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B. Widom
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Statistical Mechanics
A Concise Introduction for Chemists

Statistical mechanics is the theoretical apparatus used to study the properties of macroscopic systems – systems made up of many atoms or molecules – and relates those properties to the systems' microscopic constitution. This book is an introduction to statistical mechanics, intended to be used either by advanced undergraduates or by beginning graduate students.

The first chapter deals with statistical thermodynamics and aims to derive quickly the most commonly used formulas in the subject. The bulk of the book then illustrates the traditional applications of these formulas, such as the ideal gas, chemical equilibrium constants from partition functions, the ideal harmonic solid, and the statistical mechanical basis of the third law of thermodynamics. The last few chapters deal with less traditional material such as the non-ideal gas and the quantum ideal gases.

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He has held numerous prestigious visitorships, including ones at Amsterdam (van der Waals Professor), Oxford (IBM Visiting Professor of Theoretical Chemistry), Leiden (Lorentz Professor), and Utrecht (Kramers/Debye Professor). He has had many awards in recognition of his research in statistical mechanics, including the Boltzmann Medal of the IUPAP Commission on Statistical Physics and the Onsager Medal of the University of Trondheim. He has honorary degrees from the University of Chicago and the University of Utrecht, and has been elected to membership or fellowship of several scholarly academies including the U.S. National Academy of Sciences and the American Philosophical Society.

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Preface

This is an introduction to statistical mechanics, intended to be used either in an undergraduate physical chemistry course or by beginning graduate students with little undergraduate background in the subject. It assumes familiarity with thermodynamics, chemical kinetics and the kinetic theory of gases, and quantum mechanics and spectroscopy, at the level at which these subjects are normally treated in undergraduate physical chemistry. Ideas, principles, and formulas from them are appealed to frequently in the present work.

If statistical mechanics constituted about 10% of a physical chemistry course it would be covered in 8 to 12 lectures, depending on whether the course as a whole were taught in two semesters or three. There is enough material in these chapters for 12 lectures (or more). The instructor who has only 8 available will have to be selective. The most technical parts, and so the likeliest candidates for omission or contraction, are the treatment of *ortho*- and *para*-hydrogen, which is part of §2.4 of Chapter 2, that of molecular dynamics and Monte Carlo computer simulations in Chapter 7 (§§7.3 and 7.4), and that of the quantum ideal gases in Chapter 8, which includes a discussion of the grand partition function (§8.2).

Because only a relatively short time may be devoted to the subject it is important to arrive quickly at the usable formulas and important applications while still keeping the level consistent with that of an undergraduate physical chemistry course. The strategy adopted here is to start with the Boltzmann distribution law, making it plausible by appeal to two of its special cases (the Maxwell velocity distribution, assumed to be known from an earlier treatment of elementary kinetic theory, and the barometric distribution, which is derived, or re-derived, here), and by observing that its exponential form is required by the composition of probabilities for independent systems. The distribution law is stated with discrete-state, quantum mechanical energy-level notation at an early stage so as not to require generalizing the theory later from classical to quantum mechanical language. In a full-scale, graduate-level statistical mechanics course, where one has the leisure to devote more time to the foundations and where the students have more background in physics and mathematics, one can make a good case for starting with a classical phase-space formulation and later generalizing it to the quantum mechanical version. One would then typically start with the microcanonical rather than the canonical distribution.

Once the Boltzmann distribution law is stated the partition function appears naturally as a normalization denominator. The machinery of statistical thermodynamics – the connection of the free energy to the partition function – then follows from comparing the mean energy implied by the distribution law with that obtained from the free energy by the Gibbs–Helmholtz equation of thermodynamics. (Among earlier treatments of the subject, that in Guggenheim's wonderful little book *Boltzmann's Distribution Law* is probably that to which this one is closest in spirit.) This is followed by a qualitative discussion of energy fluctuations in a system of fixed temperature, and then the connection is made to a microcanonical system and the famous $S = k \ln W$.

What has just been outlined is the content of the first chapter, in which the machinery is set up. The next four chapters are devoted to the traditional applications: the statistical thermodynamics of the ideal gas of molecules with internal structure (Chapter 2), chemical equilibrium constants from partition functions (Chapter 3), the ideal harmonic solid (Chapter 4), and the statistical mechanical basis of the third law of thermodynamics (Chapter 5).

Much of the material in the remaining three chapters is less traditional in an undergraduate physical chemistry course but would be suitable even there and certainly at the beginning graduate level. The non-ideal gas (Chapter 6) provides the first glimpse of the problem of non-separable degrees of freedom, which appears in its undiluted and most challenging form in the liquid state (Chapter 7). The concluding chapter, on the quantum ideal gases, includes the degenerate electron gas as a model for electrons in metals, a subject that most instructors would wish to say something about even if they should choose to omit much of the detail in that section and much of the rest of the chapter.

Only equilibrium statistical mechanics is presented here. There are many topics in non-equilibrium statistical mechanics (the Nernst–Einstein relation between diffusion coefficient and mobility being an example) that are of interest and importance in physical chemistry, but given only 8–12 lectures some heartbreaking choices have to be made, as every instructor knows.

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