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Thermodynamics of Vaporization of Nuclear Materials at High Temperatures

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1. Abstract

Vaporization studies are one of the best, most convenient, and most important ways of obtaining thermodynamic properties and phase relationships of refractory nuclear materials. Measurements are made on equilibrium systems involving at least two phases. The properties of these phases are established by the proportions of the components, the properties of the pure components and their interaction parameters. Free energy-composition curves for the gas phase and the several possible condensed phases in a system are discussed in relationship to one another. The

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overwhelming effect of pressure on the free energy of the gas phase and the minute effect on condensed phases are pointed out, and their significance is emphasized. The relationship between the free energy-composition curves and the vaporization behavior of the system is described.

The several factors which are important in establishing free energy-composition curves and, hence, the mode of equilibrium vaporization are discussed. They include the stability of the gaseous molecules, the absolute and relative stabilities of the various condensed phases, the composition of the gaseous molecules, the composition of the condensed phases, and the free energies of sublimation of the elements.

A few of the principles associated with congruent vaporization processes and mass spectrometric measurements are discussed.

2. Introduction

In the previous Symposium on Thermodynamics of Nuclear Materials held in May, 1962, some general principles of vaporization processes were discussed [1]. The steps in a vaporization study, pressure-composition diagrams, and the writing of net reactions were also described. Some of these topics have been considered more recently in greater detail [2]. Kubaschewski [3] has emphasized the importance of thermodynamic properties in determining phase diagrams. He has pointed out the close relationship between the free energy diagram and the phase diagram, and has illustrated their mutual interconversion.

Thermodynamic properties of substances determine equilibrium vaporization properties just as they determine fusion phenomena. It is customary in the present decade to proceed in the opposite direction, that is, to deduce from vaporization studies thermodynamic properties of gaseous substances and occasionally of condensed substances. In fact, the importance of vaporization studies arises in part from the fact that they are one of the best and most convenient ways of obtaining thermodynamic properties and phase relationships of refractory nuclear materials.

One purpose of the present report is to show the connection between the free energy-composition diagram and the pressure-composition diagram and to discuss their relationships to the vaporization behavior of binary chemical systems. The principal difference between this discussion and that of Kubaschewski's lies in the extent to which the pressure

influences the free energy of a phase. In the fusion case, the free energies of the phases are relatively uninfluenced by the pressure; but in the vaporization case the free energy of the gas phase is determined to an overwhelming extent by the pressure. Remarks will also be made relating to the factors that influence equilibrium vaporization phenomena, congruent vaporization, the writing of chemical equations, and mass spectrometry.

3. Free energy-composition diagrams and pressure-composition diagrams

A free energy-composition diagram for a two-component system A-B is a constant temperature, constant pressure graph in which the free energy of formation of each phase per total gram atom is plotted as a function of the composition of that phase. Such diagrams have been exploited effectively by Darken and Gurry [4], as well as by Kubaschewski [3], and are now being collected by Hultgren, Orr, Anderson, and Kelley [5]. A pressure-composition diagram, like the free energy-composition diagram, is drawn for a constant temperature and is a plot of the total pressure as a function of the composition. It is a phase diagram. It has the appearance of an inverted temperature-composition diagram. This diagram is the most convenient way of summarizing information about vaporization reactions.

Several such diagrams relating to nuclear materials have been published. Diagrams for the uranium-oxygen system have been presented [1, 6, 7], and a partial one appears in the paper by Ackermann and Thorn [8] in this symposium. Alcock, Eick, Rauh, and Thorn [9] have presented one for the uranium-carbon system. Resulting from the work of Cater [10-12] is one for the uranium-sulfur system.

Figure 1 shows a schematic free energy-composition diagram for an ideal solution at a temperature of 2000°K . The composition variable is the atom fraction of component B. The upper curve is the entropy of formation for one total gram atom of an ideal solid, liquid, or gaseous solution from its constituent elements in the same state of aggregation. The lower curve shows the free energy of formation per total gram atom of the same solution from the elements. Figure-2 shows ΔS , ΔH , and ΔG for the formation of endothermic regular solutions, and Figure 3 shows the same quantities for exothermic solutions. The dashed curve gives the free energy of the ideal solution.

Figure 4 shows the free energy of formation of an ideal solid solution from the solid elements and the free energy of formation of one gram atom of an ideal gaseous solution containing no intermediate compound. The gaseous solution has a total pressure of one atmosphere. The reference state for the elements both for the solid solution and for the gaseous solution are the same, namely pure solid elements. The free energy of the gas phase is higher than the free energy of the condensed phase because the temperature is below the normal boiling point for the elements.

As the pressure is lowered, relatively little happens to the free energy of formation of the solid or liquid phase, but the free energy of formation of the gas phase diminishes rapidly. In Figure 5 we show the free energies of formation of the solid phase and the gas phase at the same temperature at a pressure P_2 , between the sublimation pressures of the components. As the pressure is lowered even more to P_1 the gas phase free energy falls as shown in Figure 6.

The criterion for equilibrium between phases in such a constant temperature, constant pressure system is that the partial molal free energy of each component be the same in all phases. A property of this kind of diagram is that a tangent to a curve intersects each vertical axis at the partial molal free energy of that component in the solution. Hence, a line tangent to two curves connects the partial molal free energies of the components with the compositions of the two phases in equilibrium with each other. The dashed lines in Figures 5 and 6 are such tangents. They show that at the lower pressure in Figure 6 both phases are richer in component B. The corresponding pressure-composition diagram for the ideal solution situation illustrated in Figures 4-6 is shown in Figure 7 in which the same shift in the composition of both phases with lowering pressure is revealed. The pressures for the three preceding figures are indicated in Figure 7. If the free energies are given, the pressure-composition diagram can be calculated and, more to the point of this symposium, vice versa.

If a system forms condensed intermediate phases instead of forming continuous solutions, its behavior may be similar to that indicated in Figure 8. The free energy range covered in this diagram is much larger than in the previous diagrams; accordingly, the gaseous free energy curve is nearly a straight line. We have exaggerated the curvature to illustrate the principles. The curves at both sides represent

the terminal solid solutions and the curve near the bottom represents the free energy of an intermediate phase which is designated AB. If the pressure is sufficiently higher than that for which Figure 8 is drawn, only condensed phases can exist in the system. The pressure shown in Figure 8 is less than the sublimation pressure of the component A, but above that for component B. If the system contains pure A, minimum free energy is achieved if only gas is present. On the other hand, in a system containing pure B, the pressure is too high to allow any vapor to be present. A common tangent to indicate a two-phase region has been drawn between the vapor curve and the curve for AB. The vapor is nearly pure A, and AB is slightly A-rich. The other side shows equilibrium between the condensed, nearly pure B phase and the slightly B-rich intermediate phase AB. In the minuscule portion at the left of the diagram, only vapor is present. At the far right side of the diagram, only solid B solution is present.

Figure 9 shows the same system at lower pressure. Now the two-phase regions on both sides of AB involve the gas phase. Figure 10 shows the free energy curves for the lowest pressures at which solids can exist. The two-phase regions on both sides of the phase AB are reduced to a single common point occurring at the composition for which the intermediate phase vaporizes congruently. The pressure-composition diagram corresponding to the free energy-composition diagrams given in Figures 8-10 is shown in Figure 11.

In Figures 12-14 we show free energy curves for the condensed and gaseous phases in a system containing the same condensed phases for the preceding drawings, but from components of greatly different volatilities. As the pressure is lowered the free energy curve for the gas phase becomes lower than that for the intermediate AB phase in such a way that the compound AB does not vaporize congruently, but rather as shown in Figure 15. In Figure 13 the dashed line with the smaller slope connects the gas phase and AB; the other, AB and B. At a unique pressure between that corresponding for Figures 13 and 14, there is a common tangent to the curves for the gas, the intermediate phase AB, and the B terminal solution, and the three phases are at equilibrium with one another.

The previous diagrams applied to a system in which there is no gaseous compound and in which the elements have volatilities differing by a factor of about 2.5×10^4 for the first set and about 10^{13} for the second set. In many systems, intermediate gaseous compounds are

important in the vapor phase. Free energy-composition diagrams of the gas phase are markedly altered, showing a very deep minimum as indicated in Figure 16. The upper dashed curve represents the behavior of the gas phase if no gaseous compound is present; and the solid curve, if $AB(g)$ exists. At a slightly lower pressure a single common tangent for the gas phase and the intermediate phase is shown in Figure 17, indicating that AB vaporizes congruently. Not shown but also following from the curves is the fact that each terminal solution tends to produce a vapor richer in the other component. The pressure-composition diagram corresponding to the free energy curves in Figures 16 and 17 is shown in Figure 18.

Systems in which two gaseous species are present would show more complicated curves as would those systems with more than a single condensed phase. Other types of free energy-composition diagrams are possible and could be drawn for more complicated systems which, for example, might contain several compounds.

4. Factors influencing equilibrium vaporization phenomena

The words mode of vaporization refer to the congruence of the processes and the variance of the system which is vaporizing. Reference to the preceding diagrams will indicate that the following factors are of greatest importance in establishing the mode of vaporization of the phases in a two-component system. These factors are arranged in approximate decreasing order of importance: (1) thermodynamic stabilities of the gaseous molecules, (2) thermodynamic stabilities of the condensed phases, (3) compositions of the gaseous compounds, (4) compositions of the condensed phases, (5) free energies of sublimation of the elements, and (6) curvature in the free energy-composition diagram. The stabilities of gaseous molecules are of almost overwhelming importance. If a gaseous molecule of great stability exists, the condensed phase of that same composition will tend to vaporize congruently and with a high pressure. Moreover, a condensed phase of a different composition will tend to vaporize incongruently to give a gas of nearly the composition of that gaseous molecule.

The next most important factor in influencing equilibrium vaporization phenomena is that of the thermodynamic stabilities of the condensed phases. We may consider the hypothetical case of a solid

intermediate phase whose stability can be altered. As the stability of that solid compound is increased without a change in the stability of the gas phase, the vapor pressure falls and the tendency for congruent vaporization to occur increases. Inasmuch as equilibrium among the gaseous constituents must also exist, the tendency to vaporize by decomposition into the elements also increases. That the compositions of the gaseous compounds and condensed phases influence their mode of vaporization has already been suggested. The differences in the volatilities of the elements themselves in the absence of gaseous molecules will, as we have seen, influence the mode of vaporization. Finally, the curvature in the free energy-composition curve for the condensed phase may render a slight effect.

5. Congruent Vaporization

A single-phase sample is said to be congruently vaporizing when the composition of the vapor and the composition of the solid are the same, so that prolonged vaporization causes no change in the composition of the sample. Such behavior has been well established for several binary systems involving nuclear materials, such as the uranium-oxygen system, the uranium-sulfur system, and the uranium-carbon system. The composition at which a sample vaporizes congruently may depend on the temperature and may also depend on the experiment.

In a system at high pressure, that is, in the viscous flow region, the transport of matter is governed by the pressure, and the composition of the vapor phase must be exactly that of the condensed phase for congruent vaporization to occur. If the vapor contains only a single species of the same composition as the solid, then the case is simple. If in addition to this species the gas contains decomposition or disproportionation products, the atom ratio in the vapor must be the same as that in the condensed phase.

On the other hand, at low pressure for the Knudsen experiment, the transport of materials is not given by the pressure alone, but rather by the molecular weight as well. If the only vapor species has the same composition as that of the condensed phase, the case is again simple. But if other species are present, then the molecular weight factor, except in the coincidental case of equal molecular weights, causes the solid composition to be slightly enriched in the heavier constituent.

The extent to which the composition in the crucible will be different from the composition in a high pressure system will depend on the ease with which the composition of the condensed phase can be changed.

The Langmuir vaporization experiment provides an interesting discussion. If the vaporization coefficients for several possible species are all the same, the transport of matter is given by the same equation as for the effusion method, and the composition of the condensed phase must be the same as in the Knudsen experiment.

Thus far in the discussion, stoichiometry has not been mentioned. The composition at which congruent vaporization occurs has just been shown to depend on the particular experiment. In neither the high-pressure case nor the low-pressure case must the congruently vaporizing composition be a stoichiometric one. Notable systems in which non-stoichiometric congruent vaporization occur are Zr-B [13] and U-C [14, 15].

It can easily be shown that in a two-component system at constant temperature and constant pressure, if two phases have the same composition, the pressure is either the maximum or the minimum. For the case of congruently vaporizing refractory nuclear materials, it is the minimum pressure case which is of importance. This minimum pressure produces an invariant system, and once a system has reached the congruently vaporizing composition it must remain at that composition as long as the temperature is held constant and no reacting species are introduced into the system. Variation of the composition from that at the minimum causes an increase in the pressure, owing to species containing relatively more of that component in which the condensed phase is rich. Hence the system tends to return to the congruently vaporizing composition.

A sample giving rise to a single vapor of the same composition will always vaporize congruently. Such a case, however, is unusual, for decomposition or disproportionation products are usually present. The partial molal free energies of vaporization of these various substances will, in general, differ from one another. The congruently vaporizing composition at one temperature will not be the congruently vaporizing composition at another. Such a behavior is suspected in a titanium-sulfur system [16] and probably in numerous other systems.

6. Chemical equations

As has been emphasized previously, the chemical equations representing chemical reactions must be balanced; they must reveal the phases that

are present; they must realistically present the compositions of those phases; they must show the gaseous species; they must be written consistent with the phase law; and they must indicate whether the process is congruent or not. Let me anticipate the work in some of the subsequent papers by writing chemical equations for the vaporization processes.

In the paper by Ackermann and Thorn [8], the pressures given in Figure 2 indicate that stoichiometric uranium dioxide vaporizes congruently and that the most important reaction is

Contributing to an extent of only about three parts per hundred is the reaction

which produces equal pressures of $\text{UO}(\text{g})$ and $\text{UO}_3(\text{g})$; and, finally, contributing to about two parts in ten thousand is the reaction

which produces equal pressures of $\text{U}(\text{g})$ and $\text{O}(\text{g})$. These equations all represent congruent vaporization processes.

When the uranium oxide is reduced to $\text{UO}_{1.95}$ the pressure of UO becomes higher than that for any other species. The most important reaction is

giving a pressure of about 1.5 that of the $\text{UO}_2(\text{g})$ pressure in equilibrium with stoichiometric $\text{UO}_2(\text{s})$, while the $\text{UO}_2(\text{g})$ pressure has fallen to about 0.6 of its value over stoichiometric $\text{UO}_2(\text{s})$. The appropriate chemical reaction for this species under these circumstances is

The pressure of the $\text{UO}(\text{g})$ and the $\text{UO}_2(\text{g})$ will remain fixed so long as the composition of the condensed phase is fixed. Apparently in the laboratory the hypostoichiometric sample is reached only by the presence

of a reducing agent such as uranium metal, another active metal, or gases in the system. If the pressures given by Ackermann and Thorn [8] are correct, a hypostoichiometric sample cannot be produced from the UO_2 phase alone for it vaporizes congruently at $2000^\circ K$. A partial molal heat of vaporization of $UO_3(g)$ from UO_2 sufficiently large to cause the sample to become substoichiometric at higher temperature should, however, be considered.

Anticipating the report by Storms [15] on the uranium-carbon system, we note that the several species of importance are $U(g)$, $UC_2(g)$ and carbon species. For the vaporization of uranium and $UC_2(g)$ from samples in this system we can write the equations in the metal region,

$$U(\text{in } UC_2 \text{ metal phase}) = U(g), \quad (6)$$

$$UC_2(\text{in } UC_2 \text{ metal phase}) = UC_2(g); \quad (7)$$

in the metal monocarbide region,

$$\left(\frac{1-d}{1-d-c}\right)UC_c(\text{metal phase}) = \left(\frac{c}{1-d-c}\right)UC_{1-d}(\text{monocarbide}) + U(g), \quad (8)$$

$$\left(\frac{2-c}{1-d-c}\right)UC_{1-d}(\text{monocarbide}) = \left(\frac{1+d}{1-d-c}\right)UC_c(\text{metal phase}) + UC_2(g); \quad (9)$$

in the monocarbide region,

$$U(\text{in } UC_{1\pm x} \text{ monocarbide}) = U(g), \quad (10)$$

$$UC_2(\text{in } UC_{1\pm x} \text{ monocarbide}) = UC_2(g); \quad (11)$$

in the monocarbide-dicarbide region,

$$\left(\frac{2-f}{1-e-f}\right)UC_{1+e}(\text{monocarbide}) = \left(\frac{1+e}{1-e-f}\right)UC_{2-f}(\text{dicarbide}) + U(g), \quad (12)$$

$$\left(\frac{1-e}{1-e-f}\right)UC_{2-f}(\text{dicarbide}) = \left(\frac{f}{1-e-f}\right)UC_{1+e}(\text{monocarbide}) + UC_2(g); \quad (13)$$

in the dicarbide region,

$$U(\text{in } UC_{2\pm y} \text{ dicarbide}) = U(g), \quad (14)$$

$$UC_2(\text{in } UC_{2\pm y} \text{ dicarbide}) = UC_2(g); \quad (15)$$

and in the dicarbide-graphite region, depending on whether the carbon-saturated dicarbide phase is hypo- or hyperstoichiometric, either

or

In these equations a letter subscript at the beginning of the alphabet gives the departure from stoichiometry at a phase boundary, and one at the end of the alphabet indicates variability in composition in a single phase region. Similar equations can easily be written for the vaporization of any of the carbon species from any of these regions.

Alternatively, and perhaps to some people more pleasing, would be the set of reactions for the vaporization of uranium and $\text{UC}_2(\text{g})$ from the various two-phase regions,

The last way of writing these equations is more suggestive of the continuity of the partial molal free energies of vaporization over the entire system. They also do not require a knowledge of the compositions of the condensed phases in equilibrium with each other and they imply, though do not state specifically, the invariance of the system at constant temperature.

7. Mass spectrometry

At the hands of many people, the mass spectrometric technique has been used for numerous vaporization studies. Originally, it was used for identification of vapor species and for obtaining temperature coefficients of intensity times temperature products so that heats of vaporization could be obtained. It has been extended to give absolute pressure measurements through the use of silver calibration, or through a self-calibration with a combined effusion and mass spectrometric experiment. More recently, particularly in Brussels, it has been used to monitor the course of a preparative reaction and to monitor the approach to a congruently vaporizing composition by revealing the changes in the pressures of the various gaseous constituents. I hope that some additional mass spectrometric results on the uranium-oxygen and uranium-carbon systems not appearing on the printed program will be presented in the discussion by the Brussels workers [17].

One important feature of the mass spectrometric technique is that partial molal free energies of individual species can be obtained from appropriate mass spectrometric studies.

8. Conclusion

We have discussed free energy-composition diagrams and have suggested that they are as useful for vaporization studies as they have been for condensed phase diagrams. The quantitative calculations would follow in a similar fashion. The relationship among free energy-composition diagrams, pressure-composition diagrams, and vaporization behaviors of binary systems have been described, and the thermodynamic properties of substances influencing vaporization behavior have been listed. So that the chemistry of vaporization processes will not be forgotten, chemical equations for vaporization reactions to be discussed in this session have been written. Some facts about congruent processes have been stated and the importance of mass spectrometry has been emphasized.

Vaporization studies can be useful for obtaining vapor pressures, heats of sublimation, partial molal heats of sublimation, heats of formation of condensed phases, dissociation energies of gaseous molecules, activity coefficients, phase diagrams, and new substances. Many of these uses will be illustrated in the following papers.

All give vapor pressures and heats of sublimation. Partial molal heats of vaporization are reported by Storms [15]. Heats of formation for condensed phases are given by Alcock, Cornish, and Grieveson [18], Ackermann and Thorn [8], Gebelt and Eick [19], and Tomilin [20]. Dissociation energies are given by Ackermann and Thorn [8] and by Murgulescu and Marta [21]. Activities have been measured by Büchler and Stauffer [22] and by Storms [15]. Phase diagrams are given by Alcock, Cornish, and Grieveson [18], Storms [15], and Tomilin [20]. Finally, new species are reported by Alcock, Cornish, and Grieveson [18], Büchler and Stauffer [22], Storms [15], and Murgulescu and Marta [21].

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Captions for Figures 1-18

Figure 1. - Free energy-composition diagram and entropy-composition diagram for ideal solutions.

Figure 2. - Free energy-composition, enthalpy-composition, and entropy-composition diagram for endothermic regular solutions.

Figure 3. - Free energy-composition, enthalpy-composition, and entropy-composition diagram for exothermic solutions.

Figure 4. - Free energy-composition diagram for ideal solid solutions and ideal gaseous solutions at a total pressure of one atmosphere. The reference states are pure solid elements for the gaseous solutions as well as for the solid solutions.

Figure 5. - Free energy-composition diagram for ideal solid solutions and ideal gaseous solutions at a total pressure between the sublimation pressures of the elements.

Figure 6. - Free energy-composition diagram for ideal solid solutions and ideal gaseous solutions at a total pressure less than that for Figure 5.

Figure 7. - Pressure-composition diagram for ideal solid solutions and ideal gaseous solutions.

Figure 8. - Schematic free energy-composition diagram for intermediate solid phase formation and ideal gaseous solutions at a total pressure between the sublimation pressures for the elements.

Figure 9. - Schematic free energy-composition diagram for intermediate solid phase formation and ideal gaseous solutions at a total pressure less than that of the sublimation pressures of the elements.

Figure 10. - Schematic free energy-composition diagram for congruently vaporizing intermediate solid phase formation and ideal gaseous solutions at the sublimation pressure of the intermediate phase.

Figure 11. - Schematic pressure-composition diagram for a two-component system containing a congruently vaporizing intermediate phase.

Figure 12. - Schematic free energy-composition diagram for elements of much greater difference in vapor pressure than in Figure 8.

Figure 13. - Schematic free energy-composition diagram at lower pressure than for Figure 12.

Figure 14. - Schematic free energy-composition diagram showing incongruent vaporization of a solid intermediate phase.

Figure 15. - Pressure-composition diagram for a two-component system containing an incongruently vaporizing solid intermediate phase.

Figure 16. - Schematic free energy-composition diagram for solid intermediate phase formation and for ideal gaseous solutions of an intermediate gaseous compound and the elements at a total pressure between the sublimation pressures of the elements.

Figure 17. - Schematic free energy-composition diagram showing the congruent vaporization of a solid intermediate phase producing primarily a single gaseous substance.

Figure 18. - Pressure-composition diagram for a two-component system showing the congruent vaporization of a solid intermediate phase producing primarily a single gaseous substance.

FIGURE 1

FIGURE 2

FIGURE 3

FIGURE 4

FIGURE 5

FIGURE 6

FIGURE 7

FIGURE 8

FIGURE 9

FIGURE 10

FIGURE II

FIGURE 12

FIGURE 13

FIGURE 14

FIGURE 15

FIGURE 16

FIGURE 17

FIGURE 18