x = 0 \qquad \textbf{(ME2.31)}$$

ME2.7 DEFINITE AND INDEFINITE INTEGRALS

In many areas of physical chemistry, the property of interest is the integral of a function over an interval in the variable of interest. For example, the work done in expanding an ideal gas from the initial volume V_i to the final volume V_f is the integral of the external pressure P_{ext} over the volume

$$w = -\int_{x_i}^{x_f} P_{\text{external}} A dx = -\int_{V_i}^{V_f} P_{\text{external}}\, dV \qquad \textbf{(ME2.32)}$$

Equation ME2.13 defines a definite integral in which the lower and upper limits of integration are given. Geometrically, the integral of a function over an interval is the area

under the curve describing the function. For example, the integral $\int_{-2.3}^{2.3}(x^3 - 5x)dx$ is the sum of the areas of the individual rectangles in Figure ME2.5 in the limit within which the width of the rectangles approaches zero. If the rectangles lie below the zero line, the incremental area is negative; if the rectangles lie above the zero line, the incremental area is positive. In this case, the total area is zero because the total negative area equals the total positive area.

The integral can also be understood as an antiderivative. From this point of view, the integral symbol is defined by the relation

$$f(x) = \int \frac{df(x)}{dx} dx \qquad \textbf{(ME2.33)}$$

and the function that appears under the integral sign is called the integrand. Interpreting the integral in terms of area, we evaluate a definite integral, and the interval over which the integration occurs is specified. The interval is not specified for an indefinite integral.

The geometrical interpretation is often useful in obtaining the value of a definite integral from experimental data when the functional form of the integrand is not known. For our purposes, the interpretation of the integral as an antiderivative is more useful. The value of the indefinite integral $\int (x^3 - 5x)dx$ is that function which, when differentiated, gives the integrand. Using the rules for differentiation discussed earlier, you can verify that

$$\int (x^3 - 5x)dx = \frac{x^4}{4} - \frac{5x^2}{2} + C \qquad \textbf{(ME2.34)}$$

Note the constant that appears in the evaluation of every indefinite integral. By differentiating the function obtained upon integration, you should convince yourself that any constant will lead to the same integrand. In contrast, a definite integral has no constant of integration. If we evaluate the definite integral

$$\int_{-2.3}^{2.3} (x^3 - 5x)dx = \left(\frac{x^4}{4} - \frac{5x^2}{2} + C\right)_{x=2.3} - \left(\frac{x^4}{4} - \frac{5x^2}{2} + C\right)_{x=-2.3} \qquad \textbf{(ME2.35)}$$

we see that the constant of integration cancels. The function obtained upon integration is an even function of x, and $\int_{-2.3}^{2.3}(x^3 - 5x)dx = 0$, just as we saw in the geometric interpretation of the integral.

Some indefinite integrals are encountered so often by students of physical chemistry that they become second nature and are recalled at will. These integrals are directly related to the derivatives discussed in Sections ME2.2–ME2.5 and include the following:

$$\int df(x) = f(x) + C$$

$$\int x^n dx = \frac{x^{n+1}}{n+1} + C$$

$$\int \frac{dx}{x} = \ln x + C \qquad \textbf{(ME2.36)}$$

$$\int e^{ax} = \frac{e^{ax}}{a} + C, \quad \text{where } a \text{ is a constant} \qquad \textbf{(ME2.37)}$$

$$\int \sin x\, dx = -\cos x + C \qquad \textbf{(ME2.38)}$$

$$\int \cos x\, dx = \sin x + C \qquad \textbf{(ME2.39)}$$

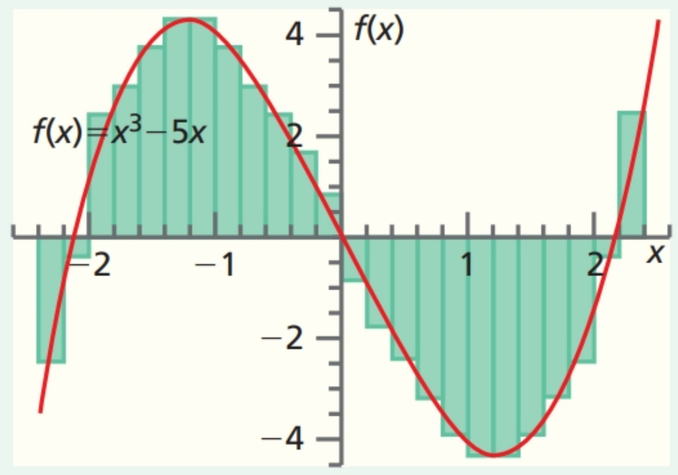


Figure ME2.5
The integral of a function over a given range corresponds to the area under the curve. The area under the curve is shown approximately by the green rectangles.

Although students will no doubt be able to recall the most commonly used integrals, the primary tool for the physical chemist in evaluating integrals is a good set of integral tables. Some commonly encountered integrals are listed below. The first group presents indefinite integrals.

$$\int (\sin ax)dx = -\frac{1}{a}\cos ax + C \quad \textbf{(ME2.40)}$$

$$\int (\cos ax)dx = \frac{1}{a}\sin ax + C \quad \textbf{(ME2.41)}$$

$$\int (\sin^2 ax)dx = \frac{1}{2}x - \frac{1}{4a}\sin 2ax + C \quad \textbf{(ME2.42)}$$

$$\int (\cos^2 ax)dx = \frac{1}{2}x + \frac{1}{4a}\sin 2ax + C \quad \textbf{(ME2.43)}$$

$$\int x\sin^2 bxdx = \frac{x^2}{4} - \frac{\cos 2bx}{8b^2} - \frac{x\sin 2bx}{4b} + C \quad \textbf{(ME2.44)}$$

$$\int x\cos^2 bxdx = \frac{x^2}{4} + \frac{\cos 2bx}{8b^2} + \frac{x\sin 2bx}{4b} + C \quad \textbf{(ME2.45)}$$

$$\int (x^2\sin^2 ax)dx = \frac{1}{6}x^3 - \left(\frac{1}{4a}x^2 - \frac{1}{8a^3}\right)\sin 2ax - \frac{1}{4a^2}x\cos 2ax + C \quad \textbf{(ME2.46)}$$

$$\int (x^2\cos^2 ax)dx = \frac{1}{6}x^3 + \left(\frac{1}{4a}x^2 - \frac{1}{8a^3}\right)\sin 2ax + \frac{1}{4a^2}x\cos 2ax + C \quad \textbf{(ME2.47)}$$

$$\int (\sin^3 ax)dx = -\frac{3\cos ax}{4a} + \frac{\cos 3ax}{12a} + C \quad \textbf{(ME2.48)}$$

$$\int (x^2\sin ax)dx = \frac{(a^2x^2 - 2)\cos ax}{a^3} + \frac{2x\sin ax}{a^2} + C \quad \textbf{(ME2.49)}$$

$$\int (x^2\cos ax)dx = \frac{(a^2x^2 - 2)\sin ax}{a^3} + \frac{2x\cos ax}{a^2} + C \quad \textbf{(ME2.50)}$$

$$\int x^m e^{ax}dx = \frac{x^m e^{ax}}{a} - \frac{m}{a}\int x^{m-1}e^{ax}dx + C \quad \textbf{(ME2.51)}$$

$$\int \frac{e^{ax}}{x^m}dx = -\frac{1}{m-1}\frac{e^{ax}}{x^{m-1}} + \frac{a}{m-1}\int \frac{e^{ax}}{x^{m-1}}dx + C \quad \textbf{(ME2.52)}$$

$$\int r^2 e^{-ar}dr = -\frac{e^{-ar}}{a^3}(a^2r^2 + 2ar + 2) + C \quad \textbf{(ME2.53)}$$

The following group includes definite integrals.

$$\int_0^a \sin\left(\frac{n\pi x}{a}\right) \times \sin\left(\frac{m\pi x}{a}\right)dx = \int_0^a \cos\left(\frac{n\pi x}{a}\right) \times \cos\left(\frac{m\pi x}{a}\right)dx = \frac{a}{2}\delta_{mn}$$

where δ_{mn} is one if $m = n$ and 0 if $m \neq n$ **(ME2.54)**

$$\int_0^a \left[\sin\left(\frac{n\pi x}{a}\right)\right] \times \left[\cos\left(\frac{n\pi x}{a}\right)\right]dx = 0 \quad \textbf{(ME2.55)}$$

$$\int_0^{\pi} \sin^2 mx\, dx = \int_0^{\pi} \cos^2 mx\, dx = \frac{\pi}{2} \tag{ME2.56}$$

$$\int_0^{\infty} \frac{\sin x}{\sqrt{x}} dx = \int_0^{\infty} \frac{\cos x}{\sqrt{x}} dx = \sqrt{\frac{\pi}{2}} \tag{ME2.57}$$

$$\int_0^{\infty} x^n e^{-ax} dx = \frac{n!}{a^{n+1}} \; (a > 0, n \text{ positive integer}) \tag{ME2.58}$$

$$\int_0^{\infty} x^{2n} e^{-ax^2} dx = \frac{1 \cdot 3 \cdot 5 \cdots (2n-1)}{2^{n+1} a^n} \sqrt{\frac{\pi}{a}} \; (a > 0, n \text{ positive integer}) \tag{ME2.59}$$

$$\int_0^{\infty} x^{2n+1} e^{-ax^2} dx = \frac{n!}{2\, a^{n+1}} \; (a > 0, n \text{ positive integer}) \tag{ME2.60}$$

$$\int_0^{\infty} e^{-ax^2} dx = \left(\frac{\pi}{4a}\right)^{1/2} \tag{ME2.61}$$

Commercially available software such as Mathematica™, Maple™, Matlab™, and MathCad™ can evaluate both definite and indefinite integrals.

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MATH ESSENTIAL 3: Partial Derivatives

Many quantities that we will encounter in physical chemistry are functions of several variables. In that case, we have to reformulate differential calculus to take several variables into account. We define the partial derivative with respect to a specific variable just as we did in Section ME2.2 by treating all other variables indicated by subscripts as constants. For example, consider 1 mol of an ideal gas for which

$$P = f(V, T) = \frac{RT}{V} \qquad \textbf{(ME3.1)}$$

Note that P can be written as a function of the two variables V and T. The change in P resulting from a change in V or T is proportional to the following **partial derivatives:**

$$\left(\frac{\partial P}{\partial V}\right)_T = \lim_{\Delta V \to 0} \frac{P(V + \Delta V, T) - P(V, T)}{\Delta V} = \lim_{\Delta V \to 0} \frac{R}{\Delta V}\left(\frac{1}{V + \Delta V} - \frac{1}{V}\right)$$

$$= \lim_{\Delta V \to 0} \frac{R}{\Delta V}\left(\frac{-\Delta V}{V^2 + V\Delta V}\right) = -\frac{RT}{V^2}$$

$$\left(\frac{\partial P}{\partial T}\right)_V = \lim_{\Delta T \to 0} \frac{P(V, T + \Delta T) - P(V, T)}{\Delta T} = \lim_{\Delta T \to 0} \frac{1}{\Delta T}\left[\frac{R(T + \Delta T)}{V} - \frac{RT}{V}\right]$$

$$= \frac{R}{V} \qquad \textbf{(ME3.2)}$$

The subscript y in $(\partial f/\partial x)_y$ indicates that y is being held constant in the differentiation of the function f with respect to x. The partial derivatives in Equation (ME3.2) allow one to determine how a function changes when all of the variables change. For example, what is the change in P if the values of T and V both change? In this case, P changes to $P + dP$ where

$$dP = \left(\frac{\partial P}{\partial T}\right)_V dT + \left(\frac{\partial P}{\partial V}\right)_T dV = \frac{R}{V}dT - \frac{RT}{V^2}dV \qquad \textbf{(ME3.3)}$$

Consider the following practical illustration of Equation (ME3.3). You are on a hill and have determined your altitude above sea level. How much will the altitude (denoted z) change if you move a small distance east (denoted by x) and north (denoted by y)? The change in z as you move east is the slope of the hill in that direction, $(\partial z/\partial x)_y$, multiplied by the distance dx that you move. A similar expression can be written for the change in altitude as you move north. Therefore, the total change in altitude is the sum of these two changes or

$$dz = \left(\frac{\partial z}{\partial x}\right)_y dx + \left(\frac{\partial z}{\partial y}\right)_x dy \qquad \textbf{(ME3.4)}$$

The first term is the slope of the hill in the x direction, and the second term is the slope in the y direction. These changes in the height z as you move first along the x direction and then along the y direction are illustrated in Figure ME3.1. Because the slope of the hill is a function of x and y, this expression for dz is only valid for small changes dx and dy. Otherwise, higher-order derivatives need to be considered.

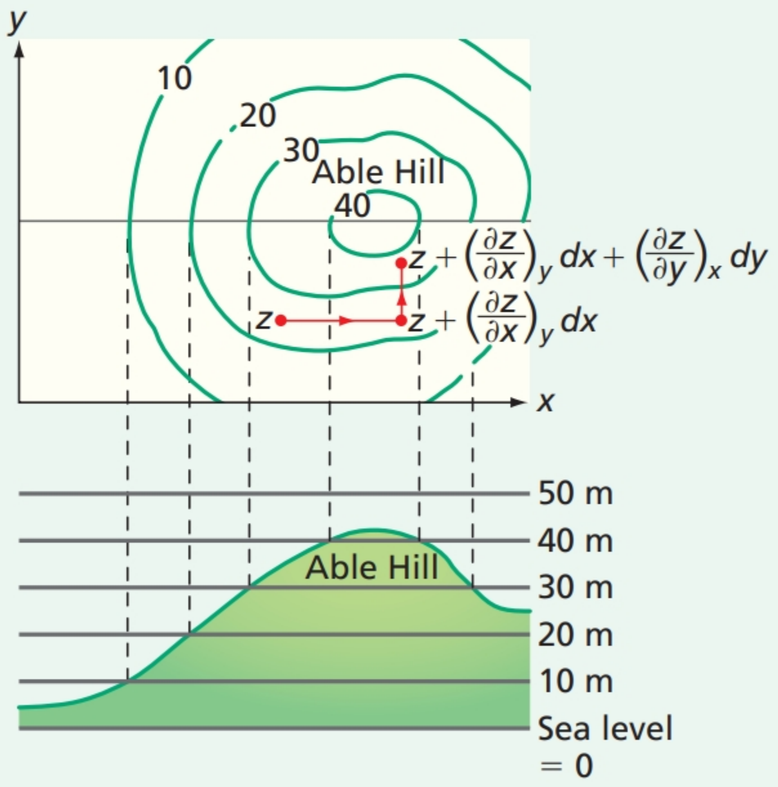


Figure ME3.1
Able Hill contour plot and cross section. The cross section (bottom) is constructed from the contour map (top). Starting at the point labeled z on the hill, you first move in the positive x direction and then along the y direction. If dx and dy are sufficiently small, the change in height dz is given by $dz = \left(\frac{\partial z}{\partial x}\right)_y dx + \left(\frac{\partial z}{\partial y}\right)_x dy$.