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CALCULATIONS OF CHEMICAL EQUILIBRIA

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РАСЧЁТЫ ХИМИЧЕСКИХ РАВНОВЕСИЙ

Сборник примеров и задач

Под редакцией
проф. Г. М. Панченкова

«ВЫСШАЯ ШКОЛА» МОСКВА

资

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CALCULATIONS OF CHEMICAL EQUILIBRIA

Examples and Problems

Edited
by Prof.
G. M. Panchenkov

Translated
from the Russian
by G. Leib

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Preface

The main object of this training aid is to teach students how to calculate chemical equilibria. A chemical engineer must be able to calculate whether or not a given chemical process will proceed, determine the stability of substances in given external conditions, compute the equilibrium and, consequently, the maximum yields of the products in given conditions, and find the optimal external parameters for conducting a process.

We have given great attention to calculating the heats of chemical reactions, heat capacities, entropies, and fugacities. Apart from problems involving the direct application of the fundamental laws of chemical thermodynamics, the book contains interesting examples showing various empirical and approximate methods of calculations. For instance, space is devoted to calculations of the heats of combustion by the methods of D. Konovalov, M. Kharasch, of increments, of introducing corrections for the substitution of hydrogen by methyl and other groups, of P. Maslov, J. Franklin, M. Souders, C. Matthews, and C. Hurd. Approximate methods, which play a great part in engineering calculations of chemical processes, are considered for heat capacities, standard entropies, and Gibbs energies.

A large section is devoted to calculating the change in the Gibbs energy as a result of chemical reactions and of the compositions of equilibrium mixtures. Since in practical work one often has to do with non-ideal systems, we have set out the basic methods of calculating fugacities, as well as the use of fugacities and activity coefficients for determining the equilibrium composition of a mixture of non-ideal systems. We have also described empirical methods of calculating the critical parameters (the method of A. Lydersen, J. Forman, and G. Thodos), and the calculation of enthalpies and heats of reactions conducted at high pressures.

We begin each chapter with a brief theoretical introduction treating the main formulas needed for solving the problems. The introduction is given only to remind our readers of the basic laws used in solving the problems, and cannot in any way replace a textbook

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in chemical thermodynamics. Each chapter gives a number of examples with detailed solutions in order to show how to apply the thermodynamic laws and formulas in solving concrete problems. Next, problems for independent work are given—the answers to which can be found at the end of the book.

The Appendices contain reference tables. They are needed, first, for solving the problems; and, second, they are of an independent significance because they will permit students to solve many thermodynamic problems proposed by the instructor or confronting them when studying special chemical subjects and chemical technology as well as when performing course or diploma work or designs. The Appendices are followed by a list of monographs and reference books that can be used in solving problems in chemical thermodynamics.

The present collection of examples and problems has been compiled using the experience gained through many years of teaching the course of chemical thermodynamics to students of the faculty of chemistry and chemical technology of the I. M. Gubkin Institute of the Petrochemical and Gas Industry in Moscow. It is based on up-to-date material published in recent years in monographs, reference books on physical chemistry and chemical thermodynamics, and in separate articles in various journals. Students study chemical thermodynamics after a course in physical chemistry. Although they are acquainted with the solution of some of the problems in the course of physical chemistry, our teaching experience has shown the great need for the proposed type of problem book, purposefully directed at training students in the methods of calculating chemical equilibria. The book will also be of interest for workers of research institutions and engineers specializing in chemistry and chemical technology.

Chapters 1 and 2 were compiled by V. A. Skoblo, and Chapters 3, 4 and 5 by A. S. Kazanskaya.

We express our deep gratitude to the late prof. V. A. Kireev, senior scientific worker A. A. Lopatkin, associate professor V. P. Dreving, and all of those in the department of physical chemistry of the Byelorussian State University headed by associate professor A. A. Vecher for their attentive critical analysis which helped us to improve the quality of the book.

G. M. Panchenkov

1

Calculation of the Heat of a Chemical Reaction

Chemical processes are attended by the liberation or absorption of heat which is called the *heat of a reaction* (or the *heat effect* by some authors). A chemical reaction consists in the breaking of a definite number of chemical bonds between the atoms in a molecule and in the formation of new bonds. If the energy liberated in the formation of the new bonds exceeds that spent for breaking the bonds in the initial molecules, the reaction is attended by the liberation of heat (an *exothermic process*); if the energy liberated in the formation of the new bonds is less than that of breaking the bonds, the reaction is attended by the absorption of heat from the surroundings (an *endothermic process*). Consequently, in chemical transformations, the internal energy of the reacting molecules changes.

The change in the internal energy dU in the course of a chemical transformation occurs, according to the first law of thermodynamics, at the expense of the absorption (or liberation) of the heat δQ and the performance of the work δW. We shall write the analytical expression of the first law of thermodynamics in the form

$$dU = \delta Q - \delta W \tag{1.1}$$

The change in the internal energy as a result of a chemical reaction does not depend on the path followed by it, but depends only on the initial and final states of the system.

The heat of a reaction in the general case is not a change in a function of state and, therefore, depends on the path of a process. In two very simple cases, however, when a process occurs at a constant pressure p or a constant volume V, the independence of the path also extends to the heat of the process (including a chemical reaction). If a reaction proceeds at $V =$ const, and no electrical or other kinds of work is performed, i.e. $W = 0$, then according to Eq. (1.1), with the temperature T constant, the heat of a reaction is

$$Q_V = U_2 - U_1 = \Delta U \tag{1.2}$$

The heat of a chemical reaction Q_V (the subscript V denotes that $V =$ const) equals the change in the internal energy as a result of the reaction. If a reaction proceeds at constant pressure and only the work of volume expansion is performed (other kinds of work are absent), the analytical expression of the first law of thermodynamics will become

$$\delta Q = dU + p\,dV \tag{1.3}$$

where the elementary work δW is represented only by the work of expansion, i.e. $\delta W = p\,dV$. Integration of Eq. (1.3) with $p =$ $=$ const yields

$$Q_p = U_2 - U_1 + p\,(V_2 - V_1)$$

or

$$Q_p = (U_2 + pV_2) - (U_1 + pV_1) \tag{1.4}$$

Since p and V are parameters of state, while U is a function of state, the sum $(U + pV)$ is also a function of state. Its change does not depend on the path of a process, but only depends on the initial and final states of the participants of a reaction. This function is called *enthalpy* and is designated by the symbol H:

$$U + pV = H \tag{1.5}$$

Consequently

$$Q_p = H_2 - H_1 = \Delta H \tag{1.6}$$

If a reaction proceeds at constant pressure, then when $T =$ const, its heat equals the change in enthalpy as a result of the reaction.

Thus, in the above cases (1.2) and (1.6), the heat of a chemical process equals the change in the functions of state; therefore, it does not depend on the path of a process, but only depends on the initial and final states.

At present, customary practice is to write the heat of a reaction as follows. The stoichiometric equation of a reaction is attended by indication of the difference between the internal energies (or enthalpies) of the products and the reactants, i.e. $\Delta U = Q_V$ (or $\Delta H =$ $= Q_p$)—the growth in internal energy (or enthalpy). If this growth is positive, the reaction proceeds with the absorption of heat; and if it is negative, heat is liberated. For example, the oxidation of liquid benzene at constant pressure to carbon dioxide and liquid water proceeding with the liberation of heat is written as follows:

$$C_6H_6(lq) + \frac{15}{2}O_2(g) = 6CO_2(g) + 3H_2O(lq)$$

$$Q_p = \Delta H = -780\,980 \text{ cal}$$

The symbols (c), (lq), and (g) are used after the chemical formula of a substance to indicate whether it is crystalline (solid), liquid, or gaseous, respectively. These symbols are usually omitted when the state of aggregation of the components of a reaction is obvious. For instance, the hydrogenation of acetylene to ethane conducted at constant pressure and at 25 °C proceeds in the gaseous phase. It may therefore be written as follows:

$$C_2H_2 + 2H_2 = C_2H_6, \quad Q_p = \Delta H = -74\,430 \text{ cal}$$

This reaction, like that in the preceding example, is exothermic.

The need to indicate the state of aggregation of reaction components is due to the fact that the heat of a reaction depends on the state of aggregation of the reactants and products. If the state of aggregation changes as a result of a chemical reaction, its heat also includes the heat of the relevant phase transition (heat of vaporization or condensation, fusion or freezing, sublimation or condensation).

The heat of a reaction depends on whether or not the temperature of the reactants and products is the same. If the products of a reaction proceeding with the liberation of heat have a higher temperature than the reactants, part of the liberated heat will go for heating the reactants. Consequently, the measured heat of the reaction will be less than when the temperature of the reactants and products is the same.

Therefore, when measuring the heat of a reaction, the temperature of the reactants must exactly equal that of the products.

For the convenience of further thermodynamic calculations, we shall denote the heat of a chemical reaction in conditions of constant pressure by the symbol ΔH, and in conditions of constant volume by the symbol ΔU. In laboratory and industrial conditions, we most often encounter reactions proceeding at constant pressure.

If ΔH is positive, the reaction, as noted above, is endothermic. For example for the thermal cracking of gas oils $\Delta H = +70$-250 kcal/kg of converted starting material; for the pyrolysis of kerosenes $\Delta H = +400$-500 kcal/kg; for platforming $\Delta H = +180$ kcal/kg; and for the catalytic cracking of petroleum fractions $\Delta H = +50$-130 kcal/kg.

If ΔH is negative, the process is exothermic. For example for the regeneration of the catalysts of catalytic cracking $\Delta H = -8000$ kcal/kg; for the hydrogenation of isooctene $\Delta H = -245$ kcal/kg; and for the alkylation of isobutane with isobutene $\Delta H = -250$ kcal/kg.

In previous publications, the thermochemical heats were used. They are denoted by the symbols $\bar{Q}_V$ and $\bar{Q}_p$ and differ from the thermodynamic heats described above (which we shall use in the following) in their sign:

$$Q = -\bar{Q}$$

This must be taken into consideration in reading chemical literature.

In the thermochemical writing of chemical reactions, the right-hand side of a reaction is followed by a term characterizing the liberation or absorption of heat as its result. Equations written in this way are called *thermochemical*. The exothermic reactions considered above have the form

$$C_6H_6(lq) + \frac{15}{2} O_2(g) = 6CO_2(g) + 3H_2O(lq) + 780\,980 \text{ cal}$$

$$C_2H_2 + 2H_2 = C_2H_6 + 74\,430 \text{ cal}$$

The endothermic reaction of formation of acetylene is written as follows:

$$2C(c) + H_2(g) = C_2H_2(g) - 54\,190 \text{ cal}$$

It is essential for thermochemical calculations that all the heats of reactions be related to identical conditions; otherwise their values will be incompatible. This is due to the fact that the heat of a chemical reaction depends on temperature and to a smaller extent on pressure. The heats of chemical reactions are customarily reduced to standard conditions. For individual solids and liquids, their state at 1 atm and the given temperature is taken as the standard one. For individual gases, their state in the form of a hypothetic ideal gas whose fugacity equals unity at the given temperature is taken as the standard one. The properties of individual gases at 1 atm do not differ too much from their properties in standard conditions; this difference is usually disregarded in calculations not requiring a high accuracy. Attention must be given to the circumstance that for a gaseous chemical reaction conducted in standard conditions it is not the total pressure that equals 1 atm, but the partial pressure of each of the gaseous reagents.

The heat of a chemical reaction conducted in standard conditions is designated ΔH_T°. The superscript indicates the standard state while the subscript is the temperature (in kelvins) at which the reaction is conducted. The standard heat of a reaction can be calculated for any temperature T, but most often 298.15 K (25.00 °C) is used. In this case, the standard heat of a reaction is denoted by ΔH_{298}°. The temperature 298.15 K is chosen because other very important characteristics of processes are given for this temperature. Calorimetric measurements are also related to it.

1.1

Relationship Between Heats of Reactions Proceeding at Constant Pressure (ΔH) and Constant Volume (ΔU)

In a chemical reaction, a change in the number of moles of one component unambiguously determines the change in the number of moles of the remaining components. We can therefore say that for systems in which a reaction occurs the internal energy will be a function not only of temperature and volume, but also of the number of moles n of one of the reagents:

$$U = f(V, T, n) \tag{1.7}$$

The total differential of the internal energy

$$dU = \left(\frac{\partial U}{\partial T}\right)_{V,\,n} dT + \left(\frac{\partial U}{\partial V}\right)_{T,\,n} dV + \left(\frac{\partial U}{\partial n}\right)_{V,\,T} dn \tag{1.8}$$

If we consider a system at $T = \text{const}$ and $p = \text{const}$, then Eq. (1.8) may be rewritten in the form

$$\left(\frac{\partial U}{\partial n}\right)_{p,\,T} = \left(\frac{\partial U}{\partial V}\right)_{T,\,n} \left(\frac{\partial V}{\partial n}\right)_{p,\,T} + \left(\frac{\partial U}{\partial n}\right)_{V,\,T} \tag{1.9}$$

Differentiation of Eq. (1.5) yields

$$\left(\frac{\partial H}{\partial n}\right)_{p,\,T} = \left(\frac{\partial U}{\partial n}\right)_{p,\,T} + p\left(\frac{\partial V}{\partial n}\right)_{p,\,T} \tag{1.10}$$

Using Eq. (1.9) in (1.10), we get

$$\left(\frac{\partial H}{\partial n}\right)_{p,\,T} = \left(\frac{\partial U}{\partial n}\right)_{V,\,T} + \left[\left(\frac{\partial U}{\partial V}\right)_{T,\,n} + p\right]\left(\frac{\partial V}{\partial n}\right)_{p,\,T} \tag{1.11}$$

For the change in volume upon the conversion of one mole, we can write

$$\Delta V = \left(\frac{\partial V}{\partial n}\right)_{p,\,T} \tag{1.12}$$

But at $V = \text{const}$, we have

$$dQ_V = (dU)_{V,\,T} = \left(\frac{\partial U}{\partial n}\right)_{V,\,T} dn \tag{1.13}$$

or

$$Q_V = (\Delta U)_{V,\,T} = \left(\frac{\partial U}{\partial n}\right)_{V,\,T} \Delta n \tag{1.14}$$

If $\Delta n = 1$, then

$$Q_V = \left(\frac{\partial U}{\partial n}\right)_{V,\,T} \tag{1.15}$$

We can prove by similar reasoning that

$$Q_p = \left(\frac{\partial H}{\partial n}\right)_{p,\,T} \tag{1.16}$$

Introducing Eqs. (1.12), (1.15), and (1.16) into Eq. (1.11), we get

$$Q_p = Q_V + \left[\left(\frac{\partial U}{\partial V}\right)_T + p\right]\Delta V \tag{1.17}$$

or

$$\Delta H = \Delta U + \left[\left(\frac{\partial U}{\partial V}\right)_T + p\right]\Delta V \tag{1.18}$$

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