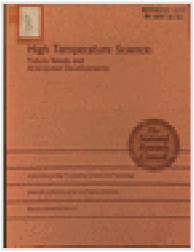

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High Temperature Science:

Future Needs and Anticipated Developments

Committee on High Temperature Science and Technology
Assembly of Mathematical and Physical Sciences
National Research Council

NATIONAL ACADEMY OF SCIENCES
Washington, D.C. 1979

NOTICE: The project that is the subject of this report was approved by the Governing Board of the National Research Council, whose members are drawn from the Councils of the National Academy of Sciences, the National Academy of Engineering, and the Institute of Medicine. The members of the Committee responsible for the report were chosen for their special competences and with regard for appropriate balance.

This report has been reviewed by a group other than the authors according to procedures approved by a Report Review Committee consisting of members of the National Academy of Sciences, the National Academy of Engineering, and the Institute of Medicine.

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PREFACE

High temperature science is concerned with chemical and physical behavior at temperatures, typically above 500 K, where the phenomena observed differ significantly from those observed at room temperature or predicted by routine extrapolation of room temperature behavior. High temperature science developed into an identifiable research field in the United States during the Manhattan Project in the early 1940's. The field has shown vigor, growth, and increasing sophistication because high temperature physical phenomena and chemical compounds -- both in the laboratory and in complex practical circumstances -- do indeed differ, sometimes dramatically, from predictions based on extrapolations of behavior at lower temperatures. Thus, new apparatus, new materials, new processes, new compounds, new understanding of chemical reactivity, and new ideas about chemical bonding in gaseous molecules and in solid phases have grown out of high temperature science.

During the past quarter of a century, high temperature science has grown into an active interdisciplinary field concerned with the investigation, correlation, and prediction of a multitude of chemical and physical phenomena. Topics covered in recent conferences and reviews of the field illustrate the varied experimental and theoretical tools which have become a part of this discipline: thermochemistry, electromotive force studies, vaporization studies, mass spectrometry, electronic spectroscopy, matrix isolation spectroscopy, high temperature laser spectroscopies, chemiluminescence, photoelectron spectroscopy, electron diffraction, X-ray diffraction, interaction of lasers with solids, solar furnaces, molecular beams (both gas-gas and gas-surface), reactivity of high temperature vapors with cold or hot substrates, electron microscopy, *ab initio* quantum mechanical calculations, and computer simulation of complex systems. These tools have been applied to diverse areas of high temperature science including the study of defect solids, corrosion, oxidation, transport under extreme conditions, flames, arcs, plasmas, liquid metals, slags, nucleation and growth of solids from the vapor, and chemical synthesis.

Practical reasons for interest in high temperature phenomena were pointed out in a 1967 National Research Council (NRC) report on this subject: "So many industrial operations -- combustion processes, electric discharges, and uses of nuclear reactors, for example -- as well as stellar processes, involve high temperature phenomena that one can regard 'high temperature' as describing a common condition of matter and, therefore, a condition deserving to be well understood." As that report anticipated, developments in high temperature science have become intimately intertwined with applied problems in such areas as energy conversion, aerospace materials, pollution, space propulsion, geochemistry, fabrication of solid state electronic components, and materials extraction.

High temperature science is now approaching a most exciting period. The technological challenge to improve the efficiency of energy utilization through high temperature processes arises directly from the second law of thermodynamics. The challenges of energy conversion and of innovative methods for extraction, production, fabrication, and recycling of materials point out serious gaps in our fundamental understanding of high temperature systems. At the same time, the enhanced understanding being gained from current research is pointing the way to new technological processes that would not have been conceived earlier.

Believing it timely to identify and call attention to areas of high temperature research where special progress might be required or anticipated in the next 10 to 25 years, the Committee on High Temperature Science and Technology (CHTST) of the NRC's Assembly of Mathematical and Physical Sciences organized the present study with support from the National Science Foundation (NSF). Suggestions were solicited from over 1,000 scientists by announcements, correspondence, and informal means in order to identify possible or probable basic research areas that high temperature scientists should, or will perforce, be concerned with because of new experimental techniques, new theoretical or computational capabilities, and advances or needs in other fields. More than 300 thoughtful contributions were received for which the Committee is greatly indebted to the corresponding contributors listed in Appendix B. Many of these responses were lengthy and detailed. After the external suggestions had been gathered, the present report was drafted at a writing workshop held in Reston, Virginia, March 19-21, 1979. The organization of report-drafting responsibilities at the workshop appears in Appendix A. By overlapping authorship and/or exchange of relevant documents, the present study was coordinated with recent NRC, Department of Energy (DOE) [formerly Energy Research and Development Administration (ERDA)], and NSF studies and workshops on chemical sciences, combustion, solid state sciences, data needs, and energy-related basic research in the materials sciences.

The report is organized as follows. Chapter 1 starts with an introduction and then summarizes some of the themes which are amplified and illustrated in the body of the report. It closes with a section which outlines the nature and history of high temperature science for those unfamiliar with the field. Chapters 2 to 7 detail basic research opportunities and needs in high temperature science. For this purpose, the field has been divided into subareas -- gases, gas-phase kinetics and combustion, solids, liquids, condensed-phase kinetics, and complex heterogeneous systems -- arranged roughly in order of complexity. Chapters 8 to 10 are of a somewhat different nature in that these focus on aspects of high temperature research that are of particular concern, and so gather together and expand upon points raised in Chapters 2 to 7. Chapter 8 describes the need for data, a problem which transcends high temperature science, but which is felt acutely by researchers in this field. Chapter 9 lists instrumentation needs and techniques; and Chapter 10 summarizes technological applications of high temperature research. Readers particularly concerned with industrial applications of high temperatures might find it helpful to read Chapter 1 *and* Chapter 10 before turning to other sections of the report. Each chapter, with the exception of the first, starts out with a section entitled "Summary and Conclusions" which highlights the findings of that chapter.

Although the present study owes much to the contributors listed in Appendix B, the CHTST and other workshop participants are responsible for this report and for any perceived deficiencies. It should be noted that the present study was funded through the Chemistry Division of the NSF; as a result, this study of the interdisciplinary field of high temperature science has an inherently chemical perspective which undoubtedly affects some of its emphases. In addition, because the writers and contributors are scientists active in high temperature research, their enthusiasm and commitment to the field cannot fail to be reflected in the report.

The Committee hopes that the report will be useful both to high temperature scientists and to science administrators by stimulating awareness of promising new research avenues, progress in areas where need for results is high, and research in dormant areas where basic advances could have significant impact on national problems.

Gerd M. Rosenblatt
Chairman

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INTRODUCTION AND SUMMARY

I. INTRODUCTION

High temperature science offers unique systems for study because the chemical species and physical processes that occur at high temperatures are often unusual and not predictable by extrapolation from conventional experimental temperatures.

High temperature behavior poses technological challenges. On the one hand, materials and processes developed for lower temperatures fail at higher temperatures; and, on the other hand, new processes and materials can be based upon high temperature behavior. Lack of recognition of unusual high temperature behavior can handicap technological progress. This would be unfortunate at a time when there is need for efficient, high temperature energy conversion processes (e.g., electric power generation and combustion), high temperature materials production processes (e.g., steel and aluminum), and precisely controlled, high temperature fabrication processes (e.g., solid state electronics devices).

Theories developed to accommodate room temperature behavior are often inadequate to deal with the unusual oxidation states, molecular complexity, and multiphase interactions encountered at high temperatures. In addition, it has been difficult to design and carry out high temperature experiments. These two difficulties have in the past caused high temperature science to take a largely empirical approach, devoted to acquiring and correlating an initial data base -- primarily thermodynamic and spectroscopic in nature. This work inherently focused on relatively simple high temperature systems that were amenable both to experimentation with limited techniques and to interpretation with limited auxiliary information.

Now, and in the coming 10 to 25 years, a potential exists for advances in both theoretical understanding and the study of chemically complex, high temperature systems. Complex high temperature systems are of fundamental interest because of the novel chemical species and physical phenomena encountered; and, at the same time, they are directly related to the difficulties and opportunities associated with harnessing high temperature technology. Recent and potential advances in theory, computer modeling, and experimental techniques -- described in the following chapters of this report -- will permit a view of high temperature processes in much greater detail, on a microscopic scale, and under much more controlled conditions. One senses an opportunity to transform a largely empirical science into one with a theoretical base providing broad predictive capabilities. In addition, this transformation will make the science even more relevant to the technology. Theory, molecular structure, macrostructure, defects, molecular interactions, atomistic mechanisms, and macroscopic rates and properties are beginning to be integrated into one coherent picture. Such unified understanding, desirable in itself, is necessary for fundamental science to have a maximum impact on the complex systems encountered in technology.

The chapters which follow make it clear that in the high temperature field an intimate and potentially rewarding relationship exists between basic and applied research. Because of this, there is an advantage in conducting high temperature research in varied institutional settings -- industry, government laboratories, different university departments -- and a need for practitioners in those different settings to be in communication with each other. There is additional motivation for university research in high temperature science: the need to train the scientists and engineers required to address the high temperature problems associated with energy, materials, and environmental needs.

II. ANTICIPATED RESEARCH DEVELOPMENTS AND NEEDS

The following chapters of this report describe research opportunities and needs in various subdivisions of high temperature science. Each leads off with a section entitled "Summary and Conclusions" which highlights some of the major findings and concerns for that subarea. The present section will focus attention on some themes that are reflected in the contents of more than one chapter and are representative of research needs and opportunities in the whole field.

The items listed are a mixture of research one *anticipates* will or could occur, based upon extrapolation of recent scientific developments, if funding is made available; and developments in experimental capability or theory which are *needed* to solve fundamental or technological high temperature problems. These are not separated into categories because, although in some cases the classification is obvious, many items fall into both. The "needs" require scientific advances (which seem probable if given adequate attention and funding, but are not guaranteed) with the exception of the need for data evaluation, compilation, and dissemination, where the major requirement is a sound, long-term funding mechanism.

Studies of Complex Systems

The emerging capability to investigate chemically and physically complex systems promises new fundamental understanding, as well as new opportunities for interactions between subfields and between basic and applied science.

Gaseous Systems

Gaseous systems at high temperature and atmospheric-or-greater pressure may consist of mixtures of currently known and unknown vapor molecules, ions, electrons, liquids, and solids. Such systems can be studied by a combination of mass spectrometric and spectroscopic techniques. Pulsed lasers offer a potential means of making the short time scale (10^{-9} to 10^{-12} sec) measurements required to study interactions in such systems.

Reactions Far Removed From Equilibrium

Studies of reactions far removed from equilibrium are needed because the reaction products and rates can be significantly different from near-equilibrium reactions. Examples range from the flash pyrolysis of biomass, and the decomposition of solid propellants and complex salts, to the chemical changes produced by large temperature gradients in nuclear reactors, magnetohydrodynamics (MHD) channels, and solar receivers.

New Materials

From the viewpoint of new materials, temperature/pressure combinations unknown in nature provide a host of opportunities. Combinations of high and low temperature techniques, selective quenching of reactants and/or products, plasma chemistry, 4000 K solar furnaces, optical or electron-impact reactant excitation, and chromatographic and mass spectrometric separation allow preparation of new reactive molecules and new materials which will offer opportunities for technological innovations beyond current conception.

Mass Transport

Mass transport along microstructural imperfections such as grain boundaries, crystallographic shear planes, dislocations, and other imperfections affects corrosion rates, component lifetimes, and materials processing. Innovative new techniques are needed to characterize the fine structure of grain boundaries and to measure diffusion in grain boundaries.

Diffusion

Diffusion under gradients of chemical potential, of temperature, and of mechanical stress are major factors in technological failures. In addition, research to determine the interactions of mechanical and chemical effects will aid development of new machine tools and will help understand such phenomena as stress corrosion cracking, erosion-corrosion, and explosions that occur when melts (metal slags, salts) drop into water.

Gaseous Atomic Aggregates

Studies of the gaseous atomic aggregates that form in high temperature vapors will lead to understanding their bonding, structure, and reactivity. High temperature clusters and their ions can be studied by combinations of nozzle beam, mass spectrometric, matrix isolation, and spectroscopic techniques.

High Temperature Reactions

High temperature reactions involving condensed phases and gaseous products occur in many technological applications including catalysis, corrosion, evaporation, sputtering, combustion, and calcination. Increased understanding of the kinetics and mechanisms of these reactions will result from use of sensitive diagnostic tools such as simultaneous Auger and energy analyzed secondary ion mass spectroscopy, laser fluorescence spectroscopy, and special reaction chambers for *in situ* electron microscopy.

Mixed Oxidants

Significant progress is anticipated in understanding high temperature oxidation by mixed oxidants, a process which is important in technology and involves complex chemistry.

New Experimental Techniques

Developments in experimental techniques and in extending the temperature range of older techniques offer new opportunities for detailed study of high temperature properties at the molecular level.

Coupling

Coupling of complementary techniques, new materials, new heating techniques (including solar furnaces), small laboratory computers, and use of field sites for complex experiments are revolutionizing the rapidity and accuracy of data acquisition and the control of experimental parameters.

New Detection Methods

Developments in use of synchrotron radiation, nozzle beam sources, lasers, and radiation detectors offer exciting potential for determining molecular structures, microstructure, composition, temperature, surface structure and composition, and local atomic-coordination environment.

Lasers

Lasers make possible high dispersion spectroscopy of both simple and complex high temperature gaseous molecules. High resolution spectra are needed both to advance chemical theory and to supply a data base for optical diagnostic studies of flames, plasmas, propellants, etc.

High Spatial Resolution

The severe environments encountered at high temperatures demand high spatial resolution in the characterization of the composition and microstructure of solid samples. These requirements are being realized in electron microscopes with 2 Å resolution. With these microscopes, diffraction may be obtained from 50 Å diameter particles. Energy dispersive X-ray spectroscopy (EDS) and electron energy loss spectroscopy (EELS) are promising supplementary techniques.

Established Techniques

Mass spectrometry, electromotive force methods, calorimetry, X-ray diffraction, matrix isolation, infrared, Raman, and electron spin resonance spectroscopies, tracer diffusion, and other established techniques continue to be important because they provide thermodynamic, molecular, and kinetic data that are needed for effective utilization of newly developed methods.

Liquids

X-ray and neutron diffraction and, particularly, extended X-ray absorption fine structure (EXAFS) provide information concerning short range order in liquids. There is a need to understand molecular interactions and structure in high temperature, strongly interacting liquids. Development of further techniques applicable to high temperature liquids is necessary.

Shock and Static High Pressures

High pressure-high temperature conditions can be reached by both shock conditions and static experiments, such as a combination of diamond anvil and laser heating.

New Spectroscopic Methods

Recently developed spectroscopic and mass spectrometric methods will enable investigations of structure and bonding in positive and negative molecular ions. This, in turn, will increase the understanding of bonding in other unusual high temperature molecules. Gaseous molecular ions are present in arcs, flames, and plasmas and are formed in mass spectrometric investigations of uncharged molecules.

Coupling of Theory and Experiment

There are major opportunities for synergistic interactions between theory, computer modeling and simulation, and experiment in advancing basic understanding and attacking technological problems.

Multiphase and Multicomponent Systems

Studies of complex systems will be enhanced by coupling theory to experiments in key, well-characterized systems to form the basis for the extensive modeling required to correlate variables in multiphase heterogeneous systems and in multicomponent liquid and solid solutions.

Computer Modeling

Computer modeling of complex high temperature phenomena is an important high temperature technique in itself. Modeling links the experimenter and the theorist, and the basic and applied researcher. It indicates gaps in basic information, allows sensitivity testing of different experimental parameters, and can reveal flaws in a data set.

Reaction Rates

Increased fundamental understanding -- both experimental and theoretical -- will enable investigators to extrapolate high temperature elementary chemical reaction rates to new conditions and to model complex nonequilibrium systems. Studies of reaction rates of state-selected species along with space-and-time probes of "real" systems, will contribute to the increased understanding required.

Quantum Molecular Theory

Quantum molecular theory should be applied and extended to calculate as accurately as possible the electronic and vibrational properties and the structure of the unusual inorganic molecules, ions, and clusters formed only at high temperatures. Fundamental theories are needed to describe the molecular structure and bonding of liquids.

Molecular Structure and Chemical Reactivity

There is a need to investigate and correlate similarities and differences of molecular structure -- and also, of chemical reactivity -- in gas, liquid, and solid states. Changes of pressure (e. g., high pressure studies) as well as temperature can provide valuable information.

Availability of a Data Base

Progress in a multidisciplinary field such as high temperature science depends upon the availability of a reliable data base, readily accessible to both basic researchers and technological problem solvers.

- Data play a particularly important role in high temperature research because of the intricacies of the experiments and the inherent complexity of high temperature systems.
- Reliable data are needed at all stages of research and development but the need is particularly acute when a technological program is first conceived.
- A wide variety of data needs to be accessible including spectroscopic data, molecular energy data, thermodynamic data, transport data, cross sections, kinetic data, etc. for pure compounds, ions, and mixtures.
- Data must be critically evaluated and broadly disseminated. This requires dedicated financial support and an organization to coordinate widely dispersed evaluation efforts.
- Because key data must be measured by the most accurate experimental techniques available, classical experimental methods which yield accurate data must not be neglected.

III. ORIGINS AND NATURE OF HIGH TEMPERATURE RESEARCH

As background for the detailed analysis of research opportunities and needs presented in the chapters which follow, this chapter closes with a brief review of the origins of high temperature research, methods to generate and measure high temperatures, and some applications of high temperatures.

Historical Background

The use of high temperatures dates back to the discovery and utilization of fire. Metallurgical processing of ores to obtain mercury, lead, and iron; the fusion of sand with other oxides to form glass, tile, and bricks; the utilization of solar heating for dehydrating biomass or for extracting salt from sea water; fire assaying of minerals; and the distillation of alcoholic beverages are examples of long-established technologies. On the other hand, the necessary ground work for science at high temperatures was only available after a coherent periodic table of the elements was constructed, an appreciation of the chemical significance of oxygen in combustion was developed, and after efficient means for generating electrical current were perfected.

Methods for generating and utilizing high temperatures have evolved from the primarily "brute force" techniques represented by the huge coke-fired furnaces of the steel industry, the electrical-heated tanks of molten glass, and the gas-fired reactors and kilns of the refractory and cement industries to a high technology based upon sophisticated devices, new materials, and scientific expertise. Not only can high temperatures be maintained over large volumes for long times but controlled pulses of energy can be used to heat individual atoms or molecules selectively for very short periods of time.

It is now routinely possible to generate temperatures of thousands of degrees in moles of material over periods of hours at low or high pressures. At the forefront of current technology it is possible to generate temperatures of tens of millions of degrees in micromoles for picosecond periods in high vacuum systems. Obviously the techniques for generating and measuring high temperatures span a wide range of disciplines and devices. High temperature scientists now have an opportunity to use a range of temperatures unprecedented in history. A variety of synthetic achievements and gains in understanding of molecular and atomic phenomena have already been made possible by application of high temperature techniques and one anticipates further significant achievements will result from new capabilities to produce controlled high temperature environments.

The Generation of High Temperatures

A system at "high temperatures" contains more energy (electronic, translational, vibrational, or rotational) than it does at a lower temperature. The usual reference "low temperature" is near room temperature (15° to 25°C) but absolute zero is also used as a reference. A combination of thermodynamics, statistical mechanics, and quantum mechanics has led to appreciation of the surprisingly subtle ways in which modern technology may generate and utilize high temperatures.

The attainment of uniform temperatures above 1500°C over an extended period of time is currently limited by the availability of suitable construction materials. Such temperatures are usually generated in the laboratory by electrical means; although where weather cooperates, the sun may be utilized directly as a source of radiant energy. Electrical-powered heating devices have been favored over chemical methods (combustion) because of simplicity of design, ease of operation, and the ability to control atmosphere and temperature. The gas-fired furnace, typical of the chemical method, has found wide application in industry because of economics; but current energy problems are changing this. There is a new surge of interest in solar augmentation of gas-fired furnaces, in the use of coal or lignite, and in other novel approaches to high temperatures. For extremely high temperatures one can use chemical explosives, electric arcs, shock waves, lasers, and fission or fusion nuclear reactors. Table 1 summarizes some of the more important and practical methods for generating high temperatures. The maximum temperatures indicated are extreme upper ranges, far above those usually achieved using the techniques described.

Measurement of High Temperatures

Temperature-measuring techniques have necessarily become more sophisticated as new temperature-generating techniques have been developed. Ideally an absolute temperature scale is based on thermodynamics and statistical mechanics and then the absolute scale is used to establish a convenient laboratory reference scale against which laboratory or plant thermometers can be compared and calibrated. Since the range of temperatures to be measured can extend from the temperature of boiling He, O_2, H_2O, or S to the temperature of the gaseous ions generated in a nuclear fireball, it is not surprising that no single measuring device or method is universally applicable. Laboratories such as those of the National Bureau of Standards (NBS) and its international counterparts have long been concerned with consistent, precise, and convenient temperature scales for use in industry and research. Through cooperative efforts international committees have devised practical temperature scales with specified limits on precision and accuracy. Table 2 summarizes some modern techniques for measuring temperatures.

The Utilization of High Temperatures

It is clear that one needs not only to be concerned with generation but also with applications of high temperatures. Some of these are obvious and many of them predate modern concepts and theories of physical and chemical phenomena. Keeping warm, cooking food, lighting the way at night, manufacturing and using fireworks, and purifying metals such as mercury, gold, silver, and copper are among the ways in which high temperatures have been utilized for at least 3,000 years. Molding bricks and blowing glass, using gun powder, preparing iron alloys, and fire assays were among the common applications of high temperatures in the Middle Ages. Applications mushroomed with the isolation of oxygen and the basic understanding that combustion required a fuel and an oxidizer. The development of batteries for producing electric current and the construction of high voltage/high current electrical machines now make it possible for any laboratory to produce temperatures ranging from a few hundred to tens of thousands of degrees.

High temperature syntheses can often be carried out simply by mixing the reactants (or compounds that will generate the reactants)

TABLE 1. Generating High Temperatures

Method	Temperature Range	Remarks
Electrical resistance heating	Up to 5000 K, depending on the conductor and the atmosphere	Neutral: most metals; Oxidizing: Pt, Ir, oxides, Alloys; Reducing: W, Ta, Mo
Chemical flames and explosions	Up to 7000 K, depending on products and reactants	Mixture of ions, electrons, and neutrals; not likely in thermal equilibrium
Exploding wires	Up to 10^4 K	Limited by heat capacity, melting point, and ionization of gases
Shock waves	Up to $2\cdot5 \times 10^4$ K in gases; high temperatures and pressures in solids	Mixture of ions, electrons, and neutrals often approaches equilibrium
Imaging and solar heating	Up to $2\cdot5 \times 10^4$ K, depending on source	Collect, concentrate, and focus to get highest temperatures
Induction heating	Up to 10^5 K	Suitable for solids, liquids, or gases; levitation possible
Electrical discharges	2×10^3 to 10^6 K	Mixture of ions, electrons, and neutrals; not likely in thermal equilibrium
Lasers	Up to 10^{10} K	Versatile and especially useful on 10^{-9} to 10^{-12} sec time scale; selective introduction of energy into molecules
Fision and fusion	10^7 to 10^{10} K	Almost limitless energy resource; couples with chemical methods for many applications

TABLE 2. Measuring High Temperatures

Method	Temperature Range	Remarks
Thermocouples	Up to 3500 K	Choice depends on atmosphere and precision desired; many available
Resistance thermometers	Up to 1500 K	Highest precision but not yet applied at extremely high temperatures
Optical pyrometry	Applicable at any temperature, as predicted by Planck's Law	Need to correct for nonideal radiating surfaces; useful for fast time response systems
Spectroscopy (relative intensities, line reversal, line broadening, etc.)	Applicable at any temperature as permitted by Planck's Law and/or Boltzmann's Distribution Law	Useful for flames, electric discharges, explosions, and astrophysical systems

and heating the mixture. Two factors determine whether a particular synthetic approach is practical: the reaction must be thermodynamically possible, and the rate of formation of product must be appreciable and must exceed its rate of decomposition. At high temperatures, reaction rates are generally fast; therefore, thermodynamic factors are often more important than kinetic factors. In electric arcs, however, species exist with the thermodynamic potential to form almost any molecule so kinetics determine which molecule results.

A few recent uses of high temperatures are summarized in Table 3. Research needs associated with these and other applications are described in the chapters which follow.

TABLE 3. Utilizing High Temperatures

Applications	Technological Uses and Remarks
Syntheses of new materials	Mixing and heating, pyrolysis, photolysis, condensation on low temperature surfaces, electrochemical methods, electric arcs and plasmas, flames
Growing single crystals of high purity and perfection	Recrystallization of solids, high pressure sintering, Czochralski and Bridgman techniques, molten zone processes, Verneuil process, hydrothermal syntheses, epitaxial growth from vapor, chemical vapor decomposition
Generating high energy fuels and oxidizers	Cycles for producing H_2, CH_4, metal hydrides, etc., electrochemical oxidations
Collecting, converting, and storing solar energy	Requires a combination of basic engineering, physics, and chemistry to accomplish process efficiently
Magnetohydrodynamics	Direct production of electricity from charged species in chemical flames

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PROPERTIES OF HIGH TEMPERATURE GASES

I. SUMMARY AND CONCLUSIONS

Currently available information concerning high temperature vapors is inadequate to supply the needs (temporal and spatial composition, temperature, thermochemistry) of the scientists and engineers investigating the phenomena occurring in this regime. Basic molecular data, particularly of ions, are required and will continue to be best obtained by a full array of experimental measurements, overlapping and interdependent, including gas phase and matrix work and employing highly developed and innovative instrumentation. Simultaneously, a data base of gas phase optical spectra, sufficiently dispersed to be useful for laser diagnostic purposes, must be built up.

Specific perceived research needs follow:

- Spectroscopic data are needed, with particular emphasis on molecular ions, to provide electronic and vibrational properties, potential energy curves, structures, etc. in ground and excited electronic states.
- Accurate molecular energy data, such as bond dissociation energies, ionization energies, etc., should be obtained by both equilibrium and impact methods.
- High dispersion spectra of high temperature gaseous species are required as a data base for laser diagnostic studies.
- Metal and nonmetal clusters, cluster ions, and their complexes should be studied by a wide range of experimental techniques.
- Theory should be applied and extended to calculate as accurately as possible the electronic and vibrational properties and structure of relevant molecules, ions, and clusters and to provide models for general understanding and prediction.

II. INTRODUCTION

Vapor species encountered in high temperature environments vary widely, from atoms and light hydrocarbon fragments, such as CH, to heavy metal-containing complex molecules such as K_2SO_4 and W_3O_9. They also include charged species and sometimes large aggregates or particulates.

In the many instances at high temperatures where gases are involved (e.g., combustion, MHD, propellants), the intrinsic properties of the vapor species and the degree of their energetic excitation determine what occurs chemically. Accordingly, measurement of the mechanisms and progress of chemical reactions in such systems requires, not only the establishment of the species present, but also the distribution of energy, i.e., among electronic, vibrational, and rotational states. It is then clear that knowledge of all of the energy levels of relevant molecules and ions is needed, perhaps up to at least 3 eV.

As is generally true in science, it is often necessary for several experimental methods to be applied to obtain the needed data. For high temperature gases these are sometimes very diverse -- involving, for example, observations of equilibrium (effusion) beams, supersonic beams, and molecules trapped in solid inert gases (matrix isolation). These techniques are usually complementary and each adds unique and essential information.

III. THERMOCHEMISTRY OF NEUTRAL SPECIES

Thermochemical data (bond dissociation energies, enthalpies and Gibbs energies of formation, entropies, ionization energies) are vital to the understanding of chemical bonding and reactivity of high temperature gaseous species. The data are also used in a wide variety of technological applications such as metallurgical processing, glass manufacture, propulsion, nuclear power generation, and MHD. Although well-developed experimental techniques for determining thermochemical properties are available, there are many frustrating discrepancies and gaps in the literature. This, together with the demand for more precise and accurate data on high temperature molecules, calls for the development of new and improved experimental techniques, as well as more innovative uses of existing techniques.

A further reason for using more innovative techniques is increasing interest in the properties of complex gaseous molecules such as the ternary species (K_2SO_4, Na_2CrO_4, Cs_2MoO_4, $AlCuCl_5$, MgW_2O_7, FeOH, $NaPO_3$, $NaAlF_4$), along with gaseous metal cluster species M_x with or without ligands (CH_2, CH_3, H, CO) attached. Suitable experimental techniques and possible new developments are described below.

Equilibrium Techniques

Most available thermochemical data for high temperature gaseous species have been determined by the technique in which mass spectrometry is used to study chemical reaction equilibria, using a low pressure effusion beam source. This has proved to be the most reliable and universally applicable technique for the study of a wide range of high temperature molecules; and it will continue to play a central role in the future.

In past studies concerned with binary compounds of metals, interferences arising from ions produced by electron-impact fragmentation in the mass spectrometer ion source have frequently been overcome through the use of low ionizing energies, a procedure that has been generally satisfactory. However, the fragmentation of ternary species, most of which are mixed dimers bonded through bridging ligands (e.g., $NaF \cdot AlF_3$, $EuO \cdot WO$) is often quite extensive even at low ionizing energies. The same is expected to be true of complex gaseous cluster species.

Therefore, the development of alternate ionization processes yielding simpler mass spectra with maximum abundances of parent ions is clearly desirable and necessary. One such approach might be multiphoton ionization. Single photon ionization using a narrow range source, such as a resonance line, may achieve the same result in some systems. Another gentle ionization process that appears to yield a high proportion of parent ions is charge-transfer ionization of the type

$$Ar^+ + NO \rightarrow NO^+ + Ar.$$

Fragmentation might be minimized by picking a projectile ion which has an ionization potential only slightly in excess of that of the target molecule.

Charge transfer calls for a somewhat complex ion source arrangement and has not yet been applied to high temperature species; but it merits serious evaluation as a method for producing simplified mass spectra. Developments of this type could produce significant advances in mass spectrometric detection and study of complex molecular species such as the ternary species and clusters discussed above.

A potentially important benefit of equilibrium studies is the determination of relatively accurate entropies from the temperature coefficients of reaction equilibrium constants (second-law method). With care, it is possible to carry out second-law determinations so that experimental entropies reliable to within 0.5 cal/deg mol are obtained. Comparisons of experimental entropies with values calculated from spectroscopic data will substantially decrease the thermodynamic uncertainties resulting from lack of information about low-lying electronic states, and will yield useful data for many applied calculations. Because of the limited data on the electronic states of the transition, lanthanide, and actinide compounds, this line of research should be pursued vigorously. The second-law method could be further enhanced by the use of highly sensitive detection methods, such as laser-induced fluorescence, to monitor species abundances.

Better diagnostic methods are also required for the sampling and study of vapors in higher pressure regimes (≥ 1 atm) characteristic of transpiration experiments. Traditionally, such experiments have been limited by uncertainties about vapor composition. Considerable effort is being devoted to the development of mass spectrometric techniques for this type of high pressure sampling. Spectroscopic techniques such as coherent anti-Stokes Raman scattering (CARS) and laser-induced fluorescence might also be very fruitful.

Impact and Beam Techniques

Several other techniques emerging as important sources of thermochemical data are dissociative photoionization with mass analysis, the crossed-beam chemiluminescent reaction technique, and the crossed-beam method of studying endothermic reactions using fast beams of neutral or ionic reactants. The advent of tunable UV lasers with suitable energy ranges will permit study of the energetics of photodissociation processes with greatly increased accuracy. So far, these techniques have been applied to only a few of the smaller high temperature molecules; but they have great potential and in the long run should be among the most accurate for determining bond dissociation energies.

IV. GAS PHASE SPECTROSCOPY

Providing Accurate Molecular Properties and a Data Base

The emergence of the laser as a powerful diagnostic tool (Eckbreth *et al.*, 1977) in extreme environments, including flames and plasmas, makes possible accurate, real time *in situ* detection and measurement of high temperature gas molecules. However, use of such laser techniques is being limited to the smaller species because of the lack of even rudimentary spectral data for poly-atomic high temperature radicals. The high resolution spectroscopic data base must be expanded, not only to include more stable molecules, but also the radicals and ions present in high temperature environments. The task is enormous. The basic researcher must make a judicious choice, from broad classes of vapor molecules, of the molecules to be studied in detail -- keeping in mind the needs of high temperature technology and also the theoretical significance of the results.

In this context there are large gaps in the available spectroscopic data on high temperature gaseous molecules (Huber and Herzberg, 1979). Unresolved spectroscopic problems are still abundant among the transition metal oxides, and particularly in the rare earth and actinide monoxides. Diatomic carbides, nitrides, sulfides, and halogens; alkaline earth hydroxides; and metal diatomics (see Section VI) all need further investigation. With the addition of triatomics the list becomes forbiddingly long. Furthermore, these are only the neutral molecules, their positive and negative ions are also important (see Section V). The length of the list emphasizes the need for careful selection of the systems chosen for study, periodic-table correlations, and coordination of experiment with theory.

As spectroscopic data improve new methods will be needed for calculating high temperature partition functions -- including anharmonicity -- and accounting for the increased number of populated electronic states.

Then it appears that, in the near future, gas phase spectroscopic data on high temperature molecules will develop along two paths -- both vital to basic knowledge and to technological progress:

Systematic Studies

Complete systematic studies of families of molecules utilizing the power of laser-induced fluorescence, multiple resonance, and Doppler-free techniques are needed to yield unambiguous information about electronic energy level diagrams. This includes full rotational analyses, detailed understanding of perturbations, and reliable measurements of electronic transition strengths. Under computer control, frequencies and parity assignment of lines can be directly recorded.

As mentioned earlier, low-lying electronic states of relevant molecules have been a concern because of their population and contribution to thermodynamic properties at high temperatures. Multiphoton laser excitation may permit these levels to be probed at IR energies and with high enough resolution to pinpoint their detailed properties.

Supersonic nozzle expansion may allow hot molecules to form a beam in which rotational and vibrational temperatures are effectively below room temperature and thereby provide, with laser probes, "cold" spectra of gas molecules which are normally present only in high temperature environments. Experiments of this type would utilize techniques recently applied to stable molecules for the more difficult investigation of high temperature molecules. The approach is promising and certainly will be attempted.

High Dispersion Spectra

Studies of high dispersion spectra of molecules should be made for diagnostic purposes as needed for practical devices or where the spectra are more difficult to analyze. Because they are formed in reactions with walls, impurities, etc., more complex high temperature species are of growing interest. Their spectra may be more difficult to observe and to analyze in great detail because of their complexity or because they contain several heavy metal atoms.

Rotational Spectra

The pure rotational spectrum of diatomic CaO was observed in the millimeter wave region by producing the molecule through oxidation of metal vapor, entrained in argon carrier gas (Creswell *et al.*, 1977). This provides a CaO molecule at ~500 K, much lower than ~3000 K to which solid CaO must be heated to produce 1 torr of CaO(g). Accurate structural and vibrational data were obtained in the ground and first excited vibrational states. This procedure circumvents some of the high temperature container problems and promises to provide accurate data for many oxides and other high temperature species.

Other Tunable Laser Applications

An excellent example of the benefits of laser state-selected spectroscopy, other than those referred to above, is in the excitation of atomic uranium -- and other actinides and lanthanides -- to particular Rydberg states to yield an accurate value of the ionization limit (Solarz *et al.*, 1976). By monitoring the photoions produced by a tuned laser and preferentially detecting Rydberg states with $n > 60$, a highly accurate ionization limit was derived by series convergence. The implications for future application to high temperature molecular species are clear and inviting.

Other Means of Generation

Multiphoton dissociation may also be used to create high temperature species and to observe their emission from excited states (Karny *et al.*, 1978; McDonald *et al.*, 1978). For example, from irradiation of acetylene at 193 nm with an ArF excimer laser, C_2 molecules are observed in emission from three excited states and CH from its excited $A^2\Delta$ state. This then is a means for producing large yields of fragments in an energy region which was previously accessible only with far-vacuum UV photolysis sources.

High peak-power lasers can be used as ablating devices or can be focused into a gas to produce very high temperatures (perhaps 10,000°C) in a short period of time, less than 100 nanoseconds. For example, vaporization of metals in an atmosphere of oxygen could produce gaseous refractory oxides which could be monitored in time by CARS, laser-excited fluorescence, saturated fluorescence, or picosecond spectroscopy. Ablation by this means was achieved many years ago, and emission observed; but now tools are available to explore the species and the chemistry occurring during, and subsequent to, the formation of the expanding plasma. Molecules and ions may be present in the reacting gases which are not present in detectable amounts when generated by other means.

Other Techniques

Electron diffraction of high temperature vapors is now routinely operating at temperatures up to ~600°C. It is likely that pulsed heating methods and pulsed electron beam scattering will be developed with gateable detector arrays. This would avoid the present limitations of photographic fogging caused by emission from heat sources.

V. MOLECULAR IONS

It has become increasingly evident in recent years that molecular ions are important contributors to many high temperature technological, and also atmospheric and astrophysical, phenomena. These include MHD devices;

other plasmas associated with lamps, lasers, and photochemical sources; flames; the ionosphere; and interstellar clouds. Compared with neutral molecules, knowledge of the properties of ions is in a rudimentary state. Besides detailed spectroscopic data, as discussed in Section IV, a primary datum for an ion is its formation energy -- the adiabatic first ionization potential of a neutral which yields the positive ion, and the electron affinity of a neutral which gives rise to the negative ion.

Accurate ionization potentials can be obtained from variable wavelength photoionization (with or without mass analysis), photoelectron spectroscopy, and from limits of Rydberg series. Correspondingly accurate electron affinities are attainable with fixed or variable wavelength photo detachment experiments on negative ions. In difficult cases, flow discharge methods have been used to set useful limits.

Photoelectron spectroscopy (PES) provides information, not only on the adiabatic first ionization potential, but also about excited states of the ion. In favorable cases, it can reveal vibrational frequencies and geometries (e.g., internuclear distance) of the ion from fine structure in electronic bands and Franck-Condon analysis of band envelopes.

Only a small amount of such information is available for species that fall in the high temperature domain, such as metal halides and metal oxides. In most cases, high temperature PES studies have not resolved vibrational structure, due to Boltzmann broadening and various limitations to apparatus resolution with high temperature samples. However, a recent study of SiO^+ reported vibrational fine structure; and this augurs well for the future.

Occasionally, the photo-induced reaction with negative molecular ions is not photo detachment,

$$h\nu + AB^- \rightarrow AB^\circ + e,$$

but rather photodissociation, i.e.,

$$h\nu + AB^- \rightarrow A^- + B.$$

Photodissociation of positive molecular ions has become a general and powerful experimental technique in ambient temperature research. It has yet to be applied to molecular ions that would be identified as high temperature species, although no fundamental obstacle exists to this extension. The high resolution available with tunable dye lasers enables one to obtain much more detailed information about these states than is generally available from PES. However, it is presently limited by the wavelength range of existing dye lasers to excitations not exceeding ~2.5 eV for single-photon processes.

Perhaps the most precise information on the spectra and structures of complex, high temperature free molecular ions derives from fluorescence studies initiated by discharges of controlled electron or photon impact. A review paper in 1971 listed 33 diatomic, 4 triatomic, and 1 polyatomic ions for which such spectra existed (Herzberg, 1971). This list included a few metal-containing systems such as BeH^+, MgH^+,

ZnH^+, CdH^+, HgH^+, and AlH^+. Since that time, the numbers have grown to include some 50 diatomic ions, 10 triatomic ions, and several polyatomic ions (Allan *et al.*, 1977). Few of those so far investigated are high temperature species; however, one can anticipate a growth in such information in the next decade. When available, such spectra can often be analyzed to yield geometries, vibrational frequencies, and electronic excitations. Laser-induced fluorescence studies of some of these ions, in the gas phase and in matrices, have already helped to unravel the vibrational structure. Rotational transitions may be probed by laser magnetic resonance spectroscopy in the far infrared. These spectroscopic experiments do not provide ionization potentials, and thus are complementary to the experiments described earlier. Such structural and spectroscopic data are needed to characterize the thermodynamic properties and chemical behavior of high temperature species.

Two recent advances warrant special mention:

- Woods and collaborators (Saykally, 1976) have succeeded in obtaining the microwave spectra of two ions, HCO^+ and HN_2^+. They produced these species in laboratory discharges, and upon analysis, were able to relate them to lines observed in the interstellar medium. Highly accurate structural information can be derived from such studies, but their importance also stems from their diagnostic value in identifying radio signals.

- Gemmell and collaborators (Gaillard, 1978) have introduced a technique whereby they accelerate molecular ions to the MeV range and direct them at a thin foil. Light molecular ions are largely stripped of their remaining electrons within a few angstroms of the entrance surface. The constituent atomic-like ions then undergo a "Coulomb explosion" as the initial potential energy is converted into kinetic energy. For carbon targets, a significant portion of the Coulomb explosion occurs downstream in the vacuum outside the target. The initial configuration can be deduced in favorable cases from a measurement of the final velocity distributions of the dissociation fragments. In a recent application of this technique, studies of H_3^+ show that its structure is an equilateral triangle, a conclusion which heretofore was based on theoretical calculations.

Finally, as the electronic spectra of molecular ions become better known, the very high sensitivity of laser-induced fluorescence may be utilized to monitor these ions, either as reactants or products, and may provide a new dimension to ion-molecule studies.

As discussed in more detail in Section VII, an increasing number of molecular ions have been matrix isolated, i.e., trapped in the solid rare gases at 4 to 10 K. This permits a range of experimental studies on "cold" high temperature molecules, some of which are not possible in the molecules' normal gaseous state.

VI. METAL ATOM AND INORGANIC GASEOUS AGGREGATES AND PARTICULATES

Over the last five years, general interest has emerged in the properties and chemistry of metal atom clusters (M_x, where $x \geq 2$) because of their relevance to such diverse areas as heterogeneous catalysis and surface chemistry, homogeneous nucleation, photographic processes, dust formation and the chemistry of interstellar space, propellant particulates, and metal dusts in chemical synthesis, in addition to their direct role in high temperature, high pressure vapors. Aggregated species are characteristic of saturated, high temperature vapors and increase in density and complexity as temperature and pressure increase. This is a significant field of research because of the direct connection it provides between gas phase molecules and condensed phases. This intermediate state of matter has been poorly explored, and it can be expected to provide new knowledge. Structural and electronic changes with increasing x and with variation of temperature are clearly of great interest.

These aggregates can occur in hot, equilibrated inorganic vapors and also can be formed from such vapors by expansion or gradual accretion. A variety of clusters [e.g., Sn_x, Pb_x, S_x, $(LiF)_x$, C_x, Si_x] have been investigated by sampling from the equilibrium vapor (effusion) in a mass spectrometer. More recently advantage has been taken of supersonic nozzles which produce relatively high concentrations of the larger clusters. Even higher concentrations can be produced and more readily studied by controlled diffusion of the smaller species when trapped (matrix isolated) in the solid rare gases at low temperatures.

At present the thermodynamic, structural, and electronic properties of almost all high temperature clusters, even most dimers, are unknown. This rich research area needs more imaginative experimental work. Undoubtedly the greatest breakthrough would occur if clusters of a single size could be generated, preferably in the gas phase, so that variation in their properties could be observed as a function of x, eventually approaching the bulk phase. In matrices, photoclustering, wherein the concentration of a particular cluster is diminished and others formed by irradiation in the absorption region of the clusters, has been useful in identification.

Research should be broadened to include clusters of all sorts of inorganic compounds, from ionic salts to refractory metal oxides. For example, condensates of silicates, oxides, and carbon -- involved in fly ash formation in a coal-fired reactor -- are of interest to astrophysicists because they form interstellar grains at very low densities. Experimental work on such clusters is just beginning.

Spectroscopic studies of many different kinds will yield useful information, including laser-induced fluorescence, Raman, Mossbauer, EXAFS, ESR, PES, magnetic circular dichroism (MCD), photoionization, mass spectrometry, and UV-visible. Intermetallic clusters are also of interest; some of them have been observed in fluorescence and via Mossbauer and mass spectrometry. Extension to the more difficult oxide and silicate aggregates should also be attempted.

Size and shape effects have been observed in light scattering from small particles of Ag, Cu, and Au (2 to 150 nm) in the gas phase (Eversole and Broida, 1977). A resonance peak at 367 nm in the spectrum of Ag particles was attributed to the collective oscillation of conduction electrons. The width of the resonance was deduced to be influenced by nonspherical shapes as well as by collisions of conduction electrons with the particle surface. Similar preparations of Zn, Cd, and Mn particles have been made using this technique, which is a promising source of gas-phase data overlapping that described above.

Allied to these studies are those on particulates, in the size range of perhaps 10 to 50 μm, as for example occur as burning metal aggregates in propellants. Here and in combustion processes in general (see Chapter 3) there is great need for understanding the oxidation of such particulates, especially when liquid droplets are involved and/or when the oxide formed on the surface is nonvolatile.

It is apparent that research into high temperature aggregates overlaps several fields of science, and it represents thereby an excellent example of the general usefulness of basic knowledge.

VII. MATRIX ISOLATION

This technique involves the trapping of high temperature vapor molecules in a matrix of a solid rare gas at 4 to 10 K so that they are isolated from each other. The benefits of spectroscopy on matrix isolated, high temperature molecules are that the spectra are simplified and the spectroscopic properties of the trapped species differ little from those of the free, high temperature, gas molecules. There is great potential for obtaining optical, ESR, MCD, and Mossbauer data for a class of high temperature molecules difficult to study spectroscopically in the gas phase.

Molecular ions (See Section V) trapped in the solid rare gases have been of increasing interest during the past five years, and it is expected that significant advances will be made in that area during the next decade. Alkali metal atoms have most often been used as donors for the formation on anions (e.g., O_2^-), but cations may be expected to be more difficult to prepare (e.g., C_2^+). Photoionization, argon discharge, proton beam, and chemical reactions have been used to produce trapped ions; additional methods to prepare the ion of choice are constantly being introduced. Once techniques for ion formation are perfected, the very successful matrix studies of neutral high temperature molecules can essentially be repeated on their ionic counterparts.

An informative technique, just gathering momentum, is the application of MCD and magnetic circular polarized luminescence (MCPL) to matrix-isolated molecules. Recently MCD has been applied to small magnesium atom clusters and to diatomic oxides such as TaO or TiO. Its value lies in providing information about the mechanism of electronic transitions (electric dipole, magnetic dipole, etc.) and their assignments. Since rotational structure is not observed in matrices, this technique supplies essential information about the many excited states often observed. Furthermore, MCD is very well suited to analyzing various cluster species because it can often differentiate among them on the basis of their differing magnetic properties.

Matrices have been a natural medium for the study of metal and salt clusters (see Section VI) since, at high enough dilution, individual atoms or ionic diatoms can be isolated. Then by careful diffusion the spectra of dimers and trimers of these monomers will gradually appear, culminating eventually in the formation of large aggregates or microcrystals. Photoclustering, i.e., photodissociation of a cluster and induced diffusion, has been helpful for identification of bands assigned to particular species. The reactions of metal aggregates with ligands such as CO and C_2H_4 are also being observed in this solid phase. Matrix studies of clusters will probably continue with the application of an expanded array of spectroscopic techniques. As mentioned above, the really desirable step would be the ability to trap only one kind of cluster at a time.

In this connection there are recent developments in nuclear magnetic resonance (NMR) of matrix-isolated molecules which show great promise. For example, chemical shifts (Knight shifts) observed in metal aggregates could provide a unique means of investigating the transition from localized bonding to delocalization as in bulk metals. The application of NMR to matrices has been a hoped-for development for many years; and recent papers indicate that it is beginning to occur. In general, the potential importance of these measurements lies in the possibility of using coupling tensors to obtain molecular geometries, and chemical shift and quadrupole tensors to obtain charge distribution and electric field gradient data. This should be a very fruitful area of research.

Over the last seven years Mossbauer spectroscopy of matrix-isolated Fe, Sn, Te, and Eu atoms and compounds has been evolving to provide isomer shift and hyperfine interaction constants, from which bonding information has been obtained. Among the species studied were Fe_2 and its reactions, and FeMn (see Section VI). A provocative result emerging from that research is the indication that Fe_2, not Fe, is the more reactive species. The Mossbauer technique can be expected to contribute to high temperature molecule data in future years.

In some spectroscopic areas the sensitivity of detection of matrix-isolated molecules has increased enormously in recent years. The laser, of course, has effected that in Raman and emission studies. The use of fourier transform infrared has already demonstrated its benefits. Another beneficial innovation has been the successful use of sputtering for the preparation of some high temperature molecules in matrices. These advances will affect future work.

It has been suggested, relevant to increasing interest in the kinetics of the reactions of these molecules (see Chapter 3), that the next step in matrix isolation should be the preparation of dilute rare gas liquid solutions. Then one could not only solve the problems of identifying the primary species, but also develop methods for rapidly generating the reactive species and determining the products of their reactions, utilizing time dependent techniques now becoming available.

VIII. THEORY

Improvements during the last decade [refinements to add higher excitations, many-body perturbation theory, improved open-shell self-consistent-field (SCF) theory, and configuration integral (CI) methods for excited states] have made possible accurate *ab initio* calculations of the potential surfaces of molecules containing two or three second-row atoms (with attached hydrogen as necessary). Methods appropriate for accurate treatment of the more difficult continuum problems of electron scattering and photoionization are being developed; and their application to diatomic molecules should be an area of rapid growth. During the next decade the calculation of ground state potential surfaces, with emphasis on chemical reactions and collisions rather than on spectroscopic properties, will probably increase. However, interest in finding diatomic potential curves for highly excited states and resonances appropriate to development of new lasers will continue.

For molecules containing heavy atoms, the state of theory can be judged by the most recent *ab initio* calculations on the diatomics MnH, FeO, FeH, MnO, FeF, NiO, and Ni_2. These are simple molecules on an experimental high temperature scale; but in some cases there is still ambiguity as to the ordering of their lowest electronic states. A review of the first-row transition-metal diatomics appearing in 1976 points out the difficulties in establishing the ground state in cases where several low-lying levels are within electron correlation energies of each other.

Extension of such *ab initio* calculations to more than one ligand attached to the metal have been meager. Recent restricted Hartree-Fock calculations for FeF_3 and other MF_3 members of the first-row transition-metal series (M = Sc to Ni) gave geometries and force constants in general agreement with existing experimental data, where such data agree. Dissociation energies were uniformly low. In the high temperature field there is clearly a need for further calculations on larger, heavier molecules, with improvements in accuracy and with extensions to ions.

Molecules containing more than one heavy atom can be expected to receive more attention in the future, particularly because of the impetus provided by the interest in metal clusters (see Section VI). Detailed calculations on homonuclear diatomics and triatomics, other than the alkali metals, are needed; and experimental work on intermetallic molecules (such as FeMn and CdHg excimers) may provide inducement for theorists. Neither experiment nor theory has presently established the ground states of the first-row transition-metal diatomics, Fe_2, etc. This can be expected to be rectified in the next few years.

As discussed in Section VI, there is still much interest in the calculation of the electronic properties and bonding in metal aggregates (so-called naked clusters) and metal cluster complexes. Aggregates offer an ideal application of the SCF-Xα-SW method; and at least in the immediate future, the method will continue to be used extensively to calculate electronic properties. CNDO, extended Hückel, and other methods have also been applied with varying degrees of success. Possible transitions from linear chains to close-packed structures as the number of atoms increases are of interest, as are transitions from solid to liquid and from atomic to collective electronic behavior. Most calculations on large clusters are moving toward incorporating bulk effects through some effective potential and/or boundary condition.

Another area of theory related to plasmas, arcs, and gaseous reactions involves intermolecular interactions or collisional behavior in high temperature gases, as opposed to interactions between ground state neutral molecules. Electronically excited species and molecular ions as interactants, reactants, and products must be better understood under these circumstances, perhaps, before sufficient generalizations are available to guide theoretical development. Chemical dynamics is not within the purview of this chapter; but it is probably the most meaningful subject in high temperature technology, if not the most complex.

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3

COMBUSTON AND OTHER HIGH TEMPERATURE GASEOUS REACTIONS

I. SUMMARY AND CONCLUSIONS

- Increased fundamental understanding of chemical kinetics -- both experimental and theoretical -- will permit reliable extrapolation of elementary reaction rates to high temperatures and will enhance the ability to model complex chemical systems. Experimental techniques for the study of reaction rates of state-selected species (as, for example, by laser excitation) will provide new insight into chemical reaction rates. Exciting and unforseen practical developments such as new materials may well follow.
- Advances in experimental and modeling studies of the chemical kinetics and fluid mechanics of turbulent, multicomponent, homogeneous, or heterogeneous flames will produce important new understanding and predictive capabilities concerning practical combustion systems.
- Increased ability to understand combustion processes -- both homogeneous and heterogeneous -- is essential for better utilization of fuels. Strong interactions between experiment and theory in this area should lead to the invention of novel or improved combustion devices.

II. INTRODUCTION

More than 90 percent of U.S. energy production comes from burning fossil fuels. These fuels are, directly or indirectly, likely to remain the country's predominant sources of energy for at least the next quarter of a century. Present and anticipated shortages of fossil fuels underscore the urgent need for improvements in our ability to extract useful work and perform efficient energy transformations using available fuel supplies.

What are the needs of society that suggest the required directions of combustion research? We seek: environmental compatibility; increased efficiency; better compatibility with engineering materials, to preserve scarce materials or to keep costs reasonable; better adaptability to widely varying fuel properties (i.e., burners or processes capable of employing "wide-spec" fuels) and to alternate fuels such as alcohols or fuels derived from coal gasification or liquefaction; and increased responsiveness to engineering design demands -- especially the development of reliable and cost-conscious scaling procedures.

The existing knowledge of combustion, extensive as it is, nonetheless requires additional effort to deal with new demands. Why? One reason is that some of the demands are, indeed, new (e.g., use of alternate fuels). However, the major reason is that in the past it has not usually been necessary to be deeply concerned with the detailed fluid physics and chemistry of practical combustion devices. Now, this has become necessary. Interactions of chemical kinetics, flow mixing processes, and, frequently, multiphase behavior dominate such pressing technological areas as pollutant formation, unburnt hydrocarbon emissions, and toleration by burners of varying types of fuels. Thus, a broadly interdisciplinary approach to the study of combustion is now, not only intellectually appealing, but technically demanded.

Such an approach should emphasize the following general areas:

- Chemical kinetics of combustion and other high temperature reactions.

- Fluid flow, transport processes, vaporization, and fuel/air mixing processes.

- Containment or treatment of hot combustion products, which requires knowledge of fluid flows and advanced cooling techniques, catalytic and corrosion reactions on hot surfaces, and particulate formation and deposition from hot gases, as well as improved high temperature materials (metals, ceramics, lubricants).

- Diagnostic techniques needed for improved measurements of local temperatures, flow velocities, and concentrations.

- Modeling of practical combustion systems involving chemical reactions in highly turbulent flows. Such systems are too complex to describe analytically in complete detail; hence mathematical models that appropriately simulate these systems must be developed to aid designers, and key experimental parameters identified to test the theories.

In high temperature gaseous reaction kinetics, continuing or increased research efforts in the following areas are foreseen:

- Improved experimental measurements by methods such as
  - -- shock tubes, conventional and novel,
  - -- discharge fast-flow reactors,
  - -- high temperature fast-flow reactors,
  - -- molecular beam reactive scattering,
  - -- laser-induced chemistry, including state-selected rates,
  - -- photolytic systems, including laser photolysis, and
  - -- premixed flame profile measurements.

- Kinetic modeling of combustion and other complex reaction systems such as plasmas.

- Compilation of critically assessed rate-constant data.

- Theories of gaseous reaction rates including
  - -- unimolecular decomposition by RRKM-type approaches,
  - -- bimolecular reactions by refined transition-state approaches,
  - -- trajectory calculations using improved potential surfaces,
  - -- ion-molecule and ion-ion reactions,
  - -- internal energy redistribution rates and state-by-state chemistry, and
  - -- electronically excited species.

In the very broad area of multiphase phenomena related to combustion systems, the following research needs exist. Some are similar to topics covered in Chapter 2, but are included here because of the additional requirements of applicability to multicomponent mixtures and to high pressure environments:

- Surface tensions of multicomponent hydrocarbon liquids in order to understand droplet atomization.

- Droplet vaporization processes including specific heats, viscosities, thermal conductivities, and mass diffusivities for liquid and gaseous multicomponent mixtures, especially at high pressures and temperatures.

- The nature of criticality or supercriticality with multicomponent mixtures.

- Vapor pressure equilibrium curves for multicomponent mixtures.

- Interactions of droplets with each other and with turbulent eddies.

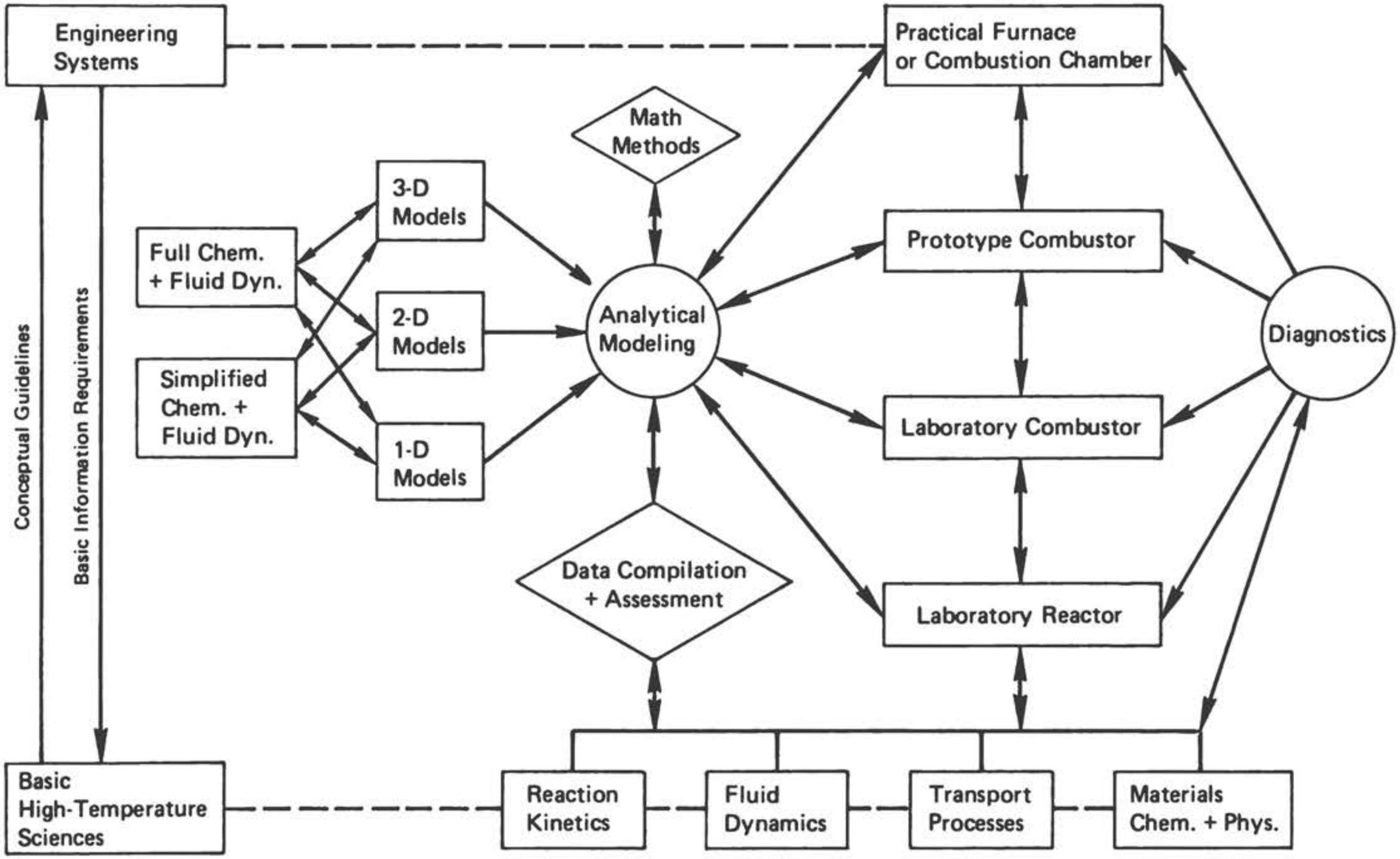
- Diagnostics for spatial resolution on the scale of a few micrometers for particulates, and on the scale of small eddies for turbulent gas-phase systems (typically, perhaps 100 μm for laboratory systems).

- Pyrolysis, oxidation, diffusion, and melting in the pores of solid fuels such as coal or biomass.
- Surface kinetics and catalyst heating in catalytic combustion.
- Effects of liquid-fuel droplet impingement on catalytic surfaces.

An interdisciplinary problem worthy of strong attention is the interplay of turbulence, chemical kinetics, and multiphase phenomena in determining certain features of combustion systems, such as pollutant emissions. Emphasis should be placed on careful experimental determinations of the most important properties that characterize these systems. In some instances, new types of instruments are available to make these measurements, and increased utilization of these advanced probes by workers in the combustion community is expected. In other instances, new types of instrumentation are needed to provide additional classes of data to which modeling theories are particularly sensitive (i.e., which will be most useful in validating these models). Both finite-difference and finite-element modeling techniques must be developed in order to solve the highly coupled, highly nonlinear, large system of partial differential equations that describes turbulent combustion phenomena. Mathematical analysis of numerical methods as well as comparative calculations on model problems are required to develop efficient, trustworthy techniques. And, asymptotic methods that will provide insights regarding flame phenomena and calibrations for numerical methods must be further developed. A general concept of how basic science is related to technology in the field of combustion has been developed by Professor R.H. Essenhigh of Ohio State University and is shown diagrammatically in Figure 1.

Certain specific subjects need thorough investigation to extend present knowledge. Among these are:

- Basic flame characteristics.
- Fuel hydrogenation and gasification.
- Fundamental data, including thermochemical and optical properties.
- Stack gas cleanup.
- Metal combustion.
- Combustion modification, including laser and plasma interaction with flames.
- Fire safety, including explosions, poisoning hazards, and detection instrumentation and methods.



NOTE: The general concept of this diagram was developed by Prof. R. H. Essenhigh of Ohio State University.

FIGURE 1 Relationships Between Basic Science and Technology

The sections to follow deal with selected subjects from the general and specific listings. Neither the lists nor the treatment of the subjects selected are comprehensive; however, an effort has been made to delineate the significant areas where high temperature research is needed and/or anticipated.

III. GASEOUS REACTION KINETICS AT HIGH TEMPERATURES

The urge to understand the chemistry of combustion processes has provided the main impetus for past investigations of reaction rates at high temperatures. In very recent years, interest in chemical lasers such as the hydrogen fluride (HF) laser has generated much additional activity in gas kinetics and especially in the production and study of gaseous reaction products having distinctly nonthermal internal energy distributions. This has led to important advances in the knowledge of vibrational and rotational relaxation rates and also of the rates of certain elementary reactions not encountered in ordinary combustion systems.

Because combustion will continue to be the major source of energy for at least the next 25 years, we expect an increasing emphasis on experimental and theoretical studies of gaseous reaction rates. The need is emphasized by the significant increase in combustion intensity, or volumetric rate of heat release, encountered in many practical systems, which brings with it a strong coupling between fluid dynamics and kinetics. To quote the NRC report on DOE research:

> "...a detailed understanding of combustion kinetics under actual conditions found in engines, flames, and in other systems requires (a) a knowledge of the elementary rate constants and (b) an equally detailed understanding of turbulent-flow hydrodynamics...rate constants, k, of elementary reactions must be known over wide ranges in temperature (often up to 3500 K)."

Additional combustion-related incentives arise in the necessity to control pollution from combustion devices; to understand the phenomena of ignition, extinction, flammability limits, and combustion instabilities; and to inhibit or prevent unwanted combustion events -- i.e., fires and explosions. In all of these, chemical kinetics plays a significant, often controlling, role. It may be noted parenthetically that the fuels or combustibles in the systems mentioned are not necessarily gaseous; yet gaseous reaction rates may control the behavior. Illustrations include the extinction of burning fuel droplets, the production of soot in burning oil sprays, and the conversion of fuel-bound nitrogen in coal to NO_x.

The past 25 years have seen great strides in the experimental measurement of gaseous kinetics and in the identification of elementary reaction mechanisms. Among the techniques used have been conventional (but increasingly well instrumented) static and flow reactors and, most notably, shock tubes and discharge fast-flow reactors. Other special systems, including flames themselves, have yielded useful data under certain circumstances. Interacting molecular beams have come into prominence in the study of molecular dynamics, although direct application of data from reactive scattering experiments to high temperature reactions lies mainly in the future.

The impact of the shock tube, which has recently celebrated its 25th anniversary as a tool for studying elementary reaction kinetics, has been crucial because of its capability of producing rate data over a wide range of temperatures. Precision of data has often been a problem with shock tubes; so that in many instances the best results have come from the combination of shock-tube data with rate data obtained at relatively low temperatures by other means. Noteworthy examples are studies of the dissociation-recombination of diatomic molecules that combine shock tube results with lower temperature data from flash photolysis. In recent years, with the use of new or improved diagnostics, better construction, and computer-aided data analysis, the precision and accuracy of shock tube data have been raised to the point where Arrhenius plots of high temperature data alone can frequently be considered reliable to within ±10 percent. (This does not, however, obviate the need for continuing experimentation on rates at lower temperatures.) The important area of vibrational relaxation rates at high temperatures has been dominated by shock tube methods.

In the next 25 years, shock tube studies will be further refined and will continue to be valuable. Some interesting modifications can be expected, such as a combined flash photolysis -- shock tube study or a combined discharge flow-shock tube study. Both of these were explored some years ago; they seem to merit new attention. Laser-induced chemistry, a new field, should be emphasized, not only because of interest in isotope separation, but also because of the importance of internal energy redistributions in elementary reactions -- including atom and radical recombinations or their inverse (unimolecular decompositions) and exothermic atom transfer reactions. The technique should be extended to elevated temperatures.

High temperature fast-flow reactors permitting study of fast elementary reactions at temperatures approaching 2000 K have been developed (Fontijn *et al.*, 1975) and are expected to multiply. In conjunction with low pressure diffusion flames and molecular beams, they can provide interesting results on reactions that are difficult to study in more conventional systems, notably certain chemiluminescent reactions between metal vapors and oxidants. This last is, incidentally, a field where much further work can be expected: a field where research on combustion is related to other research on high temperature materials. Discharge flow systems for the study of reactions of atoms and radicals with molecules are, even now, operating over a modest range of temperatures. This trend will surely continue, yielding experimental data at temperatures approaching those in typical flames.

Reactive scattering studies using molecular beams, and probably also the so-called beam-gas reacting systems, will maintain rapid development in the next 25 years. Increasingly sophisticated diagnostics will involve lasers and mass spectrometers and increasingly powerful data analysis. The coupling of theory and experiment has been effective in this area and will increase.

Finally, flames themselves (especially laminar, premixed flames) should come into their own as experimental tools for reaction kinetics. Measurements in flames have often been plagued by control problems, by problems of spatial resolution, and by diagnostic inaccuracies (in both temperature and species concentrations). Vast improvements in diagnostics have occurred and more are to be expected. When combined with modern data-acquisition techniques and with the powerful numerical methods now available for kinetic modeling (both rapidly developing areas), experimental studies of flame structure will yield valuable information on kinetics. The similarities in reactions occurring beyond the point at which the fuel has disappeared in premixed flames will allow extensive interapplicability of rate data among flame systems. The need will continue for detailed studies of the earlier stages of combustion; yet, even here, substantial data transfer may be possible because of similarities among systems.

The coupling of experiments on flame structure with kinetic modeling to obtain rate data on elementary reactions obviously requires a data base with which to begin. These data must be obtained by methods such as those mentioned earlier. One can anticipate a breakthrough since the H_2-O_2 flame is already reasonably well understood in terms of its elementary reactions and a theoretical description of the flame has been quite successful (Dixon-Lewis *et al.*, 1975). The CH_4-O_2 flame is approaching the same point (Smoot *et al.*, 1976; Tsatsaronis, 1978).

Simplified forms of rate equations must be developed for the purpose of mathematical modeling of complex combustion systems. To conduct such modeling on a wide range of flame systems, a readily available evaluated compilation of rate data on elementary reactions is essential. Strong activity is needed to couple experiments with theoretical predictions of the rates of reactions in order to describe rates in temperature regions where data are not available. Activity in both realms -- data evaluation and theory of reaction rates -- has been considerable in recent years, and is to be encouraged for the future.

Critical evaluations of high temperature kinetics have been published by the group at Leeds (Baulch *et al.*, 1972), by NBS (e.g., Hampson and Garvin, 1977), and by Jensen and Jones (Comb. Flame, 1978); there is a new effort under way at the Aerospace Corporation (Cohen and Westberg, 1979). Work of this type, done by the best scientists available, must continue, be expanded, and be periodically reassessed. There must also be an expansion of JANAF-type thermodynamic data compilations to include many species (e.g., CH_3O, C_2H_5) for which data are scanty at present. More is said on this matter in Chapter 8.

The theory of chemical reaction rates is an old subject with a distinguished history. Nevertheless, without demeaning that history in any way, activities in the last decade suggest that the coming 25 years may be remarkably fruitful, principally because of the aforementioned coupling between good experiments and sophisticated theory. A recent symposium at NBS, organized by the NRC Committee on Kinetics of Chemical Reactions (*J. Phys. Chem.*, 1979), showed that the understanding of the dissociation of diatomic molecules is reaching maturity; the application of RRKM-type theories to the unimolecular decomposition of polyatomics is nearing that point (including a detailed understanding of the whole pressure-fallout region); and progress is being made in understanding some of the fast biomolecular reactions that often exhibit nonlinear Arrhenius plots. Useful method for estimating or correlating rates of high pressure-limit unimolecular reactions and a huge array of biomolecular reactions are now available. Trajectory calculations using semi-empirical potential surfaces or, in rare cases, almost fully *ab initio* surfaces, are yielding new insight into rate behavior. Future innovations will greatly extend all of these activities.

As these areas develop, one can expect a maturing of the understanding of ion-molecule reactions (significant both in flames and in other high temperature systems such as plasmas) and of reactions involving nonequilibrium internal energy distributions and electronically excited species. Such emphases are relevant to possible future developments in chemical lasers. Several of the newer techniques for experimental studies -- such as the state-specific kinetic studies now feasible with the aid of laser excitation to selected quantum states (Brooks and Hayes, 1977) -- appropriately combined with theory, should lead to rapid progress; no doubt in directions that cannot be entirely foreseen.

IV. HIGH TEMPERATURE PYROLYSIS

In the simplest case (e.g., a diatomic molecule), pyrolysis is identical to unimolecular decomposition and falls in the realm of elementary reaction kinetics. In general, however, pyrolysis connotes a multistep thermal decomposition process that may or may not include complications such as chains (as in thermal cracking of paraffin hydrocarbons), surface reactions (as in the growth of soot particles), or catalytic influences (as in catalytic cracking). Pyrolytic mechanisms may enter into combustion processes, although pyrolysis *per se* is normally thought of as occurring in an oxidizer-free environment.

Because the chemical mechanisms of pyrolysis are usually quite complex, they are resistant to complete delineation and their rates are rarely understood on a molecular or elementary-reaction level. Thus, the pyrolysis of even the simplest paraffin hydrocarbon, CH_4, is only now approaching the state of being adequately describable in terms of an elementary-reaction scheme; others are in worse shape. For practical purposes, one relies entirely upon empiricism and hopes that the rate data will not have to be forced to conditions under which they are inapplicable.

Since pyrolysis is of substantial practical importance, this situation is very inefficient, occasionally hazardous, and certainly intellectually unsatisfying. Fortunately, intuition has often been successful, resulting in practical, well-developed pyrolytic systems such as those for making thermal carbon blacks, pyrolytic graphite, and chemical vapor-deposited films. Careful characterizations of pyrolysis products produced under well-specified conditions have yielded a body of useful correlations that have practical validity. In general, however, one cannot make predictions from such data or hypothesize reasonably reliable estimates of behavior for new pyrolytic systems. Yet such versatility is much needed. One would like to predict the rate of decomposition of coal volatiles in the pores of hot coal particles; the rate of decomposition of vapors from liquid fuel droplets as they approach the surrounding flame region or, as an extension, the behavior of fuel in the interior of a spray; the rate of degradation of a cellulosic material, or of a polymer; the rate of decomposition of a semiconducting film from a mixture of pyrolyzing inorganic gases, the rate of deposit formation in prevaporizing liquid-fuel combustors.

Some of these systems may not fully yield to study in the next 25 years; but work should proceed at a faster pace than it has so far. Present efforts in these and other areas where pyrolysis is the dominant chemistry should be intensified. Progress can be expected from pure empiricism to semiempiricism or "operational" kinetics, to rudimentary understanding on a molecular level, and ultimately to the kind of detailed understanding that is needed for full system modeling and predictions. At the very least, a full understanding of the fuel-rich combustion processes used in staged combustors should be sought because of the processes' importance in energy conversion and power production.

V. CHARACTERIZATION OF FLAMMABLE SYSTEMS

The need for intensified experiments to determine temperature and concentration profiles in premixed flames and the virtues of comparing such data with kinetic models have been pointed out. Fuel/oxidant combinations possess characteristics other than steady-state flame profiles that also merit study for their own sake (often for very practical reasons) and for comparison with predictive models. Among these are the equilibrium adiabatic flame temperature, premixed flame propagation velocity, ignition delay, ignition energy, quenching distance, flammability limits, and stability limits. To these, under special circumstances, may be added the Chapman-Jouguet detonation velocity and the response of the system to additives, especially combustion suppressants. The latter is of great practical importance with respect to pollution problems and to fire hazards. Characteristics of the diffusional combustion of fuels -- such as species and temperature distributions and radiation characteristics -- are also significant because a large number of industrial combustion systems (e.g., furnaces) normally involve diffusion flames. There is a strong need for further systematic measurement and compilation of the above characteristics that can now be measured by standard techniques.

Systematic and innovative work on flame inhibition should increase. The understanding of inhibition and suppression of both homogeneous and hetereogeneous combustion should be susceptible to rather detailed elucidation by the application of standard measurement techniques and novel diagnostics in conjunction with advanced modeling efforts.

VI. FORMATION AND DESTRUCTION OF COMBUSTION-GENERATED POLLUTANTS

The need to suppress unwanted emissions from combustion systems is altogether evident and need not be further emphasized. The NRC report on DOE research presents a perceptive and reasonably complete overview of the state of knowledge of formation rates, problems in experimental measurements, and possible lines of research on NO_x and soot. Brief mention is made of hydrocarbons, malodorous compounds, carcinogens, and lachrymators. To these may be added SO_x, CO, and inorganic solids (e.g., fly ash). All are kinetically controlled features of combustion processes.

The description and (partial) control of thermal NO_x production in practical systems by appropriate application of elementary reaction-rate data represents one of the success stories in high temperature chemical kinetics. Even so, few would consider as adequate the state of knowledge of the rates of formation and destruction of NO and/or NO_2 in flames employing a wide range of fuels over an extended range of equivalence ratios. Appreciation of the contribution of fuel-bound nitrogen to the system's chemistry is evident; but the solution to this added complication is still in the early stages, although it is an active field of research. In fact, this type of statement applies in some measure to all of the pollutants mentioned above: The problems are understood qualitatively or semiquantitatively and they are under investigation; full, quantitative understanding is seriously wanting; increased fundamental research is much needed.

Necessary technological "fixes" that are successful under limited conditions have been devised. Thus NO_x can be partially controlled by staged combustion or by adding NH_3 at a carefully selected temperature in certain systems; catalytic reduction or decomposition of NO has been quite successful in some cases; reduction of NO by carbon has been found to occur in fluid-bed combustors; soot may sometimes be controlled by metallic additives in combustors; incompletely oxidized organics can be controlled by leaning out the combustion; CO can be minimized by suitable stoichiometry and by avoiding too-rapid cooling of combustion products. These and other semi-empirical developments have been accompanied by fundamental investigations. Even when fundamental studies have not provided a rigorous answer to pollution problems , they frequently, in practice, have triggered significant progress. An enlightening example can be found in Appendix B if the NRC report on DOE.

The needs are clear: engineering design must proceed, based on the best information available; but intensified fundamental research on the formation and destruction of pollutants is essential. At worst, it will provide useful guidelines for practical modifications to be examined in engineering experiments. At best, it will provide the basis for rigorous modeling of practical systems such that new designs can be based upon first principles.

For these reasons, increased attention should be given to the following pollution-related subjects during the next 25 years:

- Thermal NO_x chemistry in flames.
- "Fuel NO_x" chemistry in flames.
- Homogeneous and heterogeneous catalytic removal of NO_x in hot or moderately hot systems.
- Chemistry of sulfur in fuels and in flames.
- Partial oxidation reactions of fuels, especially in quench layers.
- Homogeneous pyrolytic transformations of fuels to form polynuclear aromatics.
- Soot nucleation and growth.
- Soot burnout in exhaust gases.
- Aerodynamic-chemical measurements and modeling of practical systems, with emphasis on mixing rates and temperature distributions.
- Evolution of inorganic species during combustion.
- Nucleation and growth of inorganic particulates.
- Formation and oxidation of CO, especially in regions of rapidly changing temperature.

It is expected, based on recent progress and strong motivation, that most of these problems can be solved in the next 25 years if they are adequately supported.

VII. MULTIPHASE PHENOMENA

Liquid-Gas Systems

One expects that in the future many energy conversion devices (including combustors) will involve direct liquid injection into a hot gaseous environment. Atomization and vaporization are two primary problem areas associated with this two-phase flow. Mechanical, physical, and chemical aspects are associated with these phenomena; and the coupling between them is sufficiently strong (nonlinear) that neither aspect should be studied in isolation.

Atomization is significant because the droplet size distribution that results from the process has significant influence on the performance of conversion devices. The time required for vaporization of the liquid will depend upon the initial size. The mechanical properties of liquid injection momentum and kinetic energy are important but physical properties, such as surface tension, are also relevant. The detailed mechanisms for low-speed liquid-jet breakup are understood; however, for larger mass-flow systems, there is essentially no knowledge about the mechanism. Current technology is based upon empirical knowledge.

Secondary atomization processes are also relevant; droplets may break into smaller droplets for a variety of reasons. Impingement upon solid surfaces may occur; the simple problem of a cold liquid droplet striking a hot surface has not been carefully analyzed. An increase in relative velocity between gas and liquid caused by accelerating fields can result in instabilities that lead to further atomization. Finally, with a multicomponent liquid (or with an emulsified liquid), nucleation may occur in the interior of the liquid droplet, possibly resulting in a microexplosion of the droplet. In addition to mechanical and transient thermal research, information is needed on the surface tension of multicomponent liquids as a function of surface temperature and composition.

Droplet vaporization has been studied for some years. The classical case consists of a spherically symmetric, quasisteady system with a single-component liquid. Interesting practical problems of the present and the future involve: droplets moving through a gas (at best, an axisymmetric situation), transient behavior, and a multicomponent liquid. Other complications could include interactions of the droplet with turbulent eddies, liquid-phase pyrolysis of hydrocarbon fuels, and, as already mentioned, nucleation within the multicomponent liquid. Studies have begun in these areas; but much more remains to be determined over the next decade or two.

If cold liquid is injected into a hot, gaseous environment, the two phases obviously are not in equilibrium initially. Heat is continually transferred from the gas to the liquid; and mass is continually transferred from the liquid to the gas. Since droplets are small, the time scale of the event is quite short, perhaps of the order of milliseconds. Temperature gradients will occur throughout the liquid droplet and the surrounding gas film, resulting in an unsteady heat transfer with phase transition. Concentration gradients will also occur throughout both film and droplets. Since the more volatile species will vaporize preferentially from the liquid at the surface, those species will diffuse from the interior of the droplet towards the surface on account of the resulting gradient.

If the droplet is moving through the gas, a viscous boundary layer and wake will be formed over the droplet causing a shear force on the liquid surface. This force can generate internal circulation in the liquid resulting in convective heat and mass transfer in each phase.

The boiling points of heavy hydrocarbon fuels employed in high pressure combustors can be quite high; liquid temperatures can exceed 500°C. There is a need to determine viscosities, specific heats, and thermal conductivities for liquid mixtures and gaseous mixtures above these temperatures. In addition, mass diffusivities for liquids and gases must be known and latent heats of vaporization for each liquid component must be determined. It is noteworthy that at these temperatures, significant liquid pyrolysis may occur, changing the composition and properties of the liquid and possibly even leading to the formation of carbon cenospheres.

In a multicomponent liquid droplet with a temperature gradient and concentration gradients, certain interior regions may reach boiling or even superheated conditions. Studies of the nucleation process for boiling in such systems would be appropriate. If the liquid has particulate impurities, heterogeneous nucleation might occur; otherwise, homogeneous nucleation could occur. In some cases, the gas bubble growth would result in a shattering of the droplet (microexplosion).

Often combustion and fuel vaporization will occur at such high pressures that several or all of the components of the liquid fuel are at supercritical pressures. Furthermore, the components in high temperature regions may also be above critical temperature. The understanding of criticality for mixtures is vague and further study is needed. A careful and systematic determination of latent heats of vaporization and surface tensions in the near-critical domain for mixtures is required in order to resolve the main question about this phenomenon.

While large gradients of temperature and concentration exist within and around the liquid droplet, one may perhaps assume that local equilibrium occurs at the liquid surface -- that is, within a few mean free paths. Vapor-pressure equilibrium curves for the cases of multicomponent mixtures, especially at higher pressure, are urgently needed. Also, the detailed laws governing the absorption of the surrounding gas by the liquid must be determined.

Most of the existing work on droplet theory considers only isolated droplets, while most practical situations involve a spray of droplets in which the separation, on the average, will be less than 10 drop diameters. Since significant interactions may be expected in this case, a comprehensive study of these interactions will be essential

The above processes can become quite complicated when influenced by turbulent fluctuations. If the turbulent eddy is about the same size as the droplet, which is usually the case, the interaction is especially complex; the asymptotic limits of very small eddies and very large eddies are much easier to analyze. There is a need to understand the effects of the correlation of velocity with temperature, and of the correlation of velocity with concentration, upon the vaporization rate of the droplet. Also, a spray of droplets will diffuse because of turbulence.

Typically, liquid droplet diameters are in the range of 30 to 200 microns. Gradients in and around burning or evaporating droplets can be so large that substantial changes in temperature and concentration may occur in 10 microns or less. Development is clearly needed for diagnostics that can resolve temperature and concentration on the scale of a few microns in both liquids and gases. Techniques for determining the vaporization rate of each component of a multicomponent liquid are required.

To make the results of droplet vaporization theory useful to the modeler of the combustor system (and eventually to the designer), the very complex mathematical system that describes the vaporization process must be converted into a simple form. That is, at some point, insight must be employed to resolve the key mechanical, physical, and chemical aspects and to establish simplified approximate algorithms.

Innovative experiments on two-phase flow and vaporization are required. The challenge arises from the complexity of the systems that are of interest and from the small volumes and short time-scales involved. In the past, for example, ignition delays, droplet radius, flame radius, and burning times have been determined for essentially stationary, isolated droplets. Attempts must soon be made to determine these global properties, as well as temperature and composition profiles, for advecting, interacting droplets. The interaction of droplets or particles with turbulent eddies also requires experimental study. At present it is not clear how to accomplish such measurements; but when they are possible, interaction of the experimental results with theoretical models will yield important advances and, in all probability, lead to significant improvements in practical systems.

Porous Solid-Gas Systems

Many of the practical systems that have been or will be utilized to burn coal or to produce synthetic fuel from coal or biomass involve two-phase flow with either an oxidizing or reducing gas and with small porous particles. Several of the aspects that were discussed for liquid-gas systems are relevant here; other unique aspects also appear.

Again, the particles, in general, will be moving relative to the gas and a flow field with a boundary layer and wake can exist over the particle. Convective heat and mass transfers result in an unsteady heating of the particle. Gasification of particle material results. The situation is a nonequilibrium one, with large spatial gradients because of the small size of the particles. Interactions among particles and interactions between particles and turbulent eddies are similar to those for droplets. As with liquid-gas systems, there is need for high-resolution diagnostics.

An added complication is that molecular mixing and chemical reaction (pyrolysis and/or oxidation) can occur in the submicron-size pores. Furthermore, heating, and accompanying pyrolysis, can result in melting or the formation of a tar which may block the pores. These phenomena of mixing, chemical reaction, and phase transition are not well understood and further studies would be appropriate.

A clear need exists for the determination of various physical and chemical properties, especially at high temperatures and high pressures. Thermal conductivities and specific heats are required for the solid phase; thermal conductivities, specific heats, viscosities, and mass diffusivities are needed for the multicomponent gas-phase. Heats of melting, heats of gasification, surface reaction rates, and gas-phase kinetics must also be determined.

Catalytic Combustion

One of the more promising approaches to lean combustion is based upon the use of catalysts. The catalyst probably will be constructed of a honeycomb with a mesh size of several millimeters. Either a premixed, prevaporized, combustible mixture or a mixture of air and liquid fuel droplets could flow through the honeycomb catalyst. Useful experiments on such systems are under way in several laboratories, together with some modeling efforts.

In catalytic combustion systems, the mechanical, physical, and chemical aspects are strongly coupled. Viscous, thermal, and concentration boundary layers form over the catalyst surface. A transient, nonuniform heating of the catalytic material occurs and affects reaction rates.

There is a need to understand both surface and gas-phase reaction rates in these systems. Once the flame is established, it is not clear that surface kinetics still will dominate. Obviously, many of the needs for thermochemical data described in the previous two sections exist here. Note again, high pressure operation will be especially interesting.

VIII. INTERACTION OF TURBULENCE AND CHEMICAL KINETICS

The flow in nearly all practical combustion devices is turbulent. Therefore, it is of key importance to consider the effect of this turbulence on the chemistry of flames, as well as the interaction of these features with the multiphase character of most practical combustors. Since reaction rates depend critically upon temperature, often with a strongly exponential behavior, fluctuating temperatures are important in determining how various species follow the available kinetic paths.

In many instances, the chemical reaction rates are sufficiently fast from a turbulence time frame, that reactions are effectively over as soon as the reactants contact each other on a molecular scale. In other instances, chemical reactions may lag significantly behind the turbulent fluid-mixing time scales. In most complex, hot, chemically reacting systems, a mix of rates prevales; and the chemical kinetics and turbulent fluid-mixing rates are intertwined in a complex fashion. In addition, competitive rates for phase changes render the ultimate problem one of great complexity for both theoretical analyses and experimental investigations. If broad predictive capabilities for combustor design and use are to be achieved, more work is needed to unravel these complicated flame interactions, first in simplified and then more complicated environments. Already, Appleton and Heywood (1973), Gouldin (1974), and Fenimore (1977) have considered the basic effect of turbulence on NO formation from thermal and from fuel-bound nitrogen sources.

Several approaches to modeling turbulent-chemical interactions have been utilized in the last decade or so. One involves the examination of fluctuations in the Arrhenius rate term. This leads to terms with second and third correlations of concentration and temperature with themselves and with each other. Differential equations can be developed to track these scalar correlations; however, the closure problem persists and some modeling will be eventually necessary.

Another approach involves direct modeling of physical, mechanical, and chemical phenomena within an eddy of the turbulence. This appealing development is based upon a "picture" of the reacting, mixing process. At present, it is an *ad hoc* procedure that is not fully rigorous. It does indicate, however, the relative importance of three characteristic times: the eddy rotational time, the time for molecular mixing of mass and heat within the eddy, and the chemical reaction time (or, in complicated cases, more than one chemical reaction time).

Still another modeling approach involves the use of probability density functions (PDF), which describe the chance of observing particular values of the basic flame variables (i.e., temperature, species density, and velocity). These are convenient representations of experimental information and involve quantities that experimentalists can measure. However, we cannot yet calculate the variation of a PDF through space and with time, or predict the relationships between different PDF's. Little theoretical effort has been devoted to consistent development of the PDF approach; most theoreticians either avoid their use or utilize them in a limited and *ad hoc* manner. It is worthwhile to develop a body of theory that leads to a system of coupled partial differential equations describing the variations of the interesting PDF's for chemically reacting turbulent flows.

Since many questions still exist about closure and turbulent modeling, basic studies are required in which theory and experiment are compared for simple configurations (e.g., axisymmetric jet flames rather than three-dimensional confined combustion). This should not be construed as an argument against multidimensional, elliptic calculations with complex boundary conditions; it is equally important to develop computational methods. However, those calculations probably will be costly and not practical for turbulent model development for the next decade.

Additionally, more effort must be expended upon a comparison of different modeling approaches to the same set of test problems. These kinds of tests have been done on nonreactive turbulent problems but not on reactive ones. The advantages and disadvantages of each technique are not yet clear and comparisons would be quite useful.

Transference from the theoretician to the experimentalist of physical insight obtained in formulating analytical approaches is essential for efficient progress in turbulent combustion studies. The experimentalist now has at his disposal an almost bewildering variety of tools for characterizing flames, ranging from direct sampling probes to nonlinear, remote, optical measurement techniques. Flexibility in use of a wide and rapidly changing set of tools will be necessary to extract the most information from such interactive systems. Furthermore, the approach taken by experimentalists to obtain, say, simultaneous density and velocity PDF's might be *substantially* different from the equipment required to determine, for example, the temperature and its gradient at a point. Timely and physically clear descriptions of the modelers' needs must be transmitted effectively to the experimentalists in order to best utilize their advanced measurement capabilities.

IX. MATHEMATICAL METHODS

Several classifications of mathematical methods now in the development stage will have impact upon the combustion field over the next few decades. Specifically, they are: numerical techniques for solving partial differential equations, asymptotic theory for differential equations, bifurication theory, and statistical methods. It would be valuable to nurture the development of all of these methods.

Numerical Techniques

Mathematical modeling of combustor flow can involve a large system of partial differential equations. The number of equations goes well beyond the usual list of continuity, momentum, and energy for flowing systems. Since combustors usually involve large mass flows to achieve desirable power levels, the Reynolds number of the flow is typically quite large and turbulence develops. Since the turbulence profoundly affects heat and mass transport and burning rates, its characteristics must also be calculated. Typical turbulent models involve at least two additional equations to tract turbulence characteristics; a well-known example is the K, ε model. In the simplest case of one-step chemical kinetics, a small number of additional species continuity equations are required. In the more general case where detailed kinetics are considered, a large number of species continuity equations are necessary. Whenever two phases are present, additional spray transport equations must be introduced to track size, velocity, number density, and temperature of the droplet With a polydisperse spray, the initial droplet size adds an additional degree of freedom to the problem. The system can easily involve more than 10 simultaneous equations.

Intermittent combustors, such as the cylinders of an internal combustion engine, are inherently unsteady since moving boundaries are involved. Continuous combustors, as found in gas turbines, often operate in a steady mode but occasional instabilities occur causing oscillatory behavior. The combustors of interest involve at least two and often three dimensions of spatial variations. Turbulence is always three dimensional but averaged quantities may be only two dimensional.

A large system of strongly coupled partial differential equations with two to four independent variables can only be solved by numerical integration. Reinforcing this point, the equations are highly nonlinear due to inertial effects, chemical kinetic rate terms, vaporization rate terms, and the sensitivity of thermochemical properties to large temperature or concentration gradients. It is simply not feasible to seek closed-form integral solutions to these equations.

The two major schemes for numerical integration are finite-difference methods and finite-element methods. Normally, in the finite-difference method computational cells are chosen commensurate with some curvilinear coordinate system. In the finite-element scheme, the cell shapes are chosen in a more arbitrary, but perhaps more natural, manner. As adaptive grid techniques -- with resulting non-orthogonal coordinates --

are imposed upon the finite-difference scheme, the difference between finite-element methods and finite-difference methods becomes more obscure. At this point, both methods seem worthy of development, and there is likelihood of unification in the future.

Because of the multidimensional character and the appearance of various source terms resulting from chemical kinetics of vaporization (as well as for other reasons), techniques of differential-operator splitting into sequential differential operators are attractive means to simplify the numerical algorithms. However, this operator splitting can sometimes cause numerical convergence or numerical stability problems. Mathematical analysis of various splitting schemes, as well as comparative calculations on model problems, are required in order to develop efficient and trustworthy schemes.

Numerical methods should be compared to asymptotic solutions in special limit for the purpose of calibration and gaining greater physical insight. For example, the relative importance of various terms in the differential operator can be evaluated in certain asymptotic limits so that the wisdom of various operator-splitting techniques can be ascertained.

Asymptotic Methods

Equations governing reacting, mixing viscous flows contain many nondimensional similarity parameters. Often the range of interest includes very large or very small values of some of these parameters. The mathematical limit of a parameter going to zero or infinity (whereby its reciprocal goes to zero) can be both relevant and tractable via a singular perturbation approach.

The Reynolds number, Damköhler number, and nondimensional activation energy are often very large compared to unity so that such asymptotic approximations as the boundary-layer approximation, infinitely fast chemical kinetics, and delta function reaction zone become appropriate. Also, for the condensed phase, the Prandtl number and Schmidt number can be one or two orders of magnitude greater than unity. Again, a singular perturbation would be valuable.

To date, only the simplest systems have been solved via these techniques. For example, only one-step kinetics have been considered; no treatments for even two-step kinetics have been developed. Furthermore, only one-dimensional systems have been considered. The extension of the asymptotic treatment to multidimensional, multistep chemically reacting flows would be a significant achievement. No real attempt has been made to seek asymptotic solutions of spray transport equations; efforts in this direction could be quite useful.

Asymptotic solutions could be employed to check the validity of certain finite-difference or finite-element calculation schemes. These schemes could not be trusted in the general case if they failed in certain limits. Asymptotic analysis can also be useful in simplifying the form of partial differential equations via numerical integration. This avenue of research is virtually unexplored.

Bifurcation Theory

Bifurcation theory treats the behavior of solutions as a function of various parameters of the system. In combustion science, it has been applied to problems of stability, ignition, and extinction. The theory gives insight regarding the major characteristics of the system; but it has been applied only to one-step kinetic schemes in very simple geometric configurations. Extensions of this approach to multistep kinetics and multidimensions would be appropriate.

Statistical Methods

In turbulent combustion problems, many researchers are handling data or developing theory in a statistical manner. Appropriate techniques must be developed to assure results that are valid and useful. For example, with intermittent combustors, distinctions must be made between cycle-to-cycle variations and turbulent fluctuations of properties within a cycle. The same type of modeling cannot be expected to be appropriate for both kinds of fluctuations. Also, while the experimentalist often determines probability density functions, no equations for these quantities have been developed from first principles. Therefore, any theory based upon these functions is *ad hoc*. Some very fundamental thinking on that matter is required.

X. INSTRUMENTATION

The competition between analytical and experimental abilities to characterize combustion systems and processes shows experimentalists in danger of lagging behind modelers in their general capabilities for probing hot, turbulent, chemically reacting gases. The basic problem has been a lack of measurement skills for the rapidly fluctuating variables to be monitored.

Mean values are produced from sampling techniques using analyses such as nondispersive IR absorption, chemiluminescence, paramagnetic analyzers, flame ionization detectors, gas chromatographs, and wet chemistry. Fluctuations as well as mean values can be observed using probes of temperature, such as thermocouples, or using hot wires for velocity determinations; but test-system perturbation, time-response limitations, and probe survivability ultimately limit the usefulness of such devices. Thus, optical methods have received significant emphasis in recent years.

Radiative measurements in the past have been accomplished by means of absorption and emission studies. Some promising newly developed light-scattering techniques for space- and time-resolved data acquisition are now on the horizon. Because of the relative newness of these techniques to combustion applications, and because their foundations are not in the mainstream of the combustion community's technical background, an outline of information available for elastic and inelastic molecular-scattering events is presented in Table 4. Table 5 describes examples of promising measurements.

TABLE 4. Character of Information Available from Elastic and Inelastic Molecular Light Scattering

Observation	Scatterer	Scattering Process	Information	Requirements and Comments
Elastic (unshifted scattering)	Particles	Tyndall (MIE)	Some information about particle distribution	Can be difficult to interpret for nonideal particle systems
			Velocimetry	Particles small enough to follow flow fluctuations
	Gas	Rayleigh	Total density	Few particles, favorable configuration, major composition known
			Temperature	Few particles, favorable configuration, major composition known, equilibrium; difficult to instrument
Inelastic (shifted scattering)	Gas	Raman, fluorescence, nonlinear processes	Temperature and component densities	Nonequilibrium OK, wide range of signal strengths and complexities to obtain detailed data from various environments

TABLE 5. Some Promising Space and Time-Resolved Measurements from Inelastic Scattering

Information	Environment	Method	Status	Comments*
Temperature	Clean flame zones	RS	Accomplished	Do not need *a priori* composition; too weak for luminous systems
Major species densities	Clean flame zones	RS	Accomplished	Do not need *a priori* temperature for low temperatures; too weak for luminous systems
Temperature	Bright and/or particle-laden flame zone	CARS	Accomplished	Strong signal; tolerates particle loading; more difficult to instrument and interpret than RS
Major and intermediate species densities	Bright and/or particle-laden flame zone	CARS	Possible	Strong signal; tolerates particle loading; more difficult to instrument and interpret than CARS for temperature
		Raman gain	Possible	Developmental; alternative to CARS
Minor species densities	Bright and/or particle-laden flame zone	Fluorescence	Semiquantative	Strong signal
		Saturated fluorescence	Probable quantative for a few species	Reduces dependence of fluorescence on collisional quenching
		RIKES	Possible	Developmental; high experimental demands for increased quality of data

* Nonequilibrium OK for all methods
RS - Raman Scattering
CARS - Coherent Anti-stokes Raman Spectroscopy
RIKES - Raman-Induced Kerr Effect Spectroscopy

Use of any advanced state-of-the-art technique requires that compromises be made in optimizing its utilization and in tailoring its characteristics to the details of particular experiments. Thus, continuing with the example of light-scattering diagnostics, it can be shown that a tradeoff between experimental accuracy of the detected signal and test volume spatial resolution exists for Raman scattering measurements of gas density or temperature. This arises from the finite gas-breakdown (or other perturbation) limits of the flame mixture. The compromise relates to the degree of focusing (or beam expansion) used for the laser source. This example makes an important point that strong emphasis must be placed on compatible and optimal use of all the probe methods used in each experiment.

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4

PROPERTIES OF HIGH TEMPERATURE SOLIDS

I. SUMMARY AND CONCLUSIONS

Technological progress, directly related to available materials, has been strongly coupled to solid state chemistry; and in the past, research in the chemistry of materials has been driven by these needs. As a result, the data, theories, and models for solids were often developed to explain and to understand facts which were first learned empirically. The challenge for the future is to improve the quality of experimental data on selected model systems and to improve the theories and models iteratively until they are predictive, allowing materials with specific properties to be designed *a priori*. The major benefits of high temperature research on solids are:

- A coherent picture of the chemistry of solids due to the interaction of the research results on physical properties, thermodynamics, structure, theory, and models.
- Applications and development of new techniques for high temperature experimentation and for materials synthesis.
- Extension of new data (thermodynamic, structural, etc.) on well-characterized model materials and under controlled conditions to more complex systems.
- Formulation of paradigms for the extensive effects that local chemistry has on the properties of surfaces.
- Convergence of geochemical research and solid state chemistry research to further our understanding of basic principles (chemical bonding and structure) and of applications (minerals and materials processing).
- Understanding of nonstoichiometry and of defects, properties inherent in high temperature solids.

II. INTRODUCTION

The application of basic principles of chemistry to solids has been one of the keys to the technological world of the 20th century. In the past, new synthetic materials represented laboratory creations made possible by the foundation provided by simple models, descriptions, and correlations and by empirical experimentation. In the future, solid state chemistry will benefit from better predictive models and theories developed as the underpinning science is advanced by data provided by more sophisticated experiments.

Progress in this field often follows two parallel paths -- studies to advance understanding through a deliberate choice of model systems and studies with technological need as the driving force. One study might be directed toward the chemistry of alloy formation using model systems; another might take basic principles garnered from model studies to invent new alloys for a specific purpose (e.g., corrosion resistant steels). The latter approach, technology driven science, can also provide additional scientific understanding. It has been proposed that this interaction be called "molecular science and engineering." This suggests that in the right environment, the separation of disciplines and the separation between research and development need not exist (von Hippel, 1959).

The successes of molecular science and engineering in the recent past are instructive examples as one looks ahead. A mere 25 years ago, silicon was an exotic material. The chemistries of purification and doping, of crystal growth, and of surfaces and interfaces were not well understood. Today the technological forefront is to control composition, properties, and structure on a submicron scale, as large-scale integrated devices are built upon the once exotic silicon single crystal. The joining together of disciplines and talents in solid state chemistry and physics and materials science has allowed molecular engineering to be practiced on the highest scale -- a composite structure where alloys, compounds, and interfaces allow a seemingly infinite number of electronic devices.

Magnetic oxide materials have similarly blossomed because descriptive and structural chemistry provided the correlations and models which allow a material to be tailored to technological need. Hard or soft magnets, large or small initial permeabilities, remanance or coercivity, etc. all relate to understanding gained from magnetic interactions of transition elements in an oxide lattice.

In the future, solid state chemistry will respond to new technological driving forces. It will supply new materials needed because of the high cost of energy, the scarcity of certain materials (e.g., substitutes for Cr alloys), and environmental problems (e.g., replacements for asbestos). This will often entail new materials for high temperature use or new chemical processes.

There have been several reviews of the problems, promises, and future needs of high temperature chemistry applied to solids: an extensive review of the field of materials (NRC, COSMAT Report, 1974) and more recent studies on energy (ERDA Workshop Reports, 1977; DOE Panel reports on High Temperature Ceramics and on the Theory of Surfaces, 1979). A recent workshop on the *Synthesis and Characterization of Advanced Materials*, sponsored by the NRC Solid State Sciences Committee reviewed numerous sucesses and cited future needs of solid state chemistry. Each of these reports advocates better understanding of the properties and processes of condensed materials. While each technological need requires specific models, data, and correlations, common features can be grouped into eight areas of fruitful research in high temperature science. The physics and chemistry of solids can be effectively guided in the future by a set of paradigms if new experimental techniques and computational methods for matching theory and experiment with models -- expressed in terms of experimentally measurable variables -- are applied.

III. CALCULATIONS AND CORRELATIONS

Theoretical methods for calculating the electronic structure of solids, most notably the Augmented Plane Wave and Green's function methods, are beginning to provide the capability of performing meaningful calculations for some structurally uncomplicated, but nonetheless important, refractory materials such as binary oxides, nitrides, carbides, sulfides, and intermetallics (England *et al.*, 1974; Neckel *et al.*, 1975). These calculations yield detailed information about electronic states in crystalline solids which can be compared with, and used to improve upon, simplified models of chemical bonding. Simple models which have been used with varying degrees of success over the years are the ionic model, crystal field model, ligand field model, models of reduced or variable oxidation state, and hybridization models (e.g., the Brewer-Engel correlation). All such models are recognized as being simplifications. The models provide *a posteriori* rationalizations, but provide many opportunities to improve the prediction of properties or behavior of refractory systems.

Areas of solid-state high temperature chemistry which benefit from theoretical developments include: prediction of ranges of homogeneity (Anderson, 1970), prediction of order-disorder transitions (Honig, 1970), understanding changes in crystal structure (Rao, 1970), understanding charge density wave transitions (Wilson *et al.*, 1974), understanding metal-insulator transitions and changes in electrical resistance with temperature (Adler, 1968), and important factors in the adoption of a crystal structure in a given system. In some cases, the application of theory to problems will require extensions of theoretical methods -- e.g., extension of the X-alpha electronic structure calculations to catalysis (Johnson and Messmer, 1976) -- and in other cases involving existing theoretical methods, more extensive interaction is needed between solid-state theorists and experimentalists from chemistry, ceramics, and metallurgy with detailed knowledge about the behavior of refractory systems of interest.

The earliest work on the electron band theory of solids discussed the possibility that by decreasing interatomic distance, by the application of high pressures, broadening of electron bands would occur, with closure in the gap between valence and conduction bands leading towards metallic behavior. The measured shock wave properties of a number of materials are profoundly influenced by the thermal excitation of electrons across a narrowing energy level gap. In effect, these electrons anticipate the gap closure. These effects have already been seen, and theoretically interpreted, in shock compressed Ar, Xe, and I_2. Using newer ultrahigh pressure techniques, similar effects could be observed in He and in the narrowing of the alkali metal closed-core conduction band gap. Thus high temperature-generated shock compression experiments can act as probes of these energy level gaps in systems at high density.

The breaking of chemical bonds under compression is another topic of long-standing interest. Recently, a number of shock experiments have shown what appears to be breaking of the diatomic bonds in I_2 and N_2. Diatomic oxygen is also under study. Future work, at higher pressures and temperatures, could extend these studies to the remaining halogens and some small molecules. Of all the transitions of molecular substances to the metallic state, the transition of molecular to metallic hydrogen may be the most significant phase transition in the solar system. The study of this transition represents one of the major goals of contemporary high pressure physics.

Experimental methods capable of providing information about electronic structure must be brought to bear upon refractory materials. Such methods include photoelectron spectroscopy (Shirley, 1972), NMR (Knight, 1956), EXAFS (Sayers *et al.*, 1970), Mossbauer spectroscopy (Bhide, 1970), nuclear quadropole resonance (NQR) (Jeffrey and Sakurai, 1964), as well as the more indirect methods of low temperature heat capacity, magnetic susceptibility, and electrical resistivity measurements. Even in multicomponent solids, direct determinations of ionicity and polarization at the sites of individual components can be made with photoelectron spectroscopy. The interplay between experimental and theoretical results will enable a refined understanding of the nature of chemical bonding in solids stable at high temperatures. These solids are frequently atypical materials (Franzen, 1978) interesting for their unusual stoichiometry, electronic behavior, extensive nonstoichiometry, defect chemistry, or crystal structure. Unusual behavior of the kind observed provides both a basic challenge for fundamental explanation and a range of properties and behaviors with potential technological impact.

New theoretical advances -- e.g., Harwell Automatic Defect Evaluation System (HADES) calculstions (Catlow and Fender, 1975) -- are anticipated in the treatment of the effect solid state. The iterative interplay between experiment and theory will evenually result in calculation of the energies of Frenkel and Schottky defects, of dislocations and grain boundaries, of variable valence defects, of defect clusters and associates, and of defects coupled to dislocations, grain boundaries, and surfaces. New understanding of defect structures that is resulting from advanced techniques of electron microscopy and spectroscopy (EXAFS, PES, etc.) will probably lead to new theoretical breakthroughs. A growing ability exists to make detailed calculations of bond structures of defective solids, and progress continues in the application of statistical and Monte Carlo methods for the consideration of defective solids at elevated temperatures.

IV. STRUCTURE ON A MICRO SCALE

Many of the unique features of solids at high temperature are closely linked to structural features on a microscopic or atomic scale. In particular reactivity, diffusion rates, electrical conductivity, and mechanical and thermal properties are often determined primarily by deviations from perfect crystallinity; that is, by impurities, point defects, nonstoichiometry, disorder, extended defects, and grain boundaries. These deviations are inherently greatly enhanced at high temperatures. Understanding, in detail, the interrelations among these structural features, thermodynamics, and properties will form one of the major efforts of high temperature science in the next decade.

Conventional structural studies (X-ray and neutron diffraction, spectroscopy) will continue to provide important information, but more emphasis must be placed on studies at high temperature, since there is growing evidence that upon quenching, samples do not always retain their high temperature defect and structural features. The development of better X-ray techniques applicable to temperatures above 1200°C is important, including emphasis on the changes of structure (bond lengths and detailed geometry) as a function of temperature and pressure (Hazen and Prewitt, 1977) and on details of defect structure. As an example, one may cite nonstoichiometric $Fe_{1-x}O$. Structural studies at low temperatures (Koch and Cohen, 1969) suggest large defect clusters which were shown to exist at high temperatures by tracer diffusion and isotope effects (Chen and Petersen, 1975) and which have been rationalized with theoretical calculations (Catlow and Fender, 1975).

High resolution electron microscopy and lattice imaging techniques (Cowley, 1976) have proven powerful in studying structures and defects on the 3 to 50 Å scale. The extended defects seen in these studies may act as host sites for impurities, as nucleation sites and as diffusion paths when solids are heated to high temperature. High temperature studies can be performed under the electron beam, and the mechanisms of phase transition observed directly.

Solid phases, produced from high temperature vapors or liquids, which have local order on a 5 to 30 Å scale but lack long-range order, are generally called glasses or amorphous materials. There is renewed interest in low refractivity BeF_2-based glasses for laser applications and great interest in amorphous alloys for improved magnetic, mechanical and corrosion properties (Gilman, 1975) and amorphous semiconductors (Adler, 1971). Structural studies of such metastable materials encounter the same difficulties as structural studies of liquids; but the correlation of structure and properties is extremely important. Work in this area is, to a large extent, technology limited at present; but one can expect and should encourage advances in basic high temperature understanding. EXAFS, laser-Raman spectroscopy (low angle X-ray scattering), and other tools offer some structural information; and molecular dynamics simulation of glass structure and of the glass transition offers theoretical insight. For complex glasses, e.g., silicates and borates, the structure of the crystalline solids offers clues to short-range order in the glass.

On a still larger scale, grain boundaries form alternate pathways for the diffusion reactions that occur at high temperatures and indicate the location of impurities in real materials. The relation of these features to physical properties is at present mainly empirical, and often conjectural. Carefully controlled studies of the structure (Schober and Balluffi, 1970) and composition (Kingery, 1974) at grain boundaries, such as are possible with analytical instruments having great spatial resolution (transmission electron microscope with energy dispersive analyzer, electron and ion microprobe) will provide needed information. In addition, studies of real surfaces will provide a better understanding of surface tension, which is needed to understand the morphology of intergrown phases.

V. PHYSICAL PROPERTIES AT HIGH TEMPERATURES

A large fraction of available engineering materials is used at high temperatures or is processed and fabricated at high temperatures. A dichotomy between knowledge and use arises from the fact that experimental properties are most easily determined at lower temperatures and/or in ideal environments. Thus, there exists an overwhelming need to extend our experimental measurement techniques to high temperature and to develop more direct analytical tools for use at high temperatures (ERDA Workshop Reports, 1977). Excitement in this field derives, not only from the possibility of obtaining new experimental data, but also from the fact that new calculations and correlations from models can be put into a complete picture because the structure on a micro scale and the high temperature physical property measurements are importantly interrelated.

The experimental difficulties of working above several hundred degrees centigrade are large; and thus the literature is filled with inconsistancies and errors. Measurement of temperature, pressure, and composition is difficult especially as the environment around the solid becomes more complex. Other properties, such as electrical conductivity, are equally difficult to measure at high temperatures. For example, measurements of the dielectric properties of an important insulator, aluminum oxide, indicated certain reproducible variation with temperature and oxygen activity. Later, another investigator noted that the same data were obtained with the same platinum electrodes but with the crystal missing -- the reported data were for gas phase conduction (Kitazawa and Coble, 1974).

The data on magnetic, electrical, and atomic transport have been used to interpret the atomic structure and microstructure of solids. In the future the extension of these techniques to higher temperatures, under well-documented conditions and on well-characterized materials will lead to further advances in the field. Indirect measurements of atomic structure are important because direct measurement tools (e.g., X-ray diffraction) are often difficult to use at high temperatures and do not yield many pertinent details of microstructure. The major developments will come through new heating techniques and diagnostics. For example, CO_2-laser heating of most solids is possible, and thus nonreactive, cold chamber walls allow environments and temperatures not possible in other experimental methods.

High temperature studies of fundamental thermodynamic and physical properties are an obvious necessity. For example, rapid scanning differential thermal analysis at high temperatures and variable gaseous environments is a technique not currently available to high temperature chemists. Thermal expansion and compressibility data are needed at high temperatures to put the understanding of particular materials into an equation of state useful for extrapolation as well in interpolation.

Glasses constitute a large group of solids that are formed at high temperatures. Their structures resemble those of liquids, and structural information in general is lacking. In particular, long-range structural information is urgently needed. Of all properties of practical importance, chemical durability of oxide glasses is least understood. One common example is the effect of boric oxide on durability, presumably due to the ability of boron to assume both three- and four-fold coordination. Another example is the ability of zirconium-containing glasses to withstand alkali attack. The development of glasses with superior chemical durability has been the result of empirical chemistry. Structural, transport, and thermodynamic data and their utilization to predict chemical durability must be obtained and developed.

Besides chemical durability, further understanding of ionic conductivity is desired. For instance, in alkali silicate glasses, the highly anomalous "mixed alkali effect" is still not quantitatively understood (Isard, 1969). In fluoride glasses, frequently the fluoride anions, rather than the alkali ions, conduct. Reasons for this anionic conduction are unknown.

The study of glasses offers one of the best opportunities to study metastable solids because the equilibrium state is easily frozen in. Liquid-liquid phase separations give rise to composite materials containing two noncrystalline solids; and separation into crystalline phases has, in oxide glasses, produced a wide variety of useful materials. The understanding and accurate control of such phase transformations in other glass systems such as the metals, chalcogenides, and fluorides constitute an unexplored area with promise of new materials with interesting properties.

VI. HIGH PRESSURE: A PROBE AND SYNTHESIS TOOL

High pressure studies have been underemphasized by traditional high temperature science, although they have been exploited by geophysics and mineralogy as a tool for the synthesis of new materials and for the study of systematic variation of structural properties. Pressures as high as 10^6 atm have been achieved both in static experiments (Mao and Bell, 1976) and under shock conditions. The diamond-anvil cell, with laser heating, offers the possibility of simultaneously attaining pressures of 10^5 atm and temperatures of 2000°C, on a very small sample, and the measurement of X-ray, structural, spectroscopic, and electrical properties under these conditions. Although such measurements are not as accurate as those at room temperature, they open entirely new vistas, especially for phases which cannot be quenched. Other solid media pressure systems (piston cylinder, belt, tetrahedral anvil, Kawai split sphere) can attain pressures of 10^5 bars on larger samples. Lastly, shock experiments provide transient pressures approaching 10^6 atm and offer the chance to study metastable phases in a regime that allows very little diffusion to occur.

The effect of pressure on solids is in many ways opposite to that of temperature. Increasing pressure stabilizes the denser phase which is usually, but not always, the phase of lower entropy; while increasing temperature stabilizes the phase with higher entropy. Thus for determining, correlating, and predicting chemical properties, the systematics gained from studies of high pressure phases are very useful. In addition, high pressure often favors states of high electrical conductivity; thus, many insulators or semiconductors at ambient conditions become metals under high pressure (Fe_3O_4, Si, and even possibly metallic hydrogen). Thus high pressure, coupled with structural studies, is a probe for band structure and bonding.

VII. NEW SYNTHESIS TECHNIQUES AND MATERIALS

New synthetic methodologies are being developed which are capable of providing new refractory materials of basic as well as applied interest. Foremost among these are ion implantation (Poate, 1978) and molecular beam epitaxy (Cho and Arthur, 1975), techniques which provide the capabilities of tailor-making materials. Molecular beam epitaxy, which has been used with great success in the electronics industry, has yet to be explored as a technique for the synthesis of refractory materials. Numerous interesting possibilities exist for the synthesis of binary and ternary materials whose preparation is either kinetically or thermodynamically unfavorable under currently available conditions. Application of these methods to the synthesis of high temperature materials could result in the preparation of novel and potentially interesting materials with unusual stoichiometries and structural configurations.

The development of laser technology provides high temperature scientists with a tool suitable for unusual synthetic approaches. A high peak-power pulsed laser beam focused on the surface of a solid can create a unique situation: a very high temperature, ca. 10,000°C, in a very short period of time, less than 100 nanoseconds. An immense amount of chemical and physical changes occur during, and subsequent to, the formation of this high temperature situation. Ionic, atomic, and radical reactions are taking place while the laser-created plasma is expanding rapidly into the bulk gas phase, quickly cooling as it does so. The opportunity for exploring the kinetics and thermodynamics of these reactions is readily apparent.

Research in areas such as laser annealing of ion implanted semiconductors and metals is growing at a phenomenal rate. The unique ability of the laser to heat only the surface of a semiconductor wafer will offer engineers a new dimension (over batch furnace heating) in semiconductor device design. Laser surface melting of implanted metals will allow deeper penetration of implanted species, presently limited to hundreds of angstroms. The laser will be used to make surface alloys by melting plated or deposited composites, and nonequilibrium alloys will be made by rapid self-quenching. Surface alloys will be tailored to give the corrosion resistance properties of the surface alloy, while maintaining the bulk mechanical properties. The laser will be coupled to molecular beam epitaxy for *in situ* annealing of amorphous deposits. Two-dimensional high temperature chemistry will be carried out on substrates by selectively heating the surface in the presence of reactive gas mixtures -- by laser defined chemical vapor deposition (CVD) or by direct coupling to the gas phase to control gas reactions.

Other areas offering promise for synthesis of novel and useful high temperature materials are sputtering, plasma processing, and skull melting -- a technique which permits the containment of 100 cm^3 melts in temperatures in excess of 3000°C in oxidizing and reducing atmospheres. The rapid quenching of amorphous alloy strip and of metastable and finely spaced dendrites of crystallized metal powders is rapidly advancing (Grant and Giessen, 1976). A variety of powerful solid state synthetic techniques with great promise and versatility is emerging. They have yet to be applied systematically with the goal of producing useful high temperature materials.

Sight should not be lost of the fact that conventional high temperature techniques, such as have been in use in many laboratories for 10 to 20 years, continue to provide direct synthetic routes to novel inorganic materials. Two methods which remain highly productive are the simple heating of refractory materials in the 1500 to 2500°C range and vapor transport techniques. New metal-rich compounds, unusual defect-ordered solids, and intermetallic compounds fall in the first category. Since new binary compounds continue to result from these conventional methods, it is reasonable to suppose that research in this area will be productive during the next decades. It is difficult to overstate the importance of this work to the developing understanding of chemical bonding effects in solids. The general level of understanding of bonding in solids lags far behind our understanding of molecular systems, and much of the understanding of solids evolved at a time when the majority of the known compounds were saturated valence materials. The materials resulting from high temperature synthesis (reduced halides, metal-rich sulfides and phosphides, intermediate oxides, etc.) provide clear and strong indications of the importance of these materials in high temperature systems, and the structures of these materials demonstrate the importance of metal-metal bonding. In some cases, it is evident that metal clustering is an important structural feature in some high temperature materials. The further exploration and development of the synthesis of such materials, coupled with theoretical (band structure) and further experimental (PES, superconductivity, charge density wave transitions) techniques aimed at exploring the electronic behavior of the materials, will lead to an enhanced understanding of solids.

VIII. SOLID-FLUID INTERACTIONS: GEOCHEMISTRY

Phase equilibria between solid and melt have been discussed previously. However, in many industrial applications and in the geological context, solids and melts at high temperatures are in contact with aqueous fluids or water vapor. This contact greatly enhances the reactivity of the solid, usually with respect to undesirable reactions we call corrosion, but the exact mechanisms of interaction remain unclear. Several examples may be cited:

- Vaporization loss of Na_2O from alkali borosilicate glasses at high temperatures increases several orders of magnitude in a damp environment.
- The strength of crystalline SiO_2 (and very possibly other ceramic materials as well) is two orders of magnitude less for hydrothermally grown material, than for quartz which contains essentially no water.
- The viscosity of silicate melts decreases markedly as water is added.
- The melting point of $NaAlSi_3O_8$ (feldspar) is over 100°C lower at 1 kbar water pressure than at atmospheric pressure.

An understanding of the phenomena is essential to finding materials compatible with the down-hole environment of wells in natural or induced geothermal fields, and understanding the transport of ore-forming solutions in the natural environment and the possible leaching and transport of nuclear waste under similar conditions.

For high temperature chemistry, the following questions need to be answered. What are the mechanisms and thermodynamics of incorporation of water into silicate melts and of solubility of inorganic solids in aqueous fluids at high pressure and temperature? What are the mechanisms of incorporation of water in solids at both trace and major levels, and what are the phase equilibria involving hydrous phases at high temperature and pressure? The next 10 years should see a convergence of the thinking of the geochemical and high temperature science communities in these fields, since each group has much to offer the other in terms of complementary experimental and conceptual approaches.

IX. THE CHEMISTRY OF SURFACES AND INTERFACES

All materials are used in applications where interfaces and surfaces occur and most significantly where the interactions of energy or matter at these discontinuities often dominate the properties or usefulness of the materials, device, or system. The degradation of all engineering materials -- whether by aqueous corrosion or hydrogen embrittlement of steel, by electrochemical corrosion of electrodes, by erosion of concrete, or by poisoning of petroleum catalysts -- has a price too large to estimate. While it is an old problem, emerging chemical sciences and analytical techniques will allow for major breakthroughs in the control and reduction of materials degradation (ERDA Workshop Reports, 1977).

Research on surfaces and interfaces is possibly the most fruitful research topic in solids (Somerjai, 1978). Yet, compared to our understanding about bulk properties, our understanding about the properties of surfaces is in its infancy. The strucutre and chemical complexity of surfaces and interfaces are even richer in variety than bulk materials; however, because the surface is only a few atomic layers deep, only recently could its structure and chemistry be analyzed. The properties of surfaces are very sensitive, not only to atomic arrangements at the surface, but also to the underlying bulk material. The extent of influence of the structural discontinuity into the bulk of the near-surface region may be in the range of a few atomic layers in metals to many atomic layers in ionic materials. Thermodynamic and structural models that include lattice strain and electrostatic effects have not yet been formulated; but it is already apparent that large differences in the distribution of impurities and electronic or atomic defects in the near surface regions should occur for metals, semiconductors, and insulators.

The major experimental hurdle is that the sophisticated experimental techniques to study composition and structure of interfaces and surfaces (e.g., Auger, ESCA, SIMS, LEED, and STEM) are essentially low temperature, high vacuum methods, and the measured characteristics may not reflect the high temperature properties. Thus, the crucial need is for high temperature and environmental controlled stages on the instruments used in these and other new techniques, and for the careful coupling of indirect high temperature measurements of the properties of surfaces to more direct analytical methods.

The lack of fundamental understanding reaches right back to basic thermodynamics; i.e., we have very little good data or theoretical models for the surface free energy of solids, especially at high temperatures. Because a solid can support a shear stress, the surface free energy is complex to describe. It is extremely sensitive to local structure and composition; it is anisotropic and varies strongly with additives.

The understanding of the surface energy, interfacial energy, and grain boundary energy provides the fundamental physics and chemistry for many important processes and properties of solids. For example, reduction of surface energy is the driving force for the production of nearly all of the polycrystalline inorganic materials (oxides, nitrides, borides, etc.) and the interplay between the gas-solid surface and grain boundary interfaces determines the resulting microstructure. Sintered urania fuel rods with controlled porosity to avoid swelling and high surface area γ-alumina catalyst supports are possible largely due to the empirical application of these principles. Bonding, joining, adhesion, lubrication, and wear are other examples where one is reduced to empiricism.

Understanding the surface chemistry and physics of fine particulates will have immediate application in such diverse fields as stack gas cleanup and processing of materials. The physical forces between submicron powders and the extent to which applied forces (e.g., electric fields) effect particulate motion and aggregation is poorly understood. Can bulk properties be ascribed to particulates having a large fraction of their atoms at the surface? Are the atomic defects different from the bulk material? What kind of dielectric properties are expected if electrostatic precipitators or electrofluidized beds are used to capture undesired particles?

Phase transformations and chemical reactions often occur at grain boundaries, interfaces, and surfaces. The transmission electron microscope has contributed much information about the structural and topological features; but complete structural-chemical theory and understanding are not available. For example, the theories of nucleation and growth in solids, or on solids, are still limited by the lack of a basic description of the surface free energy in terms of measurable quantities. Another example is the inability to predict compounds and compositions for heterogeneous catalysts. However, recent advances in cluster calculations, using X-alpha techniques and the Auger and photoelectron spectroscopic studies of surfaces, suggest that correlations and models are possible.

A major area in which the surface chemist will be able to contribute is high temperature stress-corrosion cracking. In brittle intermetallics and ceramic materials, as well as metals, a major mode of failure at high temperatures is attributed to chemical effects from the environment at the microscopic tip of the advancing crack. What is the chemistry at the crack tip? How can the devasting effects be ameliorated by changes in the material chemistry? An enormously important technological problem awaits scientific input.

Indeed, the chemical science of surfaces looms as an important scientific challenge and one that will have great technological payoff. A key need is for theorists and new experimental techniques. The variety of instruments currently used to characterize the bulk material must be developed to analyze the surface and near-surface properties of solids. The proposed approach should complement that of surface physics (DOE Report, Theory of Surfaces, 1979). For example, the theory and measurement of electron emission from surfaces at high temperatures and nonvacuum environment will assist in understanding emission from electrodes in thermoelectric devices and magnetohydrodynamic generators, where the chemistry of the environment is probably as important as the intrinsic properties of the solid.

X. THERMODYNAMICS AND PHASE EQUILIBRIA

High temperature chemists have traditionally provided the scientific community with information about heterogeneous equilibria in binary and ternary systems. Such systems as the borides, nitrides, carbides, and oxides of the transition metals, rare earths, and actinides have been extensively studied and have provided numerous examples of complex phase behavior. The complexities arise from possibilities of mixed valence states, variable metal-metal interactions, and resultant defect formation.

The understanding of phase equilibria, although far from complete, is required for the development of high temperature technology. Areas upon which high temperature materials will have a direct impact are composites, high temperature turbine technology, reactor safety, direct production of alloys from powders, coatings, solar thermal technology, and others. Thus a continued effort in research of phase equilibria in high temperature systems should be maintained. For example, lack of phase equilibria data in the Si-Mg-O-N, Si-Al-O-N, and Si-Y-O-N has slowed the development of high temperature ceramics for turbine and diesel engines. The most interesting results in this area, scientifically, will probably be those strongly coupled to theoretical calculations with the aim of producing models describing phase behavior. For example, efforts in alloy and intermetallic compound heterogeneous equilibria will presumably be guided by close collaboration with band theorists with the goal of producing refinements in or alternatives to the Brewer-Engel or Meidema models of metal-metal interactions.

Another area in which new results will come from the study of thermodynamics of condensed phase equilibria is multicomponent systems. Many real systems that arise in corrosive environments and present difficulties in a developing energy technology (e.g., stress corrosion cracking, grain boundary effects, MHD channel corrosion, and solar collector surfaces) involve systems of greater complexity than those heretofore studied by rigorous thermodynamic analysis. Technological requirements make it imperative to enhance the understanding of such systems; and thus increasing efforts in this important area can be anticipated.

The final results of all such studies are thermodynamic data. These data, when critically evaluated and compiled, provide the structure upon which high temperature technology can advance. Using such data, the design engineer can determine under which circumstances -- i.e., in which ranges of temperature, pressure, and chemical potential -- a material will be stable, and thus, can initiate new designs to operate in more efficient regions of thermodynamic space.

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5

PROPERTIES OF HIGH TEMPERATURE LIQUIDS

I. SUMMARY AND CONCLUSIONS

Fundamental studies of high temperature liquids have lagged behind those on gases and solids because the experiments are difficult and their interpretation requires much sophistication. However, because high temperature liquid phases are present in many technological processes with potential interest, one must now address the need for reliable data and basic understanding of the liquid state so that the unique properties of high temperature liquids can be used as advantageously.

Examples of problems that would benefit from fundamental research on high temperature liquids include coal conversion and the environmentally necessary product cleanup, oil shale recovery, nuclear reactor design and novel reprocessing techniques, and new energy-conserving metallurgical methods often using lower grade domestic ores. Research on dense fluids will also help solve other important energy and environmental problems and will lead to creation of new materials and to new processes for fabrication, preparation, or extraction of materials.

Effective development of liquid-state based technologies requires research on many types of dense fluids in four areas:

- Accurate and reliable data are needed -- including thermodynamic data, data on structure and intermolecular interactions, transport data, and kinetic data -- for both pure fluids and mixtures.

- Fundamental theories are needed to understand the molecular or atomic structure and bonding of liquids.

- Usable mathematical models with obtainable parameters are needed to characterize high temperature liquid mixture behavior in terms of thermodynamics, kinetics, transport phenomena, and surface effects and phase transitions.

- Investigations must be applicable to real problems by developing, not only data and theories, but the tools to use them -- both in terms of calculational algorithms and measurement techniques.

From the history of the field one may anticipate that basic developments will translate into relevant technology. For example, the Cohen-Turnbull theory of nucleation and growth led to major advances in glass-ceramics manufacture and to the development of metallic glasses as important engineering materials.

This chapter discusses liquid metals, molten glasses, molten salts, slags, supercritical fluids, etc. -- in all cases both pure and mixed. These are categorized first in terms of possible areas of fundamental research and then with respect to their technological applications.

II. PURE MATERIALS (ONE COMPONENT)

This category includes liquid metals, salts, oxides, sulfides, and metalloids. All represent liquid states with very strong intermolecular interactions -- interactions much stronger than in the liquids to which most current data on liquid-state structures pertain. Interactions in high temperature liquids are usually considerably longer range in nature than those in well-studied, room-temperature liquids. Techniques must be developed and exploited to study the molecular physical chemistry of such high temperature fluids. Some of these techniques will be new applications of X-ray, neutron, or Raman scattering, NMR, and EXAFS to yield information on structure and on intermolecular interactions such as correlation times for translation and rotation.

Structural and molecular-level studies must be coupled with measurements of thermodynamic and transport properties, which are gradually becoming more accessible. For example, many high temperature measurements of pure liquid metals (and alloys as well) can be achieved through the use of electromagnetic levitation heating techniques and transient exploding wire methods. Reliable values of enthalpies, heat capacities, densities, surface tensions, gas solubilities, viscosities, and thermal conductivities are available for only a few melts. The most refractory metals -- Ta and W (as well as, for that matter, high melting carbides such as TaC and ZrC, and various alloys) -- offer additional opportunities for applications of containerless techniques.

Reliable measurements of basic properties of high temperature liquids will allow assessment of the accuracy of available measurements and of current estimation techniques. They will provide insight, not only into such liquids, but into the liquid state in general, because high temperature liquids have far stronger intermolecular forces than those in the well-studied low temperature fluids such as Ar, Xe, CH_4.

When key data have been obtained, statistical, mechanical, structural, quantum mechanical, hydrodynamic, and transport theories of these unusual liquids can be developed to provide a framework for a precise description of their properties. In developing a theoretical framework, the number of empirical, adjustable parameters should be minimized and those parameters which are present should have a well-defined physical meaning.

Because of anticipated advances in computer technology, molecular dynamics and other modeling calculations for liquid properties should be developed as a readily available tool for the study of the physics of high temperature liquids. If possible, quantum electronic effects should be included so that metals can be treated.

This would permit studies of the characteristics of liquids under unusual conditions and provide a guide for parallel key experiments. For example, the properties of metastable subcooled or superheated liquids -- as well as of glassy materials and their transformations -- are, not only a fundamental interest, but will have applications in industrial safety as well as in the preparation of unusual materials. High pressure, high temperature measurements are scarce. Specifically, methods for measurements near and above the critical temperatures and pressures -- especially of metals (alkali and transition) -- are important from a fundamental point of view, for nuclear and thermonuclear reactor analysis and safety (Li and Na), as well as in geophysics (Fe for understanding planetary cores). Such data, when coupled with the development of statistical mechanical and electronic theories of such liquids, should help to develop equations of state which are theoretically sound and accurate enough to describe liquids adequately for practical needs. When data cannot be measured (perhaps for transition metals such as Fe), sophisticated and, it is hoped, reliable theories should be attempted. Structural studies of simple lower melting materials (molten salts) are now underway and require no further emphasis. Studies of the structure of high melting liquids (e.g., oxides) as well as of unusual materials (glasses and their metastable devitrification products) should be undertaken to define their characteristics or the reasons for their formation. Neutron diffraction and EXAFS techniques should become more important tools with greater availability of new facilities and increased familiarity with the techniques. Other parallel studies including spectroscopic and transport measurements should prove significant in fully defining the structure and type of bonding between atoms.

Present structural tools are used largely to define nearest neighbor configurations in liquids. Developments which will serve to define longer range configurations and interactions are needed for understanding the obviously important role of long range interactions on properties (e.g., viscosity).

III. MIXTURES

In general, basic information on structure, transport, and thermodynamic properties -- needed as input for (and checks upon) theory and correlation -- is lacking for high temperature liquid mixtures. There is, of course, a need for theoretical calculations of individual properties, and correlations among the various properties, since property measurements are difficult and time consuming. At present, even if theoretical models were developed, there are insufficient reliable experimental data to check the applicability of the models.

The same structural studies and theories concerning pure materials should be extended to mixtures. It seems clear that only when enough good data are available for liquid metals can models for both pure metals and mixtures emerge. This could well lead to a general method for collection, correlation, and even prediction of liquid-metal mixture phase equilibria with a variety of important applications, as described in the next section.

Structural information is of importance for all four common types of high temperature liquid mixtures (viz., liquid metals, molten salts, molten oxides, and molten chalcogenides); and both direct structural information (e.g., X-ray diffraction, IR spectroscopy) and indirect structural information (inference from properties and crystal structures) are lacking. In addition, Knowledge is needed on variation of structures with temperatures.

Many molten oxide mixtures, for instance, the silicates, borates, and phosphates, are highly viscous liquids. Recent experiments indicate that the ambient atmosphere in contact with such viscous melts can have significant effects on the local structure of the melt, and hence on the resultant glassy phase on cooling. More research is needed in this area of atmosphere-melt interactions.

Information on viscosity and the ability to predict glass formation is needed. For molten salts, fluorides in particular, structural information is lacking. Many fluoride mixtures can be cooled to form glasses. The structures of crystalline fluorides, e.g., coordination number and linkages between polyhedra, are different from those of glass-forming oxides. Thus the direct utilization of knowledge on oxide glasses for fluorides is open to question. Molten fluorides are anionic conductors. The reasons why cations are preferably immobile are unknown. Thus, there are needs for experimental, as well as theoretical, work on transport as well as structure.

In addition to the complexities inherent in multicomponent mixtures of even simple substances, several categories of greater complexity will be of future importance.

- Electronic--Many alloy systems, such as the so-called ionic alloys (e.g., Cs-Au alloys), have unusual electronic properties which lead to unusual structural order, electrical conductivity, and thermodynamic properties. These are analogous to the similarly interesting metal -- molten-salt systems which range from electronic to ionic conductors as a function of composition.

- Structural--Many two component silicates (e.g., ortho- and metasilicates) have well-defined short-range structures. The connection between thermodynamic and other properties and structure needs better definition as a basic step in understanding these technologically important materials.

- Associative ordering--Multicomponent mixtures often exhibit a degree of ordering (or association or complexation) which governs important properties and is not found in lower order systems. The association of Al^{+3} with O^{-2}, though not fully understood, is important in aluminum smelting; interactions of C, H, O, and N with alkali metals are important in reactor technology; the interaction of metal atoms with C, O, N, and S in alloys is important in metal production.

The development of fundamental theories and some key measurements should be undertaken to broaden our understanding of these types of complexity.

Of particular importance for a number of technologies and sciences (steel, glass, MHD, coal burning, geology, cosmochemistry, metallurgy) are complex silicate liquids generally containing $CaO-Al_2O_3-SiO_2$ with other constituents such as MgO, FeO, Fe_2O_3, Na_2O, and K_2O. A detailed understanding of the properties, especially thermodynamic properties, of such liquids would be of broad significance. Complete understanding would require a coupling of experiments and theory.

Also significant for the investigation of electronic, structural, and associative complexities are structural studies such as by neutron diffraction. Details of ordering that can be deduced from accurate structural characterizations, along with information from thermodynamic, transport measurement, and other studies, provide a fundamental understanding of these materials.

Finally one further aspect of mixtures will be important in future studies -- interfaces. There will probably be a renewal of interest in surfaces between liquids and gases that will combine some of the new techniques developed to study solids, surface tension measurements (which give surface concentrations using the Gibbs adsorption equation), and new ways to control the purity of the fluids and avoid the effects of contamination on surface measurements.

IV. THE CALCULATION OF MULTICOMPONENT-MULTIPHASE EQUILIBRIA AT HIGH TEMPERATURES

The current state of the art in solution thermodynamics of organic systems at ambient temperature is that multicomponent, multiphase equilibrium data can be calculated relatively easily and accurately from a minimum of readily accessible binary data. Models of liquids permit rapid generation of vapor-liquid, solid-liquid, liquid-liquid, and even liquid-liquid-vapor equilibria by computer, using as input only pure component and binary mixture data. In fact, the binary data may often be estimated from correlations or corresponding states theory.

A goal in the coming 10 to 25 years should be to achieve the same advantageous situation for phase equilibria involving high temperature liquids. To test the possibility of achieving this goal, one needs more data on pure components and binary systems, plus workable solution theories to represent them. Multicomponent data are required to check the limited available measurements and estimates and to ascertain the possible need for ternary constants. One should be able to greatly expand present abilities to generate, from a minimum of data, needed information on high temperature liquids by development of correlations and predictive techniques.

If this can be done, it would then be possible, in principle, by computer generate and store complex phase diagrams for multicomponent systems -- including thermodynamic activities, enthalpies, and even densities over a range of temperatures. Such a capability would be an extremely valuable tool for the investigation, utilization, and optimization of high temperature processes. This capability, if available from a central facility (or better yet as a packaged program adaptable to use via remote terminal on any large computer), would permit investigators in the field to have at their fingertips data in a smoothed, critically analyzed form, plus the best available predictions.

V. APPLICATIONS OF HIGH TEMPERATURE LIQUID MIXTURE THERMODYNAMICS

Extractive Metallurgy

Experimental data, coupled with a usable mathematical model for high temperature liquid mixtures, would have important applications in many areas of extractive metallurgy. Over the next decade or two, such fundamental thermodynamics could lead to new processes. For example, one of the biggest consumers of electric power in the United States is the reactive metals industry -- aluminum production from molten salts alone represents more than five percent of total U.S. capacity.

Many new processes are being considered for the production of active metals. Alcoa has tested a new chloride process for making aluminum which uses molten salts. Carbothermic processes (e.g., for making aluminum, titanium, hafnium, zirconium, magnesium) have the advantages of simple energy sources but generally require very high temperatures. One way around the severe technological problems of high temperatures is to have the product metal dissolve in a solvent in which its activity is much less than unity.

For example, if one reduces a metal oxide (MO) by a reaction characterized as:

$$MO + C \rightleftarrows M(\text{in solution}) + CO,$$

where M is an electropositive element (e.g., Mg), the reaction is driven to the right by lowering the thermodynamic activity of the product metal. The MO and C would saturate the liquid metal solvent and hence have thermodynamic activities of unity; the CO activity depends upon its partial pressure. However, the thermodynamic activity of M can be orders of magnitude less than unity in a properly chosen solvent or solvent mixture. Thus the reaction can be driven much further to completion at a low temperature in a liquid phase, which is easy to handle, and with the suppression of carbide formation. Moreover, there would be no tendency toward retroreaction because the product metal would be retained in the liquid while the CO is taken off as a vapor.

Such a process would consist of two stages: a reaction stage with CO removal and a separation stage. In the first, the ore would be reduced in a solvent, and both thermodynamic and kinetic modeling are required. Design of the second requires good thermodynamic data.

The data and models now available indicate the molten metallic electronegative elements (such as Pb, Sn, Bi, or Sb), and perhaps some mixtures, would be suitable solvents, yielding electropositive metals at a fraction of the energy consumption required for electrochemical reduction if an economical means of separation of product metal from the solution can be devised. Data on alloys of electropositive metals with electronegative metals are needed to evaluate the potential of such processes; and a theoretical study of such alloys, many of which fall in the interesting class of ionic alloys, would help provide a scientific foundation for understanding the measured properties.

Analogous processes could well be applicable to sulfide ores. But all depends on adequate data and theories of solution behavior at high temperatures.

Separation Processes

Most new metallurgical and pyrometallurgical processes now under investigation in the nuclear industry utilize high temperature liquids (molten salts or metals). Good data and good theoretical or semitheoretical models of solution properties are needed to evaluate and develop these processes.

Supercritical fluid extraction is another novel high temperature separation technique. One of its widely heralded advantages would be the separation available by modest changes in the thermodynamic environment. At this point, however, the basic understanding of this particular type of high temperature solution is limited. A quantitative thermodynamic model applicable to the supercritical fluid state, taking into account the very sensitive solubilities of dilute species, is clearly needed.

Energy Applications

A working representation of high temperature liquid mixtures is essential to a variety of energy areas that will become increasingly important in coming years. Supercritical separations could be applied on a large scale for the recovery of coal liquids from coal and oil from shale. To an extent, CO_2 flooding for tertiary oil recovery, already in use, represents an energy application of supercritical fluid extraction.

Further, a good model of organic liquids at high temperature will be needed for the characterization and separation of coal liquids and heavy crude fractions, as some components have boiling points in excess of 1000 K. Similarly, such models are needed for design and scale-up of coal gasification and liquifaction installations; and extensive phase equilibrium models will be required to clean up the highly complex effluent streams from these processes.

Many applications of liquid metals, salts, and oxides occur in the operation of nuclear and thermonuclear reactors. Thus, behavior at extremely high temperatures must be considered and well understood. Other important energy applications include energy transfer, conservation, storage, and the concomitant problem of environmental control. Molten salts, liquid metals, and silicate melts are of primary importance in proven major technologies (glass, steel, aluminum, copper) and in nature (volcanoes, core of the earth). In addition, many new or emerging technologies utilize such liquids. Molten salts are used in the present process and in all proposed energy-conserving processes for aluminum production. Proposed methods for stack gas cleanup, waste disposal, and coal gasification as well as advanced fuel cells utilize molten carbonates. Molten halides are important in battery systems especially ones being developed for automobile propulsion and power storage for peak load periods. Molten salts are among the solvents used in some of the environmentally acceptable processes for the production of metals such as lead. Molten $ZnCl_2$ and $AlCl_3$ containing melts are involved in several processes for coal conversion. The hot corrosion of metals by combustion effluents involves molten sulfates and other oxyanions. Silicate systems, though not fully understood, are important not only in current metallurgical processes, glass production and in geology, but are of potential importance for understanding slagging during coal combustion and for minimizing the loss of the potassium seed in a MHD generator by dissolution in slag. Liquid metal mixture behavior is important in the design of heat pipes for high thermal fluxes, especially in relation to dissolution of the container material, as this now limits their application.

Expansions of work on theories and measurements, especially for complex solutions, would be essential for such technological applications.

VI. PHASE TRANSITIONS

The nucleation and growth of gas phase from a liquid are well understood theoretically. However, there has been no test of the predictions of theory either for boiling or for bubble formation by dissolved gases for any high temperature liquid. Such studies in silicates, for example, should be important in understanding volcanism as well as in high temperature safety (e.g., splattering during oxygen steelmaking). Even more important, however, is the development of a fuller understanding of nucleation and growth of crystals from a liquid. The criteria for the formation of stable and metastable materials as well as theories (such as symmetry theories) for the path of nucleation and growth and the development of different morphologies need further development. Experiments which test fundamental principles and concepts should be performed on both simple and complex high temperature molten materials.

Molten salts are often used as media for crystal growth (e.g., $BaTiO_3$ from KF) and electrodeposition (e.g., Mo). Usually, particular melts are found to be necessary to obtain desired products in an Edisonian fashion. Studies of the fundamental reasons why, for example, barium titanate crystals or better molybdenum deposits are made from fluoride melts is important and a general development of theories and concepts for such processes would be valuable.

VII. METASTABLE SYSTEMS AND NEW MATERIALS

Molten oxides and fluorides which form glasses on cooling are frequently highly viscous liquids. Some systems can be cooled to below the liquidus or solidus and maintained at these elevated temperatures without undergoing crystallization. Liquid-liquid phase transformations may occur (classical nucleation or spinodal decomposition). The extent of such transformations is controllable by chemical composition and/or cooling rate. Both theoretical and experimental studies are needed to better understand such transformations and as a means of preparing new glasses.

The more-fluid metallic alloys have been rapidly quenched (splat cooling) to yield new crystalline solids and/or new metallic glasses. The quenching of liquid oxides (nonviscous systems), molten salts, molten chalcogenides, and the less-common melts mentioned above constitutes an unexplored area of high temperature science which holds promise for new materials.

6

MASS TRANSPORT AND CHEMICAL KINETICS INVOLVING CONDENSED PHASES

I. SUMMARY AND CONCLUSIONS

Mass transport and chemical kinetic studies must focus on model systems which allow predictive capabilities and specific systems in response to national needs. Projected areas of need and future development involve more complicated systems such as multicomponent solids and gases, gas systems containing ions and electrons as well as stable molecules, solids with complicated and anisotropic crystal structures as well as glasses and polymers, and especially systems under gradients. For such systems, the following research areas appear particularly promising:

- High temperature reactions involving a condensed phase and a gaseous species may leave the condensed phase unaltered (catalysis), may slightly alter the condensed phase (energetic-particle-surface interactions resulting in ion implantation and sputtering), or may form volatile products with the disappearance of the condensed phase. The kinetics and mechanisms of these important classes of reactions are still imperfectly understood to the detriment of their application in a variety of key energy technologies. This field should develop rapidly in the next 10 to 25 years because of the availability of a variety of extremely sensitive diagnostic tools such as simultaneous Auger and energy-analyzed secondary-ion mass spectroscopy, laser fluorescence spectroscopy, and special reaction chamber designs for use in scanning electron microscopes.

- Although oxidation with a single oxidant is fairly well understood, reactions with mixed oxidants should show significant advances in the next 10 to 25 years. Recent advances in the design of high temperature environmental cells in the high voltage electron microscope will enable future investigators to observe the structure and growth of solid product layers *in situ*.

- Diffusion under gradients of chemical potential, of temperature, and of mechanical stress are major factors in determining the lifetime of many components. Research in this area is in its infancy and will become increasingly important in the next 10 to 25 years.

- The mass transport of minority constituents -- such as carbon, hydrogen, sulfur, nitrogen, water vapor, the halogens, and phosphorous -- through nonmetallic materials will be of increasing importance to high temperature technology. Research in these areas will become more active.

- Microstructural imperfections such as grain boundaries, crystallographic shear planes, and dislocations offer short circuit paths for transport. Such transport frequently limits the lifetimes of components. The characterization from thermodynamic and structural viewpoints of these gross imperfections and their role in transport will be an important research area.

II. HIGH TEMPERATURE GAS-SOLID REACTIONS FORMING GASEOUS PRODUCTS

The phenomena of mass transport and chemical kinetics at high temperatures will be discussed separately depending on whether a given condensed phase reacts with a gas to form a gaseous product or a different condensed phase.

This section deals with gaseous products put into three categories depending on whether, as a result of the interaction with the gas, the condensed phase is unaltered (catalytic type), somewhat altered (energetic particle-surface interactions), or consumed (gas complexes and volatile products).

Catalytic-type Reactions

Unique opportunities exist today, with a panoply of new experimental surface-sensitive techniques, to probe the molecular dynamics of high temperature, gas-solid reactions, and to gain a fundamental understanding of reactions which leave the surface unchanged. For example, reaction chambers of novel design allow the experimentalist to work under realistic environmental (temperature and pressure) conditions while being able to characterize the solid surface in an electron microscope. Detailed experimental information, coupled with sophisticated new models such as metal cluster *ab initio* calculations, can be expected to yield fruitful results in the next 10 to 25 years and can be expected to bring about a significant increase in our understanding of such reactions.

Energetic Particle-Surface Interactions

Although traditionally the province of the physicist and materials scientist, energetic particle-surface interactions are attracting the attention of other high temperature scientists. Reactive energetic particles (H^+, D^+, B^+, P^+, N^+, O^+) undergo chemical reactions in surface and near-surface regions with far reaching consequences to solid state chemistry and technological processes. Ion implantation and subsequent laser annealing has been shown to result in cheaper and better semiconductor junctions. Chemical and physical sputtering have been shown to be important impurity release mechanisms in magnetically confined fusion machines. A better understanding of the chemistry of ion implantation and of the effect of charge transfer processes at surfaces and ion fraction yields in sputtering can be expected to have important impact in applications as diverse as the production of amorphous semiconductor devices and the successful containment of fusion plasmas. Advances in instrumentation range from the availability of mass- and energy-selected ion beams, to simultaneous Auger and energy-analyzed secondary-ion mass spectrometry, to laser spectroscopy of Doppler-shifted atomic fluorescence lines. Progress in the next 10 to 25 years will yield not only advances in fundamental understanding but also new catalysts and substrates, semiconductor devices, protective coatings, etc.

Gas Complexation and Volatile Products

An important class of high temperature chemical reactions is that in which a gas reacts with a condensed phase to form a gaseous complex or a volatile product. Examples of the former are the chloroaluminate complexes formed with many mono-, di-, and trivalent metal chlorides by aluminum chloride gas. Examples of the formations of volatile products are the reactions of fluorine gas with many metals to form volatile metal fluorides. Although reactions of this type are extremely important technologically, their kinetics, and therefore the detailed mechanisms of the reactions, are poorly understood. The formation of volatile complexes as occurs in reactions with aluminum chloride could become important in low grade ore beneficiation, if one had a better understanding of the relation between reaction rates and the complex heterogeneous phases present in most ores. A variety of high temperature chemical vapor deposition processes, including the potentially important amorphous silicon deposition, are limited in their applicability by a lack of knowledge of the kinetics of formation and decomposition of the gaseous species. The manner of hydrogen retention and bonding in amorphous silicon films, for example, is crucial to their operation as semiconductor devices.

One can expect considerable progress in the next 10 to 25 years in these areas as a result of new experimental techniques, such as high temperature absorption spectroscopy capable of quantitative measurements of species concentrations in the gas phase. Other major advances are on the horizon as a result of improvements in plasma diagnostics.

It will be possible to measure electron, ion, and neutral densities and temperatures precisely, and therefore to make quantitative measurements of kinetic parameters in systems which heretofore have not been amenable to precise scientific study by high temperature scientists.

III. GAS-SOLID REACTIONS TO FORM SOLID PRODUCTS

High temperature solid-gas reactions in which solid products are formed are of particular importance. Kinetic studies of such reactions are needed to understand and control many high temperature corrosion processes. For example, the ability of metals and alloys to withstand the aggressive environments encountered in gas turbines and coal gasification establishes the lifetime of these materials (ERDA, 1977; ERDA-NSF, 1975). Kinetic studies with mixed oxidants can be expected to show significant advances over the next 10 to 25 years.

Microscopic interpretations of kinetic studies of these systems require sophisticated approaches. Although the initial reaction may be controlled by a phase-boundary reaction, diffusional processes in the product phase can eventually influence or control the reaction rate. Thus a major factor in the success of such kinetic studies is the ability of the investigator to identify and control important experimental variables like surface morphology, sample purity, temperature, gas pressure, and flow rates.

In many studies, the characterization of the solid product layer is essential to a detailed understanding of the reaction kinetics. For example, the coherence and imperviousness of the product layer determines whether the predominant mode of transport through the product phase is bulk diffusivity, grain-boundary diffusivity, or transport through pores or microcracks. Temperature gradients and mechanical stresses due to growth or thermal cycling can be particularly critical parameters in determining the coherency and imperviousness of solid product layers.

Recent advances in the design of high temperature environmental cells in the high voltage electron microscope (e.g., P. Swann, Imperial College, London) offer exciting potential for direct observations of the structure and morphology of solid product layers *in situ*. This instrumentation can provide, for the first time, direct observations of the nucleation and growth of the initial reaction product.

IV. TRANSPORT

Transport via bulk or lattice diffusion in solids impacts on practically every aspect of high temperature science and technology. Diffusion is frequently the limiting factor in the lifetime of components and also in the preparation of new and useful chemical products. In practical situations, this diffusive transport frequently occurs under gradients of chemical potential, temperature, or mechanical stress.

Self-Diffusion

Rates of tracer- or self-diffusion in solids (metals, nonmetals, glass, polymers) at equilibrium are needed as fundamental data and to develop models for predictions. Furthermore, diffusion isotope effects can be utilized to elucidate transport mechanisms. The availability of pure, well-characterized crystals is a major factor in obtaining such data.

Gradients and Impurities

Transport under gradients will assume greater importance in the next 10 to 25 years, as will the transport of impurities, both cation and anion, but especially of minority constituents in a gas phase -- such as carbon, nitrogen, hydrogen, water vapor, sulfur, phosphorus, and halogens (NRC, 1979).

Surfaces and Interfaces

Short-circuit transport at surfaces and interfaces -- grain boundaries, dislocations, crystallographic shear planes, and various other gross inperfections -- is often rate determining. The basic science (models, theories) of such transport presently lags far behind that for bulk lattice transport.

As an example, the corrosion of many high temperature alloys, used in both commercial and military aircraft engines, yields alumina as the major corrosion product. Short circuit paths are involved (Felten and Pettit, 1976). Model systems utilizing bicrystals of known orientation, crystals of known dislocation densities or crystallographic shear planes, or crystals under mechanical stress are needed as are studies of diffusion on free surfaces of crystals of known orientation.

Thermodynamic Variables

Methods are needed to fix thermodynamic variables quantitatively during transport. In electronics, for example, in ternary compounds such as gallium arsenide phosphide the chemical potentials of two components at constant temperature and total pressure must be simultaneously fixed for mass transport measurements to be meaningful. Likewise the ceramic components which are candidates in MHD systems and in coal gasification systems are often multicomponent (ERDA, 1977; ERDA-NSF, 1975).

In the cases of the more complex systems, novel and improved methods must be developed. The use of several different galvanic cells to fix the chemical potentials in a given compound may be explored, as may conventional gas-phase equilibration using multicomponent gas mixtures along with computer-generated solutions to the pertinent equilibria. By varying the chemical potentials and impurity levels, the number and type of lattice defects can be changed; transport studies as a function of these variables can yield information on transport mechanism as well as data for real systems.

Modern and available experimental techniques applied to bulk diffusion and surface diffusion may include Auger spectroscopy, ESCA, and SIMS, as well as more conventional microprobe analysis and radiotracer techniques.

V. REFERENCES

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7

COMPLEX HETEROGENEOUS SYSTEMS

I. SUMMARY AND CONCLUSIONS

Many research problems that relate to complex systems concern the application of high temperature chemistry to solving specific practical problems. Application of fundamental principles of high temperature chemistry, as well as reliable basic data, will be necessary for optimum solutions to these problems. One may conclude that current applied problems can be of value in setting priorities for areas of basic research, and that applied research programs could profitably support more basic research.

A recurring need is for reliable experimental data and for compilations of evaluated data. Much necessary new data can be produced from studies of gases, liquids, and solids outlined in previous chapters, including the study of model compounds particularly chosen for the insight their behavior can give to complex system behavior. New measurement techniques and instrumentation such as spatial, time-resolved probes of gas species and surface structure during gas-surface reactions would be advantageous for studying processes in complex heterogeneous systems.

Specific areas of research that may be particularly helpful in understanding complex heterogeneous systems have been identified:

- Mechanisms and rates of heterogeneous high temperature reactions need to be investigated to provide better understanding of technological processes.

- Reactions on surfaces and mass transport through surfaces and grain boundaries should be stressed. They find application in catalysis, corrosion, materials processing, and formation of particulates.

- Coupling theory to experiments in key systems as the basis for the extensive modeling required to correlate variables in complex heterogeneous systems. It is recognized that simple parametric models will be inadequate. Well-considered models can bridge the two communities of researchers, indicating gaps in basic information and ways of improving technology through better understanding.

- Studies of reactions far removed from equilibrium are needed because these reaction products and rates can differ signficantly from near-equilibrium reactions. Examples include:
    - -- the flash pyrolysis of biomass, where new formulations of mechanisms in organic reactions may be required.
    - -- solid decomposition reactions where product gases exhibit nonequilibrium compositions (e.g., propellants used in guns or rockets and decomposition of complex salts such as metal sulfates).
    - -- chemical changes brought about by large temperature gradients such as those that occur in fission or fusion reactors, MHD channels, and solar receiver materials.
- Research to determine interactions of mechanical and chemical effects will be important. Applications relate to stress-corrosion cracking at high temperature, vapor explosions that can occur when melts (metals, slags, salts) drop into water, development of new tools for machining materials, and erosion-corrosion-phenomena at high temperatures.

II. INTRODUCTION

Earlier chapters have been concerned primarily with fundamental states of matter and with homogeneous systems and reactions. This chapter deals with reactions and processes that can occur in complex heterogeneous systems.

It is important to note that technologically relevant processes almost always involve heterogeneous systems and complex reactions. From experience, it is clear that improvements in processes based on complex, multiphase high temperature reactions will require informed applications of scientific principles and reliable experimental data. New theoretical capabilities will be required, not only to guide experimental programs, but also to serve as the basis for the extensive modeling that is necessary for adequate correlation and control of the variables encountered in complex systems and reactions. Only by applying principles and processes based on reliable data can one avoid increasing the instances of semicommercial demonstrations that fail because the processes were founded on an inadequate scientific base.

Some preoccupation with applied problems can be useful in assigning priorities for the vast number of experimental studies that could be performed in complex systems. The complexities of such systems dictate the importance of fundamental high temperature chemistry research to minimize process development problems. Examples of new systems and processes related to high temperatures include plasmas, MHD gas streams, fusion reactors, coal and biomass gasification and liquefaction, chemical vapor deposition, halide lamps, thermochemical and thermoelectrochemical utilization of heat, fission reactors, and surface reactions in catalysis and corrosion.

To treat complex heterogeneous systems in some depth and still do justice to the many varied research needs, problems have been grouped into several classifications. Some of these, selected according to the interests of authors of the chapter, were expanded into discussions at some depth and the rest presented as groups of related suggestions.

III. COAL AND BIOMASS CONVERSION

With the decline in cheap oil and natural gas availability, attention is shifting once again to the derivation of fuels and chemicals from renewable resources (e.g., wood) and from the large-inventory fossil sources (e.g., coal, oil shale, tar sands). To a greater extent than is usually needed for simple combustion, one desires detailed knowledge of the chemical processes accompanying thermochemical conversion to gases, liquids, and chemical products. Furthermore, many of the processes involve rapid heating to high temperature, in steam or H_2 environments, with and without catalysts of diverse function and nature, and often at high pressure.

Starting materials are complex, heterogeneous organic substances. The exact structure and bonding in the parent material is often unknown, and the complex macromolecules and organic components are subject to reaction conditions for which classical organic chemistry provides no firm guidance. At high temperatures, sufficient energy is available for the compounds to react simultaneously through a variety of pathways and provide a multitude of products, which in turn would further react as they are formed. As an example, slow heating of wood in the absence of O_2 (pyrolysis) produces a bewildering array of gaseous species, oil, and tar -- plus a poorly characterized char containing significant residual hydrogen and oxygen. At the other extreme, flash heating of wood and its components at rates up to 10,000°C/sec produces enhanced yields of simple unsaturates such as ethylene and benzene. Similar complexity exists with coal.

A great deal of high temperature research will be needed to characterize the kinetics and mechanism of these degradation processes. Techniques will be needed to analyze the complex transient vapor species and to monitor structure, composition, and reaction centers in the condensed phase. For example, the structure of char and the factors controlling its reactivity are still poorly understood. Temperature measurements involving condensed phases undergoing both endothermic and exothermic reactions will be particularly challenging. Modeling will involve knowledge of thermophysical (e.g., thermal and gaseous diffusivities) as well as thermodynamic and kinetic properties, all in a rapidly changing environment as pyrolysis and subsequent reactions proceed.

A new regime of mechanistic description of organic reactions may emerge from studies of basic behavior of model compounds under extreme thermal stress as well as from the rapidly growing analytical field of pyrolysis mass spectrometry. Related chemical processes will occur in the more limited field of polymer ablation behavior in space and military applications.

The novelty and sophistication of these systems should attract the interest and talents of many high temperature scientists who in the past have concentrated on relatively pure, isolated, or simpler compounds. Since high temperature reactions relate to many industrial means and needs -- such as chemical conversion of coal and biomass to fuel and chemical feedstocks -- availability of new knowledge, talent, and equipment is likely to produce significant results in the solution of problems.

One can look forward, not only to basic knowledge in understanding the nature of the complex high temperature reactions, concurrent and consecutive, but also to controlling them by catalytic, stoichiometric, and physical methods. The new concepts could serve as a foundation for development of new and novel industrial processes.

Ideas related to the high temperature processing of solid fossil fuels and biomass include:

- Chemistry of radicals in fossil fuel and biomass processing.
- Quantitative measurement of atoms and radicals in combustion and gasification.
- Molten-salt reforming and catalysis of organic substances.
- Use of laser diagnostics for reactions in heterogeneous systems.
- Processing at high heating rates -- flash pyrolysis.
- Shock tube studies of dust suspensions.
- Factors determining reactivity of chars and tars.
- Coal particle ignition mechanisms.
- Pollutant formation mechanisms and control.
- Temperature measurements and sampling in particle-gas reactions.
- Coal structure studies, biomass structure, and morphological changes at high temperature.
- Transport properties in coal conversion.

- Behavior of particles in reacting turbulant media.
- Behavior of coal and model compounds above 400°C -- the reactions of organic radicals in viscous media.
- Alkali evolution from coal and slag -- hot corrosion.
- Negative ions and mineral species evaporation and condensation in coal flames.
- Catalysts for hydrogenation of coal and biomass.
- Controlled fragmentation of biomass to desired chemicals.
- Kinetic data on the homolytic cleavage of C-C and C-O bonds in lignin.
- Carbonization of lignins to fibers/foams.
- Microwave fragmentation of biomass and coal.
- Supercritical gas extraction and processing.
- Trace element behavior in fly ash.
- Evaporation and condensation behavior in fly ash formation.
- Submicron particles.
- Soot formation and properties.
- Direct fuel-cell oxidation of coal and biomass or their derivatives.

IV. FUELS AND CHEMICALS FROM PRIMARY HEAT SOURCES

Although the timing is uncertain, eventually an important fraction of fuels and many important chemicals must be produced by processes that utilize energy from primary heat sources such as high temperature fission reactors, solar-thermal power units, or high temperature regions in fusion reactor blankets. The production of hydrogen will be of prime importance since hydrogen can be used as a fuel or as a necessary intermediate in the production of other fuels, industrial chemicals, and fertilizers. Efficiency will be the major consideration in developing and selecting production processes.

It is commonly recognized that increasing temperatures imply higher efficiencies. However, this is true only if the heat requirements of the process are a near match with the temperature and heat delivery characteristics of the heat source. Certainly, no single process will be applicable to the different heat sources.

The development of new, highly efficient processes for hydrogen production will require a great deal of basic research in high temperature chemistry. Data is needed in thermochemistry and reaction kinetics even to identify potentially promising processes and also to identify and develop materials suitable for these high temperature systems.

Future production of hydrogen might be based on improved or advanced electrolysis techniques if the efficiency of power production could be improved sufficiently. Since this would require "topping cycles," it might be advantageous to utilize DC power from thermionic diode systems or MHD systems to electrolyze steam at high temperature by using ceramic ion conductors (such as ZrO_2) as the electrolyte. All these high technology systems require basic research in high temperature chemistry before optimized processes can be developed.

In principle, highly efficient hydrogen production processes can be based on the decomposition of water by means of a closed cycle of chemical reactions (commonly called thermochemical cycles). Unfortunately, it is rarely recognized that this promised efficiency can be achieved only if the thermochemical criteria required of an ideal cycle are approximated in the actual process. Briefly, there is an ideal ΔS value for the high temperature endothermic reaction (or sum of ΔS values), and corresponding ΔH values, that depend on the free energy of formation of water at the low temperature in the cycle and the difference between high and low temperatures. Since these criteria also fix the ideal high temperature, it is apparent that each heat source should have its own thermochemical cycle.

It should be emphasized that the search for ideal cycles is hampered by the lack of an adequate thermochemical data base and also by unreliable published data. Very few reaction rates and mechanisms are known. Problems of container materials and corrosion will also require a great deal of research.

V. HIGH TEMPERATURE CHEMISTRY IN FISSION REACTORS

Storage of nuclear wastes is an important problem in the nuclear power industry. Solidification of high level wastes in glasses or ceramics -- or even directly in rock formations -- is being considered because of compactness and because of the relative immobility of constituents in solids. The decay heat inherent in radioactive materials will heat the proposed solidified bodies to temperatures of the order of 1000 K at their centers. Elevated temperatures will persist for very long periods of time because of the long half-lives of fission products.

Anticipating the behavior of such a system in regard to the escape of radioactivity is a difficult problem in high temperature technology. The system is subjected not only to high temperatures but to temperature gradients which change with time. The chemistry also changes because of the selective migration of elements in the temperature gradient. Mechanical properties and stress states in the solids will be altered by combined chemical and thermal changes. Radiation damage arising from the beta and gamma decay can induce chemical and physical effects on solids. Migration of radioactivity will probably occur both through the solid and in the vapor spaces created by cracking of the affected solid. Potentially volatile species must be identified as well as the potential formation of volume accessible to vapor (i.e., the evolution of cracks, bubbles, and interconnected porosity). Because of the long periods of time which must be considered in the waste storage problem, even kinetically slow processes can be important. Thus gaseous species with normally insignificant vapor pressures may undergo vapor transport over long times. Thermomigration under small temperature gradients at moderate temperatures may also contribute to long term changes.

Another example of a complex high temperature system that requires careful modeling is an operating fuel rod in a nuclear power reactor. A fuel rod consists of pellets of UO_2 clad in a zirconium alloy. Fission generates heat which is transferred through the cladding and is eventually used to generate electricity. The temperature of the UO_2 reaches quite high values at the center of the rod and large gradients of temperature are established. The chemical nature of the system undergoes continual change because the fission process destroys uranium atoms and replaces them with fission product elements. The chemical system is thus a changing, complex, solid matrix in which 20 or more elements are being created in nonequilibrium states in a large temperature gradient. It is important to model the system to evaluate the chemical environment at the inner surface of the cladding to predict corrosion effects. Also, as the recent accident at Three Mile Island illustrates, one has to model the system at the outer surface of the cladding to anticipate chemical reactions which may take place under various unplanned for (accident and postaccident) conditions.

Models developed to date have uncovered significant gaps in information needed about the thermodynamics of the system and have shown the need for techniques to identify the chemical states of important elements and the chemical potentials of specific elements and compounds. Other fundamental information needed includes the effects of radiation on chemical reactions, and the kinetics of evaporation and condensation processes and of other gas-surface reactions, particularly those forming volatile products.

VI. MODELING HIGH TEMPERATURE PROCESSES

Complex technological processes are often simulated by mathematical models based on individual steps envisaged to occur in the overall process. The models are verified against available process information; and, where problems are identified, additional process information is sought and individual parts are simulated in the laboratory to elucidate the essential steps. This method uncovers gaps in fundamental understanding and requirements for new instrumental probes to characterize the process. Thus modeling of technologically important high temperature systems can identify needs for fundamental research.

In modeling a system or process, the reactions that can occur, including undesirable ones with container walls, are assessed; and then the kinetics of the individual steps and their influence on the path of the overall reaction are evaluated. As technological operations and analyses become more advanced, the degree of sophistication of the required fundamental information increases and even the type of information can change. Also the requirements for process information becomes more detailed and improved measurement techniques are called for. Examples of complex high temperature processes in which modeling has been important include: MHD gas streams, combustion processes, rocket propulsion systems, petroleum refining, and halide lamps.

It is illustrative to consider a model of a specific case, namely chemical vapor deposition. A useful model must relate the overall rate of formation and crystallinity of the deposit with adjustable parameters such as temperature, composition, total pressure, and gas flow conditions. The temperature and degree of supersaturation of the gas phase influence the nature of the deposit. Deposition rates increase with gas flow rate, at constant gas composition and substrate temperature. There are generally three characteristic regions: a diffusion limited region at low flow rate, an intermediate region limited by a combination of diffusion and surface kinetics, and a surface kinetics limited region at high flow rates.

In the diffusion limited region, the deposition rate is controlled by the combined effects of diffusion of reactant gases to the surface and gaseous products away through a gaseous boundary layer. The boundary layer thickness depends on the gas flow rate, the properties of the gas, and the geometry of the system. The composition of the gas at the deposition surface is different from the bulk gas. The activities of the components being deposited are functions of the local gas composition, which is not necessarily the same as the bulk gas.

In the kinetics limited region, the bulk gas composition determines the chemical activities at the process surface. The deposition mechanism presumably involves adsorption, surface reactions, and desorption of products. Information needed to quantify the model includes thermodynamic data on gaseous species and solid phases, adsorption isotherms for gases, reaction kinetics of species adsorbed on the surface, diffusivities of gaseous species in the boundary layer, and gas dynamic properties to evaluate boundary layer thickness.

Currently, those kinds of information are not generally available. Data needed to verify the model for a process include measurements of temperatures in the gas and the surface, compositions of the gas at various points in the system, rates of deposition, and, ideally, concentrations of substances on the surface. Techniques for measuring those parameters need to be developed.

VII. MATERIALS FOR USE AT HIGH TEMPERATURES

The need for materials for containment of systems at high temperature is a well-recognized problem in technology. Many processes are severely limited by materials requirements that often involve very aggressive conditions. Many such problems can be mentioned: first wall problems in fusion reactors, materials for blades of gas turbines, separators for high temperature batteries, nozzles for chemical gas lasers, electrodes in MHD channels, erosion-corrosion resistant materials for coal conversion, transparent windows for halide lamps, and containers for molten salts for chemical reactors. Development of new materials for such systems requires understanding of the degradation processes in the desired application: that is, the possible reactions and products, thermodynamic information about the reactants and products, and kinetics of the reactions.

The most common thread throughout a recent DOE workshop on basic research needs for high temperature ceramics (Panel report referenced in Chapter 4) was that ceramic parts in high temperature energy systems often fail to meet expected performance. In large part because the science and understanding basic to fabrication technologies is not available, it is difficult to consistently reproduce desired microstructures. The primary route to useful ceramic structures is by solid state reaction of particulates. The final microstructures and composition, and therefore properties of ceramic bodies, is controlled by the properties of the particulate starting material. The physics and chemistry of interaction between particles must be understood to answer the large number of relevant questions.

A novel application of the concepts of high temperature science to materials in aggressive environments relates to the wear of tools for shaping recalcitrant materials. Machining, grinding, extruding, and generally forming materials -- especially the newer generations of hard materials -- utilize tools that operate in aggressive chemical environments, not only at high temperatures, but with large temperature gradients and under mechanical stress. The processes leading to tool wear and degradation are poorly understood at present. They must certainly involve chemical reactions of the hot tool edge with the environment -- which includes the gaseous atmosphere as well as lubricants and cutting fluids possibly trapped at high pressures between tool and workpiece. Not only are improved tool materials needed but new concepts for lubricants and colants should be developed.

Understanding the processes of tool degradation will presumably involve modeling the various reactions that might occur and identifying key steps which might be altered to improve tools. Chemical steps that may occur include corrosion reactions between tool components and environmental gases and liquids; reactions between tool materials and hot chips from the workpiece; and changes in composition of the hot cutting edge caused by diffusion in the temperature gradient induced in the tip. Various fundamental high temperature properties and chemical information relating to the materials are needed for the model. In addition, instrumentational probes are needed to sense the real-time conditions in a tool during operation -- especially the temperature but also the local chemical environment.

The general topic of materials production and processing prompted specific suggestions for high temperature research.

- Study the Al-O-C-Si system for processes directed toward carbothermic reduction of aluminum ores.

- Utilize skull melting processes for the preparation of new materials.
- Generate and condense high temperature vapors to form amorphous conductors and glasses.
- Utilize the enhanced properties of liquid-vapor systems in regions of criticality to effect liquid metal separations.
- Study solubilities of materials in critical fluids.
- Develop wavelength selective filters (heat mirrors) for radiation containment during high temperature processing.
- Study bubble stirring related to heat and mass transfer to high temperature processes.

VIII. SURFACE REACTION KINETICS AT HIGH TEMPERATURES

Reactions on high temperature surfaces are fundamental to many processes and are generally not well understood. Fundamental reactions that can be cited in this connection include congruent vaporization, vaporization with decomposition, condensation on surfaces, nucleation of molecular clusters, growth of particulate solids, adsorption and desorption of gases, surface reactions between adsorbed species, reactions of adsorbates with substrate surfaces, and energy accommodation in surface reactions. Grain boundaries in solids can be considered as surfaces in a general definition, and the transport of matter across grain boundaries has features in common with normal surfaces as well as special differences. Fundamental reactions on surfaces are related to technologically important processes such as catalysis, corrosion, lubrication, particulate emission formation, ceramics and metal powder fabrication, among others.

The DOE workshop mentioned above identified grain boundary behavior as one of the most challenging areas for the development of fundamental understanding. Mechanistic models involving grain boundary structures and motions, and various material transport processes, should be developed to account for the chemical aspects of densification and establishment of microstructure. The problem is technologically significant since it must be encountered wherever a ceramic is developed or improved.

The kinetics of these reactions are especially in need of fundamental elucidation, although their thermodynamics are not well understood either. Experimental techniques for studying molecular processes on surfaces at pressures greater than vacuum level should be devised. Many sophisticated methods operate only in a vacuum (electron microscopy, LEED, Auger, etc.); however, surface conditions that prevail during reaction with gas cannot be probed by those methods. A new generation of methods is required for this purpose.

IX. PLASMA AND PROCESSING

A number of research opportunities deal with either phenomena in plasma or with the use of plasmas to effect reactions:

- Characterization of problems in multiphase interactions in MHD.
- Use of induction plasmas for processing refractories.
- Development of plasma reactions for low temperature hydrogenation of coal or biomass.
- Plasma excitation in polymer synthesis and film deposition.
- Structural changes caused by the interaction of solids with plasmas.
- Plasma processing in extractive metallurgy and inorganic synthesis.
- Plasma reduction of metal oxides to powders. Plasma arcs in synthesis.
- Organic reactions initiated with plasma generated active species.

X. LASERS IN COMPLEX SYSTEMS

Though the use of lasers is now pervasive in high temperature science, a number of new ideas are germane to heterogeneous systems.

- Laser induced chemistry in inorganic systems -- synthesis of new materials.
- Lasers in materials processing to anneal surfaces selectively, prepare surface alloys, etc.
- Laser pyrolysis mass spectroscopy.
- Lasers to simulate weapons effects, achieve flash pyrolysis.
- Lasers as probes for plasmas.
- Laser vaporization in reactive environments, e.g., carbon in H_2.

XI. DIRECT SOLAR ENERGY CONVERSION

A rapidly growing field of endeavor involving the high temperature science of heterogeneous systems exists in the diverse areas of solar energy conversion.

- Photostimulated heterogeneous catalysis, corrosion.
- Solar furnaces for ore processing, coal and biomass gasification.
- Solar heat and aerodynamic levitation for containerless studies.
- Heat-mirror furnaces for high temperature processing.
- Growth of semiconductors from high temperature melts and molten-salt electrolysis.
- Synthesis and properties of new refractory semiconductors (500° C).
- Thermal conductivity, Seebeck effect and electrical conductivity of glasses.
- Fluid semiconductors -- Te, Se and their alloys, metal-salt solutions.
- Microwave heating for junction formation in solar cells.
- Heat pipes for crystal growth in 1400 to 2200° C range.
- Effect of thermal cycling on oxidation and surface segregation of coatings.
- Study of diffusion and convective phenomena in melts in zero gravity.
- Behavior of solids in gaseous media under high solar flux.
- Heat transfer coefficients, catalyst behavior.

XII. ELECTROCHEMISTRY

High temperature electrochemical techniques may offer advantages for materials processing and for the production of specific chemicals. Suggestions for basic research and process improvement include:

- Identify factors that influence ionic and electronic conduction in ceramics.

- Study material properties of atoms, ions, and molecules in crystals and in liquids at high temperature.

- Develop electrochemical engines to convert heat to electric power, e.g., power produced by the movement of sodium ions through beta alumina under a pressure gradient or the transfer of iodide ions through an electrolyte composed of mixture of alkali iodides under a pressure gradient.

- Utilize high temperature electrochemistry for ore reduction. Develop necessary inert anodes and cathodes, e.g., titanium diboride cathodes for refining aluminum.

8

DEVELOPMENT OF A CRITICAL DATA BASE

I. SUMMARY AND CONCLUSIONS

The complexity of high temperature research provides a limit to the data which can be readily obtained. This limit requires efficient use of available data for design of new energy processes and for production and fabrication of the materials required for these processes. This nation's materials and energy development programs would be substantially assisted by expanded data evaluation and compilation. The importance of data evaluation and compilation has not been adequately recognized:

- Critically evaluated data compilations are essential for efficient progress on materials, energy, and other high temperature problems.
- Data play a particularly important role in high temperature research because of the intricacies of high temperature experimentation and the inherent complexity of high temperature systems.
- Lack of ability to find and use available data is a serious obstacle to advances in high temperature science.
- Retrieval and compilation of essential information require a unique dispersed organization.
- Reliable data are necessary for development of successful predictive models.

To provide long-term financial support and adequate manpower, it is proposed that 0.1 to 0.2 percent of the federal research and development budget ($\$27.9 \times 10^9$ in 1980) be specifically earmarked for critical evaluation and compilation of data for all fields of science. Similar proposals have been made recently by other NRC committees, namely the Committee on Chemical Sciences and the Committee on Data Needs (CODAN). It is suggested that experienced scientists in each speciality be recruited to apply 5 to 10 percent of their time to the evaluation of the data of their field. Sufficient funding would be provided for the costs of literature retrieval and storage. It is proposed that the Standard Reference Data Program of the NBS be expanded to coordinate and ensure the quality of compiled data; and that an external board of scientists help determine the order of priority of various data compilations.

Two additional aspects of such a program might be the use of postdoctoral fellows, on a temporary basis, to assist the principal scientist and thus receive training in critical evaluation of scientific data; and the support of experimental work required to resolve conflicting data in the literature.

II. INTRODUCTION

The Loss of a Kingdom for Want of a Nail ?

High temperature science plays a very important role in the preparation, fabrication, and utilization of materials for all types of uses. The nation's materials and energy development programs are hampered by the absence of an adequate, critically evaluated, readily accessible, data base.

More generally, advances in high temperature science require experimentation to obtain classical data as well as experiments at the novel frontiers of science. Because of the difficulty of making measurements under extreme conditions, one almost always has to combine high temperature measurements with measurements taken under milder conditions and apply thermodynamic and other tools to extrapolate to the conditions of interest. For example, calorimetric determinations of heat capacities and enthalpies of formation and X-ray determinations of densities provide indispensible data for extrapolation to extreme conditions in practical applications of high temperature science.

III. URGENCY OF CRITICALLY EVALUATED DATA COMPILATIONS

In the design of new high temperature processes for extraction or preparation of materials or utilization of energy sources, the ideal method would involve: first, definition of design criteria; next, the ability to predict which materials would have the desired properties; and finally, the preparation and testing of materials predicted to be most suitable. The development of new or improved theories for the prediction of properties of materials is one of the most important products of basic research. Such theoretical models involve the correlation of existing data and can be quite misleading if incorrect data are used in establishing the correlation. Correct data can mean the difference between a successful design and a failure. Although true of all fields of science and technology, this is particularly important for high temperature science because of the difficulty of obtaining data and the expense and time involved. One of the most frequent complaints of the high temperature community concerns the inadequacy of available evaluated compilations of data for a range of properties, but particularly thermodynamic and phase diagram data. Similar appeals for data compilation efforts (which affect but are not limited to high temperature research) have been made in the NRC report on the *Conference on Thermodynamics and National Energy Problems*, ERDA's *Materials Sciences Overview II. Workshop Report*, and in the NRC's *The Department of Energy: Some Aspects of Basic Research in the Chemical Sciences*.

Stockmayer (*Science*, 1978) has summarized the overall importance of critical evaluations, which is further documented in the CODAN Report. One might ask why workers in the field cannot retrieve the data they need from the literature; but this turns out to be very difficult for several reasons. Data are widely distributed in journals published in many nations and in many languages; retrieving the information is a time-consuming process. The CODAN Report documents the enormous financial loss when individual scientists must take time to search the literature for each datum that they need. A more serious aspect of literature retrieval is the unreliability of a large fraction of the data in the primary literature. This is particularily true of high temperature literature because of the difficulty of obtaining measurements under extreme conditions. It requires a great deal of experience to extract reliable information from the literature. Reliable data is even more important when no measurements exist for the compounds of interest and one must use various predictive correlation models to obtain the needed information. If the input data for the model are in error, the predictions can be greatly in error.

IV. METHODS TO PROVIDE AN ACCESSIBLE DATA BASE

The importance of evaluated compilations of data has long been recognized. In the 1920's, the International Critical Tables (ICT) compilation was initiated. Scientists active in each field devoted a portion of their time to survey the literature of their field and to arrive at a set of values that would be recommended to the scientific community. These tables made an enormous contribution to basic science and technology in this country.

Although the ICT was a successful coordinated effort in the 1920's, there was a loss of momentum after completion of the first set of tables; and critical evaluation and compilation was continued thereafter only as a disjointed effort. Because the compilation was often tied to short-term practical applications, projects were often initiated and then terminated or greatly reduced after a few years. As it takes a considerable amount of time and experience to organize an operating compilation effort, the lack of long-term support greatly reduced the efficiency of the efforts.

An example of this short-sighted view was pressure some years ago to discontinue Charlotte Moore's long-standing compilation of atomic energy levels at the NBS. This compilation had been indispensible for calculating high temperature thermodynamic properties of gaseous atoms and ions; but it was thought that such data would be of little interest in the future. This appraisal did not, of course, anticipate the laser and the resulting great demand for atomic energy level information.

Another example of the lack of long-range stable support for data compilation is the Hansen-Elliott-Shunk series of critically evaluated metallic phase diagrams, considered indispensible by metallurgists and solid state scientists concerned with high temperature behavior. This activity was disbanded with the result that the literature of the last 15 years is largely unused and essentially inaccessible to most scientists and engineers who need it. The NBS has been attempting a compilation of post-1950 thermodynamic values of inorganic materials but budgetary limitations have brought the program to a virtual standstill.

Although the availability of evaluated compilations of data is particularily important for the high temperature sciences, it is essential for all science: the needs of one field cannot be separated from those of other fields. A reliable entropy at 298 K for CO or H_2O, for example, is equally important for high temperature work as for work with room temperature aqueous solutions. Certain types of data such as thermodynamic values, phase diagrams, and kinetic data are of prime interest to the high temperature community, but many other data compilations are of importance. Areas for which compilations are needed are not listed here, since specific needs are mentioned in other chapters and the NRC, CODAN Report details needs in all fields of science. In general, the order of priority in which different types of data are evaluated should be based on the availability of theoretical models that would aid in the evaluation of experimental data and which would allow correlation of available reliable data to provide predictions of unmeasured values. It is suggested that a board of scientists representing a broad range of fields develop priorities for recovery from our present deficit of evaluated compilations.

Why is scientific progress being frustrated by lack of reliable data? In part, it is due to the enormous growth of the literature which has made it more difficult to keep up-to-date. But there are more scientists now; and if the same proportion participated as in the early days of the ICT, it would be a manageable job. Part of the problem is that many scientists become so specialized they do not realize the ways in which data from other fields could be useful to them; they think they can retrieve from the literature all the data needed for their own work. If there were organized support of evaluation and compilation activities, e.g., through the Standard Reference Data Program, many scientists might be willing to devote a fraction of their time to preparing the data in their speciality -- which they retrieve in any event -- for compilations that would make those data useful to all scientists.

A significant factor in the decline of critical evaluation and compilation has been the tightness of funding in general and an increasing emphasis upon short-term practical results.
It is difficult to anticipate which data will be key to new developments. Generally, the decline of support for critical compilations could be termed a "Tragedy of the Commons" in which activities of value to the general community cannot compete with activities of specific

interest to individual scientists. For example, the suggestion that 0.1 to 0.2 percent of federal research and development funds be earmarked for support of critical compilation efforts has received a negative response from some who anticipate that, with fixed total funding, there would be a 0.1 percent reduction in their own funding. If they considered the value of having a wide range of evaluated data available, they would recognize that their return would be many-fold the 0.1 percent contribution ($50 in a $50,000/yr research program). Peer review of proposals for data compilation, in competition with other research proposals, has generally been unfavorable to data efforts because data evaluation and compilation is considered routine and not at the frontiers of science. However, the lack of compiled data is a tremendous handicap to the development of the frontiers. Appreciation of the importance of critical compilations for the overall science and engineering effort of this country is required by those responsible for the nation's well-being. Provision must be made to provide long-term, stable support for compilation activities by a mechanism which protects them from competition by short-term interests.

Such activities cannot be carried out effectively without a long-term commitment of personnel, as well as money. An effective organizational effort, as for example by the Standard Reference Data Program of the NBS, is required to ensure the quality of the program and to utilize the rather limited manpower available for such activity. Existing full-time evaluation centers should be strengthened and expanded. But the shortage of qualified persons makes it necessary to initiate many small part-time evaluation groups. People should be recruited with the experience necessary to recognize experimental pitfalls that could introduce serious error in reported data and who would be able to sort out reliable data from misleading data. Such persons would, in general, contribute only a small fraction of their time to such activities. An unusual type of dispersed organization is needed.

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9

INSTRUMENTATION AND MODERN MEASUREMENT TECHNIQUES

I. SUMMARY AND CONCLUSIONS

- Recent developments in laser technology, synchrotron radiation sources, nozzle beam sources, and small computers suggest that major advances in high temperature instrumentation are likely to result from the use of these devices. New instrumentation techniques based on these developments should be supported.

- Standard methods exist for measuring a variety of material properties at room temperature. Frequently, these techniques must be modified, adapted, or improved before they can be used at high temperature (>1000°C). Efforts to adapt standard methods giving reliable results at lower temperatures to high temperatures should be encouraged.

- Instrumentation for characterizing gases, bulk solids, and free surfaces is relatively advanced compared to instrumentation for studying liquids or confined interfaces such as grain boundaries.

- Computer modeling of complex high temperature phenomena is a critical link in testing new theories, the performances of sensitivity checks, and the evaluation of experimental data. Such modeling efforts should be encouraged and, insofar as possible, be coordinated with complementary experimental work.

II. INTRODUCTION

The past decade has marked the development of many new measurement techniques for high temperature science (Hastie, 1979; Eckbreth *et al.*, 1977; Goulard, 1976). Significant advances include:

- Lasers for spectroscopy and as heat and excitation sources.

- Faster (100 X), less expensive (10 X), and more compact (100 X) computers for instrumentation control, data processing, modeling, and molecular orbital calculations.

- Commercial quadrupole mass spectrometers with increased compactness, ruggedness, sensitivity, stability, and decreased cost relative to the alternative magnetic and time-of-flight instruments.

- Commercial development of much improved grating (Eschelle) and etalon optical spectrometers with better sensitivity and resolution.

- Photoionization and photoelectron spectroscopy using mass spectrometric detection.

- Molecular beam sampling techniques for mass and optical spectroscopic analysis of high pressure ($\sim$1 atm), high temperature ($\sim$2000 K) gases, and nozzle beam phenomena.

- Initiation of efforts to interface sophisticated laboratory instrumentation with hostile environments, e.g., MHD test channels (optical and mass spectroscopy), rocket and jet engine exhausts (laser Raman and mass spectroscopy).

- Increased resolution (5 X) for scanning electron microscopy.

- *In situ* application of Auger spectroscopy for solids at high temperatures

- Electron spectroscopy for chemical analysis (ESCA) for room temperature analysis of high temperature materials.

- Secondary ion mass spectrometry (SIMS) and related techniques for surface analysis of solid materials.

- X-ray diffraction spectrometry adapted to *in situ* structural analysis of solids at high temperature and pressure.

Over the next one or two decades we can expect continued improvement in this type of instrumentation, as well as the development of new techniques and devices to use in high temperature systems involving gases, vapors, and plasmas; solids; interfaces; and liquids. Recent socioeconomic events and the depletion of natural resources -- e.g., oil, gas, and minerals -- will catalyze expanded R&D efforts in the following technological areas where high temperature measurements will play a key role:

- Improved combustion efficiency -- requires better understanding of processes using existing and alternative fuels.

- Reduced emissions of gaseous and particulate matter to the environment.
- Better materials durability.
- Recycling of fuels and materials.
- Extraction of metals from lower grade ores.
- Better understanding of the geochemistry deep within the earth's mantle -- in part because of depletion of high-grade natural resources closer to the earth's surface.

Most of these problem areas will require process control at higher temperatures and pressures than heretofore necessary. Thus, the measurement regime of temperature and pressure for high temperature science will require expansion to provide data-base support for these new areas of technology.

The challenge to future measurement science, then, is one of more extreme conditions of temperature and pressure, coupled with greater complexity in the chemical systems. In addition to the complexity arising from technological needs, it is essential to recognize that even simple chemical systems become more complex in their molecular chemistry and physics with increased temperature and pressure.

Another measurement requirement arises from the need to examine phenomena at reduced time scales. For instance, fluidized bed combustors, nuclear explosions for subterranean chemistry, higher pressure turbines, and nuclear fusion will each require an understanding of basic high temperature chemistry on a relatively short time scale, where unusual reaction intermediates may be significant. Also high photon fluxes resulting from newly accessible radiation sources -- e.g., lasers, synchrotrons, and solar furnaces -- will provide unusually high populations of excited states and lead to new chemical pathways and rapid reaction rates.

In the past, classical high temperature science has been characterized by measurements made under conditions of low spatial and temporal resolution. High gradients of species concentration and temperature present in laboratory flow systems such as flames, plasmas, and chemical vapor deposition (CVD) reactors, make it increasingly essential to obtain data with high spatial and temporal resolution. This may be a dominant theme in high temperature measurement science during the next 5 to 10 years.

III. MEASUREMENT CRITERIA AND NEEDS

Many measurement criteria are important in determining instrument design and operating parameters for high temperature systems. Future instrumentation developments will require extension in accuracy; sensitivity; resolution -- spatial, temporal, and spectroscopic; temperature range; pressure range; and chemical range -- e.g., dynamic concentration range, homogeneous, heterogeneous, particulate, corrosive.

The following measurements may be needed to define a high temperature system:

- Temperature.
- Species identity.
- Species concentration.
- Thermodynamic functions.
- Kinetic parameters (elementary and global).
- Transport properties (mass, thermal, and electrical).
- Structure.
- Density and other physical properties.
- Optical properties.

These system-defining measurements often cannot stand alone in the detailed characterization of complex high temperature phenomena. Complementary modeling efforts are sometimes needed -- e.g., combustion systems where chemical kinetic and gas dynamic interactions are experimentally inseparable. This aspect to measurement science is only just beginning to gain a measure of general recognition. Thus, corollary to instrumentation needs, in the conventional sense, are the needs of modelers, including:

- Improved mathematical methods and algorithms.
- Further development of sensitivity analysis techniques for identification of key experimental parameters.
- Expanded data bases.
- Mechanistic insight from appropriate high temperature experiments for selection of initial model conditions.
- Diagnostic experimental tools for testing computer-based models.

Current developments in combustion chemistry exemplify these needs and illustrate the general approach that modeling should take in other areas of high temperature science (NRC, 1979; Hastie, 1979).

IV. SPECIFIC NEEDS IN HIGH TEMPERATURE MEASUREMENT SCIENCE

In addition to the general need for extending the range of application of existing measurement methods, there are many specific areas (discussed in other chapters) where improved or new measurement methods are badly needed.

Temperature Measurement

Temperature errors are still often the greatest cause of error in high temperature data (Kollie *et al.*, 1975; Anderson and Kollie, 1976). Lack of emissivity data needed for nonblackbody optical pyrometry of solids and liquids and the poor spatial resolution of line-of-sight optical spectroscopic methods for gases are persistent problems. Computer aided tomographic imaging techniques could overcome the latter difficulty.

Cross Sections

For spectroscopic transitions and for electron impact and photoionization mass spectrometry, cross sections are needed to convert data to absolute concentrations and in some cases absolute temperatures. The related problem of complex mass spectral fragmentation requires development of new ionization methods (see Chapter 2, Section III).

Kinetic Methods

Kinetic methods are needed to bridge the gap between room temperature flow reactors and high temperature flames and shock tubes. Since high temperature elementary reactions show non-Arrhenius rate behavior and extrapolations are unreliable, it is imperative that this measurement regime be covered.

Spectroscopic and Structural Methods

For high temperature species, spectroscopic and structural methods are usually limited by thermal effects. This is particularly troublesome for complex polyatomic species where the concept of polytypic bonding has been invoked to explain electron diffraction results. New methods for reducing the population of higher vibrational and rotational states are needed to deal with these new structural problems. Matrix-isolation techniques are not always applicable, e.g., for electron diffraction. Use of adiabatic expansion of high pressure gas mixtures for producing spectroscopically cold species should be pursued (see Section V).

Nucleation and Condensation Kinetics

These phenomena are virtually unknown for high temperature species. In addition to the technological significance of particulate formation, such information would bridge a gap in the basic understanding of gas-solid phase transitions and surfaces. Extension of matrix-isolation and nozzle beam techniques should be pursued for the study of cluster formation.

Measurement Criteria

Criteria are needed to establish when systems can be described by thermodynamic equilibrium methods. Too often thermodynamic models are misapplied to nonequilibrium systems.

Transport Coefficients

The validity of engineering-type empiricisms for estimating transport coefficients needs to be tested by measurement. The empiricisms are based on permanent gas data and do not necessarily apply to high temperature systems, particularly those with strong, long-range intermolecular interactions.

Kinetic and Thermodynamic Parameters

The validity of estimation schemes for kinetic and thermodynamic parameters also needs the support of measurements on key test cases.

Long-Range Ordering

Measurement methods are needed for determining possible long-range ordering in liquids.

Electrolyte Sensors

Electrolyte sensors are needed to measure N, H, C, and S in molten metals and slags.

Levitation Calorimetry

The adaptation of levitation calorimetry to nonconducting materials is needed.

Spectroscopic Excitation Sources

More flexible spectroscopic excitation sources are needed, e.g., tunable microwave sources (and detectors) at short wavelengths (3.0 to 0.1 mm) would allow studies of high J rotational states (see Section V).

Composition and Microstructure

One anticipated demand of the more severe environments in future high temperature science is an increase in the spatial resolution required to characterize the composition and microstructure of solid samples. These requirements are realized in electron microscopes where an imaging resolution of 2 Å is possible and diffraction may be obtained from 50 Å diameter particles. Energy dispersive X-ray spectroscopy (EDS) and electron energy loss spectroscopy (EELS), two techniques currently being developed, promise to be useful in the future (Carpenter *et al.*, 1977; Silcox, 1977; Martin and Kubin, 1978) (see also Chapter 4, Section IV).

A somewhat similar situation exists in the broad area of electron spectroscopy and other methods of surface analysis. During the last decade literally dozens of modifications of these techniques have been developed, although the limits of their usefulness have not always been fairly tested (Ertl and Kuppers, 1974; Czanderna, 1975). Future efforts should concentrate on the evaluation of the most promising techniques and, in particular, on adapting them to measurements at high temperature.

Grain Boundary Problems

For many polycrystalline materials, mass transport occurs predominantly in grain boundaries over a wide range of temperatures. This phenomenon is key, for example, to the growth of reaction product layers. Real understanding of the process is stymied by an inability to characterize the fine structure of grain boundaries and, in particular, to measure diffusion in grain boundaries. Innovative new techniques are needed to study this important basic phenomenon. Transmission electron microscope techniques show promise for *in situ* high temperature studies of grain boundary structure.

Surface Analysis

Many existing electron spectroscopy techniques can only be applied under high vacuum conditions. Efforts are needed to develop new techniques for atomistic level studies of surfaces in reactive atmospheres and at pressures near and above atmospheric (see Chapter 4).

High Pressure Generation and Calibration

A need exists to expand calibration methods, such as the ruby fluorescence scale, and to facilitate interlaboratory comparisons. The United States lags in the high pressure area, except for diamond cell work, perhaps because high pressure equipment is not accessible for routine measurements (see Chapter 4).

V. DEVELOPING AREAS EXPECTED TO IMPACT FUTURE INSTRUMENTATION

There are many avenues, some unforeseen, by which major advances in high temperature instrumentation and measurement science can occur. However, the following are anticipated to have major impact: lasers, synchrotron radiation, nozzle beam sources, laboratory computers, new materials, coupling of complementary techniques, and the use of field sites for experiments.

Lasers

If current trends continue, lasers can be expected to have lower cost, greater reliability, wider spectral range, higher power, and improved spatial and temporal resolution capabilities. They will continue to find new application as heat sources -- e.g., with high temperature-pressure diamond cell devices or with photoelectron spectrometers where the stray electromagnetic radiation of conventional furnaces is limiting, or where sample containment is a problem. High heating rates (10^6°C/sec) provided by pulsed lasers may prove useful in preparing amorphous materials or in producing surface phase changes and new coating types.

Laser spectroscopy can be expected to make an even greater contribution to high temperature science than in the past (Eckbreth *et al.*, 1977; Hastie, 1979). In particular, Raman spectroscopy should become a more generally accepted tool for temperature and major species concentration measurements. More sensitive higher order scattering techniques such as coherent anti-stokes Raman scattering (CARS) will prove useful for temperature and minor species measurements. Very sensitive laser-induced fluorescence methods will be invaluable for certain minor species concentration measurements. New kinds of spectroscopy will result from greater access to lasers, as was the case with photoacoustic and optogalvanic spectroscopy. Many spectroscopic developments are already in an initial stage and demonstrations have been made on specific, relatively well-defined laboratory systems, e.g., clean laminar flames. However, limitations are apparent with more complex systems, e.g., turbulent and particulate-laden flames. The range of applicability of of these techniques should be broadened; but applications to high temperature systems may be limited by lack of data on excited state energy levels and line strengths.

More detailed accounts of recent advances and future needs for lasers in high temperature and combustion science appear elsewhere (Hastie, 1979; NRC, 1979; Goulard, 1976; Eckbreth *et al.*, 1977) (also see Chapter 3).

Synchrotron Radiation

In the next few years, high intensity, broad-band vacuum UV and X-ray beams will become available for chemical research -- e.g., at the Brookhaven Synchrotron Facility where beam intensities of 10^{13} to 10^{14} photons s^{-1} $mrad^{-1}$ $Å^{-1}$, with a wavelength spread of 0.01 λ and a wavelength range (λ) from 10 to 4000 Å, will come on line by the mid-1980's. This high intensity, tunable source can be expected to have major impact on the measurement of composition and microstructure by X-ray techniques (Winick and Bienenstock, 1978; Hodgson and Doniach, 1978). For example, advantage may be taken of the anomalous dispersion at an absorption edge to study order-disorder transformations in binary alloys whose components have similar atomic numbers. Data collection will be rapid, making possible the study of dynamic phenomena, such as phase transformations. EXAFS, made feasible by available high beam intensities, describes the local coordination environment of an atom and may be used on liquids, amorphous solids, or, by the appropriate selection of energies, in the investigation of surface atoms. Great progress is also to be expected in X-ray fluorescence techniques for detecting trace impurities (Sparks and Raman, 1979). Gas phase studies, such as the spectroscopic characterization of molecular ions and the use of photoionization mass spectroscopy for bond dissociation measurements, will also profit from the availability of the synchrotron source (Guyon, 1974).

Nozzle Beam Sources

For the high temperature scientist, nozzle beam sources provide high intensity molecular beams, spectroscopically "cold" high temperature species, a vehicle for kinetic studies of homogeneous nucleation from the gas phase, and a means of interfacing high pressure-high temperature gaseous systems with analytical devices such as mass spectrometers.

Examples of nozzle beam source mass spectrometry appear elsewhere (Hastie, 1979). The perennial problem of high temperature broadening and population of many excited states in high temperature spectroscopy can be removed through application of nozzle beam techniques utilizing expansion cooling. This approach may rival that of matrix isolation and could remove many of the uncertainties regarding molecular structure of high temperature species. Nozzle beam techniques can also be used to produce, under highly controlled conditions, molecular and particulate clusters whose importance is discussed in Chapter 2.

Laboratory Computers

Continued rapid progress in the development of inexpensive, small scale digital computers, is expected to make their use as a laboratory tool almost routine in the next decade because of the inherent chemical and physical complexity of high temperature experiments. In addition to their classical application in rapid and high volume data acquisition, computers and microprocessors will provide invaluable control for research using coupled experimental techniques. For example, tomographic imaging techniques may be used to convert integrated line-of-sight optical absorption data (e.g., in Na D-line flame temperature measurements) into point source data maps. Increased computer access will also be important for modeling to support experiments.

New Materials

Materials limitations will continue to pervade high temperature science, particularly with the need to use more aggressive conditions of temperature, pressure, and chemical reactivity. Container materials for laboratory study of heterogeneous, complex systems need further development (see Chapter 7). For some experiments, the containerless environment of a space shuttle laboratory may be of benefit. New optical materials will be needed to utilize properly new high intensity light sources (lasers, synchrotron radiation). Electronic instrumentation for use in high temperature environments will require development of temperature resistant semiconductor and related components.

Coupling of Complementary Techniques

In dealing with complex systems (e.g., combustion sources and CVD reactors), it is increasingly necessary to apply more than one experimental technique to the measurement problem. For example, simultaneous measurements of spatially and temporally resolved profiles of temperature, species concentrations, surface morphology, etc. will be needed to define and validate models for complex systems. Studies aimed at coupling complementary measurement techniques -- e.g., laser and mass spectroscopy -- should be supported as research efforts in their own right.

Use of Field Sites for Experiments

With the development of remote probe devices (e.g., lasers), it should be feasible to use field sites to complement and extend conventional laboratory studies. Experiments at great depths within the earth's mantle and in nuclear explosions, volcanoes, pilot plant combustors, solar furnaces, and so on, should yield valuable information in the coming decades.

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10

APPLICATIONS OF HIGH TEMPERATURE SCIENCE

I. SUMMARY AND CONCLUSIONS

To an unusual degree, basic research in high temperature behavior has advanced in parallel with practical applications. In some cases, technological needs have provided the impetus for basic research; in others, advances in basic understanding have guided the solution of technological problems.

- The energy crisis poses a host of specific new challenges for all subfields of basic high temperature science.
- These challenges arise in energy conversion, in the development of efficient materials extraction and production processes, and in the development of environmentally benign ways to utilize energy resources.
- University training of high temperature scientists is a necessary part of an attack on basic and applied problems relevant to high temperature technology.

II. INTRODUCTION

High temperature science deals with the most fundamental aspects of chemical bonding and structure. To an unusual degree, basic research in the field has advanced almost in parallel with practical applications. In some cases, technological needs have guided the direction of basic research; in others, basic research data and insights have guided the solution of technological problems. Clearly, the pillars of high temperature science -- the periodic table and Gibbs thermodynamics (particularly as related to entropy) -- underlie both basic research and applications.

High temperature processes are as old as the universe. They are manifested to this day by magma generation and volcanic action on the planets and by reactions in the sun and other stars. In the history of human evolution, two high temperature processes are predominant: namely, fire and (much later) metal smelting.

High temperature as a science came to fruition in the 1940's. The science has since contributed significantly to an understanding of stellar and planetary interiors, as well as to process improvements, control, and new developments in combustion and materials utilization. Basic science and applied technology have been closely interconnected in advancing both knowledge and use of combustion (from building wood fires to designing jet engines) and of materials (from smelting copper and iron to designing superalloys, semiconductors, and ceramics).

While much innovative research was carried out in high temperature behavior in the ranges of 500 to 5000 K during the 1950's and early 1960's, due to the interest of re-entry physics; much knowledge gained in this period gave only tantalizing hints as to future capabilities. However, due to the energy crisis and the need to understand the behavior of high temperature gaseous reactions -- such as occur in internal combustion engines and in high temperature rate processes connected with basic chemical production from coal and natural gas -- these studies should be expanded and emphasized.

III. PROPERTIES OF HIGH TEMPERATURE GASEOUS MOLECULES AND HIGH TEMPERATURE VAPORS

Lack of knowledge of the molecular species present in the gas phase at high temperatures has led to misinterpretation of basic research results, as well as to incorrect predictions of the practicability of proposed applications. For example, the heat of sublimation of graphite to monatomic carbon vapor is fundamental to the estimation of heats of formation of organic chemicals from bond energies. High temperature mass spectrometry showed that the vapor in equilibrium with graphite contains high concentrations of $C_3(g)$ and $C_2(g)$, as well as the monatomic $C(g)$. Failure to take into account the molecular composition of the vapor leads to erroneous heat of formation values for the desired reaction:

$$C\ (\text{graphite}) \longrightarrow C(g)$$

In the development of solid rocket propellants, specific impulse (related to payload and distance of travel) increases with increasing combustion zone temperature and decreasing molecular weight in the exhaust. The remarkable stability of complex molecules -- such as cyclic $(HBO_2)_3$ -- in the vapor phase at high temperatures limits the possibilities for achieving low molecular weight exhaust products.

Applications of high temperature processes in the metallurgical, ceramics, semiconductor, and chemical industries are legion. In developing new processes or improvements and controls for existing ones, the ability to write down mass balance equations to describe the chemistry is absolutely fundamental. If the gas phase products are not correctly identified, serious and costly errors can be made in process design. A survey of the thermodynamics data for polymeric alkali halides reveals the dearth and uncertainty of the present information base. Gaseous complexes of halides are of increasing interest and activity on several fronts including metal purification, the development of new laser systems, and lighting.

Although its use requires trained expertise, the high temperature mass spectrometer has contributed substantially to knowledge of gas phase environments present in high temperature technologies. Other research methods described in Chapter 2 have the capability for further expansion of such knowledge. For example, multiphoton absorption by complex molecules heated internally to very high temperatures may lead to selective modes of decomposition with applications to synthesis or isotope separation.

IV. COMBUSTION AND OTHER HIGH TEMPERATURE GASEOUS REACTIONS

Combustion is now, and will continue to be in the forseeable future, central in electric power generation and vehicle propulsion. The growing need to improve the efficiency of boilers and heat engines while at the same time controlling the release of environmentally damaging emissions, requires an in-depth understanding of combustion rates and mechanisms. If basic research does not proceed hand-in-hand with applications, crucial factors are likely to be overlooked in the design of new combustion systems, and optimal design is virtually impossible. Furthermore, basic research acts synergistically to broaden the range of potential alternatives that are considered in trying to meet the objectives of particular combustion applications. Demonstration projects relating to utility boilers and engines are time-consuming and costly. Basic research directed towards determining which projects have the highest probability of success can save both money and embarrassment for application-oriented agencies.

The destructive effects of combustion, in the forms of fires and explosions, are of paramount concern to every part of society. It has only recently been appreciated that the major loss of life in fires is due to inhalation of toxic fumes rather than burns. The basic research described in Chapter 3 holds a high degree of promise for identifying the gases produced in fires. Such basic data are needed to help define the nature of inhalation toxicity problems, and to guide the development of control measures. Basic research could also lead to a better understanding of the mechanisms of flame retardants. This is particularly important, since the flame retardation formulations used in the future will have to be tested for toxicity as well as for effectiveness. Some existing flame retardants, such as the notorious "tris," may be regulated out of existence; and the pressure to develop new formulations will increase. Understanding the basic mechanisms can shorten development time considerably.

V. PROPERTIES OF SOLIDS AT HIGH TEMPERATURES

The dream of being able to tailor-make materials to specified physical and chemical properties is far from reality, and is likely to remain so over the next 25 years and probably the next 100. This is more of a reflection of the distance to be traveled, however, than the anticipated rate of progress.

Anyone who has been involved in the search for materials suitable for particular applications in chemically aggressive high temperature environments has known the frustration of having no basic theoretical guidelines or models to draw. Electrodes for MHD generators, dimensionally stable anodes for aluminum electrowinning, materials for hot-end application in advanced gas turbine and diesel engine designs, selective coatings for solar thermal applications, solid electrolytes for high temperature fuel cells -- these are only a few examples of materials needs that have emerged from R&D work on energy conversion systems and energy conservation in high energy consumption industries.

For many, and perhaps most, practical applications, there are simultaneous demands for high melting point, chemical compatibility in the exposure environment, mechanical strength, thermal shock resistance, and one or more properties such as electrical conductivity, specific gravity, emissivity, heat capacity, and thermal conductivity. It is scarcely surprising that most development work has been largely empirical. Within both industry and government, however, once a need has been recognized, the effort to develop new materials is so great that any insights derived from basic research can lead to very large cost savings. The Wagner Theory of parabolic oxidation, recent advances in predicting phase diagrams, and correlations developed between structures and properties are examples of basic research that have been highly leveraged for purposes of special applications.

VI. PROPERTIES OF HIGH TEMPERATURE LIQUIDS AND MELTS

High temperature liquids and melts commonly encountered in applications include: molten metals and slags in carbothermic and metallothermic processes, molten salts in aluminum and lithium electrowinning, molten glass in container and plate glass manufacture, and molten semiconductors in a number of single crystal growth and epitaxial deposition processes. A considerable amount of basic research has been done on molten iron and steel and molten cryolite. Most was motivated by applications; and the results have been used effectively in controlling steelmaking and aluminium electrowinning processes.

Basic information that has contributed substantially to process improvement and control in steelmaking includes: ternary phase diagrams for metal and slag systems, activities in molten metals and slags, slag-metal equilibria, and kinetic data or models related to transport and interfacial phenomena. Comparable information is not available to permit design and evaluation of other pyrometallurgical processes that could assume increasing importance as the need grows to recover metals from lower grade ores. Examples are the recovery of nickel and cobalt from laterites, and the recovery of chromium from scrap. The basic data needs can be defined by analogy with the models established for steelmaking. Some of the data may indeed be available in the literature or may be amenable to estimation. Thus, critical compilation of existing data (see Chapter 8) in a form similar to that made by Elliot and Gleiser for steelmaking is a crucial first step. Then, significant gaps in the basic research framework can be given priorities for laboratory investigation.

Fundamental thermodynamic information concerning the properties of metals and oxides as solvents will be needed within the next decade. Large-scale processing technology for the evaporation of metals has led to laboratory-scale processing technology for the evaporation of metals has led to laboratory-scale demonstration of novel ways to reduce reactive metals from their oxide ores. These methods use other metals as solvents for the reactive metals, lowering the thermodynamic activity of the reactive metal product of the reduction reaction, which then can be accomplished with a relatively weak reducing agent such as carbon. The solvent metal can also be selected with a view to the elimination of impurities present in the ore, through fractional crystallization, for example. The solvent must have a volatility that differs significantly from (either much greater than or much less than) that of the reactive metal to allow its separation by high temperature distillation techniques. The overall cycle shows promise of early success as an energy and cost saving method. Examples of promising metals that might be extracted include lithium, magnesium, beryllium, titanium, zirconium/hafnium, aluminum, and uranium (and all the other actinide elements).

VII. MASS TRANSPORT AND CHEMICAL KINETICS INVOLVING CONDENSED PHASES

One of the truisms of high temperature chemistry is that everything reacts with everything else. Thus, the design of high temperature systems must take into account, not only potential corrosion and degradation reactions at surfaces of container materials, but also the effects on mechanical and chemical properties within the solid phase due to diffusion and interaction. The development of oxidation resistant coatings for high temperature service, for example, has been plagued as much by changes in coating composition due to diffusion into and from the substrates, as by lack of stability in the intended environment. Furthermore, materials which are stable in highly oxidizing environments due to rapid formation of a SiO_2, Al_2O_3, or Cr_2O_3 barrier, can fail in the less oxidizing, or even reducing, atmospheres of coal conversion and thermionic generator systems.

There is a pressing need for real-time monitoring and sensing probes for control of high temperature melt processes. There exists today only the galvanic cell zirconium probe for oxygen activity measurements. Comparable probes for carbon, nitrogen, and sulfur would find immediate application. However, if they were to be based on the same principle as the oxygen probe, suitable ionically conducting solid state electrolytes would be required. Potentially promising approaches are quite likely if investigation of basic transport phenomena in solid electrolytes is adequately supported.

VIII. PROPERTIES AND REACTIONS OF COMPLEX HETEROGENEOUS SYSTEMS

In the high temperature industries -- e.g., metals smelting and refining, glass, ceramics, thermal energy conversion -- the systems encountered in practice are generally too complex for direct basic research investigation. Typically, multicomponent gases, one or more liquid phases, and a number of solid phases are involved, with many potential thermodynamic and kinetic interactions among phases. The use of model systems and identification of key reactions for basic research investigations have proved very fruitful in providing information to put to practical purposes in real systems. There is increasing pressure, however, to narrow the time period between basic research in the laboratory and practical application. Thus, there is a need to design experiments that provide a reliable simulation of anticipated field conditions, without sacrificing the possibility of fundamental insights that basic research is traditionally designed to provide. The universal availability of programmable hand calculators, as well as the increasing use of large-scale computers in chemistry, may provide methods for modeling complex systems so that parameters selected for basic research investigation are, to a high degree of probability, key to complex applications.

The whole area of safety and hypothetical accident analysis, particularly with regard to nuclear reactors, is of primary national interest. Predictions of fission product release for given reactor designs often require knowledge of the chemistry of reactor fuels at operating and accident temperatures, which may be well above 3000 K. The broad range of fission product elements present in fuel matrices provides a wide basis for the formation of compounds. Additionally, the possibility of departure from unit activity provides incentive for the experimental verification of thermodynamic calculations when data are available. Related questions encompass fuel integrity, solid state diffusion, vaporization, and susceptibility to aerosol formation. In high level waste management, the development of experimental methods for the characterization and testing of encapsulation materials is likely to be accompanied by an elucidation of mechanisms responsible for material failure.

In fusion reactors, erosion of the internal surfaces determines to a large extent the impurities injected into the plasma. Materials experience high temperature gradients, unipolar arcing, neutron damage, and aggressive ion/surface interactions -- all of which remove surface layers by chemical and physical processes. Studies of materials suitable for reactor components have been initiated with preliminary experiments on coated refractories. These studies utilize testing techniques which simulate some aspect of the plasma environment but do not reproduce the total environment. Understanding high temperature physical and chemical reactions, including synergistic effects, at the interface between the plasma and the reactor components is essential to informed selection of materials.

In the area of pyrometallurgy, basic research efforts of past decades have resulted in an accumulation of knowledge on the thermodynamics and physicochemical properties of materials and systems of interest to high temperature technology. In recent years, increasing use of physical sciences and chemical engineering technology to better understand the workings of smelting and metal refining processes has resulted in improved methods of process control and more efficient use of energy and materials.

Diminishing resources of raw materials, necessity of energy conservation, and ecological considerations have brought an ever-increasing need for innovations in pyrometallurgy. Instead of performing a postmortem on existing processes, research must provide new concepts in smelting and metal refining processes utilizing accumulated knowledge of physical sciences and chemical engineering technology. Those engaged in basic research are well equipped to accomplish such an assignment.

For example, a new approach to steelmaking is needed: a method of making steel that would do away with the blast furnace, ore pelletizing and sintering plants, and cokemaking. The process should also be low energy intensive using a low ranking coal as the primary source. A research program with this ultimate objective would develop new knowledge in both physical sciences and chemical engineering technology.

In the area of coal gasification, there is much interest in the production of hot reducing gases for direct application in gas turbine engines, for power generation, or in metallurgical applications. The gas must be desulfurized by cyclic-regenerative methods using, for example, calcined dolomite, manganous oxide, or other regenerative sorbents in packed beds. The presence of fly ash and hot dust particles are major obstacles. Therefore, research on the fluid dynamics of dusty gases could lead to new technology needed to remove particulate matter from hot gases.

Another problem area concerns fluidized-bed reactors operating at elevated temperatures. Plastering of reactor walls and blockage of tuyeres with the carry-over dust particles are frequently encountered. More needs to be known about the mechanism of adhesion of dust particles on container walls as affected by the flow conditions, temperature, gas composition, and the nature of the particulate matter.

APPENDIX A
WORKSHOP ORGANIZATION

Gerd M. Rosenblatt, *Chairman*

Chapter

1. Introduction and Summary

   Gerd M. Rosenblatt, Pennsylvania State University
   John L. Margrave, Rice University

2. Properties of High Temperature Gases

   William Weltner, Jr., University of Florida, *Panel Leader*
   Joseph Berkowitz, Argonne National Laboratory
   Donald L. Hildenbrand, SRI International

3. Combustion and Other Gaseous Reactions

   Marshall Lapp, General Electric Company, *Panel Leader*
   Howard B. Palmer, Pennsylvania State University
   William A. Sirignano, Princeton University

4. Properties of High Temperature Solids

   H. Kent Bowen, Massachusetts Institute of Technology, *Panel Leader*
   H. Fritz Franzen, Iowa State University
   Alexandra Navrotsky, Arizona State University

5. Properties of High Temperature Liquids

   Charles A. Eckert, University of Illinois, *Panel Leader*
   Milton Blander, Argonne National Laboratory
   J. Douglas MacKenzie, University of California, Los Angeles

APPENDIX A

Chapter

6. Mass Transport and Chemical Kinetics Involving Condensed Phases

J. Bruce Wagner, Arizona State University, *Panel Leader*
Dieter M. Gruen, Argonne National Laboratory
Wayne L. Worrell, University of Pennsylvania

7. Complex Heterogeneous Systems

Melvin G. Bowman, Los Alamos Scientific Laboratory, *Panel Leader*
Daniel Cubicciotti, SRI International
Thomas A. Milne, Solar Energy Research Institute

8. Development of a Critical Data Base

Leo Brewer, University of California-Berkeley

9. Instrumentation and Modern Measurement Techniques

John W. Hastie, National Bureau of Standards, *Panel Leader*
John V. Cathcart, Oak Ridge National Laboratory

10. Applications of High Temperature Science

Joan Berkowitz, Arthur D. Little, Inc., *Panel Leader*
Charles de Hunt, Electro-Metals Corporation
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