TEACHING HIGH-TEMPERATURE MATERIALS CHEMISTRY AT UNIVERSITY

(IUPAC Technical Report)

Prepared for publication by
GIOVANNI BALDUCCI1,‡, ANDREA CICCIOLI1, GIOVANNI DE MARIA1, FIQIRI HODAJ2, AND GERD M. ROSENBLATT3

1Department of Chemistry, University of Rome, La Sapienza, Piazzale Aldo Moro 5, I-00185 Roma 34, Italy; 2SIMAP Laboratory, ENSEEG/LPTCM, Domaine Universitaire, B. P. 75, F-38402 Saint Martin d’Hères, France; 3Materials Science Division, Mail Stop 62B0203, E. O. Lawrence Berkeley National Laboratory, University of California, Berkeley, CA 94720-8253, USA

*Membership of the Division Committee during the final preparation of this report was as follows:

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‡Corresponding author: E-mail: giovanni.balducci@uniroma1.it

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Teaching high-temperature materials chemistry at university

(IUPAC Technical Report)

Abstract: Over the last four to five decades, high-temperature materials chemistry (HTMC) has become a flourishing area of scientific and applied research, spurred by both a growing demand for new inorganic materials (e.g., oxide and non-oxide modern multifunctional ceramics, intermetallics, and oxidation-resistant alloys) able to withstand extreme thermal and chemical environments and by the recognition that chemical and physical behavior at high temperatures differs from, and cannot be extrapolated from, behavior at temperatures near room temperature. Despite the important role played by HTMC in modern advanced technology and the fundamental differences in behavior encountered at high temperatures, HTMC topics are rarely covered in chemistry and materials science programs at the university level because of a lack of readily accessible resource material—no textbook exists specifically devoted to HTMC topics. IUPAC’s Inorganic Chemistry Division sponsored a project to address this gap, resulting in the present report. The report includes an introduction and seven sections covering historical background, chemical behavior of condensed-phase/gas-phase systems at high temperature, basic concepts of materials thermodynamics, experimental techniques, use of thermodynamic data and modeling, vaporization and decomposition processes, and gas–solid reactions. The ninth section covers more specific topics, primarily concerning applications of high-temperature materials and processes. Each recommended topic is accompanied by a bibliography of helpful references, a short introduction or explanation including the areas of application, and some relevant teaching suggestions. An extensive annotated resource bibliography is an Appendix to the report available as supplementary material.

Keywords: teaching; high temperature; high-temperature materials; chemical education; inorganic materials; materials thermodynamics and kinetics; high-temperature chemistry and reactions; high-temperature processes; IUPAC Inorganic Chemistry Division.

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1. INTRODUCTION

Unlike the feeling that the uninitiated might have, and in spite of the common belief prevailing in the chemistry community until some decades ago, the behavior and properties of inorganic systems at high and very high temperature may differ significantly from the chemical behavior we are used to dealing with at near room temperature.

Since the very beginning of the research field destined to become known as “high-temperature chemistry”, researchers realized that it was of special scientific interest, because high-temperature behavior of materials cannot be easily predicted by simply extrapolating the information known under ordinary conditions of temperature. Indeed, a number of phenomena and factors commonly considered marginal or negligible in the “usual” room temperature chemistry (vaporization processes, entropy effects overcoming energetic driving forces, thermodynamic rather than kinetic control of processes, formation of new and unexpected molecular species and solid phases due to stabilization of odd or unusual oxidation states of elements, etc.) become important. This importance increases more and more with in-
creasing temperature, and plays a dominant role in many physicochemical processes. Thus, it was (and still is) commonly assumed by laypersons that gas-phase systems always tend toward simplification on increasing temperature. However, different and even opposite behavior is observed when the gas phase is in equilibrium with a condensed system, since the formation of more complex species is often favored at high temperatures. On the whole, the accumulation of these observations has led to the emergence of a “new chemistry” specific to the high—and very high—temperature domain. This “new chemistry” may be complex and different from the chemistry to which students are usually introduced in their elementary courses of inorganic and physical chemistry. New and often complex species and solid phases appear, whose stability depends on high-temperature conditions.

The sequence of topics presented here represents subjects that could be included for teaching at various levels of in-depth study in university curricula for students in chemistry, industrial chemistry, and materials science. The arrangement of the topics starts from the behavior of materials at high temperatures that historically represents the emergence of the field of high-temperature materials chemistry (HTMC); it then gradually widens to reflect the evolution of inorganic materials science towards new directions. During the past decades, high-temperature science has continued to grow into an active interdisciplinary field concerned with the investigation, correlation, and prediction of a multitude of chemical and physical phenomena. High-temperature science is ubiquitous in many processes and applications, such as heat engines, combustion, nuclear power generation, high-temperature fuel cells, chemical plant and processes, etc., as well as in many geological and cosmochemical processes. Notwithstanding the well-known difficulties in conducting experiments at high and very high temperatures, the availability of reliable experimental data for binary and ternary compounds in gases and solid phases has increased considerably in the last two to three decades. Moreover, the study of high-temperature materials has benefited more recently from the parallel development of prediction models, simulation techniques, and effective use of theoretical first-principles approaches that can, for example, integrate whenever necessary the experimental thermodynamic information in the generation of new and more extensive thermodynamic databases.

The evolution in the field is clearly shown by the succession of various conferences and meetings on high-temperature materials chemistry and technology held regularly over the past five decades (see Supplementary Material: Symposium Proceedings). For example, the successful series of IUPAC conferences on HTMC is now considered the premier international venue for presenting advances of basic and applied research in the field and for gathering scientists from different areas of expertise (materials chemists, physical chemists, metallurgists, ceramists, engineers, industrial chemists, physicists). Another forum that addresses fundamental issues in high-temperature science is the Gordon Research Conference series on High-Temperature Materials Processes and Diagnostics (formerly known as the Gordon Research Conference on High-Temperature Chemistry). Other related meetings are those of the Electrochemical Society High-Temperature Materials Division. Many of the topics listed here are related to results of research reported at the above conferences.

Motivation for basic research in high-temperature science, mainly carried out at universities and other institutions, is strongly connected with the need to educate and train young scientists such as chemists, physicists, chemical and materials engineers, and materials scientists who are required to address various high-temperature materials problems associated with the needs of advanced technologies (e.g., in the fields of energy production, aerospace research, and environmental issues). To this end, it is important to recognize the task of providing students with the concepts and tools necessary to understand the behavior of materials and chemical processes at high temperatures. However, although research is actively carried out in many academic laboratories and other institutions in the field of HTMC, educational needs for preparing young scientists are relatively neglected. Indeed, as emerged from an inquiry by a Preliminary Survey Team (PST 16) promoted in the past by IUPAC Inorganic Chemistry Division Commission II.3, it seems generally difficult to introduce formal lecture courses entirely dedicated to HTMC into overcrowded university curricula in inorganic chemistry, physical chemistry, and materials science. Therefore, efforts should be encouraged to insert at least a number of selected topics.
of HTMC into other, perhaps elective, courses. IUPAC’s Inorganic Chemistry Division sponsored a project to address this gap.

The selection of topics presented here and their organization reflects in large part the actual experience of the project task group chair, who has for very many years given lecture courses on high-temperature physical chemistry to chemistry and industrial chemistry students with curricula oriented to materials chemistry (typically, sixth to ninth semester) at the University of Rome, La Sapienza.

The following list of topics is organized in eight sections. Sections 2–8 cover the “classical” corpus of topics of high-temperature chemistry dealing with high-temperature reactivity, based essentially on equilibrium thermodynamics, thermodynamic data for pure substances in vapor and solid phases, and their use in various materials problems. Section 9 presents a number of more specific topics, mostly concerning technological applications of high-temperature materials and processes. Because of their interdisciplinary nature and somewhat higher level of presentation, the study of these additional topics may need, or benefit from, a prerequisite knowledge of basic aspects of solid-state chemistry and physics, surface properties, etc. This report is intended to help teachers select the most appropriate topics to be taught in a given course.

2. HISTORICAL BACKGROUND

Aim: To give an overview of the historical development of studies of high-temperature chemical and physical behavior of inorganic materials.

Topic description and teaching suggestions: This historical introduction should follow from pioneering studies on the high-temperature behavior of inorganic materials to the recognition of the importance of high-temperature chemistry as a new area of research concerning properties, reactivity, and developments of new advanced materials for applications in extreme environments. The various definitions of high-temperature chemistry and high-temperature reactions given by the founders of this discipline can be fruitfully discussed. As discussed in some of the references given below, the term “high-temperature chemistry” is best defined in terms of characteristic chemical reactions rather than in terms of temperature ranges. Indeed, it is not possible to give a definite lower value above which temperatures may be termed “high”. Since the early stages of this area of research, studies were focused particularly on condensed-phase/gas-phase processes carried out under high-temperature/low-pressure conditions and on the characterization of high-temperature vapors and new molecules of unexpected complexity. In fact, vaporization processes become increasingly important at high temperatures, gaseous species with unfamiliar oxidation states of the elements often form and their complexity may increase with temperature. In this context, most of the studies carried out so far over the decades have been performed from 500 up to 3000 K with perhaps a large majority in the range 1200–2500 K. Also, solid phases with stoichiometries different from those usual at room temperature may be stable at high temperature.

Useful bibliography

Books

Conference proceedings
3. GENERAL CHEMICAL BEHAVIOR OF CONDENSED-PHASE/GAS-PHASE SYSTEMS AT HIGH TEMPERATURE (BREWER'S RULES)

**Aim:** To describe the behavior and properties of high-temperature vapors on a thermodynamic basis.

**Topic description and teaching suggestions:** A vapor coexisting with a condensed phase at high temperature may comprise more than one species. The relative chemical stability of, say, two vapor species may change with temperature. Brewer rationalized the unexpectedly complex molecular character of high-temperature vapors on the basis of simple empirical rules based on thermodynamic arguments. Brewer’s first rule essentially predicts that if a high-temperature saturated vapor system contains several molecular species, then the species of lower concentration will increase in relative importance as the temperature is increased. Typical cases are those where the monomer/dimer ratio in the vapor decreases on increasing temperature: the “double” role played by the vaporization enthalpy in determining the partial vapor pressure (VP) at any given temperature (Gibbs–Helmoltz equation) and their temperature dependence (van’t Hoff equation) can be underlined by assuming equal vaporization entropies as a first approximation. The role of entropy in determining the dominant species at high temperature can be analyzed in more detail on the basis of translational and internal (rotational–vibrational and electronic) contributions. Many examples illustrate this rule. Just to mention a few, the vaporization of graphite to species $C_n$ with $n = 1$ to 7, the vaporization of BeO(s) to $(\text{BeO})_n(g)$ with $n = 1$ to 6, etc. A good example of species with unusual oxidation states of the elements are: AlO, Al$_2$O, AlO$_2$, Al$_2$O$_2$ produced in the vaporization of alumina. The second Brewer’s rule indicates limitations on solid–gas reactions, and states that a gas will react endothermically with a solid to produce a significant yield of reaction product only if the reaction produces at least as large amounts of gas as are consumed in the reaction. Here again this behavior depends on the trends in reaction entropy. The interplay of enthalpy and entropy effects in determining the most important gaseous products in various gas–solid reactions can be discussed. A typical example is a solid metal which at high temperature reacts with a diatomic halogen molecule like Cl$_2$ or with molecular or atomic oxygen to give various metal halide and metal oxide gaseous species of different complexity.

This topic should be dealt with linked to subsequent topic 7.1.

**Useful bibliography**

**Books**

4. BASIC CONCEPTS OF MATERIALS THERMODYNAMICS

Aim: To review the fundamentals of thermodynamics and to re-examine these fundamentals at a higher level and with a more materials-oriented approach.

Topic description and teaching suggestions: One of the areas that is most important for HTMC is thermodynamics. A sound knowledge of theoretical and experimental aspects of thermodynamics is imperative to understand the behavior of materials under various environmental conditions and to develop processes for novel materials. Established principles from thermodynamics, general chemistry, and phase equilibria should be a prerequisite, and should include basic concepts of statistical thermodynamics usually given to students in an introductory course. These principles provide practical tools for understanding high-temperature chemical behavior of materials and processes. In the following, thermodynamic subtopics that are directly related to inorganic materials thermodynamics at high temperatures are listed. These usually cannot be addressed in-depth in the general introductory courses of the first semesters.

4.1 Gibbs energy, enthalpy, entropy relationships

4.2 Phase transformations and phase diagrams in unary systems

4.3 Thermodynamics of mixing (in metallic and ceramic systems)

4.4 Phase transformations and phase diagrams in binary systems and their relation to thermodynamic properties

Describes in particular binary Gibbs energy vs. composition diagrams with selected examples of inter-metallic and ceramic (in particular, oxide) systems.

4.5 Examples of phase diagrams for ternary systems

4.6 Basic elements of nonequilibrium thermodynamics applied to high-temperature materials problems

Useful bibliography

Books

Numerous textbooks of general thermodynamics are available. Those listed here are particularly oriented to the thermodynamics of materials.

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5. EXPERIMENTAL TECHNIQUES IN HIGH-TEMPERATURE RESEARCH

Aims: To illustrate the most important experimental techniques used to attain, control, and measure high temperatures both in laboratory experiments and in industry; to describe the main methods employed in the measurement of thermodynamic and kinetic properties at high temperatures.

5.1 Generation, measurement, and utilization of high and very high temperatures

Topic description and teaching suggestions: The concept and definition of thermodynamic temperature should be introduced. Temperature scales and International Temperature Scale (ITS-90) and their historical evolution should be described. Examples of primary and secondary thermometers should be...
given. Among the methods to produce high temperatures, in addition to the classical resistance, radiation, and radiofrequency induction heating techniques, mention should be made of laser heating and the exploding wire technique for generating extremely high temperatures (above 6000 K). Among the most used devices for temperature measurement, of special interest are resistance thermometers, various types of thermocouples, monochromatic optical pyrometers, and total radiation pyrometers.

Remarks on the suitability of different groups of materials for use as containers in experiments at high temperature under various chemical environments (vacuum-inert, reducing, or oxidizing atmosphere) should be made. Containerless processing techniques provide noncontact conditions; therefore, they are particularly useful to study liquid or glassy-state samples by avoiding interaction of the sample with the environment. Description of various levitation techniques: electromagnetic, aerodynamic, acoustic, microgravity levitation in space coupled with various modes of heating such as by induction, incandescent radiator, or laser irradiation. Remember that “at high temperature anything reacts with anything else”, therefore, these techniques are conveniently used for the measurement of thermophysical properties of advanced materials, metals, alloys, and ceramics, at high or very high temperatures (up to about 6000 K).

5.2 Experimental methods for the measurement of thermodynamic data at high temperature

**Topic description and teaching suggestions:** The most used experimental calorimetric and equilibrium techniques for obtaining thermodynamic data of materials are described

**Calorimetric methods:** Various calorimetric techniques such as direct reaction calorimetry, solution calorimetry, combustion calorimetry, differential scanning calorimetry (DSC) adapted for high-temperature conditions are employed to get thermodynamic information on various classes of inorganic materials (heats of formation, heats of solution, heat capacities, etc.).

**Equilibrium methods:** Vapor pressure (VP), electromotive force (EMF, see Section 9.5), and chemical equilibration methods. Second- and third-law analysis of equilibrium data. Among the equilibrium VP methods employed, the classical Knudsen-effusion technique, the Knudsen-effusion and torsion-effusion techniques sometimes coupled with thermogravimetry (TG) and their potentialities can be illustrated. Stress that in particular the high-temperature Knudsen cell-mass spectrometry (KC-MS) technique yields important and often unique information on the gas phase as well as on the solid phase. In fact, most available thermochemical data for high-temperature gaseous species of a wide degree of complexity have been and still are determined by this technique. To extend the area of application of HT-MS (high-temperature mass spectrometry) to higher temperature and high-pressure conditions, the mass spectrometer has been coupled with laser heating of the sample (LIV-MS, laser-induced vaporization mass spectrometry) and high-pressure molecular source (HP-MS, high-pressure mass spectrometry) for sampling and studying vapors in the higher (>1 bar) pressure regimes. The HT-MS technique significantly contributed and still contributes to the development of HTMC in many areas, particularly that concerning the characterization of high-temperature vapors and the acquisition of thermodynamic data.

5.3 Experimental techniques for determination of phase diagrams

**Topic description and teaching suggestions:** Various thermal analysis techniques: TG, differential thermal analysis (DTA), DSC, complemented by X-ray diffraction (XRD), scanning electron microscopy/energy-dispersive spectrometry (SEM/EDS) and optical microscopy, diffusion couples, Mössbauer spectrometry and neutron diffraction, all adapted for measurements at high temperatures, are currently employed to determine phase diagrams and to highlight transformations up to the melting point of inorganic materials (alloys, ceramics, and minerals), as well for the study of reaction kinetics (e.g., oxidation of metals, alloys, intermetallics, and refractory non-oxide compounds, decomposition
of solids, etc.). Give (or review where necessary) a brief description of the techniques and illustrate a few selected examples.

Useful bibliography

Books
J. O’M. Bockris, J. L. White, J. D. Mackenzie (Eds.). Physicochemical Measurements at High Temperature, Butterworths, London (1959). A volume (maybe the first to appear in the field) by pioneers in high-temperature science that offers a view of the experimental side of high-temperature physicochemical measurements as known at the time “with the purpose as a source for those who teach courses concerning high temperature work”.

Conference proceedings volumes
Papers


Consult also the following review papers dealing with the study of materials in liquid or glassy state at high or very high temperatures under containerless conditions:


Other papers published by P. Nordine, R. Weber and coworkers on the same subject and referring to specific systems might be consulted in preparing examples for students. Here, a few relevant references are cited:


6. USE OF THERMODYNAMIC DATA AND MODELING IN HIGH-TEMPERATURE MATERIALS PROBLEMS

6.1 Thermodynamic databases, compilations of data, estimation of data for pure substances

*Aims:* To provide an overview of the most useful thermodynamic functions: heat capacities; enthalpies and entropies of reaction, transformation, fusion and evaporation; entropy trends, and estimates of entropy of reaction. To show the use of thermodynamic databases for equilibrium calculations.

*Topic description and teaching suggestions:* Equilibrium calculations are an important tool to predict the phases which are stable under given conditions and to predict their composition. The availability of thermodynamic databanks for gaseous species and condensed phases is most important. The lack of necessary information is a particularly critical problem for high-temperature scientists. Knowledge of the entropy, enthalpy, and Gibbs energy changes associated with a chemical process is important in many areas of chemistry. There are many sources of thermochemical data compiled in different forms that can be used effectively for the given purpose. These databases must be prepared by
qualified people. There may be significant discrepancies in the assessed values of different databases, depending on the chemical system, and one has to be critical and to make efforts to reconcile these. In teaching students, a warning should be made in the selection of the database to be used for equilibrium calculation and modeling. However, because of both the demanding nature of experimental thermodynamics especially at high and very high temperatures and the enormous number of conceivable compounds, reliable experimental data are often unavailable or impossible to obtain. Empirical predictive models and, more recently, theoretical approaches (like DFT, density functional theory) are being used effectively for generating thermodynamic data which complement or supplement experimental data in generating extensive databases.

Useful bibliography

Web and electronic sources, compilations of data
A detailed survey of thermochemical resources in the Internet can be found in several educational and thermodynamics-related web sites. Relevant examples are:
<http://www.ca.sandia.gov/HiTempThermo/> (database specific to high-temperature applications)
<http://www.ihed.ras.ru/thermo/> by G. V. Belov
<http://www.cret.polymtl.ca/fact/index.php>
<http://www.FactSage.com>

For further readings concerning data sources, consult the general list of references given in the Supplementary Material.

Books

Papers
6.2 Types of thermochemical diagrams

Aims: To describe construction and use of Ellingham diagrams, predominance area diagrams, thermochemical volatilization diagrams.

Topic description and teaching suggestions: Thermochemical diagrams are important means to predict the stability of a material under given conditions and readily supply graphical information on the results of equilibrium calculations. As tutorial work, students may be trained to construct a simple thermochemical diagram (e.g., for a ceramic material such as SiO₂, Si₃N₄, BN) at a given temperature from the pertinent set of Gibbs energies of formation for all the condensed phases and gaseous species known for the system.

Useful bibliography

Books


Additional reading

Papers


6.3 The CALPHAD method

Aim: To introduce use of the CALPHAD approach for calculating phase diagrams.

Topic description and teaching suggestions: The coupling of thermochemical information and phase diagram information is the basis of the method, now widely used, for optimization and calculation of phase diagrams in multicomponent systems. This topic can be dealt with starting from a description of the thermodynamic models for mixture phases (substitutional solutions, sublattice models, quasichemical and association solution models for ionic melts, such as slags and molten salts). The Gibbs energy for each phase in the system is described analytically as a function of composition and...
temperature by means of models whose parameters are optimized by comparison of experimental and ab initio (quantum mechanics) information. With these functions, it is possible to calculate the equilibrium phase diagram and extrapolate thermodynamic functions to unknown regions. Lattice stabilities are obtained from estimation, extrapolation, and from ab initio techniques. One of the most important aspects in recent years has been the merging of thermodynamic models with first principles calculations. Examples of the most common software, such as ThermoCalc, LUKAS programs, FACTSAGE, PANDAT, GEMINI, etc. (see below), using the CALPHAD approach should be shown. The use of such software for a specific application can be the subject of a class tutorial. Select one or more case studies from those reported in bibliographic references. Simple examples we suggest here are Cu + Ni and Pb + Sn, showing elementary principles of coupling thermochemistry and phase diagrams.

Helpful bibliography

Books

Papers and websites
For the Lukas programs BINGSS and TERGSS for phase diagram optimization, see: H. L. Lukas, S. G. Fries. “Demonstration of the use of “BINGSS” with the Mg-Zn as example”. J. Phase Equilibr. 1, 532 (1992).
For the PanDat software by A. Chang’s group, see: <http://www.computherm.com/pandat.html>.
For the MTDATA software developed at the UK’s NPL, see: <http://www.npl.co.uk/mtdata/mtrefs.html>.

6.4 Application of thermodynamics to the modeling and prediction of high-temperature chemical processes

Aim: To present selected examples of high-temperature processes predicted by thermodynamic modeling

Topic description and teaching suggestions: Once the basic concepts and methods of thermodynamics have been presented and their practical application in databases and graphical representations assimilated by the students, a few examples of application to specific high-temperature processes (some dealt with as optional additional topics in the last part of the course) can be tackled. Appropriate examples can include the following: prediction of high-temperature corrosion of intermetallic or ceramic materials under hydrogen-oxygen-water environments; carbothermic reduction of silicon dioxide; evaluation of the distribution of components between phases in pyrometallurgical processes; equilibrium approach to dynamic processes as in the use of PVD (physical vapor deposition) and CVD (chemical vapor deposition) for synthesis of materials. The importance of a critical analysis and selection of thermochemical databases should be underlined (see Section 6.1). The limitation of using a purely
thermochemical description of dynamic processes can be shown, and the necessity to develop more sophis-
ticated approaches toward process simulation, taking into account transport phenomena, flow prop-
erties, non-isothermal conditions, etc., can be outlined.

Where possible, the results predicted by modeling should be compared with experimental data.

**Useful bibliography**


### 7. VAPORIZATION AND DECOMPOSITION PROCESSES

**Aims:** To describe the physicochemical basis and complexity of vaporization and decomposition of inorganic materials at high temperatures, the information derived therefrom and their relevance to materials characterization and processing.

#### 7.1 Vaporization processes: Thermodynamic and kinetic aspects

**Topic description and teaching suggestions:** All substances evaporate under given conditions of temperature and external pressure. The detailed study of a vaporization process yields information on the nature and energetics of chemical binding in the gaseous state; the nature of high-temperature reactions; the thermodynamic properties of solids, liquids, and gases; the kinetics of high-temperature vaporization reactions; and their use as preparative tools for new materials. For example, it may be important to consider the loss in mass and size that occurs as a result of free evaporation of an oxide ceramic (and other non-oxide ceramic materials or semiconductors) in vacuo in high-temperature environments. In this respect, it is of concern to underline the concept of evaporation and condensation coefficients. In studying vaporization reactions, a pressure-composition diagram ($P$ vs. $x$) is useful for representing occurrences in a thermodynamically effusing system. Laser-induced vaporization extends the ranges of pressure and temperature and allows information to be obtained on the behavior of materials near the critical regions. Historically, investigation of the vaporization behavior of polycrystalline and also single-crystal materials, in congruent and noncongruent modes, represented a typical and focal topic in HTMC research. Selected examples of vaporization processes of simple substances of historical relevance (like the vaporization of graphite to monatomic and polyatomic species and clusters; of alumina, etc. as anticipated in Section 3 above) may be illustrated. It is useful to underline that usually the identification and characterization of gaseous “high-temperature species” is made through the study of simple or reactive vaporization processes. This topic should be presented to students in parallel with the experimental techniques presented separately in this syllabus (see Section 5.2).

**Useful bibliography**

Among the numerous contributions on this subject appeared in contributed books, proceedings volumes, and review papers, the following bibliographic references have been selected:

**Books**


7.2 Decomposition of solids: Thermodynamic and kinetic aspects

**Topic description and teaching suggestions:** Thermal decomposition of an inorganic solid is a reaction in which a solid reactant yields a new solid phase with molar volume lower than that of the reactant, plus a gaseous product. In dealing with the analysis of the kinetics of this complex phenomenon, many features need to be considered. Nucleation, growth, sintering of the solid products, vaporization from the interface reaction, and diffusion of the gaseous product into the pores are only a few examples of processes that can have a role in determining the rate-limiting steps. Although the high-temperature thermodynamics and kinetics of decomposition reactions of inorganic solids have been dealt with in the past in a large number of studies, there is at present a renewed interest in the mechanism of thermal decomposition of different types of inorganic solids due to their various industrial applications. Indeed, the decomposition of, e.g., carbonates, sulfates, and hydroxides remains a common process in the production of oxide ceramics; knowledge of decomposition conditions and mechanism of formation of certain semiconductors is important for film growth and processing at high temperature in vacuo and in reactive environments. Illustrations for students of the basic mechanistic aspects of the decomposition reactions of solids should be accompanied by discussion of relevant examples chosen, e.g., among carbonates, sulfates, etc.
Experimental and theoretical studies aimed at interpretation of the kinetics and mechanism of thermal decomposition of solids have a history that dates back many decades. Before the 1970s, the role of the solid-state point of view was extensively explored (see books in the appended bibliography), but the implication of the vaporization theory of the gaseous products was quite neglected. At the end of 1970s and subsequently, A. W. Searcy (University of California, Berkeley) and D. Beruto (University of Genoa, Italy) developed this approach in a series of experimental and theoretical papers, mainly on the decomposition of metal carbonates (and specifically calcite), that clarified the nature of the surface step due to the vaporization of the gaseous product, the subsequent diffusion and effusion processes into the solids porous matrix, and the microstructure changes of the oxides formed due to the high-temperature chemical adsorption of the gaseous product onto the oxide surface and to the catalytic effect that the gaseous phase may have in the sintering of the oxides nanocrystallites.

From this information, a clear picture of the rate-determining steps of the thermal decomposition kinetics can be formulated in terms of a modified Langmuir–Hertz equation and of decomposition coefficients. The nature of these coefficients was clarified recently by the same authors as a function of a surface chemical step of the gaseous products and of thermodynamic activity of the solid oxide formed.

More recently, B. V. L’vov and coworkers, University of St. Petersburg, Russia, tried to extend further the implication of the vaporization theory in the thermodynamic and kinetic analysis of the decomposition reactions. They proposed a physical approach (PA), in contrast to the traditional Arrhenius plot and second-law method, through the application of the so-called “third-law methodology” which reflects a marked difference in research philosophy. The PA theory basically assumes (among other assumptions) that the primary step of thermal decomposition consists in the nonequilibrium congruent dissociative evaporation of the reactant. These assumptions seem somewhat questionable inasmuch as they are not fully substantiated by experimental facts indeed, it is extremely difficult to test experimentally the conjectured primary congruent step, even in high vacuum, considering the extremely low volatility of the oxide products at decomposition temperatures. Thus, although the author claims that the PA theory is generally better than the traditional Arrhenius plot and second-law method, at least for a great part of ceramic oxides obtained from the thermal decomposition of their inorganic salts the PA analysis can lead to results that are too speculative. In such a case, for the understanding of the kinetics of the thermal decomposition reaction it appears mandatory to couple the kinetics data from the thermal decomposition curves with the microstructure evolution of the oxides produced.

Useful bibliography

Books

Papers

8.0 HIGH-TEMPERATURE GAS–SOLID REACTIONS FORMING BOTH SOLID AND GASEOUS PRODUCTS: THERMODYNAMIC AND KINETIC ASPECTS

Aim: To describe an important type of processes almost ubiquitous in the performance of materials under extreme environmental conditions and to discuss examples for selected materials.

Topic description and teaching suggestions: Understanding this topic enables appreciation of high- or very-high-temperature corrosion of metallic and ceramic materials in various extreme environmental conditions, in particular reactive atmospheres (“hot corrosion”). This knowledge is of particular relevance for the fundamental understanding of materials problems related to aerospace (e.g., hypersonic atmospheric re-entry and rocket propulsion) and energy production systems (gas turbines operating at high temperature, coal gasification, nuclear reactors, etc.). A sound knowledge of thermodynamics and kinetics of gas–solid reactions is also important for chemical vapor transport and deposition processes (see description of the relevant topic described later in this syllabus). Among others, examples may be given and discussed of passive and active (with transport of gaseous products) oxidation; active oxidation of silicon is an outstanding example. As well, it is interesting to show the active oxidation of certain refractory metals like tungsten and molybdenum which have very low VP up to very high temperature under neutral conditions (vacuum) but are unstable due to reactive vaporization under oxidizing atmospheres even at low temperature. (It is interesting to relate this problem to the thermodynamic volatility diagrams described earlier.) The interaction of certain ceramic oxides with water vapor at high temperature is noteworthy. Indeed, the interaction of high-temperature water vapor with oxides to form volatile hydroxides leads to material loss which can be a life-limiting degradation mechanism. All these reactions may be predicted and modeled using thermochemical data for reactants and products (as dealt with in the preceding thermodynamic topics) and a Gibbs energy minimization computer code.

This topic is related to subsequent topics dealing with deposition processes, pyrometallurgical processes, and halide lamp chemistry.

Books

Papers

9.0 ADDITIONAL SELECTED TOPICS RELEVANT TO THE PHYSICAL CHEMISTRY OF HIGH-TEMPERATURE PROCESSES

Aim: To give a description of the physicochemical basis for a number of high-temperature processes and systems relevant to the synthesis, properties, and performance of materials interesting for technological applications.

The preceding topics represent in a sense the “core” of high-temperature chemistry and are based mainly on equilibrium thermodynamics, phase diagrams, thermodynamic data, and their use in materials problems and, to a lesser extent, kinetics.

This section contains a selection of additional “special” topics useful to illustrate a number of both classical and innovative processes of technological interest, where high-temperature conditions and behavior of materials play an important role. The topics reported here are not intended to be comprehensive. Indeed, there are many temperature-dependent properties that are relevant to high-temperature physicochemical behavior of inorganic materials that could be selected for teaching in a course or part of a course dedicated to HTMC. These include: defects in solids and thermodynamics of defects, solid-state diffusion, nucleation, and growth, kinetics of phase transformation, which are typical of solid-state chemistry and physics and are usually addressed in specific courses, basic or advanced, of solid-state chemistry and physical chemistry of materials. Others, such as thermophysical and thermomechanical properties, traditionally pertain more to the field of materials engineering and are not considered here explicitly. In preparing a lecture course, some of the special topics described in the following may be selected as optional.

9.1 Pyrometallurgical processes

Aims: To describe the physicochemical basis of some high-temperature processes of materials, such as extraction and recovery of metals from ores and metal refining.

Topic description and teaching suggestions: This topic encompasses various aspects and applications of high-temperature processing, in particular of individual metallic and alloy systems and also ceramic systems: reactions involving solids, metal extraction processes through carbothermal and metallothermal reduction of oxide minerals, metal refining processes through gas–solid reactions (e.g., chlorination and fluorination reactions of simple and mixed oxides), degradation of materials, etc. Pyrometallurgical treatments of materials (purification, recovery of metals, etc.) are commonly employed in nuclear reactor technology. Basic knowledge of physicochemical aspects of pyrometallurgy provide students of chemistry, industrial chemistry, materials science oriented to metallurgy, and those topics concerned with the science of producing and refining metals at high temperatures, with the information to understand how processes of industrial importance work and possibly how to improve them. A prerequisite is a basic knowledge of thermodynamics and kinetics. The instructor may select and illustrate some examples like the chlorination reactions of metal oxides and the vapor phase refining and separation of metals (relate this topic to vapor transport reactions dealt with separately; see Section 9.1.1).

Books
9.2 Synthesis of materials at high temperatures

Aims: To give an overview of the most important synthesis routes to materials at high temperature.

Topic description and teaching suggestions: There are many routes for syntheses carried out at high and ultra-high temperature to obtain inorganic materials in various forms: polycrystalline, monocristalline, amorphous, thin films, etc. Their description may be found in textbooks of solid-state chemistry at various levels. In this syllabus, we suggest including for teaching purposes a few methods of preparation of materials where high-temperature chemical processes are involved. For a compact and effective overview of methods of synthesis, see the following textbook:


Consult also:


9.2.1 Synthesis methods by physical and chemical deposition: Vapor phase transport and deposition and chemical vapor deposition processes

Aim: To give the fundamentals of theory and practice of synthetic processes, including modeling and process simulation.

Topic description and teaching suggestions: The CVD method enables the preparation of coatings of different types with the possibility of uniform thickness and low porosity, even on substrates of complicated shape. CVD is employed in many thin film applications, for instance, in the microelectronics industry. Among important CVD applications are the deposition of high-temperature materials, such as tungsten, tantalum, refractory alloys, oxide ceramics, and nitrides, which are not easily fabricated by more conventional means. (See also powder metallurgy and sintering processes, Section 9.6.) The importance should be underlined of thermochemical modeling of CVD processes, the role of high-temperature chemistry in predicting the most important gaseous precursors involved in the process, and the phases whose deposition is thermodynamically favored. Among modern, lower-temperature variants of CVD, metalloorganic CVD and plasma CVD should be illustrated. (For plasma processes, see Section 9.2.2.) Some specific examples, e.g., deposition of silicon, silicon carbide (SiC), and diamond can be illustrated.

Chemical transport along a temperature gradient is a process related to CVD. Give a description of high-temperature transport reactions, their optimal physicochemical conditions (thermodynamic and kinetic), and their relevance as preparative tools.

Besides CVD, PVD techniques are also of interest as processes for thin film deposition. The main variants of PVD are simple and reactive evaporation, sputtering, and ion plating.

Useful bibliography

Books


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9.2.2 Combustion and plasma synthesis of high-temperature materials

**Aim:** To describe the principles and operations of nonconventional high-temperature methods of synthesis of both stable and metastable materials.

**Topic description and teaching suggestions:** Combustion and plasma synthesis have emerged in the last decades as special techniques for the preparation and processing of well-characterized, high-purity, high-temperature inorganic materials.

Solid-flame combustion is a self-sustained chemical wave process that yields fully or predominantly solid products. The synthesis of materials (pure compounds or composites) via this process is generally known as self-propagating high-temperature synthesis (SHS). The SHS technique, pioneered by Merzhanov and coworkers, involves the “combustion” of (solid + solid) and (solid + gas) systems to yield high-melting materials (carbides, borides, silicides, intermetallics, etc.) by direct synthesis, starting from pure chemical elements as reactants. Once the exothermic reaction is initiated (by igniting the compacted reactants through various means), it releases sufficient heat to go to completion in a very short time (of the order of a few tenths of seconds), reaching temperatures as high as 2500–3500 K and beyond. SHS processes are approximately adiabatic, and the temperature reached in the reaction front (adiabatic temperature) can be calculated from thermochemical data where available. Physicochemical studies of SHS currently include studies of the mechanism of combustion wave propagation; mathematical simulation of combustion; establishment of relations between the product composition and operational conditions (combustion); experiments under microgravity conditions.

Considerable interest has been focused in the last two decades on plasma-assisted preparation of a number of inorganic solids in the form of fine, pure powders or films for application in many areas of advanced technology. In many cases, thermal plasma processes have been substituted for conventional synthesis techniques used for ceramic powders (nitrides, borides, carbides, oxides) with good production rates and for coatings, for example, of metals with harder ceramic materials. Thermal plasma reactors are characterized by the presence of highly reactive species (ions and excited atoms) not available under conventional processing conditions. The properties of thermal plasmas usually lead to complete vaporization with associated gas-phase chemistry. Moreover, rapid quenching of the products
can provide new and amorphous phases. A few selected examples of SHS preparation of ceramic and intermetallic materials may be illustrated, and calculation of the so-called adiabatic temperature through use of thermodynamic data may be shown.

**Useful bibliography**

Books


Conference proceedings volumes


Papers


Consult also:


Among lectures presented at the 15th International Symposium on Plasma Chemistry, Orleans, France, July 2001:


Among lectures presented at the 16th International Symposium on Plasma Chemistry (ISPC 16), Taormina, Italy, 22–27 June 2003:


Among lectures presented at the 17th International Symposium on Plasma Chemistry (ISPC 17), Toronto, Canada, 7–12 August 2005:

9.3 High- and ultra-high-temperature materials

_Aim_: To give an overview of families of materials stable at high temperature.

_Topic description and teaching suggestions_: The field of high-temperature materials embraces a wide range of metals, alloys, engineering ceramics, and composites. Their technological importance for various fields of application is ever increasing. Some are prepared at low temperature, but their use is for high-temperature applications; others may be prepared only through high-temperature processes. After the description of specific processes of high-temperature synthesis (see Section 9.2), it is useful to give students an overview of families of compounds (metallic, oxide, and non-oxide ceramics, including refractory pure metals) that are physically and chemically stable at high temperatures (e.g., up to 2500 K and beyond) in inert and in reactive atmospheres (in primis oxidation-resistant materials). These materials are important for application-oriented needs in various advanced technologies in aerospace (hypersonic flight, atmospheric re-entry, rocket propulsion, etc.) and advanced energy conversion systems (in particular gas turbines, internal combustion engines, nuclear reactors, solid oxide fuel cell (SOFCs) components, etc.) and environmental issues. Students should be aware of the physical and chemical properties that allow these materials to be used effectively in extreme environments: melting or transformation temperatures, chemical inertness, thermochemical properties, etc.

_Useful bibliography_

**Books**


For phase diagrams, see the following and other literature sources in Supplementary Material:


For others, check the American Ceramic Society website: <www.ceramics.org>.

**Additional readings**

A report useful to read focusing on present issues concerning ultra-high-temperature materials:

For a brief summary of problems and applications of high-temperature materials, see:

### 9.4 Chemistry of metal halide discharge lamps

**Aim:** To illustrate some HTMC issues in action in these energy systems.

**Topic description and teaching suggestions:** Metal halide gas discharge lamps are increasingly used in many kinds of applications. The study of total lighting systems, in which the lamp, considered as a reactor, is one important element, is highly interdisciplinary. Knowledge from several major domains (e.g., electrical engineering, plasma physics, and chemistry, and materials chemistry) is necessary in order to optimize a given light system for a particular application. Considering the discharge vessel as a reactor, it is clear that high temperatures and large temperature gradients, in combination with the presence of corrosive compounds such as metal halides (typically, mixtures of selected alkali and rare earth element halides), can lead to complex transport phenomena and corrosion processes. In this context, the major issues are, from the basic research point of view, thermochemistry and problems connected with materials transport and corrosion within the lamp bulb and the electrode. Thermodynamic modeling can help in understanding what processes are going on in these high-temperature devices. There are a lot of HTMC issues to be discussed in the operation of a gas discharge metal halide lamp: composition of the gas phase, thermodynamic and spectroscopic properties of the gaseous species and their volatility, diffusion phenomena and reactions of the hot gas with the bulb material (glass or alumina), etc. This topic may be included as optional and could perhaps be exploited in a tutorial class.

**Useful bibliography**

**Books**


**Papers**


See also:


### 9.5 Electrochemical systems at high temperature and applications of solid-state electrolytes

**Aim:** To give an overview of the basic physical chemistry of properties of materials and processes in action in various electrochemical devices.

**Topic description and teaching suggestions:** Solid-state electrochemical devices are widely used in the measurement of thermodynamic properties of metallic and ceramic materials at high temperature (see Section 5.2) and as high-temperature sensors. Examples of materials typically involved in thermo-
dynamic measurements are yttria-calcia stabilized zirconia, CaF$_2$ single crystals, etc. Solid-state electrochemical sensors can be used at temperatures up to about 1000 K with high sensitivity and response stability that contribute to improved combustion control, and result in both improved fuel utilization and reduced emissions.

Among the energy systems, SOFC and molten carbonate fuel cell (MCFC) configurations involve high-temperature materials and processes. The materials selected for use in SOFC configurations are constrained by the chemical stability in oxidizing or reducing atmospheres, and the conductivity and thermomechanical stability under high-temperature conditions. Indeed, research efforts are being made to understand the behavior of electrode and electrolyte in SOFC as thermodynamic and kinetic factors affect the stability and reactivity of cathode materials. The world-wide interest in fuel cell devices for clean and efficient electrochemical energy generation has resulted in large international research and development efforts, as demonstrated by several international symposia, scientific publications, and review papers on the subject. Education on the basic principles of processes and materials in this branch of high-temperature electrochemistry is crucial for the further development and understanding of new materials and processes at work in various systems, such as those for energy production (batteries), aircraft performance, environmental control (sensors), and slags in steel production. A prerequisite is some basic knowledge of solid-state electrochemistry, physical chemistry of surfaces, and, of course, materials thermodynamics.

Useful bibliography

Books

Papers

For a brief and pictorial summary of high-temperature materials and electrochemistry at work in an SOFC configuration, see:

9.6 Elements of powder metallurgy and high-temperature sintering processes: Examples of metallic systems and simple ceramic oxides and non-oxides

Aim: To provide teachers and students with basic principles of consolidation and sintering processes of metallic and ceramic powders.

Topic description and teaching suggestions: Sintering is the process of forming materials and components from powders under the action of thermal energy. Sintering plays an important role in con-
solidation of high-melting refractory metals and of metal oxide and non-oxide powder compacts. The main requirements for advanced materials such as electronic ceramics, structural ceramics, high toughness composite materials, etc., are high density and a very fine microstructure. The process of sintering occurs at high temperature and is of technical importance since it is used as a method of fabrication. Therefore, a basic knowledge of the physical chemistry of the sintering mechanism (driving force for densification, role of different types of diffusion, role of vaporization–condensation, etc.) is important. Although pressing and sintering can be viewed as physical processes, there are many high-temperature chemico-physical issues in action (consider, e.g., reactive sintering in ceramics consolidation). This topic is therefore included in this syllabus, and should be dealt with together with the synthesis of materials (see Section 9.2).

Basic knowledge of defects in solids and diffusion in solids is a prerequisite and it is usually given to students of chemistry, physics, and materials science in an introductory course in solid-state chemistry. Solid-state diffusion in particular is a thermally activated process that plays a very important role in sintering processes and synthesis of high- and ultra-high-temperature materials. Therefore, its fundamentals should be reviewed where necessary for students.

Useful bibliography

Books and Papers

For sintering:

Consult also:

For solid-state diffusion, see also:

To remind students about the basics of defects in solids and defect thermodynamics, consult:

9.7 Combustion

Aim: To achieve a basic understanding of combustion processes, both homogeneous and heterogeneous (e.g., flames of various types, coal combustion, metal combustion).

Topic description and teaching suggestions: High-temperature thermodynamics and kinetics are invaluable tools to understand and model the complex chemical phenomena occurring in flames and combustion processes, and in particular to predict parameters and features essential for the evaluation
of combustion systems such as equilibrium product temperature and composition, explosion limits, and oxidation mechanisms. As a basic example, calculation of the adiabatic temperature for several types of flames can be shown together with their energetics. Coal combustion and gasification are of enormous importance in energy production systems. It is important to understand how to improve the efficiency of the process and how to control emissions of dangerous pollutants. The impact of the modeling of combustion on some urgent technological problems such as better utilization of fuels and pollutant production could be discussed. A sample calculation of equilibrium combustion of a hydrocarbon in air may be illustrated. Other examples of flame chemistry may be given as well.

**Useful bibliography**

Books


Further reading


Software (CEA) widely used in combustion science to calculate chemical equilibrium product concentrations from any set of reactants and to determine thermodynamic and transport properties for the product mixture was developed by S. Gordon and B. J. McBride at NASA: <http://www.grc.nasa.gov/WWW/CEAWeb/>.

9.8 Properties of liquids and high-temperature processes involving liquids

**Aim:** To achieve basic knowledge of high-temperature liquid phases and melts.

**Topic description and teaching suggestions:** High-temperature liquid phases are present in many technological processes (liquid metals, slags, molten silicates and glasses, molten salts, etc.). Basic knowledge of the physicochemical properties of liquid and melts is important to understand the processes in which they are involved. To characterize the structure and long-range molecular interactions in such liquids, many modern diagnostic techniques such as laser beams (see topic dealing with containerless processing), XRD, neutron diffraction, NMR, and extended X-ray absorption fine structure (EXAFS), all adapted for investigation at high temperatures, provide useful information.

Students should at least be aware of the types of research problem currently encountered in industry and which techniques are useful to address a specific problem and system.

**Useful bibliography**

Books and Papers


9.9 Wettability at high temperatures

Aim: To provide students with a basic understanding of non-reactive and reactive wetting phenomena at high temperatures, and to give the basic explanation of the wetting properties of dissimilar materials (metal + metal and metal + ceramic systems).

Topic description and teaching suggestions: Wetting solids by liquids is a key aspect of many industrial processes (composite materials production, various coating processes, refining of steel, soldering and brazing processes, corrosion of solids by liquid metals, etc.) as well in laboratory preparations and property measurements. This is particularly true in processing of materials at high temperatures. It is therefore important to have a scientific understanding of wetting behavior both from theoretical models and experimental observations. An example is when liquid metals or inorganic glasses come in contact with solid metals or ceramics. It is important to know the nature of high-temperature wetting phenomena at interfaces of materials in terms of properties such as capillarity, adhesion, adsorption, and surface energies and also chemical reactions that alter the surfaces at interface. These phenomena occur, for example, when measuring some properties of a liquid in a metal or ceramic container (see Section 5.2). Remember, as always, that at high temperature everything reacts with everything else. A prerequisite is the knowledge of basic interface chemistry, thermodynamics, and kinetics.

Useful bibliography

Books

Papers

Many papers on interfacial phenomena (in particular wettability of different materials, capillarity, etc.) in high-temperature processes can be found in:
ACKNOWLEDGMENTS

This report is dedicated to Leo Brewer, the founder of modern high-temperature chemistry. The interest and collaboration of members of the former Commission II.3 of the IUPAC Inorganic Chemistry Division are acknowledged. The following colleagues expert in the field of HTMC contributed with comments and suggestions: Dario Beruto, Christian Chatillon, Guido Gigli, Daniele Gozzi, Suzana Gomez Fries, John Hastie, Don Hildenbrand, Nathan S. Jacobson, Adolf Mikula, Paul Nordine, Enrica Ricci, Alan Searcy, Giorgio Spinolo, and Rick Weber. Special thanks are due to Prof. Anthony R. West for his effective collaboration. Discussions of GB with the late Paul Gilles on teaching high-temperature phenomena were stimulating.

SUPPLEMENTARY MATERIAL

A selection of books and reference literature in English listed in chronological order for use as resources in teaching of HTMC topics at the university level.

Note: This general list of references supplements the main document as an on-line file. Most of the publications listed have been readily available to the TGC and the group to which he belongs, over several decades. The list is by no means to be considered comprehensive, especially in the area of thermodynamics of materials where there are plenty of books. Many older volumes may not be available at institutions and libraries, in particular conference proceedings. Nevertheless, those listed here, in particular the conference proceedings and, among these, primarily the IUPAC-sponsored HTMC conferences, show how the areas of research in HTMC have evolved over the decades.

Textbooks and contributed volumes


A. S. Khanna. *Introduction to High Temperature Oxidation and Corrosion*, ASM International (2002). For graduate and postgraduate courses on high-temperature corrosion, dealing with the basics and applications of high-temperature oxidation of metals and alloys in various environments.


M. H Van de Voorde, G. W. Meetham. *Materials for High Temperature Engineering Applications (Engineering Materials)*, Springer Verlag, Berlin (2000). A survey describing requirements on materials operating in high-temperature environments and the processes capable of increasing the performance and the temperature limits in use of metals, ceramics, and composites. The major part deals with materials and their specific properties. For engineering and science students, researchers, and managers in industries. Good overview of high-temperature metals giving some of the background for how these materials came into common use. A good introduction for someone who is starting in this area.

N. Eustathopoulos, M. G. Nicholas, B. Drevet. *Wettability at High Temperatures*, Pergamon Press (1999). Brings together current scientific understanding of wetting behavior gained from theoretical models and quantitative experiments. Considered are liquid metals or inorganic glasses in contact with solid metals or ceramics at temperatures of 500–2500 K. Information contained in the various chapters is useful for selection of suitable container materials of metallic and ceramic systems at high temperatures.


O. van der Biest (Ed.). *Analysis of High Temperature Materials*, Applied Science Publishers, London (1983). Lectures from a course organized by the Commission of the European Communities, J. R. C. Petten, The Netherlands, and aimed at analytical techniques appropriate to the study of high-temperature materials. Particular examples are given that are generally applicable to metallic and ceramic materials.

C. H. P. Lupis. *Chemical Thermodynamics of Materials*, North-Holland, New York (1983). For graduate students and senior students in metallurgy and materials science who have had previous introductory courses in thermodynamics. Useful also to professional metallurgists, chemists, and chemical engineers. Most applications are for metals and alloys.


Deals with the chemistry of reactive species (atoms and molecules). Although these reactive species are generated at high temperatures, and the chemistry is that of high-temperature species, the reaction chemistry is usually studied at low or extremely low temperatures.


- Volume 4, *Reactivity of Solids*, covers a great variety of “chemical reactions” in the broadest context. Particularly useful and relevant to HTMC are topics dealt with in Chap. 3 (“High-temperature reactivity”), Chap. 4 (“Decomposition reactions”), Chap. 5 (“Solid-state reactions”), and Chap. 8 (“Gas-solid reactions—Oxidation”).
- Volume 5, *Changes of State*, includes phase transformations which are at the heart of much of the chemistry and metallurgy of complex inorganic solids. Chapters relevant to high-temperature materials are topics in Chaps. 1–6 and particularly Chaps. 4–6.
- Volume 6A, *Surfaces I*, covers major surface phenomena. Particularly relevant to classical high-temperature chemistry is Chap. 3 where evaporation from solids is dealt with in a clear and thorough manner.


J. O’M. Bockris, J. L. White, J. D. Mackenzie (Eds.). *Physicochemical Measurements at High Temperatures*, Butterworths, London (1959). Deals with various aspects (mainly experimental) of investigations in the field of high-temperature physical chemistry.

**Symposium proceedings**


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Teaching high-temperature materials chemistry


Materials Research Society proceedings volumes


**Proceedings of High-Temperature Capillarity Conferences**


**Thermodynamic tables, compilations, and databases**

Equilibrium thermodynamics is a valuable tool in the analysis and prediction of high-temperature reactivity only if reliable tabulated data are available. Many compilations of tabulated thermodynamic data have been produced over the years, both in printed form and, more recently, in electronic form. Often for a given substance more recent compilations revise or incorporate data reported in older compilations.


**Other sources of thermochemical data**


Some compilations of phase diagrams


For others, check the American Ceramic Society website: <www.ceramics.org>.


For other compilations, check the American Society of Materials website: <www.asminternational.org>.
Some specific review articles on high-temperature phenomena


The above listed reviews illustrate three decades of research in the area of high-temperature science.

Journals specially dedicated to high-temperature science

Among major literature sources for high-temperature chemistry and physics are the following:

High Temperature–High Pressure, Pion, UK (1969–).
High Temperature Technology, subsequently Materials at High Temperature, Science Reviews, UK (1982–).

M. G. Hocking (Ed.). Bibliography on the High Temperature Chemistry and Physics of Materials, IUPAC-sponsored quarterly publication contributed by various scientists established for about 25 years (now discontinued).

Articles on high-temperature materials dealing with thermodynamics, phase equilibria, production, and properties (thermodynamic, kinetic, and spectroscopic), synthesis of materials by high-temperature processes, properties and reactivity of these materials, combustion processes, etc., were and are published regularly in many other journals and publications, e.g., without claiming completeness: Journal of Electrochemical Society; Journal of Chemical Physics; Journal of Physical Chemistry A, B, and C; Bulletin of Alloys Phase Diagrams (now Journal of Phase Equilibria and Diffusion); Journal of Materials Research; MRS Bulletin; Combustion and Flame; Journal of Physical and Chemical Reference Data; Carbon; Journal of Alloys and Compounds; Intermetallics; CALPHAD; Metallurgical Transactions A, B; Journal of Chemical Thermodynamics; Journal of Materials Science and Materials Science Letters; Advanced Materials—Chemical Vapor Deposition.