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CHEMICAL THERMODYNAMICS

ИЗДАТЕЛЬСТВО · МИР ·

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ХИМИЧЕСКАЯ ТЕРМОДИНАМИКА

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ИЗДАТЕЛЬСТВО «ХИМИЯ» МОСКВА

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Contents

List of Tables

Preface

The present book is intended mainly for students of higher educational establishments specializing in chemistry, and primarily for future engineers. This is why I have tried to avoid abstractness and needless theorization, which could keep the essence of the material and its practical significance concealed behind a veil of formal mathematical calculations and abundant formulas and equations. This naturally does not mean that the course ought to be reduced to a set of recipes, because such an approach cannot create a firm theoretical foundation and will not make the reader understand the great variety of practical problems.

Most thermodynamic relationships have no practical value, because they contain quantities, part of which are either unknown or can be calculated only roughly. Hence, solving a specific problem with even an approximate assessment of the numerical value of the needed quantity is frequently impossible. Therefore, while rendering my due to theory, I also give various approximate laws that make it possible to rapidly obtain the required results and predict unavailable data with an accuracy sufficient for practical purposes.

My experience in teaching physical chemistry and chemical thermodynamics convinced me that "chemization" facilitates the mastering and successful application of these courses. This prompted me to combine the introduction of elements of "empirical thermodynamics" with a depiction of the relationship between thermodynamic properties on one hand and the nature of a substance and Mendeleev's Periodic Table on the other. The limited size of the book did not permit the latter to be done entirely. It was done most completely only for entropy, whose meaning students usually find the most difficult to understand.

On the other hand, many years of lecturing on general and inorganic chemistry convinced me of the need to "thermodynamize" it. This not only improves its scientific level, but also prepares the students for comprehending the material of subsequent courses, especially physical chemistry and chemical thermodynamics, thus raising the level of teaching of the fundamental branches of chemistry as a whole and ensuring their continuity. I also attempted to do this in my book "An Introduction to the Theory of Chemical Processes" [M. Kh. Karapetyants. *Vvedenie v teoriyu khimicheskikh protsessov*, 2nd ed. Moscow, Vysshaya shkola (1975) *].

In treating the material, I give primary attention to the thermodynamics of gaseous systems while the thermodynamics of solutions is dealt with less completely, and still less space is devoted to solutions of electrolytes.

The fruitful mastering of thermodynamics in general, especially for a technologist, is conceivable only when the student sees how theory is applied to the solution of various practical problems. This is why the present volume contains many examples designed to help the student consolidate the theoretical information and acquire competence in calculations. The majority of the examples are connected with the technology of inorganic substances and of the chemical processing of fuel. The calculations have been selected as far as possible so that the results obtained can be compared with experimental data.

Most graphs have been plotted using concrete data. This should not only facilitate the understanding of the corresponding hypotheses, laws and equations, but also allow them to be used in calculations, which, in turn, should facilitate a mastery of the material.

Almost all the examples and figures have been compiled on the basis of material taken from reference books and articles in various journals (only a few were taken from monographs, textbooks and problem books).

The book has many tables containing the most important characteristics of various substances and processes. These data are given not so much to show the scale of the relevant quantities and to illustrate various relationships, as to use them in various calculations.

The bibliography at the end of the book covers training aids, monographs, problem books and reference books. References to some sources are given directly in the text.

I find great pleasure in expressing gratitude to my wife Mariya L. Karapetyants, Cand.Sc., for her great assistance in preparing the manuscript.

M. Kh. Karapetyants

* See also M. Kh. Karapetyants. In: *Sbornik nauchno-metodicheskikh statei po khimii* (A Collection of Scientific and Methodological Articles on Chemistry). Moscow, Vysshaya shkola, Vyp. 2 (1970), 3 (1974), 4 (1975) and 6 (1977).

Chapter 1

INTRODUCTION

1.1. THE SUBJECT AND METHOD OF THERMODYNAMICS

Physical and chemical phenomena in thermodynamics are mainly investigated with the aid of two fundamental laws called the **first and second laws of thermodynamics.** The former follows from the law of conservation of energy and matter. The second law characterizes the direction of processes and was formulated in the 19th century. The present century saw the discovery of the **third law of thermodynamics,** which is not as broad and universal as the first and second laws, but is of great importance for the theoretical analysis of chemical processes.

Classical (phenomenological) thermodynamics embraces a complex of laws derived mathematically from the logical development of the above laws of thermodynamics. It is constructed according to a purely deductive principle: the laws of thermodynamics are considered as experimental generalizations, and corollaries for different particular cases are derived from them.

Thermodynamics is a science of macrosystems. It does not deal with separate particles (molecules, atoms, electrons and the like) or a small number of them. The state of the objects considered in thermodynamics is determined by directly measured quantities characterizing substances. The structure of a substance and the mechanism of a process are not considered.

The merging of certain branches of thermodynamics and statistical mechanics led to the appearance of **statistical thermodynamics.** The latter helped scientists to determine the physical meaning of the quantities contained in thermodynamic equations and find the absolute values of quantities for which thermodynamics gives only relative values. The statistical method is very fruitful in considering the second law and in calculating chemical equilibria.

Thermodynamics makes it possible to determine *a priori* whether or not a process is in principle possible and thus avoid experiments destined to be unsuccessful. Thermodynamic analysis, however, by determining the "motive power" of a process, permits us to indicate only its direction. To find the rate of a process, we must know its resistance. The determination of the latter is connected with consideration of the mechanism of the process, but the latter is not studied by thermodynamics. Consequently, the thermodynamic method cannot be used in studying such phenomena as diffusion and heat transfer.*

The historically formed name of our subject does not correspond to its content. No "motion of heat" is dealt with in thermodynamics, and for this reason the similarity of the terms "thermodynamics" and "hydrodynamics" ("aerodynamics") is only linguistic.

It is customary to distinguish general (or physical), technical and chemical thermodynamics.

General thermodynamics sets out the theoretical fundamentals of thermodynamics, its laws and their application mainly to physical phenomena (to the properties of solids, liquids and gases, to electrical and magnetic phenomena, radiation, etc.).

Technical thermodynamics deals with the basic laws as applied to the processes of the mutual conversion of heat and work. Its main object is the development of the theory of heat engines to ensure their rational design and operation.

Chemical thermodynamics studies the application of the laws of thermodynamics to chemical and physicochemical phenomena. It mainly considers:

(1) the heat balances of processes, including the heat effects of physical and chemical processes;

(2) phase equilibria for individual substances and mixtures;

(3) chemical equilibrium.

Heat balances are compiled on the basis of the first law of thermodynamics. Phase and chemical equilibria are analysed on the basis of the second and third laws.

The studying of the laws describing chemical and physical equilibria is particularly important in chemical thermodynamics. A knowledge of them makes it possible to solve a multitude of very important problems encountered in production, design and research without resorting to experiments. The chief objectives here are as follows:

(1) determining the conditions in which a given process becomes possible (without performing work from outside);

(2) finding the limits of stability of a substance (or group of substances) being studied in a definite set of conditions;

(3) determining how to reduce the amount of undesirable substances produced in a reaction or even completely prevent their formation, i.e. how to suppress or eliminate secondary reactions;

* The last few decades have seen the development of the thermodynamics of irreversible processes, which analyses the course of various processes in time (see [B11, 13, 14, 34, 53, 82, 105]).