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# Thermo- dynamics of Silicates



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Translated by  
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## Preface

The intensification of the production of silicate materials and products makes a detailed theoretical study of the processes underlying their manufacture and service more and more urgent.

The thermodynamic method is of great importance for studying chemical reactions of silicate technology. Together with a study of the rate and mechanism of substance transfer, it permits obtaining necessary data for the efficient operation of technological processes.

The progress of science in recent years has solved numerous problems in the field of the physical chemistry of silicates. The great progress in deciphering silicate structures, and working out methods of the synthesis of minerals and studying their properties must be mentioned.

New methods of determining thermic constants have appeared. In future these methods should be more widely used for determining the heats of the silicate formation and related compounds in crystalline and vitreous state. This concerns in particular the system  $\text{CaO} - \text{Al}_2\text{O}_3 - \text{Fe}_2\text{O}_3 - \text{SiO}_2 - \text{H}_2\text{O}$  - which is of great importance for the technology of cement and concrete, ceramics, refractories and glass.

In the first edition of this monograph (1962), the authors collected and generalized the material on the thermodynamic study of the reactions in silicate systems available at that time in Soviet and world literature.<sup>1</sup> In the second revised edition (1965) the range of the systems considered was broadened substantially. The book aroused interest outside the U.S.S.R.: a translation was twice published by the Verlag für Bauwesen in the GDR (1965–1966), and references and reviews in both Soviet and other literature emphasized the usefulness of the work. In the third edition, using the new data of periodicals, the reaction calculations in some systems were improved, the contents of some chapters revised, and remarks and comments from references and reviews were taken into consideration.

In the present fourth edition all the sections of the book dealing with the practical application of thermodynamics to silicate and concrete technology have been substantially revised. All the calculations have been carried out with refined interrelated thermodynamic data.

The material on pyrosilicate reactions has been prepared for the most part by G. M. MATVEYEV and that on hydration reactions and corrosion by V. I. BABUSHKIN.

<sup>1</sup> A number of works should be mentioned dealing with the application of thermodynamics to technological and, in particular, geological problems [34, 56, 82, 83, 145, 162, 263, 291, 347, 550, 641].

The authors are profoundly grateful to all those who rendered assistance in writing the monograph and took part in discussing the main principles of it. All comments on the present book will be gratefully accepted by the authors.

O. P. MCHEDLOV-PETROSSYAN

# Introduction

Silicates in the form of minerals and rocks dominate in the composition of the earth crust and the products of silicate technology – cement, ceramics, refractories and glass – have a very wide range of use in building, ferrous and non-ferrous metallurgy, science, technique and home.

The chemistry of silicates represents one of the most important theoretical and engineering disciplines. It is the most complicated section of inorganic and physical chemistry and its theoretical foundations are based on most varied modern investigation methods including thermodynamics, one of the most reliable.

Thermodynamics is a mathematical science dealing with the laws of mutual transformation of heat and other kinds of energy. Chemical thermodynamics is an application of thermodynamic methods of investigation to chemical processes.

Together with kinetic methods, thermodynamics enables us to view complicated phenomena taking place in chemical interactions and phase transformations as a whole. Unlike kinetics, which deals with the rate of chemical reactions, i.e., with the transfer of the mass of a substance with time, thermodynamics studies equilibria and leaves the problem of how solutions are obtained, their rate and mechanism of the process, to kinetics.

The thermodynamic method being statistical is applicable only to the study of macrosystems with large masses. It permits determination of:

1. energy possibility and direction of the run of reactions;
2. heat alterations entrained by reactions, allowing calculation of the heat balances of processes;
3. preferability of reactions<sup>2</sup> and stability of compounds formed;
4. maximum equilibrium concentrations of the products of reactions and their maximum output;
5. ways of suppressing undesirable reactions and eliminating by-products;
6. the choice of an optimum regime of the path of the reactions (temperature, pressure and concentration of the reacting substances).

The thermodynamic investigation method should be noted as possessing one important peculiarity: it allows the theoretical solution of most problems by the use of a relatively small number of thermic constants of reacting compounds and a simple

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<sup>2</sup> As in previous works of the authors a theoretical permissibility of comparison has been shown, by the value of  $\Delta G^\circ$ , of the probability of various reactions proceeding (in one and the same system on condition of the identity of the initial structural and kinetic factors), the term "preferability" is used in this case.

mathematical apparatus, without resorting to labour-consuming and sometimes technically unrealizable experiments for the equilibrium study.

For a thermodynamic analysis of reactions only the initial state of the system and conditions affecting it need be known. This substantially facilitates handling thermodynamic ideas, but at the same time it restricts the scope of the thermodynamic method, making no allowance for the time factor.

Most phenomena of nature may be considered as equilibrium ones only at first sight; in reality, however, they are connected with non-equilibrium states and irreversible alterations. For this reason, classical thermodynamics created chiefly for equilibrium reversible processes has been supplemented of late by the thermodynamics of irreversible processes, and we found it necessary to sketch, if only in general, its essence and application to the phenomena that interest us.

As initial data for thermodynamic calculations, heats of formation, heat capacities, entropies and some other data characterizing equilibria are used.

Apart from studying equilibria, chemical thermodynamics enables us to analyze silicate systems under consideration also from the point of view of the phase rule that gives qualitative and, in certain cases, quantitative characteristics of an equilibrium [151, 468].

M. M. SHUL'TS has put forward 3 directions of the applications of thermodynamics [574] in the silicate chemistry and technology: (1) amplification of the investigations of thermodynamic properties, (2) quantitative description of phase diagrams and (3) plotting and analysis of energy balances of production silicate materials.

According to chemical processes of manufacturing and life of materials and products all reactions in silicate systems may be divided in principle into two groups: pyrosilicate ones and those of hydration and corrosion.

The first one comprises a vast range of dehydration reactions and modification transformations, reactions in solid phases and melts; the second one, the entire diversity of reactions of silicates with water and aggressive media at normal and elevated temperatures and pressures. Apart from the well-developed domain of slag melts, the thermodynamic method has been rarely applied in the study of silicates. It concerns mostly solid-phase reactions of silicate compounds first studied in systematic works by one of the authors of this book. Reactions of hydration and corrosion of silicates under normal and hydrothermal conditions are of great practical importance, but have been little studied thermodynamically until recently.

The book comprises a theoretical part, in which general thermodynamic ideas are stated, experimental and approximate methods of obtaining the necessary initial thermodynamic data are discussed and the expediency and limits of the application of thermodynamics to the study of silicates are grounded, and an applied one, in which as far as the initial data are available thermodynamic calculation of reactions in silicate systems of theoretical and practical importance are carried out and their theoretical interpretation given.

# List of Symbols

$A$	work, atomic weight, chemical affinity, frequency factor
$A_k$	activation coefficient
$a$	activity, radius of particle, coefficient of temperature conductivity
$a^*$	efficient coefficient of the substance transfer
$a, b, c$	coefficients in the equation of heat capacity as a function of temperature
$Bi$	the Biot criteria
$C$	true heat capacity, concentration
$\bar{C}$	the mean molar heat capacity
$C_p$	heat capacities at constant pressure
$C_v$	heat capacities at constant volume
$C_{vap}$	heat capacities of vapour
$C_{liq}$	heat capacities of liquid
$C_{sol}$	heat capacities of solid
1 cal	$\equiv 4,1868$ Joule
$D$	diffusion coefficient, covalent bond value in compounds, permittivity
$E$	electrical potential, bond energy, activation energy
$E_a$	activation barrier
$e$	electric charge
$F$	Helmholtz free energy, the Faraday constant ( $9.648456 \cdot 10^4$ C mol <sup>-1</sup> )
$f$	number of degrees of freedom, intensive value
$G$	the Gibbs free energy
$H$	enthalpy
$H_{ev}$	heat of evaporation
$H_m$	heat of melting
$I$	mechanical equivalent of heat, extensive value, nucleation rate
$i$	van't Hoff's coefficient
$j$	flux density
$K$	equilibrium constant
$k$	number of components, Boltzmann's constant ( $1.380662 \cdot 10^{-23}$ J K <sup>-1</sup> )
$L$	latent heat of the water evaporation, phenomenological coefficient (the kinetic coefficient of proportionality), solubility
$L_i$	the ion hydration heat
$M$	molar mass
$m$	mass, number of water moles in crystalline hydrates
$N$	the Avogadro constant ( $6.022045 \cdot 10^{23}$ mol <sup>-1</sup> ), molar fraction, serial number of cation



$n$	number of phases, concentration of ions of the solution, number of moles
$n_w$	concentration of the molecules of water
$P$	osmotic pressure
$\bar{P}$	the mean polymerization degree
$p$	pressure
$p_w$	dipole moment of the molecules of water
$Q$	heat effect of the process
$q$	heat of polymerization
$R$	gas constant ( $8.31441 \text{ J K}^{-1} \text{ mol}^{-1}$ )
$r$	number of exterior parameters, thermochemical radius
$S$	entropy
$Sp$	solubility product
$T$	absolute temperature
$T_g$	vitrification temperature
$T_m$	temperature of melting
$T_{tr}$	temperature of transformation
$U$	internal energy
$V$	volume of the system
$v$	molar volume, rate of the substance transfer
$W$	amount of electric effect (of electricity)
$W/C$	water-cement ratio
$W/S$	water-solid ratio
$w$	rate of the chemical reaction, component of the thermal flux
$x$	space variable
$y$	integration constant
$Z$	thermodynamic property, valence of the ions of the solution
$z$	ion charge
$\alpha$	degree of the dissociation, external coefficient of heat exchange
$\alpha, \beta, \gamma$	etc., particular phases
$\gamma$	coefficient of activity, components of the system
$\delta$	variation derivative, the deformation values
$\Delta$	finite change of a property
$\varepsilon$	mean bond energy, dielectric permittivity
$\lambda$	coefficient of heat conductivity
$\mu$	chemical potential, ionic strength
$\nu$	frequency, number of atoms, entropy criterion, number of ions
$\varrho$	density of the substance
$\sigma$	source in a unit of time per unit of volume
$\tau$	time, time variable
$\Phi^*$	reduced potential
$\Phi'$	different reduced potential
$\varphi$	intensive variable
$\Omega$	limiting surface, potential energy
$\omega$	potential energy of a unit mass, amount of the chemically bound water

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# Chapter I. The Basic Concepts and Laws of Thermodynamics<sup>3</sup>

## 1 Basic Concepts of Thermodynamics

In order to formulate the main principles of the thermodynamic method more precisely, the chief concepts, terms and values used in thermodynamics must be defined.

For the thermodynamic analysis of a process individual groups or individual substance, or even separate parts of it, whose interaction is to be studied, are singled out of the multitude of the substances under consideration, the scope of the investigation thus being narrowed. Only these objects, called systems are submitted to thorough analysis. The substance not included in the system is the environment and may be taken into consideration only to the extent to which it interacts with the system in question.

Systems may occur as homogeneous and heterogeneous ones the latter having boundaries between the parts of the system differing in properties. In case homogeneous systems have the same composition and properties in all the points, they are moreover uniform, whereas heterogeneous systems comprise at least two phases. Therefore the term *phase* denotes a combination of homogeneous parts of a system having identical chemical and thermodynamic properties separated by a boundary from the other phases. Phases can be subdivided into separate parts but that does not increase their number in the system, e.g., in a saturated solution of dihydrate gypsum in water, when there is any amount of crystalline particles of gypsum on the bottom of the vessel and vapour above the solution, always only one crystalline, one liquid and one vaporous phase will exist.

Components are those kinds of particles which can exist independently beyond the system. Thus in a water solution of  $\text{CaSO}_4$  at 293 K one can find the following kinds of particles: water, gypsum, anhydrite, hydrated ions:  $\text{Ca}^{2+}$ ,  $\text{SO}_4^{2-}$ ,  $\text{H}^+$ ,  $\text{OH}^-$ . There are however only three components there: water, anhydrite and gypsum, as the ions cannot be extracted from the given system separately.

Components are independent constituents of a system. Their number corresponds to that of the constituents sufficient for forming all the phases of an equi-

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<sup>3</sup> For a deeper study of the chemical thermodynamics one should consult special handbooks and monographs [1, 12, 66, 118, 149, 150, 151, 194, 234, 242, 274, 277, 302, 304, 311, 488, 527, 529, 550, 562, 603, 622, 658, 667, 672, 719]

librium system minus the number of the equations of reactions linking the concentrations of the substances in one of the phases.

The interaction of the system with the environment may manifest itself in interchange of substance and energy — open systems —. It is sometimes quite reasonable to consider a system in an idealized state, when its interaction with the environment is reduced to a minimum and its volume remains constant. In this case we deal with isolated systems in which the energy despite the processes and chemical transformations taking place remains invariable. A change of the energy of a system can be observed only in the case of its isolation being broken subsequently allowing energy interaction with the environment. If a system is not entirely isolated and can alter its volume and exchange energy with the environment, it is called (unlike the previous isolated one) closed. The values that characterize all the physical and chemical properties of a system, such as temperature, pressure, volume, internal energy, entropy, concentration etc., are denominated thermodynamic parameters of state.

For a thermodynamic analysis of the alteration of the state of a system the change of its thermodynamic parameters must be known. The number of the parameters of state depends however on the number of the degrees of freedom of a system<sup>4</sup>. An alteration of one of them results in an alteration of the state of the whole system, which causes a thermodynamic process in that system.

The process wherein a system having departed from the initial state and having undergone a few alterations returns to the initial state, is called a circular process or a cycle.

A process is called reversible when it allows the return of a system to the initial state with no alterations in the outer medium or in the system itself.

If the course of the process in a certain direction and in the reverse one results in some alterations in a system or in the environment, the process will be irreversible.

It should be borne in mind that all the processes actually taking place in Nature are irreversible. The alterations causing them go on in time with finite differences between the forces effecting the system, and they are accompanied by unavoidable losses.

Using the concept of a reversible process and other limiting notions (isolated system, ideal solution etc.) is very important, as it permits studying the processes in the most simplified idealized state which in turn simplifies the analysis. The results obtained in the limits of admissible experimental errors may be well applied to actual processes.

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<sup>4</sup> The number of the parameters of state capable of freely altering without breaking the phase equilibrium is called the number of the degrees of freedom of a system or its variance. The number of the degrees of freedom is determined for each system by the difference between the number of the parameters of the system in question and that of the equations linking them

One of these idealized notions is the idea of an equilibrium state, which is characterized by a stable state of a system in time, in which no spontaneous processes take place.

The chemical equilibrium is mobile, for the rates of direct and reverse reactions at the moment of the equilibrium are equal.

Taking into consideration that an alteration of external conditions will effect the equilibrium state of a system and may result in breaking it, for the sake of study it is necessary to choose such a system in which all extraneous influences are reduced to a minimum, i.e., to isolate the system.

The thermodynamic process in which a system passes through a continuous series of equilibrium states, is called an equilibrium process. An equilibrium process is characterized by reversibility, absence of any losses, infinitesimal difference of forces effecting a system, equality of the temperatures of a system and the external medium, an infinitely great duration of any final alteration of the state of a system.

A process going on infinitely slowly is often called quasistatic.

In chemical processes reversibility and equilibrium generally concur, i.e., any equilibrium process is always reversible.

Unlike an equilibrium process, non-equilibrium exists when finite alterations have taken place in a system. A non-equilibrium process is unidirectional. In this case owing to the finite rate of the process and because of losses, the work done by a system will always be smaller than in an equilibrium process.

A system having performed an equilibrium process may return to the initial state, passing in the reverse process the same equilibrium states that it passed in the direct process. This property, as mentioned above, is called reversibility of an equilibrium process.

As chemical thermodynamics studies the processes bringing about a system's transition from one equilibrium state to another, differing from the initial one, the need arises for more detailed knowledge of the parameters, studying the alteration laws of which produces the goal of the thermodynamic method.

The total measure of the material motion with its transformation from one kind to another is called energy. A thermodynamic system consists of an enormous number of continuously moving and interacting particles, their energy constituting the total energy of the system. The latter is divided into external and internal ones. The external energy covers the energy of the motion of a system as a whole and the potential energy of a system in the field of the forces acting. The rest of the energy of a system is called its internal energy. In chemical thermodynamics stationary systems in the absence of an external field are considered, therefore the total energy of a system will equal the internal one.

The internal energy of a system consists of that of all types of motion and interaction of the particles entering the system: the energy of the forward and rotary motion of molecules and that of the oscillatory motion of atoms, the



energy of the molecular interaction, the intra-atomic energy of the filled electron levels, the intranuclear energy etc.

At present it is not possible to calculate the absolute value of the internal energy  $U$  of any system, but for a thermodynamic analysis it is quite sufficient to measure the change of the energy  $U$ , taking place in one or another process. The internal energy depends both on the amount of the substance under consideration and on the conditions of its existence. When a thermodynamic system interacts with the environment two different ways of energy transfer from the system to the outer bodies are possible: with a change of the external parameters of the system and without such. The first method of energy transfer is called work, the second, heat, and the process itself, heat exchange.

A system that does not exchange heat with other bodies is called adiabatically isolated. The processes taking place at constant temperature are called isothermic, at constant pressure, isobaric, at constant volume, isochoric. The processes accompanied by heat release are called exothermic, those accompanied by absorption of heat, endothermic.

Enthalpy is an important thermodynamic function. Like the internal energy it is a parameter of state, i.e., its change is determined by the initial and final states of a system and does not depend on the process.

$$H = U + pV, \quad (1)$$

where  $p$ , pressure;  $V$ , volume of a system;  $U$ , internal energy.

Enthalpy is used in isobaric processes, change of the internal energy in isochoric ones.

The sum of the heat given off and the entire work over the environment excluding the work of expansion is called the heat effect  $Q$  of the process.

The heat of formation is the heat given off or absorbed during formation of a compound, and indicates the decrease or increase of internal energy of the elements of the compound.

The heat of polymorphic transformations, of dissolution, melting, sublimation etc. is that of the corresponding isothermic and reversible processes.

All energy values — internal energy, enthalpy, heat effects, heats of formation etc. — may be expressed in any energy units. They are mostly expressed in calories or joules and are referred to as moles, gram atoms or gram ions.

Heat capacity is the ratio of the amount of heat imparted: increase of the temperature.

As the heat capacity of substances depends on temperature, mean and true heat capacities are distinguished. The mean molar heat capacity of a system  $\bar{C}$  is the heat  $Q$ , expended on heating one mole of the substance divided by the difference of temperatures  $\Delta T$  of heating.

$$\bar{C} = Q/\Delta T. \quad (2)$$