

JUL 20 1965

COO-1140-123

1965, May 24.

CONF-641124-1

Thermodynamics of Materials at High Temperature and Low Pressure

A Paper Presented at, and Prepared for Publication
in the Proceedings of, the International Conference
on Applications of Fundamental Thermodynamics
to Metallurgical Processes

MASTER

Sponsored by

The Metallurgical Engineering Department
of the University of Pittsburgh

Held at

Pittsburgh, Pennsylvania, U.S.A.

on

1964, November 29-December 1

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These are topics about which I should like to talk this morning: (1) pressure -- composition diagrams, (2) the factors that influence the mode of vaporization and determine the vapor pressure of a substance, (3) the steps in a vaporization study, and (4) finally, a few suggestions of practical uses.

All substances vaporize and each does so at a characteristic rate dependent upon its temperature and its environment. The rates of vaporization of different substances vary enormously; yet at sufficiently high temperatures, every substance will vaporize at an appreciable and destructive rate.

It is now being recognized that the limiting factor in many high temperature systems will be the rate of loss of matter by vaporization. Formerly, melting temperatures were of utmost importance in the design and use

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of high temperature systems. As more highly refractory substances become available and as our temperature limits increase, vaporization becomes the most important mode of deterioration of materials. The purpose of this paper is to discuss some of the principles of vaporization phenomena and to relate them to the thermodynamic properties of substances. Pitzer and Brewer¹ have discussed some of these problems in an unexcelled way.

Vaporization phenomena are best elucidated through an investigation known as a vaporization study. Such a study frequently has purposes beyond that of simply characterizing the vaporization of a chemical system. Better than any other kind of study, a vaporization investigation can yield the thermodynamic properties of simple gaseous molecules. In some instances such properties can be obtained in no other way. These properties are of immense and critical importance in testing models and theories of chemical binding. In some systems, a vaporization study may yield even the thermodynamic properties of the condensed phases. A vaporization study also establishes the nature of high temperature reactions. It provides data on the vapor pressure which establishes the ultimate limit on the use of a material in a high temperature system. Finally, a vaporization study may be useful in the preparation of new compounds or in the preparation of single crystals. Professor Alcock² mentioned yesterday that there is no better way to obtain the partial molal free energies of components in solutions than by carrying out a vaporization study, and with that I surely agree. Some industrial processes are interrelated with vaporization reactions. Among these can be named metal preparations, vapor plating, and metal purification. Some reasons for vaporization studies are summarized in Table I.

TABLE I

PURPOSES OF VAPORIZATION STUDIES

1. To obtain for simple gaseous substances thermodynamic data essential for chemical binding theory.
2. To obtain thermodynamic data for refractory phases.
3. To investigate the stoichiometry of high temperature reactions.
4. To measure vapor pressures of pure substances.
5. To measure partial molal free energies and enthalpies of components in solutions.
6. To investigate the kinetics and mechanisms of high temperature reactions.
7. To prepare new compounds with elements in unusual oxidation states.
8. To produce single crystals.

THE PRESSURE -- COMPOSITION DIAGRAM

A pressure -- composition diagram is the most convenient way to show the results of a vaporization study. In such a diagram for a two-component system the total pressure is plotted as a function of the composition for a fixed temperature. Simple diagrams of this type are found in elementary physical chemistry texts.

Figure 1 shows the behavior of a system of two components, A and B, containing ideal gaseous solutions and ideal solid solutions. Whenever the pressure is very low, only the gas phase is present; whenever the pressure is high, only the solid phase is present. The total pressure varies linearly with the composition of the solid phase, as shown by the upper line, and varies along the lower curve with the composition of the gas phase. At in-

intermediate pressures and compositions as in the lenticular area, two phases are present; the compositions of these two phases are given by the intersections of a tie-line with the curves.

Now, if a system does not show ideal behavior, it may exhibit the behavior shown in Figure 2. In such a system there is no intermediate compound, but partial solubility of the components occurs. Again the total pressure is plotted as a function of the solid composition for the upper curves and of the gaseous composition for the lower curves. At low pressures only vapor is present. At temperatures and pressures falling within the area at the upper left which is labeled A (solution), the system contains a variable composition solid solution phase of B in A. Similarly at the upper right, mutatis mutandis. In the upper central part two solid phases, each saturated with the minor component, exist in equilibrium. The equilibrium phases in the lenticular areas are a solid solution and a gaseous solution with compositions shown at the ends of a tie-line. Along the horizontal line three phases, A saturated with B, vapor of composition P, and B saturated with A, exist in equilibrium.

In Figure 3 the same areas are shown, but both solid solutions yield vapors relatively richer in component B. Fractional distillation of the system represented in Figure 3 produces pure B in the distillate and pure A in the residue. Regardless of the initial composition, partial vaporization always produces a residue richer in A. If the residue is a single phase, its equilibrium pressure is less than that of the initial sample.

Fractional distillation of the system shown in Figure 2 causes the composition of the residue to change toward A if the original solid composition lay to the left of the point P, and toward B if to the right. Again,

if the residue is a single phase, its equilibrium pressure is smaller than that of the initial sample.

Now, if a binary system contains an intermediate phase, which a chemist is inclined to call a compound, the diagram might have the behavior shown in Figure 4. At the upper left and upper right are the component solid solutions. In the upper center is the variable composition solid solution sometimes called a compound, which is shown here as AB. Two-phase regions lie as shown between these single-phase regions. The vapor phase is at the bottom; the lenticular areas at the sides have the same significance as before, and those in the center represent equilibrium between the solid solution "compound" and vapor solution with compositions given at the ends of a tie-line.

The intermediate phase is shown as a congruently vaporizing one. At the minima in the curves in the center of the diagram, the vapor and solid have the same composition, and vaporization of the phase at this composition occurs at constant pressure without a composition change. Moreover, samples of the "compound" with different compositions produce a vapor relatively richer in the component which is in excess compared to that at the minimum, thus causing the residue to approach the composition of the minimum. Again the horizontal lines join the compositions of the three phases in equilibrium with one another.

Figure 5 shows the incongruent vaporization of an intermediate phase. The left and right sides and the bottom of the diagram have the same significance as previously. The vapor in equilibrium with the "compound" is always relatively richer in component B than the condensed phase. Accordingly, as vapor is removed, the residue must grow richer in component A.

Vaporization of "compound" ultimately produces the A solid solution. Fractional distillation of any sample ultimately produces pure solid A and pure gaseous B.

Figure 6 shows the results of an extensive experimental investigation on the titanium-oxygen system carried out in our laboratories by Drs. Q. D. Wheatley, P. G. Wahlbeck, H. F. Franzen, K. D. Carlson and Mr. G. D. Stone. In the titanium-oxygen system numerous condensed phases have been identified, and some are shown in the figure. The most important of these are TiO , Ti_2O_3 , Ti_3O_5 , and TiO_2 . Between Ti_3O_5 and TiO_2 are many phases discovered by Magnéli and co-workers^{3,4,5} whose compositions are described as $\text{Ti}_n\text{O}_{2n-1}$. These are only roughly indicated in the figure. The vaporization studies have revealed that TiO and Ti_2O_3 vaporize incongruently, always producing a titanium-rich vapor and a residue containing the next higher oxide. It is well known that TiO_2 loses oxygen, and so also do most of the complex phases. The congruently vaporizing composition has been shown to lie in the Ti_3O_5 solid solution region. These facts are summarized in the figure.

This kind of adiagram does not of course reveal the nature of the gaseous species. It is only the composition of the gas phase which is indicated. In the titanium-oxygen system, the principal species over the TiO phase are Ti(g) and TiO(g) ; over the Ti_2O_3 phase, the principal gas is TiO(g) ; over the TiO_2 phase, the principal gas is oxygen, but $\text{TiO}_2\text{(g)}$ is appreciable. The principal species over the congruently vaporizing Ti_3O_5 solid solution appear to be TiO and oxygen atoms.

The results of a related study on the titanium-sulfur system performed by Dr. Hugo F. Franzen⁶ are shown in Figure 7. The higher sulfides lose sulfur preferentially and Ti_2S loses metal preferentially. Accordingly, TiS is the congruently vaporizing phase in this particular system.

The uranium-oxygen system has been studied and discussed extensively and pressure-composition diagrams for it have been published.^{7,8,9} Figure 8 results from the work of Dr. E. D. Cater^{10, 11} who studied the uranium-sulfur system. The congruently vaporizing phase in this system is the uranium monosulfide. Similar diagrams have been presented for several additional two-component oxide systems and boride systems.^{12,13}

FACTORS INFLUENCING VAPORIZATION PHENOMENA

Turn now to some of the various factors that influence the mode of vaporization and the vapor pressure of a refractory substance.

The words mode of vaporization refer to the matters of the congruence of the processes and the variance of the system undergoing vaporization. It has been pointed out previously that meaningful pressures can be obtained only under certain circumstances.^{1, 14} For two-component systems either two condensed phases and one gas phase must exist in equilibrium or a single condensed phase and a gas phase of the same composition must co-exist.

Table II gives in approximate decreasing order of importance, the fac-

TABLE II

SOME FACTORS INFLUENCING EQUILIBRIUM VAPORIZATION PHENOMENA

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.
6. Curvature in the free energy-composition diagram.
7. The nature of the experiment.

tors which influence equilibrium vaporization phenomena. The stabilities of gaseous molecules are of almost overwhelming importance in establishing

the mode of vaporization and the vapor pressure. If a gaseous molecule of great stability exists, the condensed phase of that same composition will tend to vaporize congruently with a high pressure. The stabilities of the condensed phases are less important, but to illustrate the influence of this factor, consider the hypothetical case of a solid compound whose stability can be altered. As the stability of the solid compound is increased without a change in the stability of a gas phase, the vapor pressure falls. Inasmuch as congruent vaporization occurs at a locally minimum pressure, the tendency of the condensed phase to vaporize congruently increases. Also its tendency to vaporize by decomposition into the elements instead of into a gaseous compound increases.

Not only does the existence of a stable gaseous compound of a particular composition tend to cause a condensed phase of that same composition to vaporize congruently, but also its existence causes other solid phases to tend to vaporize incongruently. Brewer¹⁵ cites several such cases among the metal halides, for example, the titanium trihalide disproportionation. An interesting illustration is provided by the work of Hildenbrand¹⁶ on the lithium-aluminum-fluoride system; $\text{Li}_3\text{AlF}_6(\text{s})$ vaporizes incongruently primarily because of the appreciable stability of the gaseous molecule LiAlF_4 which has no counterpart in the condensed phase. This discussion also shows that the composition of the condensed phase, more particularly its relationship to the composition of gaseous molecules, influences the vaporization mode and pressure.

In the absence of gaseous molecules, vaporization proceeds by decomposition to the elements, and the heats of sublimation of these elements become the most important factor in establishing the mode of vaporization and the

vapor pressure. In a binary system with greatly different heats of vaporization for the components the usual mode of vaporization is by preferential vaporization of the component with the higher volatility. In extreme cases, the ultimate residue is the other component. A good example is the tantalum-boron system¹⁷ in which boron is preferentially vaporized from all the phases. Another example is provided by the chromium-boron system in which chromium is preferentially vaporized from all phases. If the elements have comparable volatility, then a congruently vaporizing compound frequently exists such as has been shown for zirconium diboride.¹⁸ These factors are tempered of course by the stability of the condensed phase; for as its stability increases its tendency to vaporize congruently by decomposition to the components increases.

Of perhaps some importance in some systems is the nature of the curvature in the free energy-composition diagram near the minimum but the author knows of no case in which this effect is important.

Finally, in some systems in which stabilities of condensed phases are very close to one another, different modes of vaporization might be expected for static experiments and for Knudsen experiments owing to the existence in the latter of the molecular weight dependence.

In many instances the mode of vaporization and the transport of matter in a vapor pressure experiment are not governed by these equilibrium properties. Brewer¹⁹ has pointed out numerous times that very low rates of vaporization are expected if the molecular configuration in the vapor differs radically from that in the condensed phase. High energy barriers contributing to slow rates of reaction may completely suppress the equilibrium properties. Notable among these cases are phosphorus,²⁰ As_2O_3 ,²¹ and several metallic nitrides.^{22,23} In some cases, particularly those in which incon-

gruent vaporization occurs, surface impoverishment arises because of slow rates of diffusion, and vaporization rates are much lower than equilibrium rates.

THE COURSE OF A VAPORIZATION STUDY

Ordinarily a vaporization study proceeds through several distinct parts as shown in Table III.

TABLE III

STAGES IN A VAPORIZATION STUDY

1. General characteristics of the chemical system.
2. Identification of the vapor species.
3. Writing of the net reaction.
4. Measurement of the vapor pressure.
5. Calculation of thermodynamic properties.
6. Deduction of molecular structures and constants.
7. Measurement of the kinetics of vaporization.
8. Establishment of the mechanism of vaporization.

These are listed in the order in which they might most reasonably be accomplished, but rarely is this order followed in actual practice. In the initial characterization of the vaporization process, one first investigates possible reactions between the sample and other parts of the system, which are numerous. A crucible is frequently present; residual gas is present in a vacuum system; gases in a transpiration experiment are not always pure; shields surround the vaporizing sample; and sometimes a suspension is present in the apparatus. The apparatus should be designed and operated in such a fashion so as to reduce or eliminate reactions between the sample and the other ingredients. This initial characterization also is used to establish which phases are congruently vaporizing and what is the

variance of the system. Simple, easy experiments can be used to accomplish these investigations. The crucible material may be changed; the apparatus may be altered; x-ray diffraction studies may be employed; a mass balance can be attempted; a series of step-wise vaporization experiments can be performed; chemical analyses can be performed; and the closed crucible technique may be employed. The results of the initial characterization of the chemical system are usually presented in the form of a pressure-composition diagram similar to those described previously.

After this study into the properties of the system has been accomplished, the gaseous species should be identified. The mass spectrometer has been spectacularly successful in deducing the vaporizing species²⁴ but other techniques may be used.

At this stage meaningful vapor pressure measurements may be made. The methods will depend primarily on the magnitude of the pressure to be measured. At high pressures, a static or transpiration apparatus can be used. The Knudsen method, the Langmuir method and the torsion effusion method are appropriate for measurements at low pressures. These methods are adequately described elsewhere.^{25,26,27,28,29} Two kinds of apparatus used in our laboratory are shown in Figures 9 and 10. In Figure 9, a crucible containing the sample is placed in the center of a glass apparatus and is heated inductively by 450kc rf power. Gases arising from the vaporization processes escape through a hole in the lid of the crucible and travel upward in the apparatus. The weight loss of the crucible can be measured, or the vapor escaping from the crucible can be collected on a target. After a target has been exposed to the vapor stream, it can be ejected and allowed to fall into a receiver. Meanwhile, the next target falls into the receiving position. The collected

matter can be assayed by one or more of several techniques. Modification of this technique employs an inverted tube in place of the target collection attachment so that the collected sample can be chemically dissolved and appropriately analyzed.

In Figure 10, an eddy current concentrator is shown. The sample is placed inside the concentrator and heated either directly, if it is a conducting sample, or by radiation from a susceptor. With this apparatus the weight loss of the sample is measured, although it is possible under certain circumstances to collect the vapor for subsequent assay.

Vapor pressure data obtained from the measurements can be appropriately treated by well-known methods to deduce the thermodynamic properties for the reactions that occur. Both second-law and third-law evaluations should be attempted.

Most vaporization studies terminate at this point, but one recent development illustrating the use of vaporization studies for establishing molecular constants was accomplished independently by Cubicciotti and Eding³⁰ and by Hildenbrand.³¹ They deduced values for vibrational frequencies by comparing second-law and third-law results on dihalide molecules.

Studies of the kinetics and mechanism of vaporization are underway in several laboratories. It is to be expected that activity in this field will increase rapidly in the next few years.

PRACTICAL USES

The most important uses of high temperature vaporization studies from the point of view of a chemist are those directed mainly toward establishing the principles of chemical binding; obtaining vapor pressures and thermodynamic properties of substances; and preparing new compounds. But in addi-

tion, certain practical aspects of vaporization studies can be cited. An entire industrial endeavor is associated with vapor plating. Yesterday's newspaper³² contained an article concerning a new process by which aluminum is to be plated on steel. Another interesting development which has occurred as a result of high temperature investigations was presented in the paper by Brewer and Rosenblatt³³ on the principles of the purification of metals by evaporation and by vacuum fusion.

Still another development not closely related to vaporization processes but which came from Professor Brewer and which therefore must be mentioned is his theoretical paper on the deduction of phase diagrams.³⁴ In this report he predicts about two billion phase diagrams.

ACKNOWLEDGEMENTS

The author is pleased to acknowledge the support of the United States Atomic Energy Commission through its Contract At(11-1)-1140 with the University of Kansas.

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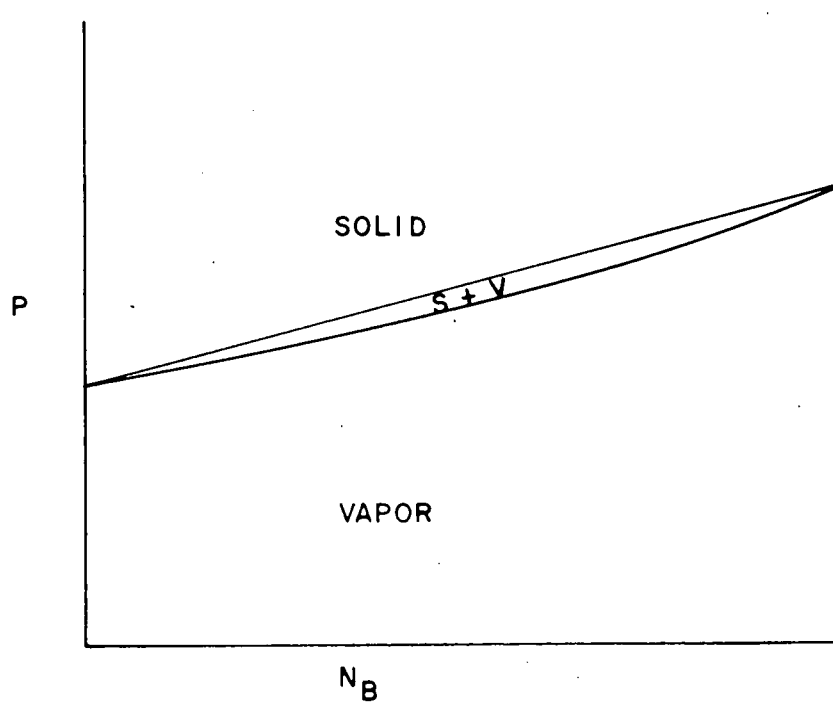


FIGURE 1. IDEAL SOLUTION

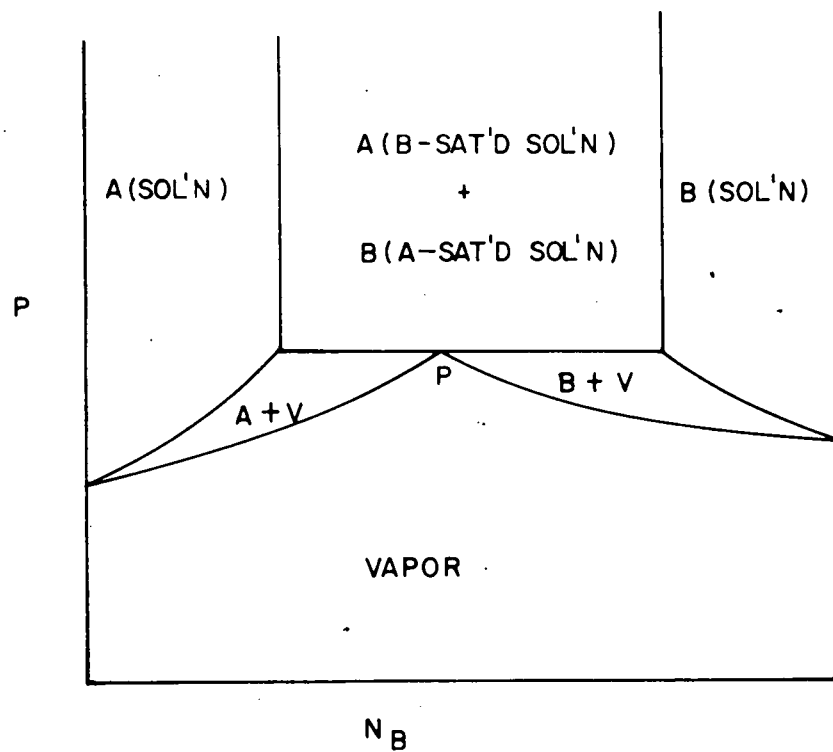


FIGURE 2 .

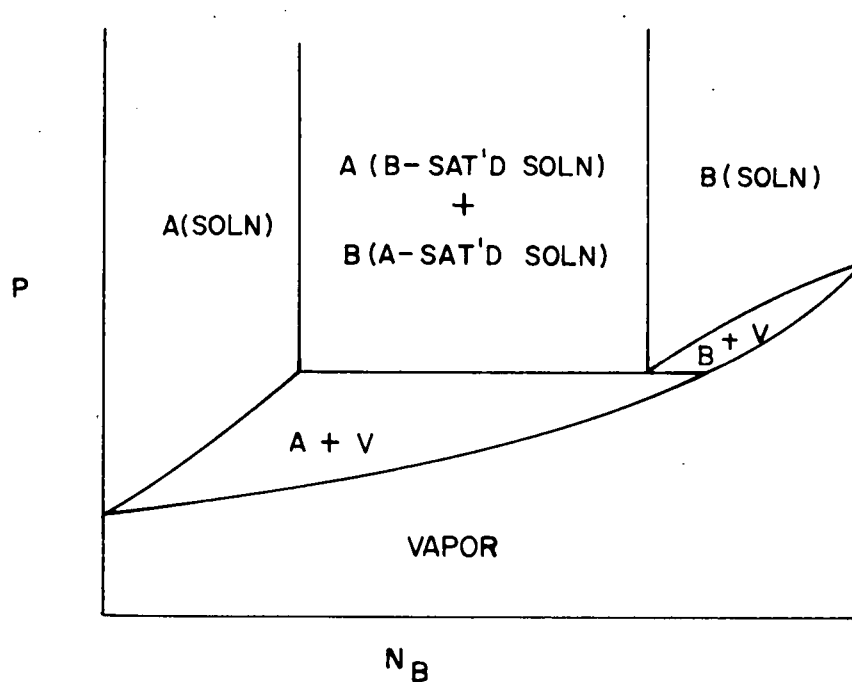


FIGURE 3

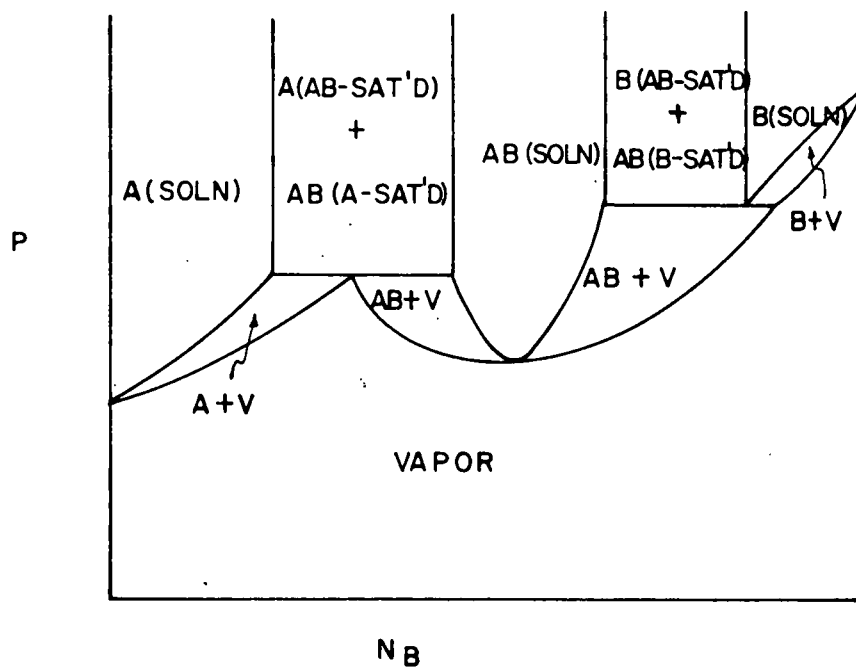


FIGURE 4

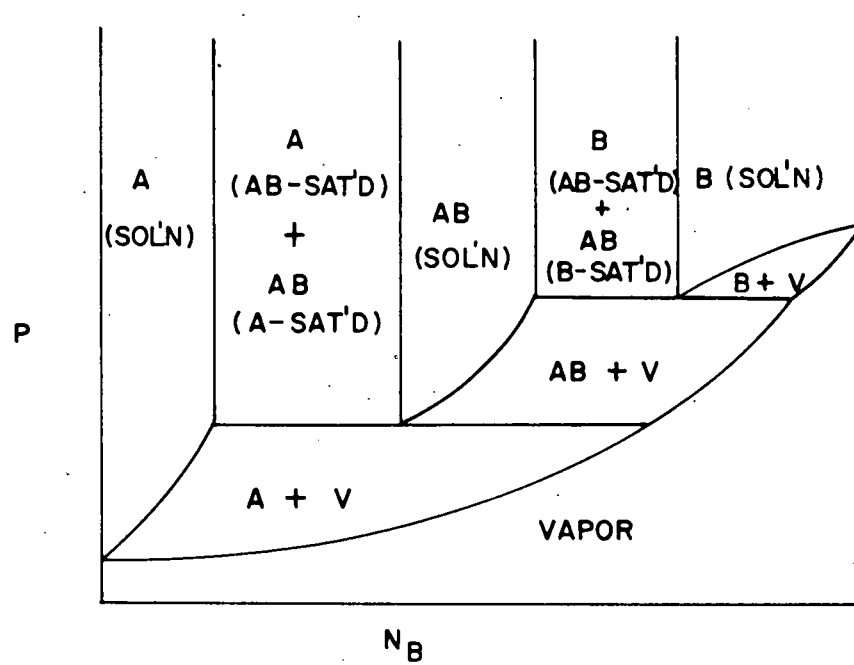


FIGURE 5 .

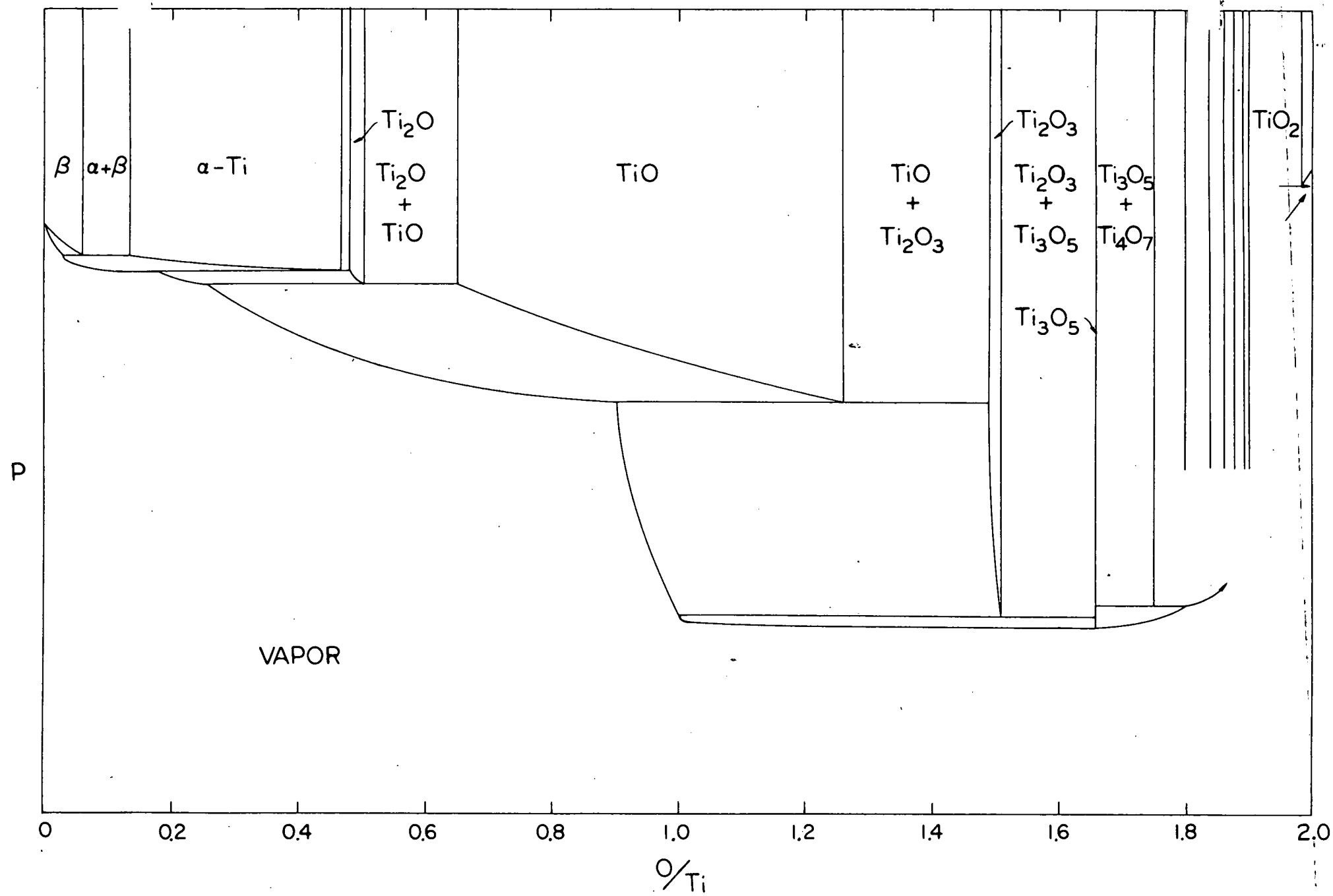


FIG. 6

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SCHEMATIC PRESSURE-COMPOSITION PHASE DIAGRAM

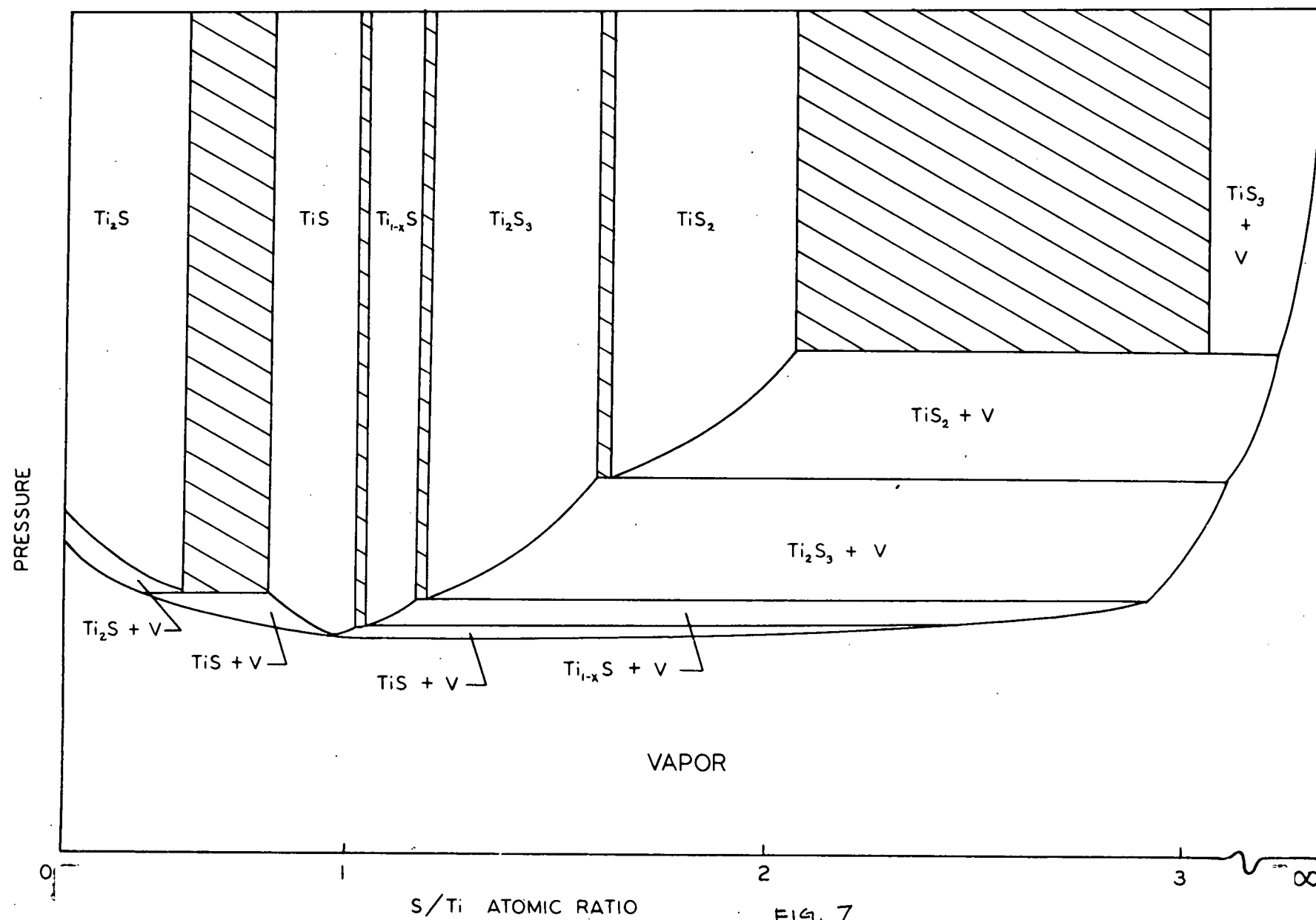


FIG. 7

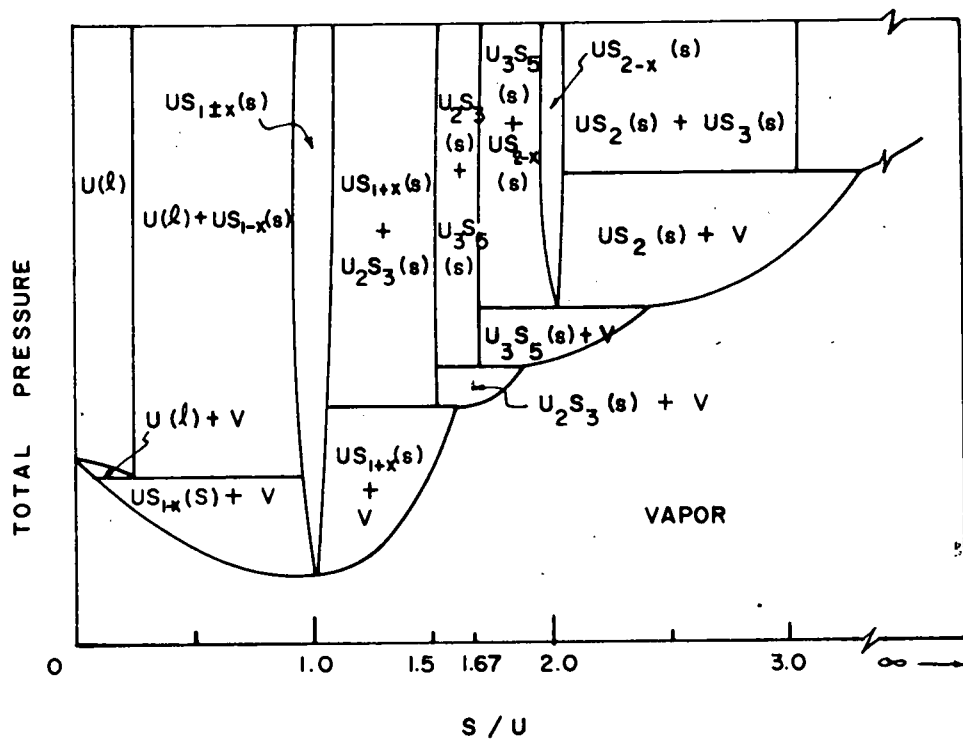
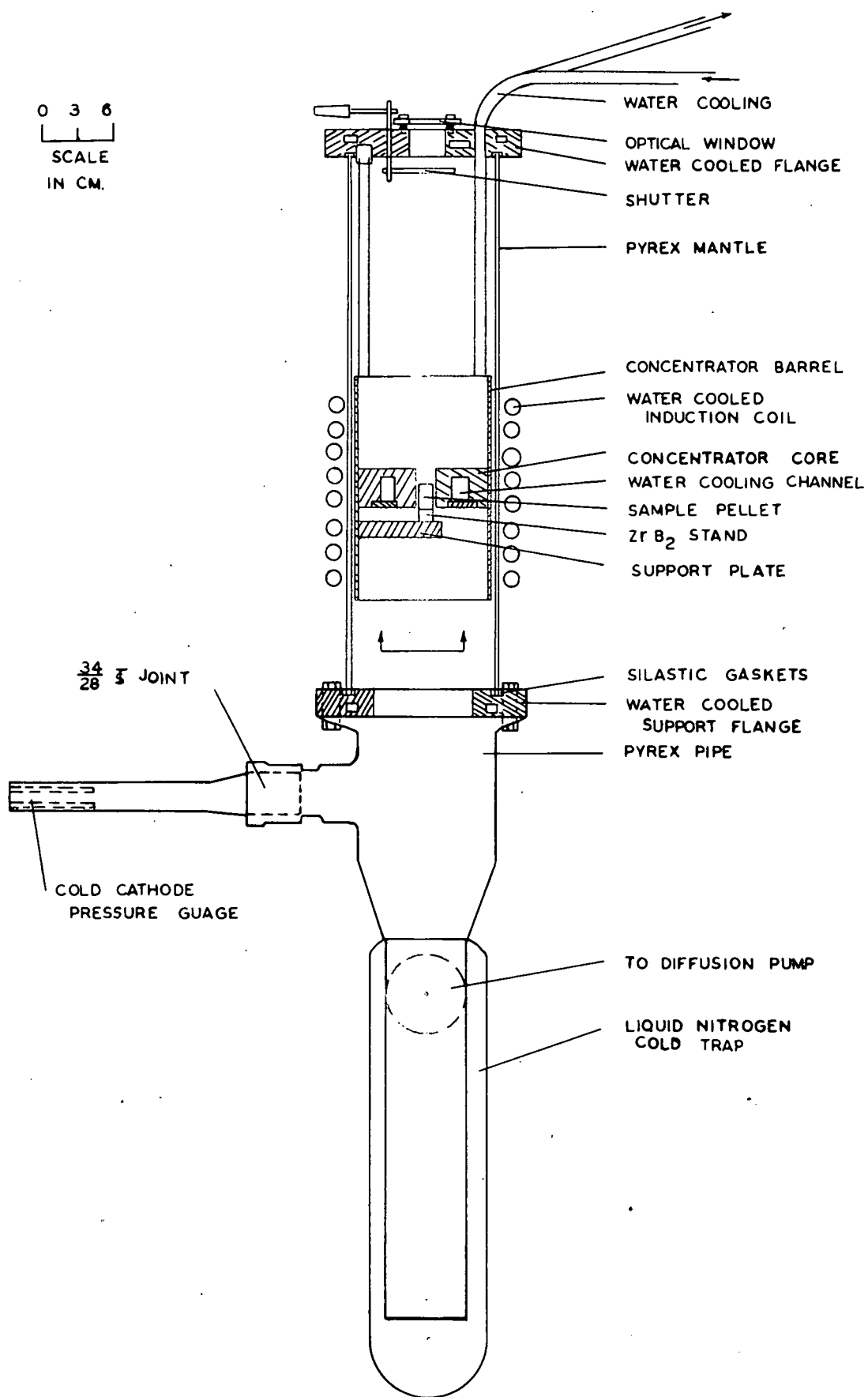


FIGURE 8

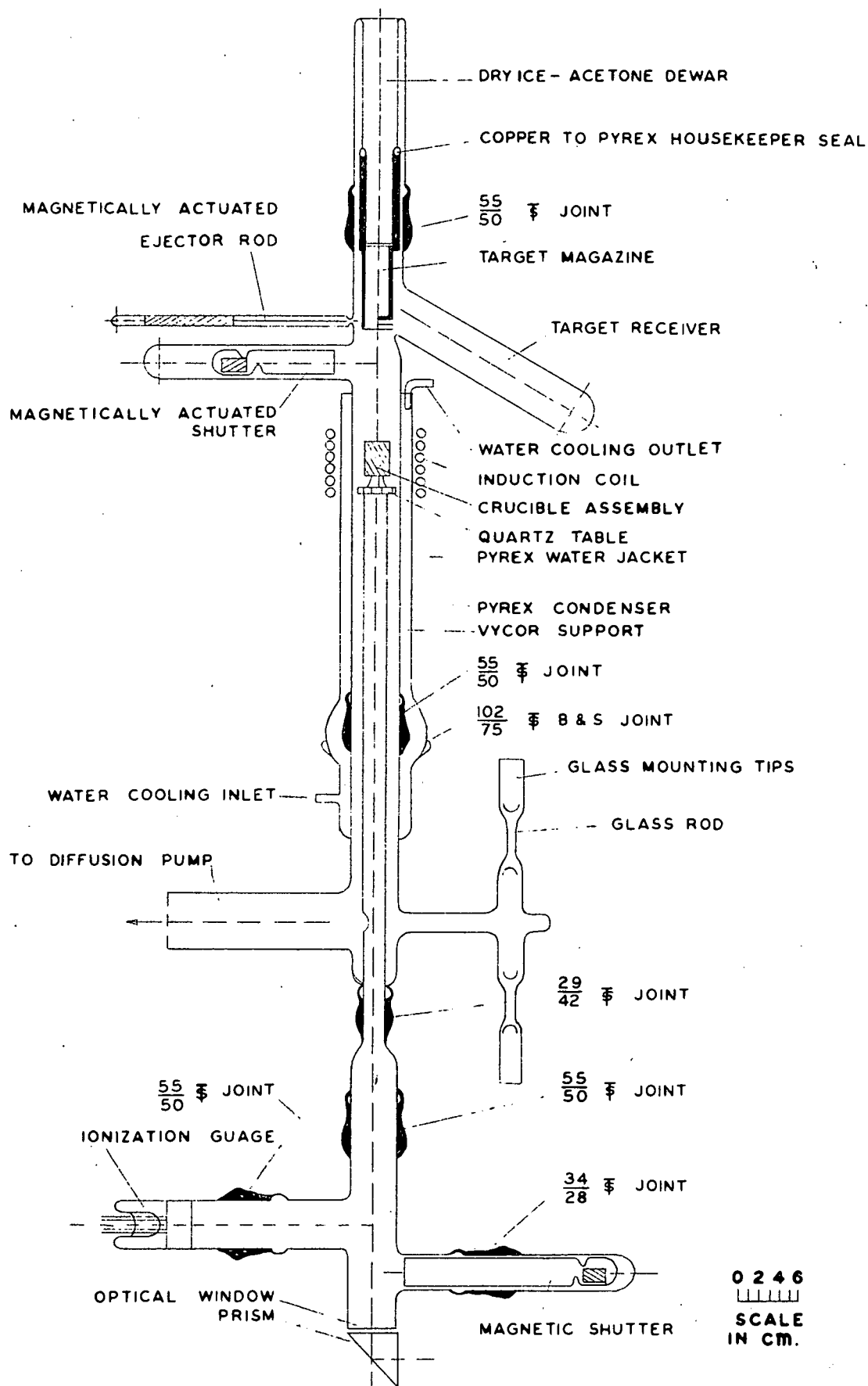
0 3 6
SCALE
IN CM.



CURRENT CONCENTRATOR APPARATUS

VACUUM SYSTEM *14

FIGURE 8-9



Vacuum Effusion Apparatus

FIGURE 8-3 10