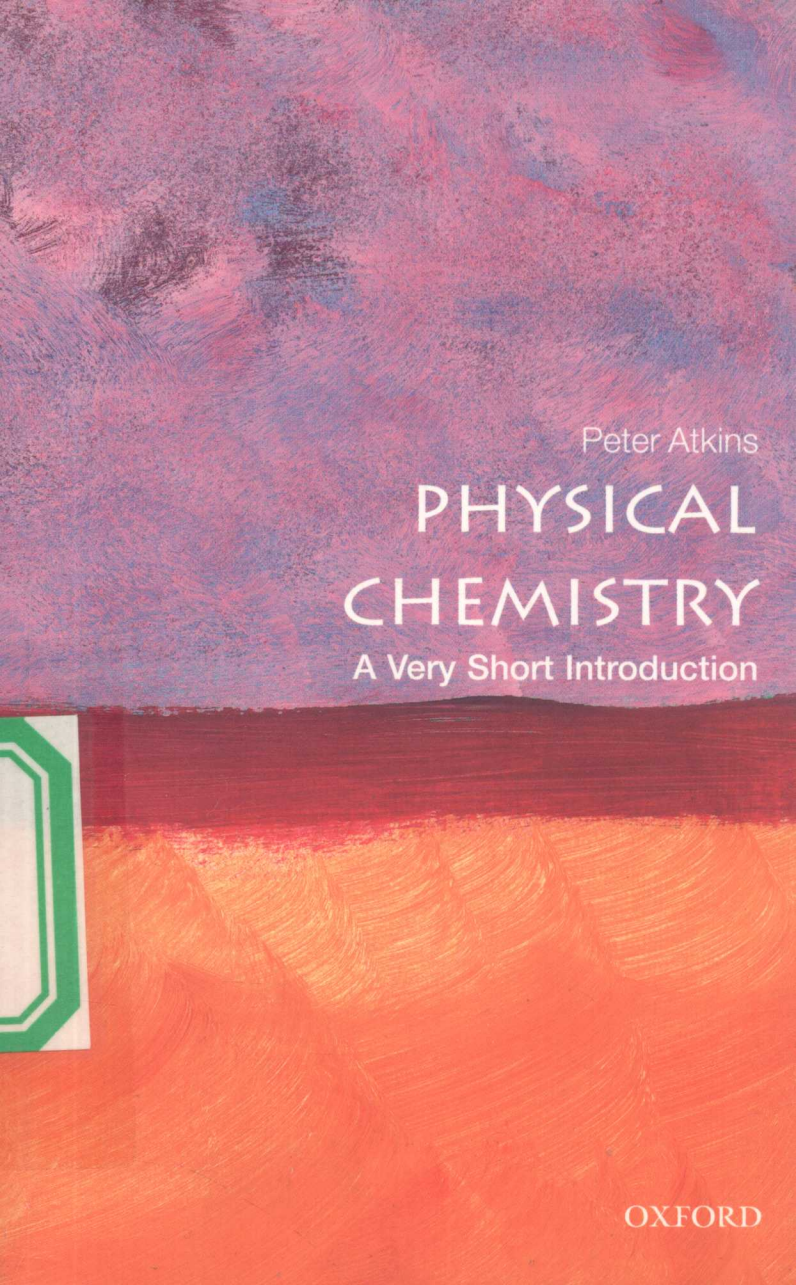
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PHYSICAL CHEMISTRY
A Very Short Introduction
OXFORD

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Preface

Physical chemistry provides the conceptual infrastructure of chemistry. It stands up to its knees in physics but has its head in inorganic and organic chemistry, the other two principal branches of chemistry. It follows that to understand modern chemistry, what it achieves, how it achieves it, and how it views the world, it is essential to understand the contributions of physical chemistry.

Physical chemistry, however, is built on a framework of mathematics. Therein lies the difficulty that aspiring students often find with the subject and which this author finds when seeking to share his vision of the subject without frightening his audience. With that in mind, I have sought to present an almost entirely verbal account of the subject so that readers can gather its attitudes and contributions to our understanding without being distracted by equations. Just occasionally, I show an equation to round out the discussion and show the basis of my verbalization; but I do that discreetly.

Standing in physics up to its knees necessarily means that physical chemistry draws on the wonderful contributions that physicists have made to our understanding of the world, and it will become apparent on reading these pages that Nobel Prizes for topics now fully part of physical chemistry have in large part been awarded to

physicists. That is just a mark of the debt that physical chemistry owes to physics. I shall introduce these topics, which include aspects of quantum mechanics and thermodynamics, but only at the level I judge sufficient.

I hope these pages will reveal the contributions that physical chemistry has made to all branches of chemistry. It provides, or at least elucidates, elaborates, and justifies, much of the language of modern chemistry, and these pages will give some insight into that language and the concepts that all chemists use in their conversations and work. I hope too that they will illustrate the cultural contributions that the subject makes to our understanding of the natural world.

Finally, I must stress that although the principles of chemistry are, as far as we know, thoroughly understood, physical chemistry is still a vibrantly alive subject. Such is the sophistication of current and emerging instrumental techniques, including computation, that the sinews of physical chemistry are stretched to wring all the information from the data that the techniques provide. Moreover, new types of matter—I have in mind soft matter and nanosystems—and elaborate 'old' matter, biological matter, are now open to study by its techniques and are providing rich fields for its application. I have tried to identify these emerging fields in the concluding 'The current challenge' paragraphs of each chapter. Perhaps those paragraphs outline what might be regarded as the research interests of a hypothetical perfect research laboratory in modern physical chemistry, where collaboration with intellectually neighbouring disciplines should be the core strategy.

Peter Atkins
Oxford, 2013

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Chapter 1
Matter from the inside

One way to understand how a physical chemist thinks and contributes to chemistry is to start at the interior of an atom and then to travel out into the world of bulk matter. The interior of an atom is where much of the explanation of matter is to be found and it is here that a chemist is most indebted to physics. Within this realm, within an atom, explanations necessarily draw on quantum mechanics, that perplexing description of the behaviour of the very small. That quantum mechanics is central to their description should not be taken to be a warning that the rest of this chapter will be incomprehensible! I shall distil from that theory only the qualitative essence of what we need.

Atoms

The ancient Greeks speculated that matter was composed of atoms. That was pure speculation unsupported by any experimental evidence and so cannot be regarded as the beginning of physical chemistry. Experimental evidence for atoms was accumulated by John Dalton (1766–1844) in the very early 19th century when the use of the chemical balance allowed quantitative measurements to be made on the reactions that matter undergoes. Dalton inferred the existence of atoms from his measurements but