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Methods of Obtaining Thermodynamic Data

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Abstract: The types of thermodynamic data needed to predict behavior of high temperature systems such as an overheated nuclear reactor in which the fuel has been exposed to water and oxygen will be discussed. Procedures for obtaining the needed data will be reviewed.

Thermodynamic data are particularly important for the understanding of high temperature behavior. It is often difficult to carry out reliable measurements under the conditions of interest. Thermodynamics is a most powerful tool to overcome this problem as one can use thermodynamic data obtained at low temperatures to make accurate predictions of the high temperature behavior. The main obstacle is the recognition of the chemical species for which data are needed. Most people expect chemistry to become simple at high temperature because of dissociation of complex molecules to simpler molecules. This is not the case and high temperature chemistry can become very complex. Consider the equilibrium between a condensed phase such as nuclear fuel and the gaseous phase in contact with it. What misleads most people when they expect chemical behavior to become simple in high temperature systems is that they are thinking in terms of heating a gas at constant pressure in an inert container. When one heats a gaseous system in contact with a condensed phase, the partial pressures of the various gaseous species will not remain constant. It will be shown shortly that the pressures will

increase fast enough to offset any simplifying effect of increase in temperature that might be expected in a gaseous system at constant pressure. In fact, high temperature gaseous systems in contact with condensed phases will become more complex the higher the temperature.

High temperature systems become more complex in three principal ways. First, the oxidation numbers and formulas of the compounds become unfamiliar at high temperatures. One is accustomed to the alkali metals having an oxidation number of 1, the alkaline earth metals having an oxidation number of 2, aluminum and the third group elements having an oxidation number of 3, and any deviations from these oxidation numbers at room temperature would be considered quite unusual. At high temperatures these are not the common oxidation states at all. One finds a variety of unusual oxidation states. Compounds like LiO , for example, are stable and compounds of barium in both the 1 and 3 oxidation states are observed. Aluminum occurs in the 1 and 2 oxidation states. At high temperatures one can just forget about the octet rule and all the other valence rules that we have been taught. Anything goes that increases entropy. That's the first complication that arises. You won't recognize some of the compounds listed in the figures or some of the compounds discussed in the text if you are accustomed to thinking of chemistry at room temperatures. Why that might be will be discussed shortly.

The second respect in which gaseous systems become more complex at high temperatures is that the molecules become very complex. There are not only diatomic and triatomic molecules but also gaseous molecules with 5, 10, and more atoms per molecule.

The third way in which these gaseous systems become more complex is that, in contrast to low temperature systems where one may have one or two principal species, one may have many different species of roughly comparable importance

at high temperatures.

In Table 1 are listed just a few examples of molecules which have been found in high temperature gaseous systems. You see that these

Table 1. Molecules in high temperature vapors.

Ba ₂ O	Mo ₃ O ₉	UO ₃	UB ₂
Ba ₂ O ₃	Mo ₄ O ₁₂	CePd	SnPbS ₂
B ₂ O ₂	Mo ₅ O ₁₂	LaH	LaIrS ₃
Si ₂ O ₂	V ₆ O ₁₄	Si(OH) ₂	LuAu ₂
Cu ₃ Cl ₃	Al ₂ C ₂	IrC	PtC ₅

are quite complex and have unusual oxidation states. Some species have been established by use of the mass action law and in recent years a very large number of new species have been detected by use of the mass spectrometer. The work of Paul Gilles and his group at the University of Kansas [1] illustrates such a study. They investigated the gaseous species in equilibrium with boron sulfide with a mass spectrometer and found molecules with varying sulfur to boron ratios and molecules with the total number of atoms per molecule extending to twenty, thirty, or perhaps more. This is typical of saturated gaseous systems at high temperatures. There are a lot of different species; there are species with many atoms per molecule; and there are unusual oxidation states.

This is customarily very bewildering to persons who have not been familiar with these facts and it would appear at first glance that chemical experience at room temperature is of no value in predicting high temperature behavior. It is useful to review very briefly a few thermodynamic arguments to show that, in fact, this complex behavior is exactly the type of behavior that one should expect in these high temperature systems. There are fortunately some general principles that can be applied to show that high tempera-

ture behavior can be related to the overall understanding of the behavior of materials at all temperatures. The basic thermodynamic relationships are

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ (1)$$

$$\frac{\Delta G^\circ}{RT} = \frac{\Delta H^\circ}{RT} - \frac{\Delta S^\circ}{R} = -\ln K \quad (2)$$

The free energy change determines whether a reaction will go or not. The standard free energy change of a reaction determines the extent to which the reaction has gone under equilibrium conditions. Customarily at room temperature, except for some unusual aqueous reactions, the difference between ΔH° and ΔG° , $T\Delta S^\circ$, is usually a small correction term. The ΔS° usually will not be decisive in determining whether the reaction will go or not. So normally we are accustomed to reactions proceeding if they are exothermic and not proceeding if they are endothermic.

It is the ΔH° which is of prime importance at ordinary temperatures. At high temperatures the order of importance of the two terms, ΔH° and ΔS° , changes. This is best seen in the Eq. (2) where the standard free energy change for a reaction is related to the equilibrium constant. For an equilibrium constant to be large, that is, for the reaction to proceed in the direction in which it is written, the standard free-energy change has to be negative. When $T\Delta S^\circ$ is small at room temperatures, it is the ΔH° term which will normally determine the sign of ΔG° . If the relative importance of the heat and entropy terms is re-examined as the temperature is increased from 300 K to 3000 K, for example, it is seen that ΔH° becomes increasingly less important in determining the sign of ΔG° and the value of the equilibrium constant. Obviously at a high enough temperature it is the entropy term which becomes the primary factor in determining whether reactions will go or not.

That essentially is the basic reason for the drastically different behavior that one finds in high temperature systems compared to low tempera-

ture systems. In low temperature systems the stable molecules are those that we are accustomed to thinking of as being saturated, those that satisfy the octet rule. They give off the greatest amount of heat upon formation. But at high temperatures it is not so important to get the most heat out of the reaction. The more important question is how much did the entropy increase? So we are not going to care at high temperatures whether we get the most stable bonds or whether we satisfy the octet rule or any of the other rules which determine the heat evolution. It turns out that the reaction which gives the most favorable entropy change need not be one which will involve a familiar oxidation number and one can observe a variety of oxidation states of a given element.

Now, to examine this problem in a little more detail, we will consider a rather simple example which can be easily generalized to any type of reaction. Consider the vaporization of some material to two possible species. One is the monomer which is designated here as A and the other is the dimer which is designated as A_2 . For one mole of liquid vaporizing to the monomer, the heat of vaporization of the monomer is designated by ΔH_1 . For two moles of liquid A going to the dimer, we have ΔH_2 , the heat of vaporization of the dimer.



In the gaseous phase there must be an equilibrium between the dimer and the monomer and the enthalpy change of the dissociation reaction is given by ΔH_D . For the process of removing 2 moles of monomer directly from the liquid,

the amount of heat required will be 2 times the heat of vaporization of the monomer. If we produce 2 moles of monomer by the two-step process, first vaporizing a mole of dimer with absorption of the heat ΔH_2 , and then dissociating the dimer to two monomers, we must add the additional heat, ΔH_D , and we obtain the final identity of Eq. (6) showing the relationship between the heats of vaporization of the monomer and dimer and the dissociation energy of the dimer.

This particular example was selected to minimize the influence of the entropies. If Trouton's rule is applied, the entropies of the first two reactions would be expected to be comparable. That is, the entropies of vaporization are determined to the first degree by the translational entropy of the gaseous molecules which would be the same for the two reactions. In the comparison of these two reactions, the order of the free energies will determine the order of partial pressures at equilibrium. Since ΔS of those two reactions should be similar, the order of the free energies should be approximately the same as the order of the heats of vaporization.

If one of these heats, say ΔH_1 , is smaller than ΔH_2 , then the standard free energy of vaporization of the monomer will be smaller than that of the dimer and the partial pressure of the monomer will be larger.

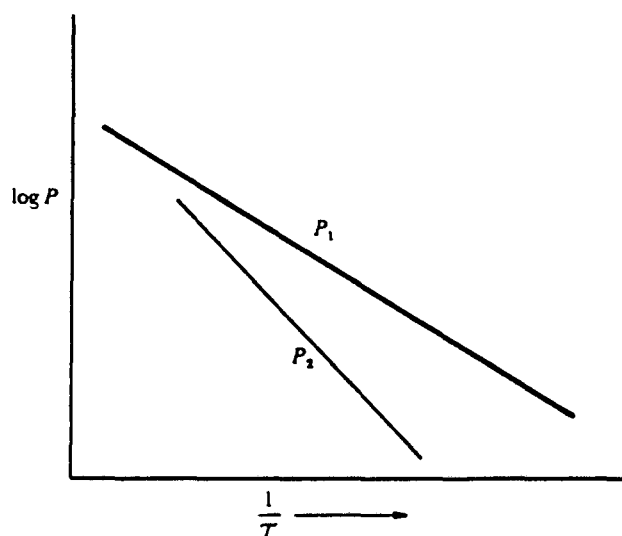
Now, consider two possible situations, one a situation where the dimer is the most important at low temperatures for equilibrium between the condensed phase and the vapor. This corresponds to a very stable dimer, that is, ΔH_D is very large. It takes a lot of heat to disrupt the dimer to monomers. Equation (6) shows that if ΔH_D is very large, then ΔH_2 is going to be small compared to ΔH_1 . So when ΔH_D is very large the heat of vaporization of the dimer will be smaller than that of the monomer and the free energy of vaporization of the dimer will be smaller than that of the monomer; the vapor at low temperatures will be predominately dimer. Aluminum trichloride would be an example.

low temperatures will be predominately dimer. Aluminum trichloride would be an example.

The above example is not the usual situation. The usual situation is one where the heat of dimerization of the ΔH_D required to dissociate the dimer is small compared to the enthalpy required to pull a monomer out of the condensed phase. Very frequently there are many bonds that have to be broken when a monomer is pulled out of the condensed phase compared to perhaps only one bond to be broken when the dimer is broken into monomers.

When that is so and ΔH_D is small compared to the heats of vaporization, then ΔH_2 must be large compared to ΔH_1 . Commonly the saturated vapor in equilibrium with a liquid at room temperatures will be predominately monomeric. There will be a much smaller proportion of dimer. Such a situation is illustrated in Fig. 1. The monomer will have a higher partial pressure because it has a low heat of vaporization. The dimer will have a

Figure 1. Vapor pressures versus temperature.



lower partial pressure because it has a higher heat of vaporization, but for the same reason, the dimer partial pressure has a much higher temperature coefficient. The species which is present at lowest partial pressure has the highest heat of vaporization and must increase the more rapidly of the two.

Therefore, the dimer must gain on the monomer and the higher the temperature of the saturated vapor, the more comparable the dimer and the monomer become.

Actually this can be easily generalized to trimers, to disproportionation reactions, ionization reactions, and any sort of vaporization reaction. This generalization can be made: The species which predominates at low temperatures, and normally there will be one species which will predominate at low temperatures over all the other possible species, will generally have the lowest heat of vaporization and all the other species which are relatively unimportant at low temperatures will have higher heats of vaporization. Therefore, the multitude of all these other species that are unimportant at low temperatures must gain more rapidly than the primary species as we increase the temperature in the saturated vapor. This means that the higher the temperature the more complex the vapor becomes with respect to the number of different species of comparable importance, and at the very highest saturation temperature, the critical temperature, one has a very large collection of species of all types.

With this very simple thermodynamic argument one can see the reason for what at first seems to be quite a paradox: That in these high temperature vapors people are discovering compounds of unusual oxidation states, compounds of very great complexity and, what is even more confusing, a tremendous variety of compounds in a given vapor.

This generalization has very great practical importance because before this was realized many people tried to extrapolate from low temperature chemical behavior directly to the expected behavior at high temperatures taking into account only those species which were known to be important at low temperatures.

One very striking example is the beryllia-steam reaction. It was known

that at low temperatures the beryllia was quite stable in contact with steam and therefore, it was not expected that anything should happen at high temperatures. However, when beryllia is taken to high temperatures in the presence of steam it vaporizes at a very rapid rate to form a complex gaseous hydroxide. And this experience has occurred time and time again in high temperature systems. Systems which show very simple behavior at low temperatures with no indication of anything abnormal become very complex and all types of unusual species come into play at the higher temperatures and completely disrupt the expected behavior.

So it becomes quite clear that if we are to anticipate the sort of problems that will arise in high temperature chemistry, we must not base our experience only upon the types of molecules that we find at low temperatures. To the first approximation, we must consider all possible combinations of the elements. Then through use of the entropy principles to sort out those which will have a favorable entropy of reaction, we can restrict ourselves to the several score species that could be of importance, eliminating the many multitudes of species which are not promising because of an unfavorable entropy of reaction. Then we can sort out from among the several scores of species the ones which will be of the greatest importance by taking into account not only entropy changes but also the enthalpy changes.

It is quite clear, then, that if we are to sort out the possible species that might be of importance we must be able to estimate entropy. In low temperature chemistry the emphasis is always placed on estimating bond energies. It is quite clear that at high temperatures the emphasis must be put equally, if not more so, on the ability to estimate entropies. Let us go into a little detail on this problem of estimating entropies of high temperature species.

There are a number of problems that must be faced if we are to estimate the entropies of molecules. In the first place, we must know something about the structure. It obviously makes a difference whether a triatomic molecule is bent or whether it is linear. Or if we have a molecule like Mo_5O_{15} , it is going to make a difference whether it has a very compact structure or whether it has a stretched-out linear structure. So one of the crucial problems of high temperature chemistry at the moment is to gain some information about the structure of these unusual and complex molecules.

At high temperatures there is considerable excitation of rotation, of vibration, and of electronic states and in a molecule of many atoms the spectrum becomes so complex that optical spectra are very difficult to use at the present. Of the new tools beginning to be applied, various molecular beam techniques are very useful. For example, the electric resonance molecular beam method can establish whether these molecules have dipole moments or not. If a molecule does not have a dipole moment, then that fact will place severe restrictions on the type of structure. Electron diffraction techniques which could give additional detail are applied to high temperature molecules only with great difficulty. The combination of molecular beam and optical techniques are providing valuable information.

Now, in addition to trying to establish the structures of these high temperature molecules, it is very important to know the various excited levels of the molecules because at high temperatures the molecule is not restricted to just a few low-lying levels. There is substantial excitation of vibration and rotation, and particularly since many of the high temperature molecules are what one would term radicals in that the electrons are not all paired, there are often quite low electronic levels which are quite extensively populated.

For the condensed phases and gaseous species that are stable at low temperatures, one can carry out various calorimetric measurements to fix heat capacities, entropies, and enthalpies of formation. One can set up electrochemical cells and measure various equilibria. These measurements can then be extrapolated with reasonable accuracy in most instances to high temperatures. The main problem is that as one increases the temperature, many of the low temperature compounds become relatively unimportant compared to the various high temperature phases and species. Some of these can be quenched to room temperature and studied calorimetrically. Some can be isolated in inert gas matrices. However, many can be studied only at high temperatures where it is difficult to get accurate measurements.

Predictive models are the key to obtaining the thermodynamic data needed to accurately predict high temperature equilibrium behavior. High temperature science is so difficult and so complicated that we cannot hope to get all of the data we need directly by experiment. What we have to do is to carry out experiments of types that will test possible predictive models. When the models are found inadequate, experiments need to be designed to provide insight to the improvement of theory. Experiments that help develop new models or test existing models are essential. Each experiment gives one not one bit of data, but yields a million-fold increase in information because the data yields a model that can then be used to predict data that would be difficult to measure.

An example that is pertinent to the reactor problem is a 1971 paper by Donald Jackson [2] on "Thermodynamics of the Gaseous Hydroxides." He used predictive models to calculate the thermodynamics of the MOH and $M(OH)_2$ gaseous species up to 3000 K for all of the elements between $M = H$ and $M = Lr$. Since his paper, some measurements have been made using mass

spectrometers. It would be very important to compare these measurements with his predictions to determine if his model needs any modification. Also since some of the fission products would form species with higher oxidation states, some attempt should be made to predict the stability of hydroxides and oxyhydroxides of high oxidation states.

At high temperatures, even more complicated species may play a significant role. Particularly, a mixture containing left-hand transition elements such as the lanthanides together with right-hand transition elements such as Ru, Rh, and Pd can yield unexpectedly stable species because of the strong generalized G. N. Lewis acid-base interactions between elements with vacant low-lying d and p orbitals and elements with non-bonding d-electron pairs.[3] K. A. Gingerich [4] has used mass spectroscopic techniques to demonstrate that these strong interactions that had been established for condensed phases also can be observed for gaseous species. The type of species that should be examined in regard to reactor fuel volatility in the presence of oxygen would be species such as CePdO . One would not expect the acid-base interactions to be as strong in diatomic species such as CePd as in the solid because all of the electrons are crowded between a single pair of metallic atoms. The oxygen could relieve the crowding by pulling some of the electrons away and thus allow all of the electrons to be used in bonding between the three atoms. Such unusual species should be considered. It might be easier to demonstrate their existence in matrix isolation experiments than with mass spectroscopic measurements in a high oxygen atmosphere.

What are the techniques that can be used to obtain sufficient high temperature data to provide the information needed to develop new theoretical models and to test existing models? In recognition of the difficulty of the field, the high temperature community promoted many symposia and publications

to encourage development of new techniques and new predictive models.

Appendix A lists a number of such publications that relate to the vaporization problems of a nuclear reactor. There are a number of additional publications that would be of value, but this selection provides a coverage of a wide-range of methods that can provide needed thermodynamic data.

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