NASA TM-83757

NASA Technical Memorandum 83757

NASA-TM-83757 19840023213

Calculation of Vaporization Rates Assuming Various Rate Determining Steps: Application to the Resistojet

Charles E. May
Lewis Research Center
Cleveland, Ohio

August 1984

NASA

CALCULATION OF VAPORIZATION RATES ASSUMING VARIOUS RATE DETERMINING STEPS: APPLICATION TO THE RESISTOJET

Charles E. May
National Aeronautics and Space Administration
Lewis Research Center
Cleveland, Ohio 44135

E-2244

SUMMARY

The various steps that could control the vaporization rate of a material are discussed. These steps include the actual vaporization, flow rate of matrix gas, chemical reaction, gas diffusion, and solid state diffusion. The applicable equations have been collected from diverse appropriate sources, and their use is explained. Rate equations are derived for conditions where more than one step is rate controlling. Calculations are made for two model materials: rhenium which vaporizes congruently, and tantalum carbide which vaporizes incongruently. The case of vaporization under thermal gradient conditions is also treated. The existence of a thermal gradient in the resistojet means that the vaporization rate of a material may be only one thousandth of that predicted under isothermal conditions. Calculations show that rhenium might have a 100 000 hr lifetime at temperature in a 2500° C resistojet. Tantalum carbide would have a life of only 660 sec under similar conditions.

INTRODUCTION

Over the past years, there has been frequent need to calculate the expected vaporization (sublimation) rates for materials to be used in various design concepts. Recently, we have made such calculations for a 2500° C version of the resistojet. The theoretical equations are well established, but their application to specific conditions is sometimes a problem. It occurred to us that it would be helpful for future use to assemble into a single document (this report) these equations as well as effective ways to use them in a practical vaporization problem. Because of the large amount of information to be covered in this report, we have divided it into four parts; a preview of each part follows: Parts I and II are concerned with the understanding of the principles and derivation of rate equations. Parts III and IV are oriented toward practical problems.

In Part I, we first discuss the general vaporization concepts and define several ways of expressing vaporization rates. In Part I, we also present equations for calculating vaporization rates if a single kinetic step controls the process. The simplest calculation of vaporization rates, of course, involves the (Langmuir) equation which gives the rate for the vaporization step, itself. This equation is applicable when a material is exposed directly to vacuum. In actual practice, this normal vaporization (nv) step may not be rate controlling. When vaporization occurs within a partial enclosure, the effective rate is slowed down, and the vapor species builds up in the container; the rate becomes controlled by the rate of escape from the container which is determined by the area of the escape hole. When a matrix gas is

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present in the system, there are several steps that might be rate controlling: the flow of the matrix gas, a chemical reaction, or the diffusion of the vaporizing species through the matrix gas. Moreover, if the material being evaluated vaporizes incongruently, solid state diffusion may become rate controlling. Incongruent vaporization refers to materials for which the ratio of the rates of vaporization of the various components of the material is not equal to their ratio in the solid material. For such materials the composition of the solid material changes as vaporization progresses. Note that this report is not concerned with vaporization induced by laser, electron, or ion bombardment.

The experimental conditions determine which step is rate controlling. Apriori, one cannot know which steps in a particular overall process are important. Therefore, in order to discuss the vaporization process, we had to direct the discussion and calculations toward a specific system. We chose the resistojet; it is a good model system because most of the aforementioned potentially rate-controlling steps might apply. As model materials we chose rhenium (Re) and tantalum carbide (TaC). These are good choices because the vaporization behavior of the one contrasts the other: the Re vaporizes congruently, and TaC vaporizes incongruently. Moreover, chemically TaC is reactive while Re is relatively unreactive under the conditions of interest. The principles applied to Re and TaC in this report apply equally well to ceramics, polymers, alloys, composites, and all other materials.

We begin Part II by giving the equations that show how kinetic steps can be combined to give kinetic rates that are controlled by two or more individual steps. Via these equations, we have derived the equations which give the vaporization rate when the steps discussed in Part I are coupled. Some of the equations are relatively complex, being dependent on both time and location in a system. Calculation of vaporization of both Re and TaC were again made; dependence of rates on time and location are illustrated graphically.

It should be noted that the actual rate of vaporization in a complex physical system can only be obtained experimentally. A calculated value is generally an equilibrium or steady state value which may never actually be reached; the calculated value should be considered to be merely a maximum. Also in this report, several approximations are used, both in parameters (such as vapor pressure) and in the derivations of the equations. Moreover, ideal behavior is assumed in most cases so that the equations will be more widely applicable. Some of the calculations are based on the parameters specific to our concept of the resistojet, so that the final conclusions as to the nature of the rate-controlling step may not be applicable to resistojet concepts with quite different parameters.

In Part III, we analyze the kinetic steps as to which are most important in an isothermal system. Our reasoning is then applied to the resistojet concept, assuming isothermal conditions. Calculated vaporization rates for Re and TaC are again given. Other topics discussed in Part II are the effect of heating and cooling periods and the use of a sacrificial vaporizing material.

In the beginning of Part IV, we discuss the vaporization rate as a function of temperature. Using two different approaches, we derive rate equations for the condition of a temperature gradient. When appropriate, the vaporization rates for Re and TaC were calculated as a function of gradient, location, and time. The significance of a temperature gradient in the resistojet is discussed. Finally, the expected lifetimes of Re and TaC are calculated using all the pertinent kinetic steps and assuming the existence of a 10° C/cm gradient. From a vaporization viewpoint, Re appears to be a satisfactory material with a potential lifetime of 100 000 hr while TaC does not.

Our findings are summarized at the end of this report in the Synopsis. As an aid to the reader in the use of the equations presented, we have included a Glossary of symbols in the Appendix. In order for this report to be useful to people of all fields for designs in which vaporization may be a problem, simple language is used and concepts are repeated where necessary. Of course, all sections cannot be of uniform simplicity. The source and use of equations are explained, but detailed derivations of equations are minimized. When derivations are given, they are intended as a method of explaining the use and meaning of the desired equation.

THE RESISTOJET

At this point it is worthwhile to give a little discussion about the resistojet (ref. 1). The parameters of one design are given because some of the vaporization equations in this report require the use of such values.

The original concept of the resistojet involved merely the resistive heating of a gas to be expelled from a spacecraft to get added thrust. A more recent concept includes an additional idea, that of converting waste material into a gas and then expelling it from the resistojet to get extra thrust. Thus, the newer concept of the resistojet would solve two problems. The design for the resistojet is continually changing. The schematic given in figure 1 is sufficient for our discussion of the vaporization problem.

The best gas for the operation of the resistojet in terms of thrust is hydrogen (H_2). However, other gases that may be expelled are: water vapor, carbon dioxide, carbon monoxide, nitrogen, ammonia, and hydrazine; these gases give less thrust than hydrogen and, in general, are more corrosive. The temperature proposed for the resistojet is 2500° C (2773 K). At present, the desired time for operation of the resistojet at this temperature is 1000 hr; but the desired time will probably increase. In our discussion of vaporization, we are interested in the hottest portion of the system, the place where the vaporization rate is expected to be the greatest. This is the final tube before the nozzle (fig. 1). This hottest portion of the system is also the place that is most susceptible to chemical reaction with the flowing gases. This tube might possibly be made from either rhenium or tantalum carbide because both of these materials have high melting points and are electrical conductors which enables direct electrical heating.

The calculations in this report are based on the following parameters for the resistojet. The tube's length (L) is assumed to be 10 cm; its inside diameter (2R'), 1 mm; and its wall thickness (S), 0.1 mm. A value of 3.16 atm is taken as the pressure (P(m)) of the flowing matrix gas. The pressure drop along the tube is presumed to be negligible. The flow rate (F') is 5000 standard cm^3/min (268 cm^3/sec at 2773 K and 3.16 atm pressure).

PART I: SINGLE STEP RATE-CONTROLLING PROGRESS

General Concepts

In the actual vaporization process, the molecules (or atoms) do not just fly off the crystal lattice of the solid. Some of the molecules on the surface are undoubtedly mobile, not bound to a particular position of the crystal lattice but free to move over the entire surface of the material. If molecules on the surface were not mobile, recrystallization would be impossible. The mobile molecules that have sufficient energy can leave the surface through vaporization. The number which vaporize per unit should be proportional to the activity (number) of the mobile molecules on the surface for any given temperature. This is a physical picture of vaporization but does not lead to an equation for the calculation of the rate of vaporization.

To obtain the desired equation, one must start with a picture of the molecules in the vapor above the solid and assume they are in equilibrium with the molecules in the solid. Equilibrium means that the number of molecules vaporizing in a given time is equal to the number condensing (returning to the solid from the gaseous state) in the same period of time. Thus, the number of molecules in the solid does not essentially change at equilibrium. The rate of condensation, N', is equal to the rate at which molecules strike a unit surface area in a unit time multiplied by the fraction, Q', that adheres. The resultant equation is known as the Langmuir equation (ref. 2, p. 278).

$$N' = 1.013\times10^{6}\ P\ Q'/\mathrm{sqr}(2\pi RTM) \simeq a\ P/\mathrm{sqr}(M) \qquad (1)$$

where N' is the rate in terms of moles/cm^2 sec, a mole being the number of molecules that has a weight in grams equal to the molecular weight. The P is the pressure in atm; the factor, 1.013×10^6, converts the pressure to dynes/cm^2; M is the molecular weight of the species in grams; R is the gas constant (8.31×10^7 ergs/K); T is the temperature in K; and the "a" is equal to $1.013\times10^6/\mathrm{sqr}(2\pi RT)$ which is 0.842 g$^{1/2}$ moles$^{1/2}$ cm^2 sec^{-1} atm^{-1} at $T = 2773$ K.

The Q' in equation (1) is called the sticking factor or accommodation coefficient and can have any value from zero to one. When Q' is set equal to one, we again have the equation that gives the number of moles of a material striking a unit area in a unit time. It is known as the Knudsen equation. The Knudsen equation is derivable from the kinetic theory of gases and has been shown to be correct experimentally under near vacuum conditions. In this report, Q' is always assigned the value of one. As alluded to before, under equilibrium conditions, the N' in equation (1) becomes the number of moles vaporizing from a square cm in a sec, P becomes the vapor pressure (P(v)), and M is the molecular weight of the vaporized species. Thus, we now have an equation that is applicable to the vaporization process under vacuum conditions. Under nonvacuum conditions, the net rate of vaporization is determined by the difference between the vapor pressure and the pressure of the vaporized species in the surrounding space. Because this pressure can be a function of the distance (Y) along the enclosure (tube), we refer to it as P(Y). It follows that

$$N' = a\ (P(v) - P(Y))/\mathrm{sqr}(M) \qquad (2)$$

One can more easily comprehend the magnitude of the vaporization rate if it is expressed in units of g/cm^2 sec. We will call this quantity, W, and the equation by which it is calculatable is obtained by multiplying equation (2) by the molecular weight of the vaporizing species.

$$W = a\ (P(v) - P(Y))\ \mathrm{sqr}(M) \tag{3}$$

When vaporization occurs into vacuum, we will term the process normal vaporization and equation (3) becomes

$$W(nv) = a\ P(v)\ \mathrm{sqr}(M) \tag{4}$$

The total rate of vaporization can always be obtained by multiplying the average rate per unit area by the inside area of the tube ($A(s) = 2\pi R'L$ with R' being the radius and L, the length).

The recession rate, G, is another way of expressing the rate of vaporization. It is the rate at which the material decreases in thickness (cm/sec). Its value can generally be obtained by dividing W by the density of the material, D. Thus,

$$G = a\ (P(v) - P(Y))\ \mathrm{sqr}(M)/D \tag{5}$$

By using the room temperature density, one can compare G with the room temperature thickness.

Throughout this report, we have endeavored to use a uniform set of symbols. However, because W always refers to the rate of vaporization, this is equivalent to continually redefining it in terms of the rate-controlling step presently being considered. In a similar manner, N', and G are likewise redefined. Doing this emphasizes the concept of loss by vaporization as well as minimizes the use of subscripts and foreign alphabets. Another symbol that we use in this way is Z, the ratio of the rate of vaporization under a particular set of conditions (pc) to the rate under normal vaporization condition (nv).

$$\begin{aligned} Z &= W(pc)/W(nv) = G(pc)/G(nv) \\ &= N'(pc)/N'(nv) \end{aligned} \tag{6}$$

The final form of the equation is only true if no chemical reaction occurs. The reason for this will become evident in a subsequent section; it involves the difference between the molecular weight of the normally vaporizing species and that of the chemically formed species. The calculation of Z for each rate-determining step eliminates the necessity of always calculating three different values: W, G, and N'. Rates that are time or space dependent cannot always be expressed in terms of Z. Therefore, at appropriate places in this report, other measures of the vaporization rate will be introduced.

Equation (4) gives the rate under normal vaporization conditions; it is generally considered to be the maximum rate of vaporization. Steps or processes that occur in series with the vaporization process can slow down the rate; but they can never speed it up. Only a process that parallels (bypasses) the normal vaporization step (e.g., chemical vaporization) can result in faster vaporization. As we shall see, any of these steps may become the sole rate-controlling step. After we have completed the treatment of normal vaporization, we will discuss the other possible factors as rate-controlling steps: partial enclosure, matrix gas flow, chemical reactions, gaseous diffusion, presence of a coating, solid state diffusion - controlled incongruent vaporization, and miscellaneous factors.

Normal Vaporization

In this section we will consider vaporization into a vacuum (eq. (4)). At this time there is no grounds for the selection of a back pressure, P(Y) (eq. (3)). However, in Part II of this report, the quantity P(Y) will be considered because it arises out of the interactions which are discussed there.

Congruent vaporization. - When equation (4) is used, the value obtained is the rate of vaporization of a material from a clean surface under vacuum conditions. To use this equation, only the vapor pressure, and molecular weight have to be known. The answer obtained is independent of all parameters associated with the experimental setup. For a material such as Re which vaporizes congruently, the calculated rate of vaporization will be virtually constant as long as the solid material remains.

The vapor pressure of rhenium is 5.92×10^{-8} atm at 2773 K (ref. 3, p. 447); its molecular weight is 186.2 g/mole. These values yield a normal vaporization rate, W(nv), at 2773 K of 6.8×10^{-7} g/cm^2 sec. In figure 2 the values of W are given as a function of temperature. Because the density of Re is 20.53 g/cm^3 (ref. 4), the recession rate, G, is 3.21×10^{-8} cm/sec or 1.19 µm/hr.

Incongruent vaporization. - Most structural materials are not pure substances. Many are one phase alloys (solid state solutions). From a vaporization viewpoint, such one phase alloys behave in a similar manner to other solutions such as aqueous solutions and polymers containing plasticizers. In general when an alloy vaporizes, the vapor consists of more than one type of species. It is likely that a different species is present for each component of the alloy. Ideally for a single phase alloy, the partial vapor pressure, P(j), for each component (j) would equal the vapor pressure of the component in its pure form, P'(j), times its mole fraction in the alloy, n(j).

$$P(j) = n(j)\, P'(j) \tag{7}$$

The corresponding value of W(j) could then be found via equation (4) and the total rate of vaporization of all components would be the sum of the individual rates.

$$W = \sum W(j) \tag{8}$$

If all the components had the same vapor pressure and molecular weight, then all of the components would vaporize in the same ratio as they are present in the solid material. Such a condition would still be called congruent vaporization. However, in the usual case of an alloy, the pressures and the molecular weights of the components are not the same, so that the composition of the material would change as vaporization proceeds. This change in composition (mole fractions of the components, n(j)'s) means that for incongruent vaporization, the actual rate of vaporization changes with time and that the rate calculated via equations (4), (7), and (8) are only initial rates when the initial values of n(j) are used.

Furthermore, most alloys are not ideal solutions so that the values of W(j) obtained assuming ideality are only approximations. If an experimental value for P(j) is available, it should be used in preference to one obtained from equation (7). Note that in some alloys, only a single component may be volatile. This is analogous to an aqueous salt solution where the water can vaporize leaving the salt behind.

Some materials such as TaC also vaporize incongruently even though they are generally considered to be compounds. No vapor species such as TaC is known to exist: the vapor species over solid TaC are Ta, C, and its polymers (e.g., the trimer, C_3). Moreover, equation (7) is not obeyed for either Ta or the C species. To understand better the vaporization of TaC, let us look at its temperature - composition phase diagram in figure 3 (ref. 5, p. 84). At the one-to-one atom ratio, the TaC phase is in equilibrium with solid carbon at 2773 K. This means that the partial vapor pressure of a carbon species arising from TaC is the same as that for the respective one from solid carbon. Also, at the stoichiometric composition of TaC (ref. 5, p. 99), the carbon vaporizes much faster than the Ta, and the dominant vapor species is the carbon trimer, C_3, because it has the highest vapor pressure above free carbon (ref. 3, p. 445). The second most important species is the carbon monomer, C.

For C_3, the value of the vapor pressure is 1.48×10^{-4} atm at 2773 K. Equation (4) requires using the molecular weight of the trimer (36.03 g/mole) for the value of M. Thus, the vaporization rate, W, is calculated to be 7.48×10^{-4} g/cm^2 sec. The vapor pressure of the C monomer species (M = 12.01 g/mole) is 7.17×10^{-6} atm, resulting in a W of only 2.09×10^{-5} g/cm^2 sec. The value of W(nv) should be taken as the sum of W(C) and W(C_3), 7.69×10^{-4} g/cm^2 sec. However, in some portions of this report, the contribution of the C monomer is disregarded because of the complications that would arise. In figure 2 are plotted the values of W for C and C_3 as a function of temperature. The graph shows that the vaporization rate of the C monomer species accounts for less than three percent of the total vaporization rate of the carbon from TaC. Here, we reemphasize that the calculated values for TaC are not expected to be constant because it vaporizes incongruently. However, as long as the distinct carbon phase exists in the surface of the TaC material, the vaporization rate will equal the initial rate. Subsequent rates of vaporization are controlled by solid state diffusion which will be discussed much later.

The vapor pressure of the Ta species over TaC is about 9×10^{-11} atm (ref. 5, p. 101). From equations (4) and (6), one finds W(Ta) to be 1.02×10^{-9} g/cm^2 sec and Z(Ta) to be 1.3×10^{-6}. This relatively low rate confirms the fact that the carbon vapor species are the dominant ones.

When a material vaporizes incongruently, the evaluation of G is not always a straight forward calculation. Assumptions are sometimes required. If TaC is a two phase region (as the phase diagram indicates; fig. 3), then G can be obtained by using the density of graphite (2.25 g/cm^3; ref. 4) in equation (5). The resultant value of G is 3.42×10^{-4} cm/sec or 1.23×10^{4} µm/hr. If one assumes that TaC consists of only a single phase and that its density is not very sensitive to carbon concentration, G is obtained by using the density of TaC (13.9 g/cm^3, ref. 4) in equation (5). The value of G from this calculation is 5.53×10^{-5} cm/sec or 1.99×10^{3} µm/hr. A third and least likely assumption involves the conversion of the TaC phase into another phase (e.g., Ta) as the carbon vaporizes. The following equation would then be applicable.

$$G = W\,(M(TaC)/D(TaC) - M(Ta)/D(Ta))\;/\;M(C) \tag{9}$$

The density of Ta is 16.6 g/cm^3. This third assumption gives a value for G of 1.89×10^{-4} cm/sec which is 6.82×10^{3} µm/hr. The phase relationships for the system under study determine which of these three methods should be used. Thus, for other types of incongruently vaporizing materials, the last method of calculation may be the most preferable. However, when one is only interested in order of magnitude values, no great care is needed in the selection of the equation. Throughout the rest of this report when G is calculated for TaC, we will use equation (5) with D equal to the density of graphite.

In discussions involving incongruent vaporization, it is helpful to use the term F(r), the fraction of the volatile component remaining in the solid material. This can be calculated as follows if W can be considered to be constant.

$$F(r) = W\,T'/D\,E'\,S \tag{10}$$

In this equation, T', is the time, S is the original thickness of the material, and E' is the original weight fraction of vaporizing species. For the incongruently vaporizing TaC, E' is M(C)/M(TaC), 0.062. Equation (10) may also be used for congruently vaporizing material (e.g., Re); in this case, E' would be unity. Another concept that is sometimes helpful is the useful lifetime, T". We have arbitrarily defined T" as the time at which F(r) = 0.5. If W is again assumed to be constant.

$$T'' = D\,E'\,S/2\,W = D\,E'\,S/2\,Z\,W(nv) \tag{11}$$

Equation (11) like equation (10) is applicable to both congruently and incongruently vaporizing material; this is due to the presence of E' in these equations. The value of T"(nv) for TaC would be 5.6 sec while T"(nv) for Re would be 42 hr. Care must be taken when comparing lifetimes between various materials; many materials are unusable long before the value of F(r) would become reduced to 0.5.

As far as vaporization is concerned, our two model materials may be called extremes. While the vaporization of rhenium is very small at 2773 K the vaporization of carbon component of the TaC is relatively large. As we shall see later, chemical vaporization can even increase the rate of vaporization for TaC. However, other factors may tend to decrease the actual rate of vaporization of TaC to a value less than the values calculated from equation (4).

<u>Presence of several phases</u>. - In many alloys, the existence of multiple phases is a necessity. The additional phases add strength or other desirable

qualities. For such a system, one must consider vaporization of each component (j) from each phase (i). One uses P(j,i) and M(j) via equation (4) to obtain the corresponding value of W(j,i). The value of W(j), the overall vaporization rate of the j^{th} component, should be obtainable as follows.

$$W(j) = \Sigma(W(j,i)\ A(i)) \ /\ \Sigma A(i) \tag{12}$$

where A(i) is the area of the i^{th} phase on the surface of the material. Equation (8) is then used to calculate the total value of W. When the phases are in equilibrium, the calculations simplify because the vapor pressure of a specified component is the same in all the phases. Equation (12) becomes unnecessary, and the calculations are the same as for a one phase system. However, while the vapor pressure of the j^{th} component is the same in all phases, its concentration is not likely to be the same. Thus, as vaporization proceeds, displacement from equilibrium may occur.

One can recall that at the stoichiometric composition of TaC (fig. 3), two phases exist: C and substoichiometric TaC. From the discussion in the previous paragraph, one can now see why the system was treatable as one phase. Another point to note from figure 3 is that if equilibrium is allowed to persist as vaporization occurs, the carbon phases will disappear, resulting in a truly one-phase system.

Evacuated Partial Enclosure

When vaporization occurs in an evacuated enclosure, the pressure closely approaches the vapor pressure of the material present; the rate of vaporization is thus controlled by the area of the exit hole. The rate of vaporization per unit area of the exit hole is given by equation (4). The average rate per unit inside area of the enclosure is obtainable by multiplying this value by the ratio of the area of the hole, A(h), to the inside surface area, A(s). Thus

$$W = a\ P(v)\ sqr(M)\ A(h)/A(s) = a\ P(v)\ R'/2\ L \tag{13}$$

The final form of the equation is applicable to our resistojet where $\pi R'^2$ is the hole area and $\pi R'L$ is the inside area. It becomes obvious that

$$Z = A(h)/A(s) = R'/2L = 0.0025 \tag{14}$$

and that Z is independent of the material used. Via equation (6) the respective values of W for Re and TaC would be 1.7×10^{-9} and 1.87×10^{-6} g/cm^2 sec. Such average values will increase with the size of the exit opening. In the present approximation, the vaporization is assumed to be uniform over the entire inside area. In a later section, we will see that when the existence of an enclosure is coupled with the vaporization process, the values of W and Z are dependent on Y, the distance along the tube (enclosure). Equations (13) and (14) may be of use in many systems. However, for the resistojet, they are applicable only during times that the exit tube may be at temperature without the presence of a matrix gas.

One should note that vaporization from an evacuated container with an orifice (small properly shaped hole) is the basis of the Knudsen method of determining vapor pressures. The vapor pressures are calculated, of course, via equation (4). Also note that in Part II of this paper, discussion of the interaction of this mode of vaporization will be minimal because this mode can interact with very few of the other modes. The other modes, in general, require the presence of a matrix gas while this mode requires it absence.

Flowing Matrix Gas

The first step in the treatment of the effect of a flowing matrix gas in an enclosure is to express its flux, F(m), in terms of its flow, F'.

$$F(m) = b\ F'\ M(m)\ P(m)/A(h) \tag{15}$$

where m refers to the matrix gas, and b is 1/RT and numerically equal to $4.4\text{x}10^{-6}$ cm^{-3} atm^{-1} ($4.4\text{x}10^{-12}$ ergs^{-1}) at 2773 K. Next, the flux of the vaporized species, F(Y), can be written in terms of the flux of the matrix gas.

$$F(Y) = F(m)\ P(Y)\ M/P(m)\ M(m) = b\ F'\ M\ P(Y)/A(h) \tag{16}$$

where Y indicates the vaporized species. The expression for W can be obtained by setting it equal to the flux of the vaporized species parallel to the flow multiplied by the ratio of the exit hole area to inside surface area.

$$W = F(Y)\ A(h)/A(s) = b\ F'\ P(v)\ M/A(s) = 3.75\text{x}10^{-4}\ P(v)\ M \tag{17}$$

The second form equation (17) results from combining its first form with equation (16). The final form of equation (17) holds for our resistojet design. Combining equations (4), (6), and (17) yields

$$Z = b\ F'\ \text{sqr}(M)/a\ A(s) = 1.66\text{x}10^{-6}\ F'\ \text{sqr}(M) = 4.45\text{x}10^{-4}\ \text{sqr}(M) \tag{18}$$

The W and Z given by equations (17) and (18) are average values. When we discuss the coupling of matrix gas flow with normal vaporization, we shall see that W and Z are dependent upon the distance along the tube or enclosure. From equation (17) the values of W for Re and TaC were found to be, respectively, $4.13\text{x}10^{-9}$ and $2.0\text{x}10^{-6}$ g/cm^2 sec. From equation (18), the respective values of Z are 0.00607 and 0.00267. Thus, the effect of the matrix gas at the prescribed velocity (for the resistojet) on the average rate of vaporization of the tube material is very roughly the same as if there were no matrix gas present: the values of Z are close to 0.0025 (eq. (14)). From equation (18), one can see that decreasing the flow rate, F', will decrease Z, and visa versa. Thus, with a slow enough flow, the value of Z could become quite small.

In the extreme where F is zero, equation (18) states that Z is also zero. This incorrect answer from equation (18) is the result of approximations used its derivation. However, closer approximations need not be used because the situation is trivial in that the matrix gas would be quickly lost into the surrounding vacuum. After the matrix gas is lost, equation (14) gives the proper steady state value for Z. Another way to look at this problem is given in the following section.

Stationary Matrix Gas

To have a stationary (nonflowing) matrix gas, the external pressure of the matrix gas (that outside the tube) must be equal to its pressure within the tube. Of course, this condition is not possible for the resistojet, but it may exist for other design problems. The logical way to attack such a problem is via gaseous diffusion. However, until we discuss the coupling of steps in Part II, the equation for this type of diffusion process cannot be set up. For now, we will be satisfied to calculate the maximum values of W and Z for this process. These are the same values given for an evacuated enclosure (eqs. (13) and (14)). Thus for all materials, Z(max) = 0.0025 when a stationary matrix gas is present; W(Re) = 1.7×10^{-9} g/cm^2 sec, and W(TaC) = 1.87×10^{-6} g/cm^2 sec.

Chemical Vaporization

The presence of a matrix gas can also give rise to the possibility of a chemical reaction between the material and the gas, itself. This could result in an increased rate of vaporization because a volatile species may be formed during the chemical reaction. For the metal, rhenium, a chemical reaction is very remote; Re should be unreactive chemically under the usual conditions of the resistojet. The situation with tantalum carbide is quite different. For the time being, the carrier (matrix) gas is assumed to be hydrogen, and the reaction product is assumed to be acetylene (C_2H_2). This is the most likely product from equilibrium considerations (ref. 6). Because of the excess of carbon in stoichiometric TaC, it is valid to write the chemical reaction as follows.

$$2C(\text{solid}) + H_2(\text{gas}) \rightleftharpoons C_2H_2(\text{gas}) \tag{19}$$

The opposing arrows indicate that both forward and reverse reactions can occur. The rate of the forward reaction should be proportional to the pressure that the hydrogen exerts (called the hydrogen partial pressure), and rate of the reverse reaction is proportional to the partial pressure of the C_2H_2. When reaction (19) is at equilibrium, the rate of the reverse reaction becomes equal to the rate of the forward reaction so that one may write

$$K(p) = P(C_2H_2)/P(H_2) \tag{20}$$

where K(p) is called the equilibrium constant for the reaction. Many such constants are tabulated in reference 6 and given in diverse sources in the chemical literature. At 2773 K, the log K(p) (base 10) for reaction (19) is equal -1.453 resulting in a partial pressure for C_2H_2 of 0.1113 atm when the partial pressure of hydrogen pressure is 3.16 atm. When chemical reactions are involved, equations (3) and (5) must be modified respectively as follows.

$$W(cs) = a\ (P(cs) - P(Y,cs))\ M'/\text{sqr}(M) \tag{21}$$

$$G(cs) = a\ (P(cs) - P(Y,cs))\ M'/D\ \text{sqr}(M) \tag{22}$$

where P(cs) is the vapor pressure of the chemical species, and P(Y,cs) is the pressure of this chemical species in contact with the material. In the present discussion, P(Y,cs) = 0. The M' is the molecular weight of the substance lost by vaporization, while M is the molecular weight of the actual vapor species which includes a weight contribution from the matrix gas (e.g., H_2) due to the chemical reaction. When considering the formation of C_2H_2, M is the molecular weight of C_2H_2 (26.036 g/mole), and M' is the molecular weight of C_2 (24.02 g/mole). Thus, W is 0.441 g/cm^2 sec, the initial rate of vaporization of carbon from TaC at 2773 K via chemical reaction with hydrogen to form acetylene. As defined in equation (6), the value of Z is equal to the vaporization rate of the chemically formed species (cs) divided by the rate for the normal vaporizing species (nv). Thus,

$$Z = P(cs)\ M'(cs)/P(nv)\ sqr(M(cs)\ M(nv)) \tag{23}$$

In the present case, "nv" refers essentially to C_3 while "cs" refers to C_2H_2 with M'(cs) = M(C_2). Examination of equation (23) indicates that when a chemical reaction is involved, it is simpler to calculate Z(cs) by dividing the numerical value of W(cs) by the numerical value of W(nv), 7.69×10^{-4} g/cm^2 sec. Thus, it follows that Z = 574; this shows that the vaporization rate by chemical reaction could be much greater than that by the normal physical process. Via equation (22) and the assumption that the loss in weight is from the carbon phase, the value of G is calculated to be 0.197 cm/sec. Remember that W, G, and Z are maximum values. If equilibrium is not reached, the actual rate could be much less, even less than that for simple vaporization. The only way to determine the real kinetic value is via experiment. The value of T" from equation (11) is 9.7×10^{-3} sec.

The TaC may also react with H_2 to form methane, CH_4.

$$C(solid) + 2H_2(gas) \rightleftharpoons CH_4(gas) \tag{24}$$

At 2773 K, the log K(p(atm^{-1})) for reaction (24) is -4.076 (ref. 6). For this case, the rate of the forward reaction should be proportional to the square of the hydrogen pressure because two hydrogen molecules are involved in the reaction. Thus,

$$K(p) = P(CH_4)/P(H_2)^2 \tag{25}$$

The value of P(CH_4) is therefore equal to 8.38×10^{-4} atm. Using equations (5) and (21) with M' = M(C) and M = M(CH_4), one obtains W = 0.00212 g/cm^2 sec and Z = 2.8. Thus, at the stoichiometric composition of TaC, the vaporization via methane formation is expected to be slower than that by acetylene formation but greater than that for C_3. The value of Z(cs) would be 577, the sum of the Z for C_2H_2 and the Z for CH_4.

When TaC is exposed to a partial pressure of oxygen, another chemical reaction can occur. The reaction can be written

$$C + O_2 \rightleftharpoons CO_2 \tag{26}$$

The value of K(p) for reaction (26) is 2.92×10^{-7}. The value of $P(CO_2)$ could be calculated in the same manner as we did for acetylene. However, this calculation can be bypassed because K(p) is very large indicating that the equilibrium is far to the right; this means that any oxygen present is almost completely converted to CO_2 as long as enough carbon species is present. At equilibrium, the partial pressure of CO_2 would be equal to the partial pressure of the oxygen originally in the system. The value of W can then be calculated from equation (21) by using this assumption. For an assumed initial oxygen partial pressure of 0.1 atm, the value of W is 0.152 g/cm^2 sec. The corresponding value of Z is 198. Note that in this case, the exact value of K(p) need not be known.

The presence of oxygen in a matrix gas of hydrogen gives rise to the following reaction.

$$O_2 + 2H_2 \rightleftharpoons 2H_2O \qquad (27)$$

The equilibrium for this reaction is far to the right; K(p) is 50.75 reciprocal atm. Thus, before the oxygen contacts the TaC, it can react with the hydrogen matrix gas, and the resultant water vapor can react with the TaC to form CO_2 along with the recovery of the hydrogen which originally reacted with the oxygen. This can give the same result as if the oxygen reacted directly with the TaC. The final partial pressure of the H_2O is many times greater than that of the O_2, but both of these are negligible when compared with the partial pressure of the CO_2. The existence of reaction (27), therefore, does not nullify any calculations made for reaction (26). Moreover, if one starts with H_2O vapor, the H_2O can also react with the TaC to form CO_2. Because there is only one oxygen atom in H_2O compared with two in CO_2, an original partial pressure of 0.1 atm H_2O would result in a final 0.05 atm of CO_2. This would result in half the rate of vaporization that would have resulted from a 0.1 atm of oxygen.

The other refractory carbides such as those of hafnium, titanium, and tungsten would be expected to react in a similar manner with hydrogen or water vapor. In fact for those of hafnium and titanium, the activity of carbon at the stoichiometric composition is unity just as it is in TaC. Therefore, the value of W(cs) for HfC (eq. (21)) would be the same as to TaC. Chemical vaporization is also a common phenomenon for the refractory metals. Metals such as tungsten, molybdenum, and even platinum will react with oxygen and vaporize chemically in the form of their respective volatile oxides. Experimentally, the rate of oxidative vaporization has been found to vary with the oxygen pressure as one would predict from the equilibrium considerations. These are only a few of the cases where materials vaporize chemically. To decide if a particular material is going to vaporize chemically, one should first ascertain what gases are present and then from equilibrium data determine to what degree reaction will occur. Of course in high vacuum or with only noble gases present, chemical vaporization is minimized.

Note that vaporization (when it is controlled exclusively by a chemical reaction step) is again not affected by parameters of the experimental setup, such as the length of the tube. Its maximum rate is determined by the thermodynamic data for the reaction that is occurring. The actual value is determined by the rate of the reaction; this would have to be found experimentally.

In addition to leading to the formation of a gas species, a chemical reaction can cause the formation of a solid phase. This is a very common occurrence for many metals such as iron. Typically, such a surface phase increases in thickness with time. If the surface phase is volatile, the calculation of its vaporization rate would be given by equation (4) with the vapor pressure used being that of the surface phase material. Vaporization of the substrate (the phase underneath) can also occur via solid state diffusion through the surface phase. This is discussed in a later section called "Surface Coating".

Diffusion Through a Gaseous Boundary Layer

Another way for a matrix gas to affect vaporization is by what we shall call back reflection. Vaporizing molecules will collide with molecules of the matrix gas, resulting in a change in their direction. Some of these vaporizing molecules will thus be directed back to the solid material and condense. One can also look at the problem in terms of a vaporizing species diffusing through the matrix gas. It is through diffusion theory that the problem can most easily be solved.

In a relatively rapid flow of the gas, one may assume the presence of a boundary layer through which the vaporizing species must move in order to leave the surface of the tube material and get to the main stream of the flowing matrix gas. The actual flow may be either laminar or turbulent, but at present we need not concern ourselves as to which it is; all that is necessary is the assumption of the existence of a boundary layer. With our symbolism, the diffusion equation (ref. 7) is written as follows:

$$\begin{aligned} W &= - D(g)\ dC''(v)/dX = - b\ M\ D(g)\ dP/dX \\ &= b\ D(g)\ M\ P/S' \end{aligned} \qquad (28)$$

$C''(v)$ is the carbon concentration in the gas phase in g/cm^3; X is the distance out from the surface of the solid material; W is the flux in that direction; $D(g)$ is the gaseous diffusion coefficient in cm^2/sec; and $dC''(v)/dX$ is the concentration gradient of the diffusing gas species perpendicular to the surface. The second form of the equation was obtained by using the ideal gas equation with $b = 1/RT$. The final form of the equation assumes planar diffusion. This assumption can be made because the thickness of the boundary layer, S'(cm), should be small compared with the radius of the tube, R'. Also, in the final form of equation (28), we assume that the partial pressure (concentration) of the vaporized (diffusing) species is zero in the bulk of the matrix gas, and that steady state conditions are achieved. One may use the vapor pressure for the value of P because this is the maximum value that P can have. The equation for Z is obtained by combining equations (4), (6), and (28).

$$Z = b\ D(g)\ sqr(M)/a\ S' = 5.21\times10^{-6}\ D(g)\ sqr(M)/S' \qquad (29)$$

The value of $D(g)$ required in equations (28) and (29) can be calculated from the following equation (ref. 2, pp. 268 and 281).

$$D(g) = sqr(V(v)^2 + V(m)^2)/3 \pi N'' Q''^2(1 + A)$$

$$= (2RT/\pi)^{3/2} sqr(1/M(v) + 1/M(m))/3 N P Q''^2$$

$$= 3.07x10^{-14} sqr(1/M(v) + 1/M(m))/P Q''^2 \qquad (30)$$

where the V's are average molecular speeds; v refers to the vaporizing species and m, to the matrix gas; N" is the number of molecules per cm^3; and Q" is the effective average molecular diameter (cm). The A' is a term to correct for persistence of direction after collision and is dependent on the interaction between molecules; having no simple way to evaluate A', we ignore it. In the final forms of the equation, we have made proper substitution for V's, etc. The N is Avogadro's number, and P is the total pressure in atm. If we select a reasonable value for Q" ($4x10^{-8}$ cm, ref. 2, p. 285), the values of D(g) for Re and TaC are, respectively, 4.3 and 4.4 cm^2/sec at 2773 K and 3.16 atm. It is also possible to estimate the value of D(g) from the known experimental data of similar molecules (e.g., ethane; its D(g) value is 5.12 cm^2/sec at 2773 K and 3.16 atm of hydrogen gas; ref. 8). Thus, our calculated value for D(g), 4.4 cm^2/sec, is deemed to serve as an approximate number that can be used later for the value of D(g) for other similar carbon-containing gaseous species.

Using the calculated values of D(g), we obtained the curves in figure 4, plots of W as a function of the boundary layer thickness, S'. From this figure, one sees that W and Z decrease with increasing boundary layer thickness. If one would assume too small of a value for S', the calculated value of Z would be greater than unity. This would represent an unacceptable physical situation. A reasonable assumption for the boundary layer is 10 percent of the diameter; this means that S' is 0.005 cm. The respective values of W for Re and TaC would be $4.16x10^{-8}$ and $2.07x10^{-5}$ g/cm^2 sec. The respective values for Z are 0.061 and 0.028. The existence of a boundary layer in the resistojet thus appears to reduce only moderately the vaporization rates for Re and TaC. Again, calculations are independent of the parameters of the experimental setup. The important parameters are the pressure of the matrix gas, the thickness of the boundary layer, and the gas diffusion coefficient.

Surface Coating

In many practical systems, materials are coated with some protective layer to inhibit heat transfer or to shield the substrate from oxidation. However, no such coating is planned for the resistojet. As discussed before, coatings may also exist due to formation via chemical reaction between the solid and the matrix gas.

The method of calculating the vaporization rate from a coating layer would again be given by equation (4) by using the proper values of P(v) and M. However here, we are more interested in the vaporization of the material underneath the coating (the substrate). A substrate may vaporize even though covered with a protective coating; it is possible for the volatile species in the substrate to diffuse through the coating and then evaporate. The solution of this problem requires the use of the steady state diffusion equation. The steady state equation for solid state diffusion has the same differential form as that for gaseous diffusion (eq. (28)).

$$W = - D(s)\ dC''(s)/dX = D(s)\ E'\ D/S'' \tag{31}$$

where $dC''(s)/dX$ is the gradient of the diffusing (vaporizing) species and $D(s)$ is its diffusion coefficient in the coating. The final form of the equation assumes planar diffusion and the gradient to be uniform across the coating with the concentration of the diffusing species equal to zero at the coating-gaseous interface. D is the density of the coating (g/cm^3), E' is the solubility (g/g) of the diffusing-vaporizing species in the coating, and S'' is the thickness of the coating. The value of Z is obtained by dividing equation (31) by equation (6).

$$Z = D(s)\ E'\ D/a\ P(v)\ S''\ sqr(M) \tag{32}$$

Any evaluation of equations (31) or (32) for our resistojet design will be extremely approximate because at the present time no coating is contemplated for the system. To apply equations (31) and (32) to the resistojet, we will assume 10 ppm solubility ($E' = 0.00001$), a density of 10 g/cm^3 for the coating, and a $D(s)$ value of 1.11×10^{-7} cm^2/sec for both Re and TaC. A low solubility is required for a coating to inhibit vaporization. This value of $D(s)$ corresponds to the value for carbon diffusion in TaC (ref. 9). By using these values and equation (31), W is plotted as a function of S'' in figure 5. For a reasonable thickness (0.01 cm), the value of W is about 1.1×10^{-9} g/cm^2 sec for both Re and TaC. The fact that W for TaC and Re are the same in our calculation illustrates that diffusion coating-controlled vaporization can be totally dependent on the diffusion parameters and independent of the vapor pressure of the substrate. Remember, we have assumed the values of the diffusion parameters; their actual values are, of course, expected to depend on the nature of the substrate. From equation (32) and our assumptions, the values of Z are found to be 1.6×10^{-3} for Re and 1.43×10^{-6} for TaC.

Solid State Diffusion-Controlled Incongruent Vaporization

Because the title to this section is quite long, we will refer to it in the future as diffusion/incongruent vaporization.

For rhenium, as well as other elements, the question of incongruent vaporization does not arise because it contains only one element. Even many compounds vaporized congruently. But as we have seen before, TaC vaporizes incongruently: the elements present do not vaporize at the same rate. The same is true for the majority of alloys and structural materials. In TaC, the carbon vaporizes first and Ta is left behind. As this happens in a one phase system, the partial vapor pressure of C decreases and so does its vaporization rate. The same sort of thing happens in other incongruently vaporizing systems. In these cases, vaporization can become controlled by the solid state diffusion of the volatile species to the surface. Thus, the time dependent form of the diffusion differential equation becomes applicable (ref. 7, p. 9).

$$dC''(s)/dT' = D(s)\ d^2C''(s)/dX^2 \tag{33}$$

where C"(s) is the concentration of the diffusing species.

The solution of this differential equation for actual systems is complex because the vapor pressure of the vaporizing species (carbon) is not necessarily a well behaved function of its concentration. Besides, all of the experimental data are not available. It is therefore necessary to make some assumptions, some of which may not be completely true. For example in the TaC system, we will assume that a single phase exists between the compositions TaC and Ta. If solid state diffusion is to be the sole rate-controlling step, one must assume that the volatile component vaporizes as soon as it reaches the surface layer. This is the same as assuming an essentially infinite vapor pressure and the surface concentration of the volatile species to be zero. With this as a boundary condition, the solid state diffusion equation (eq. (33)) may be integrated (ref. 7, p. 45). By using our symbols and assuming planar diffusion,

$$F(r) = 8 \sum_{n=0}^{\infty} (\exp(-D(s)(2n + 1)^2\ \pi^2 T'/4S^2)/(2n + 1)^2\ \pi^2) \tag{34}$$

where F(r) is the average bulk carbon concentration, F(r) being defined as unity for the stoichiometric TaC composition.

$$W = 2D\ D(s)\ M(C) \sum_{n=0}^{\infty} (\exp(-D(s)(2n + 1)^2\ \pi^2 T'/4S^2)/M(TaC)\ S) \tag{35}$$

The computer program for equations (34) and (35) are given in table I(a). The value of Z can be calculated via equation (6). The present model is referred to as Model 0 to distinguish it from models presented later which include other vaporization steps.

In figure 6, a plot of F(r) versus the square root of time shows parabolic dependence. At F(r) = 0.5, T' is 168 sec so that 168 sec may be taken as the value of the half life, T". In figure 7, the relative vaporization rate is given as a function of time. The initial value of Z is, of course, unity, meaning that W = W(nv). The final value of Z is obviously zero. This is a result of the depletion of carbon in the TaC, leaving Ta behind. Because Z is a function of time, T', for incongruent vaporization, it is convenient to define, Z', pseudo Z for an incongruent process which would be independent of time. The definition clearly requires a comparison of some time independent rate parameter with the corresponding one under the standard vaporization conditions. We chose to define Z' as follows.

$$Z' = T''(nv)/T'' \tag{36}$$

The value of Z' for the incongruent vaporization of TaC would equal 0.033.

Many times parabolic kinetics as noted in figure 6 means the formation of a new phase on the surface of the material as in the oxidation of some metals. Even though a postulate of Model 0 is the existence of a single phase, we thought it would be wise to show that Model 0 does not predict a sharp demarcation between a carbon-rich and a carbon-poor region. This is done in figure 8 where the carbon concentration profiles are plotted for various values of F(r). Again, an infinite series equation was required (ref. 7, p. 44). In figure 8, there is indeed no suggestion of such a sharp concentration demarcation.

According to equation (34), F(r) can be expressed as a function of T'/S^2. This means that T'/S^2 is a constant for any given value of F(r). It follows from this that the half life, T", is proportional to the square of the tube thickness. Thus, a slight increase in the thickness of the resistojet tube can add significantly to the value of T".

Model 0 is, indeed, an oversimplified solution to the problem. But it will probably give a correct order of magnitude answer for TaC. The total solution would involve the diffusion of C through Ta_2C as well as through TaC (fig. 3). Treatment of the problem to this mathematical depth would require a knowledge of the exact dependence of carbon activity on its concentration. Furthermore from a practical viewpoint, when the composition of Ta_2C is approached, the life of the material is essentially at an end, and calculation past this point would be only of academic interest. For other materials, a similar logic should hold so that a one phase diffusion model is sufficient for many practical problems.

Model 0 is applicable to many space problems where an alloy at an elevated temperature is exposed to the vacuum of space. The only unique parameter needed for the application of Model 0 is the diffusion coefficient of the vaporizing species in the alloy. If it is unknown, it can be approximated. Note that for Model 0, the partial vapor pressure of the vaporizing species does not have to be known. The F(r) calculated is the average fraction of the vaporizing species remaining in the alloy. Model 0 is the most severe model one can use. Models 1 and 2 to be described later requires knowledge of the vapor pressures and should result in a longer predicted life.

Miscellaneous Factors

There are still other factors that can affect the rate of vaporization of a material: adsorbed gas on the surface, roughness of the surface, grain size, and surface tension. Surface tension effects can of course be calculated, but these are second order effects on vaporization. Thus, they are not important in the present discussion. In some cases, other miscellaneous effects may have been investigated for a particular material. However, a general treatment of such effects is not available, and the effect of such factors (variables) is expected to be quite small relative to the effects discussed in this report.

Degassing of adsorbed gases may have a notable effect on the physical properties of some materials. However, we desire to keep this effect outside the scope of this report.

PART II: COUPLING OF KINETIC STEPS

General Principles

Because vaporization is a kinetic process, it couples with other kinetic steps in a predictable manner. When the process is Y and T' dependent, the process must be treated as a special case. However, when the process is Y and T' independent, general equations can be used as one will see in this present section.

For several kinetic steps that work in parallel (i.e., independently of one another using separate paths), the total rate is equal to the sum of the individual rates, W(k).

$$W(\text{total}) = \sum W(k) \tag{37}$$

It follows that

$$Z(\text{total}) = \sum Z(k) \tag{38}$$

The total rate is greater than any individual step. Also, if the rate of one step is very much faster than the others, the overall rate is controlled by the fastest rate.

A similar equation describes the effective rate, W(ef), for the combination (coupling) of several series steps if their kinetics are first order.

$$W(\text{ef}) = 1/\sum (1/W(k)) \tag{39}$$

Similarly,

$$Z(\text{ef}) = 1/\sum (1/Z(k)) \tag{40}$$

A first order step is one for which the rate is dependent on the first power of the concentration (activity) of the species involved. All the vaporization steps for Re are first order, but the normal vaporization step for TaC is expected to be third order as will be discussed later. For the combination of series steps, the overall rate is slower than the slowest individual step involved. If one of the steps is very much slower than the others, the overall rate is essentially controlled by the slowest step (ss).

$$W(\text{ef}) = W(\text{ss}) \tag{41}$$

$$Z(\text{ef}) = Z(\text{ss}) \tag{42}$$

Note that equations (39) and (40) are symmetrical with respect to the various steps which are occurring. Thus, to use equations (39) and (40), one does not need to know the chronology of the steps.

Equation (39) is easily shown to be true for a two step process. Let us call W(1) and W(2) the rates of two kinetic processes when they are occurring by themselves. When they occur in series and steady state is attained, the rates of both steps must be equal. Also, the rate of the first step is given as follows:

$$W(ef) = (1 - C') W(1) \tag{43}$$

The rate of the second step is

$$W(ef) = C' W(2) \tag{44}$$

where the 1 in the factor (1 - C') of equation (43) represents unit activity (concentration) at the start of the first step. This first step reduces the activity of the volatile component to C' on the surface of the material. The value C' will contribute to the reverse reaction so that the net forward reaction is proportional to (1 - C'). The use of this factor is similar to the use of the factor, P(v) - P(Y) (eq. (3)). The second step starts with the volatile component at an activity of C' and takes it to zero; thus, W(2) is multiplied by C', the difference between C' and zero. Elimination of C' between equations (43) and (44) yields

$$\begin{aligned} W(ef) &= W(1)\, W(2)/(W(1) + W(2)) \\ &= 1/(1/W(1) + 1/W(2)) \end{aligned} \tag{45}$$

which is equation (39) applied to a two-step reaction. Note that equation (45) holds even if the system is not ideal. For a nonideal system, C' would equal the activity but not the concentration of carbon. In spite of this, equations (43) and (44) could still be combined in the same fashion.

When a step in the overall vaporization process is not first order, equation (45) may not be valid. The most likely step not to be first order is the normal vaporization step, itself. In the case of TaC, three carbon atom in the solid must combine to form the trimer carbon vapor species.

$$3C(\text{solid}) \rightleftharpoons C_3(\text{vapor}) \tag{46}$$

Thus, the vaporization rate should be proportional to the cube of the carbon activity on the surface in the solid; such kinetics are referred to as third order. If the second rate-controlling step occurs after the third-order step, the C' in both equations (43) and (44) becomes equal to the cube of the carbon concentration, and equation (45) would still be valid. However, if the third-order step comes after the other step, equation (44) must be modified as follows.

$$W(ef) = C'^3\, W(C_3) + C'\, W(C) \tag{47}$$

We have included in equation (47) the contribution from the vaporization of the carbon monomer. By eliminating C' between equations (43) and (47) one obtains

$$1/W(ef) = 1/W(1) + 1/(W(C) + W(C_3)\,(1 + W(ef)/W(1))^2) \tag{48}$$

The equation requires use of successive approximation, but W is, nevertheless, readily calculated. The Z is given by a similar equation.

$$1/Z(ef) = 1/Z(1) + 1/(Z(C) + Z(C_3)\,(1 + Z(ef)/Z(1))^2) \tag{49}$$

In contrast with equations (39) and (40), equations (48) and (49) are not symmetric with respect to the steps involved. Equations (48) and (49) apply to the vaporization of TaC when the first step occurs before the vaporization step and the second step is either the vaporization step or one occurring after it. However, when one of the steps is much slower than the other, equations (41) and (42) can be used in place of equations (48) and (49).

To prevent our subsequent discussion from becoming too verbose, we have: limited our discussion to the coupling of two steps; used equations (41) and (42), where applicable; confined calculations to values of Z, then possible; and given much attention to the order in which the calculations are presented.

Coupling Normal Vaporization With Other Steps

Couplings independent of Y and T'. - From Part I of this report, one can note that $Z << 1$ for all steps except for normal vaporization and chemical vaporization. Therefore when dependence on Y and T' is ignored, the rate (Z) of normal vaporization coupled with one of the slow steps (ss) is given by equation (42). This equation applies to the coupling of normal vaporization with an evacuated enclosure, flowing gas, stationary gas, boundary layer, or surface coating. These values of Z have already calculated in Part I of this report. Remember that many of these values are dependent on the parameters of the design and should be recalculated when another design is involved.

Before we leave the subject of Y and T' independence, we thought it wise to derive the effective value of Z by a formal route at least once. We have chosen to do this for the evacuated enclosure. Starting with equation (39), one inserts the analytical expressions for the W's from equations (4) and (13). The resultant equation follows:

$$W(j,i) = a\ P(j,i)\ sqr(M(j))\ A(h)/(A(s) + A(h)) \qquad (50)$$

Equation (50) is written in the form for a multicomponent, multiphases system. The total contribution of the j^{th} component from all the phases is obtained by using equation (11) and the total contribution of all the components can be computed via equation (7). But for our model materials, Re and TaC, we need consider only one component and one phase, so that we can drop the i and j in equation (50). Note that in subsequent equations where i and j are not specified, one merely has to insert the i and j inside to parentheses in order to consider a multicomponent and multiphase system.

Equation (50) without the j and i is not much different than equation (13); for the resistojet with a very small hole area with respect to the inside area, the correction introduced by equation (50) is insignificant. However, when the hole area is relatively significant, equation (50) should be used.

It follows from equation (50) that W for Re is 1.7×10^{-9} g/cm^2 sec and W for TaC is 1.87×10^{-6} g/cm^2 sec. From these numbers and equation (5), Z for Re is found to be 0.0025 and Z for TaC is also 0.0025. These are the same value calculated when the effect of the evacuated enclosure was assumed to be the sole rate-controlling step (eq. (14)).

For the cases of the evacuated enclosure, flowing gas, and stationary gas, the values of Z obtained by using equation (42) should be referred to as average values, $Z(av)$, because the actual Z values can be functions of Y. From a practical point of view, we are interested in only one Y position, the place where vaporization is the greatest because that position determines the life of the entire tube. However, first one must determine the value of Y for which the vaporization rate is a maximum.

Dependence on Y for evacuated enclosure. - If the pressure caused by the vaporizing gas were high so that there would be considerable collisions between molecules, one could treat the present problem with diffusion theory. However, at the low pressures involved, a vaporized molecule will either exit through the hole or collide with the wall of the tube somewhere. Starting with this model and the concept that the direction of a molecule is random, the fraction of vaporizing molecules that exit through the hole is equal to the solid angle that the hole makes with a single molecule divided by the total solid angle. Thus,

$$\begin{aligned} W(Y) &= W\ (1 - \cos(\arctan(R'/(L - Y))))/2 \\ &= a\ Z\ P(v)\ \mathrm{sqr}\ (M)(1 - \cos(\arctan(R/(L - Y))))/2 \qquad (51) \end{aligned}$$

where W and Z refer to the steps which are being coupled with the enclosure step. It follows that

$$Z(Y) = Z\ (1 - \cos(\arctan(R'/(L - Y))))/2 \qquad (52)$$

When one is dealing with normal vaporization, $Z = 1$. Equations (51) and (52) give the rate of vaporization per unit area of the inside surface of the tube as a function of Y, the distance from the entrance. The value of $Z(Y)$ is plotted as a function of Y in figure 9. One can see that most of the vaporization occurs near the exit of the tube. Thus, the lifetime of the tube is determined by the value of $Z(Y)$ at the exit (0.5). The value of $Z(Y)$ is greatest at the exit because the molecules near the exit possess a larger solid angle of escape. At a position 1 cm from the exit the value has dropped over two orders from its value at the exit; $Z(\mathrm{entrance}) = 6.2\mathrm{x}10^{-6}$. By summing Z over the length L and dividing by L, we found the average value of Z to be 0.00249 as compared with 0.0025 given in equation (14). If the enclosure were not circular or uniform, equations (51) and (52) are still applicable with R' being the effective radius at the exit.

Flowing matrix gas. - The coupling of a vaporization step with the flowing matrix gas step can also be considered to be a function of Y. At the entrance of the tube, we can postulate that the matrix gas is free of vaporized material. It follows that this is also the location where the rate of vaporization is expected to be the greatest. At the exit hole, the matrix gas is expected to be nearly saturated with the volatile species, and so here the rate of vaporization should be the least. No longer is equation (17) valid: W is no longer proportional to $F(Y)$. Instead, the value of W should be added to the value of $F(Y)$ as one proceeds from the entrance to the exit of the resistojet tube in the following manner.

$$dF(Y) = W\ A(\text{surface area of a } dY \text{ thick slice})/A(\text{cross section})$$

or

$$\begin{aligned} dF(Y)/dY &= 2\ W\ \pi\ R'/\pi\ R'^2 = 2W/R' \\ &= 2\ a\ Z\ (P(v) - P(Y))\ \mathrm{sqr}(M)/R' \end{aligned} \tag{53}$$

where W and Z in equation (53) refer to the step being coupled with the flowing gas step, $dF(Y)/dY$ is the gradient of the vaporized species flux parallel to the length of the tube, and Y is the distance from the entrance of the tube. Note that $P(Y)$ can no longer be considered to be zero but is the partial pressure of the vaporized species in the matrix gas. Moreover, it is a function of Y. Equation (16) is again valid for $F(Y)$. Combining equation (16) and (53), followed by integration, gives an expression for $P(Y)$. Then via equation (3), one can obtain

$$\begin{aligned} W(Y) &= a\ Z\ P(v)\ \mathrm{sqr}(M)\ \exp(-Y\ R'Z\ \mathrm{sqr}(2\pi/bM)/F') \\ &= 0.842\ Z\ P(v)\ \mathrm{sqr}(M)\ \exp(-225\ Y\ Z/\mathrm{sqr}(M)) \end{aligned} \tag{54}$$

The corresponding value of $Z(Y)$ would be the exponential factor times Z.

$$\begin{aligned} Z(Y) &= Z\ \exp(-Y\ R'Z\ \mathrm{sqr}(2\pi/bM)/F') \\ &= Z\ \exp(-225\ Y\ Z/\mathrm{sqr}(M)) \end{aligned} \tag{55}$$

When the step being coupled to the flowing gas step is normal vaporization, $Z = 1$. By using the values of the parameters given before, the values of $Z(Y)$ are plotted as a function of Y in figure 10 for both Re and TaC. At $Y = L$, $Z(Y)$ is 10^{-72} for Re and 10^{-163} for TaC; $W(Y)$ is 10^{-78} g/cm^2 sec for Re and 10^{-166} g/cm^2 sec for TaC. Thus, insignificant vaporization occurs at the exit. Most of the vaporization takes place close to the entrance; here $Z(Y) = 1$, and $W(Y) = W(nv)$. Therefore, the lifetime of a resistojet tube should be governed by the lifetime of its entrance; this is the rate for normal vaporization. Our earlier calculations gave $T''(\mathrm{Re}) =$ 42 hr and $T''(\mathrm{TaC}) = 5.6$ sec. It is also interesting to compare the present findings with those for an evacuated tube. In an evacuated tube, the vaporization is greatest at its exit (fig. 9; eq. (52)) while for one with gas flow, the rate is greatest at its entrance (fig. 10; eq. (55)).

For tubes with cross sections which are either nonuniform or noncircular, the values of A in equations (16) and (53) may be expressed in terms of Y. For most cases, the resultant equations are difficult to integrate. However, equations (54) and (55) may always be used as an approximation. Regardless of the shape of the tube, the vaporization rate in a flowing gas-isothermal system does decrease as one proceeds from the entrance to the exit of the tube. This dependence of vaporization upon distance along the tube suggests a method for decreasing the actual vaporization of the tube. If a sacrificial sample of material is placed at the entrance of the tube, the matrix gas could become saturated with the vaporized species, thus inhibiting vaporization of the tube material, itself. For TaC and other carbides, the sacrificial material could be carbon.

The average value of Z over the length of the tube can be obtained via equation (56) which was obtained by summing equation (55) over Y and then by dividing by L.

$$
\begin{aligned}
Z(av) &= (sqr(M)/225\ L)\ (1 - exp(-225\ L/sqr(M))) \\
&= sqr(M)/225\ L \qquad (56)
\end{aligned}
$$

The respective values of $Z(av)$ for Re and TaC are 0.00607 and 0.00267. As expected, these are identical to the values obtained earlier via equation (18).

<u>Stationary matrix gas</u>. - When dependence on Y is considered, one must start with the gaseous diffusion equation in a form similar to equation (28).

$$F(Y) = -b\ M\ D(g)\ dP(Y)/dY \qquad (57)$$

where $F(Y)$ is the flow of the vaporizing species in the Y direction. This value of $F(Y)$ is also related to $P(Y)$ by equation (53). Combining these two equations results in a second-order differential equation. However, it is readily integrated and boundary conditions are easily assigned: the pressure of the volatile species at L is taken to be zero. Thus,

$$(P(v) - P(Y))/P(v) = \frac{cosh(Y\ sqr(Z\ sqr(2/b\pi M)/R'D(g)))}{cosh(L\ sqr(Z\ sqr(2/b\pi M)/R'D(g)))} \qquad (58)$$

Via equations (3) and (5)

$$W(Y) = \frac{a\ Z\ P(v)\ sqr(M)\ cosh(Y\ sqr(Z\ sqr(2/b\pi M)/R'D(g)))}{cosh(L\ sqr(Z\ sqr(2/b\pi M)/R'D(g)))} \qquad (59)$$

where Z again refers to the step coupled with the stationary gas step. By using equation (6),

$$
\begin{aligned}
Z(Y) &= Z\ cosh(Y\ sqr(Z\ sqr(2/b\pi M)/R'D(g)))/cosh(L\ sqr(Z\ sqr(2/b\pi M)/R'D(g))) \\
&\simeq Z\ exp((Y - L)\ (sqr(Z\ sqr(2/b\pi M)/R'D(g))) \\
&= Z\ exp(537\ (Y - L)\ sqr(Z)) \qquad (60)
\end{aligned}
$$

The last form of equation (60) holds for TaC, if no chemical reaction is involved. When the other step is normal vaporization, $Z = 1$. For this case, calculated values of $Z(Y)$ are plotted in figure 10. The vaporization behavior is similar to that for an enclosure in that the rate is greatest at the exit ($Z(Y) = 1$) and nil everywhere else. Thus, the lifetime of the tube equals the lifetime predicted for normal vaporization. At the entrance of the tube, $Z(Re) = 10^{-1545}$ and $Z(TaC) = 10^{-2330}$. For nonuniform and noncircular tubes, corrections could be made in equation (53) by expressing R' in as a function of Y.

The average value of Z can be obtained by summing equation (60) over the length of the tube, L, and then dividing by L. The result is

$$Z(av) = 1/(2L\ sqr(Z\ sqr(2/b\pi M)/R'D(g))) \qquad (61)$$

The values for Re and TaC are 1.4×10^{-4} and 9.3×10^{-5}, respectively. As should be the case, these are less than Z(max), 0.0025, calculated with the assumption that diffusion through the stationary matrix gas was the sole rate-controlling step.

Diffusion/incongruent vaporization. - The coupling of vaporization with solid state diffusion controlled incongruent vaporization requires special treatment. One begins with equation (33) but has to set different boundary conditions. We will use two different models. In Model 1, the vaporization rate of the carbon trimer is assumed to be proportional to the cube of the surface concentration of carbon, and the rate of vaporization of the carbon monomer to be proportional to the first power of its concentration as in equation (47).

$$W(ef) = Z\ W(nv) = Z\ (C'^3\ W(C_3) + C'\ W(C)) \qquad (62)$$

where Z is the value for the step that is being coupled with diffusion/incongruent vaporization. For normal vaporization Z = 1. This boundary condition makes integration of equation (33) difficult so that the calculations were made via a variable finite difference method. The computer program is given in table I(b); the program need only be run until F(r) becomes less than 0.5.

In Model 2, we assume that the rates of vaporization of both the carbon trimer and the carbon monomer are proportional to the first power of the carbon surface concentration. This boundary condition allows easy solution of equation (33) (ref. 7, p. 56). For planar diffusion and with our symbolism,

$$F(r) = 2E^2 \sum_{n=0}^{\infty} \exp(-B(n)^2\ D(s)\ T'/S)/B(n)^2\ (B(n)^2 + E^2 + E) \qquad (63)$$

and

$$Z(ef) = C' = 2E \sum_{n=0}^{\infty} (-B(n)^2\ D(s)\ T'/S)/(B(n)^2 + E^2 + E) \qquad (64)$$

where

$$B(n)\ \tan B(n) = E \qquad (65)$$

and

$$E = Z\ E(nv) = Z\ S\ W(nv)/D\ D(s) = a\ Z\ S\ P(v)\ sqr(M)/D\ D(s) \qquad (66)$$

The Z again refers to the value for the step being coupled with diffusion/incongruent vaporization. When the step is normal vaporization, Z = 1. The computer program for Model 2 is given in table I(c).

The values of F(r) for Models 1 and 2 are plotted in figure 6 as a function of the square root of time. The curves indicate roughly parabolic dependence. At all times, the values of F(r) are greater than those predicted by Model 0. This is in accord with our earlier comment that the effective rate of two combined series steps is always less than either one alone. From figure 6, the value of T" for Model 2 is 179 sec, not much more than that for Model 0 (T" = 162 sec). However, T" for Model 1 is 309 sec, definitely greater. Thus, one sees that the value of T" increases with the order of the vaporization step; remember that the order for Model 0 is zero. Plots of Z(ef) in figure 7 confirm the fact that the vaporization rate for Model 0 is the greatest, the rate for Model 2 is slightly less, and the rate for Model 1 is the least. For Models 1 and 2, carbon concentration profiles (not included in this report) were found to be similar to those for Model 0 (fig. 8). Moreover, the half lives for Models 1 and 2 were both found to be proportional to the square of the thickness, S, of the resistojet tube. One can again calculate via equation (36) a value of Z' (a pseudo values for Z). The value of Z' for Model 1 is 0.018; that for Model 2 is 0.0031.

Chemical vaporization. - Equation (38) can be used to give the value of Z(ef) for the coupling of normal vaporization with chemical vaporization. These are parallel steps. The resultant value of Z(total) for TaC is, therefore, 578. No chemical reaction is presumed for Re; therefore, Z(total) would be unity.

Coupling Chemical Vaporization With Other Steps

Coupling independent of Y and T'. - Because Z(cs) >> 1, coupling of chemical vaporization is similar to the coupling of normal vaporization. In other words, the rate of chemical vaporization is slowed down by the other steps. This in turn allows the chemical reaction involved to proceed closer to equilibrium, and the equations used will therefore have greater validity. To avoid the difficulty of defining Z values in equation (48), we begin as follows:

$$Z(ef) = W(ef)/W(nv) = W(ss)/W(nv) \tag{67}$$

Remember that "ss" refers to the slowest step. In the calculation of W(ss), one uses the P, M, and M' for chemically formed species rather than for the normally formed species. Thus, for a stationary matrix gas

$$\begin{aligned} Z(ef) &= Z(ss)\ P(cs)\ M'(cs)/P(nv)\ \mathrm{sqr}(M(nv)\ M(cs)) \\ &= Z(ss)\ Z(cs) \end{aligned} \tag{68}$$

Remember Z(cs) = 577. For a flowing matrix gas and the boundary layer effect, equation (67) leads to

$$Z(ef) = Z(ss)\ P(cs)\ M(cs)/P(nv)\ M(nv) \tag{69}$$

For TaC, this is approximately the same as equation (68). However for the coupling of coating, Z(ef) = Z(ss) because diffusion through a coating is independent of the values of P and M of the substrate material. Thus, Z(cs + flowing gas) = 1.54; Z(cs + boundary layer) = 16.1; Z(cs + stationary gas) = 1.44 and Z(cs + coating) = 1.43×10^{-6}. The values of Z for the flowing gas and the stationary gas are expected to be functions of Y. Thus, the values just given are only average values.

Flowing gas. - To determine $Z(Y)$ as a function of Y, the first form of equation (55) can be used. The Z for C_2H_2 in this equation is taken as 577 ($Z(cs)$) and M as 24.02 ($M'(C_2)$). The values of $Z(Y)$ from this equation are plotted in figure 10 as a function of Y. One sees that with chemical vaporization as well as with normal vaporization, the greatest vaporization rate occurs near the entrance of the tube. At its exit, the vaporization rate is nil while at the entrance, the rate is equal to the rate for chemical vaporization alone ($Z(Y) = 577$). The value of $Z(Y)$ for CH_4 is small, 2.8, with respect to the $Z(Y)$ for C_2H_2 at $Y = 0$, but it falls off less rapidly with Y (eq. (55)). It is interesting to note that except for small Y values, the rate of vaporization of C_3 exceeds that of C_2H_2 because the matrix gas becomes more quickly saturated with C_2H_2 than with C_3. Again from the practical standpoint, the lifetime is still controlled by the lifetime at the entrance, and the dependence of $Z(ef)$ on Y is of secondary importance.

As in the case of normal vaporization, corrections in the equation can be made for noncircular and nonuniform diameter tubes. Also, chemical vaporization could be inhibited by placing a sacrificial vaporizing material such as carbon at the entrance to the tube. This would saturate the matrix gas with C_2H_2 and prevent the chemical vaporization of the tube itself.

Stationary matrix gas. - Via equation (60), one finds the dependence of $Z(Y)$ on Y. The Z in this equation is $Z(cs)$, 577; the M is $M'(C_2)$, 24.02 g/mole. The calculated values of $Z(Y)$ are plotted in figure 10. At the exit of the tube $Z(Y)$ is 577. It is nil everywhere else, being 10^{-2104} at the entrance. The life of the tube is controlled by the life of the exit.

Diffusion/incongruent vaporization. - To couple chemical vaporization with this step, we return to Models 1 and 2. The corresponding models that include this chemical vaporization contribution are referred to, respectively, as Models X1 and X2. The boundary condition for Model X1 is obtained by modifying equation (62) to read

$$W = C'^2\, W(C_2H_2) + C'\, W(CH_4) + C'^3\, W(C_3) + C'\, W(C) \qquad (70)$$

In equation (70), the first two terms give the chemical contribution while the last two which are relatively insignificant give the normal vaporization contribution. For Model X2, equation (64) may be used by setting value of Z in equation (66) equal to 577 and M equal to 24.02.

The values of $F(r)$ and $Z(ef)$ for Models X1 and X2 can be calculated via the programs in table I. The values are plotted respectively in figures 6 and 7. The curves correspond very closely to the respective curves for Model 0. This means that the vaporizable species is vaporizing as soon as it is formed on the surface; it is due to the high vapor pressure of the chemically formed species. Rapid vaporization is the chief postulate of Model 0. The fact that the chemical vaporization rate does not exceed the rate predicted by Model 0 emphasizes that Model 0 predicts the fastest rate possible for the process if controlled by solid state diffusion.

Other Interactions with the Diffusion/Incongruent Vaporization Step

Coupling independent of Y. - Again we begin with Models 1 and 2. To incorporate other rate-controlling steps into these models, we again modify the boundary conditions. The boundary condition for Model 1 involves the definition of W. Equation (62) gives the desired condition if Z is the Z value for the particular step being coupled with diffusion/incongruent vaporization. For models derived from Model 2, the value of E (eq. (66)) determines the boundary conditions. The Z in this equation is the Z for the step being coupled with diffusion/incongruent vaporization. To distinguish these models from the original one, we refer to the ones including the boundary layer contribution as Models B1 and B2. Those including the surface coating, we call C1 and C2; those including the evacuated enclosure, E1 and E2; and those for a flow gas, F1 and F2. Because the value of Z for the stationary gas is the same as the Z for the evacuated enclosure, Models E1 and E2 will be used to represent the stationary gas effect.

The basic computer programs in table I can again be used to calculate the value of F(r) and Z. These calculated values are plotted as a function of time, T', in figures 11 and 12, respectively. In all the cases at a specified time, the carbon concentration F(r) for the coupling of rates is greater than that predicted for normal vaporization (fig. 6). Eventually, the carbon concentration for all models will go to zero. From figure 11, we can obtain the values of T" for the different models. The values of T" are as follows: Model B1 (boundary layer), 1200 sec (20 min); Model B2, 470 sec (7.8 min); Model C1 (coating), 1.2×10^{7} sec (139 days); Model C2 (coating), 5.1×10^{6} sec (59 days); Model E1 (evac. enclosure or sta. gas), 7.6×10^{3} sec (2.1 hr); E2 (evac. enclosure or sta. gas), 3.3×10^{3} sec (0.92 hr); Model F1 (flowing gas), 7.1×10^{3} sec (2.0 hr); and Model F2 (flowing gas), 3.1×10^{3} sec (0.86 hr). In all these cases, the value of T" for the models (B1, C1, etc.) involving third-order dependence on concentration is over 2 times larger than that for the corresponding models (B2, C2, etc.) involving first-order kinetic dependence. The values of Z via equation (36) are: 0.0047 for B1, 0.0119 for B2, 4.7×10^{-7} for C1, 1.1×10^{-6} for C2, 7.4×10^{-4} for E1, 1.7×10^{-3} for E2, 7.9×10^{-4} for F1, and 1.8×10^{-3} for F2.

In three of these coupling conditions (evacuated enclosure, flowing gas, and stationary gas) the values of Z(ef) are expected to be a function of Y. Thus values of Z(ef) obtained via Models E1, E2, F1, and F2 are only average values. For the flowing gas, the value of Z at the entrance is greater than the average Z from either Model F1 or F2. And for the stationary gas and evacuated enclosure, the Z at the exit is greater than the average Z from either Model E1 or E2. We will discuss the dependence of Z on Y in the next section.

Evacuated enclosure. - The coupling with the evacuated enclosure is a relatively simple problem to treat as a function of Y. We shall call the Models E'1 and E'2. The boundary condition for Model E'1 is obtained by setting Z in equation (52) equal to one, and substituting the value of Z(Y) from equation (52) for the value of Z in the boundary condition (eq. (62)). This results in a boundary condition equation which is dependent on Y.

$$W = W(nv)\ (1 - \cos(\arctan(R'/(L - Y))))/2 \qquad (71)$$

The boundary condition for Model E'2 is obtained by setting the Z in equation (51) equal to unity and substituting the value of Z(ef) for the value of Z in the boundary condition in equation (66).

$$E = E(nv)\ (1 - \cos(\arctan(R'/(L - Y))))/2 \qquad (72)$$

The calculations via the programs in table I yield F(r,Y), the average carbon concentration at a position Y along the tube (enclosure). Calculated values of F(r,Y) and Z for Model E'2 are plotted as a function of T' in figures 13 and 14, respectively. We have also plotted the result from Models E1 and E2 in these figures for comparison. The values obtained for Model E2 correspond roughly to a Y value of 9. To prevent a cluttered graph, the values for Model E'1 are not plotted. The values for Model E'1 vary from those for Model E'2 in roughly the same manner as those for Model E2 vary from Model E1. From a more detailed graph than that given in figure 13, we obtained the values of T" as a function of Y and have plotted them in figure 15. This figure gives a vivid picture of how the relative lifetime varies along the tube. Except for portions of the tube near the exit, values of T" are relatively large, but the life of a tube must be judged by shortest lifetime of any of its parts.

Flowing matrix gas. - The Y dependence of the coupling of the diffusion/incongruent vaporization step with the existence of a flowing matrix gas is relatively complicated. A two dimensional computer program would result which would be difficult to run in a reasonable time on a small computer. Moreover, the two dimensional results would be difficult to illustrate in graphic form. In addition, the calculation in most cases would be only of academic interest because all we should be interested in is the lifetime of the entrance which has already been shown to be the position of shortest lifetime. The curves for Models 0, 1, and 2 in figure 7 can be used to illustrate the vaporization at the entrance as a function of time.

Instead of setting up a rigorous model to determine the dependence of Z on Y, we set up a crude model. We will not bother the reader with the calculations or plots. This model shows that at the beginning, the greatest vaporization rate exists at the entrance. But as time proceeds, this region is depleted of carbon. Thus, the position with the greatest vaporization rate proceeds with time along the tube. The position of the maximum rate is roughly proportional to the time. Except for very short times the vaporization profile relative to the position of maximum vaporization does not change much with time. In other words, the vaporization profile proceeds along the tube in a slow single pulse fashion.

Stationary matrix gas. - A similar result would be expected for the Y dependence with a stationary matrix gas, except the maximum rate would begin at the exit of the tube and proceed toward the entrance with time in a slow single pulse manner. The dependence on time of Z at the exit for the stationary gas can be depicted by the curves for Models 0, 1, and 2 in figure 7.

Coupling of Surface Coating

Coupling independent of Y. - Four steps that can couple with the coating (ct) have not yet been discussed: gaseous boundary layer, evacuated enclosure, flow matrix gas, and stationary matrix gas. In all these cases the value of Z is much greater than the Z for the surface coating so that the value of Z(ef) = Z(ct). Therefore equation (32) is directly applicable; for Re, Z(ef) = 1.6×10^{-3}, and for TaC, Z(ef) = 1.43×10^{-6}. Note that Z(ct) is based on many hypotheses and an assumed value for the thickness of the coating. Also, remember that no coating is contemplated for the resistojet.

Coupling dependent on Y. - The equations that can be used have already been presented. For coupling with the enclosure one uses equation (52); for coupling with a flowing gas, equation (55); and for a stationary gas, equation (60). In all these equations, the Z is the one for the surface coating. The calculated values of Z(Y,Re) and Z(Y,TaC) for the enclosure are plotted in figure 9, those for the flowing gas are given in figure 16, and those for the stationary gas are given in figure 17.

Because the Z for the surface coating effect is quite small, the variation of Z(Y) with Y is small in some cases, particularly for the stationary matrix gas. Nevertheless, for the stationary gas as well as for the evacuated enclosure, the value of Z(Y) is always somewhat greater at the exit than at the entrance, and the Z(Y) for the flowing gas is always somewhat greater at the entrance than at the exit. However, this variation for Z(TaC) cannot be seen in figures 16 and 17 due to the scale of the graph.

In all these cases, we are interested primarily in the maximum value of Z(Y) which we have just discussed; the maximum rate determines the life of the entire tube. It is at the entrance for the flowing gas and is at the exit for the stationary gas where Z(Y) = Z(ct). The maximum value at the exit for the evacuated enclosure; Z(Y) = Z(ct)/2. From Part I, Z(ct,Re) = 1.43×10^{-3} and Z(ct,TaC) = 1.6×10^{-6}. If a coating exists, the life of the tube is always controlled by the diffusion through it and not by the steps involving an evacuate enclosure, a stationary gas, or a flowing gas.

Coupling Involving the Boundary Layer

Couplings independent of Y. - In the case of coupling the boundary layer effect with a flowing gas and a stationary gas, we find that the Z for the boundary layer is larger than the other two. If a much larger thickness were assumed for the boundary layer, this would not be true. However, with our assumptions, Z(av) is equal to Z for the process being coupled with the boundary layer effect. For the coupling with the flowing gas, Z(av,Re) = 0.00607, and Z(av,TaC) = 0.00267. For coupling with the stationary gas, Z(max) = 0.0025 for both Re and TaC.

Coupling dependent on Y. - Again, we can use equations (55) and (60) respectively for the coupling of the boundary layer effect with the flowing matrix gas and with the stationary matrix gas. The Z used is the Z for the boundary layer (Bl) diffusion. The calculated values for Re and TaC are plotted respectively in figures 16 and 17. As in the other examples of coupling, Z(Y) for the flowing gas is greatest at the entrance; it is equal to Z(bl). The Z(Y) for the stationary gas is greatest at the exit where it is also equal to Z(bl). Again, the life of the tube in a flowing gas is determined by the life of its entrance and the life in a stationary gas is determined by the life of the tube's exit. In both cases, the value of Z(max) is set by the value of Z(bl).

PART III: PRACTICAL CONSIDERATIONS IN ISOTHERMAL SYSTEMS

In Part IV, we will see that the existence of a thermal gradient in a practical system can tremendously influence the vaporization rate of the materials involved. Before we get into the variations that a temperature gradient gives rise to, we desire to discuss the practical aspects of a purely isothermal system because some practical systems may have to be considered as isothermal.

Part II has shown us that for isothermal systems, equations can be derived for the case of coupled kinetic steps. We limited our discussion of such equation to two-step processes to prevent verboseness in the presentation. As we will see in the following discussion, coupling two step is generally sufficient for a particular problem. Coupling of all the steps presented is never needed, and some combinations of steps cannot be coupled together. For example, a flowing gas effect cannot be coupled to an evacuated enclosure effect. Now that we have examined the equations for the single and double step processes, we are in a position in Part III to see which steps are really important for an isothermal problem.

A Look at the Kinetic Steps

Enclosures. - For this discussion, one can group together all the steps that are concerned with an enclosure; these include the evacuated enclosure, and an enclosure with either a flowing or stationary gas. As we have seen, each of these steps add a dependence upon Y. However, the life of the container (tube) is determined by the shortest lifetime of any part of tube. Moreover, this shortest lifetime is not dependent on the existence or dimensions of the tube or other enclosure. Thus, the existence of an enclosure whether evacuated or containing a matrix gas has essentially no effect on the effective lifetime of the tube. One has to consider only the position of the maximum rate of vaporization which is either at the entrance or exit depending upon the specific conditions. Remember, we are discussing an isothermal system. The existence of a temperature gradient greatly affects the calculations in systems involving enclosures.

Vaporization per se. - We may make another grouping of kinetic steps. Normal vaporization and chemical vaporization fall into a common category. They are parallel steps and thus do not interact with each other. Also, chemical vaporization interacts with every other step in the same manner as the normal vaporization step. The effective rate of their combination is merely the sum of their individual rates. Moreover, one of the two steps is generally more important than the other so that one can generally ignore one of these two parallel steps. For Re, chemical vaporization can be ignored. For TaC, normal vaporization can be ignored. But in any vaporization problem, one of these two processes must be considered. Even when a coating makes the vaporization step of the substrate unimportant, the vaporization of the coating itself must be considered as discussed in the next paragraph.

Coating. - For the resistojet, no coating is contemplated. In order for a coating to increase the life of the system, the coating would have to have a vapor pressure lower than that of the substrate. However, if it had such a low pressure, then the tube should probably be made from the coating material.

Even if a coating were used in a particular situation, the important vaporization problem would probably involve the vaporization of the coating and not the loss of substrate via diffusion through the coating. Nevertheless, a coating can certainly be used to shield from vaporization a very volatile material that has to be present in the system. Remember that our earlier calculations show that a coating can be quite effective in inhibiting the vaporization rate of a substrate.

Diffusion/incongruent vaporization. - If the material under consideration vaporizes incongruently, then this would always be an important step to consider in the overall process. If the vaporization is congruent (e.g., Re), consideration of this step does not arise.

Boundary layer. - In any system with a flowing matrix gas, a boundary layer should exist and have the effect of inhibiting the rate of vaporization as seen earlier. Thus, this effect should indeed be considered in the calculation of vaporization rates for the resistojet concept. Only for concepts involving vaporization into vacuum or very low pressure, should consideration of the boundary layer be ignored.

Application to the Resistojet

Use of Re. - By reflection on the above discussion, one can see that the steps we should consider are normal vaporization and diffusion through the boundary layer (bl). The value of Z for this combination has already been determined; $Z(bl) = 0.0607$ for a 0.005 cm thick boundary layer. Thus, $W = 4.2\times10^{-8}$ g cm^2/sec at the entrance of the tube. More accurate calculations can be made if a more accurate value of the boundary layer thickness is known. At 665 hr (28 days, value of T'') for a 0.01 cm thick tube at temperature, we predict that half the thickness of the tube at the entrance will be evaporated. The life of Re can be extended still more by the use of the sacrifical material discussed earlier in this report.

In a practical problem, one must also look at more than the time during which the tube is full of gas and is at the temperature of operation. Of course, when the tube is at room temperature the vaporization rate is nil. However, during the heating and cooling time, the tube may not always contain a matrix gas. The rate of vaporization for such periods is determined by the normal vaporization rate of the material which at temperature is faster by a factor of $1/Z(bl)$ than the rate for when the boundary layer of a matrix gas is present. As long as the time at temperature with no gas is small with respect to the time with the matrix gas, one need not be concerned with this situation for the resistojet. Also, to our advantage is the fact that without the matrix gas, the most rapid vaporization rate occurs at a different part of the tube, the exit.

As far as vaporization is concerned, Re appears to be a very good candidate for the exit tube of the resistojet and other extremely high temperature devices, especially in situations where chemical reactivity can be ignored.

Use of TaC. - For an evaluation of the vaporization behavior of TaC, one should consider the vaporization mode itself to be chiefly chemical vaporization in nature. Incongruent vaporization is also an important step as well as diffusion through the gaseous boundary layer. In the treatment of this problem, we will restrict ourselves to a modification of Model 1, which we believe is closer to reality than a variation of Model 2. We will refer to the model as Model X'1. The boundary condition is a variation of equation (70).

$$W(ef) = Z(C'^2\ W(C_2H_2) + C'\ W(CH_4) + C'^3\ W(C_3) + C'\ W(C)) \qquad (73)$$

The value of Z would be that for the boundary layer effect. The program in table I(b) can again be used.

The calculated values are shown in figure 18. From this figure, the half-life, T", of TaC is 192 sec under these conditions. This is the time required for the average composition of the TaC at the entrance to decrease to Ta_2C. This value of 192 sec is not long enough for TaC to be considered as a candidate for the exit tube of the resistojet. Moreover, the surface concentration at the entrance reaches 50 percent depletion in about 2 μs (fig. 18) and over 97 percent depletion at 192 sec, the value of T". At these degrees of depletion, the chemical and physical properties of the material are no longer that of TaC. Thus, the value of T" does not represent the lifetime of the physical properties. Such a lifetime may be much less.

There are still other factors to consider. Many of the comments made for the Re also holds for the TaC. Thus, the rate of vaporization is different during the heating and cooling periods when no matrix gas is present. However, for TaC at temperature with no matrix gas, the net rate of vaporization per time increment will be less because rapid chemical reaction will not occur. Because we may also apply the principle of sacrificial material in the case of TaC, the rate of vaporization of the TaC tube, itself, could be decreased considerably as we have mentioned several times before. Thus, the possible use of TaC in the resistojet depends upon whether and how much sacrificial material such as carbon could be incorporated into the design of the resistojet.

One must also remember that in our calculations we have assumed that the chemical reactions went to completion. We have assumed the worst situation. Under the conditions of the resistojet, chemical vaporization might not occur at all. This can only be determined by experiment. It has been reported (ref. 10) that under a static hydrogen at a half atmosphere, no reaction between TaC and H_2 could be detected. Even if no reaction occurs the value of T" (Model B1) would only be 20 min, far less than the value for Re.

PART IV: EFFECT OF A TEMPERATURE GRADIENT

Importance of a Temperature Gradient

In Part IV we shall see that the existence of a temperature gradient in a system may be one of the most important factors that should be considered for some vaporizing systems, particularly that of the resistojet. Because the existence a temperature gradient does not constitute a kinetic step, discussion up to this time has been concerned with only a single temperature. For single kinetic steps, the existence of a temperature gradient would merely mean that the rate of vaporization would be different at different locations. This is particularly evident if we consider normal vaporization. The vaporization rate would vary in an exponential manner with the absolute temperature, but vaporization at one point in space would have no effect upon the vaporization at another point in space.

However, in some cases involving coupling of kinetic steps, the vaporization rate at one location in space can have an effect upon the rate at another location. This arises from the interaction of two relationships: (1) the vaporization rate is proportional to the difference between the vapor pressure, P(v), and the partial pressure, P(Y), of the vaporized species in the matrix gas; and (2) the value of P(Y) can be affected by the value of P(v) elsewhere in the system where the temperature can be different. (If P(Y) were greater than P(v) in some cooler location, condensation would even occur). However, the interaction can only occur in some step involving an enclosed system. In an evacuated enclosure, the interaction does not occur because $P(Y) = 0$. Moreover for the case of a stationary matrix gas in an enclosure, a temperature gradient should not affect the vaporization at the exit where $P(Y) = 0$. And it is here where the vaporization rate is the greatest, and thus this is the place that determines the lifetime of the entire tube.

Therefore, when evaluating the effect of a thermal gradient, we need consider only the coupling of the flowing matrix gas in an enclosure with other relevant kinetic steps. This, of course, is the situation existing in the resistojet and in many other practical systems.

Introduction of the Temperature Gradient Effect

Many of the parameters used in this report are dependent on the temperature of the material. The existence of the coefficient of expansion makes one realize that even the radius of the tube is a function of the temperature. The use of all of the temperature dependent terms would become cumbersome and quite involved. Luckily, most of the dependencies on temperature can be ignored because they are insignificant compared with the dependence of the vapor pressure on temperature; this is exponential in nature. The vapor pressure of a substance is theoretically related to the absolute temperature as follows:

$$P(v) = k_1 \exp(-k_2/T) \tag{74}$$

where the k's are constants for the element or compound under consideration. To permit easier mathematical treatment we have approximated equation (74) as follows:

$$P(v) = k_1 \exp(k_3 T) \tag{75}$$

This is permitted because we are interested in only relatively small differences in temperature. Because the temperature dependence of the vapor pressure of Re and the C_3 component of TaC are similar (refer to the slopes of the curves in fig. 2), k_3 in equation (75) can be approximated to be the same value for both, 0.012 reciprocal degrees. If a uniform temperature gradient, G', is assumed to exist along the resistojet tube, the vapor pressure can easily be expressed as function of Y.

$$P(v,Y) = P(v,2773) \exp(0.012\, G' (Y - L)) \tag{76}$$

where G' is in units of degrees/cm, and the equation assumes the temperature at the exit, L, is 2273 K.

As discussed in the first section of Part IV, the effect of a temperature gradient in most situations is merely to produce a different rate of vaporization at the various parts of the tube. The calculations of such effects are straightforward, and thus no further detail should be required. However, when the rate a vaporization is dependent on P(Y), the applicable equations are modified considerably. In the following sections, we illustrate the modification of the kinetic equations for the practical situation of a flowing matrix gas.

Coupling With a Flowing Gas

The first quantity that is desired is, of course, the partial pressure of the vaporized gas as a function of Y because this is the quantity that inhibits the vaporization rate. This can be obtained by combining equations (3), (16), (53), and (76). If P(Y) = 0 at Y = 0, then,

$$\frac{P(Y)}{P(v,2773)} \doteq \exp(-k_3G'L)\,\frac{\exp(k_3G'Y) - \exp(-225\ Z\ Y/\mathrm{sqr}(M))}{(1 + k_3G'\ \mathrm{sqr}(M)/225\ Z)} \tag{77}$$

where 225 is $R'\mathrm{sqr}(2\pi/b)/F'$. If P(Y) equals the vapor pressure of the material at position Y = 0, that is

$$P(Y) = P(v,2773)\ \exp(k_3G'L) \tag{78}$$

then

$$\frac{P(Y)}{P(v,2773)} = \exp(-k_3G'L)\,\frac{\exp(k_3G'Y) + k_3G'\mathrm{sqr}(M)\ \exp(-225\ Z\ Y/\mathrm{sqr}(M))/225\ Z}{(1 + k_3G'\mathrm{sqr}(M)/225\ Z)} \tag{79}$$

The Z in these equations is the value for the rate-controlling step. For normal vaporization, Z = 1; for a boundary layer controlled process in a resistojet with our parameters, Z = 0.028 for TaC. For both equations (77) and (79), the relative rate Z(Y) is given as follows:

$$Z(Y) = Z\ (P(v,Y) - P(Y))/P(v,2773) \tag{80}$$

If equation (77) is assumed to be valid, then

$$Z(Y) = Z\ \exp(-0.012\ G'L)\,\frac{H\ \exp(0.012\ G'Y) + \exp(-225\ Z\ Y/\mathrm{sqr}(M))}{(1 + 0.012\ G'\mathrm{sqr}(M)/225\ Z)} \tag{81}$$

where $H = 0.012\ G'\mathrm{sqr}(M)/225\ Z$.

However, if equation (79) is a better approximation, then

$$Z(Y) = Z\ \exp(-0.012\ G'L)\,\frac{\exp(0.012\ G'Y) - \exp(-225\ Z\ Y/\mathrm{sqr}(M))}{(1 + 225\ Z/0.012\ G'\mathrm{sqr}(M))} \tag{82}$$

The values of Z(Y) for Re and TaC from equation (82) are plotted as a function of Y in figure 19 as dashed lines. Normal vaporization is assumed to be the rate-controlling step, and the value of G' is taken as 10°/cm. The solid line segments indicate how Z(Y) in equation (81) varies from Z(Y) in equation (82). The difference in the two equations is due to the postulate concerning the pressure of the vaporizing species at Y = 0. The curves for equation (81) show that the rate of vaporization is greatest at Y = 0; this is a reflection of the postulate that the pressure of the volatile species at Y = 0 is zero. The value of Z(Y) at Y = 0 for equation (82) is zero but could not be depicted on figure 20 because the abscissa involves a logarithmic scale; the zero value is a reflection of the postulate that P(Y) at Y = 0 is taken to be the vapor pressure at that position.

In a system like the resistojet, the tube leading into the exit tube would probably be made out of the same material as the exit tube itself. At least it would be a desirable situation because in such a situation the matrix gas could contain the vaporizing species near the saturation value for the entrance temperature of the exit tube. Under this condition, there would be very little vaporization occurring at Y = 0. But this is difficult to express mathematically. Nevertheless, the solution for the desired assumption should be the straight dashed lines in figure 19 with values of Z(Y) at Y = 0 being on the respective lines. Note that in the nonisothermal model, the greatest vaporization rate occurs at the exit, the position of highest temperature, rather than at the entrance as is the case for the isothermal model.

From a practical viewpoint, figure 19 is one of the most informative graphs in this report. It tells us that the vaporization rate at any spot is not as severe as predicted directly from an isothermal rate-controlling equation. The fact that the gas space already contains some vapor of the vaporizing species inhibits the rate. The vapor already present arises from the vaporization of the material in cooler portions of the system, that is, it is due to the presence of a temperature gradient. For Re, the average rate is about 1/200 of that predicted by normal vaporization; for TaC, the rate is about 1/500 of that predicted by normal vaporization. Remember these values are for a gradient of 10°/cm.

The next step is to show the effect of G' on the profile. Figure 20 is based on equation (82) and normal vaporization of TaC. For a very small gradient, G' = 0.1°/cm, the average rate is very low because the saturation value at Y = 0 is close to the saturation at Y = L. Also, the curve is almost horizontal, that is, the rate is relatively uniform from entrance to exit. For large values of gradient, G' = 100°/cm, the profile is not flat; this arises from the exponential dependence of Z(Y) on the temperature and therefore on Y. However even at Y = L, the value of Z(Y) does not approach unity. Moreover, the existence of a large value for G' is not expected in the resistojet.

By using the proper values for the parameters in equation (82), the values of Z(Y) for various rate-controlling steps can be ascertained. Figure 21 shows the effect of flow rate as well as the effect of boundary layer diffusion being the rate-controlling step. From this figure, one can infer that Z(Y) is inversely proportional to the flow rate of the gas in the range under consideration. Also, one can infer that the value of Z(Y) for boundary layer diffusion is directly proportional to its value of Z; Z(bl) = 0.028 for

TaC. Thus, the various kinetic steps which affect the vaporization rate for an isothermal process can have the corresponding effect on vaporization when a temperature gradient is present.

From the boundary layer curve in figure 21, it is not unreasonable to expect that materials for the resistojet could last more than 1000 times longer than that predicted by simple isothermal vaporization. For TaC, the existence of a chemical reaction can negate much of the effect caused by the thermal gradient: Z(Y,cs) = Z(Y,nv) x Z(cs). Thus the Z(Y)'s in figures 21 and 22 should all be multiplied by 577 to obtain Z(Y,cs).

The effect of the temperature gradient on incongruent vaporization may also be considered. We will call it Model X"1. One starts with Model 1 (see eq. (33)) using equation (73) as the boundary condition. Equation (73) includes the contribution from chemical vaporization. The Z in equation (73) would be the maximum Z(Y) value from equation (82), that is the value at Y = L. If the boundary layer is considered to control the rate, then Z in equation (73) would be $8.05\text{x}10^{-5}$, obtainable from the boundary layer curve in figure 21. Via a modification of the computer program in table I(b), the values of F(r), Z, and C' were calculated as a function of time and plotted as a function of time in figure 22. The value of T" is found to be 660 sec; this is not sufficiently long to expect TaC to be a good material for the resistojet exit tube.

However, Re was found to be a good prospect for the resistojet tube under isothermal conditions. It would have a lifetime of 665 hr. It is now expected to last even longer under thermal gradient conditions, perhaps over 100 000 hr. Of course, this presumes that no unforseen process is operative, such as chemical vaporization.

Another Approach

If the value of G' is small, we may be satisfied with an average value for Z. In Part I of this report, equation (18) (flowing gas equation) was derived by using the assumption that the gas leaving the tube was saturated with the vaporizing species, but that the gas entering contained no vaporizing species. To correct this equation for the fact that the gas entering could be saturated with the species at the temperature of the entrance, we should multiply by the factor (P(v,2773) - P(v,2773-L G'))/P(v,2773). This factor is the ratio of the pickup in the tube divided by the total pickup in the system. Through the use of equation (76), this factor can be shown to be equal to 1 - exp(0.012 G'L). Thus, for our resistojet parameters.

$$Z(av) = (1 - \exp(0.012\ G'L))(b\ F'sqr(M)/a\ A(s))$$

$$= 4.45\text{x}10^{-5}\ (1 - \exp(0.12\ G')) \qquad (83)$$

For small values of G'

$$Z(av) = 5.34\text{x}10^{-5}\ G'sqr(M) \qquad (84)$$

For TaC with a G' value of 0.1°/cm, Z(av) = $3.2\text{x}10^{-5}$; this is essentially the value obtained previously via equation (82) by using the same G'. Refer to the lowest curve in figure 20. To find Z(av) for a boundary layer diffusion controlled process, it is logical to multiply this Z(av) by the value of Z for the rate-controlling step (0.028 for the boundary layer with TaC).

Our first approach to the temperature gradient effect is more stringent than this latter one. However, this latter approach is simpler and is more easily applied than the former. Both methods point out that the existence of a thermal gradient along a tube with a flowing gas can spread out the vaporization effect over the entire area of the tube. Thereby, it can prolong the life of the tube as compared with the life predicted from simple isothermal calculation. Thus, many materials will perform much better (by perhaps a factor of 1000) than predicted by simple vaporization theory.

SYNOPSIS

In Part I, we discussed the individual effects of various kinetic steps. In some cases chemical reaction can severely enhance the rate. The existence of a gas in an enclosure slightly inhibits the rate. In some cases, the use of a diffusion barrier may be advantageous.

In Part II, the coupling of kinetic steps is considered. Parallel steps increase the rate; series steps decrease the rate. For some situations, coupling steps also introduce a dependence on position. Dependence on position suggests the use of a sacrificial vaporizing material.

In Part III, vaporization is viewed in practical isothermal systems. When a matrix gas is involved, the existence of a boundary layer is a very important factor to consider. Other important factors to consider (such as chemical reaction) depend upon the materials under consideration. Rhenium appears to be a likely candidate for use at 2500° C in the resistojet but tantalum carbide does not.

In Part IV, the existence of a temperature gradient is considered. This is found to be a very important factor. The material vaporized in low temperature locations can inhibit vaporization at higher temperature locations. This distributes the loss of material over a wider area. The lifetime of a system would thus be longer than that predicted from simple isothermal kinetic equations, perhaps by a factor of 1000. Some materials might thus be considered for use in a system such as the resistojet that might otherwise be excluded from consideration.

CONCLUDING REMARKS

Throughout this report we have calculated rates in terms of g/cm^2 sec and cm/sec. We have also expressed rates in terms of lifetime. Another useful way was in terms of Z, a relative rate with respect to the normal rate of vaporization. Actual vaporization rates are highly dependent on the properties of the material. In contrast, Z values are not grossly dependent on the properties of the vaporizing material. Note that in general the Z values for Re throughout this report do not differ significantly from the respective values of Z for TaC. See particularly figure 19. Thus Z values calculated for one material can serve as approximations for many materials. Once the normal vaporization of a perspective material (e.g., zirconium dioxide) for an application is calculated, its approximate rate under other conditions may be obtained by multiplying by the Z (for Re or TaC) under those conditions. The laborious calculations of Z from the equations given in this report are not required; an approximate value is generally sufficient.

APPENDIX

Glossary

a	$1.013\times10^6/\mathrm{sqr}\,(2\pi RT)$
(av)	average
b	$1/RT$
(bl)	boundary layer
(cs)	chemically formed species
(ef)	effective
(h)	cross section of hole through tube
(i)	phase
(j)	component
(k)	kinetic step
k_1, k_2, k_3	kinetic constants
(m)	matrix gas
n	running subscript in infinite series
n(j)	mole fraction of j^{th} component
(nv)	normal vaporization
(p)	pressure
(pc)	particular condition
(s)	inside surface of tube
(ss)	slowest step
(v)	vapor
(1)	first kinetic step
(2)	second kinetic step
A	area, cm^2
A'	term giving persistence of molecular direction after collision
B(n)	term required in infinite series; defined in equation (65)
C	carbon monomer
C'	activity of vaporizing component
C"(s)	concentration of species diffusing in solid, g/cm^3

C"(v)	concentration of species diffusing in gas, g/cm^3
C_2	carbon dimer
C_3	carbon trimer
D	density, g/cm^3
D(g)	gaseous diffusion coefficient, cm^2/sec
D(s)	solid state diffusion coefficient, cm^2/sec
E	see equation (66)
E'	initial weight fraction of vaporizing species
F	flux of gas, g/cm^2 sec
F'	gaseous flow rate, cm^3/sec
F(r)	fraction of vaporizing component remaining in solid
G	vaporization rate, cm/sec
G'	temperature gradient, deg/cm
K	equilibrium constant
L	length of tube
M	molecular weight of vapor species, g/mole
M'	molecular weight of species lost from solid, g/mole
Model	see end of glossary
N	Avogadro number, molecules/mole
N'	vaporization rate, moles/cm^2 sec
N"	molecules/cm^3
P	gas pressure, atm
P'	vapor pressure of pure component, atm
P(v)	vapor pressure, atm
P(Y)	pressure of gas as function of Y, atm
Q'	fraction of molecules that adhere to a surface upon collision
Q"	molecular diameter, cm
R	gas constant
R'	inside radius of tube, cm
S	initial thickness of tube, cm
S'	boundary layer thickness, cm
S"	coating thickness, cm
T	absolute temperature, K
T'	time at temperature, sec
T"	half-life, sec
V	velocity of gas molecules

W	vaporization rate, g/cm^2 sec
X	distance out from the surface, cm
Y,(Y)	distance from tube entrance, cm
Z	relative vaporization rate, W(pc)/W(nv)
Z'	relative vaporization rate based on lifetime, T(nv)/T

Model	all numbered models are concerned with incongruent vaporization; the rate of solid state diffusion (SSD) is always a rate-controlling step. The letter and number following the word "Model" indicates the other rate-controlling steps involved; their meanings are listed below.
0	only SSD
1	SSD plus normal vaporization proportional to cube of surface concentration
2	SSD plus normal vaporization proportional to first power of surface concentration
X1	SSD plus chemical vaporization proportional to square of surface concentration
X'1	Model X1 plus boundary layer diffusion
X"1	Model X'1 plus temperature gradient
X2	SSD plus chemical vaporization proportional to first power of surface concentration
C1	SSD plus surface coating effect; dependence on cubes of surface concentration
C2	SSD plus surface coating effect; dependence on first power of surface concentration
E1	SSD plus evaluated enclosure effect; dependence on cube of surface concentration
E'1	Model E1 including dependence on Y
E2	SSD plus evaluated enclosure effect; dependence on first power of surface concentration
E'2	Model E2 including dependence on Y
F1	SSD plus flowing gas effect; dependence on cube of surface concentration
F2	SSD plus flowing gas effect; dependence on first power of surface concentration

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```
  1 REM TABLE I(a) MODEL 0
  2 D1=13.9 @ REM density
  4 S1=.01 @ REM thickness of ma
    terial
  5 W1=.000748 @ R2=.0279 @ W=W1
    *(1+R2) @ REM give rate of v
    aporization in g/cm2-sec
  6 M2=192.96 @ M1=12.01 @ REM m
    olecular weights
  7 D2=.000000111 @ REM solid st
    ate diffusion coefficient
  8 F0=2*D2*D1*M1/S1/M2 @ REM pr
    oduct of parameters needed f
    or infinite series
 10 T1=100000000 @ REM initial t
    ime used for calculation

 11 P1=PI*PI
109 S9=-(.25*D2/(S1*S1))
110 S0=0 @ S2=0 @ S3=0 @ N0=-1 @
     REM start of calculation fo
    r time T1
111 F2=S9*T1
118 N8=1 @ T9=0 @ REM N8 is the
    number of terms added each t
    ime; T9 is the value of the
    last term
119 N0=N0+N8 @ REM counting term
    s in the full series
121 REM line 122 bypasses some s
    teps when more than one term
     is added to the series at o
    ne time
122 IF N8<>1 THEN 187
123 N2=INT(.5*N0)
124 N4=(2*N2+1)*(2*N2+1)*P1
131 T2=F0*EXP(F2*N4) @ REM term
    in series for Z with half nu
    mber of terms
187 N3=(2*N0+1)*(2*N0+1)*P1
188 T3=8/N3*EXP(F2*N3) @ REM ter
    m in series for F(r) with to
    tal terms
190 T0=F0*EXP(F2*N3) @ REM term
    in full series for Z
191 IF T0<1.E-499 THEN GOTO 315
192 S0=S0+N8*T0 @ S2=S2+.5*N8*T2
     @ S3=S3+T3*N8 @ REM adding
    the terms to the series
193 IF ABS(T9-T0)<.01*T0 THEN GO
    SUB 601
194 REM line 193 tells program t
    o average if adjacient terms
     are close; line 195 assures
     10 terms
195 T9=T0 @ IF N0<10 THEN 119
196 D4=ABS((S0-S2)/(S0+1.E-499))
197 IF D4<.0001 THEN 315
198 REM lines 196-197 tell progr
    am to stop adding terms if h
    alf series almost equals ful
    l series
199 GOTO 119
300 REM lines 315-526 print calc
    uated values
315 PRINT "T'=";T1
319 PRINT "SQR T'=";SQR(T1)
320 PRINT "Z,REL RA=";S0/W
321 PRINT "F(r),BULK CON=";S3
526 PRINT
550 T1=T1/SQR(10) @ REM determin
    es next time value for which
     to calculate the infinite s
    eries
559 REM line 560 tells program w
    hen to end
560 IF T1<.000001 THEN 700
600 GOTO 110
601 IF N0<100 THEN RETURN
604 N0=N0-4.5*N8 @ N8=10*N8 @ RE
    M when difference in terms i
    s small, 10 terms are averag
    ed
605 RETURN
700 END
```

```
  1 REM TABLE 1(b) MODEL 1
  2 Y1=1 @ REM value of Z; .028
    for Model B1; .0025 for E1;
    .00267 for F1; .00000143 for
     C1
  3 REM change the value of Y1 i
    n line 2 for the various mod
    els
  4 N1=10 @ REM specifies 10 sli
    ces
  5 DIM C0(11),A1(12)
  6 REM C0 refers to content of
    slice; A1 refers to amount t
    ransfered
  7 R1=1.8 @ REM ratio of size o
    f slice N1 to N1+1
  8 M2=192.96 @ M1=12.01 @ REM m
    olecular wts.
  9 D1=13.9 @ REM density
 10 W1=.000748 @ REM rate of vap
    orizaton under normal condit
    ions in g/cm2-sec
 11 D2=.000000111 @ REM solid st
    ate diffusion coefficient cm
    2/sec
 12 S0=.01 @ REM thickness of ma
    terial
 13 T5=0 @ REM setting of time t
    o zero
 14 A1(1)=0 @ A1(2)=0 @ A1(N1+2)
    =0 @ REM setting original tr
    ansfer values
 15 T6=.00000001 @ REM initial
    setting of the time data sho
    uld be printed
 16 C0(2)=1 @ REM setting a conc
    entration
 17 A2=0 @ REM sets the initial
    amount lost at zero
 19 REM line 20 sets the vaporiz
    ation rates of 4 vapor speci
    es
 20 G1=W1*M2/D1/M1 @ G2=G1*.0279
     @ G3=G1*574 @ G4=2.8*G1
 21 G3=0 @ G4=0 @ REM delete lin
    e for Models X1, X'1, and X"
    1
 26 REM lines 28 to 31 set the i
    nitial conc. of all slices a
    nd transfers;
 27 REM and detemines the thinkn
    ess of slice (S1) at surface

 28 S1=.000001 @ S2=S1 @ S3=S2
 29 FOR N2=3 TO N1+1
 30 C0(N2)=1 @ A1(N2)=0 @ S2=S2*
    R1 @ S3=S3+S2
 31 NEXT N2 @ S1=S1*S0/S3
 34 T3=.5*S1*S1*(1+R1)*R1/D2/2 @
     REM set a maximum time incr
    ement
 35 T0=.5*T6 @ REM lines 35 to 4
    9 select the time increment
    (T0)
 36 T4=.5*S1/(C0(2)*C0(2)*G1+C0(
    2)*G3+G2+G4)
 37 IF T4>T3 THEN T4=T3
 38 IF T4<T0 THEN T0=T4
 39 IF T5+T0>T6 THEN T0=T6-T5
 42 REM line 44 sets the amount
    of material lost at surface
    during (T0) time increment
 43 A1=(C0(2)*C0(2)*G1+C0(2)*G3+
    G2+G4)*T0*C0(2)*Y1
 44 S2=S1 @ REM lines 44 to 47 d
    etermine the amount of trans
    fer between slices in time (
    T0)
 45 FOR N2=2 TO N1
 46 A1(N2)=2*D2*T0*(C0(N2+1)-C0(
    N2))/S2/(1+R1)
 47 S2=S2*R1 @ NEXT N2
 52 REM lines 53 to 57 determine
     the new concentrations in e
    ach slice after time increme
    nt (T0)
 53 S2=S1 @ D3=D1*T0
 55 FOR N2=2 TO N1+1
 56 C0(N2)=C0(N2)+(A1(N2)-A1(N2-
    1))/S2
 57 S2=S2*R1 @ NEXT N2
 60 REM line 61 corrects slice 1
     for amount lost via vaporiz
    ation in time increment (T0)
 61 C0(2)=C0(2)-A1/S1
 62 Z=Y1*C0(2)*(C0(2)*C0(2)*G1+G
    2+G4+G3*C0(2))/(G1+G2) @ REM
     calculates Z for each time
    (T5)
 63 A2=A2+A1 @ REM calculates to
    tal amount lost in time (T5)
 64 T5=T5+T0 @ REM calculates to
    tal time
166 REM line 167 selects printin
    g or not printing
167 IF T5<T6 THEN 35
168 REM lines 169 to 180 print o
    ut calculated values
169 PRINT "T',TIME=";T5
170 PRINT "SQR T'=";SQR(T5)
174 PRINT "Z,REL RA=";Z
175 PRINT "C',SUR CON=";C0(2)
180 PRINT "F(R),BU CON=";1-A2/S0
184 PRINT
185 T6=T6*SQR(SQR(10)) @ REM set
    s new time for printing
188 REM line 189 decides whether
     to end program
189 IF T6>100000000 THEN 200
190 GOTO 35 @ REN add another ti
    me increment (T0)
200 END
```

```
  1 REM TABLE I(c) MODEL 2
  2 Y1=1 @ REM value of Z; .028
    for Model B2; .025 for E2; .
    00267 for F2 .00000143 for
    C2
  3 REM change the value of Y1 i
    n line 2 for the various mod
    els
  4 R2=.0279+2.8+574 @ REM this
    term add effect of chemical
    contribution to normal vapor
    ization
  5 R2=.0279 @ REM this term onl
    y adds effect of monomer vap
    orization; delete this line
    for X2
  8 M2=192.96 @ M1=12.01 @ REM m
    olecular wts.
  9 D1=13.9 @ REM density
 10 W1=.000748 @ REM rate of vap
    orization under normal condi
    tions: g/cm2-sec
 11 D2=.000000111 @ REM solid st
    ate diffusion coefficient
 12 S1=.01 @ REM thickness of ma
    terial
 13 W=W1*(1+R2) @ Z1=(1+R2)/1.02
    79 @ REM converts rate into
    terms of total vaporization
    rate
 14 E=Y1*S1*W*M2/D1/D2/M1 @ E1=E
    *E @ REM product of paramete
    rs needed for infinite serie
    s calculation
 15 B1=0 @ B3=0 @ N3=0 @ S9=D2/(
    S1*S1) @ REM assign initial
    values to variables
 16 T0=100000000 @ REM initial t
    ime
 17 S=0 @ S2=0 @ S3=0 @ N0=-1 @
    N8=1 @ T5=0 @ T=T0*S9 @ REM
    initial parameters for each
    time parameter
 18 REM N8 is the number of term
    s added to series at one tim
    e
120 N0=N0+N8 @ REM count of term
    s
122 B2=1 @ REM first evaluation
    for B1
130 REM lines 140 to 151 evaluat
    e B1 parameter for infinite
    series
140 B1=.9*B2+.1*B1
150 B2=ATN(E/B1)+N0*PI
151 IF ABS(B1-B2)>.000001*B2 TH
    EN 140
169 REM line 170 bypasses some s
    teps when the average of sev
    eral terms are added to inf.
     series
170 IF N8<>1 THEN 185
171 REM lines 172 to 176 calcula
    te B4 for infinite series wi
    th only half the number of t
    erms
172 N2=INT(.5*N0) @ B4=1
173 B3=.9*B4+.1*B3
174 B4=ATN(E/B3)+N2*PI
175 IF ABS(B3-B4)>.0000001*B4 TH
    EN 173
176 B6=B4*B4
177 T2=N8*EXP(-(B6*T))/(B6+E1+E)
     @ REM term for half series
    for Z
185 B5=B2*B2
186 T4=N8*EXP(-(B5*T))/(B5+E1+E)
     @ REM term for full series
    for Z
188 T3=T4/B5 @ REM term for full
     series for F(r)
190 S=S+T4 @ S2=S2+.5*T2 @ S3=S3
    +T3 @ REM adding terms to fo
    rm series
191 IF T4<1.E-400 THEN 310
192 IF ABS(T4-T5)<.01*T4 THEN GO
    SUB 600
193 T5=T4 @ REM lines 192 & 193
    decide whether term is small
     enough to take the average
    of terms
194 IF N0<10 THEN 120
195 REM line 194 makes sure that
     the fist 10 terms are not a
    veraged
196 D3=ABS((S-S2)/(S+1.E-50))
197 IF D3<.0001 THEN 310
198 REM lines 196-197 tells prog
    ram to stop adding terms if
    half series almost equal ful
    l series
199 REM line 200 says to go back
     and calculate next terms
200 GOTO 120
300 REM lines 310-526 say to pri
    nt the calculated values
310 C1=2*S*E @ F9=2*S3*E1
315 PRINT "T' =";T0
316 PRINT "SQR T'=";SQR(T0)
319 PRINT "Z,REL RATE=";C1*Z1*Y1
320 PRINT "C',SUR CON=";C1
321 PRINT "F(r),BULK CON=";F9
526 PRINT
550 T0=T0/SQR(10) @ REM determin
    es next time value for which
     to calculate the infinite s
    eries
559 REM line 560 tell program wh
    en to end
560 IF T0<.000001 THEN 700
599 GOTO 17 @ REM go back and st
    art calculation on next time
     parameter
600 IF N0<100 THEN RETURN
605 N0=N0-4.5*N8 @ N8=N8*10 @ RE
    M when difference in terms i
    s small, 10 terms are averag
    ed
649 RETURN
700 END
```

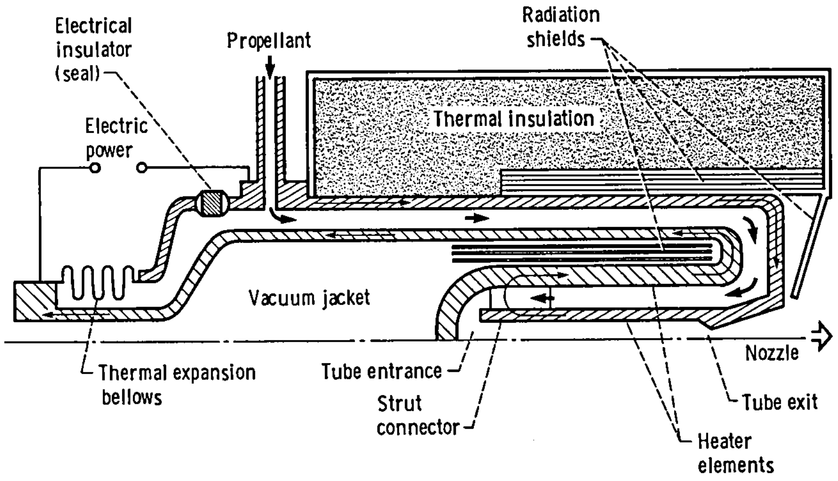

Figure 1. - Resistojet concept.

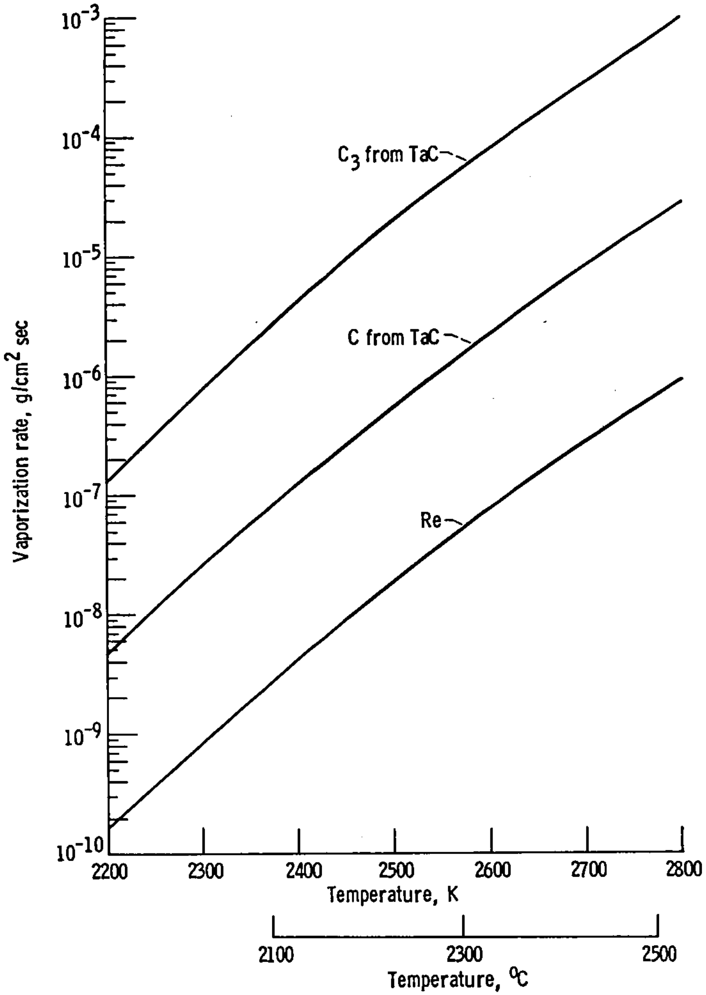

Figure 2. - Vaporization rates versus temperature.

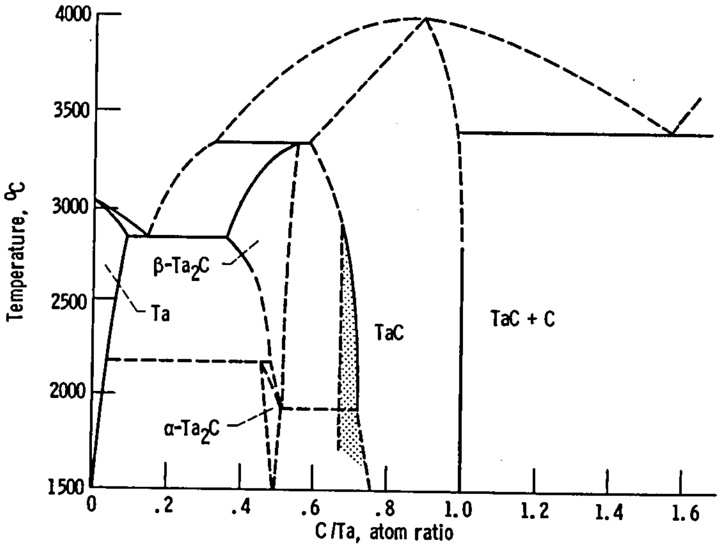

Figure 3. - Phase diagram for Ta-TaC.

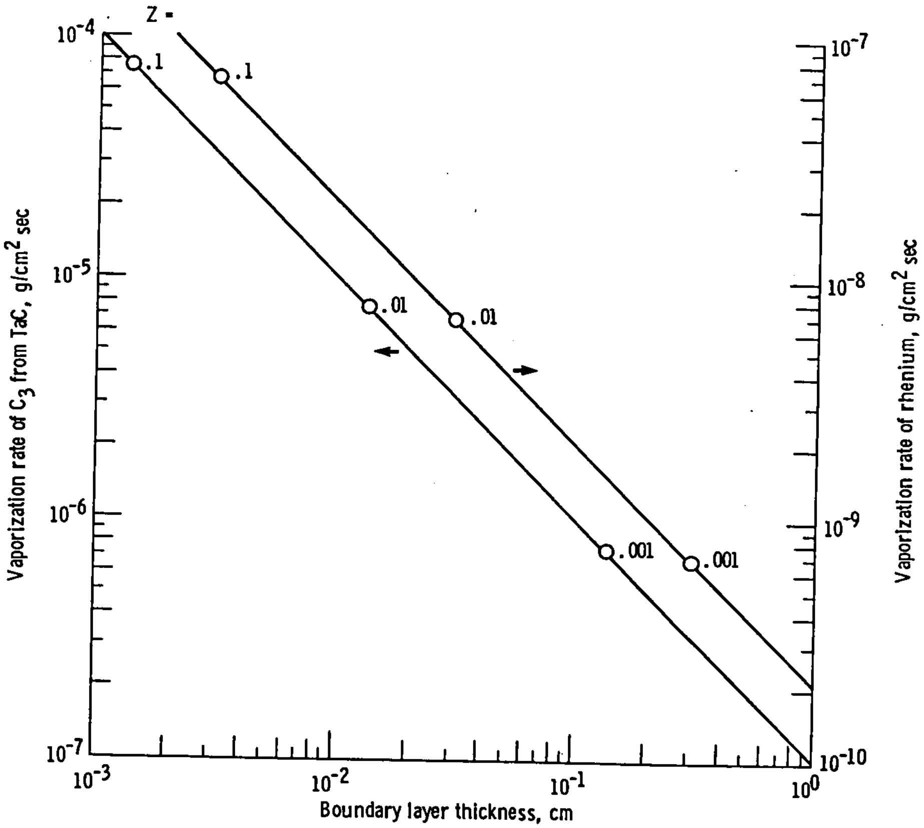

Figure 4. - Effect of boundary layer thickness on the vaporization rate.

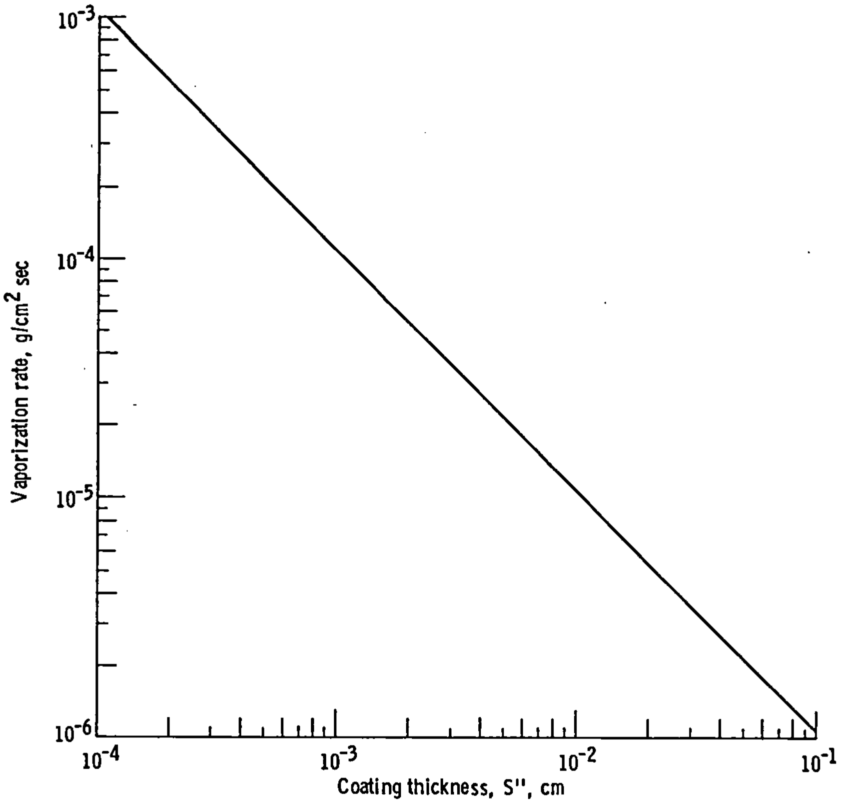

Figure 5. - Effect of coating on vaporization.

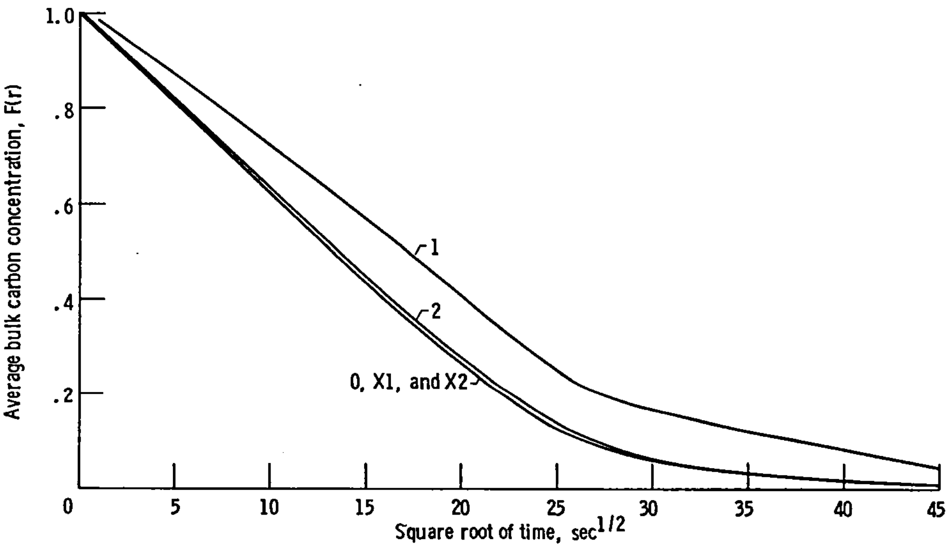

Figure 6. - Effect of solid state diffusion on the composition of TaC during vaporization [thickness = 0.01 cm; symbols on curves refer to models].

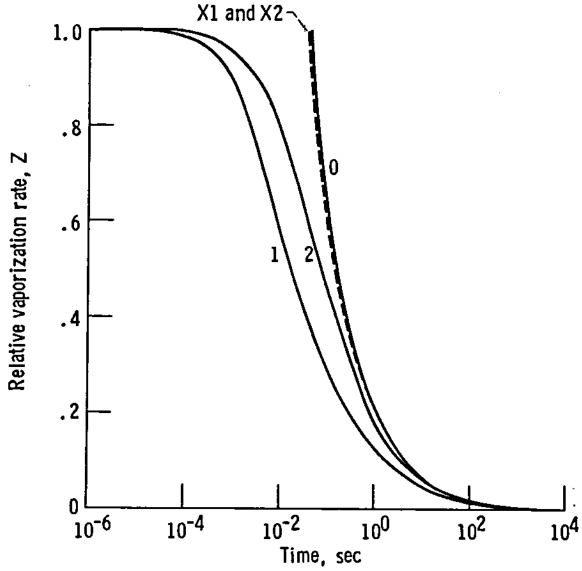

Figure 7. - Effect of solid state diffusion on the vaporization of TaC [thickness = 0.01 cm; symbols on curves refer to models].

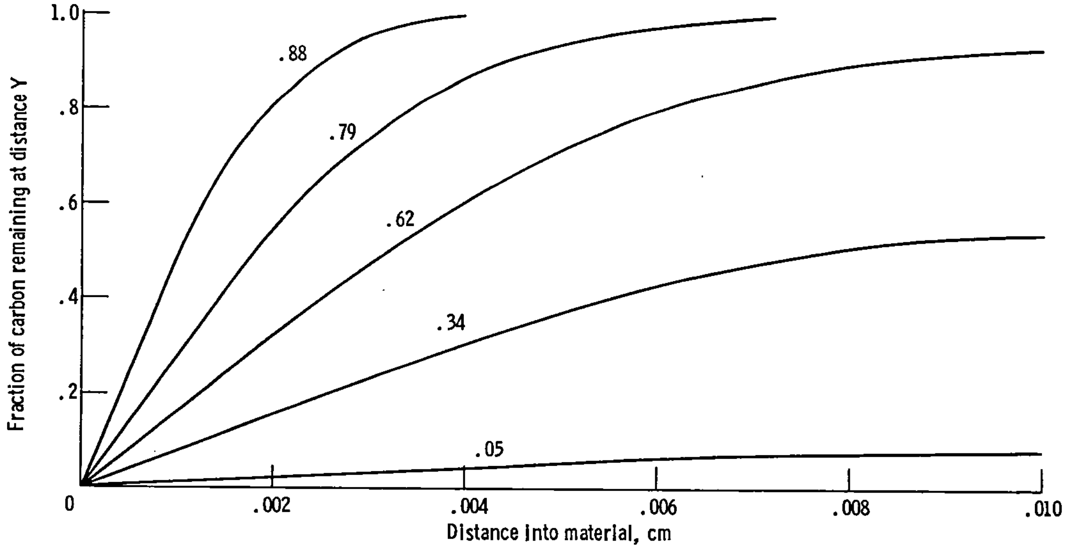

Figure 8. - Carbon concentration profile for Model 0 [numbers on curves are F(r) values].

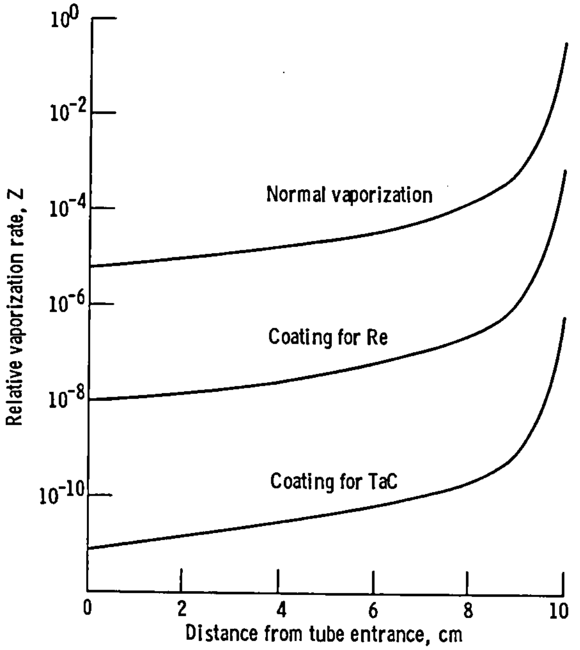

Figure 9. - Vaporization profile in an evacuated enclosure [radius of tube = 0.05 cm].

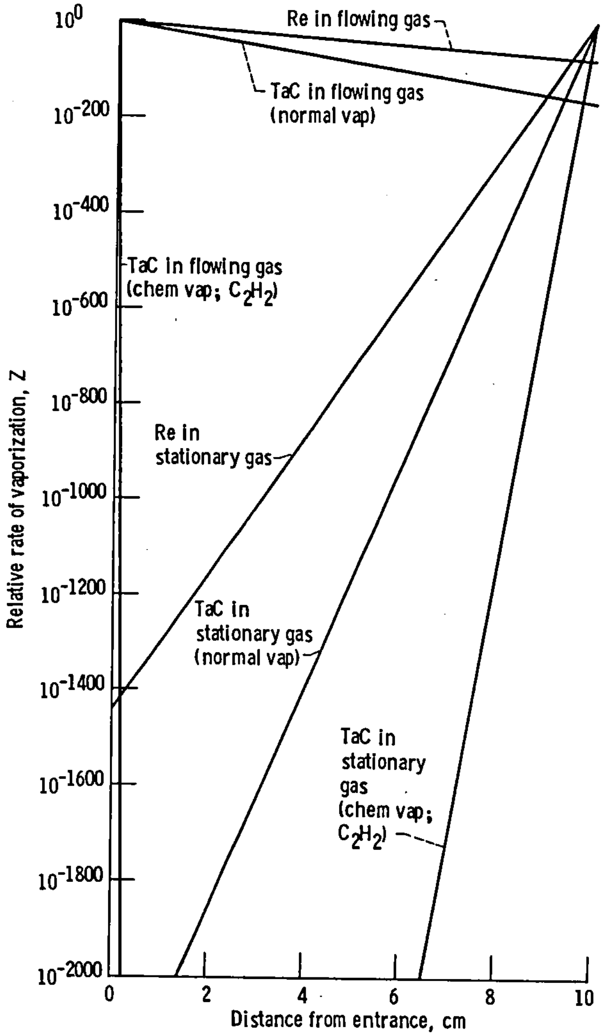

Figure 10. - Effect of matrix gas on normal and chemical vaporization in a tube [radius of tube = 0.05 cm].

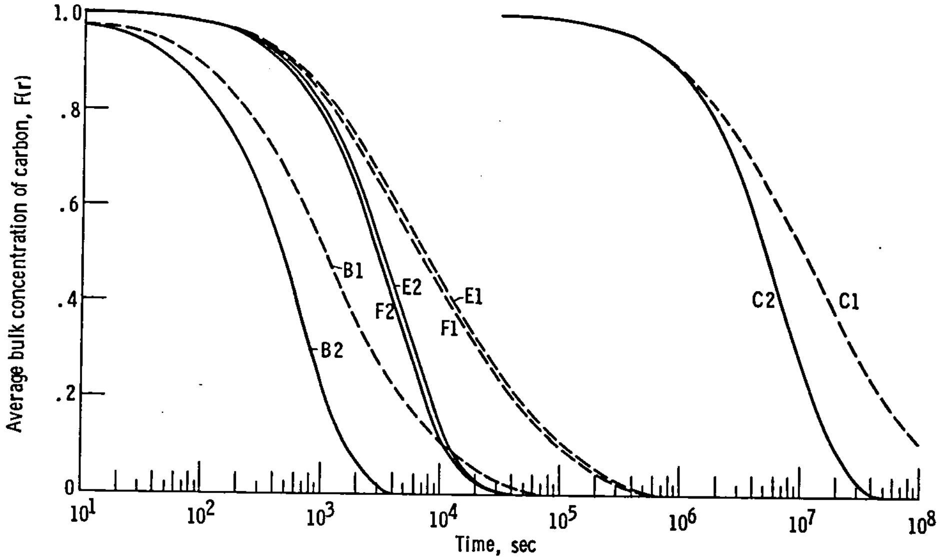

Figure 11. - TaC composition as function of time for various steps coupled with diffusion/incongruent vaporization [symbols on curves refer to models; thickness = 0.01 cm].

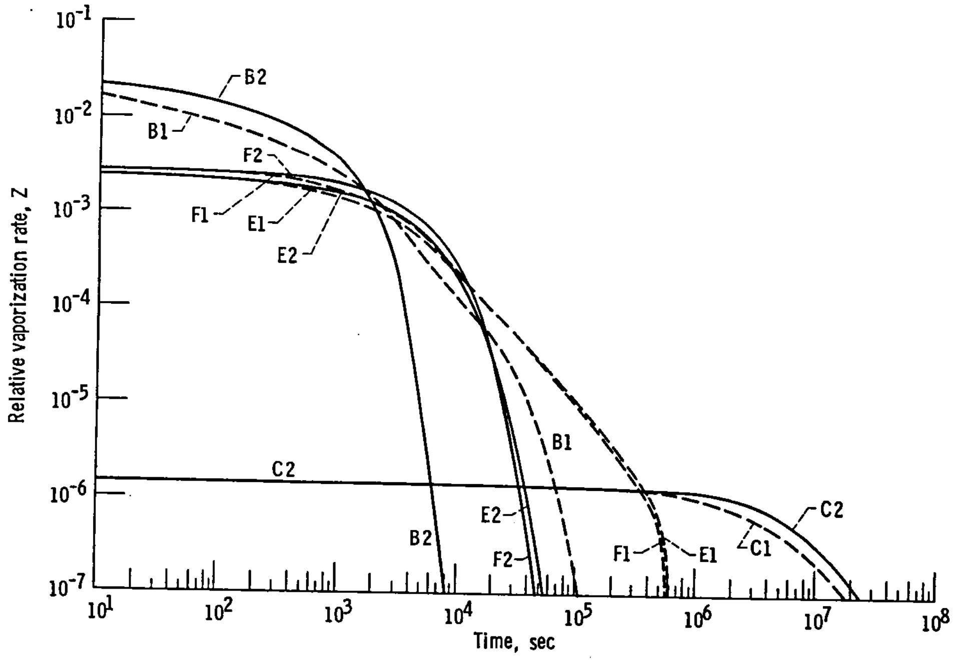

Figure 12. - Vaporization rate of TaC versus time for various steps coupled with diffusional/incongruent behavior [symbols on curves refer to models; thickness = 0.01 cm].

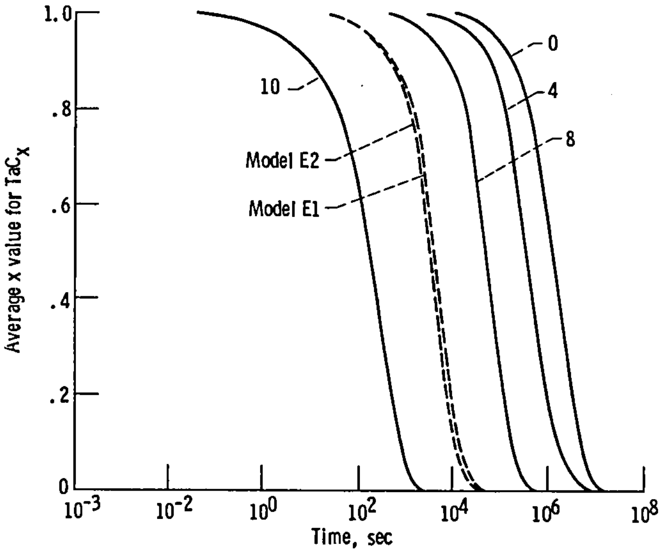

Figure 13. - Combined effects of enclosure and diffusion due to incongruent vaporization on carbon concentration in TaC [numbers on curves are Y values (cm) for Model E'2; thickness = 0.01 cm; A(h)/A(s) = 0.0025].

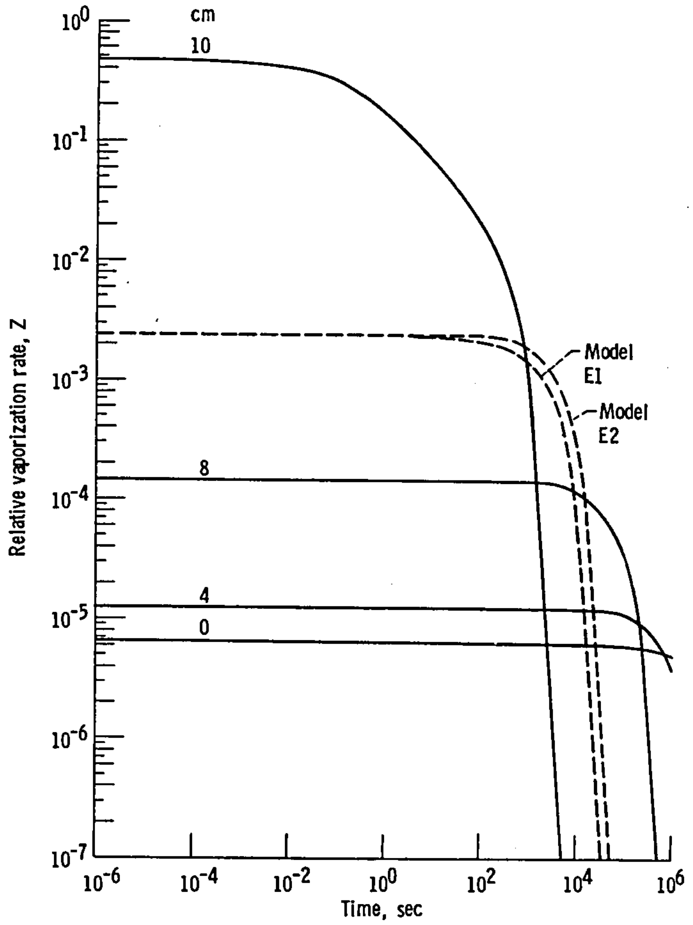

Figure 14. - Dependence of vaporization of Ta upon combined effects of enclosure and diffusion associated with incongruent vaporization [numbers on curves are Y values (cm) for Model E'2; thickness = 0.01 cm; A(h)/A(s) = 0.0025].

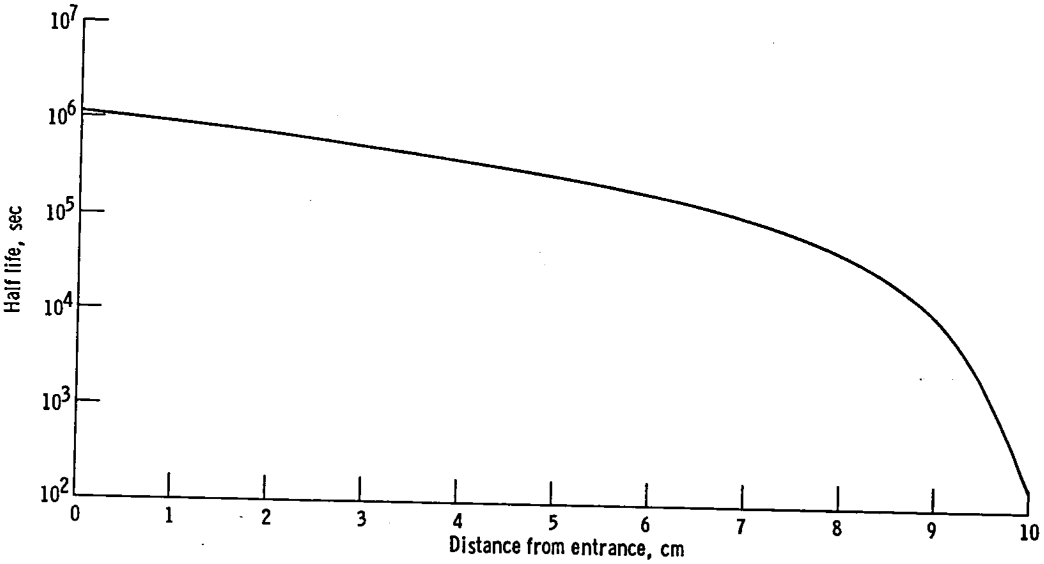

Figure 15. - Combined effects of enclosure and diffusion due to incongruent vaporization on half life of TaC [Model E2].

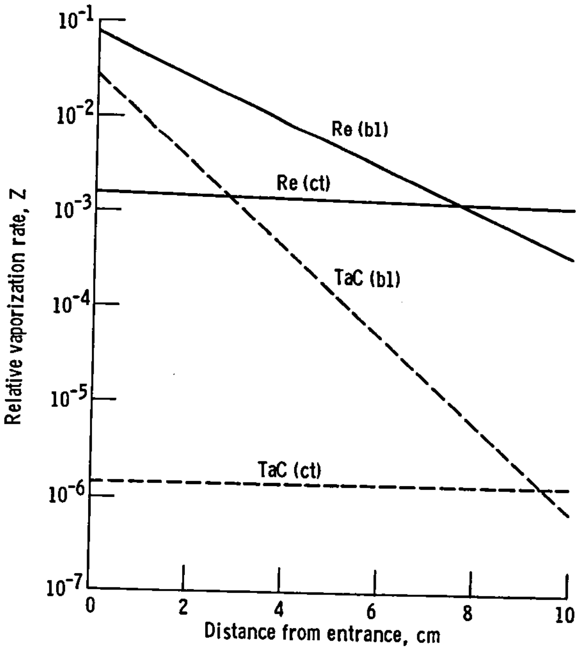

Figure 16. - Interaction of flowing gas in tube with boundary layer and coating effects.

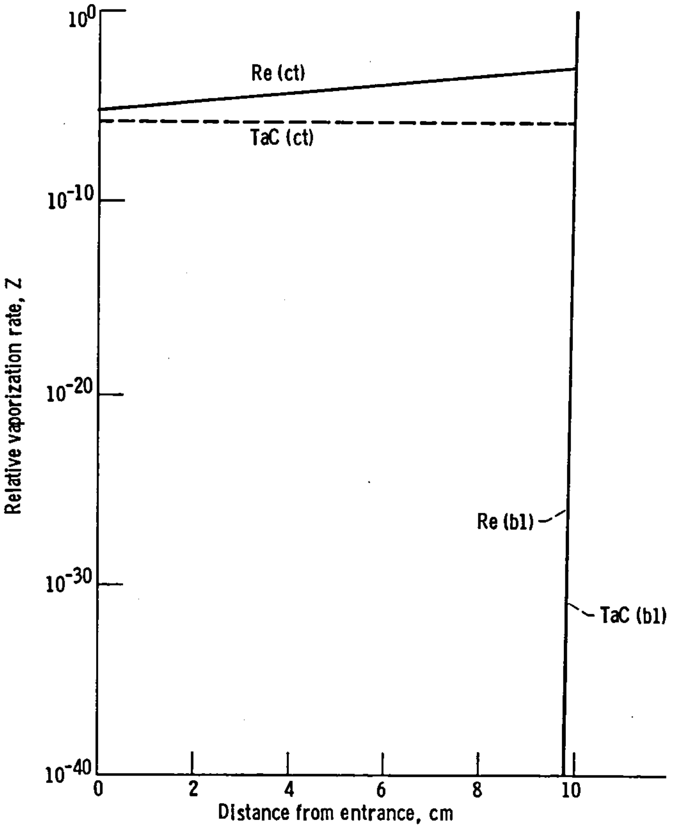

Figure 17. - Interaction of stationary gas in tube with boundary layer and coating effects.

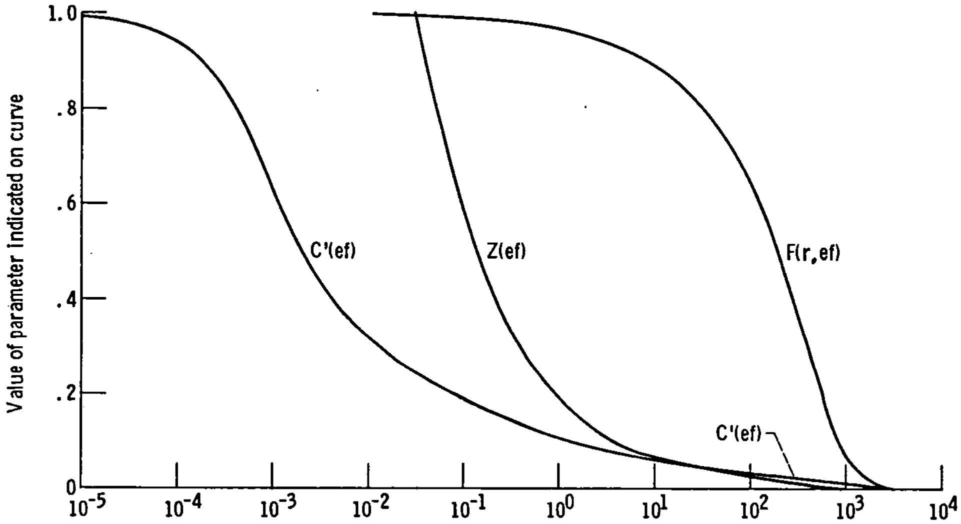

Figure 18. - Calculations for the vaporization of TaC involving chemical reaction and boundary layer diffusion.

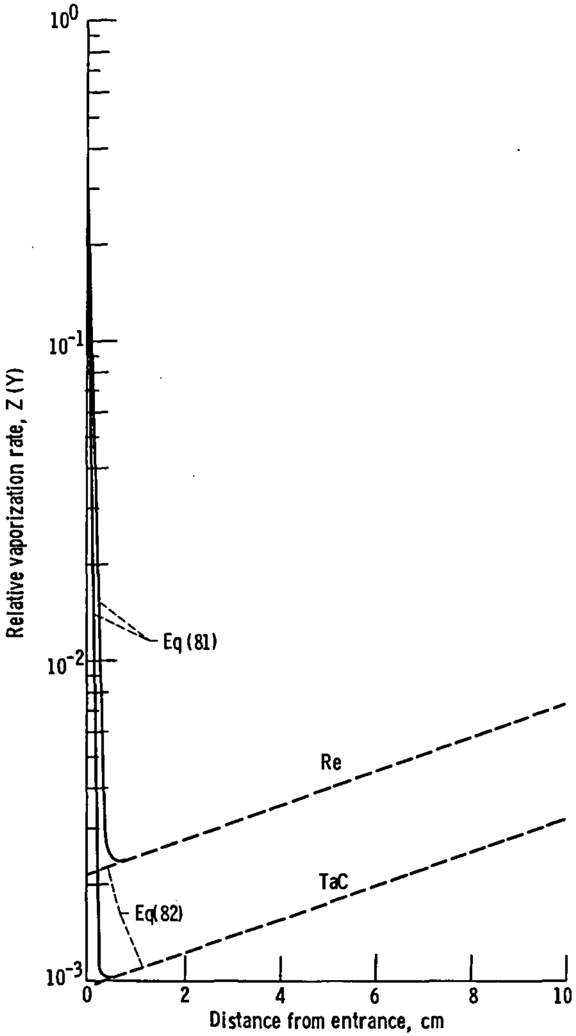

Figure 19. - Vaporization rate profile for a gradient of 10° per centimeter.

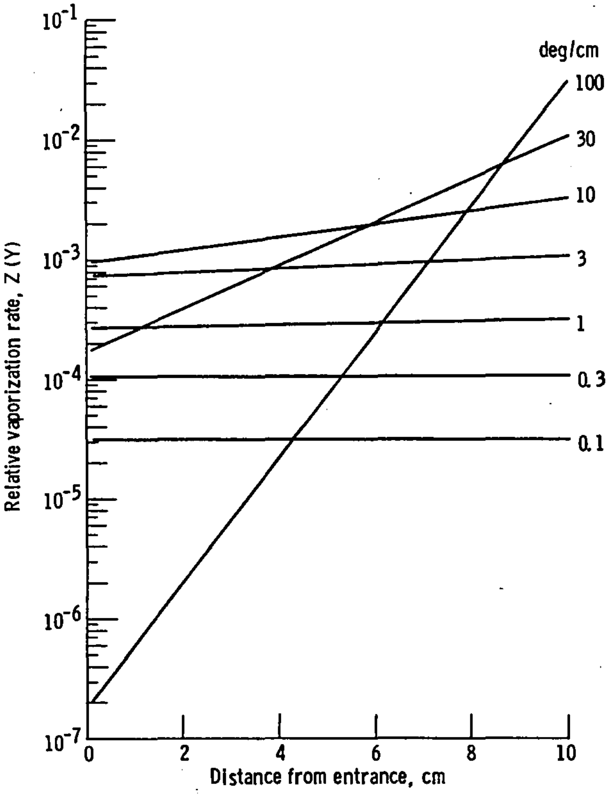

Figure 20. - Vaporization rate profile for TaC for various temperature gradients.

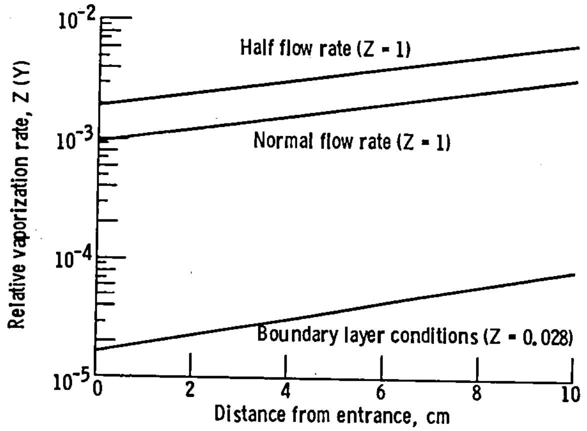

Figure 21. - Effect of various parameters on the vaporization profile of TaC with 10° per centimeter gradient.

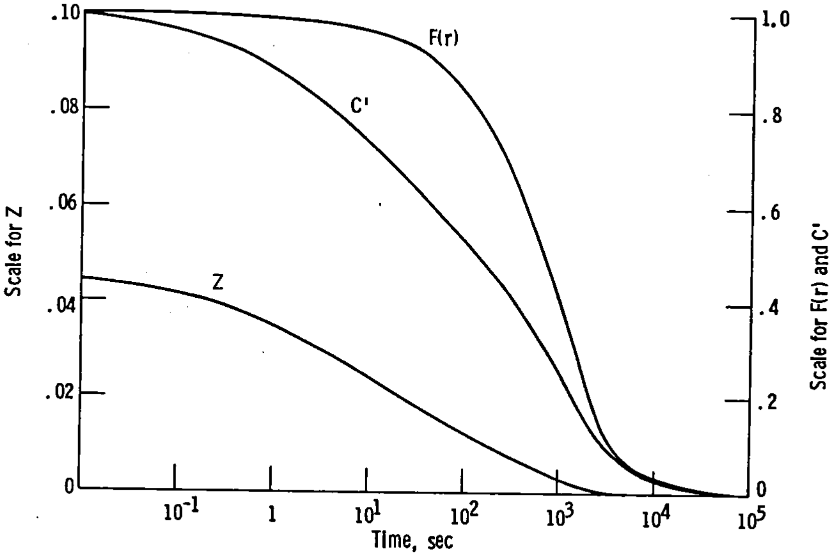

Figure 22. - Calculations for the vaporization of TaC involving temperature gradient, chemical reaction, and boundary layer diffusion [G' = 10°/cm; S' = 0.005 cm].

1. Report No.
NASA TM-83757

2. Government Accession No.

3. Recipient's Catalog No.

4. Title and Subtitle
Calculation of Vaporization Rates Assuming Various Rate Determining Steps: Application to the Resistojet

5. Report Date
August 1984

6. Performing Organization Code
506-55-24

7. Author(s)
Charles E. May

8. Performing Organization Report No.
E-2244

10. Work Unit No.

9. Performing Organization Name and Address
National Aeronautics and Space Administration
Lewis Research Center
Cleveland, Ohio 44135

11. Contract or Grant No.

13. Type of Report and Period Covered
Technical Memorandum

12. Sponsoring Agency Name and Address
National Aeronautics and Space Administration
Washington, D.C. 20546

14. Sponsoring Agency Code

15. Supplementary Notes

16. Abstract

The various steps that could control the vaporization rate of a material are discussed. These steps include the actual vaporization, flow rate of matrix gas, chemical reaction, gas diffusion, and solid state diffusion. The applicable equations have been collected from diverse appropriate sources, and their use is explained. Rate equations are derived for conditions where more than one step is rate controlling. Calculations are made for two model materials: rhenium which vaporizes congruently, and tantalum carbide which vaporizes incongruently. The case of vaporization under thermal gradient conditions is also treated. The existence of a thermal gradient in the resistojet means that the vaporization rate of a material may be only one thousandth of that predicted under isothermal conditions. Calculations show that rhenium might have a 100 000 hr lifetime at temperature in a 2500° C resistojet. Tantalum carbide would have a life of only 660 sec under similar conditions.

17. Key Words (Suggested by Author(s))
Vaporization
Sublimation
High temperature materials

18. Distribution Statement
Unclassified - unlimited
STAR Category 23

19. Security Classif. (of this report)
Unclassified

20. Security Classif. (of this page)
Unclassified

21. No. of pages

22. Price*

*For sale by the National Technical Information Service, Springfield, Virginia 22161

National Aeronautics and
Space Administration

Washington, D.C.
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