

CURRENT PROBLEMS IN RESEARCH

Chemistry at High Temperatures

New molecules will be discovered and new theories required to explain events from 1000° to 1,000,000°K.

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The scientist of today has available for laboratory investigation a temperature range from 10⁻⁶ °K all the way up to 10⁸ °K. The realm of high-temperature chemistry usually includes those chemical phenomena which occur at temperatures of 1000°K and higher, although, obviously, the boundary is not sharp. From 1000° to 10,000°K there are many molecules, atoms, and ions which are important reactant species; above 10,000°K the population of molecules gets very small, and atoms and ions become the predominant species.

In a general way, one may predict what high-temperature chemistry should be like by extrapolation of results at room temperature. Long extrapolations are dangerous, however, and one tends to underestimate the complexity of high-temperature inorganic systems when he uses the available information on organic compounds with which scientists working near room temperature are familiar. One is also tempted to overlook the possibility that useful concepts like valence and electron-pair bonding are influenced by temperature. The great variety of unusual high-temperature phenomena that have been reported in the past ten years suggests that predictions based on low-temperature analogies alone are not satisfactory and that much experimental and theoretical work remains to be done before high-temperature systems are thoroughly understood. Searcy (1), partly with tongue

in cheek, has suggested two laws of high-temperature chemistry: (i) at high temperatures, everything reacts with everything, and (ii) the higher the temperature, the more rapidly everything reacts. One may add an ultimate, third law: the products may be anything!

The aim of high-temperature chemists is, therefore, to study a selected group of materials that will illustrate the various types of behavior for high-temperature systems and allow the formulation of rules and generalizations for predicting the behavior of the many other systems for which there may never be time to carry out detailed experimental investigations.

Attainment and Measurement of High Temperatures

An important part of high-temperature work is obviously the generation and measurement of high temperatures in well-defined systems.

The concept of temperature has been discussed by physicists and chemists for many years. Among the most useful definitions are the following.

1) System A is at a higher temperature than system B if heat is transferred spontaneously from system A to system B.

2) The efficiency of an ideal Carnot cycle is given by the relation

$$\text{Eff.} = \frac{Q_{\text{in}} - Q_{\text{out}}}{Q_{\text{in}}} = \frac{T_1 - T_2}{T_1}$$

where T_1 and T_2 are the absolute temperatures between which the Carnot cycle is operating.

3) The ideal gas law equation, $PV = nRT$, as deduced experimentally and theoretically from statistical thermodynamics, yields a relationship between translational energy and temperature.

4) The factor which appears in the denominator of the Boltzmann distribution law, which describes how atoms or molecules distribute themselves over available energy states:

$$n_1/n_0 = g_1 e^{-(E_1 - E_0)/kT}$$

where n_0 is the number of particles in the single state with energy E_0 , and n_1 is the number in the state with energy E_1 and degeneracy g_1 .

It is apparent that a variety of techniques for attaining and measuring high temperatures will be available (see 2).

1) *Attainment of high temperatures.* Some of the high temperatures with which we are familiar occur in nature. Hot springs, volcanoes, lightning, and the sun and stars are examples of natural high-temperature furnaces in operation. The range of temperatures runs from a few hundred degrees up to many millions of degrees.

In terms of common devices, everyone is familiar with the generation of high temperatures by the oxidation of natural gas in ordinary flames or of gasoline in internal-combustion engines. Unusual fuels (H_2 , B_2H_6 , C_2N_2 , C_6N_6) and special oxidizers (O_3 , F_2 , ClO_3F) may produce flame temperatures up to 6000°K. Such chemical combustion processes can create temperatures of 2000° or at most 3000°K. The passage of electric current through a wire resistance, as in many common household appliances, can produce high temperatures; 3000° or even 4000°K are attainable with special conductors such as iridium, tungsten, molybdenum, carbon, tantalum carbide, or other refractories. The limitation on such methods is, of course, the melting of the conductor; at the moment the solid with the highest melting point is tantalum carbide, which melts at

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about 4200°K. It should be possible to produce heat by passing electric current through liquid metals, but the problem of containment is an extremely difficult one.

Instead of passing a current directly through a conducting wire under the influence of an electrical voltage applied at either end of the wire, one may transfer energy from an alternating-current system by a technique known as induction heating, in which a coil carrying high-frequency alternating current surrounds the object to be heated and transfers power to it by electromagnetic induction. In principle, this technique can be used for producing very high temperatures; the only requirement is an electrically conducting system. Conducting liquids and

solids can be heated inductively without contact with a container by levitation in a magnetic field.

If the system conducting electricity is no longer a condensed phase (solid or liquid) but a gas, the electrical conduction process is usually described as an electric discharge or arc. It would be very valuable to study electric conductivity at, or near, the critical temperature and pressure for fluid-gas transition, to learn more about this transition. In arcs through gases, one may supply enough energy so that some of the molecules and ions have apparent temperatures of 5000° to 100,000°K. It is true, of course, that the region of high temperature is not so well defined in such a system as in a simple furnace with a hot coil of wire wrapped around

it. By constricting the electric arc to a small volume one can create regions of more uniform and still higher temperatures. It is hoped that such constriction of electric arcs may create enough high-temperature ions to initiate thermonuclear reactions in systems that are easy to control.

Finally, one may attain high temperatures by chemical explosions that liberate large amounts of energy in a small volume and raise the temperature; by allowing a high-pressure gas to expand into a low-pressure system and create a shock wave in which the temperature of the gas is several thousand degrees Kelvin; or by passing a large amount of electric current into a small wire literally to "explode" the wire and create a region of high temperature.

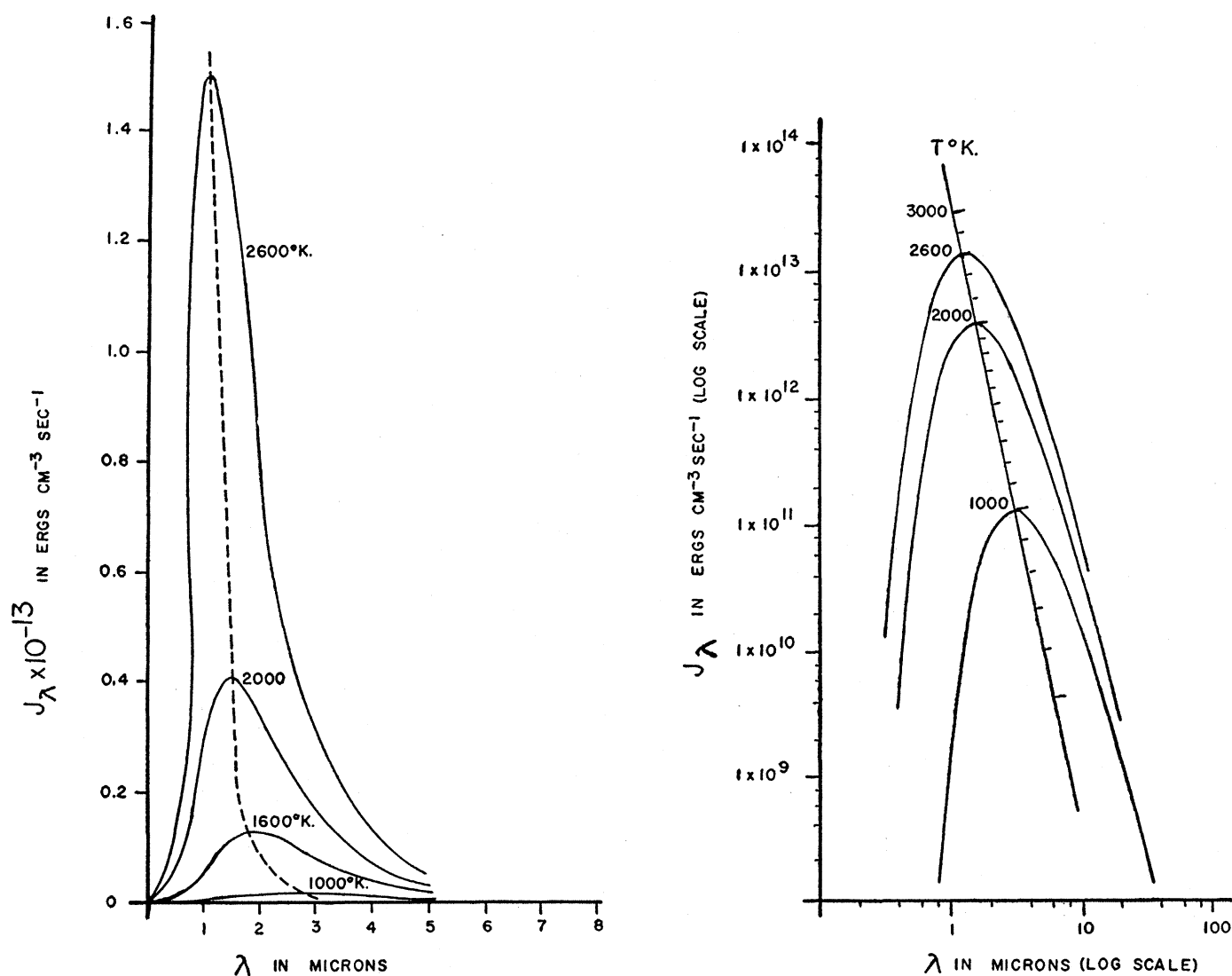


Fig. 1. Graphical representations of the Planck radiation law. (Left) Conventional plot of J_λ against λ for a series of increasing temperatures. Note that $J_{\lambda, T_1} > J_{\lambda, T_2}$ for all λ if $T_1 > T_2$, and that $\lambda_{\max}(T_1) < \lambda_{\max}(T_2)$ for $T_1 > T_2$. Also notice how little of the total radiation falls in the visible spectrum (0.4 to 0.7 μ) (5). (Right) A less familiar log-log plot of J_λ against λ at three temperatures. Note that the form of the curve is independent of T , and that radiation rates at any temperature may be obtained by a rigid displacement of the characteristic curve along the logarithmic temperature axis of slope -5 (from the λ^{-5} term in the radiation law) (6).

The very highest temperatures that have been created by human beings are those from nuclear reactions. In atomic bomb explosions, temperatures of more than a million degrees Kelvin are reached, and in a hydrogen bomb explosion, temperatures of more than 100 million degrees are attained, although only for a short time.

2) *Measurement of high temperatures.* Obviously, it is not possible to measure temperatures over the range 1000 to 100 million degrees Kelvin with any single device. Neither are the devices available at all related to the simple thermometer.

The most important difference between high-temperature systems and low-temperature systems is suggested by the Stefan-Boltzmann radiation law, which states that the radiation emitted by an object is proportional to the fourth power of the absolute temperature. Thus, an object at only 1000°K is radiating energy at a rate almost 100 times the rate of radiation of an object at 300°K. The radiation, in fact, is so much greater that it is visible and easily detected, and radiation from hot objects forms the basis for many of the methods of temperature measurement. Planck's radiation law,

$$J_{\lambda}, \tau d\lambda = \frac{C_1}{\lambda^5 (e^{C_2/\lambda T} - 1)} d\lambda \text{ erg cm}^{-2} \text{ sec}^{-1}$$

($C_1 = 2\pi hc^2$ and $C_2 = hc/k$, where h is Planck's constant, k is Boltzmann's constant, and c is the velocity of light), indicates that the energy emitted at various wavelengths from a hot object depends on the wavelength and on the temperature, and that there is a particular wavelength (λ_{\max}) at which the intensity of radiation will be a maximum (see Fig. 1).

The techniques for temperature measurement that are based on radiation phenomena include (i) location of the position of λ_{\max} , which is uniquely determined by the temperature; (ii) comparison of either total or monochromatic radiation from hot objects at unknown temperatures with the corresponding radiation from standard hot filaments which have been previously calibrated; or (iii) comparison of radiation intensities at two or three different wavelengths. Such temperature determinations are complicated by the fact that, since real objects do not emit electromagnetic radiation exactly as predicted by Planck's law, which is for an ideal emitter (black body), an emis-

sivity factor must be determined experimentally for each real emitter. Radiation techniques are especially valuable for determining astronomical temperatures, where no direct contact with the hot object is possible. The development of sensitive infrared detectors has made it possible to extend the measurement of radiation temperature down to room temperature and even below.

Another important temperature-measurement technique for high-temperature systems depends on the use of spectroscopic methods for determining the relative population of energy levels and application of the Boltzmann equation given earlier. Thus, if one can measure the intensity of a spectral line (the intensity is proportional to the population of the emitting energy level and other factors characteristic of the transition) and knows how this intensity varies from one situation to another, he has a device for measuring temperature.

For example, consider the emission of light from a system which contains three energy levels E_0 , E_1 , and E_2 . The intensity of the emission corresponding to the transition $E_2 \rightarrow E_0$ will be given by a product of factors which includes $e^{-(E_2 - E_0)/kT}$, while the intensity of the emission from level $E_1 (E_1 \rightarrow E_0)$ will depend on several factors, including $e^{-(E_1 - E_0)/kT}$. The ratio of the intensities is given exactly by

$$\frac{I_{2 \rightarrow 0}}{I_{1 \rightarrow 0}} = \frac{C_2 A_2 g_2 (E_2 - E_0) e^{-(E_2 - E_0)/kT}}{C_1 A_1 g_1 (E_1 - E_0) e^{-(E_1 - E_0)/kT}}$$

where C_2 and C_1 are geometrical factors characteristic of the experimental apparatus, g_2 and g_1 are the statistical weights of the energy states, and A_2 and A_1 are the transition probabilities for the $2 \rightarrow 0$ and $1 \rightarrow 0$ processes. Usually C_1 equals C_2 , while A_2 and A_1 are either calculated or determined experimentally in systems at known temperatures, and one can solve directly for T from the measured intensity ratio. One can also, in principle, determine C and use absolute intensities to get T .

Numerous other spectroscopic techniques for temperature measurement are valuable, including measurement of Doppler broadening caused by the rapid translational motion of high-temperature species; measurement of Holtsmark broadening resulting from Stark-effect splitting of energy levels in the fields of ions and electrons present in hot gases; or measurement of the intensity and wavelength distribution of brems-

strahlung radiation or continuous radiation from recombination of electrons and ions.

One may also observe the variation of various physical properties as a function of temperature and, with suitable calibrations, establish temperatures in this way. A very familiar technique is the measurement of electrical resistance; this approach has been highly refined for platinum resistance thermometers, used at temperatures up to 800° or 900°K. Resistance thermometers with tungsten, tantalum, or other conducting elements have been used at temperatures up to nearly 2000°K.

The junction of two dissimilar conducting materials creates a thermocouple, and the voltage generated at such junctions varies with temperature in a reproducible way. Thermocouples made of platinum metals or platinum metal alloys have been used for temperature measurements up to 2200°K, and junctions between tungsten and molybdenum or tungsten and tantalum or various refractory alloys make it possible to measure temperatures up to nearly 3000°K by thermocouple techniques.

Present Status of

High-Temperature Chemistry

One of the most important conclusions that has come out of the approximately 20 years of intensive investigation of high-temperature systems (3) is that complex species are present in high-temperature systems, and (even more surprising) that many of these systems seem to get more complicated with increasing temperature. This complexity was predicted early in the development of modern high-temperature chemistry by Brewer (4), who showed that this conclusion can be deduced from thermodynamics, which requires for a system in equilibrium, that

$$\frac{d \ln K_{eq}}{d(1/T)} = -\frac{\Delta H_T}{R}$$

where K_{eq} is the equilibrium constant, ΔH_T is the heat of reaction, and R is the gas constant.

Thus, if a solid-vapor equilibrium is being considered and if in the vapor there are monatomic and diatomic species (monomers and dimers), the rate of change of monomer concentration will be different from the rate of change of dimer concentration and will depend on the heat of formation from

the condensed phase. Both cases are known— $\Delta H_m > \Delta H_d$ and vice versa. In the former case, monomers may become predominant species at high temperatures, while in the latter case dimers may become predominant and the vapor becomes more complex. In many organic systems monomers are the important high-temperature species, while many refractories show the opposite behavior. These predictions have been dramatically supported in the studies of the vapor pressures of the chemical elements reported over the past decade.

A classical problem concerns the sublimation of elementary carbon. Before 1940 it was usually assumed that graphite sublimates primarily as atoms, and even in 1950 it was believed that the vapor consisted of atoms and diatomic molecules, C_2 , this latter species comprising a minor fraction of the vapor. The adaptation of a high-sensitivity mass spectrograph for study of vapors given off from hot filaments or escaping through the orifice of a Knudsen cell has created a very powerful tool for the characterization of high-temperature vapors. M. Inghram and W. Chupka and their associates at the University of Chicago and the Argonne National Laboratory and R. Honig at the Radio Corporation of America Laboratories have pioneered in the development of such devices. They have discovered that carbon vapor consists of C_1 , C_2 , C_3 , C_5 and probably still higher polymeric species; that germanium vapor consists of Ge_1 , $Ge_2 \dots Ge_9$; and that similar complex molecules are important in the vaporization of silicon, lead, tin, and most other elements.

As one might expect, the vaporization of compounds is also extremely complex; some of the unusual species involved in high-temperature vaporization processes are indicated in Table 1. P. Kusch and his associates at Columbia University have studied complex vapors directly by molecular-beam techniques.

From these studies it is apparent that high-temperature vapors often contain complex and unusual species not predicted from classical rules of valence or chemical bonding.

Inorganic syntheses. There are so many possible binary chemical systems that reports of new compounds prepared essentially by heating various amounts of two elements together are still common in 1961. For example, new platinum alloys and various carbides of the platinum metals have re-

Table 1. Typical complex species in high-temperature vapors.

Condensed phase	Gaseous molecules observed*
B_2O_3	B_2O_3
$B + B_2O_3$	B_2O_3 , B_2O_2 , BO
$O_2 + B_2O_3$	B_2O_3 , BO_2^\dagger
$H_2O + B_2O_3$	HBO_2 , $(HBO_2)_3$, H_3BO_3
BeO	BeO , $(BeO)_2 \dots (BeO)_6$, Be_2O
$H_2O + BeO$	$Be(OH)_2^\dagger$
Cu-Au alloy	Cu_2 , Au_2 , $CuAu$
LiF	LiF, $(LiF)_2$, $(LiF)_3$
$LiAlF_4$	$LiAlF_4$, $(LiF)_4$, $(LiF)_5$, AlF_3
Li_2O	Li_2O , LiO , $LiONa^\ddagger$
LiOH	LiOH, $(LiOH)_2$, $(LiOH)_3$
NaCN	NaCN, $(NaCN)_2$
$NaOH + HCl$	$(NaOH)_2$, $(NaOH)_3$, $(NaCl)_2$, $(NaCl)_3$, $(NaCl)_4$, $(NaCl)_5$, $(NaCl)_6$, $(NaCl)_7$, $(NaCl)_8$, $(NaCl)_9$, $(NaCl)_{10}$, $(NaCl)_{11}$, $(NaCl)_{12}$, $(NaCl)_{13}$, $(NaCl)_{14}$, $(NaCl)_{15}$, $(NaCl)_{16}$, $(NaCl)_{17}$, $(NaCl)_{18}$, $(NaCl)_{19}$, $(NaCl)_{20}$, $(NaCl)_{21}$, $(NaCl)_{22}$, $(NaCl)_{23}$, $(NaCl)_{24}$, $(NaCl)_{25}$, $(NaCl)_{26}$, $(NaCl)_{27}$, $(NaCl)_{28}$, $(NaCl)_{29}$, $(NaCl)_{30}$, $(NaCl)_{31}$, $(NaCl)_{32}$, $(NaCl)_{33}$, $(NaCl)_{34}$, $(NaCl)_{35}$, $(NaCl)_{36}$, $(NaCl)_{37}$, $(NaCl)_{38}$, $(NaCl)_{39}$, $(NaCl)_{40}$, $(NaCl)_{41}$, $(NaCl)_{42}$, $(NaCl)_{43}$, $(NaCl)_{44}$, $(NaCl)_{45}$, $(NaCl)_{46}$, $(NaCl)_{47}$, $(NaCl)_{48}$, $(NaCl)_{49}$, $(NaCl)_{50}$, $(NaCl)_{51}$, $(NaCl)_{52}$, $(NaCl)_{53}$, $(NaCl)_{54}$, $(NaCl)_{55}$, $(NaCl)_{56}$, $(NaCl)_{57}$, $(NaCl)_{58}$, $(NaCl)_{59}$, $(NaCl)_{60}$, $(NaCl)_{61}$, $(NaCl)_{62}$, $(NaCl)_{63}$, $(NaCl)_{64}$, $(NaCl)_{65}$, $(NaCl)_{66}$, $(NaCl)_{67}$, $(NaCl)_{68}$, $(NaCl)_{69}$, $(NaCl)_{70}$, $(NaCl)_{71}$, $(NaCl)_{72}$, $(NaCl)_{73}$, $(NaCl)_{74}$, $(NaCl)_{75}$, $(NaCl)_{76}$, $(NaCl)_{77}$, $(NaCl)_{78}$, $(NaCl)_{79}$, $(NaCl)_{80}$, $(NaCl)_{81}$, $(NaCl)_{82}$, $(NaCl)_{83}$, $(NaCl)_{84}$, $(NaCl)_{85}$, $(NaCl)_{86}$, $(NaCl)_{87}$, $(NaCl)_{88}$, $(NaCl)_{89}$, $(NaCl)_{90}$, $(NaCl)_{91}$, $(NaCl)_{92}$, $(NaCl)_{93}$, $(NaCl)_{94}$, $(NaCl)_{95}$, $(NaCl)_{96}$, $(NaCl)_{97}$, $(NaCl)_{98}$, $(NaCl)_{99}$, $(NaCl)_{100}$
SiC	Si_2 , Si_3 , SiC_2 , Si_2C , Si_3C , SiC , Si_2C_2 , Si_2C_3
V_2O_5	V_4O_{10} , V_4O_8 , V_6O_{14} , V_6O_{12} , V_2O_4 , $MoV_4O_{12}^\S$
WO_3	$(WO_3)_3$, $(WO_3)_4$, $(WO_3)_5$

* In most cases the positive molecule ion was actually detected in the mass spectrograph, but sometimes the parent ion loses an atom; for example, Na_2Cl^+ and $NaCl_2^-$ are the major ions from Na_2Cl_2 molecules interacting with electrons. $^\dagger BO_2$ has been identified from optical spectra only, while $Be(OH)_2$ is deduced from transpiration experiments. ‡ Impurity. § From crucible.

cently been described. Such systems are usually characterized by x-ray diffraction and melting points, to establish the composition and temperature regions of phase stability.

New ternary solids are also easily found. For example, recent studies report investigation of the $M-C-B$, $M-C-Si$, $M-O-C$, $M-O-N$, M_1-M_2-O , and other systems where M may be any one of the 70 or so available metals. H. Shaffer of Germany has synthesized a variety of oxyhalides, and the preparation of complex silicates and hydrates in high-temperature, high-pressure systems is of geochemical significance.

In addition to the synthesis of compounds by classical furnace techniques, there are various new approaches, including (i) condensation of complex vapors (suboxides and subhalides); (ii) the combination of high temperatures and high pressures to favor solid-solid reactions such as C (graphite) \rightarrow C (diamond); (iii) the creation of new species in furnaces, electric arcs, or plasma jets and the subsequent reaction of these species (molecules, atoms, or ions in various energy states) either with each other or with gases or condensed particles introduced into the system; (iv) reactions in flames where free radicals (OH, HO_2 , HCO, CH, CH_2 , and so on) can interact with each other or with materials added to the flame; and (v) electrochemical reactions with fused salts or molten metals as solvents.

Thermodynamic properties. A chemical system is uniquely characterized at T degrees Kelvin and P atmospheres by specifying any two of the quantities $\Delta F_i^{T,P}$, $\Delta H_i^{T,P}$ or $\Delta S_i^{T,P}$ which place the system with respect to the pure elements in their standard states. Such data (as functions of P and T) are vital for predicting the course of a chemical reaction—for example, whether an alloy will be oxidation-resistant, or what temperature and impulse are to be expected for a given fuel-oxidizer system.

High-temperature solid systems are usually characterized by phase diagrams (derived from free-energy relationships) that express the regions of temperature, pressure, and composition in which given phases are stable. Heats of formation of condensed phases are usually established by oxygen combustion calorimetry or by solution calorimetry, and the latter is being extensively used with liquid metals or fused salts at high temperatures. An important recent innovation in the combustion technique is the use of elementary fluorine as the oxidizing agent; this makes possible precise measurements on metal borides, carbides, nitrides, silicides, and oxides. Previously, heats of formation were often not reliable because suboxides or other products were formed in incomplete combustion processes.

The variation, with temperature, of intensities of mass spectra or of optical spectra, when obtained for systems in equilibrium, yields data on heat of formation for high-temperature gaseous species. For correlation of such thermodynamic data, the periodic table is excellent, and one can often use such a diagram to spot poor data or to predict properties of new materials.

In addition to heats of formation one needs heat capacities from 0°K to T° K and heats of transition to describe a system, since $\Delta F_i^{T,P} = \Delta H_i^{T,P} - T\Delta S_i^{T,P}$. There are many measurements of heat contents for $T < 1800^\circ$ K but almost none at higher temperatures, so that almost all thermodynamic calculations at $T > 1800^\circ$ K are based on extrapolated data. New techniques are needed to go to higher temperatures.

Structures. The existence of a variety of high-temperature species justifies research in another important area, the determination of structures.

To elucidate the structure of a high-temperature gas, one may make use of the mass spectrographic fragmentation

pattern, which shows the ionic fragments most easily formed from the parent molecule; of visible, ultraviolet, infrared, and microwave spectroscopy, which allow the establishment of energy levels; and of electron diffraction, which makes possible determination of the molecular geometries. One of the important recent advances has been the development of simple and reliable techniques for taking infrared absorption and emission spectra of high-temperature gases, by W. Klemperer and his associates of Harvard University, by D. White and his associates at Ohio State University, and by my research group at the University of Wisconsin. The infrared spectra give directly the vibrational energy levels (with some broadening) in high-temperature species without interference from electronic energy states as in visible and ultraviolet spectroscopy. The construction of a special microwave spectrometer for studying vapors at temperatures as high

as 1000°C has provided another valuable tool, although this upper limit is only the beginning of the real high-temperature range.

The technique of electron diffraction by high-temperature gases to yield characteristic patterns has been extensively developed by Akishin and his associates in Russia. In a series of outstanding papers published over the last 10 years, these workers have reported structural information on a number of compounds, ZnX_2 , CdX_2 , BeX_2 , MgX_2 , SrX_2 , GaX_3 , Li_2O , B_2O_3 , and B_2S_3 . They have shown that alkaline earth dihalides are linear molecules, that Li_2O is a bent molecule, and that B_2O_3 and B_2S_3 are probably V-shaped molecules, and thus they have answered questions that have not been resolved by other techniques up to the present time.

Bauer and his associates at Cornell University have recently used a high-temperature electron diffraction apparatus for determining the structure of

gaseous $(\text{LiCl})_2$ and also of gaseous cupric nitrate. Structures of some typical high-temperature molecules are shown in Fig. 2.

Over the past 10 years there have been published descriptions of a number of high-temperature cameras for photographing both x-ray and neutron-powder and single-crystal-diffraction patterns at temperatures up to 2000°K. The actual amount of work carried out with these cameras is quite limited, however, and much remains to be done in this area.

Transport properties and kinetics. As one would expect from the exponential dependence of reaction rates on temperature, high-temperature reactions are generally fast. Whereas, at room temperatures, reactions that have to hurdle activation energy barriers of 10 to 50 kilocalories are fairly slow, it is obvious that energy barriers of over 100 kilocalories per mole of reactant will be easily overcome at 2000°K.

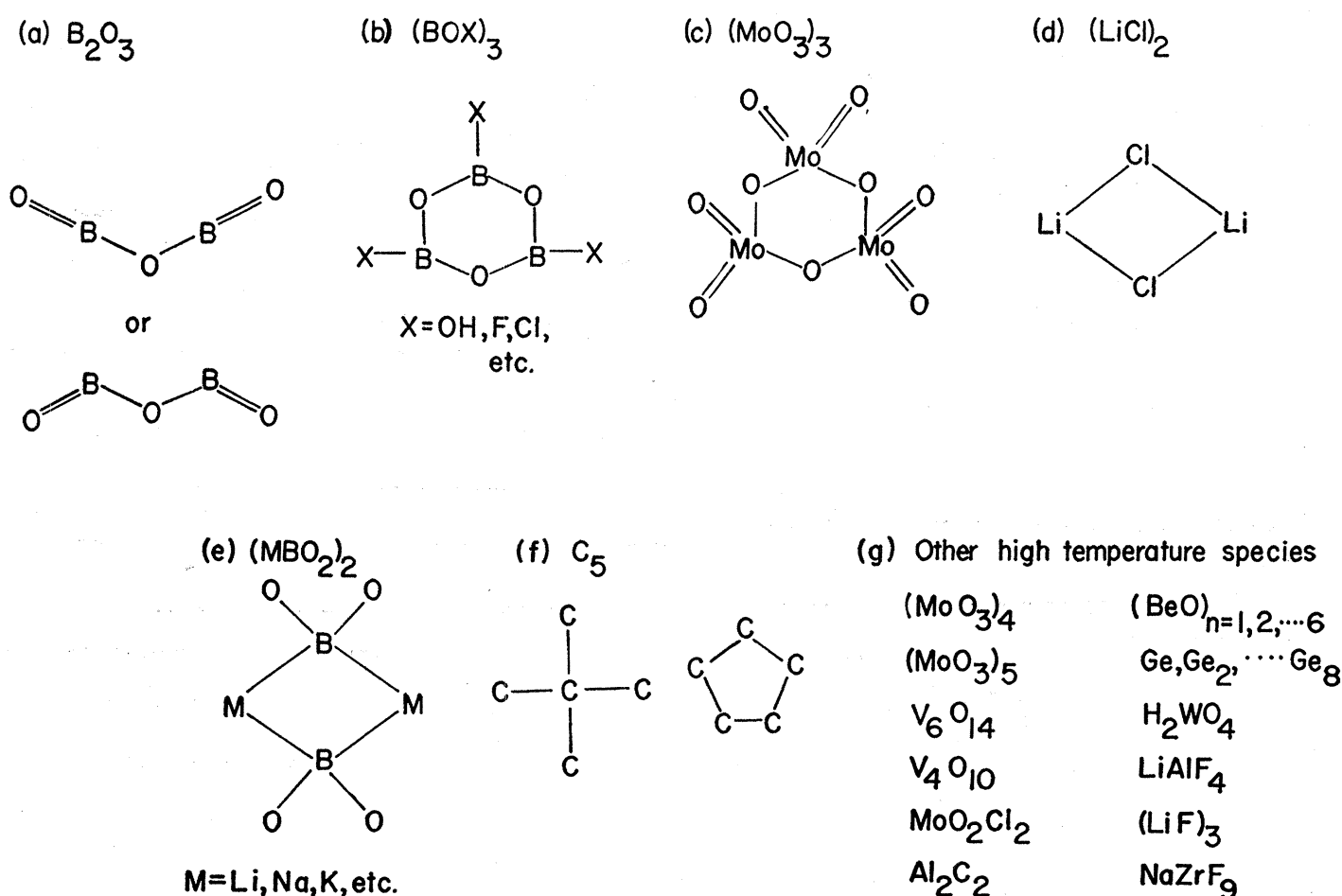


Fig. 2. Plausible structures for some high-temperature molecules. *a*, Electron diffraction favors the V-shape; *b*, no structural data, positive ion appears in mass spectrometer; *c*, no structural data, positive ion appears in mass spectrometer; *d*, electron diffraction data; *e*, no structural data except infrared absorption spectrum; *f*, no structural data, very low concentration even for mass spectrometer studies; *g*, positive ions appear in mass spectrometer.

Thus, the field of kinetics is expanded to include those types of reactions which are important at high temperatures (dissociation, ionization, and so on) and to give increased emphasis to rate processes which involve diffusion of molecules, atoms, ions, electrons, or vacancies.

Among the important types of research in this area are the measurement of rates of reaction of gases at metal surfaces; the measurement of rates of reaction between molecules, atoms, ions, and electrons in shock waves; the measurement of diffusion rates of metal *A* atoms within bulk *A*, or of metal *B* atoms in bulk *A*, or of atoms, molecules, or ions in liquid metals or in fused salts; the measurement of electrical conductance, transference numbers, and mobilities of ions in electrically conducting systems; and the measurement of viscosities, surface tensions, and other classical physical properties. In the studies of such rate phenomena, wide use is made of the available stable and radioactive isotopes in order to observe isotope effects.

The Future of High-Temperature Chemistry

The future of high-temperature chemistry is almost beyond prediction when one considers that over the past 100 years organic chemists, working in a limited temperature range, have succeeded in making over a million compounds from only five or six elements, while present-day high-temperature chemists have available more than 100 elements and a temperature range of 10^5 °K. There is no doubt that thousands of new chemical materials will be prepared within the next few years by high-temperature techniques.

One can say with some degree of certainty that these compounds will be largely endothermic molecules that have become important species in high-temperature environments, are quenched to low temperatures, and are then maintained in useful forms, because of slow reaction rates for their conversion to thermodynamically more stable systems. Some of these materials may have higher melting points than tantalum carbide or may be more chemically

reactive than our best available fuels or oxidizers of 1961.

One may formulate a number of goals, the attainment of which would greatly advance high-temperature chemistry and physics. Among these are:

1) The establishment of highly reliable standards for temperature measurement, which can be held for reference at the National Bureau of Standards and similar laboratories in other countries, and which may be used by practicing high-temperature chemists for calibration of pyrometers and other measuring instruments.

2) The development of new techniques for attaining high temperatures, especially temperatures over 4000°K, where one no longer has the conventional solids available. We must either find new solids with higher melting points or develop new techniques for creating static high-temperature systems in which experiments may be carried out. At the moment the only available techniques for this region are those in which flames or electric arcs are used, and these systems are difficult to characterize and control.

3) The development of apparatus for attaining high temperatures in highly oxidizing atmospheres. To be able to experiment in atmospheres of oxygen or even fluorine at temperatures of 2000° or 3000°K would be very valuable.

4) The development of better techniques for deducing the structures of high-temperature gaseous molecules. In many cases one has only a few millimeters of gas pressure available under conditions of high temperature, and it is extremely difficult to carry out electron diffraction. The electron diffraction technique, while promising, does not always give a unique structure, since one only compares the observed diffraction pattern with a pattern calculated for an assumed molecular model. It is always conceivable that some other model might yield a very closely related diffraction pattern. Infrared and microwave spectroscopy may give some information, but they do not usually give complete structures. There is a need for more high-temperature Raman-spectral work. Electronic spectra, especially of polyatomic molecules, are helpful but very complex, and the deduction

of a structure from electronic spectra alone could require many years of research.

5) The determination of high-precision thermodynamic data for high-temperature systems, especially heats of formation and heat capacities of high-temperature materials over wider ranges of pressure and temperature. From such data there may eventually be created complete tables of thermodynamic functions from which it should be possible to calculate chemical behavior if all the important reactant species are known.

It would be especially helpful in the collection of thermodynamic data if there were established (perhaps at the National Bureau of Standards) a "bank" for materials of high purity that are of interest in high-temperature studies, so that various kinds of high-precision measurements could be carried out on standard samples of known background and known purity. The correlation of one property with another would be more meaningful if the various measurements could be made on such high-purity materials. At present many high-temperature refractories are not even available in 95- to 98-percent purity, and published measurements in the literature are often misleading.

In summary, one must conclude that high-temperature chemistry is still in its infancy. New molecules will be discovered, new techniques will be developed, and new theories will be required to explain chemical and physical phenomena over the range 1000° to 1,000,000°K.

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