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Teaching high temperature materials chemistry at university

Final report

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Project Overview

The growth of high-temperature materials chemistry (HTMC) into an increasingly important field of scientific and technological research is due to the continuous demand for new materials and the need for systematic knowledge of their physical and chemical behaviour under the conditions required by the new technologies (e.g., space and energy technologies). These materials (e.g., oxide and non-oxide modern multifunctional ceramics, intermetallics), which offer interesting technical applications for such fields as surface coatings, electronic components, and advanced turbines, are prepared through high-temperature processing (e.g., transport reactions, CVD, combustion synthesis, laser ablation and deposition) and must be stable under extreme thermal and chemical conditions.

HTMC now encompasses many fields of science and technology. Its advancement has involved a synergic interchange between basic and applied research, with the application of thermodynamics, kinetics, and a variety of physical, chemical, and modelling techniques to investigate processes and behaviour of materials at temperatures as high as 3000 K to 5000 K.

More than 50 years of studies have demonstrated that the general behaviour of materials and reactions at high temperatures often differs dramatically from those that we are educated to expect near room temperature. HTMC topics are rarely addressed in chemistry and materials science programs at university. Therefore, it is important to introduce to students of chemistry and materials science the concepts underlying the behaviour of materials and chemical bonding at high temperatures.

This project provides a resource book of topics in the area of properties and behaviour of high-temperature materials for those teaching materials science or physical or inorganic chemistry at various levels. Each recommended topic is followed by: a statement of the aims in teaching that particular topic; a brief description of the topic, including the areas of application, together with some specific teaching suggestions; a bibliography of relevant references. A more extensive bibliography is given in the Appendix together with some comments on specific features of many of the publications listed.

List of topics

1. Introductory remarks

Unlike the feeling that the uninitiated could have, and in spite of the common belief prevailing in the chemistry community until some decades ago, the behaviour and properties of inorganic systems at high and very high temperature may differ significantly from the chemical behaviour 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 behaviour of materials cannot be easily predicted by simply extrapolating the information known under ordinary temperature conditions. Indeed, a number of phenomena and factors commonly considered marginal or negligible in the "usual" room temperature chemistry (vapourization 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.) come on stage and their importance increases more and more with increasing temperature, playing a dominant role in many physicochemical processes. Thus, it was (and still is) commonly assumed by laypersons that gas phase systems always tend towards simplification on increasing temperature. However, different and even opposite behaviour is observed when the gas phase is in equilibrium over a condensed system since the formation of more complex species is often favoured under high temperature conditions. 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 is only obtained under 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 the university curricula for students in chemistry, industrial chemistry and materials science. The arrangement of the topics starts from the behaviour of materials at high temperatures that historically represents the emergence of the field of research known as high temperature materials chemistry; it then gradually widens parallel to 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 to many processes and applications, such as heat engines, combustion, nuclear power generation, high temperature fuel cells, chemical plant and processes, etc., as well as to many geological and cosmo-chemical processes. Notwithstanding the well-known difficulties in making 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 benefitted more recently from the parallel development of prediction models, simulation techniques and effective use of theoretical first-principles approaches as, for example, in the generation of new and more extensive thermodynamic databases.

The evolution in the field is clearly evidenced by the succession of various conferences and meetings on high temperature materials chemistry and technology held regularly in the last five decades (see Appendix: Symposium Proceedings). For example, the successful series of IUPAC conferences on High Temperature Materials Chemistry (HTMC) is now considered the premier international venue for presenting advances of basic and applied research in the field and for gathering together scientists from different areas of expertise (materials chemists, physico-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 researches reported at the above conferences.

Motivation for basic research in high temperature science, mainly carried out at university and other institutions, is strongly connected with the need to train young scientists such as chemists, physicists 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, the importance is recognized of providing students with the concepts and tools necessary to understand the behaviour 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 of 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.

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 of 6th to 9th semester) at the University of Rome La Sapienza.

The following list of topics is organized in eight sections. Section 2 to 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 vapour and solid phases, and their use in various materials problems. The last section 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 behaviour of inorganic materials.

Topic description and teaching suggestions: This historical introduction should draw the route from the pioneeristic studies on the high temperature behaviour 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 the condensed phase-gas phase processes carried out under high temperature-low pressure conditions and on the characterization of high temperature vapours 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 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

J.W. Hastie, *"High Temperature Vapors. Science and Technology"*, Academic Press, New York, 1975

J.L. Margrave, editor, *"The Characterization of High Temperature Vapors"* Wiley & Sons, New York/London/Sidney, 1967

L. Eyring, editor, "*Advances in High Temperature Chemistry"* Academic Press, New York, Volume 1, 1967

"Thermodynamics" by Kenneth Pitzer and Leo Brewer (revision of Lewis and Randall) second edition, McGraw-Hill International Student Edition, 1961. Chap. 33 is particularly relevant to high-temperature vaporization chemistry

Conference proceedings volumes:

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, editor "*Characterization of high temperature vapors and gases*", Proc. of the 10th Materials Research Symposium held at NBS, Gaithersburg, Maryland, September 1978, published as NBS Spec.Publ. 561 / Vol 1-2, U.S.G.P.O.,Washington, DC., 1979

Review papers, selected among others, of historical relevance:

R.J. Thorn, *Chemical Phenomena at High Temperature*, Ann. Rev. Phys. Chem., 1966, **17**, 83-118

V.A. Kireev, *Some aspects of high-temperature chemistry from the viewpoint of thermodynamics*, Russian Chem. Reviews, 1964, **33**, 330-342

J. Drowart and P. Goldfinger, *High Temperature Chemistry*, Ann. Rev. Phys. Chem., 1962, **13**, 459

A. Searcy, "*High temperature inorganic chemistry*", in *Progress in Inorganic Chemistry* (F.A.Cotton, editor) Vol. III, Interscience Publishers, 1962 pp. 49-127., and references cited therein

P. W. Gilles, *High Temperature Chemistry,* Ann. Rev. Phys. Chem., 1961, **12**, 355-79

J. L. Margrave, *High Temperature Chemistry*, Ann. Rev. Phys. Chem. 1959, **10**, 457-85

L. Brewer and A. W. Searcy, *High Temperature Chemistry*, Ann. Rev. Phys. Chem. 1956, **7**, 259-85

3. General chemical behaviour of condensed phase-gas phase systems at high temperature (Brewer's rules)

Aim: To describe the behaviour and properties of high temperature vapours on a thermodynamic basis.

Topic description and teaching suggestions: A vapour coexisting with a condensed phase at high temperature may be constituted of more than one species. The relative chemical stability of, say, two vapour species may change with temperature. Brewer rationalized the unexpectedly complex molecular character of high temperature vapours on the basis of simple thermodynamic arguments. The so-called Brewer's first rule essentially predicts that if a high temperature saturated vapour system contains several molecular species, then the lower concentration species will increase in relative importance as the temperature is increased. Typical cases are those where the monomer/dimer ratio in the vapour decreases on increasing temperature: the "double" role played by the vaporization enthalpy in determining the partial vapour pressures 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 analysed in more detail on the basis of translational and internal (roto-vibrational and electronic) contributions. Many examples illustrate this rule. Just to mention a few, the vaporization of carbon-graphite to C_n with n=1-7 species, the vaporization of BeO (s) to BeO_n (g) with n=1-6, 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. A 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 many moles of gas as are consumed in the reaction. Here again this behaviour 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. 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 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* N.B. Hannay, editor, "*Treatise on Solid State Chemistry*", Vol. 4, "*Reactivity of Solids*", Plenum Press, New York / London, 1976, chapter 3

J. Hastie, *"High Temperature Vapors. Science and Technology"* Academic Press, New York, 1975; Chapter 1, in particular for defining high temperature vapors.

A. W. Searcy, David V. Ragone, Umberto Colombo, editors, *"Chemical and Mechanical Behaviour of Inorganic Materials"* Wiley Interscience, New York/ London/ Sydney/ Toronto, 1970, chap.5

"Thermodynamics" by Kenneth Pitzer and Leo Brewer (revision of Lewis and Randall) second edition, McGraw-Hill International Student Edition, 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), Mc Graw-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 in Appendix. See *e.g.*

L.Brewer, *"Principles of high temperature chemistry",* in Proc. Of the Robert A. Welch Foundations Conferences in Chemical Research,VI Topics in Modern Inorganic Chemistry; Houston TX, 1962, pp.47 ff.

4. Basic concepts of materials thermodynamics

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

Topic description and teaching suggestions: One of the areas that is most important for high-temperature materials chemistry is thermodynamics. A sound knowledge of theoretical and experimental aspects of thermodynamics is imperative to understand the behaviour of materials under various environmental conditions and to develop processes for novel materials. Established principles from thermodynamics, general chemistry and phase equilibria (their basic knowledge should be a pre-requisite, including basic concepts of statistical thermodynamics usually given to students in introductory courses) provide practical tools for understanding high-temperature chemical behaviour of materials and processes. In the following, thermodynamic sub-topics 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 free 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

Describe in particular binary free-energy vs composition diagrams with selected examples of intermetallic and ceramic (in particular oxide) systems

4.5 Examples of phase diagrams for ternary systems

Useful bibliography

Books

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

D.R. Gaskell, "*Introduction to the thermodynamics of materials*", 4th edition, Taylor & Francis, New York, 2003: excellent for the purpose.

Hae-Geon, "*Chemical thermodynamics for metals and materials",* ICP Imperial College Press, London, 1999; with CD-ROM

M. Hillert, "*Phase equilibria, phase diagrams, and phase transformations: their thermodynamic basis*"; Cambridge University Press, 1998;

E.S. Machlin, "*An introduction to aspects of thermodynamics and kinetics relevant to materials science*", revised and updated edition, Giro Press, Croton-on-Hudson, N.Y., 1999

D.V. Ragone, "*Thermodynamics of materials*", Voll. I and II, Wiley MIT Series in Materials Science & Engineering, New York, 1995;

N.A Gokcen., R.G Reddy, *"Thermodynamics"* 2nd edition, Plenum Press, New York, 1996 pp 400, with floppy disk for chemical equilibrium calculations;

R.T. De Hoff, "*Thermodynamics in materials science*", McGraw-Hill, 1993, 281pp.

C.H.P Lupis, "*Chemical thermodynamics of materials*", North Holland New York/Amsterdam/Oxford, 1983, a more advanced text.

C.G. Bergeron, S.H. Risbud, *"Introduction to Phase Equilibria in Ceramics"*, The American Ceramic Society, Columbus, Ohio, 1984, pp. 158

K.E Spear *"High-temperature reactivity" in* N.B. Hannay, editor, "*Treatise on Solid State Chemistry"*, Vol. 4, "*Reactivity of Solids*" Plenum Press, New York / London, 1976.

A. Prince, "*Alloy phase equilibria*", Elsevier, Amsterdam, 1966

Consider also the classical textbook used by generations of chemistry students and researchers:

Thermodynamics by Kenneth Pitzer and Leo Brewer (revision of Lewis and Randall) second edition, McGraw-Hill International Student Edition, 1961. Chaps 32 and 33 are particularly relevant to high-temperature chemistry.

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 Equilibria* 1997, **18**, 426. (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 practical Temperature Scale (ITS-90) should be described also in their historical evolution. 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 (6000K+). 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 oxidising atmosphere). Containerless processing techniques provide non-contact conditions; therefore, they are particularly useful to study liquid or glassy-state samples avoiding interaction of the sample with environment. Give a description of various levitation techniques: electromagnetic levitation, aerodynamic levitation, acoustic levitation, microgravity levitation in space coupled with various modes of heating such as by induction, incandescent radiator, or laser irradiation. Remember that "*at high temperature anything reacts with anything else*"; therefore, these techniques are conveniently used for the measurement of thermophysical properties of advanced materials, metals, alloys and ceramics, at high/very high temperatures (up to 6000 K or so).

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, DSC adapted for high temperature conditions are employed to get thermodynamic information on various classes of inorganic materials (heats of formation, heats of solution, specific heats, etc.).

Equilibrium methods: vapour pressure methods, electromotive force methods and chemical equilibration methods. Second-law 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 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 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 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 vapours in the higher (> 1 atm) pressure regimes. The HT-MS technique under many aspects, significantly contributed and still contributes to the development of high temperature materials chemistry, particularly in the area concerning the characterization of high-temperature vapours and the acquisition of thermodynamic data.

5.3 Experimental techniques for phase diagram determination

Topic description and teaching suggestions: Various thermal analysis techniques: TG, DTA, DSC, complemented by XRD, SEM-EDS and optical microscopy, diffusion couples, Mössbauer, 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, ceramic, 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 refresh where necessary) a brief description of the techniques and illustrate a few selected examples.

Useful bibliography

Books

J.-C. Zhao (ed.), "*Methods for Phase Diagram Determination*", Elsevier Science, 2007.

N Saunders and A.P Miodownik, "*CALPHAD- Calculation of Phase Diagrams. A comprehensive guide*", Pergamon Materials Series, Pergamon/Elsevier Science, Oxford, 1998; see Chapter 4, for experimental determination of thermodynamic data and phase diagrams.

V. Stolyarova and G. Semenov, "*Mass spectrometric study of the evaporation of oxide systems",* Wiley 1994.

O. Kubaschewski, C.B. Alcock, P.J. Spencer, "*Materials Thermochemistry"*, 6th edition revised of *"Metallurgical Thermochemistry"*, Pergamon Press, Oxford/New York, 1993.

Quinn T.J., "*Temperature*" 2nd edition, Academic Press, London 1990.

Sime "*Physical chemistry-methods, techniques, experiments"*, Saunders College Publishing, 1990.

H. Rickert., " *Electrochemistry of solids. An introduction"*, Springer-Verlag, Berlin, 1982, useful chapter 8.

J.L. Margrave, "*High temperature techniques*", chap VI of *Techniques of chemistry Vol. IX-Chemical experimentation under extreme conditions*, Bryan W. Rossiter editor, Wiley, New York 1980.

G. Chaudron and F Trombe, eds. "*Les hautes temperatures et leurs utilization in physique et en chemie*" Vol I and II, Masson, Paris, 1973.

R.C Mackenzie (Editor), "*Differential thermal analysis*", in 2 Volumes; Vol.1, *Fundamentals*, Vol.2 *Applications*, Academic Press, London, 1970.

R. Rapp, editor, “*Physicochemical measurements in metals research”*, Vol IV, Part 1 of *Techniques of metal research*, Wiley Interscience, 1970, Chapters 1 to 5

J.L. Margrave, editor, “*The characterization of high temperature vapors”*, Wiley 1967

I.E.Campbell and E.M. Sherwood (Editors), *“High-temperature materials and technology*”, John Wiley & Sons, New York 1967. This is an old but comprehensive contributed book which contains a great deal of high temperature materials property data and major investigation known at the time.

J. O’M.Bockris, J.L.White, J.D.Mackenzie (Editors), “*Physicochemical measurements at high temperatures”*, Butterworths, London, 1959, pp.394 with seven appendixes. A volume (maybe the first to appear in the field) contributed by pioneers in the high temperature science. It offers a picture of the experimental side of high temperature physicochemical measurements as known at the time.. “*with the purpose as a source for those who teach courses concerning high temperature work”.*

“Temperature measurement “, in Kirk-Othmer Encyclopedia of Chemical Technology Vol. 23, 809-832, Wile & Sons, New York, 1997

R.M. Perkin, “*Electrically generated heat*” in Ulmann’s Encyclopedia of Chemical Technology, Fifth revised Edition, Vol. B3 chapter 15; R.M. Perkin, “*Radiation heating”,* ibidem, chapter 16, VCH, Weinheim, 1988.

Conference proceedings volumes

J.W. Hastie, editor "*Characterization of high temperature vapors and gases*", Proc. of the 10th Materials Research Symposium held at NBS, Gaithersburg, Maryland, September 1978, published as NBS Spec.Publ. 561 / Vol 1-2, U.S.G.P.O.,Washington, DC., 1979.

Papers

J. Drowart, C. Chatillon, J. Hastie, D. Bonnell *“High-temperature-mass spectrometry: instrumental techniques ionization cross-sections, pressure measurements and thermodynamic data”* Technical Report published in *Pure Appl. Chem*.77(4), 683-737(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(11) 2111-2126 (2000)

F. Righini, G.C. Bussolino, J. Spisiak, “*Pulse calorimetry at high temperatures*”, Thermochimica Acta 247, 93-102 (2000).

A. Navrotsky, "*Progress and new directions in high temperature calorimetry*" in Phys. Chem. Minerals 24 (1997) 222-241

C. Colinet, "*High temperature calorimetry: recent developments*" in J. Alloys Compounds 220 (1995) 76-87

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

J.K.R. Weber, J.A. Tangeman, T.S. Key and P. Nordine, "*Investigation of liquid-liquid phase transitions in molten aluminates under containerless conditions*", Journal of Thermophysics and Heat Transfer 17 (2003) 182-185

P.C. Nordine, J.K.R. Weber, J.G. Abadie, "*Properties of high temperature melts using levitation*", Pure Appl. Chem. 72 (2000) 2127-36.

Other papers published by Paul Nordine, Richard Weber and coworkers on the same subject referred to specific systems might be consulted in preparing examples for students. Here few references are cited:

J.K.R.Weber, "*Behaviour of molten oxides under containerless conditions*", European Journal of Solid State and Inorganic chemistry 34 (1997) 847-859

T. Baykara, R.H. Hauge, N. Norem, P. Lee, J.L. Margrave, "*A review of containerless thermophysical property measurements for liquid metals and alloys*" in High Temperature Science 32 (1991) 113-154

6. Use of thermodynamic data and modelling in high temperature materials problems

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

Aims: To provide an overview of 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 data banks 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 free 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 data bases 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 use criticism and to make efforts to reconcile these. In teaching students, a warning should be made in the selection of database to be used for equilibrium calculation and modelling. 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) 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.openweb.ru/thermo/index_eng.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,* (1973) American Society for Metals: Metals Park, OH, USA.

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. Fourth Edition, M.W. Chase, Jr., Journal of Physical and Chemical Reference, 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 Appendix

Books

H. L. Lukas, S. G. Fries, Bo Sundman, "*Computational thermodynamics- Assessing thermodynamic data and creating multicomponent databases using the Calphad method*", Cambridge University Press, 2007

T.G. Grimvall., "*Thermophysical properties of materials*" enlarged and revised edition, North-Holland-Elsevier Science B.V., Amsterdam, 1999, pp 424

F.R. de Boer, R.Boom, W.C.Mattens et al., "*Cohesion in Metals-Transition Metal Alloys*", Vol.1, North-Holland, Amsterdam/Oxford/New York/Tokyo, 1988, 758 pp.

Papers

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

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

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 edition, Taylor & Francis, New York, 2003.

P. Haasen, (ed.) Materials Science and Technology. A Comprehensive Treatment-Volume 5 *"Phase transformations in materials"*, R.W. Cahn (ed), P Haasen (ed) E.J Kramer, (ed), VCH, 1990

N. Birks, G.H. Meier, *"Introduction to High Temperature Oxidation of Metals*", Edward Arnold Publisher, London, 1983; see chapter 2 and references cited therein. Consult the new enlarged edition: N. Birks, F.S.Pettit, G.H. Meier, *"Introduction to High Temperature Oxidation of Metals",* Cambridge University Press, Cambridge, 2006, pp. 272 ; chapter 2.

A.H Heuer, and 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 (1990) 2785-3128

V.L.K Lou, and 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 (1985) 49-58, a review

T. Reed, *"Free Energy of Formation of Binary Compounds: An Atlas of Charts for High-Temperature Chemical Calculations"*, MIT Press, Cambridge Mass, 1971; very useful booklet

E. A. Gulbransen and S.A Jansson, in "*Heterogeneous kinetics at elevated temperatures"*, ed. G.R Belton, and W.F Worrell, 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*, edited by P.Nash and B. Sundman, The Minerals, Metals & Materials Society, Warrendale, PA. 1995, pp. 19-27

6.3 CALPHAD

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 optimisation and calculation of phase diagrams in multi-component systems. This topic can be dealt with starting from a description of the thermodynamic models for solution and compound 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* information. With these functions, it is possible to calculate the equilibrium phase diagram, and extrapolate thermodynamic functions to unknown regions. For that, 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 solution models with first principles calculations. Examples of the most common softwares, such as ThermoCalc, BINGSS etc. (see below) developed 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, 2007 ; see chapter 9 for selected case studies

N. Saunders and A.P Miodownik,"*CALPHAD- Calculation of Phase Diagrams. A comprehensive guide*", Pergamon Materials Series, Pergamon/Elsevier Science, Oxford, 1998

U.Kattner, "*Thermodynamic modeling of multi-component phase equilibria*", JOM 49 (1999) 20-26

L. Kaufmann and H. Bernstein, “*Computer calculation of phase diagrams*”, Academic Press, New York 1970

THERMOCALC software: http://www.Thermocalc.se/index.html

For the Lukas programmes 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 Equil. 13 (1992) 532.

For the PanDat software by the A. Chang’s group see: http://www.computherm.com/pandat.html

For the MTDATA software developed at the UK’ NPL see: http://www.npl.co.uk/mtdata/mtrefs.html

“MTDATA-Thermodynamic and Phase Equilibrium Software from the National Physical Laboratory”

R.H.Davies, A.T.Dinsdale, G.A.Gisby, J.A.J. Robinson, S.M.Martin, CALPHAD 26 (2002) pp.229-271

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 modelling

Topic description and teaching suggestions : Once the basic concepts and methods of thermodynamics have been gone through 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 and CVD for materials synthesis. The importance of a critical analysis and selection of thermochemical databases should be underlined (see above 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 towards process simulation, taking into account transport phenomena, flow properties, non-isothermal conditions, etc., can be outlined. Where possible, the results predicted by modelling should be compared with those of the experiments

Useful bibliography

The SGTE Casebook – Thermodynamics at work (Second edition) edited by K.Hack, Woodhead PublishingLtd., Cambridge, UK, 2008; pp 256. The second edition, substantially revised and enlarged, of this standard reference explores both the theoretical background to thermodynamic modelling and its wide range of practical applications

The SGTE Casebook – Thermodynamics at work edited by K. Hack, The Institute of Materials, London, UK 1996 ; pp.228

7. Vaporization and decomposition processes

Aims: to describe the physico-chemical bases 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 explanation 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 ; their use as preparative tools for new materials. For example, it may be important to consider the loss in weight 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. Under this respect to underline the concept of evaporation and condensation coefficients is of concern. In studying vaporization reactions, a pressure-composition diagram (P-x) is useful for representing occurrences in a thermodynamically effusing system. Laser- induced vaporization extends the ranges of pressure and temperature and allows information on the materials behaviour near the critical regions to be obtained. Historically, investigation of the vaporization behavior of polycrystalline and also single-crystal materials, in congruent and non-congruent mode, represented a typical and focal topic in HTMC research. Selected examples of vaporization processes of simple substances of historical relevance (like the vaporization of carbon to monoatomic and polyatomic species and clusters; of alumina, etc. as anticipated in Topic 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 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 and G. Semenov, "*Mass spectrometric study of the evaporation of oxide systems",* Wiley, 1994 *;*

O. Kubaschewski, C.B. Alcock, P.J. Spencer, "*Materials Thermochemistry"*, 6th edition revised of *"Metallurgical Thermochemistry",* Pergamon Press, Oxford/New York, 1993

G.M. Rosenblatt "*Evaporation from solids*" in N.B. Hannay, editor, "*Treatise on Solid State Chemistry"*, Plenum Press, New York / London, vol.6A, chapter 3, 1976;

R. Rapp, editor, *Physicochemical measurements in metals research*, Vol IV, Part 1 of *Techniques of metal research*, Wiley Interscience, 1970, Chapters 1 to 5

A.W. Searcy "*The kinetics of evaporation and condensation reactions",* in Alan W. Searcy, David V. Ragone, Umberto Colombo, editors, *"Chemical and Mechanical Behaviour of Inorganic Materials"* Wiley Interscience, New York/ London/ Sydney/ Toronto, 1970, chapter 6

J.L. Margrave, editor, *The characterization of high temperature vapors"*, Wiley, 1967, chapters 2 to 8;

P.J. Ackermann, R.J. Thorn and G.H. Winslow "*Some fundamental aspects of vaporization"*, in J.L. Margrave, editor, *The characterization of high temperature vapors*, Wiley, 1967, chapter 14; J.P. Hirth*, "Kinetic aspects of evaporation and sublimation processes"*, ibidem chapter 15

Conference proceedings volumes

J.W. Hastie, editor "*Characterization of high temperature vapors and gases*", Proc. of the 10th Materials Research Symposium held at NBS, Gaithersburg, Maryland, September 1978, published as NBS Spec.Publ. 561 / Vol 1-2, U.S.G.P.O., Washington, DC., 1979; see Vol.1, chapters I to III.

Papers

J. Drowart, C. Chatillon, J. Hastie, D. Bonnell *"High-temperature-mass-spectrometry: instrumental techniques ionization cross-sections, pressure measurements and thermodynamic data",* Technical Report published in *Pure Appl. Chem*., 77(4), 683-737(2005) and references 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(11) 2111-2126 (2000)

G.M. Rosenblatt, "*Vaporization rates, surface topography, and vaporization mechanisms of single crystals: a case study"*, in Accounts of Chemical Research, 9 (1976) 169

W.A. Chupka, M.G. Inghram "*The heat of vaporization of carbon*"., J. Chem. Phys., 21 (1953), 371-2.

J. Drowart, G. De Maria, R.P. Burns, "*Thermodynamic study of Al_2O_3 using a mass spectrometer"*, J.Chem.Phys. 32 (1960)1366-69; G. De Maria, J. Drowart, M.G. Inghram, "*Mass spectrometric study of Al_2O_3* " J.Chem.Phys. 30 (1959) 318-20

7.2 Decomposition of solids: thermodynamic and kinetic aspects

Topic explanation and teaching suggestions: Thermal decomposition of inorganic solids are reactions where a solid reactant yields a new solid phase with molar volume lower than that of the reactant, and a gaseous product. In dealing with the kinetics analysis of this complex phenomenon many features need to be considered. Nucleation, growth, sintering of the solid products, vaporization from the interface reaction and diffusion in to the capillary of the gaseous one are only a examples of processes that can have a role in determining the rate limiting steps. Although the HT 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 and 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. Illustration to 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 an history that dates back to many decades. Before the 1970's 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 1970's and subsequently, Alan W. Searcy (University of California, Berkeley, USA) 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 formed oxides 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 these informations a clear picture of the rate determining steps of the thermal decomposition kinetics can be formulated in terms of modified Langmuir-Hertz equation and of decomposition coefficients. The nature of this coefficient was clarified recently by the same authors as a function of surface chemical step of the gaseous products and of thermodynamic activity of the formed solid oxide.

More recently a russian group (Boris V.L'vov, University of St. Petersburg, Russia, and coworkers), tried to extend further the implication of the vaporization theory in the thermodynamic and kinetic analysis of the decomposition reactions by proposing 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 cases 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 produced oxides.

Useful bibliography

Papers

D.T. Beruto, Alan W. Searcy, Mun Gyu Kim, *"Microstructure, kinetic, structure, thermodynamic analysis for calcite decomposition: free-surface and powder bed experiments*", Thermochimica Acta 424 (2004) 99-109 and references cited therein

Boris V. L'vov "*Application of the third-law methodology to the investigation of decomposition kinetics"*, Thermochimica Acta 424 (1-2) (2004) 183-199. A review and refs cithed therein

D.L. Hildebrand, K. H. Lau, R. D. Brittain," *Mechanistic aspects of metal sulfate decomposition processes*" High Temp. Science 26 (1988-1989) 427-440.

B.V. L'vov, *"The physical approach to the interpretation of the kinetics and mechanism of thermal decomposition of solids: state of the art*", Thermochimica Acta 272 (2001) 97-124

C.H.Bamford, C.F.Tipper, *"Comprehensive chemical kinetics, Vol.22. Reactions in the solid state"*, Elsevier, Scientific Publishing Co.,1980

D. Beruto, J. Ewing, A.W. Searcy: "*The nature of the CaO produced by calcite decomposition in vacuum and in CO_2* ", J. Amer. Cer. Soc. 62 (1979), 580

D. Beruto, L. Barco, A.W. Searcy,: *"CO_2-catalyzed surface area and porosity changes in high surface area CaO aggregates"* J. Amer. Cer. Soc.67(1984)512.

A. Searcy and D. Beruto, "*Kinetics of endothermic decomposition reactions.I. Steady-state chemical steps. II. Effects of solid and gaseous products"*, Journal Physical Chemistry 80 (1976) 425 ; ibidem 82 (1978) 163-67.

F.C. Tompkins *Decomposition reactions*, in N.B. Hannay, editor, "*Treatise on Solid State Chemistry"*, vol.4, chapter 4, Plenum Press, New York / London 1976

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

A.D. Young., "*Decomposition of solids*", Pergamon Press, Oxford 1966, in particular chapters 2 and 3

8. High-temperature gas-solid reactions forming both solid and gaseous products: thermodynamic and kinetic aspects – Applications to corrosion and protection of materials at high temperature

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 explanation and teaching suggestions: Understanding of this topic enables appreciation of high/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 HT, 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 vapour pressure up to very high temperature in neutral conditions (vacuum) but are unstable due to reactive vaporization under oxidizing atmospheres even at low temperature (it is interesting to relate with thermodynamic volatility diagrams described earlier). The interaction of certain ceramic oxides with water vapour at high temperature is noteworthy. Indeed the interaction of high temperature water vapour 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 free energy minimization computer code.

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

C.B. Alcock "*Thermochemical processes: Principles and Models*" Elsevier Science&Technology Books (Publisher: Butterworth-Heinemann), 2001, chap.8

A.S. Khanna, "*Introduction to high temperature oxidation and corrosion*", ASM Intl., 2002

N. Birks, F.S.Pettit, G.H. Meier, *"Introduction to High Temperature Oxidation of Metals",* Cambridge University Press, Cambridge, 2006, pp. 272.

V. Per Kofstad, *"High Temperature Corrosion",* Elsevier Applied Science, London/New York, 1988;

L.K Lou and 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 (1985) 49-58, a review

A.H Heuer and 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 (1990) 2785-3128

E.J.Opila, N.S. Jacobson, D.L.Myers, E.H. Copland, "*Predicting oxide stability in high-temperature water vapour*", JOM 58 (1) (2006) 22-28

N.S. Jacobson, D.L.Myers, E.J.Opila, E.H. Copland, "*Interaction of water vapour with oxides at elevated temperatures*", Proc. HTMC XI Conf., in J. Phys. Chem. Solids 66 (2005) 471-478.

9. Additional selected topics relevant to the physical chemistry of high temperature processes

Aim: to give a description of the physico-chemical 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 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 materials behaviour play an important role. The list reported here is not intended to be comprehensive. Indeed, there are so many temperature-dependent properties that are relevant to high-temperature physico-chemical behaviour of inorganic materials that could be selected for teaching in a course or part of a course dedicated to HTMC. These include: defects in solids and thermodynamics of defects, solid state diffusion, nucleation and growth, kinetics of phase transformation, which are typical of solid state chemistry and physics and are usually addressed in specific courses, basic or advanced, of solid state chemistry and physical chemistry of materials; others, such as thermophysical and thermomechanical properties traditionally pertain more to the field of materials engineering and are not explicitly considered here. In teaching 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 physico-chemical basis of some high temperature processes of materials, such as extraction and recovery of metals from ores, and metal refinement.

Topic description and teaching suggestions: This topic encompasses various aspects and applications of high temperature processing in particular of individual metallic and alloys 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 physico-chemical aspects of pyrometallurgy provide students of chemistry, industrial chemistry, materials science oriented to metallurgy and those concerned with the science of metal-making and refining 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 teacher 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 with the vapor transport reactions dealt with separately; see section 9.2.a).

K. Gupta Chiranjib, "*Chemical metallurgy*", Wiley-VCH 2003, chap.4 (p. 343-457).

C.B. Alcock "*Thermochemical processes: Principles and Models*" Elsevier Science&Technology Books (Publisher: Butterworth-Heinemann), 2001, 386 pp.

T. Rosenqvist, *Principles of Extraction Metallurgy*", Tapir Forlag., 2nd edition, 2004, 528 pp

C.B. Alcock,*"Principles of Pyrometallurgy",* Academic Press, London/ New York/ San Francisco, 1975; see in particular chapter 3.

F. Habashi, "*Principles of Extractive Metallurgy. Volume 3: Pyrometallurgy*", Gordon & Breach, 1986, pp. 479.

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 synthesis routes carried out at high and ultrahigh 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 to include for teaching and describe in the following a few peculiar methods of materials preparation where high-temperature chemical processes are involved. For a compact and effective overview of synthesis methods, see the following textbook:

A.R. West, "*Basic solid state chemistry*" second edition, John Wiley & Sons, New York, 1999, Chapter 9

Consult also:

J.I.Gerstein and F.W. Smith, "The physics and chemistry of materials", Wiley Interscience, New York, 2001; Chapter 21 "Synthesis and processing of materials" and relevant topics at Web site W21 (ftp://wiley.com/public/sci_tech_med/materials)

9.2.a) Synthesis methods by physical and chemical deposition: vapour phase transport and deposition and chemical vapour deposition processes

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

Topic description and teaching suggestions: The CVD (Chemical Vapour Deposition) process technique enables the preparation of coatings of different types with 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, that are not easily fabricated by more conventional means (see also powder metallurgy and sintering processes, 9.6). The importance should be underlined of thermochemical modelling of CVD processes and the role of high temperature chemistry in predicting the most important gaseous precursors involved in the process and the phases whose deposition is thermodynamically favoured. Among modern, lower temperature variants of CVD, MetalloOrganic CVD and Plasma CVD should be illustrated (for plasma processes see the following sub-topic 9.2.b). Some specific examples, *e.g.* deposition of silicon, SiC, and carbon diamond can be illustrated.

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

Besides CVD, Physical Vapour Deposition (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*" Elsevier Science & Technology Books (Publisher: Butterworth-Heinemann), 2001; chapters 1 and 3.

H.O. Pierson, "*Handbook of chemical vapor deposition (CVD)-Principles, technology, and applications*", 2nd edition, Noyes Publications, New York, 1999; for fundamentals see chapters 1 to 3.

H.O. Pierson "*Handbook of carbon, graphite, diamond and fullerenes-Properties, processing and applications*", Noyes Publications, 1993, Chapter 13

J. Hastie, *"High Temperature Vapors. Science and Technology"* Academic Press, New York, 1975

M. Faktor, I. Garrett, "*Growth of crystals from the vapour*", Chapman & Hall, London, 1974

H. Schaefer, *"Chemical Transport Reactions"*, Academic Press, New York/London, 1964, 161 pp

Papers

G. Whal, O. Stadel, O. Gorbenko, and A. Kaul, "High-temperature chemical vapour deposition. An effective tool for production of coatings", Pure Appl. Chem. Vol.72, No.11, pp.2167-76, 2000.

K.A. Spear and R.R. Dirkx, "*Role of high temperature chemistry in CVD processing*", High Temperature Science Vol.27 (1990) 107-129

K.E. Spear, "*Diamond-Ceramic coating for the future*" in: J. Am. Ceram. Soc. 72, No.2 (1989) pp. 171-91.

W.A Bryant, "*The fundamentals of chemical vapour deposition*" J. Materials Science 12 (1977) 1285-1306

A useful reading for students is also the introductory paper by K.E. Spear, "*Chemical Transport Reactions",* in J. Chem. Educ. 49 (1972) 81

Consult also:

G. Whal et al., "*Thin films*" in: Ullmann's Encyclopedia of Chemical Technology Vol. A26, VCH, Weinheim, 1995, pp.681-747.

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

9.2.b) Combustion and plasma synthesis of high-temperature materials

Aim: to describe the principles and operations of non-conventional high-temperature methods of synthesis of materials, both stable and metastable.

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 which yields fully or predominantly solid products. The synthesis of materials (pure compounds and/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 reaction is initiated (by igniting the compacted reactants through various means), being highly exothermic it releases sufficient heat to go to completion in a very short time (of the order of few tenths of seconds), reaching temperatures as high as 2000-3000°C and beyond. SHS processes are approximated to be adiabatic and the temperature reached in the reaction front (adiabatic temperature) can be calculated from thermochemical data where available. The physico-chemical studies of SHS currently include studies of mechanism of combustion wave propagation; mathematical simulation of combustion; establishment of relationship 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; thermal plasma properties 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; calculation of the so-called adiabatic temperature through use of thermodynamic data may be shown.

Useful bibliography

Books

A.A. Borisov, L. De Luca and 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, Editor, "*Chemistry of advanced materials*", A 'Chemistry for the 21st century' monograph, International Union of Pure and Applied Chemistry, Blackwell Scientific Publications, Oxford,tec., 1993, 388 pp.

Z.A. Munir, J.B. Holt, editors, *"Combustion and Plasma Synthesis of High-Temperature Materials",* VCH, New York/Weinheim/Basel/Cambridge, 1990, pp.501. A contributed volume dealing with preparation and processing of high temperature materials. Among papers collected see in particular papers 1 and 35.

H.V. Boenig, *"Fundamentals of Plasma Chemistry and Technology*", Technomic Publishing Co, Lancaster, 1988, pp. 413. See chaps. VI, XVI and XVI

Conference proceedings volumes

Chang-Chun Ge and A.S. Rogachev, (eds.) "*Progress in Self-Propagating High-Temperature Synthesis*", Proc. of the Workshop held 21-24 Sept 2000 in Bejing; published in: Key Eng. Mater. 2002, 217, Trans. Tech. Publication, Switzerland, pp. 228.

Papers

A.G. Merzhanov, "*The chemistry of self-propagating high-temperature synthesis*", J. Mater. Chem., 14 (2004) 1779-1786; a review of the chemistry of SHS method with examples of production of refractory materials

A.G. Merzhanov, "*Combustion and explosion processes in physical chemistry and technology of inorganic materials"* Russian Chem. Rev. 72 (2003) 289-310

J.J. Moore, H.J Feng, "*Combustion synthesis of advanced materials; Part I. Reaction parameters*" in Progress in Materials Science Vol.39, 1995, pp 243-273, Pergamon*; Part II.Classification, applications and modelling,* ibidem pp. 275-316;

V. Hlavaceck, "*Combustion synthesis: a historical perspective*", Ceramic Bulletin 70 (1991) 240-243

Z.A. Munir and U. Anselmi Tamburini, "*Self-propagating exothermic reactions: the synthesis of high- temperature materials by combustion*", Materials Science Reports Vol.3 (1989) pp.267-365

Consult also:

Lectures presented at the 15th International Symposium on Plasma Chemistry, Orleans, France, July 2001 and published in Pure Applied Chemistry Vol 74 (3) 2002. For example: Pere Roca i Cabarrocas et al., "Plasma production of nanocrystalline silicon particles and polymorphous silicon thin films for large-area electronic devices" Pure Appl.Chem. 74(3) 359-367, 2002.

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

P. Fauchais, M. Vardelle, J.F. Coudert, A. Vardelle, C. Delbos, and J. Fazilleau, "Thermal plasma deposition from thick to thin coatings and from micro-to nanostructures" Pure Appl. Chem., Vol.77, No.2, pp.475-485, 2005

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

Toyonobu Yoshida, "Toward a new era of plasma spray processing", Pure Appl. Chem. Vol.78, No.6, pp.1093-1107, 2006.

H. Brachhold, R. Mueller, G. Pross, "*Plasma reactions*" in Ullmann's Encyclopedia of Industrial Chemistry, Vol. 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 high temperature synthesis processes (see previous topic 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 2000°C 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 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/transformation temperatures, chemical inertness, thermochemical properties, etc.

M.H. Van de Voorde, G.W. Meetham,”*Materials for high temperature engineering applications (Engineering materials)”* Springer Verlag, 2000, 164 pp

T.Ya. Kosolapova, editor “*Handbook of high temperature compounds: properties, production, applications*” Taylor&Francis 1990, 958 pp

M.G. Hocking, V.Vasantasree & P.S/.Sidky, *"Metallic & Ceramic Coatings: Production, High Temperature Properties & Applications"*, Longman Scientific & Technical (John Wiley), New York etc., 1989, 670 pp

E. Bullock, editor, *"Research and Development of High Temperature Materials for Industry",* CEC-JRC Petten-The Netherland (Elsevier Applied Science), New York/London, 1989, 680 pp.

I.E. Campbell E.M.Sherwood, editors*"High Temperature Materials and Technology* Electrochemical Society (Wiley), New York, London, 1967, 1022pp

For phase diagrams see literature sources in Appendix e.g

Phase Equilibria Diagrams- *Phase Diagrams for Ceramists*, Vol I(1964)---> Vol XIII (2001)

The American Ceramic Society, Columbus/Westerville, OH ; see in particular Vol X for borides, carbides, nitrides

T. Massalski (ed.) *Binary alloy phase diagrams,* ASM International, 2nd Edition, 1990

For others, check on the American Ceramic Society Web-site: www.ceramics.org

Additional readings:

A report useful to read focused present issues concerning ultra high temperature materials:

HTM Workshop Report (W.G. Fahrenholtz and G.E. Hilmas eds) sponsored by NSF Division of Materials and AFOSR Ceramic and Non-metallic Materials, July, 2004, Arlington, VA, USA; see literature cited therein. This report was also summarized in: *Refractory applications and news*, vol. 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”,* Electrochemical Society Interface (2006), 48-51.

9.4 Chemistry of metal halide discharge lamps

Aim: to enlight some high temperature materials chemistry 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, 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 major issues are, from the basic research point of view, thermochemistry and problems connected with material transport and corrosion within the lamp bulb and the electrode. Thermodynamic modelling can help in understanding what processes are going on in these high temperature devices. In summary, there is a lot of high temperature materials chemistry 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.

Helpful bibliography

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

W. van Erk, "*Trasport properties in metal halide gas discharge lamps*", Pure Appl. Chem, 72(11)2159-2166 (2000) and literature cited therein.

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

J. Hastie, *"High Temperature Vapors. Science and Technology",* Academic Press, New York, 1975, Chapter 3

See also:

Contributions presented in "High temperature metal halide chemistry" edited by D.L.Hildenbrand and D. Cubicciotti, Proc.Vol. 78-1 The Electrochemical Society, 1978

Z. Toth, "*Chemistry of material science phenomena in high intensity discharge light sources*", plenary lecture presented at the 12th International IUPAC-Conference on High Temperature Materials Chemistry-HTMC XII, held in Vienna September 17-22, 2006; published in *Pure and Applied Chemistry*, Vol. 79, n.10, p. 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 materials properties and processes in action in these 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 the description of the preceding topic dealing with experimental thermodynamics, section 5.2) and as high temperature sensors. Examples of materials typically involved in thermodynamic measurements are yttria-calcia stabilized zirconia, CaF_2 single crystals, etc. Solid state electrochemical sensors can be used at temperatures up to 700°C with high sensitivity and response stability to improve combustion control, resulting in both improved fuel utilization and reduced emissions.

Among the energy systems solid oxide fuel cell (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 and/or reducing atmospheres, the conductivity and thermomechanical stability in high temperature conditions. Indeed, research efforts are being made to understand the behaviour of electrode and electrolyte in SOFC as thermodynamic and kinetic factors affect their 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 R&D 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.

S. Singhal, K. Kendall, "*High temperature solid oxide fuel cells: fundamentals, design and applications*", Elsevier, 2003. A contributed book in 13 chapters

T. Kawada and H. Yokokawa, *Materials and characterization of solid oxide fuel cells*, Key Engineering Materials Vols. 125-126 (1997) pp. 187-248

P.G. Bruce, editor, "Solid state electrochemistry", Cambridge University Press, Cambridge, UK, 1997, pp.360

H. Rickert, Electrochemistry of solids. An introduction, Springer-Verlag, Berlin, Heidelberg, New York, 1982; in particular chapter 8 deals with galvanic cells with solid electrolytes for thermodynamic investigations

H. Rickert, *Solid state electrochemistry* in N.B. Hannay, editor, "*Treatise on Solid State Chemistry*", vol.4, chapter 6, Plenum Press, 1976

R. Rapp, editor, *Physicochemical measurements in metals research*, Vol IV, Part 2 of *Techniques of metal research*, Wiley Interscience, 1970

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

K.A.Spear, "*High temperature materials*" in: *What is Electrochemistry? Electrochemistry and Solid State Science*, fourth edition, The Electrochemical Society, Pennington, NJ, 1997, pp. 24-27 and refs. cited therein

K.E. Spear, S. Visco, E.J. Wuchina, E.D. Wachsman, *"High temperature materials",* Electrochemical Society Interface (2006), 48-51.

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 consolidation 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 considered for inclusion in this syllabus, and should be dealt with together with the synthesis of materials (see 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 HT and UHT materials, therefore its fundamentals should be refreshed, where necessary, to students.

C.B. Alcock., "*Thermochemical processes: Principles and Models*" Elsevier Science&Technology Books (Publisher: Butterworth-Heinemann), 2001; particularly useful chapters 5 to 7

M. Glicksman, "*Diffusion in solids*" Wiley, New York, 2000

C.B. Alcock, *Principles of Pyrometallurgy*, Academic Press 1976, chap.5

W.D. Kingery, H.K. Bowman D.R. Uhlmann, "*Introduction to ceramics*", Wiley & Sons, 1976, chap. 10.

For sintering:

Suk-Joong L. Kang "*Sintering: Densification, Grain Growth and Microstructure*", Butterworth-Heinemann, 2005, 280 pages.

G. Weidmann, P. Lewis, N. Reid (eds.), "*Structural Materials*", Materials in Action Series, The Open University, Butterworths, 1990, London, pp. 195-206.

Consult also:

A.W. Searcy, Dario Beruto, "*Theory and experiments for isothermal and nonisothermal sintering*", Science of Ceramics 14 (1988) 1-13. A review

W.A. Kaysser, W. Weise, "*Powder metallurgy and sintered materials*" in Ullmann's Encyclopedia of Industrial Chemistry, Fifth Edition, Vol. A22, VCH, Weinheim, FRG, 1993, pp.105-142

J.S. Moya, C. Baudin, P. Miranzo, "*Sintering*" in: Encyclopedia of Physical Science and Technology, Vol.12 p.700-712, Academic Press, 1987

For solid state diffusion see also: R.J. Borg and G.J. Dienes, "*The physical chemistry of solids*", Academic Press, 1992

For reminding students about the basics of defects in solids and defect thermodynamics, consult A.R. West, *"Basic solid state chemistry" second edition, John Wiley & Sons, 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 explanation 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, 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 modelling 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.

J. Warnatz, U. Maas, R.W. Dibble, "*Combustion: physical and chemical fundamentals, modelling and simulation, experiments, pollutant formation*", Springer, 3rd edition, 2001

S.R. Turns, "*An introduction to Combustion: Concepts and Applications w/Software*", McGraw-Hill Science, 2nd edition, 704 pp., 2000.

Glassman, "*Combustion*", Third Edition, Academic Press, 1996

G. Chaudron and F Trombe, eds. "*Les hautes temperatures et leurs utilization in physique et en chemie*" Vol I, Masson, Paris, 1973.

J. Hastie, *"High Temperature Vapors. Science and Technology",* Academic Press, New York, 1975, chapter 5, and literature cited therein for literature source prior to 1975

Further reading :

R. Sharifi, S.V. Pisupati, A.W. Scaroni, "*Combustion science and technology*" in: Kirk-Othmer Encyclopedia of Chemical Technology, Fourth Edition, Volume 6, pp. 1049-1092, Wiley Interscience, 1993

A 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 explanation and teaching suggestions: High temperature liquid phases are present in many technological processes (liquid metals, slags, molten silicates and glasses, molten salts...). Basic knowledge of the physico-chemical properties of liquid and melts is important to understand the processes in which they are involved. To characterize the structure and long range bond interactions in such liquids, many modern diagnostic techniques such as lasers-beams (see topic dealing with containerless processing), X-ray diffraction, neutron diffraction, NMR and 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.

C.B.Alcock, "*Thermochemical processes: Principles and Models*" Elsevier Science&Technology Books (Publisher: Butterworth-Heinemann), 2001, see Part 3

F. D. Richardson "*Physical Chemistry of Melts in Metallurgy*", Academic Press, London/New York, 1974.

P.C. Nordine, J.K.R. Weber, J.G. Abadie, "*Properties of high temperature melts using levitation*", Pure Appl. Chem. 72 (2000) 2127-36.

T. Baykara, R.H. Hauge, N. Norem, P. Lee, J.L. Margrave, "*A review of containerless thermophysical property measurements for liquid metals and alloys*" in High Temperature Science 32 (1991) 113-154

Alan W. Searcy, David V. Ragone, Umberto Colombo, editors, *"Chemical and Mechanical Behaviour of Inorganic Materials"* Wiley Interscience, New York/ London/ Sydney/ Toronto, 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 of liquids on solids 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 materials processing at high temperatures. It is therefore important to have a scientific understanding of wetting behaviour both from theoretical models and experimental observations for example when liquid metals and/or inorganic glasses come in contact with solid metals or ceramics. It is important to know the nature of high-temperature wetting phenomena at materials interfaces 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 the previous topic 5.2 dealing with experimental thermodynamics). Remember, as always, that "*at high temperature everything reacts with everything else*". A prerequisite is the knowledge of basic interface chemistry, thermodynamics and kinetics.

N. Eustathopoulos, M.G.Nicholas, B. Drevet, "*Wettability at high temperatures*", Pergamon Press, 1999, pp.437. This book in ten chapters is comprehensive and almost unique in treating high-temperature wetting phenomena

Y. V. Naidich *"The wettability of solids by liquid metals"* in Progress in Surface and Membrane Science, vol. 14, pp. 354-485 (1981). Edited by D.A. Cadenhead and J.F. Danielli. Academic Press, New York.

M.M. Schwartz.“*Brazing”*, 2nd edition, ASM International, 2003.

M.G. Nicholas, “*Joining processes: an introduction to brazing and diffusion bonding”,* Kluwer Academic Publishers, 1998, 368pp

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

"Proceedings of High Temperature Capillarity Conference 2004" edited by A. Passerone and N. Eustathopoulos. J. Materials Science. vol 40 (9-10) 2005, pp. 2119-2761.

"Proceedings of High Temperature Capillarity Conference 2007" edited by N. Eustathopoulos, E. Louis and A. Mortensen. To be published in Materials Science and Engineering.

A plenary lecture and some papers on wetting properties of materials have been presented at *the IUPAC sponsored- Conference on High-Temperature Materials Chemistry, HTMC XII*, held in Vienna, September 2006: N. Sobczak et al. “*The factors affecting wettability and bond strength of solder joint couples*”, published in *Pure and Applied Chemistry*, Vol. 79, n.10, p. 1755, 2007

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Appendix

A Selection of Books and Reference Literature in English listed in chronological order for use as resource in teaching of HTMC topics at University

Note: This general list of references arranged in chronological order constitutes an Appendix to the document. Most of the listed publicatons have been available to the TGC off the shelf over the decades. Many old volumes might not be at present available at institutions and libraries, in particular conference proceedings. Nevertheless those listed here, the conference proceedings volumes in particular and, amomg these, primarily the IUPAC sponsored HTMC conferences, show how the areas of research in HTMC evolved over the decades.
In the list of topics, appended to each topic a selected bibliography is given whereas possible including more recent publications and books presumably more readily available.

BOOKS

Textbooks and Contributed Volumes

N. Birks, F.S.Pettit, G.H. Meier, *"Introduction to High Temperature Oxidation of Metals",* Cambridge University Press, Cambridge, 2006, pp. 272.

In this book the intent is to introduce the subject of high temperature oxidation of metals and alloys to students and to professional engineers whose works demands familiarity with the subject.The emphasis of the book is placed on supplying an understanding of the basic, or fundamental, processes involved in oxidation. Examples of the application of the principles described are given.

D.R. Gaskell,"*Introduction to the thermodynamics of materials*", 4^{th} edition, Taylor & Francis Kumar, New York, 2003.

An introductory text particularly written for students of materials science & engineering underlying the principles and their applicability, with worked examples. In particular, chapters 9 to 13 are relevant to the high temperature thermodynamics of materials

Gupta Chiranjib, "*Chemical metallurgy*", Wiley-VCH 2003, 811 pp.

A book in seven chapters. Particularly relevant are chap.s 2 and 4 dealing with mineral processing and pyrometallurgy

A.S Khanna ., "*Introduction to high temperature oxidation and corrosion*"
ASM Intl,, 2002, 324 pp.

A textbook for graduate and postgraduate courses on high temperature corrosion.It deals with the basics and applications of high temperature oxidation of metals and alloys in various environments

C.B Alcock ., "*Thermochemical processes: Principles and Models*"
Elsevier Science&Technology Books (Publisher: Butterworth-Heinemann), 2001, 384 pp in three parts with appendices

This volume, companion to Kubaschevski's et.al *Materials Thermochemistry*, deals primarily with the kinetic and transport theory of high-temperature chemical reactions for students who have already absorbed the basic courses in classical thermodynamics required before they study materials processing. It describes the application of physical and chemical concepts to processing
and degrading metals, ceramics, semiconductors, plastics and composites, from the atomic scale to that of industrial processes.

M.H Van de Voorde, G.W Meetham .,"*Materials for high temperature engineering applications (Engineering materials)"*
Springer Verlag,2000,164 pp

A survey book describing in 16 chapters the requirements on materials operating in high-temperature environments and the processes increasing temperature capability of metals, ceramics and composites. The major part deals with the applicable materials and their specific properties. The book is written for engineering and science students, researchers and managers in industries.
The book is a good overview of high temperature metals and gives some of the background for how these materials came into common use. A good intro for someone who needs an entrèe to this area and to lay the groundwork.

N.Eustathopoulos, M.G.Nicholas, Beatrice Drevet, "*Wettability at high temperatures*",
Pergamon Press, 1999, 437 pp

A book in ten chapters written with the purpose to bring together current scientific understanding of wetting behaviour that has been gained from theoretical models and quantitative experimental observations. The materials considered are liquid metals or inorganic glasses in contact with solid metals or ceramics at temperatures of 200-2000°C. Informations given in the various chapters are
useful for selection of suitable container materials of metallic and ceramic systesms at high temperatures.

A Pechenik ., R.K. Kalia,Vashishta Priya, editors, "*Computer-aided design of high-temperature materials (Topics in physical chemistry)"*
Oxford University Press, 1999, 538pp

This volume collects recent work from experimental and computational scientists on high-temperature materials and emphasizes the potential for collaboration. It features state-of-art materials modeling and recent experimental results

E.S. Machlin ., "*An introduction to aspects of thermodynamics and kinetics relevant to materials science*", revised and updated edition, Giro Press, Croton-on-Hudson, N.Y., 1999

The book covers in several chapters topics of materials science required for seniors and graduate students

H.O.Pierson, "*Handbook of chemical vapor deposition (CVD)-Principles, technology, and applications*", 2nd edition, Noyes Publications, New York, 1999; for fundamentals see chapters 1 to 3.

An up-to-date description of principles, technology and applications of CVD processes. Fundamentals of the process are described in chapters 1 to 3. Plasma and metallo-organic CVD – two major factors in the rapid growth of CVD market – are illustrated with many examples.

Lee Hae-Geon, "*Chemical thermodynamics for metals and materials",* ICP Imperial College Press, London, 1999

A book of classical thermodynamics with CD-ROM for computer-aided learning. Primarily
written for students and graduate materials engineers, it is useful as well for students of chemical sciences

TG Grimvall ., "*Thermophysical properties of materials"* enlarged and revised edition, North-Holland-Elsevier Science B.V., Amsterdam, 1999, pp 424

A book in 19 chapters and 9 appendices which provides an overview in a specific field of materials science such as thermophysical phenomena. Written primarily for graduate students in condensed matter physics, metallurgy, inorganic chemistry or geophysical materials. Particularly useful chapters: 7, 12-14, 16 and 17.

N.Saunders and A.P Miodownik .,"*CALPHAD- Calculation of Phase Diagrams. A comprehensive guide*"
Pergamon Materials Series, Pergamon/Elsevier Science, Oxford,1998, 479pp, 12 chapters

Mats Hillert, “*Phase equilibria, phase diagrams, and phase transformations: their thermodynamic basis*”
Cambridge University Press, 1998

M.Barsoum, “*Fundamentals of ceramics*” McGraw-Hill, 1997, 668pp

The SGTE Casebook – “*Thermodynamics at work”*
Edited by K.Hack
The Institute of Materials, London, 1996

Purpose of the book is to illustrate how thermodynamic calculations can be used as a basic tool in the development and optimization of materials and processes of many types

J.J Moore ., H.J., Feng “*Combustion synthesis of advanced materials; Part I. Reaction parameters*” in Progress in Materials Science Vol.39, 1995, pp 243-273, Pergamon*; Part II.Classification, applications and modelling,* ibidem pp. 275-316

David V. Ragone, “*Thermodynamics of materials*”, Vols. I and II, Wiley MIT Series in Materials Science & Engineering, New York, 1995

M.N Rahaman ., “*Ceramic processing and sintering*”, Dekker, 1995

, N.A Gokcen ., R.G Reddy, ., *“Thermodynamics”* 2nd edition, Plenum Press, New York, 1996 pp 400, with floppy disk for chemical equilibrium calculations

A textbook of classical thermodynamics in 16 chapters plus 6 appendices with emphasis on the application of thermodynamics to chemical, materials and metallurgical problems. It is intended for students and specialists in materials sciences, metallurgical engineering, chemical engineering, chemistry and related fields. It contains also a thermodynamic database for inorganic compounds

V.L.Stolyarova, G.A. Semenov, "*Mass Spectrometric Study of the Vaporization of Oxide Systems*",
Wiley, Chichester/ U.K., 1994, 434pp

An invaluable book collecting in eight chapters various aspects, fundamental and applications, of
vaporization thermodynamics of oxide systems …..

O. Kubaschewski, C.B.Alcock, P.J.Spencer, "*Materials Thermochemistry"*, 6th edition revised from *"Metallurgical Thermochemistry"*, Pergamon Press, Oxford/New York, 1993, 363pp

This volume in its latest revised and updated edition (warning, it contains many typographical and other types of errors!) is a classic and excellent book dealing with applications (practical) of thermochemistry to the optimization of materials and materials processes. It contains many examples and problems and useful tables of thermochemical data

Hugh O.Pierson, "*Handbook of carbon, graphite, diamond and fullerenes- Properties, processing and applications*", Noyes Publications, Park Ridge, NJ, 1993

A review in fifteen chapters of the science and technology of the element carbon and its allotropes. There is a good deal of high-temperature chemistry of carbon in its various forms.

C.N.R.Rao, Editor, "Chemistry of advanced materials", A 'Chemistry for the 21st century' monograpph, International Union of Pure and Applied Chemistry, Blackwell Scientific Publications, Oxford,tec., 1993, 388 pp.

R.J.Borg and G.J.Dienes, "*The physical chemistry of solids*", Academic Press, San Diego etc., 1992, **584 pp.**

A.Fontijn, editor, *"Gas-Phase Metal Reactions*", North-Holland, 1992, 700pp

D. Porter and K Easterling, "*Phase transformation s in metals and alloys*", 2nd edition, Chapman & Hall 1992

R.W.Cahn, P.Haasen, E.J.Kramer,editors, "*Materials Science and Technology – A comprehensive treatment"* in 18 Vols. See topics in Vols. 5 and 11

Vol.5 "*Phase transformations in materials*", edited by P. Haasen, VCH, Weinheim, 1991 in 10 chapters. Particularly useful is Ch. 1: "Thermodynamics and phase diagrams of materials"
Vol.11, "*Structure and properties of ceramics*" edited by M. Swan, VCH, Weinheim,1994. Useful is Chap. 10 (High-temperature engineering ceramics)

T.Ya.Kosolapova, editor "*Handbook of high temperature compounds: properties, production, applications*"
Taylor&Francis 1990, 958 pp.

Z.A.Munir, J.B.Holt, editors, *"Combustion and Plasma Synthesis of High-Temperature Materials",* VCH, New York/Weinheim/Basel/Cambridge, 1990, 501 pp

A volume contributed by an international group of experts (originating from a meeting held in San Francisco, October 1988), It reports in detail on various aspects of current research and development activity in combustion and plasma synthesis of high temperature materials

John W.Hastie, editor, "*Materials Chemistry at High Temperatures"*, 2 Vols. A selection of papers based on the Proceedings of IUPAC Sixth International Conference on High Temperature-Chemistry of Inorganic Materials, Humana Press, Clifton, NJ, USA, 1990

T.J. Quinn, *"Temperature*" 2nd edition, Academic Press, London 1990

A comprehensive treatment of the principles of temperature measurement over the range 0.5 to 3000 K

M.G.Hocking, V.Vasantasree & P.S/.Sidky, *"Metallic & Ceramic Coatings: Production, High Temperature Properties & Applications"*, Longman Scientific & Technical (John Wiley), New York etc., 1989, 670pp

J.D.Gilchrist, "*Extraction Metallurgy*", Pergamon Press, 3rd edition, 1989,431 pp

H.V. Boenig, *"Fundamentals of Plasma Chemistry and Technology*", Technomic Publishing Co, Lancaster, 1988, pp. 413

Per Kofstad, *"High Temperature Corrosion",* Elsevier Applied Science, London/New York, 1988, 558pp

Aim of this classical book is to survey the main aspects and mechanisms of gas-metal reactions at high temperature. Descriptions and treatments of the principles of the various corrosion phenomena are emphasised. A book of value to those who are (or will be) engaged in materials science, metallurgy, corrosion and high temperature materials and technology. Particularly useful material of chapter 1 and parts of chapters 5,6,10,11,13,14

E.Bullock, editor, *"Research and Development of High Temperature Materials for Industry",* CEC-JRC Petten-The Netherland (Elsevier Applied Science), New York/London,1989, 680pp

The book reports a study carried out by J.R.C. Petten, The Netherlands and reviews materials requirements in high temperature technologies at the time. It identifies the priorities for research and development in the short-term future (approximately ten years) of structural materials operating in major high temperature technologies

F.R. de Boer, R.Boom, W.C.Mattens et al., "*Cohesion in Metals-Transition Metal Alloys"*,Vol.1, North-Holland, Amsterdam/Oxford/New York/Tokyo, 1988, 758 pp

Alan Jones, Brian D. McNicol,*"Temperature-Programmed Reduction for Solid Materials Characterization*", Marcel Dekker, New York/Basel, 1986, 199 pp

course in phase equilibria designed for students in ceramic engineering and associated disciplines

P.C.Hayes," *Process selection in extractive metallurgy*", Hayes Publishing Co, Brisbane,1985, 406 pp

R.J.Fruehan,"*Laddle Metallurgy principles and Practices"*, Iron and Steel Society Inc.,1985, 52pp

L.Condurier, D.W.Hopkins, I.Wilkomirsky, "*Fundamentals of metallurgical processes*", 2nd edition, Pergamon Press, 1985, 404pp

V.I.Babushkin, G.M.Matveyev, O.P.Mchedlov-Petrossyan, *"Thermodynamics of Silicates"* Springer Verlag, Berlin/Heidelberg/New York/Tokyo, 1985, 459 pp

A book in two parts, theoretical and applied,dealing with the application of thermodynamics to the study of silicate systems

R.H.Doremus, "*Rates of phase transformations*", Academic Press, 1985, 176pp

An introduction to the kinetics of phase transformations.An understanding of rates of transformations control the properties of materials being processed

C.H.Bamford, C.F.H. Tipper, R.G.Compton, editors
"Chemical Kinetics. Vol. 21, Reactions of Solids with Gases"
Elsevier, Amsterdam, 1984, 237 pp

Particularly useful chap. 1 on the oxidation of metals

J.L.Margrave, editor, *"Modern High Temperature Science*", Humana Press, Clifton, N.J., 1984, 462pp

A collection of papers dedicated to Leo Brewer on theoccasion of his 65th birthday

F.A.Hummel, *"Phase Equilibria in Ceramic Systems"*, Marcel Dekker, New York, 1984, 388 pp

This book in eight chapters seems particularly adequate for use in teaching equilibria in ceramic systems at undergraduate level. It enables the student to move into highly specialised textbooks or treatises in the subject.

C.G.Bergeron, S.H.Risbud, *"Introduction to Phase Equilibria in Ceramics"*, The American Ceramic Society, Columbus, Ohio, 1984,pp. 158

A textbook in eight chapters plus four appendices shaped to serve the needs of an introductory

E.Lang, editor, *"Coatings for High Temperatures Applications"*
Applied Science Publishers, London, 1983, xxxpp

O. van der Biest, editor, *"Analysis of High Temperature Materials*"
Applied Science Publishers, London, 1983, xxxpp

The book contains the lectures of a course organised by the Commission of the European Communities, J.R.C. Petten, The Netherlands. It is aimed at the analytical techniques appropriate to the study of high temperature materials, and particular examples of this type are given, although generally applicable to metallic and ceramic materials

Lupis, C.H.P. "*Chemical thermodynamics of materials*", North Holland New York/Amsterdam/Oxford, 1983. pp581, with 5 appendices

A book written for graduate students and senior students in metallurgy and materials science who have had previous introductory courses in thermodynamics, useful also to professional metallurgists, chemists and chemical engineers. Most applications in the text are for metals and alloys

T.Rosenqvist, *Principles of Extraction Metallurgy*", McGraw-Hill Boopk Co., 2nd edition, 1983, 503 pp

D.R.F.West, "*Ternary equilibrium phase diagrams*", Chapman-Hall, 1982

U.R.Evans, *An Introduction to Metallic Corrosion,* Edward Arnold, 3rd edition,1981

H. Schmalzried,*"Solid State Reactions", 2nd edition*
Verlag Chemie, Weinheim, 1981, 254 pp
This "classic" monograph in nine chapters provides a quantitative understanding of solid state reactions.

H.A.J.Oonk, „*Phase theory-The thermodynamics of heterogeneous equilibria*”
Elsevier, Amsterdam 1981

> Thermodynamic principles of heterogeneous equilibria, in particular the relation between phase diagrams and Gibbs energy

V.Guttmann, editor, „*Phase stability in high temperature alloys*“
Applied Science Publishers, London, 1981, 154 pp

> The book contains the lectures of a course organised by the Commission of the European Communities, J.R.C. Petten, The Netherlands. It presents in five chapters a summary of the relevant theoretical and practical aspects of metal structures with emphasis on their possible changes during service. The fundamental thermodynamic aspects and computational techniques of phase diagrams are dealt with.

T.I.Barry, editor, *"The Industrial Use of Thermochemical Data"*
The Chemical Society Special Publ. No. 34, London, 1980, 427pp

B.W. Rossiter, editor, *"Chemical Experimentation Under Extreme Conditions"*, Vol IX of Techniques of Chemistry, Wiley, New York/Chichester/Brisbane/Toronto, 1980, 369 pp

Relevant to the scope is chapter 6: "*High Temperature Techniques*", J.L.Margrave and R.Hauge, (pp 277-360) where the topics of generation, measurement and utilization of high temperatures are reported in detail

K.J.Klabunde,*"Chemistry of Free Atoms and Particles"*
Academic Press,New York, 1980, pp. 238

> A book in ten chapters dealing with the chemistry of reactive species (atoms and molecules) .Although these reactive species are generated at high temperatures, so the chemistry investigated is that of high-temperature species, however the reaction chemistry is usually studied at low or extremely low temperature.

E.T.Turkdogan, *"Physical Chemistry of High Temperature Technology"*
Academic Press, New York/London/Toronto.Sydney/San Francisco, 1980,447 pp

> A book in two parts, fundamentals and applications, and ten chapters which present in compact and comprehensive form topics of the physical chemistry of materials and systems at elevated temperatures and pressures

“High Temperature Science: Future Needs and Anticipated Developments”
A monograph prepared by the Committee on High Temperature Science and Technology, Assembly of Mathematical and Physical Sciences, National Research Council
Published by National Academy of Sciences, Washington, D.C., 1979, 139pp

P. Davidovits & D.L McFadden.,editors, “Alkali halide vapors – Structure, spectra and reaction dynamics”
Academic Press, New York 1979, 542pp

This book in fifteen chapters reviews and summarizes various aspects of alkali halide chemistry as structural and spectral properties and gas phase chemistry

O. Kubaschewski, C.B.Alcock, *"Metallurgical Thermochemistry"*, 5th edition
Pergamon Press, Oxford/New York/Toronto/Sydney/Paris/Frankfurt,1979, 449 pp

R.H.Parker, “*An introduction to chemical metallurgy*” 2nd edition,
Pergamon Press, Oxford, 1978, 361pp

An introduction to the applications of thermodynamics and reaction kinetics to chemical metallurgical processes

G.S. Updhayaya and R.K.Dube, *"Problems in Metallurgical Thermodynamics and Kinetics",*
International Series In Materials Science &Technolgy, Vol.25
Pergamon Press, Oxford/New York/Toronto/Sydney/Paris, 1977, 252pp

A text in nine chapters dealing with basic metallurgical thermodynamics and kinetics with worked numerical problems. Advantageous for undergraduate and postgraduate students at universities, polytechnics and technical colleges

F.P.Glasser and P.E.Potter, editors, *"High Temperature Chemistry of Inorganic Materials",* The Chemical Society Special Publ. No. 30, London, 1977, xxxpp

W.D.Kingery, H.K.Bowen, D.R. Uhlmann, *"Introduction to Ceramics" (second edition)*
Wiley Interscience, New York, 1976, 1032pp

A classical book (“ treatise”) in four parts and nineteen chapters on

structure,phase

equilibria,phase transformations, reactivity and properties of ceramics

J.Szekely, J.W.Evans, H. Yong Sohn, “*Gas-solid reactions*”, Academic Press, NY, 1976, 400pp.

A monograph in eight chapters; see, chaps. 5 to 8

R. Pampuch, *"Ceramic Materials-An Introduction to their Properties*", Elsevier, Amsterdam, etc., 1976, 344pp

Chapters: 2 & 3

N.B.Hannay, editor, "*Treatise on Solid State Chemistry"*, Vol. 1-6
Plenum Press, New York / London, 1974 - 76

The central theme of this *Treatise* is the exposition of unifying principles in the chemistry, physical chemistry and chemical physics of solids
Useful chapters of Vols. 4,5 and 6A
Volume 4, *"Reactivity of Solids"* in eleven chapters written by specialists in the field covers a great variety of "chemical reactions" in the broadest context. Particularly useful and relevant to high-temperature materials chemistry are typical topics dealt with in chapter 3 ("High-temperature reactivity"), chapter 4 ("Decomposition reactions"), chapter 5 ("Solid-state reactions") and chapter 8 ("Gas-solid reactions – Oxidation").
Volume 5, *"Changes of State".* This includes phase transformations which are at the heart of much of the chemistry and metallurgy of complex inorganic solids. Of the eleven chapters constituting the book, relevant to high temperature materials are topics in chapters 1 to 6 and particularly those chapters 4 to 6.
Volume 6A " *Surfaces I"*, in five chapters covering major surface phenomena. Particularly relevant to classical high-temperature chemistry is the topic of chapter 3 where the "evaporation from solids" is dealt with in a clear and thorough manner

A. Cottrell, *"An Introduction to Metallurgy", 2nd edition*
Edward Arnold, London, 1975, 548 pp

John Hastie,*"High Temperature Vapors. Science and Technology"*
Academic Press, New York, 1975, 480 pp

A reference monograph summarizing three decades of research efforts in characterizing and understanding high temperature phenomena with emphasis on the vapor state

C.B.Alcock,*"Principles of Pyrometallurgy"*
Academic Press, London/ New York/ San Francisco, 1975, 348 pp

This volume deals with the application of high temperature chemistry of individual metallic systems to the various extractive unit operations in three major sections: reactions involving solids, metal extraction processes, metal refining processes: This book is essential reading for students of metallurgy and materials science and for those concerned with the science of metal-making at high temperature.

G.Chaudron and F Trombe, *"Les Hautes Temperatures et leurs Utilization en Physique et en Chimie",* 2 Vols., Masson, Paris, 1973

A reference treatise dealing with high temperatures and their utilization in science and industry

R.A.Swalin, "*Thermodynamics of solids*", John Wiley & Sons, 2nd edition, 1973, 400pp

Marc M. Faktor, Jan Garrett, *"Growth of Crystals from the Vapour"*, Chapman and Hall, London, 1974, 300 pp

This monograph has as its theme one of the most versatile, cheap and widely used methods of growing crystals: chemical vapour transport. Particularly useful chapters on the thermodynamic basis of chemical vapour transport.

A.G.Guy, "*Introduction to materials science*", McGraw-Hill, New York, 1972, 604pp

Thomas B. Reed,*"Free Energy of Formation of Binary Compounds: An Atlas of Charts for High-Temperature Chemical Calculations"*
MIT Press, Cambridge Mass, 1971, 81 pp

Alan W.Searcy, David V.Ragone, Umberto Colombo, editors, *"Chemical and Mechanical Behaviour of Inorganic Materials"*
Wiley Interscience, New York/ London/ Sydney/ Toronto, 1970, 715 pp

A book in twenty-nine chapters which contains the written versions of the course of lectures presented at the First International Course on Materials Science held in Tremezzo, Italy, September 1968. The first nineteen chapters present a systematic development of the thermodynamic and kinetic principles that underlie the behaviour of solids and illustrate applications of these principles to understanding chemical and mechanical processes. Of particular interest to high-temperature materials chemistry are chapters 1 to 6 and chapter 13.

Robert A.Rapp, editor, *"Techniques of Metal Research*," Vol. IV. Physicochemical Measurements in Metal Research, Part 1 and Part 2
Wiley Interscience, New York/London/Sydney/Toronto 1970, 562pp

This volume covers the important techniques involved in the study of physical chemical properties of metallic materials. Particularly useful are the chapters covering vapor pressure methods, calorimetry, chemical equilibria, phase equilibria and transformations, electrochemistry, oxidation and corrosion:

Chapter 1; Chapters 2A,2B,2C,2D; Chapters 3A,3B; Chapters 4A,4B,4C; Chapters 5A,5B; Chapters 6A,6B,6C; Chapters 10A,10B; Appendix

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a treatise on phase diagrams in three volumes contributed by various specialists:
Vol.I, *Theory, principles and techniques of phase diagrams*, edited by Allen M. Alper, Academic Press, 1970
Vol.II, *The use of phase diagrams in metal refractory, ceramic and cement techniques*, edited by Allen M. Alper, Academic Press, 1970
Vol.III, *The use of phase diagrams in electronic materials and glass technology*,, edited by Allen M. Alper, Academic Press, 1970

Leroy Eyring, editor, "*Advances in High Temperature Chemistry"*
Vol. 1-4, Academic Press, New York, 1967-71
Volume 1, 1967, 333pp; Volume 2,1969, 283pp; Volume 3,1971, 286pp, Volume 4, 1971, 281pp

N.A.Toropov, editor, *"Chemistry of High -Temperature Materials"*, trans. from Russian, Consultants Bureau, New York,1969, 237pp

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A sort of "bible" collecting problems and techniques in the area of research concerning the characterization of high-temperature vapors based on the results of the first twenty-five years of high-temperature chemistry. All chapters 1 to 15 + 3 Appendices are useful; in particular chap.s 2 to 8 relative to vapor pressure methods

I.E. Campbell E.M.Sherwood,editors*"High Temperature Materials and Technology*
Electrochemical Society (Wiley),New York, London, 1967, 1022pp

Useful topics dealt with in Chapters 1-4; Chapters 18-27

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A.Prince, "*Alloy phase equilibria*", Elsevier, Amsterdam, 1966, 298pp

The main body of this text in fifteen chapters comprises a discussion on binary, ternary and quaternary systems. Binaries are treated in full, while ternaries and quaternaries more selectively.

D.A.Young, “Decomposition of solids”, Pergamon Press, Oxford, 1966, 209pp

Harald Schaefer, *"Chemical Transport Reactions"*, Academic Press, New York/London, 1964, 161 pp

A.W. Searcy, “*High temperature inorganic chemistry*” in “Progress in Inorganic Chemistry Vol. III”, F.A.Cotton editor, Interscience Publishers/ Wiley, New York, 1962, pp 49 - 127

A.W. Searcy, “*High temperature reactions*” in “*Survey Progress in Chemistry*”, A. Scott, editor, Academic Press, New York, 1963 pp 35 - 79

W.D.Kingery, *" Property Measurements at High Temperatures"* John Wiley, New York/ Chapman & Hall, London, 1959, 416 pp

An introductory book in fourteen chapters and appendices presenting description of measurements at high temperatures

J. O'M Bockris, J.L.White & J.D.Mackenzie, editor, *"Physicochemical Measurements at High Temperatures"*,Butterworths, London, 1959, 394 pp

A book in fifteen chapters and seven appendices dealing with various aspects (mainly experimental) of investigations in the field of high temperature physical chemistry

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> Contributions relevant to thermochemical and kinetic aspects of high-temperature gas-solid reactions, in particular oxidation of metals

“*Thermodynamics of nuclear materials 1974* “, Vols I and II, Proc. Symp. held by IAEA in Vienna, 1974
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E.Rutner, P.Goldfinger, J.Hirth, editors, *"Condensation and Evaporation of Solids"*
Proc. of an Int. Symposium held in Dayton, Ohio, September 1962; Gordon and Breach, New York, 1964

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Proc. of a Symposium, McGraw Hill, New York, London, Toronto,1959

Stanford Research Institute, "*High Temperature. A Tool for the Future"*
Proc. of a Symposium, Stanford Research Institute, Menlo Park, 1956

Materials Research Society Proceedings volumes:

The Hydrogen Cycle- Generation, Storage and Fuel Cells, Volume 885E, 2005 (only available as electronic version)

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The series of proceedings of High Temperature Capillarity Conferences:

"Proceedings of High Temperature Capillarity Conference 1994" edited by N. Eustathopoulos. Bratislava 1994. pp. 1-425.
"Proceedings of High Temperature Capillarity Conference 1997" edited by N. Eustathopoulos and N. Sobczak. Cracow 1998. pp. 1-419.
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Thermodynamic Tables, Compilations and Data Bases

Equilibrium thermodynamics is a valuable tool in the analysis and prediction of high-temperature reactivity only if reliable tabulated data are available

There are many compilations of tabulated thermodynamic data produced over the years, both in printed form and, more recently, in electronic form. Often for a given substance recent compilations revise and/or incorporate the data reported in older compilations.

M.W.Chase,Jr., C.A.Davies, J.R.Downey,Jr., D.J.Frurip, R.A.McDonald, A.N.Syverud editors, *JANAF Thermochemical Tables*, Third edition, JPCRD, Vol.14, Suppl., Washington, 1985; M.W.Chase,Jr. NIST-JANAF Thermochemical Tables, 4th ed.; J.Phys.Chem.Ref.Data; Monograph 9, American Chemical Society and American Physical Society for National Bureau of Standards, New York, 1998

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O.Knacke, O.Kubaschewski, K.Hesselmann, "*Thermochemical properties of inorganic substances*", 2nd ed., Spring Verlag, Berlin, 1991

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Other sources of thermochemical data:

Landolt-Bornstein, *Numerical Data and Fuctional Relationships in Science and Technology*, New Series, Vol. 5 sub vol b, B.Predel editor, Springer Verlag, 1992

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R.A.Robie and B.S.Hemingway, *Thermodynamic Properties of Minerals and Related Substances at 298.15 K and 1 Bar Pressure and Higher Temperatures*, U.S. Geological Survey Bulletin 1452; U.S GPO, Washington, 1978. This deals primarily with mineral compositions.

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

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A useful journal article summarizing the use of tabulated thermochemical data is:
Nathan Jacobson, "*Use of tabulated thermochemical data for pure compounds*" J.Chem.Ed. 78 (2001) 814 and refs cited therein

Inserire i data bases sul web elencati nelle Topics ?

Some Phase Diagrams Compilations

Phase Equilibria Diagrams- *Phase Diagrams for Ceramists*, Vol I(1964)---> Vol XIII (2001)
The American Ceramic Society, Columbus/Westerville,OH
For others check on the American Ceramic Society Web-site: www.ceramics.org

P.Villars, A.Prince, H.Okamoto, *Handbook of ternary alloy phase diagrams* (10 volumes set, 7380 systems), ASM International, 1995

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T.B.Massalski et al. editors, *Binary Alloy Phase Diagrams*, (3-Volume set) ASM International, Materials Park,OH, 2nd edition,1990. See also a version od this second edition plus updates on CD-ROM

For other compilations check on the ASM Web-site: www.asminternational.org

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Leo Brewer and Alan W. Searcy, *High Temperature Chemistry*, Ann. Rev.Phys.Chem. 1956,**7**, 259-85

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Journals specially dedicated to high temperature science

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"*High Temperature* ", english translation from russian of *Teplofiz. Vysok. Temp.* (1963→)

"High Temperature Science", subsequently "*High Temperature and Materials Science*," Humana Press, USA (1969→1997, discontinued)

"*High Temperature – High Pressure"*, Pion, UK (1969→)

"*High Temperature Technology"*, subsequently "*Materials at High Temperature"*, Science Reviews,UK (1982→)

"*Bibliography on the High Temperature Chemistry and Physics of Materials*", IUPAC sponsored project, M.G.Hocking (ed.), contributed from various scientists (now discontinued)

High temperature materials articles dealing with high temperature thermodynamics, phase equilibria, production and properties (thermodynamic, kinetic and and spectroscopic) of high temperature molecules, synthesis of materials by high temperature processes and properties and reactivity of these materials,combustion processes etc. were and are regularly published in many other journals and publications, e.g., without claiming completeness:

Journal of Electrochemical Society, Journal of Chemical Physics, Journal of Physical Chemistry A and B, Bulletin of Alloys Phase Diagrams (now Journal of Phase Equilibria), Journal Materials Research, MRS Bulletin, Combustion and Flame, Journal of Physical and Chemical Reference Data, Carbon, Journal Alloys and Compounds, Intermetallics, CALPHAD, Metallurgical Transactions A,B, Journal of Chemical Thermodynamics, Journal Materials Science and Materials Science Letters, Advanced Materials-Chemical Vapor Deposition.