
THERMOCHEMICAL AND THERMODYNAMIC PROPERTIES OF ORGANOMETALLIC COMPOUNDS

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PREFACE

In the world chemical literature, any up-to-date monograph on the thermodynamics of organometallic compounds is absent which reviews the theory, the experimental methods and all results on the thermodynamics and thermochemistry of organometallic compounds. Their thermodynamic properties and functions are significant to design the most efficient modern processes of industrial application of organometallic compounds in various fields of technics such as electronics, machine-building, chemical, gas and oil industries and others. Moreover, these fundamental data are useful for understanding the problems of stability and instability of organometallic compounds and their reactivity in various processes.

The authors of the presented monograph are the representatives of Nizhny Novgorod chemical thermodynamics school founded by Professor I. B. Rabinovich and well known in the chemistry world. Many experimental and theoretical studies in the field of chemical thermodynamics of organometallic compounds of transition and nontransition metals were carried out under the supervision of Professor I. B. Rabinovich. The data obtained as the result of those studies are extremely accurate and the most reliable. This school has many scientific contacts with the leading chemists in the world thermodynamics. The monograph presented is a useful handbook for foundations of thermodynamics and the experimental data on thermodynamics and thermochemistry of organometallic compounds.

The monograph contains three parts. Part 1 consists of description of the principles of chemical thermodynamics. It contains six chapters covering major topics of chemical thermodynamics (the fundamental laws of thermodynamics, the theory of heat capacity, definitions of enthalpy and entropy and their calculation, the fundamental equations for closed and open systems, criteria for the proceeding and the equilibrium of chemical processes). Part 1 written by Prof. I. B. Rabinovich may be used as a short but excellent complete manual on the theory of chemical thermodynamics and thermochemistry for chemists. This part precedes the following parts containing experimental data since the principles of chemical thermodynamics constitute the basis for both the experimental and calculation methods used to obtain all the original data of this monograph. This basis also serves for developing the evaluation methods of optimal conditions of various chemical processes with participation of the organometallic compounds used in catalysis, material science (MOCVD), plasma- and laser-chemistry.

Part 2 is devoted to the thermochemical properties of organometallic compounds. The enthalpies of formation of organic compounds of transition and nontransition metals as well as the average

enthalpies of breaking the metal - organic ligand chemical bonds are evaluated and discussed. This part contains the standard enthalpy values for 630 organometallic compounds. These compounds include metals of almost all groups of the Periodic Table of elements. The chapters of this part are subdivided into sections devoted to the similar types of compounds with the same ligands. The average values of breaking enthalpies of 260 metal - ligand bonds are listed and discussed. Their dependencies on the metal and ligand nature are demonstrated in tabular and graphic forms.

Part 3 deals with the thermodynamical properties of organometallic compounds. It consists of descriptions of experiment conditions on determining the thermodynamic data of substances studied. Many tables and plots of experimental data show temperature dependencies of heat capacities of substances. The values of the heat capacity, entropy, enthalpy and Gibbs functions in a wide temperature range as well as the standard enthalpies and Gibbs functions of formation for 90 organometallic compounds are tabulated. All the data presented have been verified by authors on the basis of many publications of various authors and as well as the data obtained in the authors laboratory. They are consistent with each other. This part is divided into chapters according to the types of organometallic compounds reviewed.

The monograph collects the experimental data on thermodynamics and thermochemistry of all the organometallic compounds studied by Russian and foreign authors during many years up to the present time. All the data are critically considered and the most reliable ones are chosen as a basis. These thermodynamic and thermochemical data have a fundamental character. They may be used independently of their origin time. Because of this, the monograph is of a great value for many potential users.

This monograph can serve as a handbook and simultaneously as manual to thermodynamics and thermochemistry of organometallic compounds for chemist-researchers and technologists. It may also be recommended as an educational textbook and methodic manual to chemical thermodynamics for students, post-graduate students and post-doctoral students as well as for scientific workers. It will be interesting to students and specialists in the field of organic, inorganic, organometallic and coordination chemistry, physical chemistry and chemical physics as well as scholars in the material science field.

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PRINCIPLES OF CHEMICAL THERMODYNAMICS

1.1 INTRODUCTION. THE FIRST LAW OF THERMODYNAMICS AND THERMOCHEMICAL CALCULATIONS

1.1.1. The Subject and Basic Concepts of Thermodynamics

For many years scientists searched for the laws determining the conditions, directions and results of spontaneous processes in Nature for both research and practical purposes. Quite a number of hypothesis proved to be inconsistent when experimental data were accumulated. Nevertheless, such laws were finally discovered in nineteenth - the beginning of twentieth centuries. The First Law of thermodynamics is concerned with energy properties of systems. It corresponds to the law of conservation of energy which had been foreseen long before it was substantiated in experiments. This was established by Mayer, Joule and Helmholtz in the 1840s.

The Second Law of thermodynamics is the law showing the direction of spontaneous processes in Nature. This law was established by Clausius and Thomson on the basis of the analysis of Carnot's work of heat machines.

The Third Law of thermodynamics that was discovered by Nernst (1906) and Plank (1911) is concerned with thermodynamic properties of substances at the temperature of absolute zero. These three laws of thermodynamics (especially the First and the Second ones) to be considered in detail below, are general laws of Nature that integrate and generalize vast human experience.

On the basis of these laws Gibbs, Helmholtz, Vant-Goff and other scientists deduced a harmonious theory to describe the physical and chemical processes under given conditions and equilibrium phase and chemical composition of systems as a final results. This theory operates with differential equations and other various relations between temperature, pressure, volume, concentration and some of their functions, which are also the properties of reacting systems. This is the main subject of thermodynamics. The principal theoretical technique of thermodynamics is the method of characteristic functions (or the method of thermodynamic potentials) that is a powerful tool for investigation of physical and chemical systems as well as of their properties and various transformations. In spite of the absence of equations for liquid and solid states, which strongly complicates integration of differential equations of

thermodynamics, the use of appropriate empirical relations and wide application of calorimetry enabled researchers to accumulate rich quantitative material about thermodynamic properties of substances.

Basic Concepts of Thermodynamics.

A thermodynamic system is a macroscopic body or an ensemble of bodies capable of exchanging energy and/or substance with surroundings and/or with each other. Such a system consists of a great number of microparticles, consequently the laws and methods of statistical physics can be applied to its investigation. Thermodynamic methods do not require knowledge about separate particle properties or any assumptions concerning structure of the body investigated. On the other hand the thermodynamic laws are not applicable to microscopic bodies and give no information about microparticles.

A *homogeneous system* is a system which has identical properties at its every point in macroscopic sense, or these properties change continuously in the transition from one point to another, i.e., there is no region where these properties are discontinuous or change sharply. Such a homogeneous system is referred to as "phase".

A *heterogeneous system* contains more than one phase, with the properties changing sharply at boundaries of phase.

An *isolated system* is a system whose parts may exchange energy and substance, but such an exchange is excluded with surroundings (i.e., the system is inside a medium with tight, incompressible, adiabatic¹ walls). Constant volume and internal energy are the principal characteristics of this system.

A *closed system* is the system which is capable of exchanging energy but not substance with surroundings. Both energy and substance exchange between its components is possible inside this system.

An *open system* is capable of exchanging energy and substance both between its components and with surroundings.

Thermodynamic properties of a system are the properties that depend only on temperature, pressure², volume, and its quantitative chemical compositions. The thermodynamic properties dependent on quantity of substance are referred to as *extensive properties* (for example, volume of the system, its internal energy). These properties are additive.

The properties that do not depend on the quantity of substance are defined as *intensive properties* (for example, temperature, pressure, concentrations of components, heat capacity).

Thermodynamic state of a system is determined by quantitative values of all its thermodynamic properties.

If we change only one of these properties, we change the thermodynamic state of this system, it passes from one state to another and we say that we have the *thermodynamic process*.

Energy is a general measure of motion and interaction of material objects. In accordance with various types of motion and interaction we distinguish various kinds of energy. In particular, *chemical energy* is the energy of atoms' interactions in molecules, radicals, ions, and atomic crystals, i.e., it is the energy of chemical bonds.

Van der Waals energy is the energy of isotropic interaction of molecules which are not bound.

Mechanical energy is the energy of movement and gravitational interaction of macroscopic bodies.

Energy of directed electron and ion motion is defined as *electric current energy*.

However, all kinds of energy are essentially unified and interconvertable.

Heat (q) and *work (A)* have dimension of energy (*J*) and represent two forms of energy conversion from one system to another:

1) by thermal conductivity (and simultaneously by radiation) as a result of chaotic molecular collisions in adjoining bodies; in such cases we speak about heat conversion;

¹ Adiabatic (or adiathermal) walls are the walls which prevent any thermal interaction with surroundings

² Pressure describes interaction of the system with environment. It is determined by a force applied to the surface area unit perpendicular to it.

2) by directed motion of macroscopic bodies or ensemble of particles (compression or expansion of gas, various actions of electrical currents passing through the system or formed in it); in these cases the energy is converted by the work done on the system.

One should distinguish the work of expansion of the system (when it is heated or under chemical reaction leading to an increase of the total mole number of gases) and the “so-called” useful work expended on producing some useful actions (in the case of chemical reactions this is the work of an electric current).

Thus, the heat and work are not the properties of a thermodynamic system. They are the characteristics of a thermodynamic process.

The amount of heat and work depends on a path of the transition of the system from one state to another. (The process may be reversible or irreversible and may take place under constant pressure or constant volume.)

Heat and work of a very small action on the system are expressed through δq and δA , respectively, because they are not differentials but very small quantities.

Thermodynamic equilibrium is the state of closed or open systems which do not change in time until external conditions (contact of the system with surroundings, temperature, pressure) begin to change.

With a time any isolated system always reaches a state of thermodynamic equilibrium and can not depart from it spontaneously. This is one of the main postulates of thermodynamics.

Thermodynamic equilibrium includes three kinds of equilibrium:

- 1) *mechanical equilibrium*, requiring an identical pressure in the entire volume of the system;
- 2) *thermal equilibrium*, demanding an identical temperature in the entire volume of the system; and
- 3) *chemical equilibrium* requiring constant compositions and masses of all substances in the system.

The Zeroth Law of thermodynamics is concerned with the properties of the system in thermal equilibrium. The statement of the law is as follows: “If system 1 is separately in thermal equilibrium with system 2 and system 3, then systems 2 and 3 must also be in thermal equilibrium with each other”. The concept of empirical temperature (T)¹ follows directly from this law. If we have equalities $T_1 = T_2$ and $T_1 = T_3$ we know that $T_2 = T_3$. This is the main criterion of thermal equilibrium - the equality of temperatures of the contacting systems. The general conditions for thermodynamic equilibrium as functions of the state of the system will be presented below.

If the system passes through a continuous series of equilibrium states, it is said that we have the *thermodynamic equilibrium process*.

During this process a deviation of the system from mechanical, thermal and chemical equilibrium should be infinitely small. Hence, such process should be extremely slow.

Thermodynamically reversible process is the equilibrium process, admitting a possibility for the system to return to its initial state without changes in its surroundings. The process, which does not allow for such a possibility is said to be a thermodynamic irreversible process.

Thermodynamic equilibrium and, especially, thermodynamic reversibility are theoretical models of high importance. Many processes are described very well with these models. In some other cases, theory of equilibrium and reversible processes facilitates investigation of real systems.

In particular, processes proceeding in a system which is in the state of chemical equilibrium are almost reversible. This is extremely important, because the laws and methods of equilibrium thermodynamics and reversible processes are valid for their investigations. Classical thermodynamics considers only equilibrium systems. Consequently, the terms “thermodynamic system” and “thermodynamic property” concern equilibrium systems.

Thermodynamics considers spontaneous or initiated processes for which both the initial and final states are thermodynamic equilibrium states. But the intermediate states should not necessarily be equilibrium ones.

If thermodynamic calculations show that the system is in equilibrium relative to the processes of interest but, at the same time, another process occurs in it, then, given infinitesimal velocity of the latter,

¹ Thermodynamic definition of temperature and corresponding interpretation are given in sections 1.4.1 and 1.4.2.

we can assume the system to be near to equilibrium. Consequently, the laws and equations describing thermodynamic equilibrium are applicable to it.

For example, gaseous mixture of hydrogen and oxygen in any ratio at room temperature and atmospheric pressure can be regarded to be nearly equilibrium, if the formation of water under these conditions without catalyst proceeds with infinitesimal velocity.

Thermodynamic Parameters and Functions of the System

The properties of the system are interconnected, because all of them are determined by nature of the system.

The minimal number of the properties chosen as independent variables, which are necessary and sufficient for the description of all other properties, are referred to as thermodynamic parameters of the system. All other properties of the system are called the functions.

Temperature, pressure, volume, entropy¹ and mole number or molar ratio of components (in the case of solution) are usual parameters of the system.

If a thermodynamic function is defined uniquely by thermodynamic parameters of the system, then it is said to be a function of state.

Mathematically it means that the differential of the function of state is a total differential. For example, in the case of only two parameters of state (x and y , ideal gas) for any function of state Z the equation (1.1) is true:

$$dZ = \left(\frac{dZ}{dX} \right)_Y dX + \left(\frac{dZ}{dY} \right)_X dY. \quad (1.1)$$

The linear integral of such a function over any closed curve is equal to zero, $\oint dZ = 0$. Hence, the change of the function of state in any process does not depend on its path and is defined only by the initial and final states of the system.

One of such functions is the internal energy of the system (U). It is the total energy of different kinds of motion and interaction of all types of particles in the system. The energy of motion of the system and its macroscopic bodies as a whole, as well as their potential energy in a force field are not included to the internal energy.

Motion energy of all kinds of particles (kinetic energy) is the positive part of internal energy, and energy of all kinds of particles interactions (potential energy) is a negative quantity in internal energy. It means that the internal energy of system is increased (system adsorbs energy) by increasing of motion energy of particles (an increase of amplitude of atoms' and molecules' vibrations, a growth of velocity of molecule translation, an increasing of electron level excitation and others), and it is decreased (system gives energy back) by the increasing of energy of interaction (a formation of chemical bonds, an increase of intermolecular interactions, in particular, condensation of vapor or crystallization of liquid).

Usually, the thermodynamic processes are carried out at the constancy of certain parameters of system, that is reflected in their terms:

Isothermal process occurs at constant temperature, $T = \text{const}$.

Isobaric process - at constant pressure - $p = \text{const}$.

Isochoric process - at the constant volume of system, $V = \text{const}$.

Isoentropic process occurs at the constant entropy of system, $S = \text{const}$.

Adiabatic process is process with absence of heat exchange between system and surroundings, $q = 0$.

Isobaric-isothermal - process occurs at $p = \text{const}$, $T = \text{const}$.

Isochoric-isothermal - at $V, T = \text{const}$.

Isobaric-isoentropic - at $p, S = \text{const}$.

Isochoric-isoentropic - at $V, S = \text{const}$.

¹ Thermodynamic function (parameter) entropy (S) will be introduced and defined in section 1.3.

Thermodynamic Terms and Designations

In thermodynamics any change of function of state and parameters during a process are expressed as a difference of their values after (state 2) and before (state 1) the process takes a place. So, for example, change of the internal energy of system, its temperature, and volume are expressed accordingly:

$$\Delta U = U_2 - U_1; \Delta T = T_2 - T_1; \Delta V = V_2 - V_1.$$

Consequently, if the internal energy of system is increased during the process, then $\Delta U > 0$, etc.

If the system gives energy back in the form of heat (q), then q is a negative value. If the system gets energy in the form of heat, then q is a positive amount. However, if the system makes a work (A) against the external force by using internal energy, which may be compensated by heat adsorption (it occurs, for example, at expansion of gas in thermostat), then the value A is considered to be positive. If the external force makes a work on the system (it transfers the energy to the system in the form of a work), then A is a negative value. By the other words, the change of internal energy of system ΔU during the process, and the change of its energy in the forms of heat (q) and work (A), are referred to as energy, heat and work of this process.

In thermodynamics the designations of parameters concerning to functions are written down near the last ones. So, temperature is written in round brackets near the function, and pressure - as the superscripted index to the right of it. If the function of its change are related to pure compound, then the formula of this compound is following the brackets with temperature. The phase state of compound at the given T and p is shown in brackets following its chemical formula as the subscripted index. After the symbol “ Δ ” there is the designation of process as the subscripted index. For example, $\Delta_{\text{soln}} \hat{H}^\circ(298)\text{NH}_3(\text{g})$ - means the value of the enthalpy of solution of gaseous ammonia at the pressure 1 atm. = 101.325 kPa and temperature 298K (“ $^\circ$ ” means standard thermodynamic pressure; “soln” is related to the process of solution; “g” means gaseous state).

1.1.2. The First Law of Thermodynamics. Thermochemical Calculations.

As early as 1755, the French Academy of Sciences, having considered on abundance of projects on perpetual motion machine (*Perpetuum Mobile*) all of which proved to be unsound, announced that projects of a machine performing work without expending energy on it would no longer be considered. But almost 100 years later it was proved rigorously, that such a machine is unrealistic.

In 1842-1855, Mayer, Joule and Helmholtz on the basis of their experimental results discovered the principle of quantitative equivalence of heat and work. In the middle of the nineteenth century the law of conservation of energy was formulated: “*The internal energy of an isolated system is constant. Under various processes, the energy passing from one system to another, can convert from one kind to another, but in strictly equivalent amounts*”.

Before the international system of measures was introduced into practice (SI, 1960) the energy of an electric current had been measured in “Joules” (J), the energy transferred in the form of heat, in calories (cal), and the energy converted to mechanical work was measured in kilogram{force}meters (kg{f}·m). Joule (1842) found a mechanical equivalent of heat - the amount of work equivalent to a unit of heat. Its refined modern value is:

$$1 \text{ cal} = 0.4268 \text{ kg}\{\text{f}\}\cdot\text{m}.$$

of pure substances, calculation of enthalpies of substances, and also calculation of entropy and Gibbs function, except for their values at 0K, by temperature dependence of heat capacity [18, 20, 21].

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