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UNDERDEVELOPED AREAS IN HIGH TEMPERATURE CHEMISTRY

Berkeley, California

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June 21, 1963

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> "The division of the year into two distinct seasons--dry and wet--impresses those who have been accustomed to the variable climate of the Atlantic States unfavorably. The dry appearance of the country in summer and the difficulty of moving about in winter seem to impose serious difficulties in the way of agricultural prosperity, while the many and decided advantages resulting from the mildness of winter, and the bright, clear weather of summer, are not appreciated."
>
> From a report on California addressed by the Hon. T. Butler King to the Hon. John M. Clayton, Secretary of State, United States of America, March 22, 1850.

High temperature chemistry is not a new field for investigation. But it is still a young field in the sense that within it large areas remain underdeveloped or even almost unexplored, although other areas by virtue of easier accessibility, popular prejudice, or historical accident may have been extensively investigated and may be relatively well understood. The effects of a reawakened interest in high temperature chemistry were just beginning to make themselves felt at the time of the first of these Symposia on High Temperature Technology, which was jointly sponsored by Stanford Research Institute and the University of California on the Berkeley Campus of the University in 1956. At this third Symposium, it is appropriate to assess our knowledge of the field of high temperature chemistry after seven years of an unprecedented level of research activity.

While any addition to our knowledge is a gain, in a young field we can expect greater gain from expending our effort in those areas about which least is known and for which, in consequence, we experience the greatest difficulty in guessing the behavior of systems that we have not yet been able to study. It is important that we recognize and explore the underdeveloped areas of high temperature chemistry. We should not, metaphorically speaking, expend all our efforts on an exhaustive exploration and settlement of the land along each little creek that flows into Massachusetts Bay before we make even a cursory survey of the coast of California.

The purpose of this paper is to call attention to areas of high temperature chemistry that the author considers to be underdeveloped, to suggest theoretical or practical gains that may result from study of these areas, and, sometimes, to suggest experimental approaches that may be appropriate to these areas of investigation.

There has not been universal agreement that the development of California is prudent or pleasant; there will without doubt be disagreement with suggestions of this paper. But if the paper stimulates analysis and discussion of what are the underdeveloped areas of high temperature chemistry, some good will have been accomplished.

COMPOSITION STUDIES

Gas Phase Molecules

The first problem in any chemical study is the determination of the composition and temperature limits of the stable condensed phases and determination of the formulas for stable gas molecules. That vapors at high temperatures may contain an exceedingly complex mixture of molecules is now one of the more familiar facts of high temperature chemistry. Lists of new vapor molecules, identified largely by means of mass spectrometry, are included in various review articles.[1,2,3]

Studies of vapor complexity are being pursued vigorously, and the only point that need be emphasized here is one originally made by Brewer which can guide us in our studies of vapor complexity: The ratio of the concentration of any minor species in a saturated vapor to the concentration of the major species can always be expected to increase with the temperature at which the saturated vapor is studied.[4,5] No high temperature vapor composition studies appear to be in disagreement with this generalization, and none are expected since the generalization is based on thermodynamic principles.[5]

Figure 1 illustrates this principle with a logarithmic plot of the partial pressures of sulfur vapor species against 1/T.[6] Note that the partial pressures of all the species that are at low concentrations at low temperatures increase more rapidly than does the partial pressure of S_8 so that near 1 atm. pressure S_8, S_7, and S_6 all have comparable pressures.

An obvious deduction is that investigations aimed at revealing the existence of new vapor species can best be carried out at the highest temperatures for which the saturated vapor can be studied. Reduction in the pressure of the vapor below the pressure that is at equilibrium with the condensed phase, on the other hand, rapidly reduces the concentrations of the higher polymer species. Thus, for example, Klemperer and Rice[7] failed to observe the presence of dimer molecules in their initial studies of the vapors above alkali metal halides, apparently because in their system the vapor was at lower than the equilibrium saturation vapor pressure.[8]

Studies of high temperature vapors at and above the normal boiling point and perhaps even above the critical point can be expected to reveal the presence of species whose concentrations are too low for observation at lower pressures. Ultimately, of course, studies of the molecular composition of fluids above their critical temperatures and at hundreds of thousands of atmospheres of pressure will become possible and will be made. Then we can study on earth some of the molecules that we know must exist in dense stars.

At sufficiently high pressures, van der Waals attractions would hold even rare gas atoms together in complexes sufficiently stable so that they might for some purposes be dignified by the name "molecules". Furthermore, with the temperature high enough so that the populations of atoms in excited electronic states become comparable with the populations of atoms in the ground states, ordinarily nonreacting atoms can form molecules by reaction of the excited atoms. Some of these molecules would have shorter interatomic distances than shown by the van der Waals complexes formed by the corresponding ground state atoms and would show longer half-lives for decomposition back to the constituent atoms because of deeper potential wells for the dissociation process. In these two senses, then, these excited state molecules would become as significant molecular species as are any molecules under comparable conditions. For example, at 2×10^5 °K, the concentration of He atoms in the ^3S state, which lies 455 kcal above the ground state,[9] is essentially equal to that in the ^1S ground state. At this temperature and at a pressure of the order of one million atmospheres, the reaction $2\ He \rightarrow He_2$, which at ordinary temperatures has a heat of approximately +400 kcal, would go effectively to completion if no new unforeseen process interfered.

High Temperature Liquids

The liquid state of matter is in many respects the most difficult to study. Nevertheless, valuable progress has been made in studies of high temperature liquid solutions. To the author the most spectacular result of such investigations has been the demonstration that the alkali metals and their highly ionic salts may become completely miscible at, or only a little above, the melting point of the solid salt.[10] These metal-salt solutions must owe their existence to the fact that compatible combinations of metallic and ionic bonds are possible for these solutions. Perhaps the

bonding in these liquid solutions is basically similar to the bonding in the so-called interstitial carbides, nitrides, and borides of the transition metals, whose properties can also be interpreted as reflecting a combination of metallic and ionic bonding. A theoretical discussion of the bonding in fused alkali metal-alkali metal halide systems has been presented by Pitzer.[11]

A relatively familiar fact is that tin undergoes a crystallographic transition at approximately 13°C[12] from a low temperature, semiconducting, grey modification, which has the diamond structure, to a high temperature, metallic modification in which each tin atom has six neighbors at approximately the same distance.[13] This transformation may be looked on as reflecting a change in electronic state for solid tin.

Somewhat less familiar is the fact that several of the semimetals and compounds of semimetals undergo similar electronic transitions from nonmetallic to metallic states as an accompaniment to melting.[14]

Germanium and silicon are semiconductor solids which crystallize in the diamond structure, which is characterized by four nearest neighbors. But both elements melt with abnormally high entropy changes and form liquids which are more dense than the solids at the melting points. Both elements form liquids that have metallic conductivity. X-ray studies of liquid germanium show each atom to be surrounded by six nearest neighbors. Krebs has demonstrated a similar structural relationship between solid and liquid antimony, bismuth, and the isoelectronic compound GeTe, for which the atoms have three nearest neighbors in the solid and six in the liquid.[14]

Further experimental and theoretical studies of the liquids of these semimetals and semimetal compounds can contribute significantly to our understanding of the nature of bonding in the condensed state.

High Temperature Solid Solutions

Previous papers[15], have stressed the importance of even minute changes in composition on physical properties of solids. The discussion need not be repeated here. Instead, the author wishes to draw attention to the fact that high temperature solid solution widths in inorganic systems are probably often wider than indicated on existing phase diagrams. Several examples can be cited to illustrate this point, the first a relatively undramatic, but significant, example from the author's own experience.

Alan R. Miller and the author found during the course of an investigation of the vaporization behavior of solid In_2S_3 that the phase which appears as a vertical line on the temperature vs composition phase diagram reported by Stubbs and coworkers[16] clearly had a measurable composition range at 600° to 800°C. Careful studies of composition vs X-ray diffraction patterns for quenched samples indicated that the composition could be varied from the stoichiometric composition when the sulfur pressure was equilibriated at near 1 atm. pressure to about $InS_{1.38}$ at the indium-rich phase boundary.

Studies of partial pressures of the vapor species vs composition at constant temperatures in the 600° to 800°C range, however, showed the solid solution range to be even wider than indicated by the X-ray studies of the quenched samples. The indium-rich phase boundary determined by this more direct means lies at about $InS_{1.25}$.[17]

X-ray examination of quenched samples of zirconium-hydrogen mixtures led to the identification of Zr_4H, Zr_2H, ZrH, and ZrH_2 as the stable solid phases.[18] Subsequent pressure vs composition studies, however, show the system to consist at high temperatures only of solutions of hydrogen in the metal lattice and of a second solid solution of wide composition limits.[19]

For the cerium-oxygen system, two independent X-ray investigations of quenched samples led to the conclusion that samples of compositions between $CeO_{1.81}$ and $CeO_{2.00}$ when annealed at 700°C were two-phase mixtures of $CeO_{1.81}$ and $CeO_{2.00}$.[20,21] However, a composition vs hydrogen pressure study by Brauer and Gingerich indicated that a single phase extended across this entire composition range at 700°C.[22] They, therefore, studied this composition region by use of a high temperature X-ray diffraction camera and obtained results in complete agreement with their pressure vs composition measurements.[23]

Increased emphasis on performance of studies of solid solution composition ranges at the temperatures of interest rather than at room temperature with quenched samples is clearly desirable, except for glass-forming substances, for which quenching is effective. On the other hand, efforts should be made to find annealing temperatures at which substances now known only to form continuous solid solutions (such as, for example, the ThO_2-UO_2 solid solution) will decompose into two or more phases of relatively narrow composition limits. All solid solutions must decompose into phases of narrow composition limits if equilibrium can be established at sufficiently low temperatures.[24,25]

THERMODYNAMICS AND REACTION EQUILIBRIA

Heats of Reactions and Free Energies of Reactions

Under ideal conditions, heats of reaction can be measured with high precision. The standard heats of formation at 298.16°K of most common solid metal oxides from the metal and oxygen are believed to be known usually to within 1 kcal per gram atom of combined oxygen for those systems in which careful measurements have been carried out.[26] That we may sometimes place too much confidence in the reliability of calorimetric measurements, however, is illustrated by recent findings for the heat of formation of quartz.

Despite the fact that the heat of formation of quartz had apparently been firmly established by several independent calorimetric investigations as -209.9 ± 1 kcal/mole,[26] the results of several recent investigations

demonstrate convincingly that the correct value is about -217.5 kcal/mole.[27,28,29] The error in the earlier determinations of the heat by silicon combustion in oxygen may have arisen because a large fraction of the silicon was burned to an amorphous form of silicon monoxide whose presence went undetected even though the investigators were aware of this source of experimental error and made earnest efforts to eliminate it or to correct for it.

This startling experience with quartz lends emphasis to a fundamental point with respect to calorimetric measurements. The difficult problem of precise calorimetric determinations is not the problem of obtaining an accurate measurement of heat evolved during the experiment. It is the inorganic and analytical chemistry problem of determining the completeness of reaction, of determining total chemical content of starting materials and products, and of determining the degree of crystallographic order in the phase or phases produced by reaction.

Calorimetric heats of formation should whenever possible be confirmed by studies of equilibrium properties of the materials concerned. Under favorable circumstances, such properties as free energies of dissociation of a solid to a second solid plus a gas can be determined to within one calorie times the absolute temperature of measurement, i.e., to 1 kcal at 1000° K and 2 kcal at 2000° K. That, for example, the heat of formation of silicon carbide derived from calorimetric determinations was somewhat in error was suggested by measurements of the vapor pressure of silicon and of the silicon partial pressure of silicon carbide in equilibrium with graphite.[30,31] These measurements indicated that the heat of formation was not -13 kcal/mole, but at least 2 kcal/mole more negative. From analysis of all data, calorimetric and equilibrium studies of various types, Rein and Chipman conclude that the heat of formation of β-SiC is -15.6 kcal at 298° K.[32]

Use of fluorine bomb calorimetry and other less familiar calorimetric techniques to supplement the oxygen bomb calorimeter and solution calorimetry should be expanded. Several laboratories are taking steps in this direction.

At the previous Asilomar Conference, the author expressed his opinion of the great importance of increased attention to activities, partial and integral free energies, and other partial molal and integral thermodynamic quantities as functions of compositions in the single-phase regions of inorganic systems.[15] That two recent publications have appeared in which calculation of some of these quantities is illustrated in some detail should be mentioned.[33,34]

Heat Capacity and Entropy Data for Solids

The free energy of reaction as a function of temperature is given approximately by the expression $\Delta F = \Delta H - T\Delta S$, where ΔF is the free energy of reaction, ΔH is the heat of reaction, ΔS is the entropy of reaction, and T is the absolute temperature of reaction. Ten or fifteen years ago

our ability to calculate the free energy of reactions at any desired temperature was usually limited by the precision with which we could measure the heat or free energy of reaction at some particular temperature. In the event that the entropy of reaction were unknown, it could usually be estimated with a reliability comparable with the reliability of measurement of the heat or free energy of reaction. And, in the event that the data were sufficiently precise to warrant correction for the variations in heat and entropy of reaction with temperature, heat capacity changes in the reaction could also be estimated satisfactorily. These heat capacity corrections are second-order corrections that need usually only be applied when precise calculations are necessary. Methods for estimation of entropies or heat capacities can be found in previous publications.[35,36,24]

The situation has now changed in two important respects. First, the number and precision of the free energy and heat of formation measurements available has increased markedly in recent years. Second, our knowledge of, and interest in, reactions which involve rather complex gas phase molecules is much higher than formerly. As will be demonstrated in the next section, uncertainties in values for entropies of complex gas molecules may be very high. In this section we are concerned with the availability of reliable entropy values for solids.

If the heat capacity of a solid and heats of transition have been measured to well above the Debye temperature from temperatures near absolute zero, the entropy at 298° K can be calculated from familiar relationships, and the results are usually reliable to within a few tenths of a cal/deg/gram atom of solid. It even appears possible to extrapolate such heat capacities and the derived entropies to high temperatures with relatively little error,[37,38] although reliable heat capacity measurements for solids and liquids at 2000° K and above can be included among data that are needed.

Our problem here is not one of lack of reliability of the entropy data for those solids for which experimental measurements have been made, but rather with the lack of any data at all for many solids of considerable technological and theoretical importance. For example, to the best of the author's knowledge, Mo_3Si is the only transition metal silicide for which a value of the entropy at 298° K is available. Few entropy values are available for transition metal carbides and borides, and apparently no entropy values have been determined as functions of composition for a carbide phase even though solid solution ranges in carbide phases are often wide.

In evaluating high temperature data, the assumption has commonly been made that the entropy of formation of these phases from the solid elements is zero. This approximation is satisfactory for rough calculations intended only to warn an investigator about whether or not he can expect the materials to react at high temperatures. But the estimated entropies are too highly uncertain, for example, to make a comparison between heats of formation values, which are usually measured near room temperature,

and free energy values, which may be measured 2000° K higher. In a recent evaluation of entropy data for the diborides of the titanium and vanadium family metals, investigators for the Manlabs, Inc.[39] concluded that the entropies of formation vary from -7.5 cal/deg/mole for TiB_2 to +1.5 cal/deg/mole for TaB_2.

Properties of these diborides are of interest to temperatures at least as high as 3000° K. An estimate of ΔS formation = 0 when the true ΔS formation is -7.5 cal/deg/mole would introduce an error of 19 kcal/mole in calculations of the free energy of formation at 2500° K from room temperature calorimetric data for the heat of formation.

Recently Mr. Alan R. Miller and the author required an entropy for solid In_2S_3 in order to carry out a third-law evaluation of vapor pressure data. An investigation of the literature revealed that not only was there no entropy measurement for solid In_2S_3 but there was no entropy measurement for <u>any</u> solid indium compound. From the assumption that the entropy of In_2S_3 is the sum of the entropies of the constituent solid elements, $S_{298°K}$ was estimated to be 50.7 cal/deg/mole for In_2S_3. But this assumption has been found to predict the correct entropies for sulfides for which entropies are known to within an average deviation of ±2 cal/deg/gram atom of sulfur,[40] so as a check of the estimate a semiempirical method due to Latimer was also used.[41] This method leads to S_{298} = 29.9 cal/deg/mole for In_2S_3. The large discrepancy between these entropies estimated by two standard methods obviously meant that a third-law evaluation of vapor pressure data for In_2S_3 could be of little reliability even if the entropies for the gaseous species could be successfully estimated.

To resolve the difficulty, Mr. Miller prepared several hundred grams of In_2S_3 with which Mr. King[42] of the Pacific Experiment Station of the U.S. Bureau of Mines determined the heat capacity of In_2S_3 between 53° K and 297° K. The data yielded S_{298} = 39.1 ± 0.6 cal/deg/mole, a value which happens to be about the average of those estimated by the two methods.

It should be mentioned that the program for measurement of entropies and other standard thermodynamic quantities which is carried on by the Bureau of Mines, and probably the programs of other agencies as well, is often limited by the availability of suitable pure samples. Investigators who have prepared pure solids whose entropies and heat capacities are unknown should explore the possibility that one of these thermodynamic laboratories may be able to use the samples.

Entropies and Heat Capacities of Gases

The accuracy with which entropies and related thermodynamic quantities can be calculated from statistical mechanics represents one of the most impressive triumphs of scientific theory. For essentially all gaseous atoms, for most diatomic molecules, and for many molecules of greater complexity, the heat capacities, entropies, and heat contents can probably be calculated more precisely by application of theory to the spectroscopic data for the molecules than the quantities can be measured directly.

However, there are frightening gaps in the available information. To quote from a 1961 review article by Brewer and Rosenblatt: "No spectroscopic data are available for molecules of any gaseous metal dioxide. There are no data that yield internuclear distances, vibrational frequencies, configuration, or degree of electronic excitation for these molecules."[43]

Evaluation of the heat of a sublimation reaction from the measured free energy of reaction, from the entropies of gas species as determined from spectroscopic data (sometimes estimated), and from entropy data for the condensed phase, the so-called third-law method, is now usually considered to be more reliable than evaluation of the heat of sublimation from the slope of the free energy plot, the so-called second-law method, even when thermodynamic functions for the gas must be estimated.[44,45] There is reason to believe, however, that for reactions that produce gaseous molecules the reliability of the third-law method is not as high as usually estimated. The uncertainties in evaluation of entropies of gas molecules probably often is sufficient to introduce uncertainties of 10 kcal or more in the heats of sublimation derived from use of these entropies. It is important to understand when entropy and other thermodynamic functions for gases can be considered precisely known, to understand when they cannot, and to consider what research can be performed to augment and improve the available data. Let us consider the steps employed in evaluation of the entropies of gas molecules in order to see at what points uncertainties may arise.

The entropy of a gas molecule is usually viewed as being separable in the following manner: $S = S_t + S_r + S_v + S_e$, where S_t is the entropy of translation, S_r is the entropy of rotation, S_v is the entropy of vibration, and S_e is the entropy of electronic excitation. The translational entropy can be unambiguously estimated for any gas molecule provided only that its molecular weight is known.[46] The rotational states of all molecules, except for the hydrogen molecule, are excited to the classical values even at temperatures very close to absolute zero. Calculation of the rotational entropy requires knowledge only of the moment of inertia and of the symmetry number. So the problem of estimating the rotational entropy resolves itself into the problem of determination of the shape and bond distances for the molecule. Estimation of bond distances for simple gas molecules presents no particular problem because these distances are simply related to distances in related solids. The structure or shape of the molecule may, however, be difficult to measure and difficult to guess if unmeasured.

The simplest possible question about the shapes or structures of gas molecules would seem to be the question of whether triatomic molecules are linear or nonlinear. Until about a year ago, the problem of estimation of whether a triatomic molecule with a central metal atom and no nonbonding valence electrons was linear or nonlinear appeared to be a relatively simple one. High temperature electron diffraction data for the gaseous alkaline earth halides and for some of the subgroup metal dihalides had

been interpreted as showing all of these molecules to be linear.[47] This was the expected result either on the basis of a simple covalent model or on the basis of an ionic model in which polarization of the inner shell electrons of the central atoms was considered to have negligible influence on the molecular shape. For gaseous triatomic molecules of the transition metals, some uncertainty as to linearity or nonlinearity existed, because the role played by the nonbonding d electrons in determination of molecular shapes was unknown.

For triatomic molecules in which the central atom was a nonmetal and the terminal atoms were metals, prediction of linearity or nonlinearity appeared to depend on whether one favored an ionic or covalent model. For molecules of this class, e.g., Li_2O, Al_2O, Al_2S, and In_2S, a simple ionic model would predict linearity while a covalent model would predict nonlinearity.

Interpretation of the electron diffraction data for Li_2O led to the conclusion that the bond angle in that molecule was roughly 110 deg.[48] This result seemed to imply that molecules in which the central atom is a nonmetal could be expected to be bent in most cases. The apparently settled state of affairs has been dramatically upset, however, in the last year. William Klemperer and his associates[49] at Harvard have shown that molecular beams of the vapors of all barium dihalides, strontium difluoride and dichloride, and calcium difluoride when passed through a quadruple electric field are deflected and refocused in a manner that can only be expected if these molecules have dipole moments. When a beam from lithium oxide or from several other alkaline earth dihalides, including $CaCl_2$, $CaBr_2$, $SrBr_2$, and SrI_2, is subjected to the same experiment, however, essentially all the beams are deflected in a manner expected only for nonpolar molecules. Various ingenious experiments were performed to insure that the characteristics measured were those of the normal alkaline earth dihalide gas molecules and of the Li_2O gas molecule. There appears no reason to doubt the results. Furthermore, some of the results obtained by Klemperer and his associates have already been confirmed by work performed by Buchler and associates, who have performed the same kind of experiments performed by Klemperer and his group but with substitution of a mass spectrometer as a detector in place of the hot wire detector[50] used by Klemperer.

The results of Klemperer, Buchler, and their associates demonstrate the need for vigorous programs of research on the basic shapes of high temperature molecules. Various mass spectrometer groups are actively at work to adapt their instruments for studies similar to those now being carried on by Buchler. For many-atom high temperature gas molecules, the process of structure determination is formidable. Microwave studies can give very precise structural information, but rotational-vibrational spectra are only developed by molecules that have dipole moments. This problem can sometimes be overcome in matrix-isolation studies because the matrix may provide an environment which reduces the normal molecular symmetry.[51]

Even when a molecule has a dipole moment, however, its structure determination may be a difficult and time-consuming task. Some nine different papers have appeared on the structure of the boric oxide gas molecule alone,[52] and boric oxide is less complex than many high temperature gas molecules are expected to be. The problem of structure determination for gases at high temperatures is one that will continue to require hard and ingenious experiment and analysis.

At present high temperature electron diffraction results appear too imprecise even for bond angle determinations in triatomic molecules, but the bond distance values, which are less subject to error, are probably reliable, and improvements in technique may make electron diffraction a very useful high temperature tool. For complex molecules, reasonable estimates of the moment of inertia can often be made even though the actual shape and structure of the molecule is unknown, but for such molecules the uncertainty in the symmetry number which also contributes to the rotational partition function may introduce a considerable uncertainty into the estimated thermodynamic functions. For example, one of the significant species in the vapor above molten sulfur appears to be S_5.[6,53] From various arguments it can be concluded that S_5 is almost certainly a ring molecule. Sulfur atoms are known to bond at approximately 103 deg bond angles.[54] This angle is very close to the angle that would be found in a strictly planar S_5 molecule (108 deg). For a strictly planar S_5 molecule the symmetry number is 10 and the contribution of the symmetry number to the entropy or free energy function is R ln 10 or approximately 4.6 cal/deg/mole, while for either a puckered ring or a linear S_5 molecule the symmetry number would be 1 and the contribution to the entropy would be 0 cal/deg/mole. The uncertainty in the symmetry number, therefore, can produce an uncertainty in heats or free energies calculated from estimated entropies of the order of 4.6 x T cal/mole of S_5, or 4.6 kcal at 1000° K.

The sources of errors in calculation or estimation of the vibrational partition function and thus in determination of the vibrational contributions to thermodynamic functions for the gas overlap, and to a limited extent cancel, the sources of error in determination of the rotational functions. For a linear molecule the number of rotational modes of excitation is one less than the number for a nonlinear molecule, while the number of vibrational modes is one greater. The need for knowledge of the molecular structure is common to both.

The necessary parameter for calculation of vibrational partition functions is the fundamental modes of vibration of the molecule. Vibration frequencies for the molecules can be obtained from spectroscopic measurements, but some of these frequencies are usually degenerate (that is characteristic of two or more modes). Analysis of how many frequencies are to be expected and of which frequencies are degenerate requires evaluation of the molecular structure.

The vibrational modes of excitation can be considered as belonging to two major subclasses: stretching modes and bending modes. Unfortunately,

from the point of view of accurate thermodynamic calculations, the low-energy bending modes are the vibrational modes that make the largest contributions to the magnitudes of the thermodynamic functions, while these low-energy modes are the most difficult to measure spectroscopically. Even for those molecules for which stretching frequencies are known, the bending frequencies commonly must be calculated by difference from the frequencies of the higher energy modes. The process usually results in calculated bending frequencies that are highly uncertain. Often, even such unreliable calculations are not possible and frequencies must be estimated. No schemes for making such estimates can be used with a high degree of confidence.

The approaches outlined by Brewer and Rosenblatt[43] and by Brewer, et al.[55] for estimating free energy functions of dioxides and dihalides appear as good as presently can be devised for use with gases for which so little spectroscopic and structural information is available. The approach used is basically one of estimating the contributions of translational, rotational, electronic, and stretching mode contributions to the functions and estimating the bending mode contributions by subtracting the sum of these from functions calculated by the second-law method from what appear to be the best experimental data. It need hardly be pointed out that this procedure implies acceptance of the thesis that carefully determined second-law data can be better than our present estimates of thermodynamic functions <u>for these molecules</u>.

Electronic contributions to thermodynamic functions for gas molecules are usually described in textbooks on chemical thermodynamics as particularly simple to evaluate. A statement is often made that only in rare instances will any electronic state other than the ground state make a significant contribution to the thermodynamic functions. The electronic contribution then is just R ln d to the entropy or free energy function (where d is the degeneracy of the ground state) and is zero to the heat content and heat capacity. However, for high temperature studies the evaluation of the electronic contribution may, in fact, be very difficult to assess within acceptable limits.

In the first place, for most triatomic and more complex molecules we do not have any spectroscopic data and consequently can only guess what the ground states are, while Brewer has recently argued that even for many diatomic molecules which have been extensively studied, the ground states may have been incorrectly assigned. Recent studies indicate that the ground state for Se_2 is a $^3\Pi$ state rather than a $^1\Sigma$ state as previously believed,[56] while the ground state of C_2 is $^1\Sigma$ rather than $^3\Pi$.[57]

In the second place, the idea that excited electronic states make negligible contributions is based on the tacit premise that only moderate temperatures will be of interest. Now we often need reliable thermodynamic functions at temperatures above 3000°K, and excited electronic states may often contribute significantly to the thermodynamic functions within the range of experimental interest. Compilations of electronic energy levels

necessarily can include only levels deduced from observed and identified transitions. Often low-lying electronic states may undergo no readily observed transitions because all the allowed transitions involving these states lie in an inaccessible region of the spectrum. Sometimes the species may have been observed but the chemical species that gives rise to the transition has not been identified.

From trends in the energy level separations between various states of isoelectronic diatomic molecules, Professor Brewer deduces that the ground states for gaseous MgO and CaO are very probably $^3\Pi$ rather than $^1\Sigma$ states. Even if the $^3\Pi$ state is as much as 1000 wave numbers higher in energy than the $^1\Sigma$ state, the $^3\Pi$ state would make the larger contribution to the entropy and free energy functions at 2000° K because the $^3\Pi$ state would be highly populated at 2000° K and has a degeneracy of 6, while a $^1\Sigma$ state is not degenerate.[5] Furthermore, the $^3\Pi$ state is expected to have a lower vibrational frequency and a higher moment of inertia than expected for a $^1\Sigma$ state and these differences would further increase the partition function over the quantity expected on the assumption that only $^1\Sigma$ states are important.

To provide enough information to make possible even intelligent guesses as to the electronic configurations of many of these substances would require a huge spectroscopic effort. Fortunately, it appears possible to obtain information that can at least serve as a guide to improved thermodynamic calculations by means which will be experimentally much simpler. Klemperer and his associates have used an inhomogeneous magnetic field resonance apparatus combined with a hot wire detector to demonstrate that $BaCl_2$[49] does not contain unpaired electrons in the ground state. In the author's laboratory, and probably elsewhere, an apparatus is in construction in which an inhomogeneous magnetic field will be used to deflect paramagnetic constituents from a molecular beam which passes into a mass spectrometer. Use of the mass spectrometer will make possible a much wider range of experiments than is possible with the hot wire detector. The apparatus may be usable for determinations not only of whether the ground states of gases are paramagnetic but also of the approximate separation between electronic states for molecules that have paramagnetic and diamagnetic states that are not far separated in energy.

It should be apparent from the foregoing discussion that for various reasons high temperature thermodynamic functions may be uncertain by several cal/deg/mole. This fact is not altered when the calculations are performed by a machine which reports data to .001 cal/deg/mole.

Machine calculations have frequently been extended to very high temperatures with use of the harmonic oscillator, rigid rotator approximation. Anharmonicity corrections contribute .8 cal/deg/mole to both the heat capacity and entropy of gaseous KI at 4000° K and .5 cal/deg/mole to these quantities for I_2. Techniques for incorporating anharmonicity corrections are well known,[46] simple to use in machine calculations, and should be routinely incorporated in machine programs.

REACTION KINETICS

Kinetics of Sublimation Reactions

The rate of evaporation or sublimation from a free surface into a vacuum, and probably also the rate of evaporation or sublimation into a fast-moving stream of inert gases, is related to the pressure of the evaporating species by the Hertz-Langmuir equation:

$$Z_i = \alpha_i P_i / (2\pi M_i RT)^{1/2} ,$$

where Z_i is the number of moles of the particular gas molecule that evaporate per unit time per unit area, P_i is the equilibrium pressure, M_i is the molecular weight of the gas molecule, and α_i is the evaporation or sublimation coefficient. Discussions of the use of this expression for evaluation of equilibrium pressures can be found in previous publications.[58,59]

A fortunate circumstance in the prediction of sublimation reaction rates is that for a number of important kinds of chemical substances the value of α is unity, or very close to unity, and the rate of sublimation can be calculated immediately from knowledge of the equilibrium pressure. This equilibrium pressure can, of course, be obtained directly from the free energy for the reaction, since for any reaction $\Delta F^\circ = -RT \ln K$, where ΔF° is the standard free energy of the reaction and K is the equilibrium constant. For a simple sublimation reaction, such as NaCl(s) = NaCl(g), $K = P_{eq}$, where P_{eq} is the equilibrium pressure of the gas, i.e., monomeric NaCl in the example chosen.

Available data seem to indicate that α for metals lies in the range 0.3 to 1, provided, of course, that their surfaces are clean. α also seems to be unity for nonpolar solids and liquids that contain in the condensed phase the same molecules that are present in the vapor, e.g., for carbon tetrachloride and various other nonpolar organic molecules.[60]

On the other hand, the value of α may be orders of magnitude smaller than unity if the lattice consists of units which are markedly different from those of the equilibrium vapor species. Thus, for example, the sublimation coefficient for metallic arsenic is about 0.05,[61] while the sublimation coefficient for solutions of As in liquid thallium in which the arsenic presumably is present as As_4 molecular units, which also constitute the principal vapor species, appears to be unity to within the experimental error.[62]

Before turning our attention to the rates of other types of sublimation reactions, it will be profitable to analyze how α can be expected to vary with temperature. We can write $\alpha = P_{eq}/P_{apt}$, where P_{apt} is the apparent pressure that is calculated from the rate of sublimation from a surface by means of the Hertz-Langmuir equation with α assumed equal to 1. The free energy of activation ΔF^* for sublimation can be expressed as $\Delta F^* = -RT \ln P_{apt}$. This free energy of activation must obey an equation

of the general form $\Delta F^* = \Delta H^* - T\Delta S^*$, where ΔH^* is the heat of activation and ΔS^* is the entropy of activation. And so long as the rate-determining step of the reaction remains unchanged, ΔF^* will vary linearly with temperature, and P_{apt} is an exponential function of temperature. But P_{eq} is another exponential function of temperature, and since $\alpha = P_{apt}/P_{eq}$, α must also, except in the limiting case of $\alpha = 1$, vary exponentially with temperature.

For an evaluation of the kinetics of sublimation reactions, therefore, a determination of α at one temperature or over a narrow range of temperatures is insufficient unless α proves to be unity. The temperature dependence of α must be determined as well.

The experimental difficulties in determining α over a range of temperatures can be appreciated when we remember that the value of α for water at room temperature is still in dispute. The results of two investigations were reported in talks presented a week apart at the University of California last year. The conclusion from one investigation was that the vaporation coefficient is unity; the conclusion from the second was that the evaporation coefficient is about .02.

But the situation is not hopeless, at least for carefully selected systems and experimental designs. The principal problem in determination of evaporation ceofficients appears to be the determination of the true surface temperature.[63] This problem can be minimized for systems whose evaporation or sublimation coefficients are very low so that by the principle of microscopic reversibility,[64] the rate of the reverse reaction is negligible. The evaporating surface can then be immersed in a nearly isothermal environment which supplies thermal energy to the surface by radiation or gas phase conduction or convection. Under such conditions, the sample surface temperature must be that of the environment.

One method for establishing a known temperature at the subliming surface is to place the surface directly on a hot plate.[65] The close contact with the plate and thermal energy transferred by the film of vapor established by the subliming solid between the two surfaces assure maintenance of the plate temperature at the surface of sublimation. This method obviously can only be applicable to studies of solids with very low sublimation coefficients because the vapor has many opportunities for collision with the sample surface before escaping from between the plate and sample.

The hot plate method has recently been used by R. F. Chaiken et al. to measure the rate of sublimation and the heat of activation for sublimation of several ammonium halides by reactions of the type $NH_4X(s) = NH_3(g) + HX(g)$.[66] These salts show activation energies that are about one-third of the heats of sublimation.

Dr. Zuhair A. Munir and the author have recently measured the rate of free surface sublimation of gallium nitride by the reaction: $GaN(s) = Ga(g) + 1/2\ N_2(g)$.[67] To perform the measurements, disks of gallium

nitride were placed in the positions normally occupied by the orifices of a torsion-effusion cell.[58] The disks and cell were heated by radiation from a tantalum tube under identical conditions to those which had been demonstrated to yield vapor pressure data that agree with the best available data to within 15% or better. There appears to be no reason to believe that the temperature uncertainty under these experimental conditions should be higher for the gallium nitride study than for a conventional torsion-effusion study.

Apparent pressures were of the order of 10^{-6} times the equilibrium pressures. The heat of activation and entropy of activation for the gallium nitride decomposition reaction were calculated from the temperature dependence of the apparent pressure data in the conventional manner. The values obtained were then compared with the heat and entropy obtained by treating the data by the third-law method, just as though the reaction were an equilibrium process. The third-law calculation involved the assumption that the entropy of formation of the activated complex is the same as the entropy of the reaction $GaN(s) = Ga(g) + 1/2\ N_2(g)$. The heat and entropy of activation at 298°K calculated from the slope of a $-R \ln Q$ vs $1/T$ plot were 125.4 kcal/mole and 54.85 cal/deg/mole. The corresponding third-law values were 127.5 kcal/mole and 52.92 cal/deg/mole.

The agreement is closer than is often obtained between second- and third-law data in equilibrium vapor pressure studies. The results lend strong support to the view that, in contrast with ammonium halide sublimation, gallium nitride sublimation is characterized by a high energy barrier to reaction, with the activated complex being essentially free gallium atoms and nitrogen molecules.

An examination of the literature for formation and decomposition of metal nitrides suggests that nitride sublimation reactions must often occur at rates slower than predicted by the Langmuir equation on the assumption that there is no barrier to the process in excess of the free energy of reaction. A significant item of evidence is that metal nitrides can sometimes be formed from reaction of the metal with ammonia at temperatures and pressures for which the metal nitride is thermodynamically unstable with respect to decomposition to the metal and nitrogen and for which ammonia is unstable relative to decomposition to nitrogen and hydrogen.[68] Apparently nitrogen atoms produced during ammonia decomposition become adsorbed to the solid surface and experience a high energy barrier to N_2 gas formation.

Some time ago Soulen, Sthapitanonda, and Margrave reported evidence that sublimation of magnesium nitride is a nonequilibrium process.[69] Recently, Dreger, Dadape, and Margrave[70] have reported that the rates of decomposition of boron nitride and aluminum nitride are 10^{-3} to 10^{-2} times the rates to be expected if there is no excess free energy barrier to the decomposition reactions. Probably Professor Margrave will describe these results and unpublished results of Dreger and Margrave for TiN in the next paper of this Symposium.

Comparison of Knudsen effusion and Hertz-Langmuir sublimation rates for beryllium oxide,[71] plumbous oxide,[71] and tungsten trioxide[72] have been interpreted as indicating that the sublimation rates are within experimental error of the rates to be expected if the sublimation coefficient is unity. From variation in the apparent pressures with orifice area in Knudsen effusion studies, the conclusion has been derived that the sublimation coefficient for lithium oxide is unity while that for silica near the melting point is low.[71]

The determination of sublimation coefficients from variation of apparent rates of evaporation with orifice area is dangerous, however. Clarence L. Hoenig and the author found no dependence in apparent pressures of stannic oxide with orifice area in a Knudsen study, and the weight losses calculated were in excellent agreement with those predicted from independent thermodynamic data. Nonetheless, free surface sublimation studies by the Hertz-Langmuir method yielded sublimation rates only about 1% of those obtained from the Knudsen cell.[73]

The calculation of sublimation coefficients from the variation of apparent pressures with orifice area are based essentially on use of the equation $P_{eq} = P_{apt}(\alpha A + \underline{a})/\alpha A$, where A is the sample surface area and $\underline{a}$ is the orifice area. Clearly if measurements are made with two different, and known, ratios of A to $\underline{a}$ both P_{eq} and α can be calculated. But for porous solids the pores act like small Knudsen cells which, if α is small, contribute a much higher flux of vapor molecules to the cell chamber above the sample than do equivalent areas of sample surface. This pore contribution has usually been ignored. But a recent paper by Rosenblatt describes a model by which the effect of pores can be taken into account so that equilibrium pressures and sublimation coefficients can be calculated from Knudsen data.[74]

Results recently obtained by Somorjai for cadmium sulfide and cadmium selenide[75] and by Alan R. Miller and the author for indium sulfide[76] demonstrate the sublimation coefficients for these chalcogenides to be of the order of .1 to .01 in the pressure range near 10^{-6} atm.

Since a factor of 100 in the rate at which a refractory sublimes at high temperatures may mean the difference between its being useless or useful in some materials application, there is clearly great need for further study of the sublimation behavior of oxides and other refractories as functions of temperatures. These studies constitute the fifth step of six that Paul Gilles has outlined in the orderly development of understanding of vaporization reactions.[77] When we have reliable kinetic data as functions of temperature, we will be ready to attempt the sixth step of deriving a detailed mechanism for these very important reactions.

Reactions of Gases with Solids to Yield Gaseous Products

Reactions of gases at low pressures with solids or liquids to yield only gaseous reaction products have received relatively little attention

from the time of Langmuir's pioneering experiments[78] until the last few years. The behavior of materials under such conditions may be important to their usefulness in rocket and space applications, and interest in the field is growing.

These reactions are extremely interesting from a theoretical point of view, also. Whenever the equilibrium concentration of the gaseous products is higher than the pressure of the reactant, the rate of reaction must be limited by the rate at which the gaseous reactants strike the reaction surface. The Hertz-Langmuir equation can be used, therefore, to calculate an upper limit to the rate of reaction. The ratio of the actual rate of reaction to the rate possible in terms of the rate of arrival of the gaseous reactant is then a measure of the reaction efficiency.

The reaction of this type which has been most extensively studied is the reaction of oxygen with tungsten to produce gaseous tungsten oxides. Several general points of interest can be illustrated with data for this tungsten-oxygen reaction.

For simplicity we will restrict discussion to studies made of temperatures in excess of 2000°K where the problem of procurement of a clean tungsten surface is relatively slight. As a result of studies by a number of different investigators, the rate of the reaction has been measured over the pressure range from 10^{-6} mm to 3 mm Hg. The most striking feature of the data is that a maximum in the rate of reaction is observed in each curve of reaction rate vs temperature. The results of several of these investigations[79-81] as summarized by Perkins, Price, and Crooks[81] are presented in Fig. 2.

Until recently the reaction product was presumed to be WO_3, and the decrease in reaction rate at high temperatures was attributed to the decrease in the stability of WO_3 with increased temperature. If the available thermodynamic information is correct, however, WO_3 is not sufficiently stable at the low pressures and high temperatures of some of the studies to be the observed reaction product, and recent mass spectrometer experiments by A. Buchler and Joan Berkowitz-Mattuck[50] have demonstrated that, in fact, while WO_3 and polymers of WO_3 are important reaction products at lower temperatures, in the temperature range that we are presently considering, the principal reaction product is WO_2. At constant pressure the free energy for the reaction $W(s) + O_2(g) = WO_2(g)$ must change monotonically with temperature.[24] The interpretation proposed first by Becker, Becker, and Brandes,[82] that the decrease in reaction rate at very high temperatures is to be attributed to competing reactions of revaporization of unreacted oxygen and oxygen atoms, must be correct.

The available data seem to be best interpreted as implying that the rate-limiting step is one that occurs upon the sample surface. The efficiency of reaction of impinging oxygen molecules remains relatively constant, 1 to 6%, at 10^{-5} to 10^{-3} mm and 2000-2600°K.[80]

Attempts to interpret the mechanism of the reaction in terms of the dependence of the reaction rate on oxygen pressure and on temperature are not really satisfactory. It is apparent that improved knowledge of the concentration of oxygen adsorbed on the surface as a function of pressure and temperature is needed so that attempts can be made to formulate the reaction kinetics in terms of the concentration of adsorbed oxygen rather than of the oxygen gas pressure.

A point that has been accorded insufficient attention for reactions of this general class is that when the gas molecules that reach the surface are at a different temperature from the surface upon which the reaction occurs, the rate at which the reaction occurs may sometimes be limited by the efficiency with which the impinging molecules are heated to a temperature sufficiently high for the reaction to take place. Gomer and Meyer[83] noted that methane gas does not undergo thermal decomposition on a clean graphite surface held in the vicinity of 2000°K despite the fact that methane is thermodynamically highly unstable under the temperature and pressure conditions used. Subsequently, they demonstrated that nonreacting gases that strike a hot graphite surface are revaporized with the adsorption of energies much lower than those which would be necessary to raise the gases to the temperature of the surface. Meyer and Gomer concluded that the decomposition of methane on a clean graphite surface is limited by the fact that the methane is revaporized at an effective temperature below that necessary for the decomposition to take place.[83,84]

De Poorter and Searcy[85] have found that nonreacting gases show the same kind of behavior on a tungsten surface as that reported by Meyer and Gomer on a graphite surface. Furthermore, the rate of reaction of cold carbon dioxide with tungsten appears to be limited by the efficiency with which the carbon dioxide is heated by the tungsten surface. An oxygen molecule, on the other hand, interacts strongly with the surface during the time of a collision and reacts with relatively high efficiency.

The efficiency with which energy is exchanged between a gas and a surface has thus been demonstrated to play sometimes a critical role in determination of reaction rates under conditions of considerable practical interest. Further studies of energy exchanges and of reactions of solids with gases, now carried on with use of a mass spectrometer, are in progress in the author's laboratory.

Disproportionation Reactions Which Yield a Gaseous Product

Reactions of the type $AB(s) = A(s) + B(g)$ must show many features in common with sublimation reactions but are complicated by additional factors. For reactions that yield a solid product, there may be an induction period during which the rate of reaction is too low to observe because of the necessity of forming stable nuclei of the condensed phase reaction product. After the condensed phase reaction product has formed, the rate of the subsequent reaction may be governed by the rate at which the gaseous

reaction product can effuse or diffuse through the product layer. Diffusion-controlled reactions have been extensively studied, but the effect of effusion through a porous reaction product on the reaction rate is somewhat neglected.

It is desirable, in order to obtain improved understanding of the influence of the effusion step in limiting reaction rates, that disproportionation reactions be studied for which the sublimation coefficient is known. Otherwise, the effect of effusion on the reaction rate cannot be readily distinguished from the effect of a slow step on the surface of the decomposing solid. Suitable materials for such study might be intermetallic compounds because there is no particular reason to expect that the surface forces in such compounds will be significantly different from the surface forces in pure metals. The sublimation coefficient for the disproportionation reaction can thus reasonably be inferred to be near unity for intermetallic compounds.

Solid State Reaction Kinetics

The author cannot discuss solid state reactions in detail but would like to mention several points which deserve special attention or more attention than they presently receive.

Correlations of the rates and of the activation energies for solid state diffusion with readily available thermodynamic parameters can be of immense theoretical and practical value. Essentially all experimental studies of diffusion as functions of composition in solid solutions of known thermodynamic parameters have been made with substitutional metallic solutions.[86] These metallic solutions seldom show much deviation from perfect solution behavior and are, therefore, insensitive to flaws in the models chosen for description of diffusion. Needed are studies of diffusion as functions of composition and thermodynamic stabilities of the nonmetals and metals in transition metal hydrides, carbides, nitrides, and silicides. Since little thermodynamic information for interstitial solids is yet available, coordinated studies of kinetic and thermodynamic properties are required.

Interstitial solutions encompass a much wider range of stabilities than do metal solutions. Furthermore, interstitial solutions usually have high equilibrium concentrations of vacancies in the nonmetal positions. Vacancy formation, a necessary step in diffusion in substitutional metallic solutions, is not a necessary step in the diffusion process for nonmetals in interstitial solutions.

Samsonov and Latisheva[87] have reported and Weinberg, Hudson, Yang, and Carpenter[88] have confirmed the observation that diffusion of carbon is slowest into those metals whose carbides have the most negative free energies of formation. From admittedly limited observation, the author has formed the opinion that for interstitial solutions the diffusion of a nonmetal is more rapid in phases of high nonmetal content than in those of low nonmetal content for any particular metal-nonmetal system. Observations such as these should be extended and made quantitative.

Quantitative studies that can be interpreted in terms of thermodynamic parameters should be made not only for binary solid solutions but also for ternary solutions that contain two nonmetals. Such studies would provide us with additional parameters with which to test and improve our theories of diffusion and could lead, as well, directly to development of useful new materials. Suppose, for example, that small concentrations of nitrogen in certain metal carbides should be found to drastically reduce the rate of diffusion of carbon in these phases. Such a finding could lead to development of more effective protective coatings for graphite.

Our understanding of diffusion in temperature gradients, and of the steady state concentration gradients established in temperature gradients, is still primitive. The behavior of a solid solution in temperature gradients may well limit its usefulness for some long-term high temperature applications. The usefulness of materials in thermoelectric devices in particular may depend on the compositional changes produced in the severe temperature gradients that characterize such devices.

Semiconducting materials should be particularly suitable subjects for studies of the concentration gradients developed in temperature gradients because the electrical properties of semiconductors are well-known, sensitive functions of composition. For studies of diffusion of elements heavier than phosphorus at concentrations of one percent or more, microprobe analysis appears to be a particularly valuable new technique.[89]

CONCLUSION

High temperature technology has reached a point beyond which further advances must depend more and more on sound understanding of the underlying physical and chemical principles of materials behavior in high temperature environments. If high temperature technology is to progress at the most rapid possible rate in future years, an increased fraction of the money and scientific effort expended in high temperature studies must be devoted to basic research in scientifically underdeveloped areas of the high temperature field. The author hopes that this paper will stimulate increased research in some of these areas.

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FIGURE LEGEND

Fig. 1 Variation in partial pressures of sulfur vapor species with temperature.

Fig. 2 Rates of reaction of tungsten (in grams/cm^2/min) as a function of temperature for various pressures of oxygen (in mm).

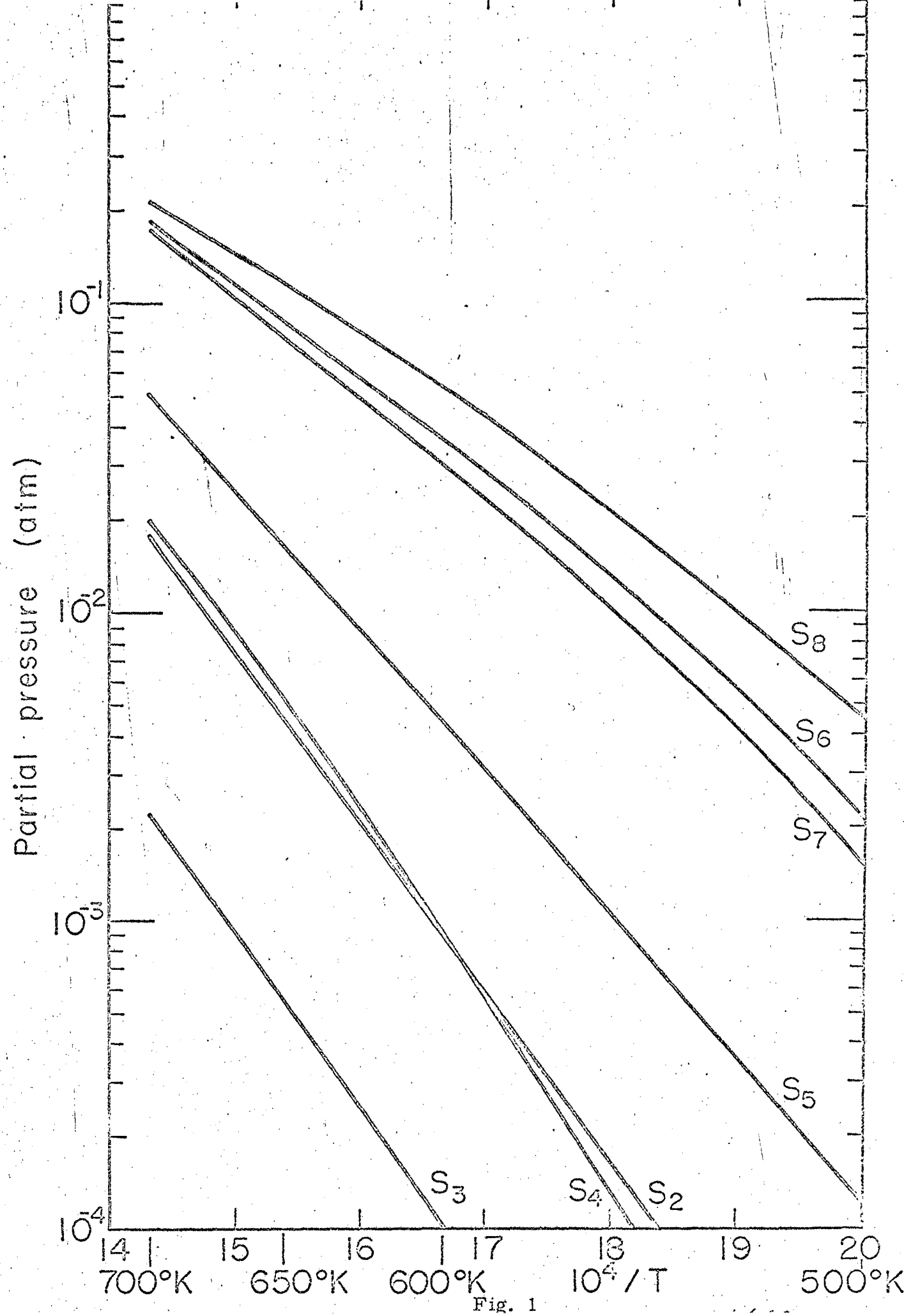
Partial pressure (atm)
10^{-1}
10^{-2}
10^{-3}
10^{-4}
S_8
S_6
S_7
S_5
S_3
S_4
S_2
14
15
16
17
18
19
20
700°K
650°K
600°K
$10^4/T$
500°K

Fig. 1

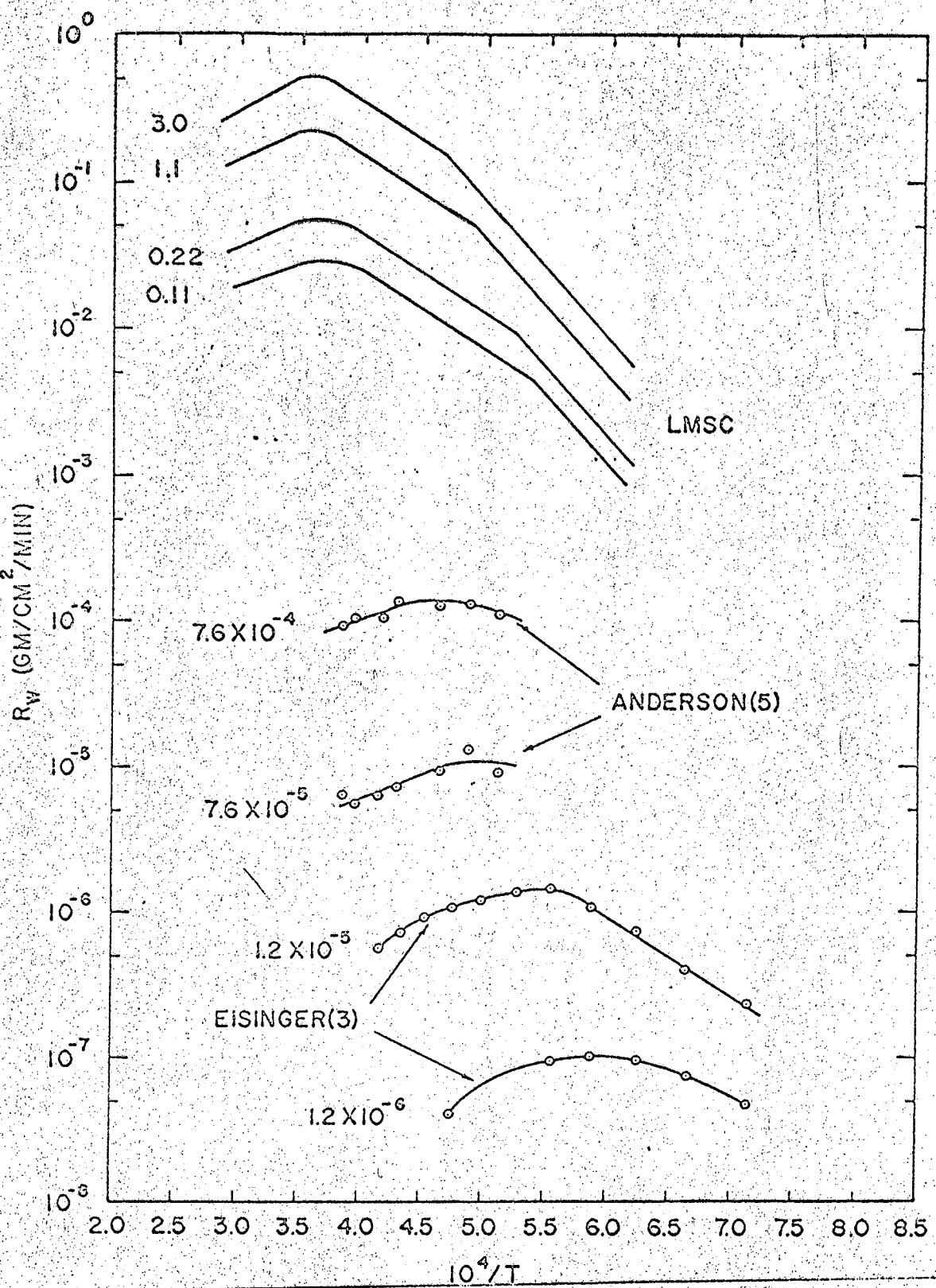
10^0
10^{-1}
10^{-2}
10^{-3}
10^{-4}
10^{-5}
10^{-6}
10^{-7}
10^{-8}
R_W (GM/CM^2/MIN)
3.0
1.1
0.22
0.11
LMSC
7.6×10^{-4}
ANDERSON(5)
7.6×10^{-5}
1.2×10^{-5}
EISINGER(3)
1.2×10^{-6}
2.0 2.5 3.0 3.5 4.0 4.5 5.0 5.5 6.0 6.5 7.0 7.5 8.0 8.5
$10^4/T$

Fig. 2

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