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CHEMICAL THERMODYNAMICS

BY

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EXTRACTS FROM PREFACES TO FIRST EDITIONS

THE importance of the thermodynamical method in chemistry is now widely recognised and scarcely needs emphasizing. While there are several excellent larger treatises on the subject, which are suitable for the advanced student and for reference, the need has been felt of an elementary introduction to the subject which shall stress the underlying principles and at the same time give due attention to their applications. I have therefore ventured to prepare the present work, which is the outcome of several years' experience in teaching the subject. I have tried to present the subject in a logically precise, yet simple form, having in mind not only the student who intends to specialise in Physical Chemistry, but also that class of chemistry students which has only a very moderate knowledge of mathematics and little sympathy with mathematical methods. I shall be content if the book may help to promote the introduction of the thermodynamical method into the chemical curriculum at an early stage, as an essential part of the training of a chemist.

The applications of the theory to chemical processes have been selected from as wide a field as possible, and some topics have been included, which although not strictly thermodynamical, are most conveniently studied

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in this connection. The data given are to be taken as specimens of the results available, and are not intended to be exhaustive. Since it is not possible for the student to obtain a thorough grasp of the subject without working through numerical examples, I have added a collection of exercises to each chapter. For those who require a somewhat more limited course, I have marked with asterisks a number of sections which may be omitted at first reading, without loss of continuity.

Part II is concerned with the thermodynamical functions, energy, free energy and entropy, and their partial derivatives. In my experience it is desirable that the student should have some familiarity with the calculation of maximum work and the simpler applications of the first and second laws of thermodynamics before he embarks on the study of these quantities. This I endeavoured to provide in Part I, and my readers will find that they have already met some of these quantities, and in these circumstances the transition to the new methods will present no great difficulty.

It has been inevitable on this plan that I should cover again, in greater detail and from a more advanced point of view, some of the ground traversed in Part I, but I do not think this will be found to be a disadvantage. The exact distribution of material between the two parts is a matter of expedience, and I can only claim that the arrangement I have adopted has worked well in practice, the material of Part I forming a first course, and that of Part II a second course, which are studied in consecutive years. But this could easily be modified to suit other circumstances.

FOREWORD

THE fact that both Part I and Part II need to be reprinted at this time gives me the opportunity of bringing them both within the covers of one volume. I sincerely hope that this will not be considered an infliction by my former readers and users of Part I, and that they will be encouraged to look a little further and sample at least the earlier chapters of Part II. To teachers it will give a greater latitude in their courses and the possibility of introducing the concept of entropy (Chap. XI) at a much earlier stage, if they so desire.

I have also taken the opportunity of giving Part II a thorough revision so that it now covers most of the advances of the last decade. The book remains essentially practical in its outlook: it deals at length with applications, even when they take it out of the strictly thermodynamical field. It treats of thermodynamics as something to be used in everyday chemistry, a necessary tool of the chemist in the laboratory and in industry.

To this edition, the late Dr. W. J. C. Orr contributed, shortly before his untimely death, an Appendix on the Statistical Derivation of Thermodynamical Functions, which gives a concise but lucid treatment of this valuable method. I believe it will be of assistance to those who require at least a nodding acquaintance with the subject and a vantage point from which they may embark on the study of the larger works. I have also to express my indebtedness for his valuable suggestions and data for Chapter XIII.

J. A. V. B.

THE thermodynamical problem of the equilibrium of heterogeneous substances was attacked by Kirchhoff in 1855, when the science was yet in its infancy, and his method has been lately followed by C. Neumann. But the methods introduced by Professor J. Willard Gibbs, of Yale College, Connecticut, seem to me to be more likely to enable us, without any lengthy calculations, to comprehend the relations between the different physical and chemical states of bodies.

J. CLERK-MAXWELL

(as reported *Amer. J. of Science*, 1877)

INTRODUCTION

THERE are two points of view from which the study of a chemical or physical process may be approached. In the first place, it may be pictured in terms of atoms and molecules and their motions. Thus in this, the kinetic aspect of things, the pressure of a gas is looked upon as a consequence of the bombardment of the containing vessel by the gas molecules in rapid motion. The vapour pressure of a liquid is that at which equal numbers of molecules leave the liquid and enter it from the gaseous phase in a given time. The study of processes from this point of view gives as a rule a definite picture of the mechanism of the change, but it is limited by the complexity of the laws governing the motions of atoms and molecules and by our ignorance of them.

There is another viewpoint from which such processes can be studied, namely, from a consideration of the energy changes involved. In the early part of the nineteenth century two general laws of energy were formulated which are believed to be universally true. The first states that in any change no energy is lost. The second gives a means of distinguishing processes which can occur of their own accord in any given circumstances from those which cannot. This is precisely what the chemist needs, a means of predicting whether under any particular circumstances a reaction can take place or

not. In addition, if the laws of energy and their detailed consequences are to hold good for any given change, we find various relations which must hold between the properties of the substances undergoing change. We are thus able to predict the effect of changes of conditions on the equilibrium state of a system.

Thermodynamics is a deductive science. It takes as true the broad generalizations on which it is based, and seeks to deduce their detailed consequences in particular cases. It applies, moreover, to the behaviour of matter in bulk; that is, to quantities so great that the behaviour of any individual molecule is not observed. While, in kinetic theory, the motion of the individual particle is taken as the basis, and the attempt is made to deduce from it the behaviour of matter in quantity, in thermodynamics we are concerned with the observed behaviour of quantities of substances which contain innumerable individual particles. The laws of thermodynamics are the laws of the behaviour of assemblages of vast numbers of molecules.

An analogy to the two possible ways of studying material processes might be found in the two possible ways of approaching the study of social phenomena. Corresponding to the kinetic method we might study the behaviour of individuals and on that basis seek to interpret the behaviour of large assemblages of individuals. If we adopted the "thermodynamical" method we should observe directly the behaviour of large assemblages of individuals. Just as any generalization which we might be able to deduce from our study of the behaviour of crowds would not help much in predicting the movements of isolated individuals, so the laws of

thermodynamics do not tell us anything about the behaviour of individual molecules. The application of thermodynamics to molecular systems could, in fact, be made without any reference to the atomic or molecular constitution of substances, but it is usually convenient, however, to make use of the language of atomic and molecular theories.

We shall make frequent use of the relation between the pressure and the volume of a gas. According to Avogadro's principle, in the limiting case at low pressures, equal volumes of gases under the same conditions of temperature and pressure contain equal numbers of molecules. The amount of a gas which occupies the same volume as the molecular weight of hydrogen (2.016 grams), when these conditions are fulfilled, is termed the *mol*. Strictly, the mol as a unit of quantity applies only to the gaseous state. When we speak, for example, of a mol of a substance in the liquid state we mean the amount of substance which gives rise to a mol of gas when the liquid is vaporised. It has nothing to do with the actual molecular weight of the substance in the liquid.

The relation between the pressure and volume of one mol of any gas at sufficiently low pressures is given by the *perfect gas equation* :

$$pv = RT$$

where R is a universal constant, which will be evaluated later. While this equation is true in the limit at low pressures for any gas, at higher pressures actual gases may deviate from it to a greater or less extent.

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PART I.—ELEMENTARY THEORY AND ELECTROCHEMISTRY

CHAPTER I

THE FIRST LAW OF THERMODYNAMICS

The Conservation of Energy. The mechanical theory of heat had its origin in the observations of Count Rumford, published in 1798, on the great quantity of heat produced in the boring of cannon. According to the prevailing theories, heat was an imponderable fluid called caloric,* contained in matter in various amounts. The production of heat would, on this view, be ascribed to the escape of caloric in the reduction of massive metal to fine turnings, so that the turnings should contain in a given weight, less caloric than the massive metal. Rumford thought that a change in the amount of caloric should show itself by a change in the heat capacity, and determined the specific heats of the metal in a massive state and in fine turnings. He found that they were the same, and thus came to the conclusion that there was no escape of caloric in the boring and that the heat produced had its origin in the mechanical work performed. After

* Bacon, in his *Novum Organum*, defines heat as "a motion, expansive, restrained and acting in its strife upon the smaller particles of bodies." (Book II., Aphorism XX.) He seems to have come very near to a mechanical theory of heat.

describing experiments on the production of heat by friction, he says :

“ We have seen that a very considerable quantity of heat may be excited by the friction of two metallic surfaces, and given off in a constant stream . . . without any signs of diminution or exhaustion It is hardly necessary to add, that anything which any insulated body or system of bodies can continue to furnish without limitation cannot possibly be a material substance ; and it appears to me to be extremely difficult, if not quite impossible, to form any distinct idea of anything capable of being excited and communicated in these experiments, except it be MOTION.”

Humphry Davy also experimented (1799) on the production of heat by friction and concluded that the observable motion of massive bodies was converted by friction into motions of the small particles of which they are composed. Joule made many careful experiments (1840-1878) to determine the amount of heat produced by the expenditure of a given amount of mechanical work. He found that the same amount of heat is always produced by the same amount of work whatever the substance used and the method of working. He determined with considerable accuracy the amount of work required to produce a unit quantity of heat, a quantity which is known as the *mechanical equivalent of heat*. Mayer also determined this quantity (1842) by finding the change in the temperature of a gas when it performed a known amount of work by expansion against the atmosphere.

The earlier development of mechanics had led to the concept of the *energy* of a body, expressing the amount of work done in bringing it into a given position and state of motion. In mechanics two kinds of energy are

recognised, kinetic and potential. Kinetic energy is the energy of motion ; it is the amount of work expended in bringing a body from rest into a given state of motion. Potential energy is the energy of position ; when a body is moved from one position to another under the action of forces exerted on it by other bodies (*e.g.* the force of gravitation), its potential energy increases by the amount of work done in changing its position.

The discovery by Joule of the equivalence of heat and work led to the recognition of heat as a third form of energy, so that when mechanical work is expended in frictional processes, the mechanical energy lost is accounted for by the energy of the heat produced. Other kinds of energy were soon recognised. Thus by the expenditure of work in a dynamo it is possible to produce an electric current, the energy of which can be converted into heat. Energy may be defined in general as work or anything which can be produced from or converted into work.* Energy of different kinds is often measured in different units. Thus work may be measured in ergs or foot-pounds, heat in calories, electrical energy in joules. The relations between these units must be determined by experiment.

The equivalence of the different forms of energy, approximately verified in a few cases, led to the enunciation, in different forms by Helmholtz, Clausius and Kelvin, of a general law of nature, the principle of the *Conservation of Energy*. This may be stated most simply as follows :

When a quantity of energy of one kind disappears an equivalent amount of energy of other kinds makes its appearance