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FUNDAMENTAL MATERIALS LIMITATIONS IN HEAT-EXCHANGER NUCLEAR ROCKETS*

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ABSTRACT

Part I

Materials limitations are delineated for gas-heating propulsion reactors for the distant future. The method cannot deal with gaseous reactors, so in that sense they are excluded. Liquid reactors are permitted by the implicit assumption that their design is achievable.

Once a gaseous species is formed, it is assumed lost from the reactor, thus reducing performance by lowering specific impulse. Chemical reactions leading to material losses are considered, as are means of minimizing losses caused by reaction with the hydrogen propellant. Pessimistic performance predictions based on thermodynamic equilibria are made. Where performance is limited by material loss, UC dissolved in more refractory carbides will give a high temperature capability, but one not greatly superior to simple binary solutions of uranium in refractory metals.

Part II

A review of graphite Rover and BeO Pluto reactors reveals the most serious material limitation to be that associated with the reaction of the coolant and moderator, indicating good reason to remove the moderator from the core. A strong case is made for ignoring the supposed thermal stress problems of carbides. Thus, several indications point to carbides as the ultimate materials for heat-exchanger nuclear rockets, operating below the melting point in the immediate future, and perhaps far above the melting point in the distant future.

*Work performed under the auspices of the U. S. Atomic Energy Commission.

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INTRODUCTION

The success of the nuclear propulsion program has from the start been dependent upon the development of materials science and technology. The promise of nuclear energy with its virtually limitless capability for high temperatures and its very high energy production per unit mass has stimulated an enormous effort directed toward utilization of this potential, and the result has been the evolution of materials, capabilities and techniques which are presently being applied to nuclear propulsion. The first generation of nuclear reactors for propulsion has been designed and successfully tested; we now look to the future.

As we would expect from an initial venture, our first generation devices have utilized the simplest approach; they are nuclear heat exchangers which impart the maximum possible enthalpy to the propellant. Their performance is limited, at present, by the characteristics of the materials which comprise the heat exchanger. It is to this class of propulsion device that we have turned our attention, with special emphasis on the hydrogen propelled nuclear rocket. The reason for this is very simple: now that we know they can be built and operated, we should do our utmost to establish, conceptually at least, the ultimate limits to which we can expect them to perform. We must do this to make an intelligent decision as to future courses of action--do we make plans for new generations of higher temperature reactors? Or will parametric studies show that we have paid too dearly for the higher temperature, with its inevitable accompanying complications?

* Work performed under the auspices of the U. S. Atomic Energy Commission.

The heat exchanger type of nuclear engine, affectionately termed "Old Pokey" by many, is relatively unsophisticated in concept, but has one great virtue: it is the only high thrust nuclear rocket we know how to make with our existing technology. But what is its ultimate capability? To answer this question, we should look to the limitations which are implicit in its operation, and in our opinion the most fundamental of these are the high temperature chemical processes which lead to failure of the reactor.

PART I

In the first part of our paper, we will consider the chemical aspects of hydrogen propelled nuclear rockets operating above 3500°K. To make the task simpler, we will ignore all reactor features except the heat exchanger materials and the propellant. Further, we have chosen not to take melting as failure, since ingenious engineering can undoubtedly result in heat exchangers based on constrained liquids.^(1,2,3) We have excluded from consideration "gas core" reactors which hope to separate and recover the heavy gaseous fuel from the propellant, or which use a transparent membrane to confine the fuel. Our only assumption is that once a gaseous species is formed, it is lost from the system; thus the production of volatile species is a truly fundamental limitation. It is fundamental not only in that vital components of the reactor will be lost, but more important, the transfer of heavy molecules or atoms into the propellant will increase its molecular weight, resulting in decreased specific impulse. Others^(2,3) have pointed out that since vaporization losses increase with increasing temperature, a degraded specific impulse will eventually result as the temperature rises.

Effect of Propellant

Hydrogen must be our propellant; its low molecular weight is unique. Further, the onset of dissociation with its corresponding increase in enthalpy enhances potential performance even more.

We must consider the effect of propellant on the reactor materials. In the simplest case of an all metal reactor, the role of the propellant will be simply to remove the vapors formed. For such a reactor it is better to operate at high pressures; the partial pressure of the vaporizing species will be reduced, and losses minimized. If the heat exchanger contains non-metals, these will react with the hydrogen to form gases which are lost from the system. The pressure of such gases will increase with increasing hydrogen pressure; if the increase follows the first power, the concentration is pressure independent.

One may ask if the hydrogen and the reactor materials will achieve equilibrium. If our heat exchanger is to perform efficiently, the residence time of the propellant-coolant must be sufficient to reach near-thermal equilibrium. Since the mass transfer and heat transfer equations are so similar in form, it seems likely that we may reach chemical equilibrium as well. The reactions between hydrogen and possible reactor materials are considered in more detail later in the paper.

Behavior of Fuel

The most essential, and usually the most costly component of a reactor is the nuclear fuel. It is well, then, to turn our attention first to the problem of retaining the fuel within the system. Unfortunately, uranium is only a moderately refractory element. Its melting point is 1133°C , and its enthalpy of vaporization at $3500^{\circ}\text{K} \sim 102 \text{ kcal}$. No reactor based on pure, liquid uranium will be practical at 3500°K ; the vapor pressure of $\text{U}_{(g)}$ is 0.025 atm, and losses would be prohibitive. Two possibilities are suggested: (1) The uranium could be enclosed in some inert, refractory container, and (2) the chemical activity of the uranium can be lowered by dilution with other materials or by the formation of compounds.

If one considers (1) above, it is found that even at temperatures far below 3500°K , no materials exist which can long contain molten uranium. If it is assumed that the container must be a solid, there are very few materials which have not melted by 3500°K , and all of these would be rapidly dissolved by the molten metal. It is therefore necessary to combine the uranium in some form which will

be more inert towards high melting materials. Thus topics 1 and 2 should be considered together; first a sufficiently refractory uranium-containing compound must be found, then suitable enclosure material used. If one is considering solid heat exchangers, this approach is the obvious one.

Compound Formation

A large reduction in the chemical activity of uranium can occur when an element or elements are added with which it forms strong bonds. The stronger the bonds formed, the more stable the compound, and the greater the reduction in uranium activity. From the literature it is known that the most stable compounds of uranium are with the first row elements: B, C, N, O and F. One further consideration is necessary; if stable, gaseous molecules are formed, the fuel loss may be prohibitive, even though the activity of uranium, referred to uranium atoms, is small. The formation of uranium-containing gaseous molecules rules out fluorides, and also makes the use of oxides unattractive, since the uranium loss above UO_{2-x} in contact with hydrogen exceeds the loss above pure uranium.⁽⁴⁾

If gaseous, uranium-containing molecules are unimportant, as appears true for borides, nitrides and carbides, one can use the free energies of formation to calculate the tendency of the uranium compound to dissociate to the gaseous atoms. The compounds of uranium with boron and nitrogen are insufficiently stable for use at temperatures of 3500°K and greater. The carbides of uranium thus appear the best choice if only binary mixtures are considered. Unfortunately, although formation of the carbide lowers the vapor pressure of uranium dramatically, reactions with the propellant rule out the use of pure UC. This aspect of the problem will be discussed subsequently.

Solution Formation

Another means of reducing the activity of uranium is by solution in a second refractory metal such as Ta, W, Re or Mo - or refractory alloys of more than one metal. At low temperatures the refractory metals have a very small solubility

for uranium, but above the melting points, the liquids are probably miscible in all proportions. The most refractory metal is tungsten, which is used subsequently for illustration.

The reduction in activity which will result from this approach is expected to be only that which comes from the entropy of mixing; no strong bonds would be expected between the metals. At temperatures of the order of 4000°K , it seems likely, therefore, that the behavior of solutions of uranium in refractory metals can be approximated by Raoult's law. If this is true, the maximum reduction in volatility which can be expected at any temperature is the volatility of pure uranium at that temperature multiplied by the mole fraction of uranium in the solution. As an illustration of a solution of metals, consider a hypothetical solution of tungsten in uranium. At 4000°K , the equilibrium vapor pressure of uranium is 0.21 atm, which would certainly be intolerable if the propellant gases were to become saturated. At the same temperature, the vapor pressure of pure tungsten is 4.6×10^{-4} atm. The mole fraction of uranium required to reduce $U_{(g)}$ to the point where it equals the pressure of $W_{(g)}$ is 2.3×10^{-3} , a W/U ratio of about 400.

For illustration, we have presented in Fig. 1 the performance of several metal diluted systems. As a figure of merit, we have chosen the vacuum specific impulse, $I_{sp}(\text{vac})$ as taken directly from King's⁽⁵⁾ tables.

The results given in Fig. 1 show that a respectable performance can be achieved by dilution. Further reduction in the concentration of uranium in the solution will only raise the maximum in the curve slightly, since even at dilutions of 100:1, the loss of refractory metal, not the uranium, is the major contributor to degradation in impulse. A curve for pure tungsten would reach its maximum at 5000°K , with a vacuum I_{sp} of about 1600. This number undoubtedly represents the maximum which can ever be achieved by a simple heat exchanger system, since in high pressure hydrogen, tungsten is the least volatile substance known.

The performance of other metal diluents will be poorer, depending on their vapor pressures. Niobium is a promising choice, combining the advantages of relatively low atomic weight, low vapor pressure and a fairly low absorption of thermal neutrons.

To get an idea of the loss of uranium associated with some specific mission, it is necessary to impose an energy requirement; we have chosen 1000 MWh. In Fig. 2 is plotted the flow rate of hydrogen required to extract 1 MW, and in all further examples we will assume 100 atmospheres total pressure. Using flow rates from the chart, and assuming the propellant is saturated with vaporized metal, we can then calculate uranium loss at the maxima of the curves in Fig. 1. For pure uranium at 3800°K, a 1000 MWh mission would lose 3600 kg! For a 100:1 Nb:U solution at 4600°K, the loss would be 450 kg U^{235} , and would yield a specific impulse of 1410 rather than 1140. If the reactor could operate at a lower uranium concentration, the U^{235} losses would be decreased in direct proportion.

It seems that if a constrained liquid reactor is feasible, fairly promising performance can be obtained by simple dilution with refractory metals. At "fast" compositions (U:Me $\sim$ 1) the loss rate would be enormous, however, and the performance poorer.

Solutions of Compounds

It would seem that the ultimate in reduction of the activity of U will be through a combination of compound and solution. For example, uranium carbide can be dissolved in other refractory carbides; the resulting pseudo-binary systems can then be expected to obey Raoult's law, at least roughly. The activity of $U_{(g)}$ will be lowered in accordance with its mole fraction, in addition to the lowering due to formation of U-C bonds. The activity of carbon is not truly constant in this pseudo-binary, since UC is not as stable as some of the carbides of the refractory metals, and the carbon activity will vary slowly with the metal atom ratio. Thus the reaction with hydrogen to form hydrocarbons will remain an important consideration.

Predicting the Behavior of Components in Single Phase Carbides

We are confronted with the task of predicting the loss of material from a single phase containing two or three components. It should be kept in mind that in treating such systems properly, either solid or liquid, we should consider them as solutions, rather than compounds. As an illustration, in Fig. 3 is a tentative phase diagram for Nb-C. In this diagram there are phase regions, rather than sharp, stoichiometric compounds, and the properties within the single phase regions are best treated as though the "compounds" were highly non-ideal solutions of the component materials. In the NbC system at $\sim 3100^{\circ}\text{C}$, for instance, "NbC" can exist within the composition limits $\text{NbC}_{0.98}$ to $\text{NbC}_{0.6}$, and its properties vary continuously over this interval. If we are calculating reactions which cause loss of components, we must know the chemical activity of each component at the desired temperature and composition. Such data are not available for most of the systems discussed in this paper. In a binary system we know that as the activity of one component increases, the other must decrease, but the exact variation in activity with composition is not simple. Recently Kaufman⁽⁶⁾ has investigated this subject quite extensively, and his results appear very encouraging.

This paper was written not for the purpose of precise thermodynamic calculation, but for a more general behavior prediction. In all cases the ultimate performance proved to be in the liquid region, where virtually no data exist. We chose to base our predictions on what we think are reasonable thermodynamic calculations. The assumptions and methods of calculation are described in Appendix I.

In all our predictions we assumed thermodynamic equilibrium; that is we consider all reactions have time to go to completion. Especially for the formation of hydrocarbons, there are serious doubts as to the validity of this assumption.

Reaction With Hydrogen to Form Hydrocarbons

One can use the thermodynamic data to calculate the vapor pressures of the metal, $C_{(g)}$ and other polyatomic species of carbon vapor above carbides. In this way a loss rate can be calculated, but it is probably not worth doing. Rather than the simple volatilization that was found in the metal systems, the incorporation of carbon into our material has raised the problem of chemical interaction between hydrogen and carbon to form hydrocarbons. The severity of this problem is difficult to assess in a paper of this type, in which no specific reactor system is discussed, since the tendency to form hydrocarbons is dependent on hydrogen pressure, carbon activity and temperature. We have chosen 100 atmospheres as before for our total pressure. Only the two most important hydrocarbons, C_2H and C_2H_2 , are considered. In predicting hydrocarbon importance, it is necessary to know the activity of carbon, since their formation depends on $(a_c)^2$, and in the compositions calculated, a_c is a fraction considerably less than 1. The assumptions made for calculating the hydrocarbon pressure are given in Appendix II.

At a fixed total pressure, it is possible, in principle, to calculate the loss from any metal-carbide system if the activities of the individual components are known as a function of composition. The procedure is to assume an initial composition, calculate all reactions causing loss of each component, and then re-adjust the composition until the losses of the components are in the same proportion as they occur in the solid, i.e., congruency. In ZrC_{1-x} , for example, the metal is lost only by vaporization of $Zr_{(g)}$, but C is lost through vaporization of $C_{(g)}$, $C_3(g)$ and a host of hydrocarbons. The composition will therefore adjust itself until the Zr:C ratio in the solid is the same as that of the equilibrium gas. (There must be strong negative deviations from ideality for such congruency to occur; we have assumed this to be true in the molten carbides.)

In practice, this type of calculation requires too many laborious iterations, and also the thermodynamic data are insufficient to warrant the effort. We have chosen to make a few calculations which demonstrate trends, but we did not perform sufficient iterations to optimize. The results of several calculations are shown in Fig. 4.

The lower curve in Fig. 4 shows the initial loss rate which would occur from a solution of Zr:U:C of atom ratios 100:1:85. For solid ZrC, the congruently (in vacuum) vaporizing compound occurs at $\sim \text{ZrC}_{0.85}$ near the melting point, and we have assumed this to be the congruent composition in the liquid also. This assumption plus the free energy of formation of the carbide allows calculation of the activity of both C and Zr. Using these activities and the known vapor pressures of the pure components, it is then possible to calculate the partial pressures of the individual species at 100 atmospheres total pressure. In Table I are given the pressures of the gases evolved initially from Zr:U:C atom ratio of 100:1:85; similar calculations were made to obtain the curves in Fig. 4.

Table I

Species	4000°K	4500°K	5000°K
	$a_C = 0.125$ $a_{Zr} = 0.113$	$a_C = 0.132$ $a_{Zr} = 0.155$	$a_C = 0.17$ $a_{Zr} = 0.326$
C	8.1×10^{-3}	0.07	0.69
C ₃	5.6×10^{-4}	8.0×10^{-3}	0.125
Zr	9.6×10^{-3}	8.6×10^{-2}	0.82
C ₂ H	0.646	2.47	7.36
C ₂ H ₂	0.528	1.17	1.74
U (no bonding)	2.0×10^{-3}	1.0×10^{-2}	4.0×10^{-2}
H	14.4	27.5	43.4
H ₂	84.4	69	46

It is apparent from the data that although $\text{ZrC}_{0.85}$ is very stable in vacuum or in an inert gas, it is strongly attacked by hydrogen. As time passes, the C will deplete, the activity of carbon fall, and the activity of Zr rise. At some point the solution will achieve congruency for these conditions. We feel that it is impossible to predict the final composition, at least until better thermodynamic data are available for the molten carbides. The middle curve on Fig. 4 shows the loss rate above a solution of unknown composition, but whose Zr activity was fixed at 0.5. Again assuming a quantity for the free energy of formation of the condensed phase, we can calculate the activity of carbon and thus the pressures of hydrocarbons. At this very high activity of Zr, the carbon loss through formation of hydrocarbons is less than the Zr loss; a congruent system would be slightly richer in carbon.

As to the loss of fuel, we assumed that at the very low carbon activity required to resist hydrocarbon formation, there would be very little bonding to the uranium; the zirconium is a stronger competitor for bonds. We therefore made the very pessimistic assumption of no bonding at all, only a Raoult's law dilution effect. At a Zr:U ratio of 100:1, the loss of uranium is a minor contributor to the degradation of I_{sp} at all temperatures considered; our assumption therefore made the fuel loss the same as would occur from a metal solution of Zr:U = 100:1.

Since Nb has a lower vapor pressure than Zr, it seems that a Nb:U:C ternary will have a higher temperature capability, even though the stoichiometric carbide of Nb is not as stable as that of Zr. Again we used the rather tenuous thermodynamic data to calculate the loss from $\text{NbC}_{0.x}$, assuming a Nb activity of 0.5. The result of this calculation is shown in Fig. 4. Our results indicate a higher performance potential for NbC, but not much more information can be obtained from this type of calculation.

What has been gained from the addition of carbon? If our calculations are valid, the carbon must be present at very low activity if it is to resist loss via hydrocarbon formation. This low carbon activity implies a correspondingly high metal activity, and thus there can be no great reduction in metal vapor pressure, and the carbon containing systems are little better than the metal solutions. If the assumption is made that the carbon can reduce the metal activity to 0.33, a Nb-C system would optimize at an I_{sp} of 1530 at 5000°K, a gain of 8 percent over Nb alone. But it is apparent that the hydrocarbon formation has wiped out the large gains that the thermodynamic stability of the carbides seemed to imply.

Conclusion - Part I

In concluding the first part of this paper, it would seem well to enumerate a few of the areas which require further investigation. First, all our predictions of ultimate capability imply a liquid heat exchanger. The problems associated with this design have been discussed by several authors⁽²⁾, and we can only encourage their continued efforts. Second, we can never expect heat exchangers to operate above ~ 5000°K; even a pure tungsten exchanger would have passed its optimum at this temperature and at 100 atmospheres pressure of hydrogen. Third, we cannot really predict behavior unless better high temperature data are available for both solid and liquid systems. In the mixed metal system, it would be desirable to have experimental partial molal quantities for all components, so their vapor pressures can be precisely calculated as a function of composition. Perhaps an interim goal should be a good treatment of the molten materials using regular solution considerations.

It is always proper, in summing up any paper in which equilibrium thermodynamic calculations are used to make predictions, to re-emphasize that one can use the calculations to predict only the maximum extent of the reaction. Any sluggish step in the process can thus cause the predictions to be invalid. The author's experience in high temperature chemistry has indicated, however, that at the very high temperatures discussed in this paper, kinetics of reaction are not apt to be slow.

PART II

In the recent KIWI and NERVA reactors if one were to raise temperatures until an intolerable situation were encountered, that situation would arise due to chemical interaction between graphite in the fuel elements and the hydrogen propellant⁽⁷⁾. This statement per se is probably an oversimplification in that some design changes might be needed to avoid overheating of structural components. The current temperature levels have been attained because a protective coating technology has developed which now uses a thin layer of niobium carbide as a barrier between carbon and hydrogen which otherwise react⁽⁸⁾.

In the most developed of the Pluto reactors (Tory II-C) such a conceptual temperature elevation process needs to consider two alternatives:

1. If the reactor temperature were elevated with perhaps minor design changes to provide additional cooling for structural components, then the limit would be imposed by oxidation (likely by ignition) of the uncooled coated Nb alloy baseplates⁽⁹⁾.

2. After sufficient data was available on the temperature limits associated with the Nb alloy it was apparent that enlarging the fuel element passages could result in a lower base plate temperature for the same performance⁽¹⁰⁾.

This is possible for Pluto reactors because in performance terms there is a trade-off between exit gas temperature and pressure drop through the reactor. Another alternative which produces for our purposes the same end is to eliminate the refractory metal. The technology was rather well developed in this direction⁽¹¹⁾. This technology is available for eliminating cooled or other metal structure in hydrogen cooled reactors in favor of materials with higher temperature capability which are generally brittle.

Either of the above alternative courses, followed sufficiently, would have led to the situation where a continued elevation of temperature would produce intolerable loss of BeO in the fueled BeO elements. This would occur due to reaction between BeO and water in the atmosphere. Technology was proceeding satisfactorily toward extending this limit with another protective coating when the program terminated.

A comparison of these limitations in the Pluto and the Graphite Rover reactors reveals a similarity (ignoring the Pluto refractory metal problem, which would have been eliminated in the course of time). In both cases the limitation encountered was that of a thin protective coating, the function of which was to protect the neutron moderator from reacting with the propellant. The implication clearly is to eliminate the moderator.

While the possibility is now somewhat academic, it seems clear that for Pluto application some fuel element compositions are available which would have much less tendency to react with the gaseous environment than does BeO. Of more certain future interest is the fact that several fuel element compositions have much better chemical compatibility with hydrogen than does graphite. Those involving tungsten are receiving considerable attention. Those classified as ceramics are receiving practically no attention insofar as specific development for reactor application is concerned. Carbides have extremely high melting points and a compatibility with hydrogen much better than that of graphite. One objection often cited for the carbides is that cracking due to thermal stresses may cause serious difficulties⁽¹²⁾. In this connection it is pertinent to cite some data obtained in connection with the Pluto program.

When similar questions about the integrity of cracked fuel elements arose it was decided to test an array of deliberately precracked dummy alumina ceramic fuel elements in search for deleterious effects. The element cross section is as in Fig. 5.

Fig. 5 Dummy Fuel Element Cross Section

These elements had length between 1-1/2" and 4". There were 66 in the cross section arranged to form an equilateral triangle. The one assembly was tested with pressure drops of up to 100 psi and temperatures to 1375°C. There were half a dozen or so runs on this assembly with a total accumulated time over 1100°C of about 40 minutes. Visual inspection through the holes showed no apparent change. Fig. 6 shows the extent of the pre-cracking in all the tubes. Fig. 7 shows an end view of the test assembly. Axial support was provided by a ceramic plant on the downstream end. Fig. 8 shows where the one small piece which was found to be missing upon disassembly was located. Clearly carbides should not be rejected on the basis that thermal stress cracking can cause difficulty.

In conclusion to Part II, it seems clear that carbides deserve increased attention.

ACKNOWLEDGEMENT

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THERMODYNAMIC DATA SOURCES

Other than those specifically referenced, the following sources were used: Vapor pressures of W, Nb, Zr and U were taken from Hultgren, R., Orr, R. L., Anderson, P. D., and Kelley, K. K., "Selected Values of Thermodynamic Properties of Metals and Alloys", John Wiley and Sons, Inc., New York, 1963; and Vapor Pressure of C and C_3 from JANAF Thermochemical Tables, Dow Chemical Co., Midland, Michigan.

APPENDIX I - Calculation of Activities in Carbides

For ZrC, the data on free energy of formation of $ZrC_{(1)}$ were taken directly from the JANAF tables. From this, the equilibrium constant for the reaction $Zr_{(1)} + C_{(s)} = ZrC_{(1)}$ can be obtained. If the ZrC activity is taken as unity, there are two unknowns; the activity of Zr, a_{Zr} , and the activity of carbon, a_C . Since the vapor pressures of the pure components are known, only the product of the reduced pressures above the compound is known.

In vacuum, ZrC is thought to achieve congruency at a composition approaching $ZrC_{0.85}$ near the melting point⁽¹³⁾. In the absence of better information, the same value was assumed for the liquid to obtain the lower curve in Fig. 4. It is realized that the assumption of a congruent composition constant with temperature cannot be correct, but for the purpose of this paper, it is probably satisfactory.

The free energy of formation of the non-stoichiometric compound was assumed proportional to the composition, i.e., the ΔF° was assumed to be $1.85/2.00$ that of "stoichiometric" ZrC, which actually has a composition slightly less than stoichiometric.

For the calculations in which the metal activity was assumed to be 0.5, the free energy of formation was taken to be $3/4$ that of ZrC. This undoubtedly gives an unrealistically low value for the carbon activity.

For NbC, there is no tabulation of estimated data for the liquid or solid. We extrapolated the solid enthalpy data given by Storms⁽¹³⁾ to the assumed melting point, 3900°K, and obtained a heat of fusion based on an estimated entropy of fusion. The entropy of fusion of NbC was assumed to be the sum of the entropy of fusion of Nb (2.3 e.u.) and an estimated entropy of fusion of carbon of 5.3 e.u.⁽¹⁴⁾ The entropy of NbC_(l) was assumed to be the sum of the entropy of the liquid components plus the entropy of mixing.

NbC was assumed to vaporize congruently at NbC_{0.7}. The free energy of formation was varied with composition in the same way as that for ZrC. The ΔH°_{298} of formation of NbC was taken as -33,600 kcal;⁽¹³⁾ that of NbC_{0.7} = 28,500.

APPENDIX II - Thermodynamic Data for C₂H and C₂H₂

A very large number of hydrocarbons are stable under the conditions considered in this paper. Unfortunately, precise thermodynamic data are rarely available, and estimates must be made. Duff and Bauer⁽¹⁵⁾ have published an extensive study of this subject.

We have chosen to consider only the hydrocarbons which are formed in the greatest concentrations. Ignoring the remainder should affect the total hydrocarbon concentration by at most a factor of two.

C₂H₂ -- We have estimated the high temperature free energy functions and assumed a ΔH°_{298} of formation of 54.33 kcal/mole. Our results agree quite closely with those of Duff and Bauer.

C₂H -- Neither free energy functions nor enthalpy of formation are known for this molecule. We estimated both; our enthalpy of formation was 100 kcal/mole, compared with 117 kcal/mole estimated by Duff and Bauer.

REFERENCES

- (1) McCarthy, J., "Nuclear Reactors for Rockets", Jet Propulsion 24, 1954, p. 36.
- (2) Nelson, S. T., Gray, J., and Williams P. M., "Conceptual Study of a Liquid-Core Nuclear Rocket", AIAA Paper No. 64-385, 1st AIAA Annual Meeting, June 29-July 2, 1964.
- (3) Barret, W. L., "Liquid Core Nuclear Rocket", AIAA Paper No. 64-541, May 4-6, 1964.
- (4) Ackerman, R. J. and Thorn, R. J., "Progress in Ceramic Science", edited by J. E. Burke. Pergamon Press, New York.
- (5) King, C. R., "Compilation of Thermodynamic Projects and Theoretical Rocket Performance of Gaseous Hydrogen", NASA Technical Note D-275, April 1960.
- (6) Kaufman, L. and Sarney, A., "Thermodynamic Properties of Transition Metal Monocarbides". International Symposium on Compounds of Interest in Nuclear Reactor Technology, edited by Waber, J., Chiotti, P., and Miner, W. N., August 3,4,5, 1964.
- (7) Bussard, R. W., "Nuclear Rocketry - The First Bright Hopes", Astronautics, Dec., 1962.
- (8) Unclassified abstracts of several classified papers presented at "Fuel Element and Materials Technology I" Session of AIAA Propulsion Joint Specialist Conference, USAF Academy, Colorado Springs, Colo., June 14-18, 1965. AIAA Bulletin V2, no. 5, May 1965, pp. 235-236.
- (9) Ibid, "Fuel Element Material Technology II" Session, paper by Robinson and Wells, p. 248.
- (10) Ibid, "Reactor Design" Session, paper by Moyer and Goldberg, p. 206.
- (11) Wells, W. M., Brown, N. J., and Myers, W. B., "Tory III Reactor", classified portion of presentation at Classified Nuclear Propulsion Conference sponsored by ARS, ANS and IAS and held at Monterey, California, August 15-17, 1962.

- (12) Cooper, R. S., "Fast Reactor Rocket Engines - Heat Transfer", LA-2746, Los Alamos Scientific Laboratory, Los Alamos, New Mexico, October 8, 1962.

Various verbal discussions indicate the thermal stress fracture fear is often given more credence than this particular reference suggests.

- (13) Storms, E. K., "A Critical Review of Refractories", LA-2942, Los Alamos Scientific Laboratory, Los Alamos, New Mexico, August 1964.

- (14) Kaufman, L., and Clougherty, E. V., "Thermal Dynamic Factors Controlling the Stability of Solid Phases at High Temperatures and Pressures", Vol. 22, Metallurgy Society Conferences, Gordon and Breach Science Publishers, New York-London, p. 331.

- (15) Duff, R. E. and Bauer, S. H., "The Equilibrium Composition of the C/H System at Elevated Temperatures", LA-2556, Los Alamos Scientific Laboratory, Los Alamos, New Mexico, 1961.

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Fig. 1 Degradation in Specific Impulse due to Equilibrium Vaporization
Refractory Metal - Uranium Solutions
Pressure 100 Atm.

Fig. 2 Hydrogen Flow Rate Required to Extract 1 MWh Enthalpy

Fig. 3 Phase Diagram of Nb-C System

Fig. 4 Degradation in Specific Impulse due to Equilibrium Vaporization and Hydrocarbon Formation
Carbide Systems - Pressure 100 Atm. Hydrogen

Fig. 6 Fluorescent penetrant photo of typical cracked tube.

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Fig. 7 End view of test assembly.

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MISSING FRAGMENT

Fig. 8 Cracked tube assembly after testing showing one missing fragment.