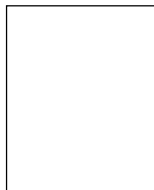


# Physical Chemistry

**Mohammed Farooq Ahmed**



*Physical Chemistry*

G K Vemulapalli

Prentice Hall of India, New Delhi, 1997

ISBN-81-203-1142-6, pp.991, Rs295.00

Since physical chemistry is a discipline which is concerned with the theoretical and quantitative basis of chemistry, the practitioner of every discipline of chemistry must be familiar with physical chemistry in order to understand his own subject. Similarly physical chemistry is necessary for a geologist, metallurgist, biologist and an engineer. Thus a text book in physical chemistry needs to cater to a wide spectrum of readership. Without doubt as is confessed by many an eminent physical chemist, physical chemistry is a difficult subject as a lot of mathematics and physics is applied in its elucidation which tends to make the subject abstract. Hence a course in physical chemistry should avoid excessively mathematical treatment that would obscure the physical ideas and at the same time the treatment should not be so qualitative as to mask its conceptual logic. The conceptual logic and beauty of physical chemistry will be evident only if the subject is presented with mathematical precision without losing sight of physical reality. Secondly, at present the domain of physical chemistry is not confined to thermodynamics and kinetics

alone but encompasses a wide range of topics such as quantum mechanics, spectroscopy, statistical mechanics, photochemistry, macromolecules and so on. Consequently, a single course in which such varied areas are treated can be valuable if it provides coherence to the study of these different topics by providing a conceptual link among them. I would classify the book under review among those attempts that have tried to achieve the above mentioned two objectives and therefore consider it as a welcome addition to the genre of physical chemistry text books.

The book consists of five parts. Part-I deals with introductory aspects, part-II with equilibrium thermodynamics, part-III with quantum chemistry and spectroscopy, part-IV with chemical kinetics and part-V with statistical thermodynamics and some selected topics. Various topics have been grouped into 33 separate chapters based upon their conceptual framework and appear in appropriate parts. Under this scheme of organization, it appears that some of the usual physical chemistry topics like macromolecules and surface chemistry have been neglected. But actually some aspects of the former, for instance determination of molecular weights by sedimentation are discussed in chapter 33 and those of the latter in chapters 12 and 28.1. Similarly the topic of electrochemistry is dispersed in chapters 11, 28 and 33. The wholeness of a topic thus suffers but it is inevitable as the author has aimed at providing a conceptual



link among the various topics. There is no chapter devoted to colloids.

The bulk of the material pertains to equilibrium thermodynamics (part-II), quantum chemistry (part-III) and chemical kinetics (part-IV) as in most other text books but the organization within each area and within different chapters differs significantly from other text books and much instruction is provided by the author in the preface for the efficient use of the book. For example, only an elementary account of statistical theory is given in chapter 2 before the introduction of thermodynamics so as to enhance the understanding of classical thermodynamics which follow in chapters 3, 4, 5 and 8.9 and a more rigorous account of it is given much later in chapter 29 so as not to intimidate the average student in the beginning itself. Similarly spectroscopy is introduced before the discussion of bonding theory which makes quantum theory more interesting and less abstract.

Part-II which deals with equilibrium thermodynamics comprises 10 chapters (3–12) which include in addition to the usual topics, chapters on phase equilibria, electrochemical equilibria and surface thermodynamics. This part gives a fairly detailed account of entropy and reversibility and a complete and logical account of the origin and use of chemical potential.

In part-III quantum chemistry and spectro-

scopy is presented in careful detail. The introduction of quantum mechanical principles in chapters 13 and 14 is immediately followed by its application with two chapters (15 & 16) one each on rotational and vibrational spectroscopy. This is followed by three chapters (17-19) which include a discussion of quantum mechanical treatment of hydrogen atom, qualitative discussion of basis functions and approximate methods and finally electronic structure and spectra of atoms. Chapter 20 discusses bonding theory and electronic spectra of diatomic molecules. Chapter 21 starts with an introduction to symmetry and group theoretical principles followed by bonding and electronic spectroscopy of polyatomic molecules. Part-III ends with Chapter 22 on magnetic resonance. The juxtaposition of theory and experiment in this part has made the subject less arduous and interesting to read. The matter presented is fairly upto date except that spectroscopic techniques like PES, ESCA have not been discussed.

Part-IV on chemical kinetics starts with three chapters (23-25) on gas phase kinetics followed by chapter 26 on kinetics in solution, chapter 27 on energy transfer and photochemistry and chapter 28 on heterogeneous and electrochemical reactions. The author has been successful in maintaining the balance between classical and modern kinetics. Topics such as energy transfer, photochemistry and lasers have been described from a kinetic viewpoint and are therefore included in this part of the book.



Part-V contains one chapter (29) on statistical thermodynamics. This is a continuation of the discussion in chapter 2 but treated in greater detail. It contains complete information on par with the requirements of an undergraduate curriculum. The remaining four chapters (30-33) in this part cover topics like optical and magnetic properties of molecules, the solid state, intermolecular forces and irreversible processes in liquid phase. Each of these sections is self-contained.

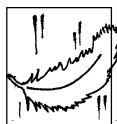
Overall the book is well written and readable. The treatment of the subject is neither too rigorous nor too qualitative but well balanced. It gives intuitive insights and clear verbal descriptions of the theory presented. A large number of figures that are well designed and easy to understand, supplement the book. A particularly appealing aspect of the book is the worked out examples at the end of each chapter that explore both the theory and practical aspects of the subject. These are helpful in building skills for the solution of similar but not identical problems that follow the exercises. For a book of its

length and scope, typographical errors are rare. I am unable to cite any really serious scientific or pedagogical deficiencies in this text book. Some minor drawbacks that can be pointed out are that the bibliography cites references only to books. No references have been made to important and relevant research articles. No appendix is devoted to mathematical concepts which would be a useful adjunct to a general reader. Similarly it does not contain exhaustive tables of physical data as is found in many other text books.

In summary although the book is meant as an undergraduate text book, it contains more detailed discussions on theoretical topics like reversibility, entropy, chemical potential, Schrödinger equation, wave functions and basis set than in many undergraduate physical chemistry text books. It can therefore serve as a useful reference book for many of the graduate students of Indian universities as well.

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**Mohammed Farooq Ahmed, Department of Chemistry, Bangalore University, Bangalore 560 054, India.**



The most beautiful thing we can experience is the mysterious. It is the source of all art and science. He to whom this emotion is a stranger, who can no longer pause to wonder and stand rapt in awe, is as good as dead; his eyes are closed.

Einstein



# They Make Space and Give Time

## The Engineer as Poet

**Gangan Prathap**



*Flying Buttresses, Entropy and O-Rings*  
*The World of an Engineer*  
 James L. Adams  
 Universities Press (India) Limited 1997  
 pp. 264 Rs 190

Perhaps the most poetic description of the role of an engineer in Society was made by Shelley, when he wrote about the role of technology in his *A Defence of Poetry*:

“Undoubtedly the promoters of utility, in this limited sense, have their appointed office in society. They follow the footsteps of poets, and copy the sketches of their creations into the book of common life. They make space and give time”.

“This is a book about engineering,” is the modest first line of the book. It is also a book about technology. Engineering and technology are not well understood by most people; even less well understood is the difference between science and technology. James L. Adams’ book goes a long way to communicate the bigger picture of the world of the engineer, from cathedrals (flying buttresses) to the Challenger (O-Rings), in this well organised, well written and easily accessible book. It is a must read for any

young aspirant to an engineering career and an equally valuable book for every parent who hopes to pilot a ward into the engineering profession. Most practising engineers, and even teachers of the various engineering disciplines “are so caught up in their particular activity that they have not developed a good sense of the whole.” It is a book for them, as well as for general readers, people who are not engineers.

Chapter One offers a brief history of technology. Technology was with us (man, the skilful, *Homo habilis*) far before Science (man, the thinker, *Homo sapiens*). It might be of interest to the Resonance reader to know that anthropologists classify us as *Homo sapiens sapiens* (too clever by half, perhaps!):- not only do we “take better care of ourselves,” we also have the “unprecedented ability to exploit others and destroy ourselves”.

Chapter Two gives a glimpse of the complexity of engineering and the profile of the profession (aeronautical to petroleum) and where they are distributed by function (only 0.5% do basic research but 9% are in management of R & D!). Most engineers (30%) work on development (design, testing and prototyping associated with new products), and significantly large numbers are in general management (19%) or perform production and inspection functions (17%). Engineering is classified according to “industry” (I work in the aerospace industry), “field” (I am an aeronautical engineer; the point to be made is that each industry is



multi-disciplinary – there are electrical engineers, electronics engineers, chemical engineers, mechanical engineers, etc. in the aerospace industry), “discipline” (I am a structural engineer) and sub-discipline (computational mechanics).

Chapter 3 elucidates how the “technology pushes” and the “market pulls” define modern engineering and technological practice. Design and innovation is the subject of chapter 4. Technology (derived from the Greek words *techne* = art or craft and *logos* = reason) requires ingenuity apart from art and skill. The word engineer is drawn from the Latin word *ingeniatorem*, implying ingenuity at innovation. Unfortunately, in English-speaking countries, there is a tendency to confuse engineering with those who run “engines”. There is a common lazy attitude to dismiss engineering and technology as “applied science”. Technology is not only distinct from science, it is enormously richer and autonomous (courtesy R Narasimha, *Current Science*, 1993, **64**, 494-502). While science deals with economy and unity of understanding, engineering or technology has to do with utility, and its economy thereof.

The language of science and engineering is of course mathematics and this is used to symbolically manipulate the basic physical principles. Chapter 5 is devoted to the unreasonable effectiveness of mathematics in science and engineering and chapter 6 shows how the familiar term “research and

development” (R & D) covers the entire chain from pure science (concept) to product development (cash). It was during the Scientific Revolution that science for the first time began to overlap technology.

Technology development is about trial and error, about conceiving, designing, testing, failing and learning from failure. Chapter 7 details the kind of experiments engineers perform to perfect failure. The process of development and “debugging” can be excruciatingly tiresome and failures can be devastating. The O-rings of the Challenger Space Shuttle tragedy is a modern parable of this. Adams also draws examples from the aircraft industry to show how “the codification of knowledge that becomes the directive of innovation” (a phrase borrowed from Professor R Narasimha) takes place.

Chapter 8 is devoted to the nitty-gritty of engineering - the art of manufacturing and assembly. Next comes the business of money. “No man except for a blockhead ever wrote for anything except money,” said Samuel Johnson. No engineer, or engineering industry, is free from this compulsion either. Money is the grease that makes the chain of technological innovation run. Chapter 9 captures this well, how engineering is inseparable from “money, people and business strategy”.

Technology cannot run free. Things do go wrong often, leading to large scale failures. The first reference to an engineer in the



English language appears in Shakespeare where he mockingly and despairingly talks of the “engineer hoist on his own petard.” Regulation is a must to ensure the safety of the planet from a technology grown wild. Progress involves failure and large scale projects can lead to devastatingly large losses of life and limb unless strictly regulated. Adams covers the “painful inevitability” of this in the penultimate chapter.

In the last chapter, Adams gazes into the crystal ball to speculate about the future. He suggests how the impending changes will influence the professional lives of engineers to come. “Increasingly complex technology and social problems will result in more constraints and requirements and require stronger interaction between the community

of engineers and the larger society.” The book ends with a very valuable bibliography of sources and suggested reading, arranged chapter-wise.

James L Adams is a Professor in the Department of Values, Technology, Science and Society at Stanford University. The book reflects all these values, using, as the quotation from Peter Likins on the blurb puts it, an “engaging, personal style of a letter to a young friend considering an engineering career.” Engineers as people, if not as poets, is the picture that is painted in this enlightening tour.

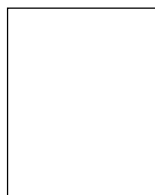
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**Gangan Prathap is with the National Aerospace Laboratories and the Jawaharlal Nehru Centre for Advanced Scientific Research in Bangalore.**

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## Thermodynamics: An Exposition for the Layman

**R Srinivasan**



*The Refrigerator and the Universe  
Understanding the Laws of Energy*  
Martin Goldstein and Inge F Goldstein  
Universities Press (India) Limited, 1997  
pp.443, Rs 225/-

Thermodynamics has a hoary past. The laws of thermodynamics have stood the test of time and have remained unchanged even after the revolutionary developments in physics with the advent of quantum

mechanics and special theory of relativity. Thermodynamics covers processes resulting in the interconversion of heat and work. It therefore has a wide range of applicability from heat engines to chemical reactions to black holes. Thermodynamics deals with the relationships between macroscopic properties such as energy, entropy and work. It does not depend on the microscopic mechanisms responsible for such properties. This is one of the reasons for its success and is also a cause for its limitation. While thermodynamics can say that a chemical reaction is possible it cannot state with certainty that it will occur.



In teaching thermodynamics at the undergraduate level, one finds it very difficult to put across the concept of entropy successfully to the student. In the calculation of entropy one must always limit oneself to reversible processes. But entropy is a state variable and hence independent of the path followed to reach the state, even if the path is irreversible. It is this idea that the student finds difficult to comprehend. The second law also has the consequence that only processes in which the total entropy of the system increases or stays constant are possible processes. Here the emphasis is on the total entropy of the system and not the entropy of its constituents. What constitutes the total system is also a matter of confusion and often leads to situations in which one sees an apparent contradiction to the second law.

In this book the authors aim to trace the development of thermodynamics from its early days of caloric theory to its application to the current ideas of an expanding universe in astrophysics. It is a very daunting task to take on such a wide sweep and it is more challenging to do this without the aid of mathematics. It is one of the special features of the book that even the elementary mathematical equations are relegated to an appendix and an attempt is made to present the basic concepts in simple language understandable to a layman. The authors have succeeded eminently in this task.

The concepts of energy, work and temperature in the early chapters of the book are

developed from simple every day examples which will appeal to a general reader. The authors then go on to point out the equivalence of mechanical and heat energies and the experiments of Joule which proved the death knell for the early caloric theory of heat. They then introduce the kinetic theory and present a microscopic picture of heat energy as the average kinetic energy of the atoms.

The concept of entropy is introduced as a development of experience with early steam engines. A heat engine always needs a hot and a cold reservoir for its operation and one could never convert all the heat into mechanical work. The concept of reversible and irreversible paths by which a change of state can occur is explained lucidly. It is pointed out that it will not be possible to get a direct proof of the second law of thermodynamics and one can only deduce certain consequences of the law which can be verified, such as the lowering of the melting point of ice with pressure.

The connection between entropy and disorder expounded in Chapter 7 is one of the clearest expositions that I have come across. The concepts of micro- and macro-states are introduced lucidly and the connection between entropy and the number 'W' of micro-states associated with a definite macro-state is explained very clearly. I would specially recommend teachers at the undergraduate level to use such a presentation in their classes.



The gross failure of the equipartition theorem in explaining black body radiation is then pointed out. This leads to the genesis of the quantum theory and the authors again explain, with the aid of a simple diagram, how the average energy of a linear harmonic oscillator will fall below the value of  $kT$  when the separation of energy levels is large compared to  $kT$ .

The applicability of thermodynamics to chemical reactions and to living systems forms the subject matter of Chapters 11 and 12. The argument of creationists that the second law is violated in the evolution of order in going from single celled to complex living organisms is refuted reasonably effectively.

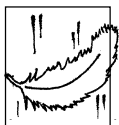
Kelvin's deduction of the age of the earth from the rate at which the earth cooled and the controversy it generated with the geological evidence is discussed in some detail in Chapter 13. The controversy was resolved with the discovery of radioactivity and the realisation that this provided a source

of heat not included in Kelvin's calculations. The last few chapters deal with Quantum Mechanics and the third law of thermodynamics, and the applicability of the first and second laws of thermodynamics to an expanding universe. The reader is taken on brief excursions through the basics of quantum mechanics, special and general theories of relativity. In an expanding universe the first law breaks down. But the authors conclude on the basis of existing evidence that the second law is still valid.

I found reading this book very enjoyable. I would suggest that every college library should acquire a copy as it will help the undergraduate science student get a better grasp of thermodynamics. It will also provide a serious non-science student with enough material to ponder on the power, the sweep and the limitations of one of the most long-standing and successful theories of science.

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**R Srinivasan, Raman Research Institute, C V Raman Avenue, Sadashivanagar, Bangalore 560 080**



### Why did the chickens cross the road?

The Sphinx: You tell me.

Joseph Stalin:

It was clearly a conspiracy. Take all the chickens out and shoot them.  
At Once!

Thomas de Torquemada:

Give me ten minutes with the chicken and I'll find out.

From: *Internet*

