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THE CHEMICAL IMPORTANCE OF UNUSUAL MOLECULES OBSERVED AT HIGH TEMPERATURES

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Almost every careful study of a chemical system at high temperatures that has been made in recent years has resulted in the detection of new gaseous molecules or solid phases. For example, neutral gaseous molecules such as Al_2O, B_2O_2, Cu_3Cl_3, C_2, C_3, C_5, Ge_1 through Ge_8, Cu_2, Ag_2, Au_2, CuAu, Mg_2, H_3BO_3, HBO_2, MoO_2Cl_2, SiO, $SiO_2 \cdot 4H_2O$, and $NaAlCl_4$ have been reported, as have many new solid phases. In several high-temperature vaporization processes ions are found and, in the mass spectrograph, ion fragments of every imaginable variety persist for a sufficient length of time to be detected. The chemical importance of such unusual molecules, for which our normal ideas of valence and electron-pair bonds seem invalid, is very great. Any satisfactory theory of chemical bonding must be able to explain and to justify the existence of these species. High-temperature phenomena will offer a fertile proving ground for the theoretician in chemistry.

The species commonly observed at high temperatures are "unstable" toward cooling. They may condense, polymerize, or disproportionate. The production of unusual and unstable molecules in arcs and discharges and often in flames involves nonequilibrium processes; for this reason thermodynamic arguments are not too useful. In resistance-heated, solar-heated, or induction-heated furnaces one may, however, observe unusual molecules present in equilibrium amounts. Their stabilities, measured in terms of heats of atomization or of bond energies, may be very high or very low, as indicated in TABLE 1.

In spite of the relatively weak bonds found in some molecules, the latter occur at high temperatures and may even become more important as the temperature increases. For example, $D(Mg_2)$ is only 0.31 eV (7.2 kcal.), but $Mg_2(g)$ makes up $\sim$0.3 per cent of saturated Mg vapor at the boiling point, 1399° K., and becomes still more important in the saturated vapor at higher temperatures; $D(Na_2)$ = 0.75 eV (17.3 kcal.), but Na_2 increases in importance from 0.1 mol per cent at 400° K. to 12 mol per cent at 1100° K. in

TABLE 1
HEATS OF ATOMIZATION
(MOLECULES → GROUND STATE ATOMS)
All Are Found at High Temperatures

B_2O_3	663 kcal./mol
B_2O_2	500 kcal./mol
C_3	311 kcal./mol
C_2	144 kcal./mol
Cu_2	48 kcal./mol
Mg_2	7.2 kcal./mol

saturated Na vapor. At first glance this increase of importance of complex species may seem anomalous, but Brewer[1] has shown that it can be explained by simple thermodynamic considerations.

In this discussion of the chemical importance of the unusual, "unstable" molecules observed at high temperatures, it seems reasonable to consider their importance: (1) in elucidating the simpler high-temperature processes such as dissociation, vaporization, and thermal decomposition; (2) in explaining more complex high-temperature phenomena such as solid-gas reactions, solid-solid reactions, combustion processes, and reactions in electric arcs and discharges; (3) in chemical syntheses; (4) in chemical kinetics; and (5) in providing verification of present theories and new bases for more improved theories.

The Simpler High-Temperature Processes

In the group of "simple" high-temperature processes are included those reactions that are endothermic in nature and have little tendency to proceed at room temperature on the basis of thermodynamic equilibrium calculations. Typical processes include: (1) the vaporization or sublimation of most metals, most ionic compounds, some covalent compounds, some nonmetallic elements, and some element-compound mixtures to form neutral species or ions; (2) the thermal decomposition of stable compounds when simple vaporization or sublimation does not occur; and (3) the dissociation of complex molecules into simpler units and of neutral species into ions.

Simple vaporization and thermal decomposition of condensed phases. A few years ago, chemists would not have been at all dismayed to see the equation for vaporization of C written simply as

$$C\ (\text{graphite}) \rightleftarrows C\ (\text{gas})$$

or that for the vaporization of $B_2O_3(l)$ as

$$B_2O_3(l) \rightleftarrows B_2O_3(g)$$

At present, however, there is considerable doubt that such simple, straightforward transfer of atomic or molecular units to the gas phase usually occurs. Often more complex molecules are involved. The most reasonable procedure for obtaining information about vapor species is to examine the equilibrium vapors with a mass spectrograph. Work of this type has been done by Inghram and Chupka[2a-2c] on C; Honig[3a-3d] on C, Ge, Sn, Si, Pb; Kane[4] on As and P; Köhl[5] on Ge, B, Si, and Sn; Inghram, Porter, Schissel, and Chupka[6a-9] on SiO_2, BaO, SiO, MgO, Al-Al_2O_3 mixtures, B_2O_3, and B-B_2O_3; Bichel and Holroyd[10] on SrO and BaO; Pelchowitch[11] on Ni, SrO, CaO, and BaO; Friedman[12] on LiI; and by Rosenstock, Sites, Walton, and Baldock[13] on CuCl.

Alternative techniques involve the use of a torque-Knudsen cell with which one can measure both total weight loss from a cell and average molecular weight of the effusing species,[14a, 14b] or a chemical method such as that used by Brewer and Lofgren on CuCl.[15]

Some amazing results have been reported. Graphite vapor contains

$C(g)$, $C_2(g)$, $C_3(g)$, possibly $C_5(g)$ and also $C^-(g)$, $C_2^-(g)$, and $C_3^-(g)$; germanium vapor includes all the species from $Ge(g)$ to $Ge_8(g)$; boron and gallium appear to vaporize as atoms; B_2O_3 yields $B_2O_3(g)$ monomers, while B-B_2O_3 mixtures yield $B_2O_2(g)$; Al_2O_3 decomposes to $AlO(g)$ but Al-Al_2O_3 mixtures vaporize as $Al_2O(g)$; $CuCl(l)$ is found to vaporize as the trimer, $Cu_3Cl_3(g)$; LiI yields > 2 per cent of $(LiI)_2$, and other alkali halide vapors appear to contain polymers.[16, 17] The mass spectrograph offers quick and unequivocal evidence for the existence of complex vapor molecules. By observing the temperature dependence of the intensity of a given mass signal, one can deduce the heat involved in molecule formation and, thus, the heats of vaporization or sublimation for the various species.

In addition to the mass-spectrographic technique, one can make use of emission or absorption spectra of the atoms or molecules formed on heating. Atomic emission lines from heated gases are well known, especially in astronomy, and ions have been detected in shock-wave studies at temperatures up to 18,000° K.[18] The advantage of optical spectra of molecules is that they reflect intrinsically the details of the molecular structure if the experimenter can only interpret them. Recent studies of Cu, Ag, and Au vapors at high temperatures indicate visible spectra of Cu_2, Ag_2, $CuAu$, and Au_2 molecules.[19-22b] Visible spectra characteristic of electronic transitions have been useful in identifying the green color observed when boron compounds are burned with the $B_2O_3(g)$ molecule.[23-25] Since electronic spectra are complicated by vibrational and rotational fine structure, infrared or Raman spectra offer more hope of providing molecular structure data, and Klemperer[26a-26c] has recently reported high-temperature studies on $AlCl_3(g)$, $HgCl_2(g)$, $HgBr_2(g)$, and $LiH(g)$. The fundamental frequencies and intensities observed allow formulation of reasonable molecular models.

Many compounds are not stable enough to vaporize directly as gaseous molecules, and thus they undergo partial or complete decomposition at high temperatures. In a case of thermal decomposition one may use mass-spectrographic and optical techniques for detection of species. In addition, thermochemical calculations assuming direct decomposition to the elements will serve to establish whether a complete decomposition is involved, or whether gaseous intermediate substances are formed. In the case of Mg_3N_2 and TeO_2, Soulen, Sthapitanonda, and Margrave[23] considered

$$Mg_3N_2(s) \rightleftharpoons Mg_3N_2(g)$$
$$\text{or } 2\ MgN(g) + Mg(g)$$
$$\text{or } 3\ Mg(g) + N_2(g)$$

and

$$TeO_2(s \text{ or } l) \rightleftharpoons TeO_2(g)$$
$$\text{or } TeO(g) + \tfrac{1}{2}\ O_2(g)$$
$$\text{or } Te(g) + O_2(g)$$

as possible vaporization processes. One can calculate the partial pressures of the elements and, by measuring the rate of weight loss in either flow or effusion apparatus, can decide if decomposition to elements is the process occurring or if some other species is involved. For $Mg_3N_2(s)$ the correct

reaction is decomposition to the elements; for TeO_2(s and l) weight loss occurs by forming TeO_2(g) molecules.

Similar studies of the thermal decomposition of Na_2CO_3,[27] $MgSO_4$,[28] K_2MnO_4,[29] Li_2O and Na_2O,[30] MgO,[31] and UO_2[32] have recently been made.

In the decomposition of Li_2O some support for the existence of either Li_2O(g) or LiO(g) was obtained. During the Mg_3N_2 studies there was observed a spectrum that is associated with Mg_2(g) molecules that apparently are unstable intermediates formed in the decomposition process.

Dissociation of complex molecules. Dissociation of diatomic molecules to atoms has recently been reviewed by Gaydon.[33] The atomic products are usually well known, although several interesting chemical systems are not completely understood because of uncertainties about the atomic states of the dissociation products. For example, ClF, BrF, and IF molecules dissociate to halogen atoms, but the question as to which atom is $^2P_{3/2}$ and which $^2P_{1/2}$ is unanswered.[34-36] Careful high-temperature mass-spectrographic and spectroscopic studies could settle the problem.

A number of common but fairly complicated systems have been studied. One would suppose in systems of the CX_4 type (X = H or halogen) that dissociation would occur, giving CX_3, CX_2, and CX molecules. For CF_4, spectra of the CF_2 and CF molecules have been observed on decomposition in an electric arc[37-39] and in thermal equilibrium at high temperatures.[40] No evidence for CF_3 spectra has been reported, although mass-spectral and kinetic data indicate that there must be large concentrations when CF_2 and CF are observed. C_2F_4 also undergoes decomposition to yield CF_2 and CF.

CH_4 decomposes thermally at about 1000° C. to graphite and hydrogen. Thus, there is slight opportunity to obtain CH_3, CH_2, and CH by a simple dissociation process. However, further heating of C and H_2 to very high temperatures yields emission spectra of CH molecules.[41, 42] CH_2 and CH_3 are not easily identified, but probably will be distinguished by infrared or ultraviolet spectra.

Two new techniques of great importance are the "shock-tube" method for creating a high-pressure, high-temperature shock wave in a gas[43, 44] and flash photolysis for photodissociation processes.[45-47] Spectral studies of emitted and absorbed light in flash-photolysis and shock-tube experiments have indicated the presence of such unusual molecules as S_2, CS, ClO, CH_3CO, OH, CH, C_2, C_3, CN, NH, and NH_2, all of which are important at high temperatures.

Complex High-Temperature Phenomena

Reactions considered in this section are distinguished from those discussed previously because there is more than one reactant involved and therefore the mechanism for the reaction is somewhat more complex.

Solid-solid reactions.[48-50] Reactions of this type are rapidly becoming of major practical importance as the influence of small amounts of impurities on physical and chemical properties is being recognized and applied in semiconductors, transistors, phosphors, catalysts, and so on. Solid-solid reactions necessarily occur by a diffusion mechanism as impurities, added mate-

rials, or imperfections move through the crystal lattices. High temperatures and high pressures, of course, make these reactions take place more rapidly by increasing migration rates. Another important process of this type is sintering.

In discussing the reactivity of solids Rice[50] has attributed enhanced surface reactivity in solids to: (1) special surface conditions arising because of the preparative method used; (2) weakening of the lattice on approaching a crystallographic transition temperature; and (3) distortion of the lattice because of the presence of impurities of different size or charge type. In addition, reactivity depends on particle size, thermal treatment (adsorbed gases present), and magnetic and ferroelectric properties, and can be influenced by photoexcitation and by supersonic vibrations.

Solid-liquid reactions. In high-temperature systems the major solid-liquid reactions of interest concern solubilities and equilibria in ceramic[51] and metallic systems[52] and their practical application, for example, in zone melting purification methods.[53a, 53b] Again, such reactions are diffusion-controlled, but in the liquid state the diffusing species is an atom or an ion instead of a lattice imperfection.

Solid-gas reactions. This type of reaction is of great importance, since it represents the primary step in such processes of corrosion as rusting, weathering, and the high-temperature scaling and oxidation of surfaces. The reactions of solids with oxygen, nitrogen, and hydrogen—both dry and with various amounts of water—have been studied by many investigators, primarily from a kinetic viewpoint.[54-55b] In general, the results favor a mechanism involving diffusion of ions, electrons, or positive holes through lattice defects in the protective film, without actual formation of new molecules. The "unstable" units involved in these processes are the lattice defects; and their potential ability to "react" and form "stable" lattices containing the reactant gas atoms accounts for metal corrosion. At high temperatures where metal vapor pressures become high, corrosion may actually take place by means of a gas-gas reaction.

An example of the useful type of information obtained is to be found in the nitridation studies on Mg and Al by Sthapitanonda and Margrave.[56] These authors found that at temperatures below 460° C. the rate of nitridation of Mg is actually faster than the rate of oxidation; thus, low-temperature corrosion of Mg is primarily by nitridation, while at high temperatures oxidation is predominant. Al, on the other hand, oxidizes faster than it nitrides, at all temperatures.

Another type of solid-gas reaction that has been studied involves the burning of finely divided Al or C in O_2.[57] When such highly exothermic reactions occur, emission spectra of the hot intermediates and products are obtained.

Simple gas-gas reactions. Gas-gas reactions represent the most studied types of high-temperature systems. For example, the reactions between N_2 and O_2, NO and O_2, H_2 and F_2, H_2 and Cl_2, H_2 and Br_2, and H_2 and O_2 have been carefully studied. The products are usually well-known molecules,[58-60] but the "unstable" intermediates are sometimes interesting and

unusual molecules. For example, in the H_2-O_2 reaction, in addition to OH(g), there has been considerable evidence for the production of H_2O_2 and a suggestion that gaseous HO_2 molecules are formed during the reaction.[61a-61c]

"Combustion"; complex gas-gas reactions. When hydrocarbons or other complex molecules react with such molecules as oxygen, NO, NO_2, and fluorine, with evolution of heat and light, deposition of C, and formation of CO_2, CO, H_2O, and other substances, a "combustion" process is taking place. The practical importance of increasing the efficiency of "combustion" reactions is apparent; in addition, combustion reactions are excellent sources of information about "unstable" high-temperature intermediates because the sequence of events following introduction of a hydrocarbon-oxygen mixture into a burner is very much more complicated than the final reaction products, CO_2 and H_2O, would indicate.

In a Bunsen flame, for example, optical spectra show that C_2, CH, CO, and OH molecules are predominant,[62, 63] while mass-spectroscopic studies[64] also show C_2H_2, CO, CH_2O or C_2H_6, CH_4O, and C_4H_2 in methane-oxygen flames. In flames supported by fluorine, spectra of C_2, C_3, CH, CN, and OH are observed with organic compounds; in addition, BrF and IF have been found in fluorine flames with organic halides or elementary halogens.[65a-65c] Studies of NH_3-O_2 flames indicate NH_2, NH, and OH as the principal molecular species, and NH_3-NO flames yield mainly NH and OH.[66] NH_3 burned with NO_2 yields spectra of NH_2, NH, and OH, and an NH_3-fuming nitric acid flame shows mainly NH and OH spectra.[67] The C_2N_2-O_2 flame, which produces temperatures over 5000° K. when operated under pressure, shows emission spectra of CN, CO, N_2, C_2, and NO molecules, as well as atomic features.[68-70] The HCO(g) spectrum has also been identified in flames. Modern theories of flame propagation require, and spectral evidence proves, the existence of acetylene, aldehydes, peroxides, and other complex intermediates in hydrocarbon-oxygen flames.[71] The general subject of free radicals in flames has been reviewed by Pannetier.[72]

Sugden and his associates[73a-73c] have reported a number of interesting studies of flames into which alkali metals have been introduced. From microwave attenuation measurements they deduced the existence of gaseous hydroxides—LiOH, KOH, RbOH, CsOH—in the flame, as well as appreciable amounts of OH^-, and they have established heats of formation and the electron affinity of OH.

Flame-photometer studies in analytical chemistry are complicated by "interferences" that enhance or reduce certain emission intensities in ways that are certainly connected with the formation of gaseous molecules in the flame. Huldt and Lagerqvist[74a, 74b] have demonstrated the formation of gaseous alkaline earth oxides and of MnO(g) and CrO(g) under equilibrium conditions in a flame and have calculated their dissociation energies. Various investigators have examined interferences in flame-photometer studies[75, 76] and have interpreted them in terms of ionization and molecule formation at high temperatures.

Electric arcs and discharges. Most of the early information about unusual high-temperature molecules came from studies of electric arcs and dis-

charges. For example, in their compilation on molecular spectra Pearse and Gaydon[77] cite arcs and discharges most often as sources of molecular spectra. Despite the fact that our knowledge of the details of the reactions in arcs and discharges is relatively incomplete because of the complex processes involved, the use of these sources still represents the best way of attaining extremely high temperatures.[78, 79]

High electronic excitation is available in arcs, and they are good sources of ultraviolet and vacuum-ultraviolet light. New, high-energy, "unstable" molecules are still being discovered by careful study of the radiation from arcs and discharges.[80]

Another interesting event that could occur in arcs and discharges is the capture of electrons by ions of appreciable electron affinities to form gaseous negative ions. Although such gaseous ions as OH^-, CN^-, F^-, Cl^-, and O^- undoubtedly exist, no one has definitely established a spectrum or obtained energy-level data for a negative gaseous ion. Schuler[81] has obtained in a discharge through water vapor a spectrum that he tentatively attributed to OH^-.

Chemical Synthesis

Chemical syntheses, both natural and artificial, may involve high-temperature molecules. The distribution of elements on the earth and the composition of the exhaust gases from volcanoes and hot springs[82]—indeed, even the creation of living matter itself—have been explained by high-temperature processes.

Important industrial chemical syntheses at high temperatures include: (1) the preparation of pure metals and alloys from their ores; and (2) the preparation of industrially useful hydrocarbons from both heavier and lighter hydrocarbon molecules. Metal reductions are always high-temperature processes. Sheer and Korman[83, 84] have shown that high-intensity arcs can be useful high-temperature sources for extracting rare metals from ores. Arc casting and vacuum melting, with and without containers, are now widely used in metallurgical laboratories.[85-87] The crystallization of graphite from coke, the preparation of SiC and CS_2, and the many fused electrolysis reactions—for example, of NaCl and Al_2O_3—are other typical high-temperature processes. In the CS_2 synthesis, it is likely that the intermediate molecule CS(g) is formed first.

Fixation of nitrogen is accomplished at 2000° C. and higher by direct reaction with oxygen to form NO. This can be accomplished with ordinary gas-air furnaces,[88, 89] electric furnaces,[90, 91] or in an arc.[92] The desired NO, which is thermodynamically unstable at room temperature but has a slow rate of decomposition, can be cooled very quickly, oxidized to NO_2, and used for nitric acid production.

In studies of a discharge through gaseous mixtures (CH_4, NH_3, H_2O, H_2), Miller[93] has shown that various complex and useful molecules can result from this treatment alone. It appears possible that the high temperatures produced by solar energy could be instrumental in the synthesis of such industrially important materials as CS_2, C_2H_2, NO.[94, 95] Patents for the

manufacture of C_2H_2, SiO, NO, and various hydrocarbons in arcs have been granted in recent years.

Chemical Kinetics

The chemist interested in synthesis or in equilibrium phenomena asks: "What are the reactants and what are the products?" The kineticist seeks to answer a more fundamental question: "What pathway was followed as the reaction occurred?" In almost every case studied the chemical highway from reactant to product is far from straight and simple. However, the laws of classical and quantum mechanics still apply, and the favored mechanisms of reaction usually involve hurdling the minimum potential barrier that must be exceeded to permit formation of the products. This "potential barrier" between reactants and products is measured by the activation energy, E_A. The reaction rate constant, k, varies with temperature according to an Arrhenius-type equation

$$k = ae^{-E_A/RT}$$

where a is a constant, or a function of T, and is often called the frequency factor. The magnitude of k thus depends on E_A, T, and the constant a, which may include a steric factor. At high temperatures, reactions with small E_A's will proceed rapidly and will be difficult to study. High-temperature studies are best for reactions with high activation energies and/or low frequency factors. If the activation energy is too high, however, the reaction rate will vary rapidly with T and may be hard to study over a wide temperature range.

Typical high-temperature kinetic studies are those of Daniels and his associates,[96] of Wise and Frech,[97] and of Kaufman and Kelso[98] on the decomposition of NO up to 1900° C., of Rosser and Wise[99] on the decomposition of NO_2; of Wall and Michaelsen[100] on the thermal decomposition of Teflon; and of Gulbransen and Andrew[101a-101d] and Cubicciotti and associates[102-105] on the oxidation and nitridation of metals.

Extremely fast reactions, such as the recombination of halogen atoms, have been studied by flash photolysis and by photoelectric-oscillographic techniques.[106, 107] Fast reactions at high temperatures have also been studied by shock-wave procedures.[108, 109]

The Theoretical Significance of Unusual High-Temperature Molecules

When a theory is to be justified, one tests it by checking the available experimental data against it and by making predictions that can be tested in new experiments. Theories of chemical bonding are rigorously put to the test by the existence in high-temperature systems of many types of molecules, ranging from light and simple ones, such as LiH(g), to complex, heavy molecules, such as U_2O_4(g), suggested recently as a significant vaporizing species from UO_2 at 2000° K. and higher.

H_2 and H_2^+ bond energies are known and can be calculated from theory. The bond energy for LiH is calculable and is in good agreement with the spectroscopic dissociation energy. For more complex molecules there is

little satisfactory theoretical work, although the "magic formula" of Mulliken[110] has been applied for CH, N_2, O_2, F_2, CH_4, C_2H_6, C_2H_4, C_2H_2, H_2^+, and He_2^+ and represents a beginning in the attempt to solve these problems. Recent reports have indicated that most elements form diatomic species of some stability, and spectra of Si_2, Cu_2, Ag_2, Au_2, and Mg_2 have been reported in high-temperature systems. Bond-energy calculations are needed for these and similar molecules. Herzberg[111] lists over 400 diatomic species (mainly elements, oxides, halides, hydroxides, nitrides, and sulfides) but experimentally obtained dissociation energies accurate to more than ± 10 kcal./mol are available for less than 200 molecules.

In addition to dissociation energies (or bond energies), one of the more useful properties of a molecule to ascertain is a description of the ground (lowest-energy) electronic state. Correlation rules considering the atoms involved are of aid but, for many simple diatomic molecules and most polyatomic molecules, no clear-cut determination has been made. Among the diatomic molecules with uncertain ground states are: AgBr, AgCl, AgI, As_2, AuCl, BiH, BN, CaH, CaI, CaO, CdBr, CdF, CeO, Cl_2^+, CrO, CuO, GdO, HgBr, HgF, HgI, InO, IO, LuO, MgBr, MgI, MgO, MnCl, MnF, MnI, MnO, NBr, NiBr, NiO, PbBr, PbH, PbI, PrO, Se_2, SeO, SO, SrI, SrO, TiO, TlH, VO, YbCl, ZnBr, ZnI, ZrO.

In summary, better theories of chemical bonding are needed (1) to account for the existence of such molecules as $C_3(g)$,[2a-3d] $Al_2O(g)$,[8, 9] $CF_2(g)$,[37-40] $Na_2B_4O_7(g)$[112, 113] (or $NaBO_2$), $NaAlCl_4(g)$,[114] $NaAlF_4(g)$,[115] MoO_2Cl_2,[116] $H_3BO_3(g)$ and $HBO_2(g)$,[117, 118] at high temperatures; (2) to provide explanations for the difficulty in identifying and proving the presence of $CH_3(g)$ and $CH_2(g)$ in C-H systems; and (3) to make possible a better correlation of the structures of gaseous molecules with the structures of the condensed phases from which they were formed.

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