Physical Chemistry in Action

Miloslav Pekař

The Essentials of Thermodynamics

Springer

Physical Chemistry in Action

Physical Chemistry in Action presents volumes which outline essential physicochemical principles and techniques needed for areas of interdisciplinary research. The scope and coverage includes all areas of research permeated by physical chemistry: organic and inorganic chemistry; biophysics, biochemistry and the life sciences; the pharmaceutical sciences; crystallography; materials sciences; and many more. This series is aimed at students, researchers and academics who require a fundamental knowledge of physical chemistry for working in their particular research field. The series publishes edited volumes, authored monographs and textbooks, and encourages contributions from field experts working in all of the various disciplines.

Miloslav Pekař

The Essentials of Thermodynamics

Springer

Miloslav Pekař
Faculty of Chemistry
Institute of Physical and Applied Chemistry
Brno University of Technology
Brno, Czech Republic

ISSN 2197-4349 ISSN 2197-4357 (electronic)
Physical Chemistry in Action
ISBN 978-3-031-60320-4 ISBN 978-3-031-60321-1 (eBook)
https://doi.org/10.1007/978-3-031-60321-1

© The Editor(s) (if applicable) and The Author(s), under exclusive license to Springer Nature Switzerland AG 2024

This work is subject to copyright. All rights are solely and exclusively licensed by the Publisher, whether the whole or part of the material is concerned, specifically the rights of translation, reprinting, reuse of illustrations, recitation, broadcasting, reproduction on microfilms or in any other physical way, and transmission or information storage and retrieval, electronic adaptation, computer software, or by similar or dissimilar methodology now known or hereafter developed.
The use of general descriptive names, registered names, trademarks, service marks, etc. in this publication does not imply, even in the absence of a specific statement, that such names are exempt from the relevant protective laws and regulations and therefore free for general use.
The publisher, the authors and the editors are safe to assume that the advice and information in this book are believed to be true and accurate at the date of publication. Neither the publisher nor the authors or the editors give a warranty, expressed or implied, with respect to the material contained herein or for any errors or omissions that may have been made. The publisher remains neutral with regard to jurisdictional claims in published maps and institutional affiliations.

This Springer imprint is published by the registered company Springer Nature Switzerland AG
The registered company address is: Gewerbestrasse 11, 6330 Cham, Switzerland

If disposing of this product, please recycle the paper.

Essentially, all known physical laws
were discovered by watching
how things move,
whether they are planets or atoms[1]

---

[1] Michor F., Liphardt J., Ferrari M., Widom J. What does physics have to do with cancer? *Nature Reviews* **11**, 657–670 (2011).

Dedicated to the memory of Ivan Samohýl
(www.fch.vut.cz/vav/sapelite/is)

Preface

Why another book on thermodynamics? Well, because each author is convinced that he will finally interpret it better, clearer, more comprehensibly than anyone before. This text has at least one more motivating source. It is meant to serve as a precursor to our not-so-long-ago published, more advanced monograph on the non-equilibrium thermodynamics of linear fluids [1]. A precursor, which, similarly to the monograph, draws a great deal from C. A. Truesdell's[2] efforts to cleanse thermodynamics from strange, too intuitive, even mystical procedures and to place it on a solid mathematical foundation such as mechanics. This foundation, however, is also firmly connected with practical knowledge and experience, which it simply tries to generalize or to model in a correct mathematical way.

Despite the attempt to follow a correct mathematical procedure, perhaps not perfect in this basic implementation, this writing attempts to be clear, illustrative and maintains a connection with the experience of both common and experimental reality. Therefore, it resorts quite often to a historicizing approach, so that readers do not get the impression that equations, relations and quantities simply appear in the mind of thoughtful scientists; on the contrary, they will get a basic idea of the building of thermodynamics over time and its logical development. This should contribute to the aforementioned better clarity and understanding of what thermodynamics is all about. As W. F. Giauque[3] said—thermodynamics is not difficult if you can keep track on what it is you are talking about. Historical considerations in the interpretation are recommended by educational experts in chemistry [2].

And yet another insight of contemporary pedagogy readers will find applied here. The interpretation is not strictly a sequence of logically closed, single-topic units, but a single stream of reasoning in which related topics may occur in different places, as the logic of the mainstream requires. This instructional approach appears to promote

---

[2] Clifford Ambrose Truesdell (1919–2000), American mathematician, creator and promoter of rational thermodynamics, spent most of his academic career at Johns Hopkins University.

[3] William Francis Giauque (1895–1982), American physical chemist, was a professor at the University of California, Berkeley, best known for his research on very low temperatures, for which he received the 1949 Nobel Prize in Chemistry.

desirable rehearsal, leading to a more permanent retention of the discussed content in memory [3–5]. The progression of explanation through completed and closed topics may show better scores on immediate tests of learning, but it affects long-term memory less effectively. Ideally, this book is primarily concerned with permanently embedding the essence of thermodynamics in readers' memories.

One last motivating element. Although the substantial part of the interpretation concerns classical thermodynamics, we systematically include time as the fundamental quantity. This is in contrast to the traditional interpretation where time has completely disappeared, and in line with, for example, Truesdell's approach or Müller's position [6]: "Traditionally, starting with Clausius, there is the strangest reluctance to mention time in thermodynamics, although there is no good reason for the omission of time."

In (text)books like this, it is not customary to place references at every point, but to give a summary of the sources of inspiration. This is also the case here; direct references in the text are limited to necessary cases; most items listed inspired the entire text. Two principal sources used throughout this text were [7, 8], more advanced mathematics was taken from [9–12], personal lockets from [13–16].

There is an accompanying website to this book, please look at https://www.fch.vut.cz/en/rad/poester.

Brno, Czech Republic Miloslav Pekař

References

1. Pekař, M., Samohýl, I.: The thermodynamics of linear fluids and fluid mixtures. Springer, Cham (2014). See also https://www.fch.vut.cz/vav/sapelite
2. Olsson, K.A., Balgopal, M.M., Levinger, N.E.: How did we get here? Teaching chemistry with a historical perspective. J. Chem. Edu. **92**(11), 1773–1776 (2015)
3. Dunlosky, J., Rawson, K.A., Marsh, E.J., Nathan, M.J., Willingham, D.T.: Improving students' learning with effective learning techniques: promising directions from cognitive and educational psychology. Psycholog. Sci. Pub. Int. **14**(1), 4–58 (2013)
4. Karpicke, J.D., Blunt, J.R.: Retrieval practice produces more learning than elaborative studying with concept mapping. Science **331**, 772–775 (2011)
5. Roediger, H.L., Pyc, M.A.: Inexpensive techniques to improve education: applying cognitive psychology to enhance educational practice. J. App. Res. Mem. Cogn. **1**(4), 242–248 (2012)
6. Müller, I.: Max Planck-a life for thermodynamics. Ann. Phy. **17**(2–3), 73–87 (2008)
7. Truesdell, C.: The tragicomical history of thermodynamics 1822–1854. Springer, New York (1980)
8. Truesdell, C., Bharatha, S.: The concepts and logic of classical thermodynamics as a theory of heat engines, rigorously constructed upon the foundation laid by S.Carnot and F. Reech. Springer, New York (1977)
9. Jarník, V.: Differential Calculus I. Praha: Academia (1974). In Czech
10. Kvasnica, J.: Mathematics in physics. Praha: Academia (1989). In Czech
11. McQuarrie, D.A.: Mathematical methods for scientists and engineers. Sausalito: University Science Books (2003)
12. Rektorys, K. et al.: Overview of applied mathematics. Praha: SNTL (1981). In Czech
13. Laidler, K.J.: The world of physical chemistry. Oxford: Oxford University Press (1995)

14. Partington, J.R.: A short history of chemistry. New York: Dover (1989)
15. Pitzer, K.S., Shirley, D.A.: William Francis Giauque 1895–1982. A biographical memoir. Washington: National Academies Press (1996)
16. Tanner, R.I., Walters, K.: Rheology: An historical perspective. Amsterdam: Elsevier, (1998)

Contents

Chapter 1
Introduction

In the summer of 1827, a Scottish botanist, Robert Brown,[1] observed an interesting phenomenon in a microscope, which he also published about a year later [1]. Brown watched the pollen grains scattered in a drop of water and noticed their chaotic, jerky, incessant motion. It was also the time of the rebirth of the atomic theory of the structure of matter. About 80 years later, Einstein[2] and Smoluchowski[3] explained this phenomenon as the result of the permanent motion of water molecules (composed of oxygen and hydrogen atoms). Vast quantities of these building blocks of water are constantly bumping into tiny pollen grains. An enormous number of chaotic impacts move the grain back and forth, and it travels through the liquid medium on a winding, shaky and constantly wobbling path. Brown was probably not the first to observe such *motion* in a microscope, Einstein or Smoluchowski were not the first to explain the behavior of material bodies or solids by means of the unobservable, tiny particles that make up those bodies, but Brown's motion is historically the best-known case of observing microscopic motion (or its consequences) with the naked eye (albeit supported by lens). Microscopic motion has thus taken a firm place in our understanding and description of the events and phenomena we observe around us, alongside macroscopic motion, that is, the motion of bodies actually visible to the naked eye. By microscopic motion we mean the motion of the structural particles of material bodies, not the motion associated with the microscope as an instrument. In the case of water, these particles are molecules, and sometimes we will loosely confuse the terms particles and molecules. After all, the etymology of the word molecule lies in the expression for very small particle, very small matter in Latin or French.

---

[1] (1773–1858), one of the first to describe the nucleus of plant cells.

[2] Albert Einstein (1879–1955), a famous German physicist, was a professor at Princeton University in the USA from 1933; he is known as the creator of the theory of relativity but was awarded the Nobel Prize in Physics in 1921 for his discovery of the photoelectric effect.

[3] Marian Smoluchowski (1872–1917), an Austrian-born Polish physicist and one of the pioneers of statistical physics, worked at the universities of Lvov and Cracow.

M. Pekař, *The Essentials of Thermodynamics*, Physical Chemistry in Action,
https://doi.org/10.1007/978-3-031-60321-1_1

Brownian motion—of pollen or similar particles—is a consequence of motion—of molecules—which we have come to call *thermal motion* (and which we certainly cannot see with a light microscope alone). The adjective thermal refers to the commonly used concept of heat, which, as we shall soon see, also resonates in the term of the science we want to discuss here—thermodynamics. Furthermore, it probably also wants to capture an experimentally observed fact—thermal, or Brownian, motion responds to changes in temperature, and is more intense (faster) at elevated temperatures. Temperature (and its changes) is a concept that we associate closely with heat.

When the water molecules hit the pollen grains they "transfer part of their motion" to the pollen grains, thus moving them or changing the direction or speed of their motion. If we already know something of mechanics, let's say, somewhat more technically, that the particles (molecules) impart to the grains some of their energy, which is a certain measure of motion.

Temperature, heat and energy are central concepts of thermodynamics. Why? The translation of the name "thermodynamics" itself suggests this. It is formed from the Greek words heat (*θερμός*) and force (*δύναμις*). So thermodynamics could be the study of the force of heat, which indeed corresponds to the time of its formation, its origin and that coincidentally is also roughly the first half of the 19th century. That was the time when steam engines, devices that really harnessed the "force of heat", were developing rapidly. Nowadays, thermodynamics has progressed far beyond the steam engine, as we shall show in turn. But first, let's stop with those central concepts and look at their meaning and significance. Before doing so, let us just say that thermodynamics can be understood simply as a description of the thermal behaviour of bodies, of the consequences of thermal motion, as a science that handles all our experiences of heat and cold.

Reference

1. Duplantier, B.: Brownian motion, "diverse and undulating". Progr. Math. Phys. **47**, 201–293 (2006)

Chapter 2
Basic Concepts. Thermal Experience

Abstract Basic concepts of human experience with hotness or coldness are introduced—temperature and heat. They are characterized empirically and approached operationally. The thermometer and its role are also discussed. The differences between temperature and heat, two sides of the same coin, are stressed.

2.1 The Way to Temperature and Thermometer

Each of us has personal experience of feeling hot or cold. We feel that warm warms, hot burns, cold cools and frosty really freezes (and as a result, it can also “burn”). These subjective feelings are not always common or distinguishable—in the same room, in the same place, one person may feel cold, another warm and a third “just right”. However, in many cases, we can agree on a ranking of bodies from coldest to warmest. Everyone will agree that water in a summer pool is warmer than water frozen in ice, but colder than boiling water. We can no longer distinguish minor differences—e.g., similarly sorting differently cold ice or differently lukewarm water. But it is only a question of the imperfection of our senses. If we can find a more sensitive and objective (feeling-independent) measure, we can rank the bodies from coldest to warmest, preferably by means of a suitable numerical quantity which this measure will give us:

$$\begin{aligned}&\textit{body 1 warmer than body 2} \quad \Leftrightarrow \\ &\qquad \textit{numerical quantity of the body 1} > \textit{numerical quantity of body}\end{aligned} \tag{2.1}$$

This numerical quantity is called *temperature*. If we denote it in this section with a letter θ, we can rewrite relation (2.1) in a more concise and illustrative way:

$$\textit{body 1 warmer than body 2} \quad \Leftrightarrow \quad \theta_1 > \theta_2 \tag{2.2}$$

(θ_i is the temperature of body i) or generalize it to some extent:

M. Pekař, *The Essentials of Thermodynamics*, Physical Chemistry in Action,
https://doi.org/10.1007/978-3-031-60321-1_2