TERNARY SPECIES AT HIGH TEMPERATURES

P. W. GILLES

Department of Chemistry, University of Kansas, Lawrence, Kansas, U.S.A.

INTRODUCTION

Gaseous species containing three kinds of atoms have been well known and characterized for many decades. Most of them are organic molecules, such as alcohols, esters, and acids and halides, but others, such as phosphorous oxychloride, carbonyl chloride, hydrogen cyanide and the metal carbonyls are familiar. These substances are relatively low temperature ones. It has been only recently that high temperature ternary species have been studied.

Quite properly, the systematic study of high temperature gases began with the elements. Even though there be only one element present, the complexity of the gaseous species may be considerable. Dimerization in the gases of the alkali metals is well known; the importance of polymers in carbon vapour was demonstrated a little over a decade ago; and polymers in the vapour of silicon, germanium and tin have also been reported. Most of the experimental work associated with these simple systems has been accomplished at low pressures. Considerably more work at much higher pressures at which polymers are expected to be more important remains to be done.

The status of the theoretical calculation of the binding energies and the molecular constants for these single element polymers is not well advanced. We can hope for additional effort and results in this area. An attempt was made by Pitzer and Clementi[1] to calculate the properties of polymeric carbon vapour, but relatively little other work of this nature has been reported.

Virial coefficients, viscosities, and much higher vapour pressures must be measured in order to provide suitable data on which to base additional theoretical work.

Since the field of high temperature chemistry began fifteen to twenty years ago, the largest proportion of effort has been associated with systems containing two elements. Most of the work has been associated with the oxides, but a significant proportion has been concerned with the halides. The metallic borides, carbides, nitrides, silicides, phosphides and sulphides have received some attention, particularly in the condensed state.

The vaporization properties of many binary systems have been examined. The present evidence indicates that few gaseous diatomic or polyatomic molecules containing a metal and boron, carbon, nitrogen, silicon, phosphorous, or sulphur exist. On the other hand, a multitude of gaseous metallic oxides and halides are well known and need not be listed here. Inasmuch as there has been great effort associated with the properties of gaseous metallic oxides and halides, this field has been rather well explored, and, recently, workers have been studying systems producing gases containing three kinds of atoms.

In almost every instance, these ternary gaseous species have been produced by studies of vaporization processes, and many of their properties have been measured in the course of such studies. Unusual ternary species can be prepared at high temperatures by at least six kinds of evaporation reactions.

In one of these, a ternary condensed phase evaporates congruently as in the reaction[2]

$$UOS(s) = UOS(g) \tag{1}$$

In the second, a ternary gas is produced from a liquid or solid solution as in the reaction[3]

$$LiAlF_4(soln) = LiAlF_4(g) \tag{2}$$

The third kind is the most common and accomplishes the formation of a ternary gas from one condensed phase and a reacting gas. Many gaseous hydroxides are obtained from reactions of this type, which can be illustrated by the reaction[4]

$$Ta_2O_5(s) + 3TaCl_5(g) = 5TaOCl_3(g) \tag{3}$$

In the fourth type, two different gaseous species are formed by the reaction of a condensed phase and a gas as in the reaction[5]

$$2\ UF_4(s) + O_2(g) = UF_6(g) + UO_2F_2(g) \tag{4}$$

The fifth type involves the reaction of two condensed phases to give a ternary gas and another condensed phase in the reaction[6]

$$MgF_2(s) + 2B_2O_3(liq) = 2BOF(g) + MgB_2O_4(s) \tag{5}$$

The sixth kind involves the reaction of two condensed phases to produce two gases as in the reaction[7]

$$3\ BeO(s) + W(s) = BeWO_3(g) + 2Be(g) \tag{6}$$

The importance of vaporization processes for all high temperature studies, and, in particular, for the study of ternary gaseous species, makes a discussion of the physical chemical principles involved in such research desirable, and this paper is directed towards that end. We shall also try to summarize the present state of our knowledge concerning the preparation and properties of ternary gaseous species.

VAPORIZATION PROCESSES

The study of a vaporization process serves to establish the nature and energetics of chemical binding in the gaseous state; to establish the nature of high temperature reactions; to measure the thermodynamic properties of solids, liquids and gases; to study the kinetics of high temperature reactions; and to prepare new substances. Many of the data required for the testing of chemical binding come from high temperature vaporization studies.

Usually the study of a vaporization process proceeds through six stages: (*i*) the general behaviour of the system is established; (*ii*) the gaseous species are identified; (*iii*) the net reaction is deduced; (*iv*) the vapour pressure is measured; (*v*) the kinetics of the evaporation process may be measured, and (*vi*) finally, the detailed mechanism of the vaporization process might be established. Most of our present studies in connection with vaporization processes are in the first four stages.

The general behaviour of the system

The initial characterization of a vaporization process should reveal any reactions between the sample and other parts of the system, the congruence of the process, and the variance of the system. Relatively simple kinds of experiments can, and should, be used for this characterization.

One of the first matters to examine in the study of a vaporization process is the tendency of the ingredients, *i.e.* those substances originally present in the system, to react to form condensed phases. It must always be remembered that, in addition to the sample, both the crucible material and the residual gases in a system are also ingredients and may be capable of reacting.

The next matter is the tendency of the ingredients to react to form gaseous substances. Such a reaction can produce gases alone, or another condensed phase may be produced simultaneously.

The next consideration concerns the vaporization of a single-phase sample which does not react with other substances. The phase may vaporize in a congruent fashion to give a gas of the same composition as the condensed phase, or it may vaporize incongruently to give another condensed phase and a gas of a different composition.

The next matter concerns the invariance of the vaporization process. A system must be invariant or pseudo-invariant in the phase rule sense before meaningful pressure measurements can be made.

Several techniques may be employed in the initial characterization of the vaporization process. A chemical analysis of all the starting materials and of the residual substances should be performed. X-ray diffraction studies can be used to identify the phases. Mass balance observations and calculations can sometimes reveal what is occurring in the system. The closed crucible experiment[8] may be especially suitable.

In this technique the sample is contained in a closed crucible instead of in an ordinary Knudsen effusion cell containing an orifice in the lid. Heating in vacuum to an appropriate temperature can be prolonged to any desired extent. The particular design of crucible and lid will be adjusted to the experimenter's particular purposes, but four pairs of choices are immediately apparent: (*i*) the crucible may be inert or reactive; (*ii*) it may be in a temperature homgeneous region or in a temperature gradient; (*iii*) the lid may be welded soundly or be fitted in a tight yet removable fashion; (*iv*) the sample may or may not be isotopically enriched.

The technique may be used to reveal possible reaction between the crucible and the sample; to reveal possible leakage or diffusion of the sample through the crucible walls; and, if the latter occurs, to estimate diffusion coefficients, to indicate the composition of gases leaving the exterior surfaces, and to identify the migrating species. A non-isothermal closed crucible experiment can be used to reveal the presence of two or more important gaseous species and to obtain thermodynamic information for them. Finally, it can be used for the preparation of crystals for X-ray crystallographic investigations.

Another technique which will frequently indicate reaction of the sample with the crucible is to change the crucible substance. Ackermann and Thorn[9] have refined this technique by observing the total weight loss from the crucible and oxide sample as the sample is completely evaporated from metallic crucibles.

The congruence of a process can be demonstrated by examining the residue after successive evaporation experiments with the same sample. If the residue always has the same composition, the process is a congruent one; but if the over-all composition of the residue changes, the process is incongruent.

The invariance of the system can be established by conducting a succession of pressure measurements on the same sample at the same temperature. If the pressure remains the same during the entire course of the evaporation, then the process is an invariant one.

The initial characterization of the vaporization behaviour of a sample should demonstrate whether there is reaction between the sample and the other parts of the system, whether the process is congruent, and whether it is invariant.

Identification of the gaseous species

After the general vaporization behaviour of the system has been established, the gaseous species should be identified. The most satisfactory instrument for this purpose is the mass spectrometer. The next most satisfactory is an appropriate spectrograph. Other less direct methods utilize a velocity selector and molecular beam apparatus, or a momentum detector, or a torsion effusion cell, or an electron diffraction apparatus, or a transpiration technique.

The mass spectrometer has yielded the most spectacular high temperature results during the past few years. The instrument is positive and specific for each individual substance and will indicate all the species that are present. It has a high sensitivity, and its specificity makes impurities relatively inconsequential. Several papers to be given at this meeting result from mass spectrometer studies.

Spectroscopic techniques can serve not only to identify molecules but also to obtain necessary molecular structure and constants. Ultra-violet, visible, infra-red, and microwave techniques have all been employed. As the complexity of the molecule increases, the difficulties of interpreting the spectra also increase.

The velocity selector is a rotating mechanical device with adjustable angular velocity which can be placed in a molecular beam. In such a beam, the distribution of molecular velocities depends on the temperature and the molecular weight of the gas according to the Maxwell-Boltzmann distribution law. When the selector is rotating at a particular speed, only molecules within a rather narrow range of velocity will pass through. By changing the speed of rotation, it is possible to obtain the distribution of molecular velocities of the gas molecules entering it and, hence, to deduce the molecular weight. Miller and Kusch[10] have used such a selector to study alkali halides, and Hostettler and Bernstein[11] have designed a new selector consisting of six slotted discs.

A momentum detector may be a vane interposed in the path of molecules such that it measures directly the pressure. This quantity, when coupled with some other measurement, such as mass transport, can be used to obtain molecular weight. The torsion effusion method employs an effusion cell suspended by a torsion fibre. The cell contains two holes on opposite sides displaced in opposite directions from the centre. Gases escaping through the holes cause a torque to be exerted on the cell, and the rotational displacement gives the pressure directly. A more nearly complete discussion of this technique has been presented[12].

An electron diffraction technique appears to be suitable for identifying the molecules arising in vaporization reactions, and it should also produce molecular geometries that are needed for the calculation of thermodynamic data.

In the transpiration technique, the pressure of a reacting gas can be varied to indicate the stoicheiometry of the product gases. Several papers in this meeting result from such work.

The phase law and conditions for meaningful pressure measurements

We shall now consider the circumstances under which meaningful pressures can be obtained. The phase law

$$F = C - P + 2$$

gives the number of degrees of freedom F in terms of the number of components C and the number of phases P. In order for a pressure to be fixed, the number of degrees of freedom in the system must be zero.

The simplest cases arise for one-component systems for which the number of degrees of freedom is $3 - P$. When three phases are present, the entire system is fixed; and both the temperature and pressure are fixed. When a gas and either a liquid or a solid are present one degree of freedom remains, and the pressure is a function of the temperature alone. Although many one-component systems are complicated because of the existence of polymers in the gaseous state, the pressure of each constituent depends only on the temperature.

For systems of two components the phase rule gives the number of degrees of freedom as $4 - P$, and four cases are of interest. If only one condensed phase and a gas phase are present, there are two degrees of freedom which may be taken to be the temperature and the composition of one of the phases. For such a system, it is possible to make meaningful pressure measurements only if these two variables are fixed. Extensive solid solubility frequently exists in high temperature systems; often a solid solution is the only condensed phase, and it is essential that its composition be fixed. If two condensed phases and one gas phase are present, F is one, and the pressure depends solely on the temperature. It is possible in principle to measure the equilibrium pressure of this system, but the experimental study may not be straightforward, owing to preferential vaporization of one of the components and the accompanying surface impoverishment of that component.

If three condensed and a gas phase are present, no degrees of freedom remain, and the pressure and temperature are both fixed. Such a case, however, rarely occurs.

Another case of a two-component system in which the pressure depends only on the temperature occurs if a single phase undergoes a congruent vaporization process. Such a system can be considered either as a single-componentone or as a two-component one with an additional restriction which reduces the number of degrees of freedom to one. The additional restriction is that the composition of the two phases be the same. In either case, the pressure depends only on the temperature.

For three-component systems, the number of degrees of freedom is $5 - P$, and the number of additional phases or restrictions must be increased by one to make the pressure a function of the temperature alone. If a gas phase and one, two, or three condensed phases are present, one must specify the temperature and two, one, or no composition variables, respectively, to fix the pressure. The case of five phases is not likely to occur. The same experimental difficulties as described for two-component systems will also occur for a three-component system containing three condensed phases.

The previous discussion emphasizes the importance of the component number of the system. This number is not necessarily the number of ingredients. It is well known, for example, that calcium carbonate forms a two-component system. Similarly, systems containing two ingredients may be three-component ones. Some of the chemical properties of the system must be known in order to establish the number of components. It is for this reason that the general behaviour of a system should be investigated first. With these points in mind, we turn now to the writing of the net reactions for the processes occurring in a vaporizing system.

The net reaction: vaporization of a single phase

Vaporization processes are chemical reactions which always can, and should, be written. First, the equation must be balanced; second, it must show the phases that are actually present in the system; third, it must be consistent with the phase law; and finally, it must reveal the gaseous species.

To illustrate these principles, we shall look first at the vaporization reactions of a single phase for which three groups of reactions are of interest. Consider the first group consisting of the reactions

$$\mathrm{H_2O(liq)} = \mathrm{H_2O(g)} \tag{7}$$

$$\mathrm{Na_2O(liq)} = 2\ \mathrm{Na(g)} + 1/2\ \mathrm{O_2(g)} \tag{8}$$

$$\mathrm{A_2B_3(s)} = \mathrm{AB(g)} + \mathrm{AB_2(g)} \tag{9}$$

These reactions are all congruent ones, and are alike in the phase rule sense, for the systems they represent may be considered either as single-component ones or as two-component ones with the additional restriction of congruence. In either case, the pressure depends only on the temperature. To be sure, if excess oxygen is added to vaporizing sodium oxide, the vapour no longer has the same composition as the condensed phase, and the pressure then depends on the composition of the vapour as well as on the temperature.

These reactions are, however, very different on a molecular scale. In reaction (7) molecules maintain their identity as they pass into the vapour phase. In reaction (8) the products are gaseous elements, and in reaction (9) the products are gaseous molecules both having different composition from that of the solid.

Turn now to reactions

$$2\,NaO_2(s) = Na_2O_2(s) + O_2(g) \tag{10}$$

$$3\,MoO_2(s) = Mo(s) + 2\,MoO_3(g) \tag{11}$$

$$2\,A_2B_3(s) = AB(g) + A_3B_5(s) \tag{12}$$

These are incongruent vaporization reactions in two-component systems in which a sufficient number of phases are present so that the pressure depends on the temperature alone. Each reaction gives a gas and a condensed phase, but they are quite different on a molecular scale. In reaction (10) a gaseous element is produced; in reaction (11) a condensed element is formed; and in reaction (12) a gaseous binary gas molecule of a composition different from the original phase is produced.

The reactions in the third group

$$H_2O\ (KCl\ soln) = H_2O(g) \tag{13}$$

$$O_2(FeO_x) = O_2(g) \tag{14}$$

$$TiO\ (TiO_y) = TiO(g) \tag{15}$$

are incongruent ones in two-component systems containing an insufficient number of phases; thus, the pressure depends on the one-composition variable as well as the temperature. Reaction (13) represents the evaporation of water from a potassium chloride solution. Reaction (14) represents the evaporation of oxygen from the wüstite solid solution in the iron–oxygen system and also describes the equilibrium between oxygen in the solid and in the gas. Reaction (15) describes the vaporization of TiO from the solid solution of TiO_y to form TiO(g). When the composition of the condensed phase and the temperature are specified in each of these cases, the pressure is fixed. These reactions are different in that the solvent is vaporized in (13); an element is vaporized in (14) from a solution in which it is the solute; and a substance is vaporized in (15) from a solution containing no other elements.

To clarify the principles of writing the proper equation, let us consider the two-component system containing titanium and oxygen and show the incorrect and correct way of writing the equations. In this system the condensed phases TiO, Ti_2O_3, Ti_3O_5 and TiO_2 are well characterized. A constitution diagram has been given by de Vries and Roy[13]. The first has a wide solid solution on both sides of the stoicheiometric composition;

Ti_2O_3 and Ti_3O_5 have narrow homogeneity ranges; and TiO_2 shows wide solid solution on the oxygen-deficient side. In addition to these phases, Magnéli and co-workers[14] have recently reported several having the general formula Ti_nO_{2n-1}. The vaporization properties of the phases in the titanium–oxygen system have been investigated[15], and are summarized as follows. All compositions in the TiO phase region vaporize incongruently giving Ti(g) and TiO(g). The Ti_2O_3 phase evaporates incongruently giving TiO(g) as the most important gas. The Ti_3O_5 phase evaporates congruently, and the most important gaseous species possibly are TiO(g) and TiO_2(g). The intermediate phases Ti_nO_{2n-1} lose oxygen and TiO_2(g) preferentially, and the TiO_2 phase loses oxygen preferentially to give initially the reduced TiO_{2-x}.

Consider first the vaporization of TiO. The equation

$$\mathrm{TiO(s)} = \mathrm{TiO(g)}\ \text{(incorrect)} \qquad (16)$$

is not correct because it demands that the process be congruent, which it is not. The equation

$$\mathrm{TiO}_y\mathrm{(s)} = \mathrm{TiO(g)}\ \text{(incorrect)} \qquad (17)$$

is not correct because it is not balanced. The equations

$$\mathrm{Ti}\cdot(z)\mathrm{TiO(soln)} = \mathrm{TiO(g)} + \mathrm{Ti}\cdot(z-1)\mathrm{TiO(soln)} \quad \text{(incorrect)} \qquad (18)$$

and

$$\mathrm{O_2}\cdot(w)\mathrm{TiO(soln)} = \mathrm{TiO(g)} + \mathrm{O_2}\cdot(w-1)\mathrm{TiO(soln)} \quad \text{(incorrect)} \qquad (19)$$

are not appropriate for vaporization studies, because they imply that two different condensed phases are present, whereas in reality there is only one. Equations such as equation (18) and (19) may be written for calorimetric studies in which the over-all change in the calorimeter is disclosed, but we are now considering equilibrium processes. The proper equations for the vaporization of any composition in the TiO region are reaction (15) and the reaction

$$\mathrm{Ti(TiO}_y) = \mathrm{Ti(g)} \qquad (20)$$

in which the quantity y is the composition variable in the solid phase. Whenever y is specified, the pressure of Ti(g) and TiO(g) are both fixed.

Consider now TiO_2. The equation

$$3\ \mathrm{TiO_2(s)} = 1/2\ \mathrm{O_2(g)} + \mathrm{Ti_3O_5(s)} \quad \text{(incorrect)} \qquad (21)$$

is not correct because it implies that Ti_3O_5 and TiO_2 are in equilibrium with each other but such is never the case. Instead of producing a separate phase, TiO_2 loses oxygen preferentially to produce a reduced rutile phase according to the equation,

$$\mathrm{O_2(TiO_{2-x})} = \mathrm{O_2(g)} \qquad (22)$$

An equation of the type

$$3\mathrm{TiO_2(TiO_{2-x}\ soln)} = 1/2\ \mathrm{O_2(g)} + \mathrm{Ti_3O_5(TiO_{2-x}\ soln)} \quad \text{(incorrect)} \qquad (23)$$

should not be written for the same reason given for (18) and (19).

Consider now Ti_3O_5 and Ti_2O_3. The equation

$$Ti_3O_5(s) = O_2(g) + 3\ TiO(s) \quad \text{(incorrect)} \tag{24}$$

is incorrect because it implies that Ti_3O_5 and TiO are in equilibrium with each other, but they cannot be because of the intermediate compound, Ti_2O_3. An equation incorrect in a more subtle way is

$$Ti_2O_3(s) = 1/2\ O_2(g) + 2\ TiO(s) \quad \text{(incorrect)} \tag{25}$$

The difficulty with this equation is that it implies that stoicheiometric Ti_2O_3 and TiO are in equilibrium with each other. If the TiO and Ti_2O_3 phases are in equilibrium the composition of the former must be the oxygen-saturated one, and of the latter, the titanium-saturated one. The correct equation for the loss of oxygen from the Ti_2O_3 phase to produce the TiO phase is,

$$Ti_2O_{3-a}(s) = (1 - a - 2d)/2\ O_2(g) + 2\ TiO_{1+d}(s) \ \text{(incorrect species)} \tag{26}$$

in which a gives the composition of the titanium-saturated Ti_2O_3 phase, and d gives the composition of the oxygen-saturated TiO phase. The quantity a is probably no larger than 0·02, but d is about 0·25. Even though this reaction is formally correct, it does not describe what occurs in the system. Instead of losing oxygen to the gas phase, Ti_2O_3 primarily loses TiO(g) and produces the titanium-saturated Ti_3O_5 phase. The proper equation to write showing the most important reaction in the vaporization of the Ti_2O_3 phase is

$$Ti_2O_{3+b}(s) = \left(\frac{1 - 3b - 2c}{2 - c}\right) TiO(g) + \left(\frac{1 + b}{2 - c}\right) Ti_3O_{5-c}(s), \tag{27}$$

in which b gives the composition of the oxygen-saturated Ti_2O_3 phase, and c gives the composition of the titanium-saturated Ti_3O_5 phase.

The net reaction: vaporization of two phases

The reactions we have been considering show the vaporization of a single phase. We turn now to vaporization reactions involving two reactants in two-component systems. The reaction

$$Pt(s) + O_2(g) = PtO_2(g) \tag{28}$$

accomplishes the formation of a gas by oxidation of a metal. This reaction is of the same type as reaction (3). Only two phases are present; the reaction is an incongruent one; and the pressure depends on the composition of the gas phase. Reactions of this particular type are particularly amenable to study by transpiration techniques as Alcock and Hooper[16] and Schäfer and Tebben[17] have recently shown.

The reaction

$$C(s) + 2S(s) = CS_2(g) \tag{29}$$

is one in which there are a sufficient number of phases so that the pressure of CS_2 depends only on the temperature. The reaction,

$$C(s) + S(s) = CS(g), \tag{30}$$

involves the same reactants, has a sufficient number of phases, and accordingly the pressure of CS(g) also depends on the temperature alone.

Three-component systems

It is important to recognize a three-component system when it appears. For example, in a system formed by mixing magnesium oxide and graphite, the reaction,

$$MgO(s) + C(s) = Mg(g) + CO(g) \tag{31}$$

occurs. Under these circumstances, the system is one of two components, and the pressure depends only on the temperature. If, however, additional carbon monoxide is added to the system, then it has three components, and the pressure depends on the composition of the gas phase as well as on the temperature. This reaction is of the same type as the reaction (6). One can regard the system formed by mixing the two condensed phases as a three-component system with the additional restriction that the composition of the gas phase is indicated by the right-hand side of equation (31), or with an additional restriction that no other gas be added.

In a system formed by mixing tricalcium phosphate and silica, the reaction occurring is,

$$2\ Ca_3(PO_4)_2(s) + 6\ SiO_2(s) = P_4O_{10}(g) + 6\ CaSiO_3(s) \tag{32}$$

This reaction is of the same type as reaction (5). The system has three components for it is not possible to express the composition of each phase in terms of any two substances. For this particular reaction there are four phases present, and the pressure of P_4O_{10} depends on the temperature alone.

Let us suppose that we have a system prepared by mixing these two ingredients with a deficiency of silica. Consider the changes in the system as P_4O_{10} is removed. As long as the three condensed phases are present, the pressure remains fixed. When the SiO_2 is consumed, a ternary condensed phase, $Ca_5SiP_2O_{12}$, is produced. The appropriate reaction under these circumstances then is

$$3\ CaSiO_3(s) + 4\ Ca_3(PO_4)_2(s) = 1/2\ P_4O_{10}(g) + 3\ Ca_5SiP_2O_{12}(s) \tag{33}$$

In this system enough phases are still present to make the pressure dependent on the temperature alone, but since one condensed phase is different from the previous case, the equilibrium pressure will be lower than the previous value.

Properties of vaporization products

After the system has been characterized, the gaseous species identified, and the net reaction established; the vapour pressure may be measured. For this purpose the various techniques include the static, boiling point, transpiration, Knudsen and Langmuir methods. These have been discussed by Margrave[18] and need not be repeated. In the lowest pressure regions the Knudsen and Langmuir techniques are appropriate. Frequently, the sensitivity of these methods can be increased by using a mass spectrometer, radiochemical techniques, or microchemical analytical techniques. At higher pressure, the transpiration method is appropriate.

Entropies and heats of formation of gaseous substances can be obtained from vaporization data if sufficient data are available for the condensed phases. Of course, in complex systems, such data may not be available. The resultant entropies of the gaseous molecules can be compared for reasonableness with those empirically calculated.

The structures of high temperature ternary species are much more difficult to obtain. Adequate theory is lacking for the calculation of reliable structures. Spectroscopic methods are about the only useful ones. Studies on HOBO(g) have been made with infra-red spectrometers, and it is conceivable that microwave spectrometers can be used for certain high temperature species.

If the structures are adequately known, then, of course, the thermodynamic functions can be calculated from the usual statistical thermodynamic formulae. If the structures are not available, certain empirical entropy calculations may give approximate values to compare wth those derived from vapour pressure measurements.

SUMMARY OF TERNARY GASEOUS SPECIES

Some of the ternary gaseous species that have been recently recognized are shown in *Tables 1* to *4*, arranged according to reaction type, which are typified by equations (1), (2), (3) and (4), respectively.

A glance at the tables shows that the alkali metals have been studied more than any other group of metals. The species produced are somewhat unusual and surprising, yet they usually have the metal in the normal oxidation state. The theories are insufficient and the data are still sufficiently scarce to permit many worthwhile generalizations of thermodynamic properties to be made.

Table 1. Ternary gaseous species produced by congruent vaporization

Gas	*Investigators*	*Reference*
UOS	Cater	2
NaOH	Rao and Schoonmaker	19
MoO_2Cl_2	Basitova, Davydovskaya and Bekhle	20
ReO_3Cl	Basitova, Davydovskaya and Bekhle	20
$NbOCl_3$	Schäfer and Kahlenberg	21
$Cu(NO_3)_2$	Addison and Hathaway	22
$Cu(NO_3)_2$	Porter, Schoonmaker and Addison	23
$LiBO_2$	Büchler and Berkowitz-Mattuck	24
$NaBO_2$	Büchler and Berkowitz-Mattuck	24

Table 2. Ternary gaseous species produced from solutions

Gas	*Investigators*	*Reference*
$LiAlF_4$	Porter and Zeller	3
$NaAlF_4$	Howard	25
$NaAlCl_4$	Dewing	26
$LiZr_2F_9$	Sense and Stone	27
$LiBeF_3$	Sense and Stone	28
$NaBeF_3$	Novoselova, Muratov, Reshetnihova and Gordeev	29
$LiNaF_2$	Schoonmaker	30
$NaKCl_2$	Milne and Klein	31
$LiNaO$	Berkowitz, Chupka, Blue and Margrave	32
$GeSiC$	Drowart, De Maria, Boerboom and Inghram	33
$NaFeCl_4$	Cook and Dunn	34
$KMgCl_3$	Schrier and Clark	35

Table 3. Ternary gaseous species produced by reactions of the type (s) + (g) = (g)

Gas	*Investigators*	*Reference*
$TaOCl_3$	Schäfer and Sibbing	4
$LiOH$	Berkowitz, Meschi and Chupka	36
$Be(OH)_2$	Grossweiner and Seifert	37
$Zn(OH)_2$	Glemser, Völz and Meyer	38
$MgOH$	Brewer and Trajmar	39
$WO_2(OH)_2$	Glemser and Völz	40
$WO_2(OH)_2$	Meyer, Oosterom, and Oeveren	41
$TeO(OH)_2$	Glemser and Haesleler	42
HBO_2	Margrave	43
HBO_2	Meschi, Chupka and Berkowitz	44
$(HBO_2)_3$	Meschi, Chupka and Berkowitz	44
H_3BO_3	Meschi, Chupka and Berkowitz	44
$(BOF)_3$	Hildenbrand, Theard and Saul	6
$MoO_2(OH)_2$	Elliott	45
$SiO(OH)_2$	Elliott	45
$(NaOH)_2$	Schoonmaker and Porter	46

Table 4. Gaseous species produced by reactions of the type (s) + (g) = (g) + (g)

Gas	*Investigators*	*Reference*
UO_2F_2	Fried and Davidson	5
MoO_2Cl_2	Hultgren and Brewer	47
$VOCl_3$	Schäfer	48
$NbOCl_3$	Schäfer, Sibbing and Gerken	49
$TaOCl_3$	Schäfer, Sibbing and Gerken	49

CONCLUSION

The first four stages of a vaporization investigation, the establishment of the general behaviour, the identification of the gaseous species, the deduction of the net reaction, and the measurement of the vapour pressure and thermodynamic properties have been described and applied to ternary gaseous species. Those species thus far identified have been tabulated.

It is surely true that additional research will reveal ternary gases of other metals, and our experience with binary gases indicates that many more uncommon stoicheiometries will be found. Hopefully, new techniques for such studies will be developed.

More important, probably, is the need for additional theoretical work on the binding energies of the gaseous species and for vigorous experimental investigations on the last two stages of vaporization studies, the kinetics and mechanism of vaporization.

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