# INTRODUCTION
TO
# STATISTICAL MECHANICS

BY

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# PREFACE

THIS book has been written in an attempt to provide an introduction to statistical mechanics suitable for students who, while of limited mathematical experience, require, nevertheless, to appreciate something of the content and importance of modern statistical theories, especially in the field of physical chemistry. It is based on lectures given during the past two or three years, while I was a member of the Department of Physical and Inorganic Chemistry in the University of Leeds, to third-year Honours chemistry students and young research workers. I could have wished no better audience, and should like here to acknowledge my indebtedness to the lively discussions which often followed these lectures and contributed very greatly to my own understanding of the subject.

The emphasis of the book is on the fundamental principles and techniques of statistical mechanics, rather than on their application to specific physical or chemical problems. Inevitably, however, some application of these principles to definite experimental phenomena must be made: both in order to confirm the validity of the basic statistical postulates and to illustrate the kind of understanding which statistical interpretations afford. I hope that my choice of these illustrations will not seem too arbitrary. For the most part the examples chosen are of quite fundamental importance (as, for instance, the statistical interpretation of the specific heats of gases): others have been included either on account of their mathematical suitability or because of current interest within the department in which I was lecturing. For this latter reason I have dealt in some detail with the theory of non-ionic solutions. But I must emphasize that these lectures were not intended in any way to cover the ground in theoretical chemistry. Nor is this book. Its aim is simply to take a student with no previous knowledge of statistical mechanics, and little mathematical equipment, sufficiently far for him afterwards to be able to read original papers and standard treatises (see bibliography) with some understanding and not too much effort.

Until the last chapter, when something is said, briefly, of their interconnexion, statistical mechanics and thermodynamics are regarded as largely independent disciplines both bearing on our field of inquiry: some acquaintance, therefore, with the basic concepts of thermodynamics is presupposed. Nevertheless, I think that all the thermodynamic formulae which have been used have been derived from first principles either in the text or in appendixes at the end of the book. Mathematically, no knowledge is presupposed apart from that which is indispensable to any scientist: acquaintance with logarithmic and exponential functions, elementary algebra, and the fundamentals of differential and integral calculus. Although there are problems of statistical mechanics which require for their satisfactory solution very powerful instruments of pure mathematics, it is quite surprising how much progress is possible with the help only of simple and elementary tools.

Any book which makes no special claim to originality necessarily owes much to current standard treatises, and while I have tried to avoid conscious plagiarism my indebtedness to the works listed in the bibliography will be apparent to all who are familiar with them. I only hope that the result of this present text will be that many others are enabled to enjoy those weightier publications, indispensable to serious research workers. It has seemed inappropriate, in an exposition which is primarily theoretical, to make detailed reference to the origin of experimental values listed in the half-dozen tables of physical measurements. Most of these tables, which give the experimental values that I quoted in my lectures, were derived from miscellaneous sources: in so far as many of these can be traced in the reference books already mentioned, I hope that this expression of my indebtedness to them may be taken as sufficient acknowledgement. Table II is rather exceptional in that its columns were taken as they stand from the corresponding table on p. 90 of Fowler and Guggenheim's *Statistical Thermodynamics*. I am very grateful to Professor Guggenheim, F.R.S., and the Syndics of the Cambridge University Press, for their kind permission to use this table.

It gives me much pleasure to express my gratitude to the many friends who have helped me in this work. Particularly must I thank Professor C. A. Coulson, who was not only responsible for my starting to write the book but has read the whole manuscript and corrected many of its errors, and Professor M. G. Evans, F.R.S., with whom I have had countless invaluable discussions: for their kind encouragement I am especially grateful. I must also thank by name Dr. N. B. Slater and Mr. J. S. de Wet for their help in correcting the proofs and checking the examples.

Finally, I am much indebted to the officers of the Clarendon Press for their unfailing patience and helpfulness, which have made my share in the business of publication so agreeable and pleasurable a task.

G. S. R.

OXFORD
*January 1949*

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APPENDIXES

# I

# INTRODUCTION

1. Statistical mechanics is concerned with interpreting and, as far as possible, predicting the properties of macroscopic physical or chemical systems in terms of the properties of the microscopic systems (atoms, molecules, ions, electrons, etc.) of which these aggregates are composed. It is, moreover, primarily concerned with the equilibrium properties of macroscopic systems and not with the velocity with which this equilibrium is reached. The theory of rate-processes is called kinetic theory and, although of great importance, is still very much in process of development and hardly yet on as sound or final a basis as is the theory of the properties of thermodynamic systems which have attained complete equilibrium. This book will deal only with the latter field, in which the rules are already well established.

The field is, of course, by no means an unimportant one. For we shall be concerned with the theory underlying the interpretation, in terms of molecular structure and intermolecular forces, of such diverse physical or chemical properties as the specific heat of a gas, the partial vapour pressures of a solution or the melting-point of a solid. We shall not, however, attempt to deal with all existing applications of statistical mechanics. Some of these, e.g. to the melting-point of a solid, are necessarily either superficial or mathematically very involved: and most are already easily available either in standard treatises (such as Fowler and Guggenheim; see Bibliography) or in original papers. The present book aims rather at preparing the ground so that such more detailed and elaborate works may be read with profit. The basic concepts and principles of statistical mechanics are introduced, it is hoped, both simply and systematically, and the examples chosen to illustrate the application of the principles, and to further a clear understanding of them, are generally of quite fundamental importance. Some examples of rather minor interest, however, have been included when these have served to extend the mathematical technique. For statistical mechanics is essentially a mathematical science, and besides introducing the basic concepts and principles of the theory an elementary book must also develop some of the necessary mathematical tools. Here, however, we have deliberately kept to the very simplest methods.

The theory is called *statistical* mechanics because it evidently has to do with average behaviour, in much the same way as an actuary is concerned with average behaviour when dealing with population statistics. The pressure of a gas, for example, on the walls of its container, is clearly some kind of *average* rate of destruction of the momenta of the gas molecules on collision with the walls. For, by definition, pressure is force per unit area and, by Newton's laws of motion, force is rate of change of momentum. Strictly, the pressure will be subject to fluctuations, but these will usually be too small to measure. The existence of local fluctuations in the pressure, or density, of a gas is revealed by the blue colour of the sky (Rayleigh); the Brownian movement of colloidal suspensions and the shot effect in electronics are other well known instances of fluctuation effects. The theory of fluctuation phenomena is a branch of statistical mechanics, but one with which we cannot start off: it constitutes a rather specialized field, which is largely outside the scope of this book.

**2.** Before the development of statistical mechanics, there were two major theoretical sciences which dealt with the behaviour of bulk matter: classical mechanics and thermodynamics. These, associated respectively with the names of such men as Newton, Euler, and Hamilton on the one hand and Carnot, Joule, and Planck on the other, formed well-established sciences, valid in their own proper domains, but with little or nothing by way of a link between them.

By classical mechanics we mean mechanics based on Newton's laws of motion, in distinction to the more recent quantum or wave mechanics which, we now know, replaces the older theory when very small bodies, of atomic size, are considered. Although one of our main concerns in subsequent chapters will be to emphasize the differences in macroscopic properties resulting from quantal rather than classical behaviour (of the atomic systems of which bulk matter is composed), in the present paragraph it will be sufficient to confine attention to the more familiar classical concepts. These concepts of classical mechanics are simply time; displacement, mass, velocity, energy, force, etc., and the equations of classical mechanics describe the motion, in time and space, of bodies, generally macroscopic bodies, acted upon by given forces. The equations can be solved accurately only when very few bodies, such as those of a planetary system, are involved.

Thermodynamics, by contrast, deals with the general laws governing heat effects: the total conservation of energy, whether mechanical or thermal, the existence of entropy, the phase rule, and so on: a field having at first sight no intimate connexion with classical mechanics. It is concerned only with very general properties of bulk matter: a typical thermodynamic formula, for instance, being that connecting the difference between specific heats at constant pressure and constant volume, respectively, with compressibility and the coefficient of thermal expansion, i.e.

$$C_p - C_v = -T\left(\frac{\partial P}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_P^2.$$

A certain familiarity, on the part of the reader, with the basic concepts of thermodynamics and some knowledge of the more important formulae, are assumed throughout this book. For easy reference, however, most of the formulae required, together with a concise derivation of them from statements of the first and second laws of thermodynamics, are collected together in Appendix I.

Now just because the fundamental laws of thermodynamics are so general, applying equally to a litre of hydrogen and a block of ice, thermodynamics, as such, is completely unconcerned with specific molecular behaviour. Why, at the same temperature and external pressure, $H_2O$ molecules can form a solid while $H_2$ molecules form a gas, is a question thermodynamics alone cannot answer.† Yet the limitations of classical mechanics are equally profound. It is easy to suppose that *if* we could solve the $3.10^{23}$ formulae of Newtonian mechanics for a thermodynamic system

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† It is, however, not quite true to say that thermodynamics is altogether unconcerned with molecular models: cf. the last chapter.

of $10^{23}$ atoms we should possess a complete description of the properties of the bulk matter. Quite apart from the possibility of so doing, this is not true. Our answer would still be in terms of space–time concepts (mass, position, velocity of each atom, etc.) and not in terms of thermodynamical concepts such as heat content, entropy, or specific heat. There is a gap here which has to be bridged by some entirely new ideas. It is the theory of Statistical Mechanics, due to Boltzmann, Gibbs, Fowler, and others, which provides the bridge.

**3.** Before stating the fundamental problem of statistical mechanics explicitly, we must give rather more precision to our terminology. So far, as the reader will have observed, we have employed the word *system* to denote two very different entities.

In the first place it has been used, e.g. in the phrase thermodynamic system, to describe any collection of macroscopic bodies (solids, liquids, or gases) among which thermal, physical, or chemical changes can occur. Secondly, it has been used, e.g. in the phrase microscopic system, to describe one of the basic particles (atom, molecule, ion, or electron) the statistical behaviour of a very large number of which gives rise to the measurable properties of a macroscopic body. Such dual usage is liable to produce confusion, and we shall, therefore, use the word *assembly* to denote what we have so far called a thermodynamic, or macroscopic, system; and we shall reserve the word system, by itself, for what we have hitherto called an atomic, or microscopic, system. This terminology is not universal, in the literature of statistical mechanics, though it is used in the writings of Fowler and Guggenheim and has a great deal to commend it. More precisely, then:

(i) We shall refer to a thermodynamic system, no matter how many, or few, phases and constituents it comprises, as an assembly.

(ii) We shall reserve the word system as a generic term for any of the atoms, molecules, ions, etc., of which the assembly is composed.

There are two other related words which we shall use in a restricted technical sense, and it is convenient to give their definitions here. They are the words *species* and *components*. The systems of an assembly can be of differing species. Thus we may take for our assembly a piece of brass: the systems then comprise two species, copper atoms and zinc atoms (or, if we wish to be more precise, there are three species, copper ions, zinc ions, and electrons). Alternatively, we might consider a quantity of gaseous HCl. In this assembly HCl systems preponderate, but there are also necessarily some $H_2$ and $Cl_2$ molecules in dissociative equilibrium with them. When these traces of $H_2$ and $Cl_2$ can be ignored, as, for instance, in the theory of the specific heat of gaseous HCl, we shall say that there is only one species present, namely HCl molecules. But if we are particularly interested in the value of the equilibrium constant between HCl, $H_2$, and $Cl_2$ then we must recognize that our assembly contains (at least) three types of system, and we shall refer to each distinct type of system as a distinct *species*. In the present instance we should recognize (probably) three species in the assembly: $H_2$ molecules, $Cl_2$ molecules, and HCl molecules. Quite generally,

(iii) The number of species present is the number of different types of system which we recognize as existing as distinct entities in the assembly. Each distinct type constitutes a species.

In the above example, however, the numbers of systems of the three species, $H_2$, $Cl_2$, and HCl, are not independent. If we add more systems of the type $H_2$, then the number of HCl systems will also change, on account of the chemical reaction. We shall refer to the *independent* chemical constituents of an assembly as its *components*. Thus, in the above example, there are two components: though whether we regard $H_2$ and $Cl_2$ or $Cl_2$ and HCl or HCl and $H_2$ (molecules) as specifying these components does not matter. Actually we should, in this case, probably not choose any of the three species as components, but take the two components of the assembly to be H atoms and Cl atoms, from which all three species are built up. In general,

(iv) the number of components of an assembly is the number of independent types of system from which we may regard