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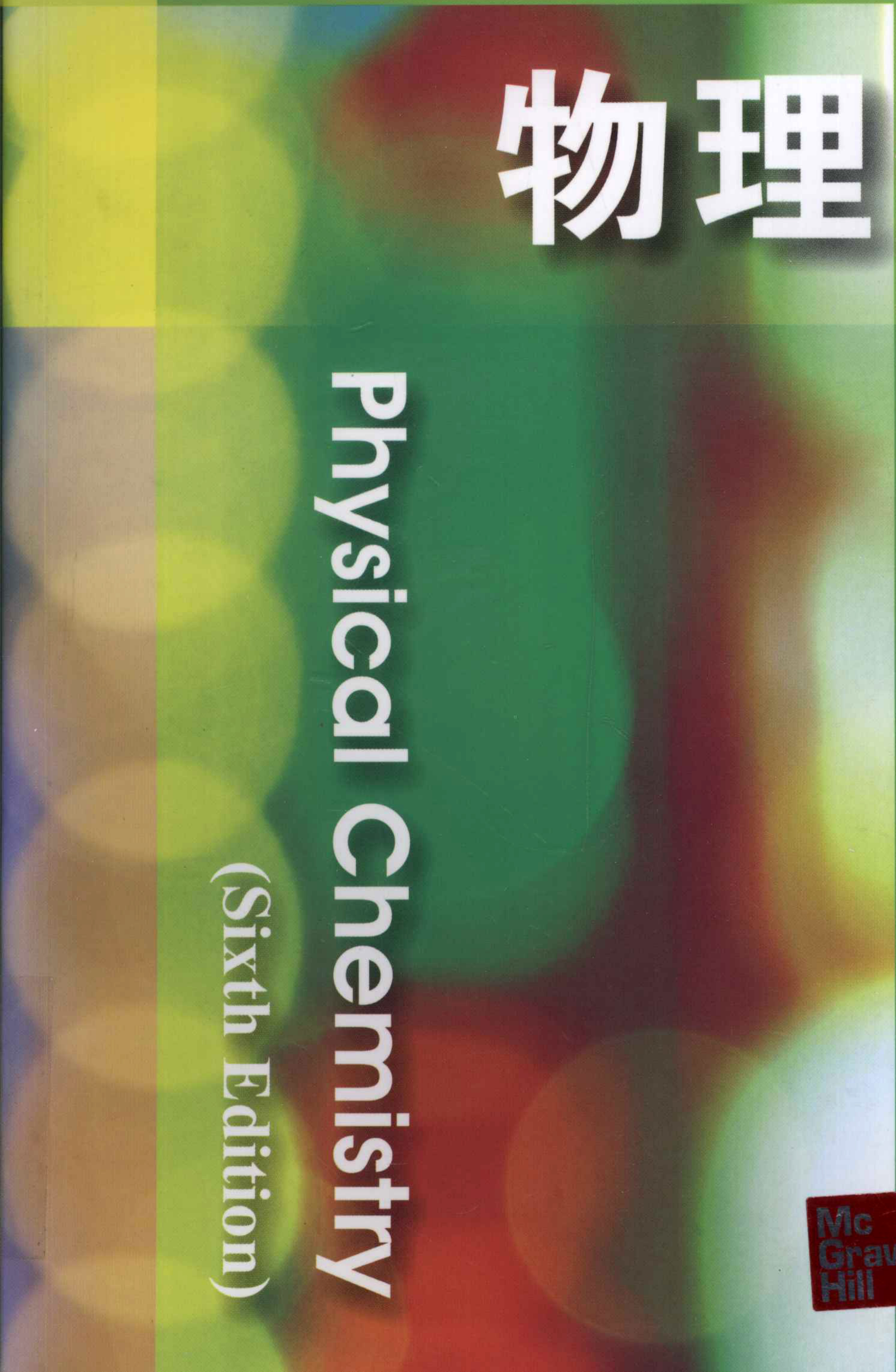

物理化学

（第6版）

Physical Chemistry

(Sixth Edition)

［美］ Ira N. Levine

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清华大学出版社

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出版前言

随着经济全球化、教育国际化趋势的逐渐增强，迫切需要既精通专业知识又精通外语的高素质人才。化学是自然科学的“中心学科”，高等化学教育应面向世界，适应时代的需要，吸收国外先进的教学理念和教育教学形式，培养学生适应国际形势需要的综合素质。

为反映国外化学类教材的最新内容和编写风格，同时也为提高学生阅读专业文献和获取信息的能力，为高等学校使用英文原版教材进行双语教学服务，我们精选了国外优秀的化学类教材，组成“国外高校优秀化学教材——影印版”，本书即为其中的一册。所选教材均在国外广泛采用，多数已再版，书中不仅介绍了有关概念、原理及应用，给出了丰富的实例和数据，还反映了作者不同的学术观点。

我们希望这套丛书的出版能对高等学校师生有所帮助，并对我国高等化学教育的发展做出贡献。

清华大学出版社
2012年10月

Preface

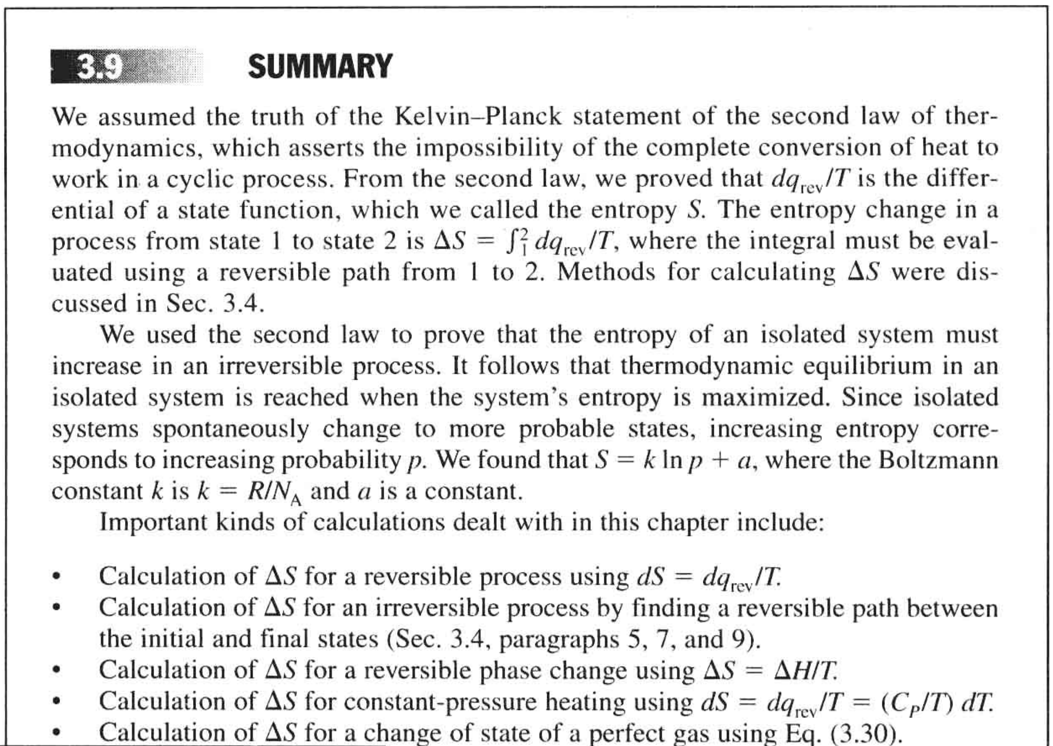
This textbook is for the standard undergraduate course in physical chemistry.

In writing this book, I have kept in mind the goals of clarity, accuracy, and depth. To make the presentation easy to follow, the book gives careful definitions and explanations of concepts, full details of most derivations, and reviews of relevant topics in mathematics and physics. I have avoided a superficial treatment, which would leave students with little real understanding of physical chemistry. Instead, I have aimed at a treatment that is as accurate, as fundamental, and as up-to-date as can readily be presented at the undergraduate level.

LEARNING AIDS

Physical chemistry is a challenging course for many students. To help students, this book has many learning aids:

- Each chapter has a summary of the key points. The summaries list the specific kinds of calculations that students are expected to learn how to do.



3.9 SUMMARY

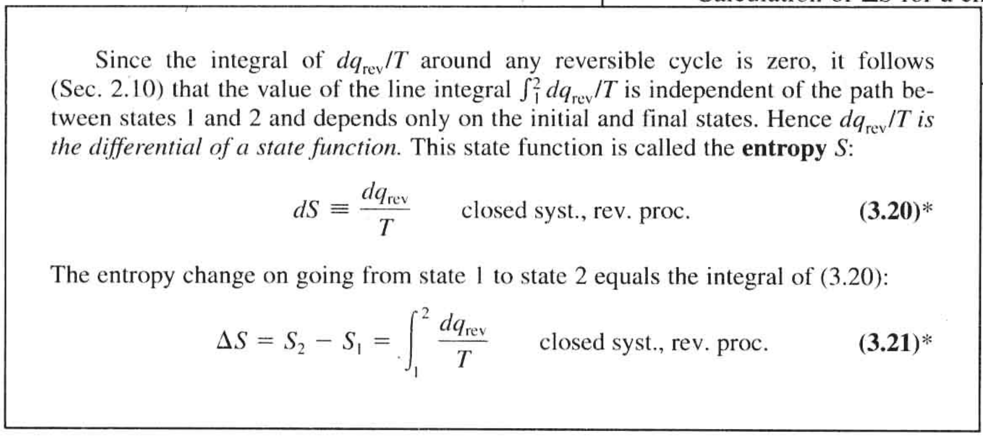
We assumed the truth of the Kelvin–Planck statement of the second law of thermodynamics, which asserts the impossibility of the complete conversion of heat to work in a cyclic process. From the second law, we proved that dq_{rev}/T is the differential of a state function, which we called the entropy S. The entropy change in a process from state 1 to state 2 is $\Delta S = \int_1^2 dq_{rev}/T$, where the integral must be evaluated using a reversible path from 1 to 2. Methods for calculating ΔS were discussed in Sec. 3.4.

We used the second law to prove that the entropy of an isolated system must increase in an irreversible process. It follows that thermodynamic equilibrium in an isolated system is reached when the system's entropy is maximized. Since isolated systems spontaneously change to more probable states, increasing entropy corresponds to increasing probability p. We found that $S = k \ln p + a$, where the Boltzmann constant k is $k = R/N_A$ and a is a constant.

Important kinds of calculations dealt with in this chapter include:

- Calculation of ΔS for a reversible process using $dS = dq_{rev}/T$.
- Calculation of ΔS for an irreversible process by finding a reversible path between the initial and final states (Sec. 3.4, paragraphs 5, 7, and 9).
- Calculation of ΔS for a reversible phase change using $\Delta S = \Delta H/T$.
- Calculation of ΔS for constant-pressure heating using $dS = dq_{rev}/T = (C_P/T)\,dT$.
- Calculation of ΔS for a change of state of a perfect gas using Eq. (3.30).

ing perfect gases at constant T and P using Eq. (3.33).



Since the integral of dq_{rev}/T around any reversible cycle is zero, it follows (Sec. 2.10) that the value of the line integral $\int_1^2 dq_{rev}/T$ is independent of the path between states 1 and 2 and depends only on the initial and final states. Hence *dq_{rev}/T is the differential of a state function.* This state function is called the **entropy** S:

$$dS \equiv \frac{dq_{rev}}{T} \qquad \text{closed syst., rev. proc.} \qquad \mathbf{(3.20)}^*$$

The entropy change on going from state 1 to state 2 equals the integral of (3.20):

$$\Delta S = S_2 - S_1 = \int_1^2 \frac{dq_{rev}}{T} \qquad \text{closed syst., rev. proc.} \qquad \mathbf{(3.21)}^*$$

- Equations that students should memorize are marked with an asterisk. These are the fundamental equations and students are cautioned against blindly memorizing unstarred equations.

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- A substantial number of worked-out examples are included. Most examples are followed by an exercise with the answer given, to allow students to test their understanding.

EXAMPLE 2.6 Calculation of ΔH

$C_{P,\mathrm{m}}$ of a certain substance in the temperature range 250 to 500 K at 1 bar pressure is given by $C_{P,\mathrm{m}} = b + kT$, where b and k are certain known constants. If n moles of this substance is heated from T_1 to T_2 at 1 bar (where T_1 and T_2 are in the range 250 to 500 K), find the expression for ΔH.

Since P is constant for the heating, we use (2.79) to get

$$\Delta H = q_P = \int_1^2 nC_{P,\mathrm{m}}\,dT = n\int_{T_1}^{T_2}(b + kT)\,dT = n\left(bT + \tfrac{1}{2}kT^2\right)\Big|_{T_1}^{T_2}$$

$$\Delta H = n\left[b(T_2 - T_1) + \tfrac{1}{2}k(T_2^2 - T_1^2)\right]$$

Exercise

Find the ΔH expression when n moles of a substance with $C_{P,\mathrm{m}} = r + sT^{1/2}$, where r and s are constants, is heated at constant pressure from T_1 to T_2. [*Answer:* $nr(T_2 - T_1) + \frac{2}{3}ns(T_2^{3/2} - T_1^{3/2})$.]

- A wide variety of problems are included. As well as being able to do calculational problems, it is important for students to have a good conceptual understanding of the material. To this end, a substantial number of qualitative questions are included, such as True/False questions and questions asking students to decide whether quantities are positive, negative, or zero. Many of these questions result from misconceptions that I have found that students have. A solutions manual is available to students.
- Although physical chemistry students have studied calculus, many of them have not had much experience with science courses that use calculus, and so have forgotten much of what they learned. This book reviews relevant portions of calculus (Secs. 1.6, 1.8, and 8.9). Likewise, reviews of important topics in physics are included (classical mechanics in Sec. 2.1, electrostatics in Sec. 13.1, electric dipoles in Sec. 13.14, and magnetic fields in Sec. 20.12.)
- Section 1.9 discusses effective study methods.

Integral Calculus

Frequently one wants to find a function $y(x)$ whose derivative is known to be a certain function $f(x)$; $dy/dx = f(x)$. The most general function y that satisfies this equation is called the **indefinite integral** (or *antiderivative*) of $f(x)$ and is denoted by $\int f(x)\,dx$.

$$\text{If} \quad dy/dx = f(x) \qquad \text{then} \quad y = \int f(x)\,dx \qquad \textbf{(1.52)*}$$

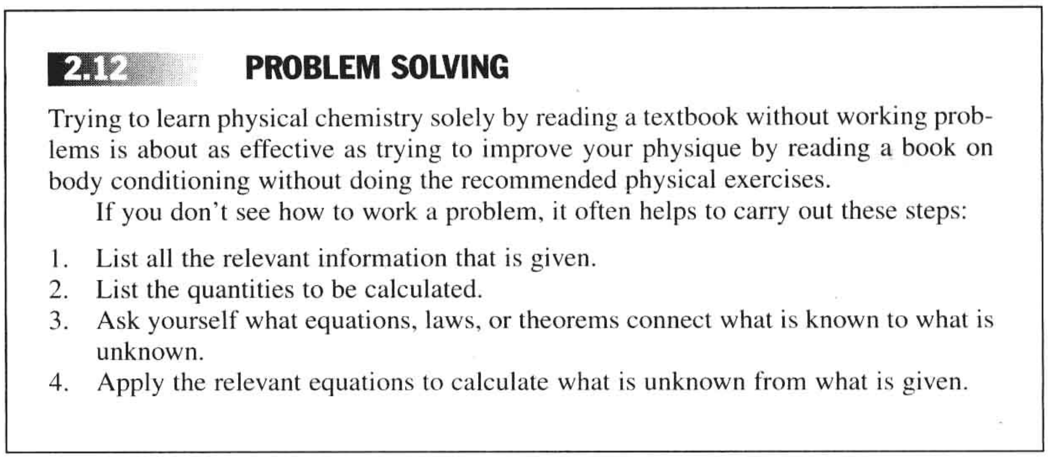
The function $f(x)$ being integrated in (1.52) is called the **integrand.**

1.9 STUDY SUGGESTIONS

A common reaction to a physical chemistry course is for a student to think, "This looks like a tough course, so I'd better memorize all the equations, or I won't do well." Such a reaction is understandable, especially since many of us have had teachers who emphasized rote memory, rather than understanding, as the method of instruction.

Actually, comparatively few equations need to be remembered (they have been marked with an asterisk), and most of these are simple enough to require little effort at conscious memorization. Being able to reproduce an equation is no guarantee of being able to apply that equation to solving problems. To use an equation properly, one must understand it. Understanding involves not only knowing what the symbols stand for but also knowing when the equation applies and when it does not apply. Everyone knows the ideal-gas equation $PV = nRT$, but it's amazing how often students will use

- Section 2.12 contains advice on how to solve problems in physical chemistry.



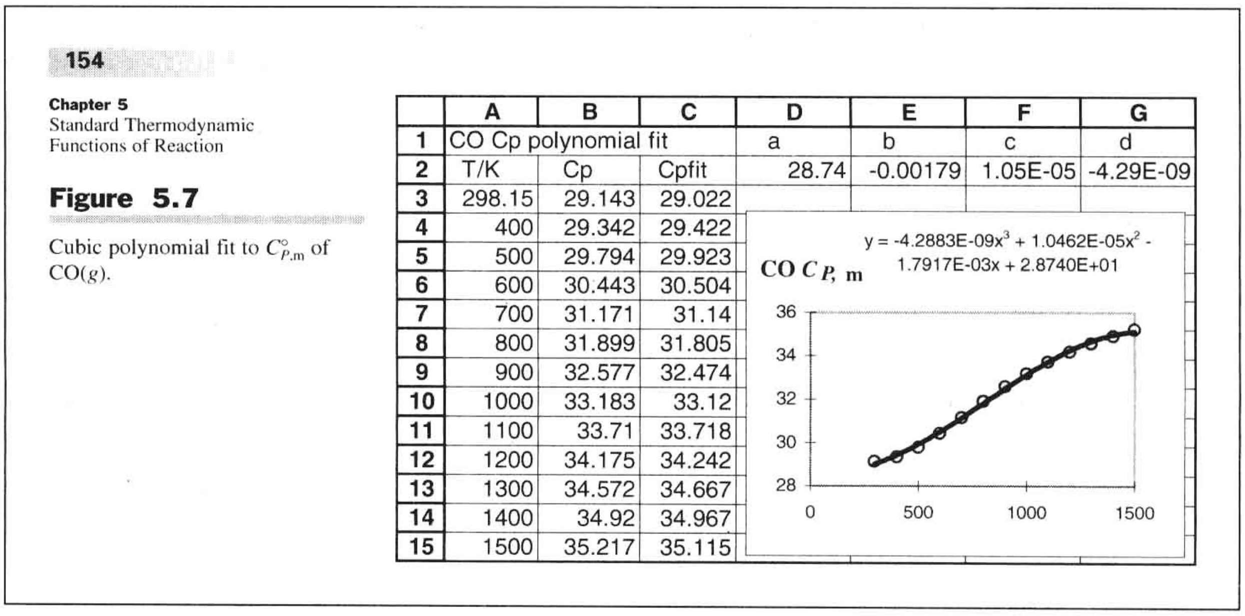
2.12 PROBLEM SOLVING

Trying to learn physical chemistry solely by reading a textbook without working problems is about as effective as trying to improve your physique by reading a book on body conditioning without doing the recommended physical exercises.

If you don't see how to work a problem, it often helps to carry out these steps:

1. List all the relevant information that is given.
2. List the quantities to be calculated.
3. Ask yourself what equations, laws, or theorems connect what is known to what is unknown.
4. Apply the relevant equations to calculate what is unknown from what is given.

- The derivations are given in full detail, so that students can readily follow them. The assumptions and approximations made are clearly stated, so that students will be aware of when the results apply and when they do not apply.
- Many student errors in thermodynamics result from the use of equations in situations where they do not apply. To help prevent this, important thermodynamic equations have their conditions of applicability listed alongside the equations.
- Systematic listings of procedures to calculate q, w, ΔU, ΔH, and ΔS (Secs. 2.9 and 3.4) for common kinds of processes are given.
- Detailed procedures are given for the use of a spreadsheet to solve such problems as fitting data to a polynomial (Sec. 5.6), solving simultaneous equilibria (Sec. 6.5), doing linear and nonlinear least-squares fits of data (Sec. 7.3), using an equation of state to calculate vapor pressures and molar volumes of liquids and vapor in equilibrium (Sec. 8.5), and computing a liquid–liquid phase diagram by minimization of G (Sec. 12.11).



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Chapter 5
Standard Thermodynamic Functions of Reaction

Figure 5.7

Cubic polynomial fit to $C^\circ_{P,\mathrm{m}}$ of CO(g).

	A	B	C	D	E	F	G
1	CO Cp polynomial fit			a	b	c	d
2	T/K	Cp	Cpfit	28.74	-0.00179	1.05E-05	-4.29E-09
3	298.15	29.143	29.022				
4	400	29.342	29.422				
5	500	29.794	29.923				
6	600	30.443	30.504				
7	700	31.171	31.14				
8	800	31.899	31.805				
9	900	32.577	32.474				
10	1000	33.183	33.12				
11	1100	33.71	33.718				
12	1200	34.175	34.242				
13	1300	34.572	34.667				
14	1400	34.92	34.967				
15	1500	35.217	35.115				

CO C P, m
y = -4.2883E-09x^3 + 1.0462E-05x^2 - 1.7917E-03x + 2.8740E+01
36
34
32
30
28
0
500
1000
1500

- Although the treatment is an in-depth one, the mathematics has been kept at a reasonable level and advanced mathematics unfamiliar to students is avoided.
- The presentation of quantum chemistry steers a middle course between an excessively mathematical treatment that would obscure the physical ideas for most undergraduates and a purely qualitative treatment that does little beyond repeat what students have learned in previous courses. Modern ab initio, density functional, semiempirical, and molecular mechanics methods are discussed, so that students can appreciate the value of such calculations to nontheoretical chemists.

IMPROVEMENTS IN THE SIXTH EDITION

- Students often find that they can solve the problems for a section if they work the problems immediately after studying that section, but when they are faced with an exam that contains problems from a few chapters, they have trouble. To give practice on dealing with this situation, I have added review problems at the ends of Chapters 3, 6, 9, 12, 16, 19, and 21, where each set of review problems covers about three chapters.

REVIEW PROBLEMS

R3.1 For a closed system, give an example of each of the following. If it is impossible to have an example of the process, state this. (*a*) An isothermal process with $q \neq 0$. (*b*) An adiabatic process with $\Delta T \neq 0$. (*c*) An isothermal process with $\Delta U \neq 0$. (*d*) A cyclic process with $\Delta S \neq 0$. (*e*) An adiabatic process with $\Delta S \neq 0$. (*f*) A cyclic process with $w \neq 0$.

R3.2 State what experimental data you would need to look up to calculate each of the following quantities. Include only the minimum amount of data needed. Do not do the calculations. (*a*) ΔU and ΔH for the freezing of 653 g of liquid water at 0°C and 1 atm. (*b*) ΔS for the melting of 75 g of Na at 1 atm and its normal melting point. (*c*) ΔU and ΔH when 2.00 mol of O_2 gas

- One aim of the new edition is to avoid the increase in size that usually occurs with each new edition and that eventually produces an unwieldy text. To this end, Chapter 13 on surfaces was dropped. Some of this chapter was put in the chapters on phase equilibrium (Chapter 7) and reaction kinetics (Chapter 16), and the rest was omitted. Sections 4.2 (thermodynamic properties of nonequilibrium systems), 10.5 (models for nonelectrolyte activity coefficients), 17.19 (nuclear decay), and 21.15 (photoelectron spectroscopy) were deleted. Some material formerly in these sections is now in the problems. Several other sections were shortened.
- The book has been expanded and updated to include material on nanoparticles (Sec. 7.6), carbon nanotubes (Sec. 23.3), polymorphism in drugs (Sec. 7.4), diffusion-controlled enzyme reactions (Sec. 16.17), prediction of dihedral angles (Sec. 19.1), new functionals in density functional theory (Sec. 19.10), the new semiempirical methods RM1, PM5, and PM6 (Sec. 19.11), the effect of nuclear spin on rotational-level degeneracy (Sec. 20.3), the use of protein IR spectra to follow the kinetics of protein folding (Sec. 20.9), variational transition-state theory (Sec. 22.4), and the Folding@home project (Sec. 23.14).

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I welcome any suggestions for improving the book that readers might have.

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To the memory of my mother and my father

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