

INTERNATIONAL UNION OF PURE AND APPLIED CHEMISTRY

INORGANIC CHEMISTRY DIVISION*

TEACHING HIGH-TEMPERATURE MATERIALS CHEMISTRY AT UNIVERSITY

(IUPAC Technical Report)

Prepared for publication by

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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.

CONTENTS

1. INTRODUCTION
2. HISTORICAL BACKGROUND
3. GENERAL CHEMICAL BEHAVIOR OF CONDENSED-PHASE/GAS-PHASE SYSTEMS AT HIGH TEMPERATURE (BREWER'S RULES)
4. BASIC CONCEPTS OF MATERIALS THERMODYNAMICS
 - 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
 - 4.5 Examples of phase diagrams for ternary systems

- 4.6 Basic elements of nonequilibrium thermodynamics applied to high-temperature materials problems
- 5. EXPERIMENTAL TECHNIQUES IN HIGH-TEMPERATURE RESEARCH
 - 5.1 Generation, measurement, and utilization of high and very high temperatures
 - 5.2 Experimental methods for the measurement of thermodynamic data at high temperature
 - 5.3 Experimental techniques for determination of phase diagrams
- 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
 - 6.2 Types of thermochemical diagrams
 - 6.3 The CALPHAD method
 - 6.4 Application of thermodynamics to the modeling and prediction of high-temperature chemical processes
- 7. VAPORIZATION AND DECOMPOSITION PROCESSES
 - 7.1 Vaporization processes: Thermodynamic and kinetic aspects
 - 7.2 Decomposition of solids: Thermodynamic and kinetic aspects
- 8. HIGH-TEMPERATURE GAS–SOLID REACTIONS FORMING BOTH SOLID AND GASEOUS PRODUCTS: THERMODYNAMIC AND KINETIC ASPECTS
- 9. ADDITIONAL SELECTED TOPICS RELEVANT TO THE PHYSICAL CHEMISTRY OF HIGH-TEMPERATURE PROCESSES
 - 9.1 Pyrometallurgical processes
 - 9.2 Synthesis of materials at high temperatures
 - 9.2.1 Synthesis methods by physical and chemical deposition: Vapor phase transport and deposition and chemical vapor deposition processes
 - 9.2.2 Combustion and plasma synthesis of high-temperature materials
 - 9.3 High- and ultra-high-temperature materials
 - 9.4 Chemistry of metal halide discharge lamps
 - 9.5 Electrochemical systems at high temperature and applications of solid-state electrolytes
 - 9.6 Elements of powder metallurgy and high-temperature sintering processes: Examples for metallic systems and simple ceramic systems oxides and non-oxides
 - 9.7 Combustion
 - 9.8 Properties of liquids and high-temperature processes involving liquids
 - 9.9 Wettability at high temperatures

ACKNOWLEDGMENTS

SUPPLEMENTARY MATERIAL

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

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J. L. Margrave (Ed.). *The Characterization of High Temperature Vapors*, John Wiley, New York (1967).
L. Eyring (Ed.). *Advances in High Temperature Chemistry*, Vol. 1, Academic Press, New York (1967).
K. S. Pitzer, L. Brewer (revision of Lewis and Randall). *Thermodynamics*, 2nd ed., McGraw-Hill International Student Edition, New York (1961). Chapter 33 is particularly relevant to high-temperature vaporization chemistry.

Conference proceedings

- L. Brewer. “Conference overview of the role of chemistry in high-temperature materials science and technology”, pp. i–ix in *Materials Chemistry at High Temperatures*, Vol. 1, J. W. Hastie (Ed.), Humana Press, Clifton, NJ (1990).

J. W. Hastie (Ed.). *Characterization of High Temperature Vapors and Gases*, Proc. of the 10th Materials Research Symposium held at NBS, Gaithersburg, Maryland, September 1978. NBS Spec. Publ. 561, Vols. 1–2, U.S. Government Printing Office, Washington, DC (1979).

Selected review papers of historical relevance

R. J. Thorn. “Chemical phenomena at high temperature”, *Annu. Rev. Phys. Chem.* **17**, 83 (1966).

V. A. Kireev. “Some aspects of high-temperature chemistry from the viewpoint of thermodynamics”, *Russ. Chem. Rev.* **33**, 330 (1964).

J. Drowart, P. Goldfinger. “High temperature chemistry”, *Annu. Rev. Phys. Chem.* **13**, 459 (1962).

A. Searcy. “High temperature inorganic chemistry”, in *Prog. Inorg. Chem.*, F. A. Cotton (Ed.), Vol. III, pp. 49–127, Interscience, New York (1962).

P. W. Gilles. “High temperature chemistry”, *Annu. Rev. Phys. Chem.* **12**, 355 (1961).

J. L. Margrave. “High temperature chemistry”, *Annu. Rev. Phys. Chem.* **10**, 457 (1959).

L. Brewer, A. W. Searcy. “High temperature chemistry”, *Annu. Rev. Phys. Chem.* **7**, 259 (1956).

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 $(BeO)_n(g)$ with $n = 1$ to 6, etc. A good example of species with unusual oxidation states of the elements are: AlO , Al_2O , AlO_2 , Al_2O_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

K. E. Spear. “High-temperature reactivity”, in *Treatise on Solid State Chemistry*, Vol. 4, N. B. Hannay (Ed.), *Reactivity of Solids*, Chap. 3, Plenum Press, New York (1976).

J. Hastie. *High Temperature Vapors: Science and Technology*, Academic Press, New York (1975); Chap. 1 in particular for defining high-temperature vapors.

- A. W. Searcy, D. V. Ragone, U. Colombo (Eds.). *Chemical and Mechanical Behavior of Inorganic Materials*, Chap. 5, Wiley-Interscience, New York (1970).
- K. S. Pitzer, L. Brewer (revision of Lewis and Randall). *Thermodynamics*, 2nd ed., McGraw-Hill International Student Edition, New York (1961). Chap. 33 is particularly relevant to high-temperature vaporization chemistry.
- L. L. Quill (Ed.). *The Chemistry and Metallurgy of Miscellaneous Materials: Thermodynamics*, National Nuclear Energy Series IV, Vol. 19B, McGraw-Hill, New York (1950).

Papers

Several papers by L. Brewer and other authors discuss this topic; some among these are reported in the list of references given in the Supplementary Material. See, e.g.,

- L. Brewer. "Principles of high temperature chemistry", in *Proc. Robert A. Welch Foundation Conferences in Chemical Research*, VI. Topics in Modern Inorganic Chemistry, Houston, Texas (1962); p. 47 ff.
- L. K. Nash. "Trouton and T-H-E rule", *J. Chem. Educ.* **61**, 981 (1984).

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.

- M. Hillert. *Phase Equilibria, Phase Diagrams, and Phase Transformations: Their Thermodynamic basis*, 2nd ed., Cambridge University Press (2008).
- D. R. Gaskell. *Introduction to the Thermodynamics of Materials*, 4th ed., Taylor & Francis, New York (2003). Excellent for the purpose.
- H.-G. Lee. *Chemical Thermodynamics for Metals and Materials*, ICP Imperial College Press, London (1999); with CD-ROM.
- E. S. Machlin. *An Introduction to Aspects of Thermodynamics and Kinetics Relevant to Materials Science*, revised and updated ed., Giro Press, Croton-on-Hudson, NY (1999).
- D. V. Ragone. *Thermodynamics of Materials*, Vols. I and II, Wiley-MIT Series in Materials Science and Engineering, New York (1995). See Vol. II, Chap. 8 for nonequilibrium thermodynamics.
- N. A. Gokcen, R. G. Reddy. *Thermodynamics*, 2nd ed., Plenum Press, New York (1996); with floppy disk for chemical equilibrium calculations.
- R. T. De Hoff. *Thermodynamics in Materials Science*, McGraw-Hill, New York (1993).
- C. H. P. Lupis. *Chemical Thermodynamics of Materials*, North-Holland, Amsterdam, (1983); a more advanced text.
- C. G. Bergeron, S. H. Risbud. *Introduction to Phase Equilibria in Ceramics*, American Ceramic Society, Columbus, OH (1984).
- K. E. Spear. "High-temperature reactivity", in *Treatise on Solid State Chemistry*, Vol. 4, *Reactivity of Solids*, N. B. Hannay (Ed.), Plenum Press, New York (1976).
- A. Prince. *Alloy Phase Equilibria*, Elsevier, Amsterdam (1966).

Consider also the classical textbook widely used by chemistry students and researchers.

- K. S. Pitzer, L. Brewer (revision of Lewis and Randall). *Thermodynamics*, 2nd ed., McGraw-Hill International Student Edition, New York (1961). Chaps. 32 and 33 are particularly relevant to high-temperature chemistry.

Papers

- E. Gamsjäger. "A concise derivation of the contact conditions at a migrating sharp interface", *Philos. Mag. Lett.* **88**, 363 (2008).
- J. Svoboda, J. Vala, E. Gamsjäger, F. D. Fischer. "A thick-interface model for diffusive and massive phase transformations in substitutional alloys", *Acta Mater.* **54**, 3953 (2006).
- J. Svoboda. "Utilization of the thermodynamic extremal principle for modelling in materials science", in *Moving Interfaces in Crystalline Solids, CISM Courses and Lectures No. 453*, F. D. Fischer (Ed.), p. 117, Springer, Vienna (2004).

Web and electronic sources

- X. Lu, Z. P. Jin. PHDT: Phase Diagram Tutor. An animated phase diagram tutor. Free download from: <<http://www.mse.kth.se/utbildning/4H1302/phdt.htm>>, *J. Phase Equilib.* **18**, 426 (1997). A simple tutorial software for phase diagram and solution models.

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 thermo-physical 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 transpiration 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

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- J.-C. Zhao (Ed.). *Methods for Phase Diagram Determination*, Elsevier Science, Amsterdam (2007).
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- “Temperature measurement”, in *Kirk-Othmer Encyclopedia of Chemical Technology*, Vol. 23, p. 809, John Wiley, New York (1997).
- R. M. Perkin. “Electrically generated heat”, in *Ullmann’s Encyclopedia of Chemical Technology*, 5th revised ed., Vol. B3, Chap. 15; R. M. Perkin. “Radiation heating”, *ibid.*, Chap. 16, VCH, Weinheim (1988).

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- J. Drowart, C. Chatillon, J. Hastie, D. Bonnell. "High-temperature-mass spectrometry: Instrumental techniques: ionization cross-sections, pressure measurements and thermodynamic data", *Pure Appl. Chem.* **77**, 683 (2005).
- J. W. Hastie, D. W. Bonnell, P. K. Schenck. "Development and application of very high temperature mass spectrometry: Vapor pressure determinations over liquid refractories", *Pure Appl. Chem.* **72**, 2111 (2000).
- F. Righini, G. C. Bussolino, J. Spisiak. "Pulse calorimetry at high temperatures", *Thermochim. Acta* **247**, 93 (2000).
- A. Navrotsky. "Progress and new directions in high temperature calorimetry", *Phys. Chem. Miner.* **24**, 222 (1997).
- C. Colinet. "High temperature calorimetry: Recent developments", *J. Alloys Compounds* **220**, 76 (1995).

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:

- J. K. R. Weber, J. A. Tangeman, T. S. Key, P. Nordine. "Investigation of liquid-liquid phase transitions in molten aluminates under containerless conditions", *J. Thermophys. Heat Transf.* **17**, 182 (2003).
- P. C. Nordine, J. K. R. Weber, J. G. Abadie. "Properties of high temperature melts using levitation", *Pure Appl. Chem.* **72**, 2127 (2000).

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:

- J. K. R. Weber. "Behavior of molten oxides under containerless conditions", *Eur. J. Solid State Inorg. Chem.* **34** 847 (1997).
- T. Baykara, R. H. Hauge, N. Norem, P. Lee, J. L. Margrave. "A review of containerless thermophysical property measurements for liquid metals and alloys", *High Temp. Sci.* **32**, 113 (1991).

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

IVTANTHERMO for WINDOWS—Thermodynamic database and thermodynamic modeling Software. Version 3.0. Glushko Thermocenter of Russian Academy of Sciences. <http://www.ihed.ras.ru/thermo/ivt_weng.htm>.

R. Hultgren, P. D. Desai, D. T. Hawkins, M. Gleiser, K. K. Kelley, D. D. Wagman. *Selected Values of the Thermodynamic Properties of the Elements*, American Society for Metals, Metals Park, OH (1973).

SGTE databases. Scientific Group Thermodata Europe. <<http://www.sgte.org/>>.

NIST databases. National Institute of Standards and Technology: <<http://www.nist.gov/srd/thermo.htm>>, and in particular <<http://webbook.nist.gov>>. Among NIST compilations covering thermodynamic data for inorganic substances, see the last edition of JANAF tables: NIST-JANAF Thermochemical Tables, 4th ed., M. W. Chase Jr. (Ed.), *J. Phys. Chem. Ref. Data Monograph 9* (1998).

HSC Chemistry (Outokumpu): <http://www.outotec.com/pages/Page____21783.aspx>.

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.crct.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

H. L. Lukas, S. G. Fries, B. Sundman. *Computational Thermodynamics: Assessing Thermodynamic Data and Creating Multicomponent Databases using the CALPHAD Method*, Cambridge University Press, Cambridge, UK (2007).

T. G. Grimvall. *Thermophysical Properties of Materials*, North-Holland-Elsevier Science B.V., Amsterdam (1999).

F. R. de Boer, R. Boom, W. C. M. Mattens, A. R. Miedema, A. K. Nissen. *Cohesion in Metals: Transition Metal Alloys*, Vol. 1, North-Holland, Amsterdam (1988).

Papers

J. Hafner, C. Wolverton, G. Ceder (guest Eds.). "Towards computational materials design: the impact of density functional theory on materials research", *Mater. Res. Soc. Bull.* **31**, 659 (2006).

L. Glasser, H. D. B. Jenkins. "Predictive thermodynamics for condensed phases", *Chem. Soc. Rev.* **34**, 866 (2005).

N. Jacobson. "Use of tabulated thermochemical data for pure compounds", *J. Chem. Educ.* **78**, 814 (2001) and refs. cited therein.

C. M. Wai, S. G. Hutchison. "Free energy minimization calculation of complex chemical equilibria", *J. Chem. Educ.* **66**, 546 (1989).

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 SiO_2 , Si_3N_4 , 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

- D. R. Gaskell. *Introduction to the Thermodynamics of Materials*, 4th ed., Taylor & Francis, New York (2003).
- P. Haasen (Ed.). "Materials Science and Technology. A Comprehensive Treatment", Vol. 5, *Phase Transformations in Materials*, R. W. Cahn, P. Haasen, E. J. Kramer (Eds.), VCH, Weinheim (1990).
- N. Birks, G. H. Meier. *Introduction to High Temperature Oxidation of Metals*, Edward Arnold, London (1983); see Chap. 2 and refs. cited therein. Consult the new enlarged edition: N. Birks, F. S. Pettit, G. H. Meier. *Introduction to High Temperature Oxidation of Metals*, Chap. 2, Cambridge University Press, Cambridge, UK (2006).
- T. Reed. *Free Energy of Formation of Binary Compounds: An Atlas of Charts for High-Temperature Chemical Calculations*, MIT Press, Cambridge (1971); very useful booklet.
- E. A. Gulbransen, S. A. Jansson. In *Heterogeneous Kinetics at Elevated Temperatures*, G. R. Belton, W. F. Worrell (Eds.), Plenum Press, New York (1970).

Additional reading

- N. S. Jacobson. "Carbothermal reduction of silica in high temperature materials", in *Applications of Thermodynamics in the Synthesis and Processing of Materials*, P. Nash, B. Sundman (Eds.), pp. 19–27, The Minerals, Metals & Materials Society, Warrendale, PA (1995).

Papers

- A. H. Heuer, V. L. K. Lou. "Volatility diagrams for silica and silicon carbide and their application to high-temperature decomposition and oxidation", *J. Am. Ceram. Soc.* **73**, 2785 (1990).
- V. L. K. Lou, A. H. Heuer. "Graphical displays of the thermodynamics of high-temperature gas-solid reactions and their application to oxidation of metals and evaporation of oxides", *J. Am. Ceram. Soc.* **68**, 49 (1985); a review.

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, MT-DATA, 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

- H. L. Lukas, S. G. Fries, B. Sundman. *Computational Thermodynamics—Assessing Thermodynamic Data and Creating Multi-component Databases using the CALPHAD Method*, Cambridge University Press, Cambridge, UK (2007); see Chap. 9 for selected case studies.
- N. Saunders, A. P. Miodownik. *CALPHAD—Calculation of Phase Diagrams. A Comprehensive Guide*, Pergamon Materials Series, Pergamon/Elsevier Science, Oxford (1998).
- L. Kaufmann, H. Bernstein. *Computer Calculation of Phase Diagrams*, Academic Press, New York (1970).

Papers and websites

- G. V. Belov, A. L. Emelina, W. I. Goriacheva, I. A. Uspenskaya, G. F. Voronin. “PhDi-Software package for calculation of binary phase diagrams”, *J. Alloys Compd.* **452**, 133 (2008).
- R. H. Davies, A. T. Dinsdale, G. A. Gisby, J. A. J. Robinson, S. M. Martin. “MTDATA-Thermodynamic and Phase Equilibrium Software from the National Physical Laboratory”, *CALPHAD* **26**, 229 (2002).
- U. Kattner. “Thermodynamic modeling of multi-component phase equilibria”, *JOM* **49**, 20 (1999).
- THERMOCALC software: <<http://www.Thermocalc.se/index.html>>.
- 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 Equilib.* **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 sophisticated approaches toward process simulation, taking into account transport phenomena, flow properties, non-isothermal conditions, etc., can be outlined.

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

Useful bibliography

The SGTE Casebook—Thermodynamics at Work, 2nd ed., K. Hack (Ed.), Woodhead Publishing, Cambridge, UK (2008). The 2nd edition, substantially revised and enlarged, of this standard reference first published in 1996, explores both the theoretical background to thermodynamic modeling and its wide range of practical applications.

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

- V. Stolyarova, G. Semenov. *Mass Spectrometric Study of the Evaporation of Oxide Systems*, John Wiley, New York (1994).
- O. Kubaschewski, C. B. Alcock, P. J. Spencer. *Materials Thermochemistry*, 6th ed. revised of *Metallurgical Thermochemistry*, Pergamon Press, Oxford (1993).
- G. M. Rosenblatt. “Evaporation from solids”, in *Treatise on Solid State Chemistry*, Vol. 6A, N. B. Hannay (Ed.), Chap. 3, Plenum Press, New York (1976).

- R. Rapp (Ed.). *Physicochemical Measurements in Metals Research*, Vol. IV, Part 1 of *Techniques of Metal Research*, Chaps. 1–5, Wiley-Interscience, New York (1970).
- A. W. Searcy. “The kinetics of evaporation and condensation reactions”, in *Chemical and Mechanical Behavior of Inorganic Materials*, A. W. Searcy, D. V. Ragone, U. Colombo (Eds.), Chap. 6, Wiley-Interscience, New York (1970).
- J. L. Margrave (Ed.). *The Characterization of High Temperature Vapors*, Chaps. 2–8, John Wiley, New York (1967).
- P. J. Ackermann, R. J. Thorn, G. H. Winslow. “Some fundamental aspects of vaporization”, in *The Characterization of High Temperature Vapors*, J. L. Margrave (Ed.), Chap. 14, John Wiley, New York (1967); J. P. Hirth. “Kinetic aspects of evaporation and sublimation processes”, *ibid.*, Chap. 15.

Conference proceedings volumes

- J. W. Hastie (Ed.). *Characterization of High Temperature Vapors and Gases*, Proc. 10th Materials Research Symposium held at NBS, Gaithersburg, Maryland, September 1978, *NBS Spec. Publ.* **561**, Vols. 1–2, U.S. Government Printing Office, Washington, DC (1979); see Vol. 1, Chaps. I–III.

Papers

- J. Drowart, C. Chatillon, J. Hastie, D. Bonnell. “High-temperature-mass-spectrometry instrumental techniques: ionization cross-sections, pressure measurements and thermodynamic data”, *Pure Appl. Chem.* **77**, 683 (2005) and refs. cited therein.
- J. W. Hastie, D. W. Bonnell, P. K. Schenck. “Development and application of very high temperature mass spectrometry: Vapor pressure determinations over liquid refractories”, *Pure Appl. Chem.* **72**, 2111 (2000).
- G. M. Rosenblatt. “Vaporization rates, surface topography, and vaporization mechanisms of single crystals: A case study”, *Acc. Chem. Res.* **9**, 169 (1976).
- W. A. Chupka, M. G. Inghram. “The heat of vaporization of carbon”, *J. Chem. Phys.* **21**, 371 (1953).
- J. Drowart, G. De Maria, R. P. Burns. “Thermodynamic study of Al₂O₃ using a mass spectrometer”, *J. Chem. Phys.* **32**, 1366 (1960).
- G. De Maria, J. Drowart, M. G. Inghram. “Mass spectrometric study of Al₂O₃”, *J. Chem. Phys.* **30**, 318 (1959).

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

- C. H. Bamford, C. F. Tipper. *Comprehensive Chemical Kinetics*, Vol. 22, *Reactions in the Solid State*, Elsevier Scientific, Amsterdam (1980).
- F. C. Tompkins. “Decomposition reactions”, in *Treatise on Solid State Chemistry*, Vol. 4, N. B. Hannay (Ed.), Chap. 4, Plenum Press, New York (1976).
- A. D. Young. *Decomposition of Solids*, Pergamon Press, Oxford (1966); in particular, Chaps. 2, 3.

Papers

- D. T. Beruto, A. W. Searcy, M. G. Kim. “Microstructure, kinetic, structure, thermodynamic analysis for calcite decomposition: Free-surface and powder bed experiments”, *Thermochim. Acta* **424**, 99 (2004) and refs. cited therein.
- B. V. L'vov. “Application of the third-law methodology to the investigation of decomposition kinetics”, *Thermochim. Acta* **424**, 183 (2004). A review and refs, cited therein.
- D. L. Hildenbrand, K. H. Lau, R. D. Brittain. “Mechanistic aspects of metal sulfate decomposition processes”, *High Temp. Sci.* **26**, 427 (1988–1989).
- B.V. L'vov. “The physical approach to the interpretation of the kinetics and mechanism of thermal decomposition of solids: state of the art”, *Thermochim. Acta* **272**, 97 (2001).
- A. de La Croix, R. English, M. E. Brown, L. Glasser. “Modeling the thermal decomposition of solids on the basis of lattice energy changes. Part 1: Alkaline-Earth Carbonates,” *J. Solid State Chem.* **137**, 332 (1998); “Part 2: Alkaline-Earth Peroxides”, *J. Solid State Chem.* **137**, 346 (1998).
- D. Beruto, J. Ewing, A. W. Searcy. “The nature of the CaO produced by calcite decomposition in vacuum and in CO₂”, *J. Am. Ceram. Soc.* **62**, 580 (1979).
- D. Beruto, L. Barco, A. W. Searcy. “CO₂-catalyzed surface area and porosity changes in high surface area CaO aggregates”, *J. Am. Ceram. Soc.* **67**, 512 (1984).
- A. Searcy, D. Beruto. “Kinetics of endothermic decomposition reactions. I. Steady-state chemical steps. II. Effects of solid and gaseous products”, *J. Phys. Chem.* **80**, 425 (1976) 425; **82**, 163 (1978).

D. Beruto, A. W. Searcy. "Use of the Langmuir method for the kinetic studies of decomposition reactions: Calcite", *J. Chem. Soc., Faraday Trans.* **70**, 2145 (1974).

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

- W. Gao (Ed.). *Developments in High Temperature Corrosion and Protection of Materials*, Woodhead Publishing, Cambridge, UK (2008).
- D. Young. *High Temperature Oxidation and Corrosion of Metals*, Elsevier, Amsterdam (2008).
- N. Birks, F. S. Pettit, G. H. Meier. *Introduction to High Temperature Oxidation of Metals*, Cambridge University Press, Cambridge (2006).
- A. S. Khanna. *Introduction to High Temperature Oxidation and Corrosion*, ASM International, Materials Park, OH (2002).
- C. B. Alcock. *Thermochemical Processes: Principles and Models*, Chap. 8, Elsevier Science & Technology Books (Publisher: Butterworth-Heinemann), Oxford (2001).
- V. P. Kofstad. *High Temperature Corrosion*, Elsevier Applied Science, London (1988).

Papers

- V. L. K. Lou, A. H. Heuer. "Graphical displays of the thermodynamics of high-temperature gas-solid reactions and their application to oxidation of metals and evaporation of oxides", *J. Am. Ceram. Soc.* **68**, 49 (1985); a review.
- A. H. Heuer, V. L. K Lou. "Volatility diagrams for silica and silicon carbide and their application to high-temperature decomposition and oxidation", *J. Am. Ceram. Soc.* **73**, 2785 (1990).
- E. J. Opila, N. S. Jacobson, D. L. Myers, E. H. Copland. "Predicting oxide stability in high-temperature water vapour", *JOM* **58**, 22 (2006).

N. S. Jacobson, D. L. Myers, E. J. Opila, E. H. Copland. "Interaction of water vapor with oxides at elevated temperatures", Proc. HTMC XI Conf. *J. Phys. Chem. Solids* **66**, 471 (2005).

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 thermo-mechanical 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

K. G. Chiranjib. *Chemical Metallurgy*, Chap. 4, Wiley-VCH, Weinheim (2003).

Y. Waseda, M. Isshiki (Eds.). *Purification Process and Characterization of Ultra High Purity Metals. Application of Basic Science to Metallurgical Processing*, Springer B.V., Berlin (2002).

C. B. Alcock. *Thermochemical Processes: Principles and Models*, Elsevier Science & Technology Books (Publisher: Butterworth-Heinemann), Oxford (2001).

- T. Rosenqvist. *Principles of Extraction Metallurgy*, 2nd ed., McGraw-Hill/Tapir Forlag (2004).
C. B. Alcock. *Principles of Pyrometallurgy*, Academic Press, London (1975); see in particular Chap. 3.
F. Habashi. *Principles of Extractive Metallurgy*, Vol. 3: *Pyrometallurgy*, Gordon & Breach Science, Amsterdam (1986).

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, monocrystalline, 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:

A. R. West. *Basic Solid State Chemistry*, 2nd ed., Chap. 9, John Wiley, New York (1999).

Consult also:

J. I. Gersten, F. W. Smith. *The Physics and Chemistry of Materials*, Chap. 21, Wiley-Interscience, New York (2001); synthesis and processing of materials and relevant associated material in electronic form as Chap. W21 downloadable from <ftp://wiley.com/public/sci_tech_med/materials>.

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

- C. B. Alcock. *Thermochemical Processes: Principles and Models*, Chaps. 1, 3, Elsevier Science & Technology Books (Publisher: Butterworth-Heinemann), Oxford (2001).
H. O. Pierson. *Handbook of Chemical Vapor Deposition (CVD)—Principles, Technology, and Applications*, 2nd ed., Noyes Publications, New York (1999); for fundamentals, see Chaps. 1–3.

- H. O. Pierson. *Handbook of Carbon, Graphite, Diamond*, Chap. 13, Noyes Publications, Ridge Park, NJ (1993).
- J. Hastie. *High Temperature Vapors. Science and Technology*, Academic Press, New York (1975).
- M. Faktor, I. Garrett. *Growth of Crystals from the Vapour*, Chapman and Hall, London (1974).
- H. Schaefer. *Chemical Transport Reactions*, Academic Press, New York (1964).

Papers

- G. Whal, O. Stadel, O. Gorbenko, A. Kaul. "High-temperature chemical vapour deposition. An effective tool for production of coatings", *Pure Appl. Chem.* **72**, 2167 (2000).
- K. E. Spear, R. R. Dirks. "Role of high temperature chemistry in CVD processing", *High Temp. Sci.* **27**, 107 (1990).
- K. E. Spear. "Diamond-ceramic coating for the future", *J. Am. Ceram. Soc.* **72**, 171 (1989).
- W. A. Bryant. "The fundamentals of chemical vapor deposition", *J. Mater. Sci.* **12**, 1285 (1977).
- A useful reference for students is the introductory paper by K. E. Spear. "Chemical Transport Reactions", *J. Chem. Educ.* **49**, 81 (1972).

Consult also:

- G. Whal et al. "Thin films", in *Ullmann's Encyclopedia of Chemical Technology* **A26**, 681 VCH, Weinheim (1995).

Other papers dealing with this topic can be found in *High Temperature Science*, Vol. 27, Humana Press, Clifton, NJ (1990).

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

- A. A. Borisov, L. De Luca, A. G. Merzhanov (Eds.). *Self-propagating High Temperature Synthesis*, Taylor & Francis, New York (2002); a collection of papers on the subject.
- C. N. R. Rao (Ed.). *Chemistry of Advanced Materials*, IUPAC/Blackwell Scientific Publications, Oxford (1993).
- Z. A. Munir, J. B. Holt (Eds.). *Combustion and Plasma Synthesis of High-Temperature Materials*, VCH, New York (1990). A contributed volume dealing with preparation and processing of high-temperature materials. Among papers collected, see in particular 1 and 35.
- H. V. Boenig. *Fundamentals of Plasma Chemistry and Technology*, Technomic Publishing, Lancaster (1988); see Chaps. VI, XVI, XVI.

Conference proceedings volumes

- C.-C. Ge, A. S. Rogachev (Eds.). *Progress in Self-Propagating High-Temperature Synthesis. Key Eng. Mater.* **217** (2002).

Papers

- A. G. Merzhanov. "The chemistry of self-propagating high-temperature synthesis", *J. Mater. Chem.* **14**, 1779 (2004). A review of the chemistry of the SHS method with examples of production of refractory materials.
- A. G. Merzhanov. "Combustion and explosion processes in physical chemistry and technology of inorganic materials", *Russ. Chem. Rev.* **72**, 289 (2003).
- J. J. Moore, H. J. Feng. "Combustion synthesis of advanced materials; Part I. Reaction parameters", *Prog. Mater. Sci.* **39**, 243 (1995). "Part II. Classification, applications and modelling", **39**, 275 (1995).
- V. Hlavacek. "Combustion synthesis: A historical perspective", *Ceram. Bull.* **70**, 240 (1991).
- Z. A. Munir, U. A. Tamburini. "Self-propagating exothermic reactions: The synthesis of high-temperature materials by combustion", *Mater. Sci. Rep.* **3**, 267 (1989).

Consult also:

- R. G. Reddy, L. V. M. Antony. "The thermal plasma processing of fine powders", *JOM* **55**, 19 (2003).

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

- P. Roca i Cabarocas, A. Fontcuberta i Morral, S. Lebib, Y. Poissant. "Plasma production of nanocrystalline silicon particles and polymorphous silicon thin films for large-area electronic devices", *Pure Appl. Chem.* **74**, 359 (2002).

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

- P. Fauchais, M. Vardelle, J. F. Coudert, A. Vardelle, C. Delbos, J. Fazilleau. "Thermal plasma deposition from thick to thin coatings and from micro- to nanostructures", *Pure Appl. Chem.* **77**, 475 (2005).

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

- T. Yoshida. "Toward a new era of plasma spray processing", *Pure Appl. Chem.* **78**, 1093 (2006).

Consult also:

- H. Brachhold, R. Mueller, G. Pross. "Plasma reactions", in *Ullmann's Encyclopedia of Industrial Chemistry*, **A20**, VCH, Weinheim (1992).

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

- M. H. Van de Voorde, G. W. Meetham. *Materials for High Temperature Engineering Applications (Engineering Materials)*, Springer Verlag, Berlin (2000).
- T. Ya. Kosolapova (Ed.). *Handbook of High Temperature Compounds: Properties, Production, Applications*, Taylor & Francis/Hemisphere Publishing, New York (1990).
- M. G. Hocking, V. Vasantasree, P. S. Sidky. *Metallic & Ceramic Coatings: Production, High Temperature Properties & Applications*, Longman Scientific & Technical, Harlow/John Wiley, New York (1989).
- E. Bullock (Ed.). *Research and Development of High Temperature Materials for Industry*, Elsevier Science, New York (1989).
- I. E. Campbell, E. M. Sherwood (Eds.). *High Temperature Materials and Technology*, Electrochemical Society (Wiley), New York (1967).

For phase diagrams, see the following and other literature sources in Supplementary Material: Phase Equilibria Diagrams—*Phase Diagrams for Ceramists*, Vols. I (1964) to XIII, The American Ceramic Society, Columbus/Westerville, OH (2001); see, in particular, Vol. X for borides, carbides, nitrides.

- T. Massalski, H. Okamoto, P. R. Subramanian, L. Kacprzak (Eds.). *Binary Alloy Phase Diagrams*, 2nd ed., ASM International, Materials Park, OH (1990).

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: W. G. Fahrenholtz, G. E. Hilmas (Eds.). HTM Workshop Report, NSF Division of Materials and AFOSR Ceramic and Non-metallic Materials, July 2004, Arlington, VA; see literature cited therein. Summary: *Refractory Applications and News* **10** (1) (2005).

For a brief summary of problems and applications of high-temperature materials, see:
K. E. Spear, S. Visco, E. J. Wuchina, E. D. Wachsman. "High temperature materials", *Electrochem. Soc. Interface* **15**, 48 (2006).

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

J. Hastie. *High Temperature Vapors. Science and Technology*, Chap. 3, Academic Press, New York (1975).

Papers

T. Markus, U. Niemann, K. Hilpert. "High temperature gas phase chemistry for the development of advanced ceramic discharge lamps", *J. Phys. Chem. Solids* **66**, 372 (2005).

W. van Erk. "Transport properties in metal halide gas discharge lamps", *Pure Appl. Chem.* **72**, 2159 (2000) and refs. cited therein.

K. Hilpert, U. Niemann. "High temperature chemistry in metal halide lamps", *Thermochim. Acta* **299**, 49 (1997).

See also:

D. L. Hildenbrand, D. Cubicciotti (Eds.). "High temperature metal halide chemistry", Proc. 78-1, The Electrochemical Society, Pennington, NJ (1978).

Z. Toth. "Chemistry of material science phenomena in high intensity discharge light sources", *Pure Appl. Chem.* **79**, 1771 (2007).

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

- S. Singhal, K. Kendall. *High Temperature Solid Oxide Fuel Cells: Fundamentals, Design and Applications*, Elsevier, Amsterdam (2003).
- P. G. Bruce (Ed.). *Solid State Electrochemistry*, Cambridge University Press, Cambridge, UK (1997).
- H. Rickert. *Electrochemistry of Solids. An Introduction*, Springer Verlag, Berlin (1982); in particular, Chap. 8 deals with galvanic cells with solid electrolytes for thermodynamic investigations.
- H. Rickert. "Solid state electrochemistry", in *Treatise on Solid State Chemistry*, Vol. 4, N. B. Hannay (Ed.), Chap. 6, Plenum Press, New York (1976).
- R. Rapp (Ed.). *Physicochemical Measurements in Metals Research*, Vol. IV, Part 2 of *Techniques of Metal Research*, Wiley-Interscience, New York (1970).

Papers

- J. W. Fergus. "Materials challenges for solid-oxide fuel cells", *JOM* **59**, 56 (2007).
- T. Kawada, H. Yokokawa. "Materials and characterization of solid oxide fuel cells", *Key Eng. Mater.* **125–126**, 187 (1997).

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

- K. E. Spear. "High temperature materials", in *What is Electrochemistry? Electrochemistry and Solid State Science*, 4th ed., p. 24, The Electrochemical Society, Pennington, NJ (1997); also refs. cited therein.
- K. E. Spear, S. Visco, E. J. Wuchina, E. D. Wachsman. "High temperature materials", *Electrochem. Soc. Interface* **15**, 48 (2006).

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

- C. B. Alcock. *Thermochemical Processes: Principles and Models*, Elsevier Science & Technology Books (Publisher: Butterworth-Heinemann), Oxford (2001); Chaps. 5 to 7 are particularly useful.
- M. Glicksman. *Diffusion in Solids*, John Wiley, New York (2000).
- C. B. Alcock. *Principles of Pyrometallurgy*, Chap. 5, Academic Press, London (1976).
- W. D. Kingery, H. K. Bowman, D. R. Uhlmann. *Introduction to Ceramics*, Chap. 10, John Wiley, New York (1976).

For sintering:

- S.-J. L. Kang. *Sintering: Densification, Grain Growth and Microstructure*, Butterworth-Heinemann (2005).
- G. Weidmann, P. Lewis, N. Reid (Eds.). *Structural Materials, Materials in Action Series*, The Open University, Butterworths, London (1990).

Consult also:

- A. W. Searcy, D. Beruto. “Theory and experiments for isothermal and nonisothermal sintering” *Sci. Ceram.* **14**, 1 (1988).
- W. A. Kaysser, W. Weise. “Powder metallurgy and sintered materials”, in *Ullmann’s Encyclopedia of Industrial Chemistry*, 5th ed., Vol. A22, p. 105, VCH, Weinheim, FRG (1993).
- J. S. Moya, C. Baudin, P. Miranzo. “Sintering”, in *Encyclopedia of Physical Science and Technology*, **12**, 700, Academic Press (1987).

For solid-state diffusion, see also:

- R. J. Borg, G. J. Dienes. *The Physical Chemistry of Solids*, Academic Press, New York (1992).

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

- A. R. West. *Basic Solid State Chemistry*, 2nd ed., John Wiley, New York (1999).

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

- J. Warnatz, U. Maas, R. W. Dibble. *Combustion: Physical and Chemical Fundamentals, Modeling and Simulation, Experiments, Pollutant Formation*, 3rd ed., Springer Verlag, Berlin (2001).
- S. R. Turns. *An Introduction to Combustion: Concepts and Applications with Software*, 2nd ed., McGraw-Hill Science, New York (2000).
- I. Glassman. *Combustion*, 3rd ed., Academic Press, New York (1996).
- G. Chaudron, F. Trombe (Eds.). *Les Hautes Températures et Leurs Utilization en Physique et en Chimie*, Vol. I, Masson, Paris (1973).
- J. Hastie. *High Temperature Vapors. Science and Technology*, Chap. 5, Academic Press, New York (1975); also literature cited therein for sources prior to 1975.

Further reading

- R. Sharifi, S. V. Pisupati, A. W. Scaroni. "Combustion science and technology" in *Kirk-Othmer Encyclopedia of Chemical Technology*, 4th ed., Vol. 6, p. 1049, Wiley-Interscience, New York (1993).

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

- H. Fukuyama, Y. Waseda (Eds.). *High-Temperature Measurements of Materials*, Springer, Berlin (2009).
- C. B. Alcock. *Thermochemical Processes: Principles and Models*, Part 3, Elsevier Science & Technology Books (Publisher: Butterworth-Heinemann), Oxford (2001).
- F. D. Richardson. *Physical Chemistry of Melts in Metallurgy*, Academic Press, London (1974).

- P. C. Nordine, J. K. R. Weber, J. G. Abadie. "Properties of high temperature melts using levitation", *Pure Appl. Chem.* **72**, 2127 (2000).
- T. Baykara, R. H. Hauge, N. Norem, P. Lee, J. L. Margrave. "A review of containerless thermophysical property measurements for liquid metals and alloys", *High Temp. Sci.* **32**, 113 (1991).
- A. W. Searcy, D. V. Ragone, U. Colombo (Eds.). *Chemical and Mechanical Behavior of Inorganic Materials*, Wiley-Interscience, New York (1970).

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

- M. M. Schwartz. *Brazing*, 2nd ed., ASM International (2003).
- N. Eustathopoulos, M. G. Nicholas, B. Drevet. *Wettability at High Temperatures*, Pergamon Press, Oxford (1999). Comprehensive and almost unique in treating high-temperature wetting phenomena.
- M. G. Nicholas. *Joining Processes: An Introduction to Brazing and Diffusion Bonding*, Kluwer Academic, Dordrecht (1998).

Papers

- Y. V. Naidich. "The wettability of solids by liquid metals", *Prog. Surf. Membr. Sci.* **14**, 354 (1981).

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

- N. Eustathopoulos, E. Louis, A. Mortensen (Eds.). "Proceedings of high temperature capillarity conference 2007", *Mater. Sci. Eng. A* **495** (1–2) (2008).
- N. Sobczak, A. Kudyba, R. Nowak, W. Radziwill, K. Pietrzak. "Factors affecting wettability and bond strength of solder joint couples", *Pure Appl. Chem.* **79**, 1755 (2007).
- A. Passerone, N. Eustathopoulos (Eds.). "Proceedings of high temperature capillarity conference 2004", *J. Mater. Sci.* **9–10**, 2119 (2005).
- R. Asthana, N. Sobczak. "Wettability, spreading and interfacial phenomena in high-temperature phenomena", *JOM-e* **52** (1) (2000).

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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

- H. Fukuyama, Y. Waseda (Eds.). *High-Temperature Measurements of Materials*, Springer, Berlin (2009).
- H. L. Lukas, S. G. Fries, B. Sundman. *Computational Thermodynamics: Assessing Thermodynamic Data and Creating Multicomponent Databases using the CALPHAD Method*, Cambridge University Press, Cambridge (2007). See Chap. 9 for case studies.
- M. Hillert. *Phase Equilibria, Phase Diagrams, and Phase Transformations: Their Thermodynamic Basis*, 2nd ed., Cambridge University Press, Cambridge (2008).
- K. Hack (Ed.). *The SGTE Casebook Thermodynamics at Work*, 2nd ed., Woodhead Publishing, Cambridge, UK (2008). Illustrates how thermodynamic calculations can be used as a basic tool in the development and optimization of materials and processes of many types.
- B. D. Fahlman. *Materials Chemistry*, Springer, Dordrecht (2007).
- S. Bose. *High Temperature Coatings*, Butterworths-Heinemann, Oxford (2007).
- N. Birks, F. S. Pettit, G. H. Meier. *Introduction to High Temperature Oxidation of Metals*, Cambridge University Press, Cambridge (2006). Introduction to high-temperature oxidation of metals and alloys for students and professional engineers whose works demand familiarity with the subject. The emphasis is on understanding the fundamental processes involved in oxidation. Examples of the application of principles described are given.
- D. R. Gaskell. *Introduction to the Thermodynamics of Materials*, 4th ed., Taylor & Francis Kumar, New York (2003). Introductory text for students of materials science and engineering with underlying principles, their applicability, and worked examples. In particular, Chaps. 9–13 are relevant to the high-temperature thermodynamics of materials.
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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.

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

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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*.