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RESEARCH LABORATORY

TECHNICAL REPORT

CHEMICAL CORROSION OF ROCKET LINER
MATERIALS AND PROPELLANT
PERFORMANCE STUDIES

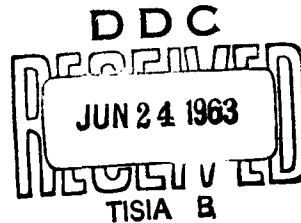
Fourth Quarterly Technical Summary Report

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ABSTRACT

Studies on the theoretical equilibria resulting from interaction of candidate refractory nozzle wall materials with various chemical species resulting from combustion of rocket fuels have continued. Tantalum carbide has been considered in detail, with composition diagrams and saturation parameters reported for its interaction at 1000 psia with AlF_3 , BF_2 , BF_3 , BOF , BeF_2 , CO , CO_2 , HCl , HF , H_2 , H_2O , LiF and N_2 . Similar computations are reported for tungsten interacting with BOF , CO , and CO_2 , these results representing a revision of data reported in the previous quarterly report under this contract, as necessitated by a recent revision in the thermodynamic data for the tungsten oxides. The oxides are considered briefly as a class for application in oxygen-containing atmospheres, with results given for MgO , HfO_2 and ThO_2 in CO_2 . The stability of carbides in nitrogen is also considered.

The possibility of extending the isothermal saturation results for pure components at 1000 psia to mixtures at other pressures has been considered in some detail, with results that look promising except where multi-atomic species are important which are not considered in the individual cases (e.g., HCN is important in a N_2 - H_2 mixture in equilibrium with graphite, but is not considered with the individual pure reactants). A "catalog" of ablation reactions for studies reported previously is included.

Plans for future work are described briefly. Certain errata for previous reports are appended.

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SECTION 1

INTRODUCTION

This is the fourth quarterly report in a program which has two parts, the first being the theoretical appraisal of various refractory rocket liner materials from a chemical standpoint and the second being the computation of theoretical performance of certain rocket propellant combinations. Work in this past quarter has been concerned only with the evaluation of refractory nozzle materials.

Refractory materials under study include graphite, tungsten, and various high melting carbides, nitrides, borides, and oxides. The procedure in use for comparing these materials is to compute the theoretical amounts of these refractory materials required to "saturate" a unit mass of reacting gas or solid which represents a component of a rocket combustion stream; the details of the procedure were given in the Volume I of the Second Quarterly Report¹. As explained therein, stability is expressed in terms of both an isothermal saturation parameter (the value "A") and an adiabatic saturation parameter (the value "B"). The adiabatic saturation parameter is proportional under certain conditions to the rate of attack by a flowing stream. Both parameters include effects of simple vaporization, which factor becomes important² even in the absence of chemical reactions at temperatures greater than about 3500°K, especially with low molecular weight gas streams and with more volatile refractories. The computational technique is arbitrarily extended to temperatures above the melting point without modification, a technique which is valid in terms of chemical stability but obviously not significant in terms of physical stability.

Thermochemical data used in these calculations have been obtained for the most part from the JANAF³ compilations. It has in addition been necessary to accumulate thermodynamic data for certain heavy metal species not available in these tables, and this has been, prior to this quarter, represented a significant portion of the effort in this program.

Chemical compatibility studies are reported herein for tantalum carbide with various pure gases and solids, and for tungsten in oxygen-containing gases (with the exception of H_2O). In addition oxides as a class are discussed briefly for application in oxidizing atmospheres, as well as nitride-carbide equilibrium. The tungsten-oxygen calculations represent a revision of results reported previously², necessitated by recent revisions in the JANAF tabulations of data for tungsten oxides. Equilibrium systems in which $H_2WO_4(g)$ may appear have not been reported, as revision of $H_2WO_4(g)$ thermodynamic data is expected in the near future⁴.

The use of an averaging technique to predict the "A" saturation parameter for real combustion gas mixtures is discussed.

SECTION 2

CHEMICAL CORROSION STUDIES

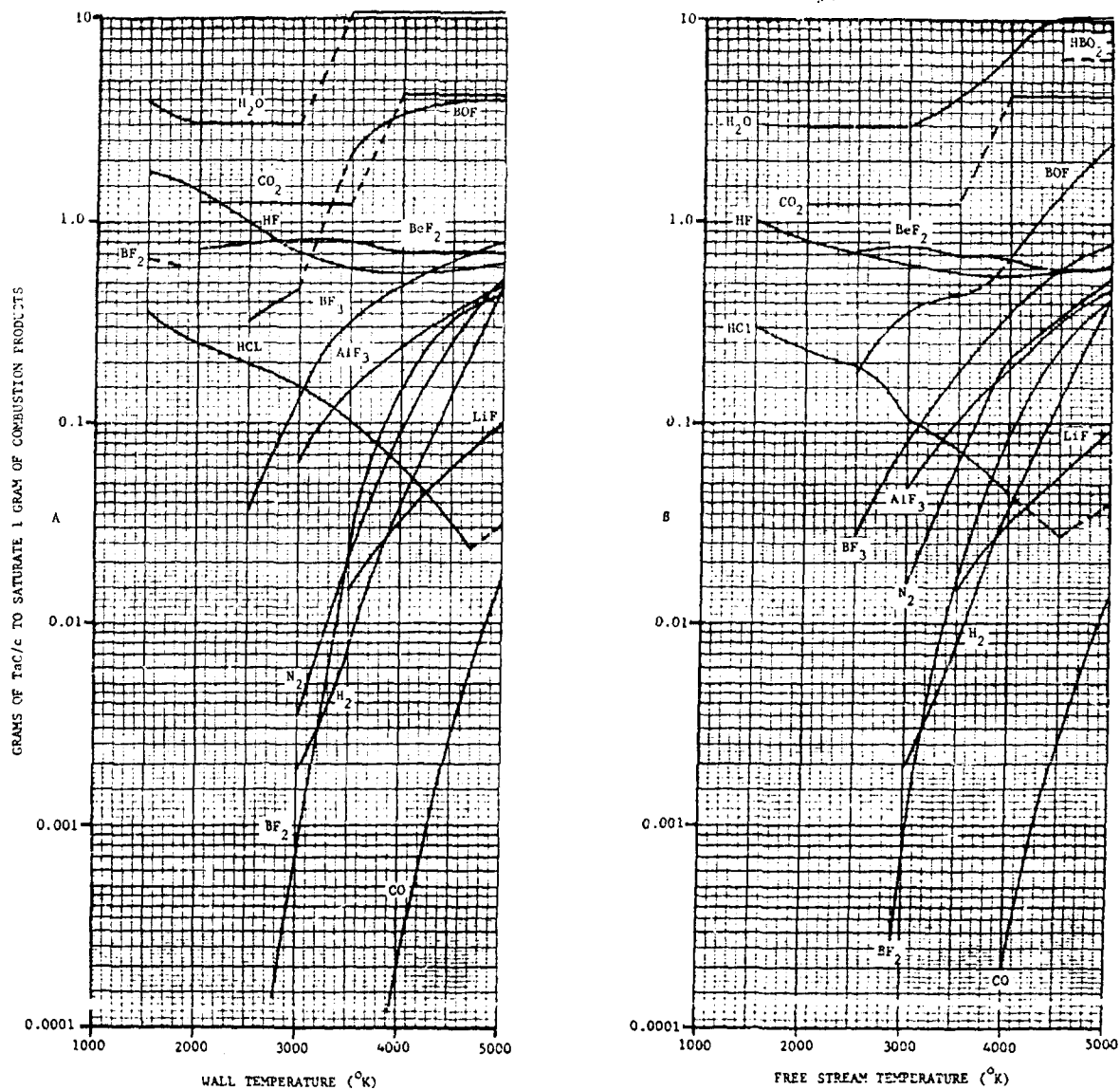
2.1 CHEMICAL CORROSION OF TANTALUM CARBIDE

2.1.1 GENERAL

The chemical stability of tantalum carbide in fourteen different atmospheres was calculated as described in previous reports^{1,2} under equilibrium conditions at 1000 psia and various temperatures; the atmospheres were formed by equilibration of the nominal species AlF_3 , BF_3 , BF_2 , BOF , BeF_2 , CO_2 , CO , HCl , HF , H_2 , H_2O , LiF and N_2 . (The nominal species specifies the overall stoichiometry; the species itself may, however, be largely dissociated at the temperature and pressure under consideration.) The results are presented as "A" and "B" plots in Figure 1; equilibrium compositions are given in Figures 2 through 6. Principal species contributing to corrosion are shown in Table I.

It is apparent from Figure 1 that in many cases TaC is severely attacked (B values greater than unity) by species containing "loosely" bound oxygen, such as CO_2 and H_2O ; species such as BF_3 and BeF_2 which contain "excess" fluorine are less damaging. Exothermic effects are noted for the species HCl , HF and N_2 , and endothermic effects with AlF_3 , BF_3 , BF_2 and BOF .

The species HBO_2 was considered but again gave rather meaningless results as no gas phase was found to be present below about 4500-5000°K, (as



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FIGURE 1. CHEMICAL CORROSION OF TaC BY COMMON COMBUSTION PRODUCTS
AT 1000 PSIA

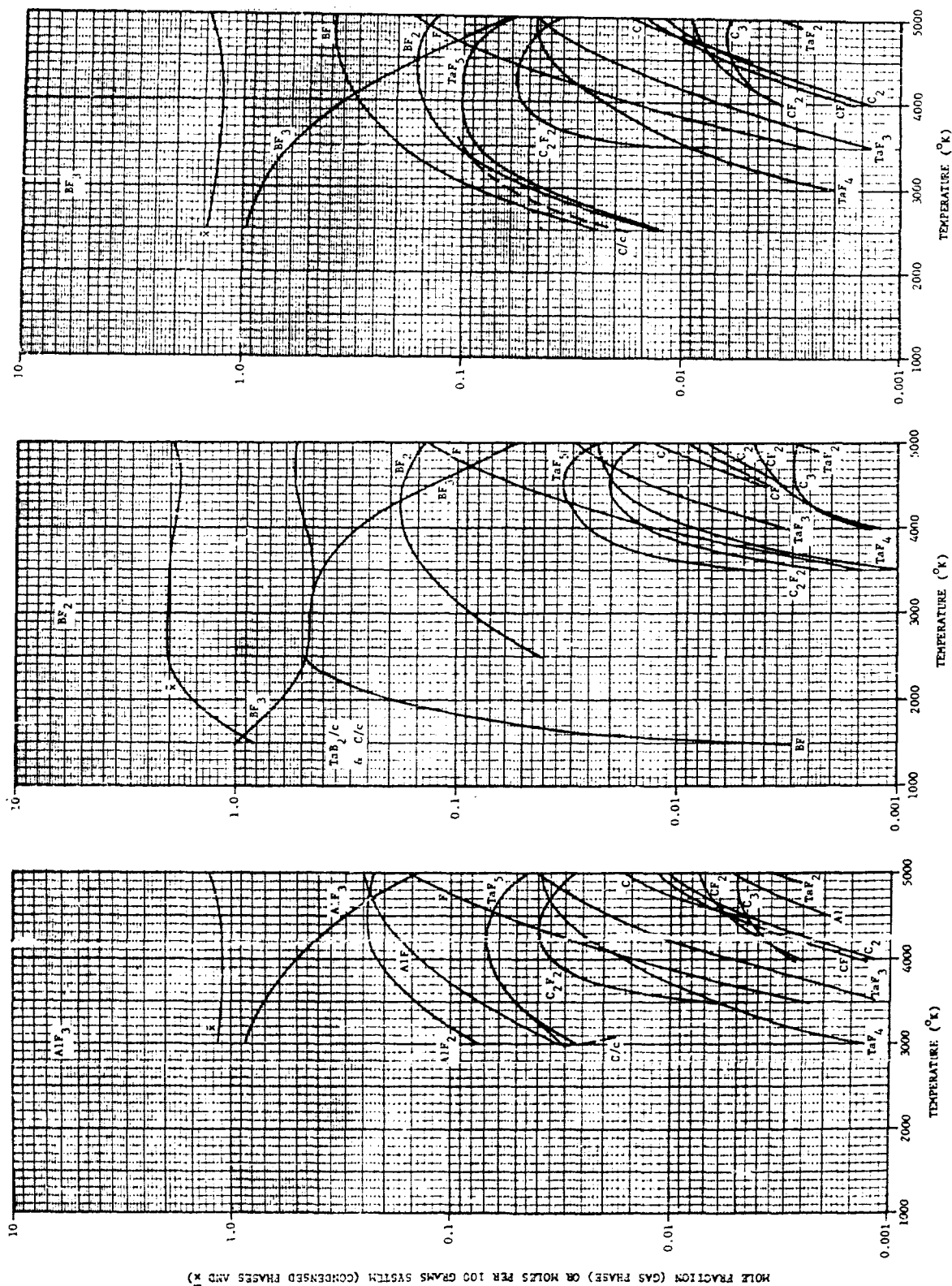
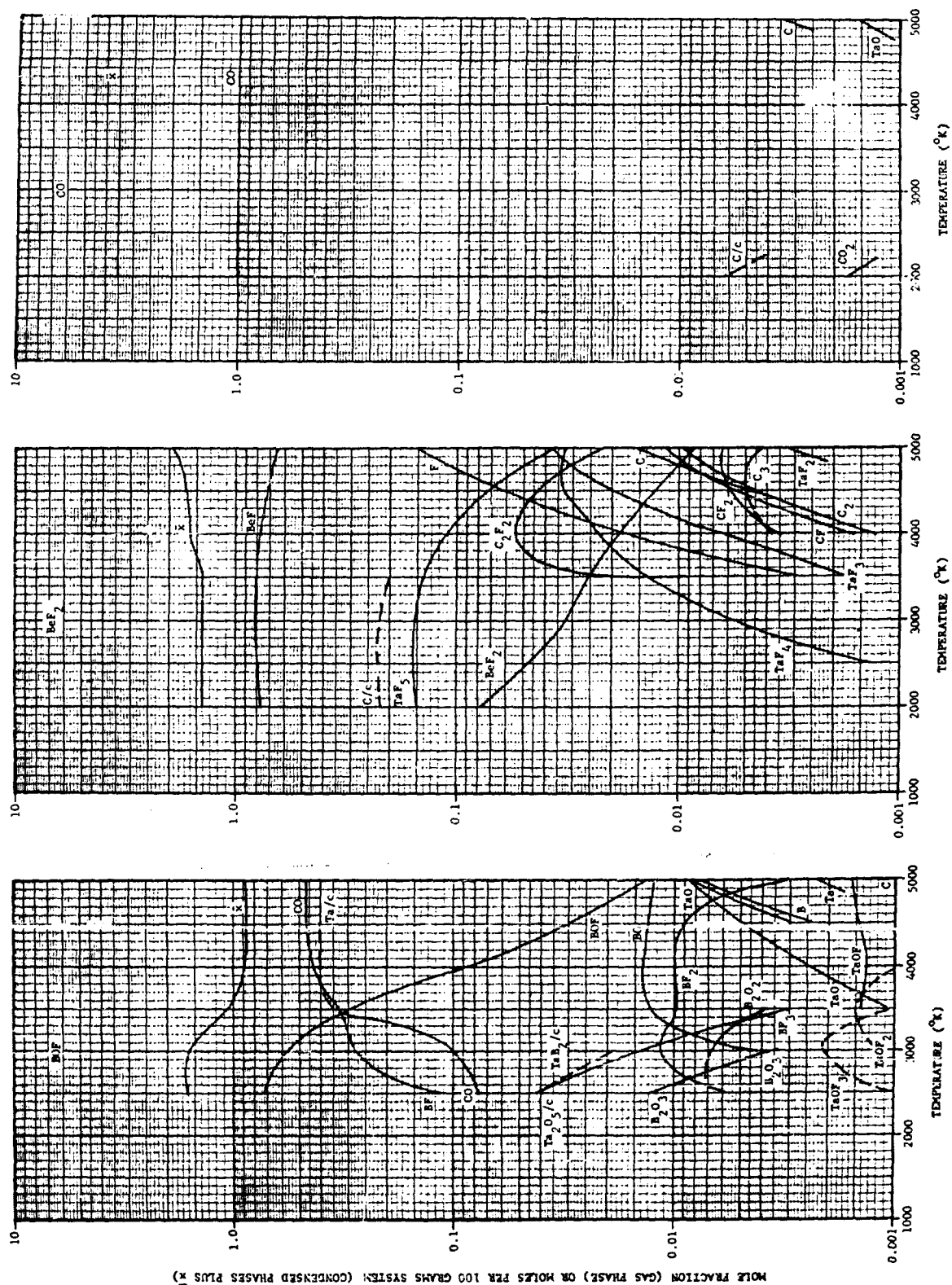


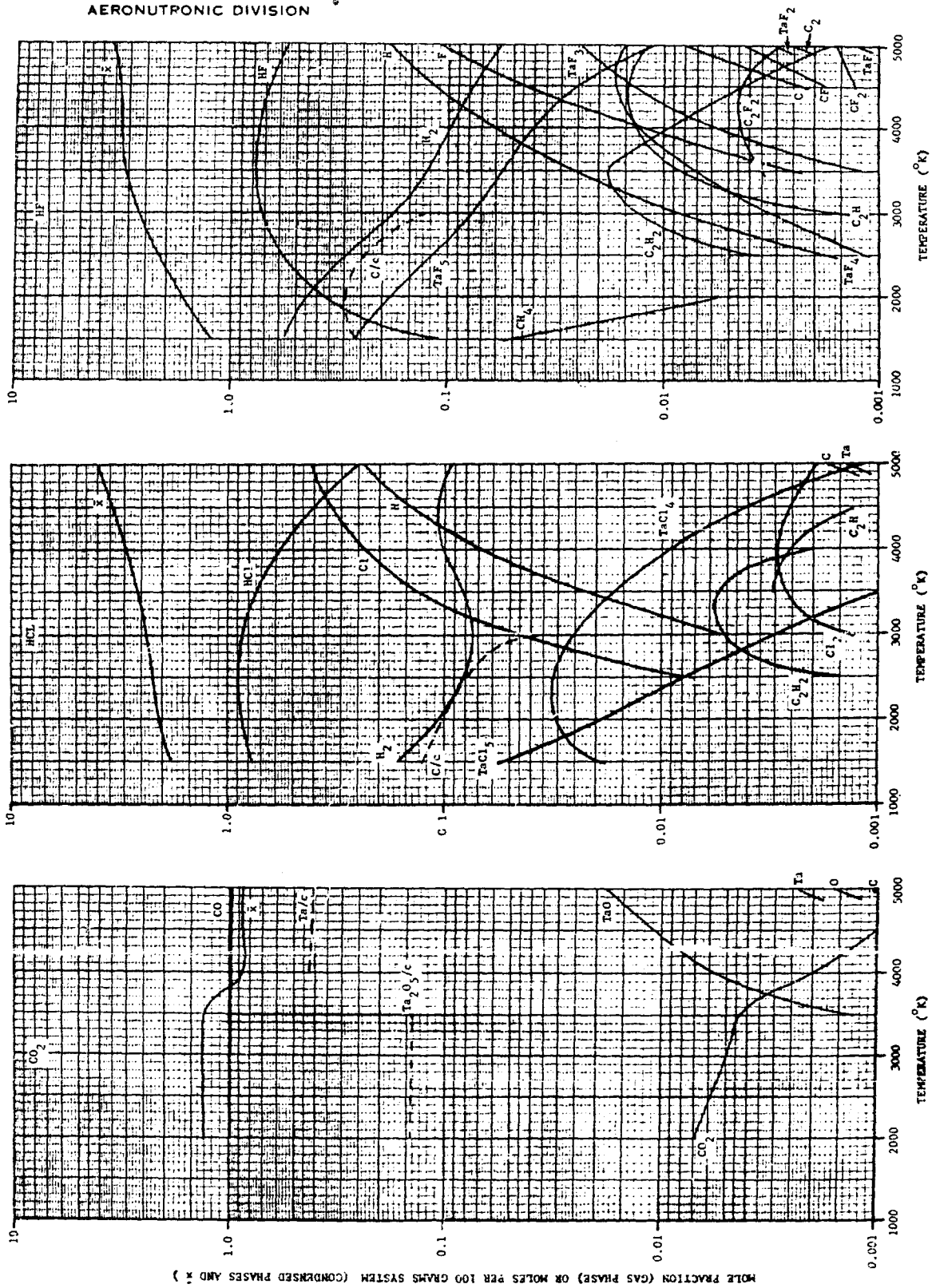
FIGURE 2. SPECIES PRESENT UNDER EQUILIBRIUM CONDITIONS AT 1000 PSIA
FOR TaC AND AlF_3 , BF_2 , AND BF_3

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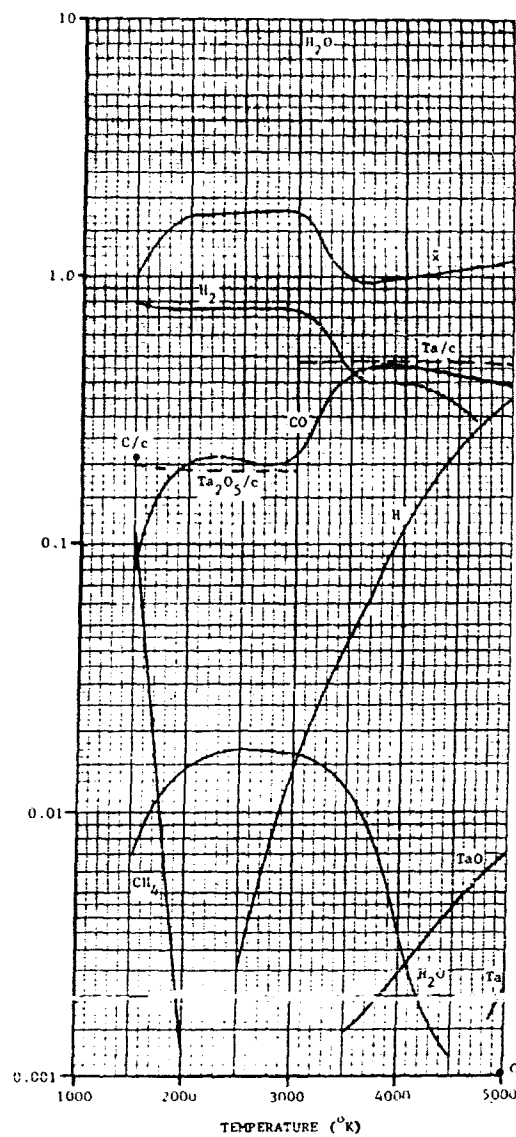
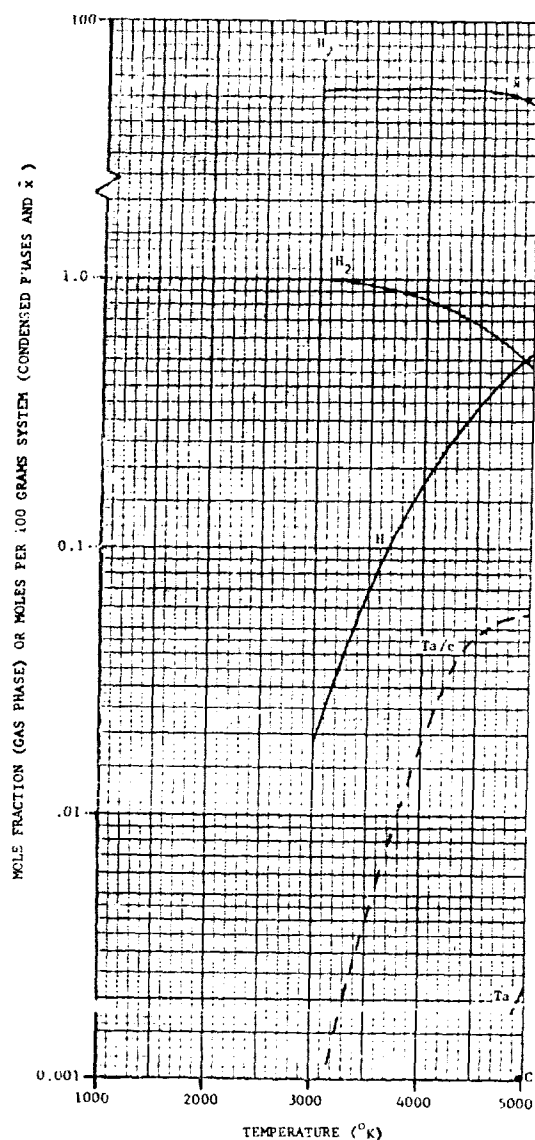
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FIGURE 3. SPECIES PRESENT UNDER EQUILIBRIUM CONDITIONS AT 1000 PSIA
FOR TaC AND BOF, BeF₂, AND CO



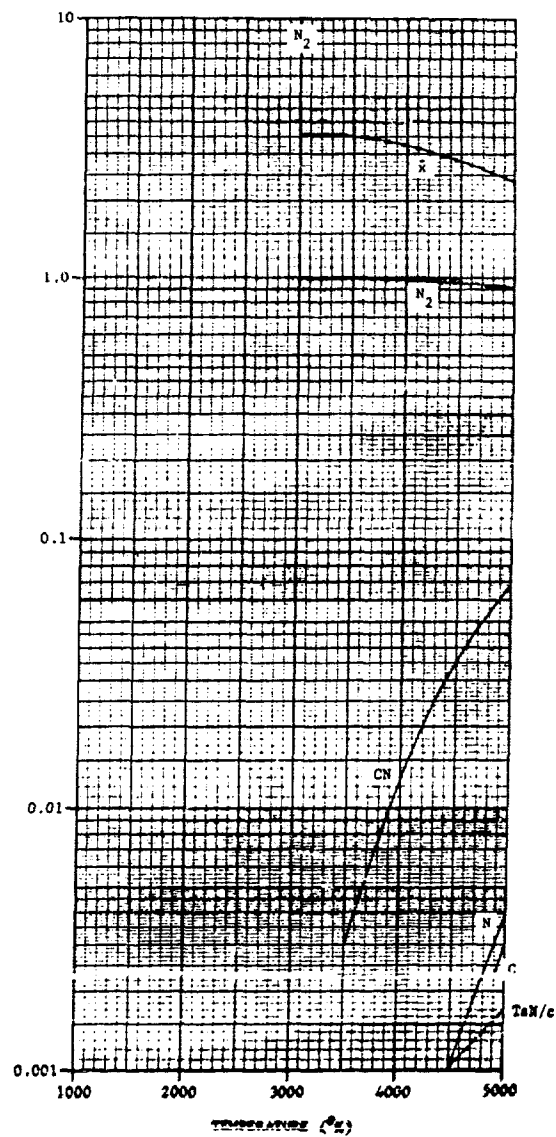
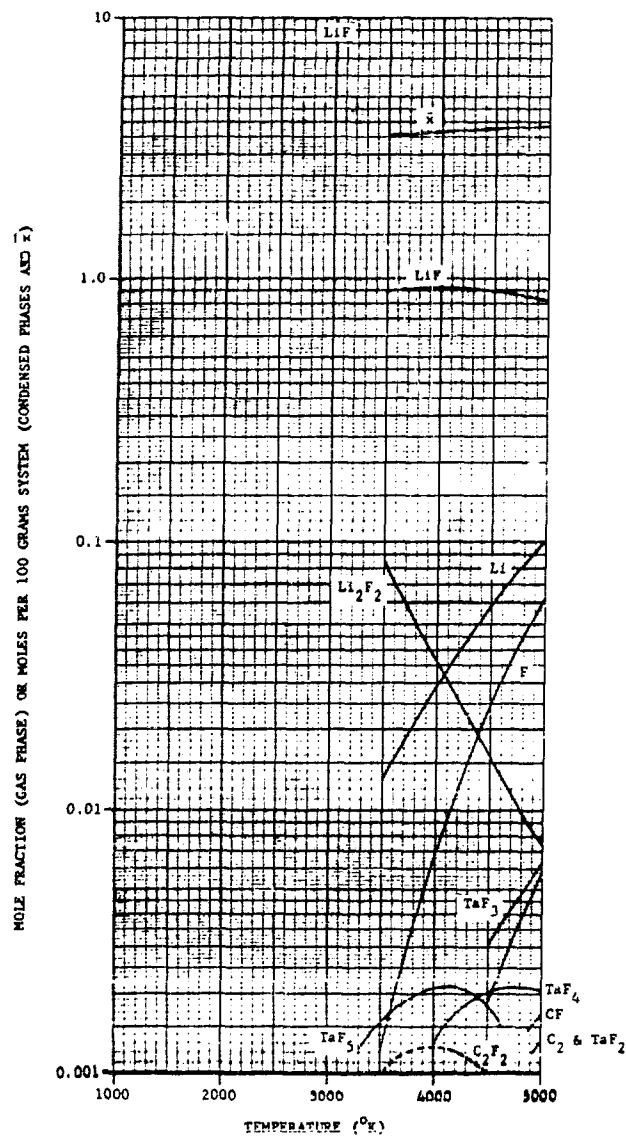
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FIGURE 4. SPECIES PRESENT UNDER EQUILIBRIUM CONDITIONS AT 1000 PSIA
FOR TaC AND CO₂, HCl, AND HF



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FIGURE 5. SPECIES PRESENT UNDER EQUILIBRIUM CONDITIONS AT 1000 PSIA
FOR TaC AND H₂ AND H₂O



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FIGURE 6. SPECIES PRESENT UNDER EQUILIBRIUM CONDITIONS AT 1000 PSIA
FOR TaC AND LiF AND N_2

TABLE I

PRINCIPAL SPECIES CONTRIBUTING TO THE ABLATION OF
TANTALUM CARBIDE AT 1000 PSIA

Combustion Product	Principal Species at the Nozzle Wall	Approximate Temperature Range (°K)	Remarks
AlF ₃	TaF ₅ , C(c), C ₂ F ₂	3000-5000	No gas phase below about 3000°K.
BF ₂	TaB ₂ (c), C(c)	1500	
	TaF ₅ , TaF ₄ , TaF ₃ , C ₂ F ₂ , C	3500-5000	
BF ₃	TaF ₅ , C(c), C ₂ F ₂ , TaF ₄ , TaF ₃	2500-5000	
BOF	Ta(c), CO	3500-5000	
	Ta ₂ O ₅ (c), TaB ₂ (c)	2500-3000	
BeF ₂	C(c), TaF ₅ , TaF ₄ , TaF ₃ , C ₂ F ₂	2000-5000	
CO	TaO	4500-5000	
CO ₂	Ta ₂ O ₅ (c)	2000-3500	
	Ta(c), TaO	4000-5000	
HCl	C(c)	1500-3000	
	TaCl ₄ , TaCl ₅	2000-5000	Decrease with temp.
HF	C(c), TaF ₅	1500-5000	Decrease with temp.
	TaF ₃ , TaF ₄ , C ₂ H	3000-4500	Increase with temp.
H ₂	Ta(c)	3000-5000	
H ₂ O	C(c), Ta ₂ O ₅ (c), Ta(c)	1500-3000-5000	Solids exist in three separate temp. ranges
	CO	1500-5000	
LiF	TaF ₃ , C	4500-5000	
N ₂	CN, TaN(c)	3500-5000	

was the case with tungsten²) and this result was considered unreliable in view of the lengthy extrapolation used in preparing the thermodynamic tables for this species in this region. It accordingly has not been reported in detail.

2.1.2 DISCUSSION OF INDIVIDUAL CASES

AlF₃

The saturation numbers increase over the temperature range investigated, with a fairly constant cooling of about 200°. The cooling can be attributed to endothermic reactions involving formation of tantalum and carbon fluorides.

BF₂ and BF₃

The general behavior of these systems is similar to the AlF₃ system. Cooling is slightly greater in the case of BF₃.

BOF

This system forms solid phases which have a vapor pressure less than 1000 psia below about 2500°. At about 3000-3500°, the reduction of the carbide to the metal with formation of CO produces a substantial cooling effect with the equilibrium wall temperature over 1000° cooler than the free stream temperatures.

BeF₂

This system shows essentially a constant saturation number as was found also for tungsten with this gas². Basically the BeF₂ is dissociating to BeF and F, the free fluorine then reacting with the condensed phase. The overall reaction is endothermic at low temperature (640° at 2500°) and exothermic at high temperature (1100° at 4500°). It should be mentioned that these results are based on the JANAF value of -88.34 kcal/mole for the standard heat of formation of BeF at 298°K; a less negative value which now appears probable⁵ would presumably materially alter the results.

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CO

Very little reaction takes place over the whole temperature range, as would be expected. Some cooling occurs at very high temperatures (53°K at 5000°K ; 11°K at 4500°K) due to volatilization.

CO₂

The corrosion is essentially due to oxygen from dissociation of CO_2 . At temperatures below 3500°K , $\text{Ta}_2\text{O}_5/\text{c}$ is formed; at temperatures somewhat above 3500°K , Ta/c is formed. The latter reaction results in a larger saturation value than the former. The reaction becomes strongly exothermic at high temperature (-211° at 2500° , $+255^{\circ}$ at 3000° and 1497° at 4500°).

HCl

This gas reacts primarily (and exothermically) with TaC/c to form H_2 , solid carbon, and gaseous tantalum chlorides. Saturation numbers decrease with temperature due to decreasing stability of the tantalum chlorides and increase in the fraction of chlorine that remains in the elemental form. The equilibrium wall temperature is some $100\text{--}400^{\circ}$ greater than the free stream.

HF

This gas behaves chemically in a fashion similar to HCl . The heating effect is greater at low temperatures (nearly 1000°K) and less at high temperatures (about 100°K at 5000°).

H₂

Very little reaction occurs below about 3000°K , at which temperature the saturation reaction is slightly exothermic (23°K). The saturation numbers increase with temperature as more gaseous hydrocarbons and elemental metal are formed; the net heating effect decreases gradually until at 5000°K the net reaction is endothermic by 1.3°K .

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H₂O

Up to 3000°K, Ta₂O₅ is the primary reaction product, and is formed nearly quantitatively. At higher temperatures elemental tantalum forms. The saturation numbers are high over the whole range indicating that H₂O is extremely corrosive to TaC. The reactions are exothermic in the lower temperature region and strongly endothermic where Ta₂O₅ is not stable and Ta/c forms.

LiF

No gas phase is computed below about 3500°K. Gaseous products include tantalum and carbon fluorides along with gaseous lithium. The overall reactions are very slightly endothermic (15°K-50°K) over the 3500-5000°K range.

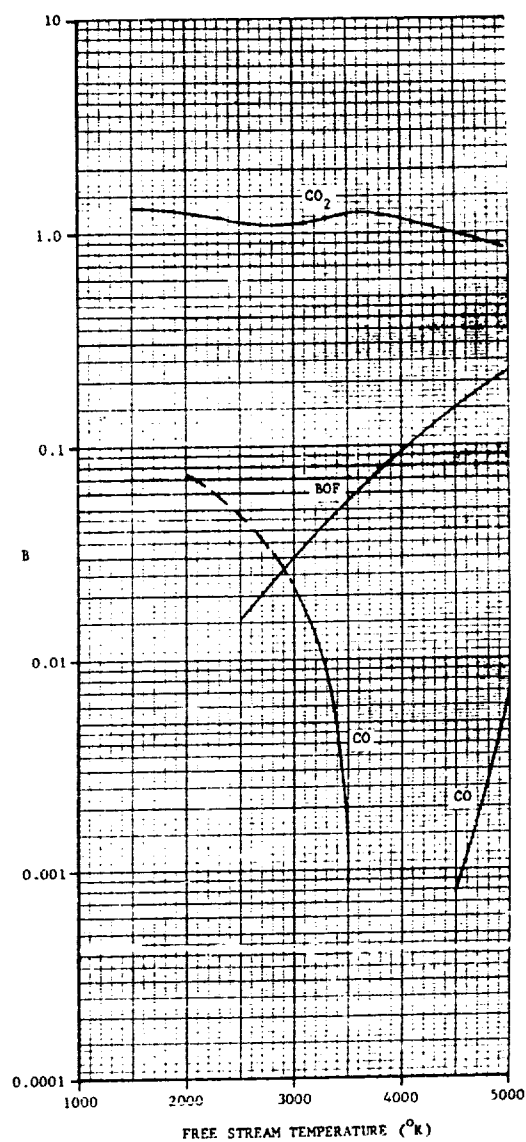
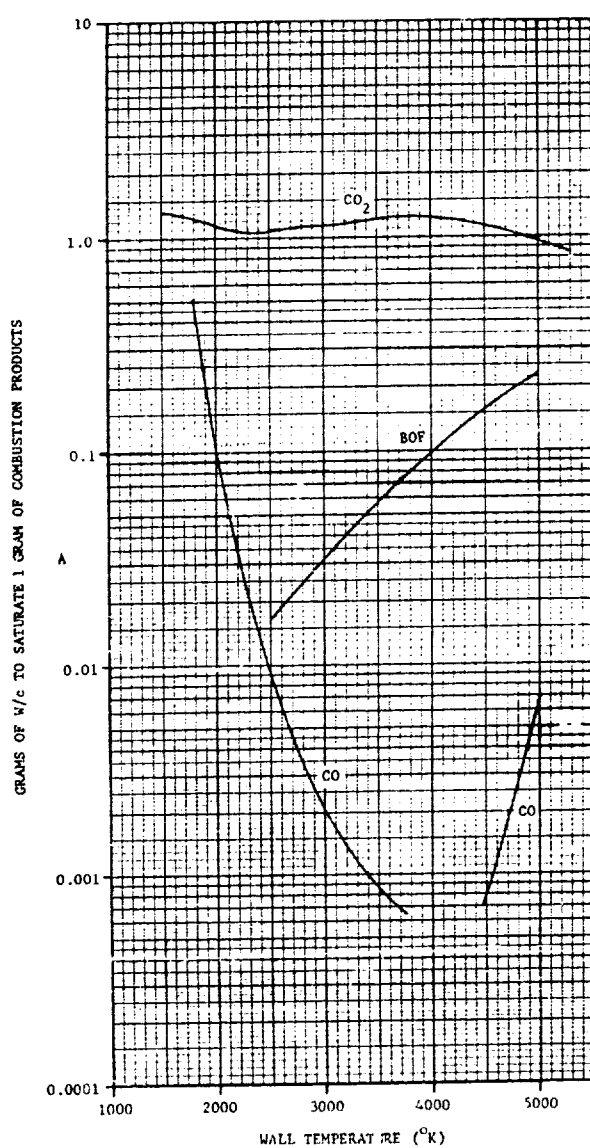
N₂

TaC reacts quantitatively with N₂ to form TaN and carbon at low temperatures (see Section 5). At 3000° the reaction is exothermic, so that the adiabatic wall is some 400°K hotter than the free stream. The reaction is exothermic to about this same degree to 4500°K; at 5000°K the reaction is only 38°K exothermic due to increase in endothermic volatilization effects. CN is the primary gaseous reaction product.

2.2 RECALCULATION OF THE CORROSION OF TUNGSTEN BY BOF, CO AND CO₂

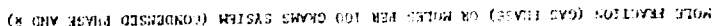
Since publication of the Third Quarterly Report², revised or new data sheets have been issued for the JANAF tables³ on the WO₃/c, WO₃(g), W₃O₉(g) and W₄O₁₂(g) species. As substantial changes were involved, computations for cases where these oxides might be significant were repeated. (The tungsten-water case has again been held up pending anticipated receipt of new information on H₂WO₄(g)⁴. The HBO₂ case was not recomputed in view of the rather meaningless results obtained before², with no gas phase present at 1000 psia below about 4500°K.)

Results are given in Figures 7 and 8.



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FIGURE 7. CHEMICAL CORROSION OF TUNGSTEN BY BOF, CO AND CO₂ AT 1000 PSIA (REVISED CALCULATIONS)



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Comparison of the results with the new and old data can be made by examining Table II. The most striking effect is on the 3500°K point with CO₂; the revised data show a substantial (592°K) increase in adiabatic saturation temperature over free stream temperature whereas the older data showed a significant (205°) cooling effect. This is due to a reduction in the enthalpy of saturated system at a given temperature with the revised data, as shown by the "hsw" values given in Table II. "B" values are not greatly affected, inasmuch as the revised data show W₃O₉ concentrations which are roughly one-third of the WO₃ concentration computed earlier. This is shown in Table III.

Comments on the individual systems follow.

BOF-W

This system is all condensed at 1500 and 2000°K at 1000 psia (WOF₄/c and B₂O₃/c). B₂O₃/c disappears above 2000°K. The polymeric tungsten oxide vapor species are not particularly important. The reactivity increases with temperature.

CO-W

At 1500°K and 1000 psia this system is all condensed, forming WC/c and WO₂/c. A gas phase appears between 1500 and 2000°K and reactivity decreases to nearly zero at about 4000°K at which point it begins to increase due to simple volatilization of tungsten. These results are of course sensitive to the thermodynamic data used for WC/c, which are not well known. No gas phase tungsten oxide is significant.

CO₂-W

This system also forms WC/c and WO₂/c at 1500°K. WC/c disappears below 2000°K; WO₂/c disappears below 2500°K. The polymeric tungsten oxide species are primary contributors to the ablation. (WO₃(g) was indicated to be the primary contributor in the last Quarterly Report².)

TABLE II

COMPARISON OF RESULTS OF ABLATION COMPUTATIONS USING
"OLD" AND REVISED JANAF THERMODYNAMIC DATA FOR TUNGSTEN OXIDES

1000 psia				
Free Stream Temp., °K	Wall Temperature, °K		B Parameter	
	"Old"	Revised	"Old"	Revised
System W-BOF				
3000	2962	2969	.0307	.0292
3500	3412	3443	.0631	.0526
4000	3901	3947	.1275	.0943
4500	4459	4478	.2257	.1563
5000	5021	5004	.3098	.2234
System W-CO				
2000	2057	2057	.0773	.0773
3500	3501	3501	.0009	.0009
4000	4000	4000	.00004	.00004
4500	4498	4498	.0008	.0008
5000	4981	4981	.0065	.0065
System W-CO ₂				
3000	2843	2804	1.008	1.148
3500	3295	4092	1.153	1.240
4000	4611	4659	1.227	1.141
4500	5232	4984	1.241	0.984
5000	5624	5312	0.911	0.814

TABLE III

COMPARISON OF EQUILIBRIUM GAS MOLE FRACTIONS
CO₂ plus W, 1000 psia

"Old" and "Revised" as in Table II

Species	3000°		3500°		4000°	
	Old	Revised	Old	Revised	Old	Revised
CO	.7222	.7781	.6704	.8058	.6947	.8032
CO ₂	.1839	.1401	.1051	.1035	.0644	.0829
O	.0001	--	.0017	.0014	.0099	.01104
WO	--	--	--	--	.0004	.0004
O ₂	.0001	.0001	.0009	.0006	.0031	.0038
WO ₂	.0001	--	.0011	.0008	.0045	.0056
WO ₃	.0912	.0005	.2203	.0037	.2231	.0145
W ₃ O ₉	.00238	.0656	.0004	.0730	--	.0709
W ₄ O ₁₂	--	.0155	--	.0111	--	.0076
WO ₃ /c*	.169					
$\bar{x}^{**}$	1.190	1.137	1.334	1.120	1.326	1.143
hsw***	-40.16	-41.52	-15.02	-30.77	-4.15	-18.67

* Moles/100 grams of system on an excess tungsten-free basis

** Moles gas on same basis

*** In kcal/100 grams on same basis $[\sum x_i (\Delta H_{f298}^{\circ} + H_{298}^+)]$

2.3 REFRACTORY OXIDES FOR USE IN OXYGEN-CONTAINING ATMOSPHERES

Equilibrium calculations have been made during the course of this work on a variety of refractory materials, including graphite and tungsten as well as certain carbides and borides. All of these materials have been found to be subject to fairly severe attack in oxygen-containing atmospheres (such as CO_2 and H_2O), a fact which leads immediately to consideration of refractory oxides as materials for such applications. Unfortunately, the oxides generally melt at much lower temperatures than do the other materials of interest so that they are not obviously attractive for high temperature application. This is shown by the figures in the following list:

<u>Compound</u>	<u>Melting Point, $^{\circ}\text{K}$</u>
TaC	4100
HfC	4160
W	3650
C	~ 4100 (sublimes at 1 atm)
HfN	3580
HfB ₂	3520
ThO ₂	3323
HfO ₂	3170
MgO	3073
BeO	2823

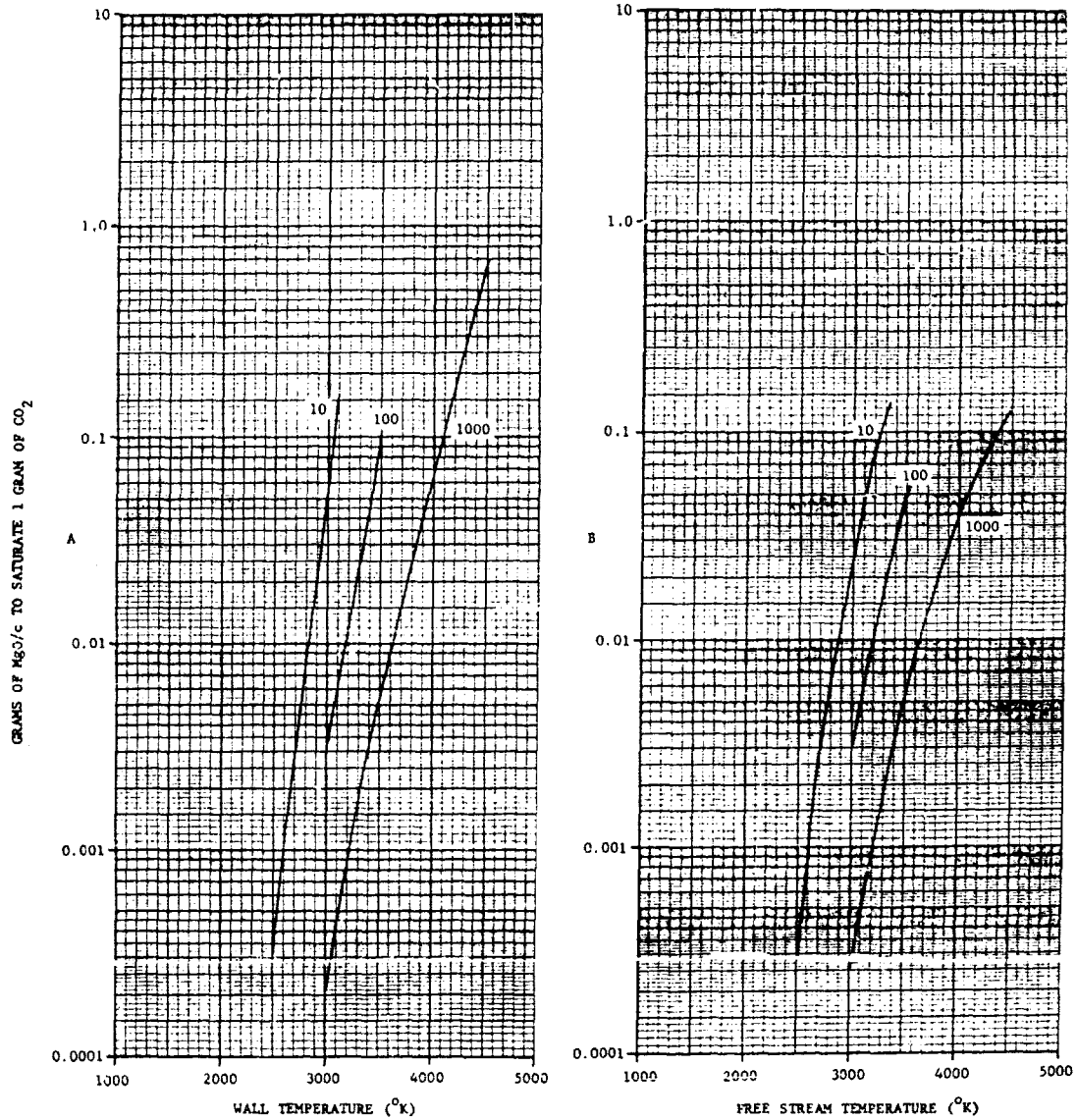
The highest melting oxide is ThO₂, which melts at a temperature of 3323 $^{\circ}\text{K}$ or 5521 $^{\circ}\text{F}$, a temperature far below that expected with many advanced propellant systems of interest. There did, however, appear to be some possibility that these materials would be self-cooled by their own vaporization processes, which if appreciable, could make their usefulness somewhat greater than would be immediately apparent. A brief study was thus made of the cooling effect involved with CO_2 as a nominal gas using the refractory oxides MgO, HfO₂ and ThO₂. MgO was studied because it is, in

the region of interest, the most volatile of the high melting oxides; HfO_2 because it is the last volatile⁶, and of course ThO_2 because it is the highest melting oxide.

The procedure used was the same as that employed in other cases studied, except that attention was devoted to the cooling effect during adiabatic saturation as a function of pressure. Thermodynamic data for the MgO system were based on the JANAF tables to the melting point (3073°K)⁷ at which a heat of fusion of 18.5 kcal/mole was assigned and above which a constant heat capacity of 14.0 cal/mole- $^\circ\text{K}$ was used. The data for HfO_2 and its compounds was that reported previously in this work². These two cases were computed using the Aeronutronic machine ablation program^{1,2}; the ThO_2 case was considered only by relatively crude hand computation methods inasmuch as the thermodynamic data available for ThO_2 ⁸ have not been worked up into a form suitable for inclusion in our machine program.

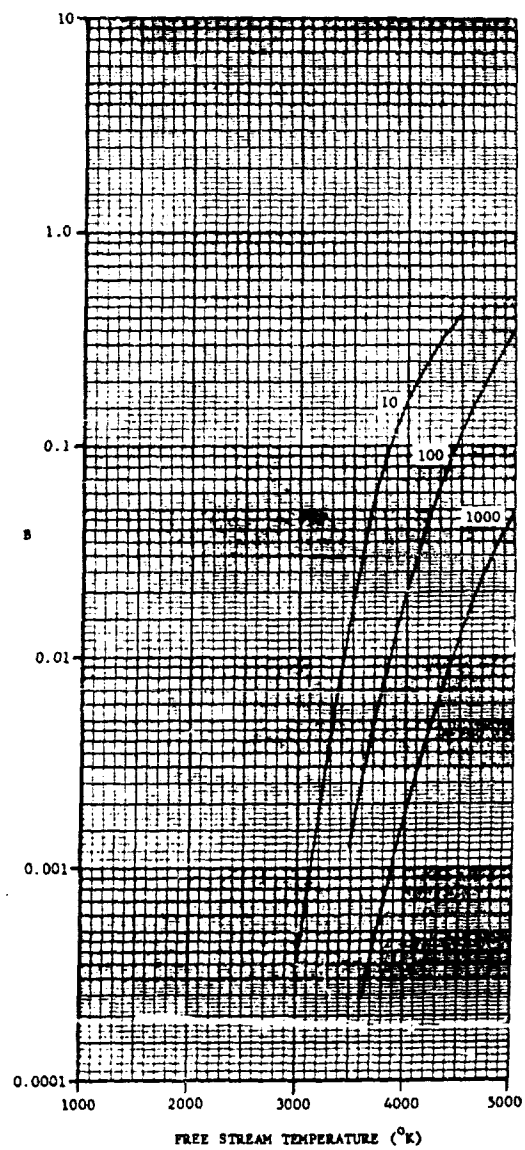
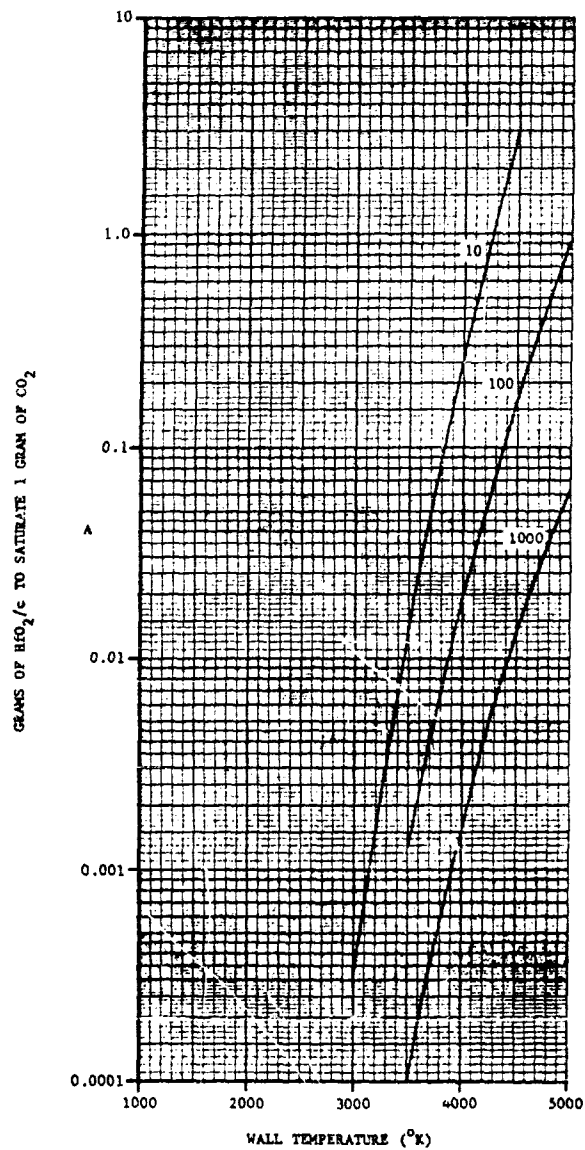
Equilibrium computation results for MgO and HfO_2 are shown for the three cases studied in Figure 9 through 13. Examination of the "A" and "B" plots reveals that relatively little cooling effect can be anticipated in the vicinity of the melting point, and that where cooling is substantial, saturation values are high. The cooling effect in the CO_2 case is made more clearly evident in Figure 13; a similar plot for the HfO_2 case would show substantially less deviation from the 45° line. (At 3500°K and 10 psia, the cooling effect with HfO_2 is only 5°K .)

The self-cooling effect due to volatilization of the oxides is summarized along with "B" values, at the melting point, for the three cases studied in Table IV. The cooling effect, which is shown in the final column, denotes the difference between the free stream stagnation temperature and the wall temperature at the melting point (under, of course, the assumptions used in this work). Obviously, the cooling effect is greater at lower pressure but in no case is it very great. With MgO , for example, the free stream stagnation temperature can be only approximately 270° above the



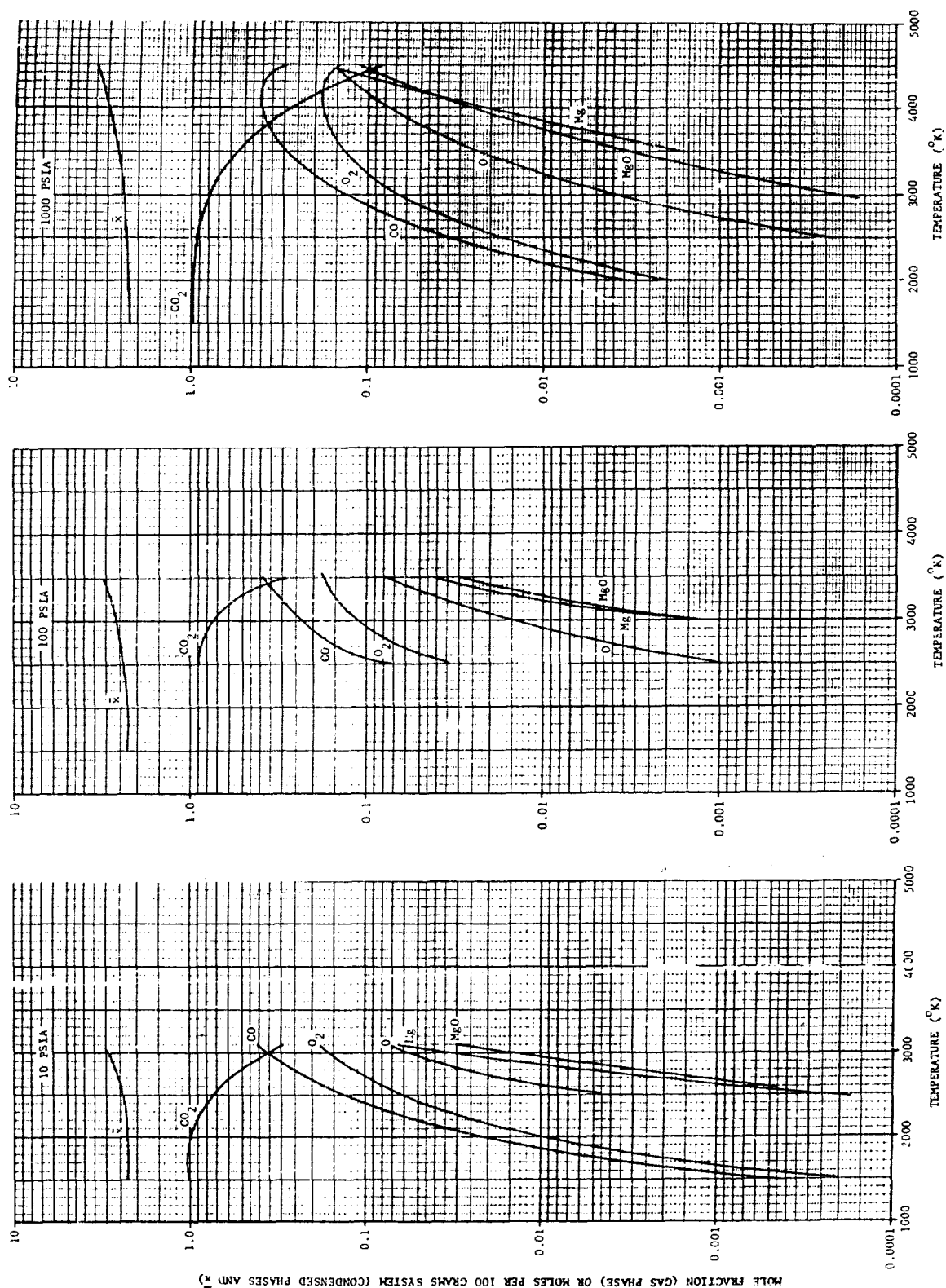
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FIGURE 9. CHEMICAL CORROSION OF MgO BY CO₂ AT THREE PRESSURES



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FIGURE 10. CHEMICAL CORROSION OF HfO_2 BY CO_2 AT THREE PRESSURES

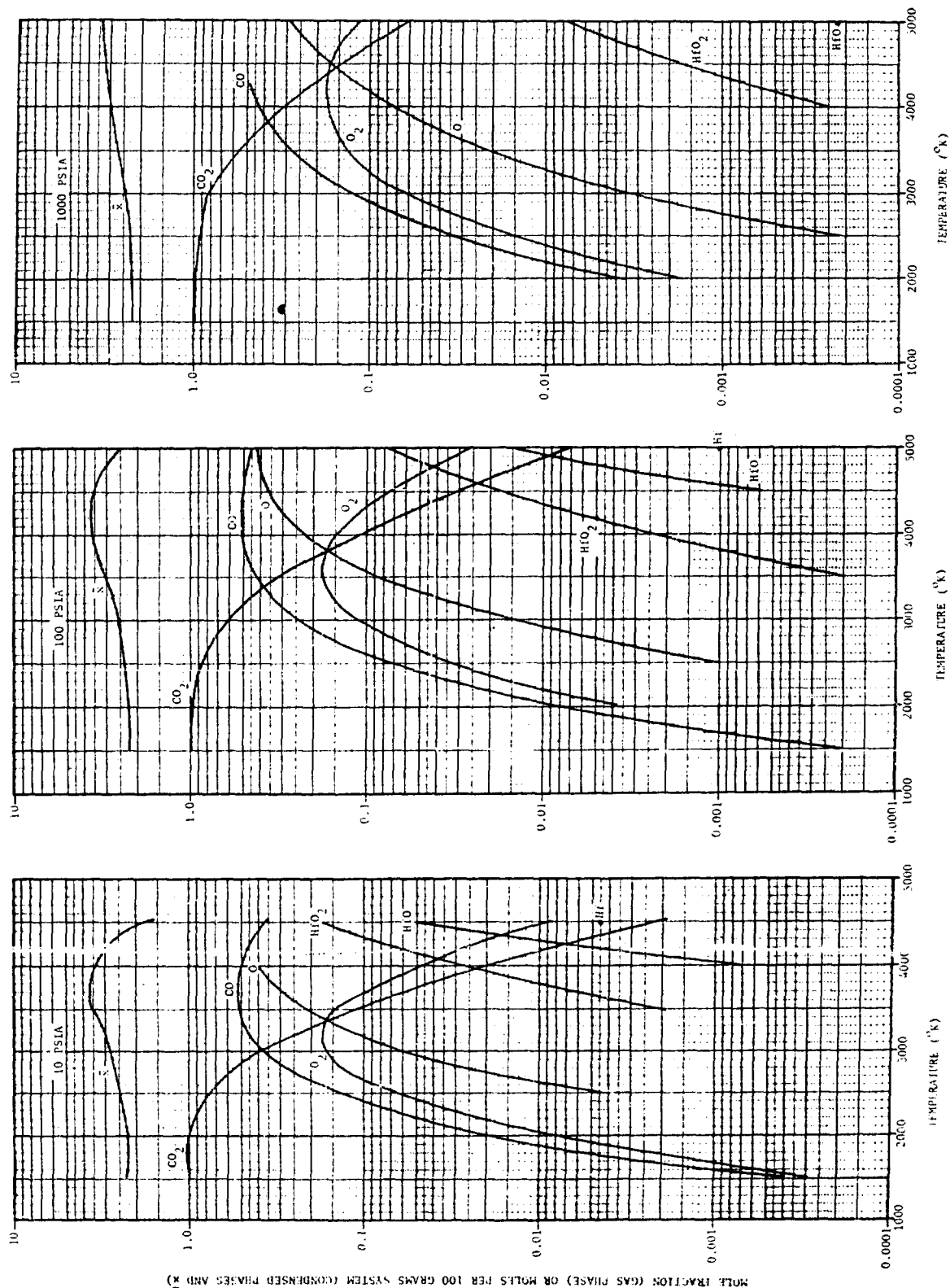


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FIGURE 11. SPECIES PRESENT UNDER EQUILIBRIUM CONDITIONS AT THREE PRESSURES FOR CO₂ AND MgO

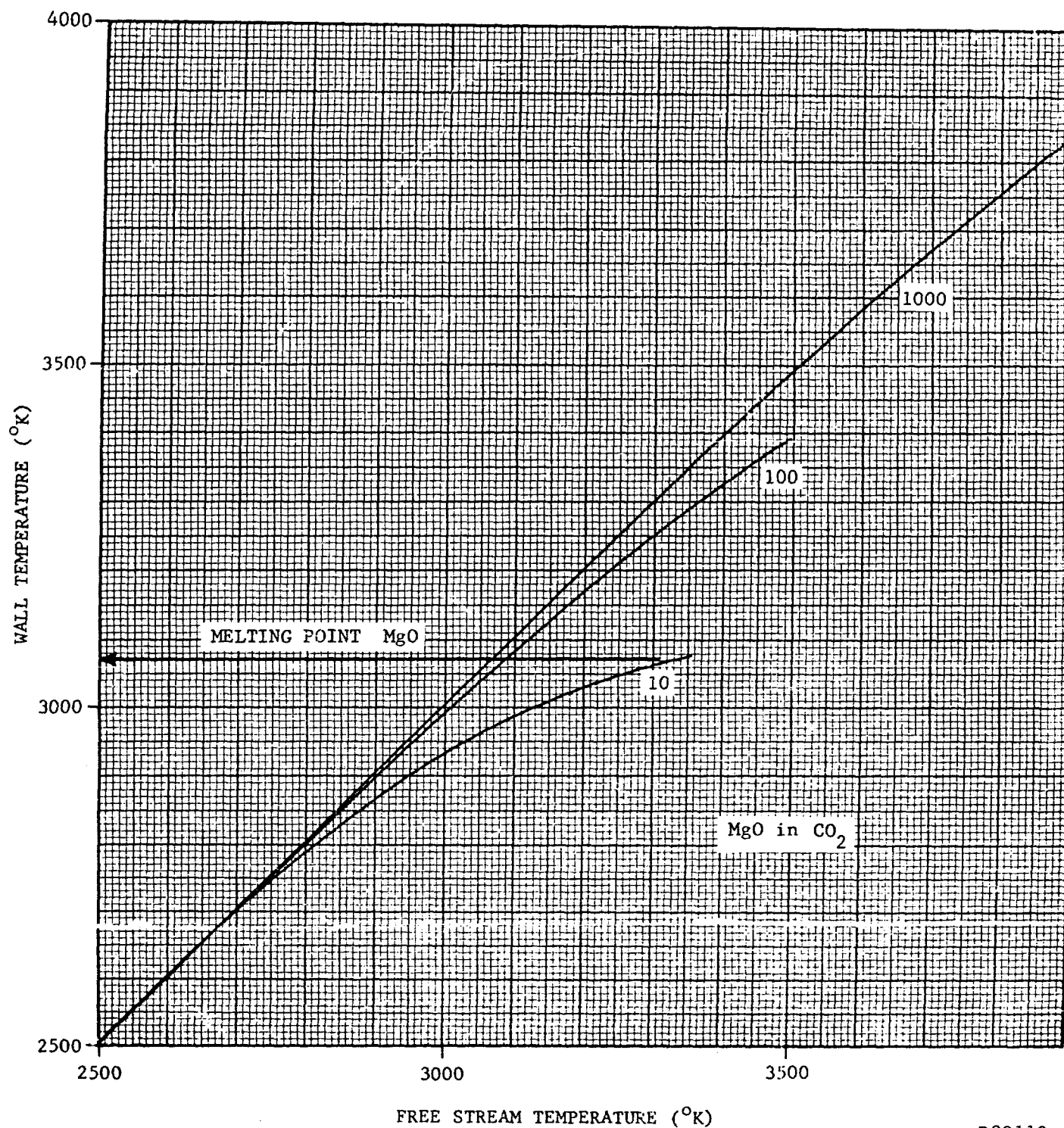
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FIGURE 12. SPECIES PRESENT UNDER EQUILIBRIUM CONDITIONS AT THREE PRESSURES FOR CO_2 AND H_2O .



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FIGURE 13. ADIABATIC WALL TEMPERATURE VS. FREE STREAM TEMPERATURE FOR MgO IN CO_2 AT THREE PRESSURES

TABLE IV

WALL COOLING EFFECTS WITH MgO, HfO₂ AND ThO₂ AT THEIR
MELTING POINTS IN A CO₂ ATMOSPHERE AT VARIOUS PRESSURES

<u>Oxide</u>	<u>Melting Point, °K</u>	<u>Pressure, psia</u>	<u>"B" $\frac{\text{grams}}{\text{grams}}$</u>	<u>Cooling Effect, °K</u>
MgO	3073	1000	4.1×10^{-4}	~3
		100	6.1×10^{-3}	~18
		10	1.4×10^{-1}	~270
HfO ₂	3170	1000	~0	~0
		100	9.0×10^{-4}	~1
		10	1.3×10^{-3}	~3
ThO ₂	3323	1000	$\sim 2 \times 10^{-4}$	~1
		100	$\sim 3 \times 10^{-3}$	~5
		10	$\sim 4 \times 10^{-2}$	~60

3073°K melting point of MgO or 3340°K, even at 10 psia, before melting would be expected. With ThO₂ the maximum free stream temperature could be only about 3380°K even at 10 psia before melting would occur; the saturation parameter and thus the regression rate would be smaller than with MgO. With HfO₂, as expected, the cooling effect is very slight. In no case is the cooling effect of any real significance at pressures of interest in most rocket combustion systems.

Based on the foregoing limited analysis, the oxides do not appear attractive for high temperature oxygen-containing propellant systems. This of course does not preclude their consideration for all applications.

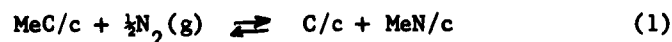
2.4 STABILITY OF CARBIDES IN NITROGEN

As refractory metal carbides are among the highest melting materials known, they are of considerable interest as possible nozzle materials and have been under investigation in this program in terms of their chemical stability. These studies have been limited in the case of the carbides reacting with nitrogen in that below certain temperatures at given pressures nitrogen reacts quantitatively with these carbides to form a condensed system consisting of metal nitrides and carbon; the program gives relatively little worthwhile information under these conditions. The nitrides are, however, lower melting than the corresponding carbides, as shown in the following tabulation:

<u>Carbide</u>	<u>Melting Point, °K</u>	<u>Nitride</u>	<u>Melting Point, °K</u>
HfC	4160	HfN	3580
TaC	4100	TaN	3363
ZrC	3765	ZrN	3225
TiC	3410	TiN	3200

so that it becomes important to know under what conditions carbides are thermodynamically unstable in nitrogen. (Tungsten apparently forms no nitrides of interest².) A brief study carried out in this direction ensues.

The pressure of nitrogen in equilibrium with the three condensed phases, C, nitride, and carbide, was computed from previously reported^{1,2} and JANAF thermodynamic data, based on the equation:



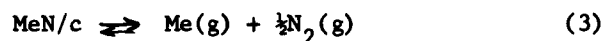
where

Me = Ti, Zr, Hf or Ta.

At the nitrogen pressures and temperatures involved in the study, the extent of the nitrogen dissociation reaction



and the carbide and nitride dissociation reactions

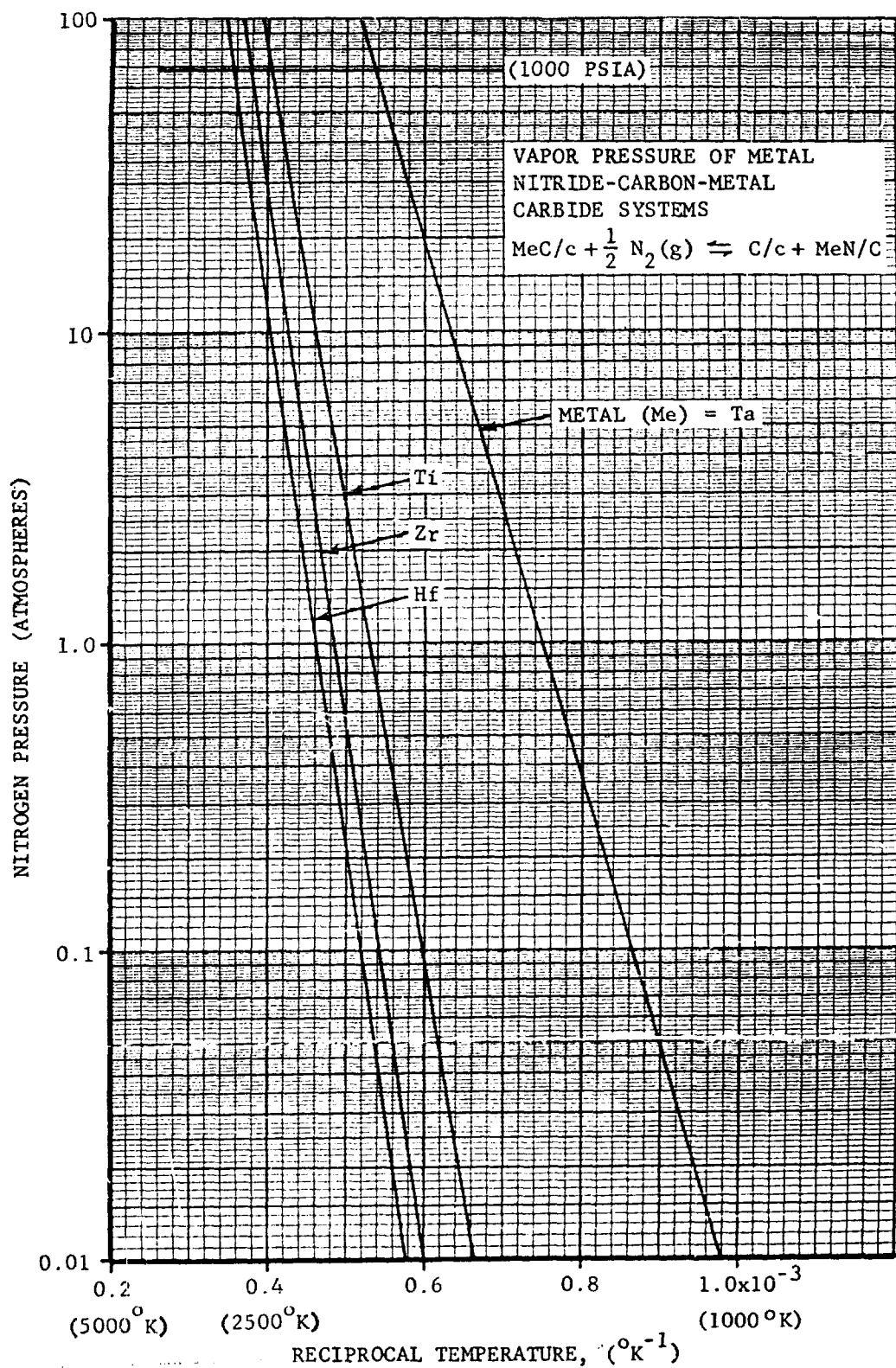


and



was found to be negligible so that it was necessary to consider only the primary reaction (Reaction 1). Hand computational methods were thus used.

The N_2 pressure results are plotted against reciprocal temperatures in Figure 14. It is evident from the plot that at a given temperature TaC requires the greatest nitrogen pressure to convert it to the carbide and HfC requires the least. The relative stabilities of the carbides in nitrogen can thus be said to decrease in the order TaC, TiC, ZrC and HfC. Even HfC, the least stable of these, however, requires a N_2 pressure of greater than 1000 psia at 2780°K to convert the carbide to the lower melting nitride; at higher temperatures (nearer the melting point) a pressure greater than 1000 psia would be required. If nitride formation is to occur in a carbide nozzle under neutral conditions in a nitrogen atmosphere, it would form thermodynamically only during the transient heat up period and would not be of concern at the higher temperature conditions normally of interest. These



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FIGURE 14. VAPOR PRESSURES OF REFRACTORY NITRIDES IN EQUILIBRIUM WITH BOTH CARBON AND THE CARBIDE

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computations are of course valid only for the unique conditions considered. Should an additional reactant be present so that solid carbon is not present, nitrides may form with specified nitrogen pressures at considerably higher temperature conditions.

For the sake of completeness, the computations given in previous reports for the various carbide-nitrogen cases can be extended into the all-condensed regions in terms of the "A" saturation parameter, using the information presented in Figure 14*. These computations were made for 1000 psia nitrogen pressure so that at temperatures below the corresponding temperature in Figure 14 the carbide would be quantitatively converted to nitride and the "A" value would be simply:

$$A = \frac{\text{grams metal carbide}}{\text{gram nitrogen}} = \frac{\text{molecular weight of the carbide}}{14.007}$$

In the case of TaC for example at 1000 psia below 1850°K, the A value would be simply

$$A = \frac{192.96}{14.007} = 13.8$$

At temperatures above 1850°K at 1000 psia, the A value would be zero until temperatures at which CN gaseous species become significant. The corresponding temperature at 1000 psia for the other systems would be about 2440°K for TiC, 2630°K for ZrC, and 2780°K for HfC. Figure 14 is useful for other systems and other pressures in a similar way. For example, at 1500°K the equilibrium nitrogen pressure with TaC is 5.5 atmospheres or 81 psia. Below this pressure there is no tendency for reaction to occur; above this pressure the A value would be 13.8.

Values for the adiabatic saturation parameters can not be readily determined using this simple approach.

* The equilibrium composition plots in these cases actually start at temperatures considerably above the all-condensed region, inasmuch as finite quantities ($>10^{-6}$ mole/100 grams) of vapor species formed from the reactant solid must normally be present in the Aeronutronic computer program for computation to proceed. Thus where the gas is 100% N₂ and the solid is simply TaC the ablation program rejects the problem and goes to a higher temperature. In the TaC case at 1000 psia, the first machine results are at 3000°K where CN(g) is present at a mole number of 5×10^{-6} ; Figure 14 however shows that conversion to all condensed occurs only below 1850°K.

SECTION 3

PREDICTION OF ISOTHERMAL SATURATION NUMBERS FOR MIXTURES FROM DATA ON "PURE" COMPONENTS, WITH ALLOWANCE FOR TOTAL PRESSURE EFFECTS

3.1 INTRODUCTION

In order to extend the utility of isothermal and adiabatic saturation numbers being determined under this contract for nozzle materials corroded by "pure" combustion system components (CO, H₂O, BOF, etc.), a tentative approach has been developed for predicting from these numbers the corrosivities of complex mixtures of combustion products and at total pressures other than those reported. Initially, the method has been confined to the estimation of isothermal saturation numbers "A" for such mixtures. Whereas the prediction of adiabatic saturation numbers "B" for mixtures based on data for the pure components appears next to impossible, such numbers for complex systems might be correlated empirically, knowing the general relationship between "A" and "B" for the individual components. Accordingly, corrosion rates might be estimated for actual propulsion applications, assuming the adiabatic saturation model.

The method thus developed is not intended to replace the rigorous calculation of saturation numbers, using the ablation equilibrium computer program. Rather, it is designed to permit rapid estimation of "A" values for cases where a computer or suitable program is not available, or in which rigorous computation would require excessive use of machine time.

The basis of the approach first will be outlined, including the preliminary "additivity" assumption, and the more elaborate model subsequently developed. Mathematical treatments then will be given for four typical cases, and possible extensions to other situations will be indicated. Finally, two examples will be presented, showing actual comparisons between predicted and rigorously computed isothermal saturation numbers.

3.2 THEORETICAL BASIS

A simple assumption which might be used to estimate isothermal saturation numbers "A" for complex systems is the rule of "additivity", in which the overall "A" would be taken as a linear, weighted average of the "A's" of each of the individual combustion species. In applying this approach, the "A" for each component would be taken at the total system pressure, rather than at its own partial pressure, since otherwise, "A" values of infinity might be determined for some trace species. Even with this technique, an "A" value for a certain species may be undefined, if a question exists as to whether the species yields a gaseous phase in equilibrium with the ablator at the specified temperature and pressure.

As will be shown, the "additivity" model by itself yields correct predictions of isothermal saturation numbers only for a very limited number of systems. Two obvious factors tending to invalidate this assumption are: (1) partial pressure effects on equilibria involving a change in gaseous moles, and (2) chemical interaction between two corrodant species. The method herein developed is concerned primarily with applying "corrections" based upon factor (1) for the case of dilution of the attacking species by an essentially inert carrier gas. By some modification, the approach can be expanded to include dilution by an independently corrosive agent, or, under factor (2), even dilution by a second species entering into the same equilibrium reaction. The only situation not amenable to direct analysis is that in which a new ablation species appears upon going to the complex system.

3.3 A CATALOG OF ABLATION REACTIONS

In order to characterize ablation reactions for possible pressure effects, four main groupings were defined, as shown in Table V, according to whether the net mole change was zero, positive, negative, or independent of the gaseous species. Various ablation reactions, involving corrosion of C/c, TiC/c, ZrC/c, ZrB₂/c and W/c nozzle materials have been classified according to this scheme; the results are presented in Table VI. As an approximation, any reaction involving a mole change of less than 50 percent ($2 \rightarrow 3$, or $3 \rightarrow 2$), has been considered as having zero change in gaseous moles.

TABLE V
CLASSIFICATION OF ABLATION REACTIONS

<u>Case</u>	<u>Description</u>	<u>Type</u>	<u>Gas-Phase Mole Reaction</u>
I	No change in gaseous moles	I	$n \rightarrow n$
II	Increase in gaseous moles	II	$1 \rightarrow 2$
		II'	$2 \rightarrow 3$
		II''	$1 \rightarrow 3$
		II'''	$1 \rightarrow 4$
		II(4)	and higher $0 \rightarrow n$
III	Decrease in gaseous moles	III	$2 \rightarrow 1$
		III'	$3 \rightarrow 2$
		III''	$n \rightarrow 0$
IV	Inert gas feed; simple decomposition or vaporization of ablator	IV	$0 \rightarrow n$

TABLE VI
A CATALOG OF ABLATION REACTIONS
(Pressure = 1000 psia)

Corrodant	Principal Reaction	Type	Temp., °K	Ablator: C/c	
				A	B
H ₂ O	C/c + H ₂ O → CO + H ₂	II	2000	0.66	0.44
H ₂ O	C/c + H ₂ O → CO + H ₂	II	3000	0.77	0.63
H ₂ O	3C/c + H ₂ O → CO + C ₂ H ₂	II	4000	1.50	0.86
H ₂	C/c + 2H ₂ → CH ₄	III	2000	0.15	0.14
H ₂	2C/c + H ₂ → C ₂ H ₂	I	3000	0.84	0.18
H ₂	2C/c + H ₂ → C ₂ H ₂	I	4000	6.6	1.20
CO ₂	C/c + CO ₂ → 2CO	II	2000	0.26	0.082
CO ₂	C/c + CO ₂ → 2CO	II	3000	0.27	0.22
CO ₂	C/c + CO ₂ → 2CO	II	4000	0.28	0.31
HF	2C/c + 2HF → C ₂ F ₂ + H ₂	I	2000	0.0008	0.0008
HF	2C/c + 2HF → C ₂ F ₂ + H ₂	I	3000	0.018	0.013
HF	2C/c + 2HF → C ₂ F ₂ + H ₂	I	4000	0.24	0.076
N ₂	2C/c + N ₂ → 2CN	II	3000	0.0027	0.0020
N ₂	2C/c + N ₂ → 2CN	II	4000	0.11	0.020

TABLE VI: A CATALOG OF ABLATION REACTIONS (Pressure = 1000 psia) (page 2)

Corrodant	Principal Reaction	Type	Temp., °K	A	B
Ablator: C/c (continued)					
HCl	2C/c + 2HCl → C ₂ H ₂ + 2Cl	II'	3000	0.0022	0.0018
HCl	2C/c + HCl → C ₂ H + Cl	II	4000	0.095	0.038
CO	3C/c → C ₃	IV	4000	0.0072	0.0044
Al ₂ O ₃ /c	3C/c + Al ₂ O ₃ /c → 2Al + 3CO	II ⁽⁴⁾	3000	0.51	---
Al ₂ O ₃ /c	3C/c + Al ₂ O ₃ /c → 2Al + 3CO	II ⁽⁴⁾	4000	0.36	0.056
HBO ₂	2C/c + 2HBO ₂ → H ₂ + 2CO + B ₂ O ₂	II	2000	0.37	0.13
HBO ₂	2C/c + 2HBO ₂ → H ₂ + 2CO + B ₂ O ₂	II	3000	0.60	0.26
HBO ₂	4C/c + HBO ₂ → C ₂ H + 2CO + B/c	II''	4000	0.74	0.43
BOF	C/c + BOF → CO + BF	II	2000	0.013	0.013
BOF	C/c + BOF → CO + BF	II	3000	0.25	0.094
BOF	C/c + BOF → CO + BF	II	4000	0.27	0.15
BF ₂	C/c + 12BF ₂ → 8BF ₃ + B ₄ C/c	III'	2000	0.012	0.0084
BF ₂	-----	---	3000	~0	~0
BF ₂	2C/c + 2BF ₂ → C ₂ F ₂ + 2BF	II'	4000	0.023	0.010
BeF ₂	2C/c + 2BeF ₂ → C ₂ F ₂ + 2BeF	II'	2000	0.004	0.022
BeF ₂	2C/c + 2BeF ₂ → C ₂ F ₂ + 2BeF	II'	3000	0.14	0.087
BeF ₂	2C/c + 2BeF ₂ → C ₂ F ₂ + 2BeF	II'	4000	0.23	0.25

TABLE VI: A CATALOG OF ABLATION REACTIONS (Pressure = 1000 psia) (page 3)

Corrodant	Principal Reaction	Type	Temp., °K	A	B
<u>Ablator: C/c (continued)</u>					
BeO/c	$3C/c + BeO/c \rightarrow Be_2C/c + CO$	II ⁽⁴⁾	3000	0.0001	0.0001
BeO/c	$C/c + BeO/c \rightarrow Be + CO$	II ⁽⁴⁾	4000	0.73	0.67
BF ₃	$2C/c + 2BF_3 \rightarrow C_2F_2 + 2BF_2$	II'	3000	0.0033	0.0026
BF ₃	$2C/c + 2BF_3 \rightarrow C_2F_2 + 2BF_2$	II'	4000	0.088	0.038
AlF ₃	$2C/c + 2AlF_3 \rightarrow C_2F_2 + 2AlF_2$	II'	3000	0.0024	0.0021
AlF ₃	$2C/c + 2AlF_3 \rightarrow C_2F_2 + 2AlF_2$	II'	4000	0.045	0.025
LiF	$2C/c + 2LiF \rightarrow C_2F_2 + 2Li$	II'	4000	0.019	0.013
<u>Ablator: TiC/c</u>					
H ₂ O	$2TiC/c + 5H_2O \rightarrow Ti_2O_3/c + 2CO + 5H_2$	I	2000	1.28	1.29
H ₂ O	$TiC/c + 2H_2O \rightarrow TiO/c + CO + 2H_2$	II'	3000	1.67	1.39
H ₂ O	$TiC/c + H_2O \rightarrow Ti + CO + H_2$	II''	4000	2.86	2.05
H ₂	$2TiC/c + H_2 \rightarrow 2Ti/c + C_2H_2$	I	3000	0.0068	0.0062
H ₂	$2TiC/c + H_2 \rightarrow 2Ti + C_2H_2$	II''	4000	0.70	0.35
CO ₂	$2TiC/c + 5CO_2 \rightarrow Ti_2O_3/c + 7CO$	I	2000	---	---
CO ₂	$2TiC/c + 5CO_2 \rightarrow Ti_2O_3/c + 7CO$	I	3000	0.55	0.58
CO ₂	$TiC/c + 2CO_2 \rightarrow TiO/c + 3CO$	II'	4000	0.75	0.81

TABLE VI: A CATALOG OF ABLATION REACTIONS (Pressure = 1000 psia) (page 4)

<u>Corrodant</u>	<u>Principal Reaction</u>	<u>Type</u>	<u>Temp., °K</u>	<u>A</u>	<u>B</u>
<u>Ablator: TiC/c (continued)</u>					
HF	$\text{TiC/c} + 4\text{HF} \rightarrow \text{C/c} + \text{TiF}_4 + 2\text{H}_2$	I	2000	0.84	0.89
HF	$\text{TiC/c} + 4\text{HF} \rightarrow \text{C/c} + \text{TiF}_4 + 2\text{H}_2$	I	3000	2.2	1.13
HF	$2\text{TiC/c} + 2\text{HF} \rightarrow \text{C}_2\text{H}_2 + 2\text{TiF}$	II'	4000	2.9	1.79
N ₂	$2\text{TiC/c} + \text{N}_2 \rightarrow 2\text{TiN/c} + 2\text{C/c}$	III''	2000	---	---
N ₂	$2\text{TiC/c} + \text{N}_2 \rightarrow 2\text{Ti} + 2\text{CN}$	II'''	3000	0.0024	0.0021
N ₂	$2\text{TiC/c} + \text{N}_2 \rightarrow 2\text{Ti} + 2\text{CN}$	II'''	4000	0.042	0.020
HCl	$\text{TiC/c} + 4\text{HCl} \rightarrow \text{TiCl}_4 + 2\text{H}_2 + \text{C/c}$	I	2000	0.33	0.28
HCl	$2\text{TiC/c} + 6\text{HCl} \rightarrow 2\text{TiCl}_3 + 3\text{H}_2 + 2\text{C/c}$	I	3000	0.27	0.28
HCl	$2\text{TiC/c} + 2\text{HCl} \rightarrow 2\text{TiCl} + \text{C}_2\text{H}_2$	II'	4000	0.49	0.41
CO	$2\text{TiC/c} + 3\text{CO} \rightarrow \text{Ti}_2\text{O}_3/\text{c} + 5\text{C/c}$	III''	2000	---	---
CO	$2\text{TiC/c} + 3\text{CO} \rightarrow \text{Ti}_2\text{O}_3/\text{c} + 5\text{C/c}$	III''	3000	---	---
CO	$\text{TiC/c} \rightarrow \text{Ti} + \text{C}$	IV	4000	0.0084	0.0056
<u>Ablator: ZrC/c</u>					
H ₂ O	$\text{ZrC/c} + 2\text{H}_2\text{O} \rightarrow \text{ZrO}_2/\text{c} + \text{C/c} + 2\text{H}_2$	I	2000	1.3	2.0
H ₂ O	$\text{ZrC/c} + 3\text{H}_2\text{O} \rightarrow \text{ZrO}_2/\text{c} + \text{CO} + 3\text{H}_2$	I	3000	2.4	2.0
H ₂ O	$\text{ZrC/c} + \text{H}_2\text{O} \rightarrow \text{Zr/c} + \text{CO} + \text{H}_2$	II	4000	5.4	3.7

(page 5)

TABLE VI: A CATALOG OF ABLATION REACTIONS (Pressure = 1000 psia)

Corrodant	Principal Reaction	Type	Temp., °K	A	B
<u>Ablator: ZrC/c (continued)</u>					
H ₂	2ZrC/c + H ₂ → 2Zr/c + C ₂ H ₂	I	3000	0.0008	0.0008
H ₂	2ZrC/c + H ₂ → 2Zr/c + C ₂ H ₂	I	4000	0.041	0.051
CO ₂	ZrC/c + 3CO ₂ → ZrO ₂ /c + 4CO	I	3000	0.77	0.81
CO ₂	ZrC/c + 3CO ₂ → ZrO ₂ /c + 4CO	I	4000	0.82	2.1
HF	ZrC/c + 4HF → C/c + ZrF ₄ + 2H ₂	I	2000	1.3	2.4
HF	ZrC/c + 2HF → C/c + ZrF ₂ /c + H ₂	III	3000	2.4	2.5
HF	2ZrC/c + 2HF → C ₂ H ₂ + ZrF ₂ /c	III	4000	2.5	2.5
N ₂	2ZrC/c + N ₂ → 2ZrN/c + 2C/c	III'	2000	---	---
N ₂	2ZrC/c + N ₂ → 2Zr/c + 2CN	II	3000	0.0059	0.0059
N ₂	2ZrC/c + N ₂ → 2Zr/c + 2CN	II	4000	0.074	0.065
HCl	2ZrC/c + 6HCl → 2C/c + 2ZrCl ₃ + 3H ₂	I	2000	0.94	0.94
HCl	2ZrC/c + 6HCl → 2C/c + 2ZrCl ₃ + 3H ₂	I	3000	0.95	1.03
HCl	2ZrC/c + 2HCl → 2ZrCl + C ₂ H ₂	II'	4000	1.32	1.32
CO	ZrC/c + CO → C + ZrO	II	4000	0.0007	0.0007
<u>Ablator: ZrB₂/c</u>					
H ₂ O	ZrB ₂ /c + 5H ₂ O → ZrO ₂ /c + B ₂ O ₃ /c + 5H ₂	I	2000	1.29	1.43
H ₂ O	ZrB ₂ /c + 4H ₂ O → ZrO ₂ /c + 2BOH + 3H ₂	I	3000	1.48	1.48
H ₂ O	ZrB ₂ /c + 4H ₂ O → ZrO ₂ /c + 2BOH + 3H ₂	I	4000	1.57	1.61

TABLE VI: A CATALOG OF ABLATION REACTIONS (Pressure = 1000 psia) (page 6)

Corrodant	Principal Reaction	Type	Temp., °K	A	B
Ablator: ZrB ₂ /c (continued)					
H ₂	ZrB ₂ /c → Zr/c + 2B	IV	3000	0.0006	0.0006
H ₂	ZrB ₂ /c → Zr + 2B	IV	4000	0.053	0.051
CO ₂	ZrB ₂ /c + 5CO ₂ → ZrO ₂ /c + B ₂ O ₃ /c + 5CO	I	2000	1.1	---
CO ₂	ZrB ₂ /c + 4CO ₂ → ZrO ₂ /c + B ₂ O ₂ + 4CO	I	3000	0.59	0.62
CO ₂	ZrB ₂ /c + 4CO ₂ → ZrO ₂ /c + 2BO + 4CO	II'	4000	0.62	0.73
HF	ZrB ₂ /c + 10HF → ZrF ₄ + 2BF ₃ + 5H ₂	I	2000	0.57	0.91
HF	ZrB ₂ /c + 4HF → ZrF ₂ /c + 2BF + 2H ₂	I	3000	1.25	1.08
HF	ZrB ₂ /c + 4HF → ZrF ₂ /c + 2BF + 2H ₂	I	4000	1.39	1.30
N ₂	2ZrB ₂ /c + 3N ₂ → 2ZrN/c + 4BN/c	III''	2000	2.7	---
N ₂	2ZrB ₂ /c + 3N ₂ → 2ZrN/c + 4BN/c	III''	3000	---	---
N ₂	ZrB ₂ /c → Zr + 2B	IV	4000	0.0021	0.0021
HCl	2ZrB ₂ /c + 18 HCl → 2ZrCl ₃ + 4BCl ₃ + 9H ₂	I	2000	0.27	0.35
HCl	2ZrB ₂ /c + 18 HCl → 2ZrCl ₃ + 4BCl ₃ + 9H ₂	I	3000	0.42	0.43
HCl	2ZrB ₂ /c + 10 HCl → 2ZrCl ₃ + 4BCl + 5H ₂	I	4000	0.43	0.44
CO	ZrB ₂ /c → Zr/c + 2B	IV	3000	0.00054	0.00055
CO	ZrB ₂ /c → Zr + 2B	IV	4000	0.011	0.010

TABLE VI: A CATALOG OF ABLATION REACTIONS (Pressure = 1000 psia) (page 7)

Corrodant	Principal Reaction	Type	Temp., °K	A	B
	Ablator: W/c				
AlF ₃	W/c + 4AlF ₃ → WF ₄ + 4AlF ₂	I	2000	0.0045	0.0039
AlF ₃	W/c + 4AlF ₃ → WF ₄ + 4AlF ₂	I	3000	0.165	0.079
AlF ₃	W/c + 2AlF ₃ → WF ₄ + 2AlF	II'	4000	0.59	0.33
BF ₂	W/c + 3BF ₂ → WB/c + 2BF ₃	III'	2000	1.15	0.64
BF ₂	W/c + 4BF ₂ → WF ₄ + 4BF	I	3000	0.045	0.026
BF ₂	W/c + 4BF ₂ → WF ₄ + 4BF	I	4000	0.57	0.30
BF ₃	W/c + 2BF ₃ → WF ₄ + 2BF	II'	2000	0.0069	0.0066
BF ₃	W/c + 2BF ₃ → WF ₄ + 2BF	II'	3000	0.36	0.128
BF ₃	W/c + 2BF ₃ → WF ₄ + 2BF	II'	4000	1.02	0.53
BOF	W/c + 6BOF → WF ₄ + 2B ₂ O ₃ + 2BF	I	3000	0.032	0.031
BOF	3W/c + 9BOF → 3W ₃ O ₉ + 9BF	I	4000	0.136	0.121
HBO ₂	-----	---	---	---	---
BeF ₂	W/c + 4BeF ₂ → WF ₄ + 4BeF	I	2000	0.88	---
BeF ₂	W/c + 4BeF ₂ → WF ₄ + 4BeF	I	3000	0.94	0.92
BeF ₂	W/c + 4BeF ₂ → WF ₄ + 4BeF	I	4000	0.96	0.78

(page 8)

TABLE VI: A CATALOG OF ABLATION REACTIONS (Pressure = 1000 psia)

Corrodant	Principal Reaction	Type	Temp., °K	A	B
<u>Ablator: W/c (continued)</u>					
CO	W/c + 2CO → WC/c + CO ₂	III	2000	0.10	0.10
CO	W/c + 2CO → WC/c + CO ₂	III	3000	0.0032	0.0032
CO	W/c + 2CO → WC/c + CO ₂	III	4000	0.0001	0.0001
CO ₂	3W/c + 9CO ₂ → W ₃ O ₉ + 9CO	I	2000	1.3	---
CO ₂	3W/c + 9CO ₂ → W ₃ O ₉ + 9CO	I	3000	1.12	1.06
CO ₂	-----	---	4000	1.23	1.25
HCl	2W/c + 10HCl → 2WCl ₅ + 5H ₂	I	2000	0.056	0.056
HCl	2W/c + 10HCl → 2WCl ₅ + 5H ₂	I	3000	0.023	0.021
HCl	W/c + 2HCl → WCl ₂ + H ₂	I	4000	0.021	0.021
HF	W/c + 4HF → WF ₄ + 2H ₂	I	2000	1.67	1.40
HF	W/c + 4HF → WF ₄ + 2H ₂	I	3000	1.30	1.17
HF	W/c + 4HF → WF ₄ + 2H ₂	I	4000	1.07	1.03
LiF	W/c + 4LiF → WF ₄ + 4Li	I	4000	0.085	0.080

3.4 ANALYTICAL SOLUTIONS FOR TYPICAL CASES AND COMMENTS

3.4.1 MATHEMATICAL DEVELOPMENTS

Mathematical treatments are presented in the following (Case I, Case II, Case III and Case IV) to show how isothermal saturation numbers for typical ablation reactions with inert diluents are determined for each of the four main classes.

Case I: No change in gaseous moles



Assume: X/c is essentially non-volatile.

Gaseous component Z is inert.

a. For pure Y in feed:

$$p_Y = \left(\frac{1}{K+1} \right) \pi \quad (2)$$

$$p_{XY} = \left(\frac{K}{K+1} \right) \pi \quad (3)$$

and $A_Y = \left(\frac{K}{K+1} \right) \left(\frac{M_X}{M_Y} \right) \quad (4)$

b. For mixture of Y and Z in feed:

$$[1 \text{ mole feed} = f \text{ moles } Y + (1-f) \text{ moles } Z] \quad (5)$$

$$p_Y = \left(\frac{1}{K+1} \right) f \pi \quad (6)$$

$$p_{XY} = \left(\frac{K}{K+1} \right) f \pi \quad (7)$$

$$p_Z = (1-f) \pi \quad (8)$$

and
$$A_{Y+Z} = \frac{\left(\frac{K}{K+1}\right) f M_X}{f M_Y + (1-f) M_Z} \quad (9)$$

or

$$A_{Y+Z} = \left[\frac{f M_Y}{f M_Y + (1-f) M_Z} \right] A_Y \quad (10)$$

or, in other words

$$\left(\frac{A_{Y+Z}}{A_Y} \right) = \left(\frac{\text{weight Y in feed}}{\text{total weight feed}} \right) \quad (11)$$

showing the linear relation for additivity when no mole change is involved.

c. For mixture of Y and XY in feed:

$$[1 \text{ mole feed} = f \text{ moles Y} + (1-f) \text{ moles XY}] \quad (12)$$

$$p_Y = \left(\frac{1}{K+1} \right) \pi \quad (13)$$

$$p_{XY} = \left(\frac{K}{K+1} \right) \pi \quad (14)$$

Assume that $\left(\frac{K}{K+1} \right) > (1-f)$, i.e., A_{Y+XY} positive:

Then
$$A_{Y+XY} = \frac{\left[\left(\frac{K}{K+1} \right) - (1-f) \right] M_X}{M_Y + (1-f) M_X} \quad (15)$$

or

$$A_{Y+XY} = \frac{\left[\left(\frac{K}{K+1} \right) - (1-f) \right] M_X}{f M_Y + (1-f) M_{XY}} \quad (16)$$

or in other words,

$$A_{Y+XY} = \frac{1}{f} \left[A_Y - (1-f) \left(\frac{M_X}{M_Y} \right) \right] \left(\frac{\text{weight Y in feed}}{\text{total weight feed}} \right) \quad (17)$$

where $\frac{1}{f} \left[A_Y - (1-f) \left(\frac{M_X}{M_Y} \right) \right]$ is always less than A_Y
In this case although there is no change in moles on reaction, the simple additivity rule would fail.

Case II: Increase in gaseous moles



Assume: X/c is essentially non-volatile.

Gaseous component Z is inert.

a. For pure WY in feed:

$$p_{WY} = \pi - 2K \left(-1 + \sqrt{1 + \frac{\pi}{K}} \right) \quad (2)$$

$$p_{XY} = p_W = K \left(-1 + \sqrt{1 + \frac{\pi}{K}} \right) \quad (3)$$

and
$$A_{WY} = \left[\frac{K \left(-1 + \sqrt{1 + \frac{\pi}{K}} \right)}{\pi - K \left(-1 + \sqrt{1 + \frac{\pi}{K}} \right)} \right] \left(\frac{M_X}{M_Y} \right) \quad (4)$$

b. For mixture of $WY + Z$ in feed:

$$[1 \text{ mole feed} = f \text{ moles } WY + (1-f) \text{ moles } Z] \quad (5)$$

$$p_{WY} = f\pi - K \left(\frac{1+f}{2} \right) \left[-(1+f) + \sqrt{(1+f)^2 + 4f \left(\frac{\pi}{K} \right)} \right] \quad (6)$$

$$p_{XY} = p_W = \left(\frac{K}{2} \right) \left[-(1+f) + \sqrt{(1+f)^2 + 4f \left(\frac{\pi}{K} \right)} \right] \quad (7)$$

$$p_Z = (1-f) \left\{ \pi - \left(\frac{K}{2} \right) \left[-(1+f) + \sqrt{(1+f)^2 + 4f \left(\frac{\pi}{K} \right)} \right] \right\} \quad (8)$$

and

$$A_{WY+Z} = \frac{\left(\frac{K}{2} \right) \left[-(1+f) + \sqrt{(1+f)^2 + 4f \left(\frac{\pi}{K} \right)} \right] M_X}{\left\{ \pi - \left(\frac{K}{2} \right) \left[-(1+f) + \sqrt{(1+f)^2 + 4f \left(\frac{\pi}{K} \right)} \right] \right\} [f M_{WY} + (1-f) M_Z]} \quad (9)$$

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or

$$A_{WY+Z} = \left[\frac{f M_{WY}}{f M_{WY} + (1-f) M_Z} \right] A'_{WY} \quad (10)$$

or

$$A_{WY+Z} = \left(\frac{\text{weight } WY \text{ in feed}}{\text{total weight feed}} \right) A'_{WY} \quad (11)$$

where

$$A'_{WY} = \frac{\left(\frac{K}{2} \right) \left[-(1+f) + \sqrt{(1+f)^2 + 4f \left(\frac{\pi}{K} \right)} \right]}{f \left\{ \pi - \left(\frac{K}{2} \right) \left[-(1+f) + \sqrt{(1+f)^2 + 4f \left(\frac{\pi}{K} \right)} \right] \right\}} \left(\frac{M_X}{M_{WY}} \right) \quad (12)$$

$$\text{But } A'_{WY} \neq A_{WY} \quad (13)$$

Given:

$$A_{WY} = \frac{\left[-1 + \sqrt{1 + \left(\frac{\pi}{K} \right)} \right]}{\left\{ \left(\frac{\pi}{K} \right) - \left[-1 + \sqrt{1 + \left(\frac{\pi}{K} \right)} \right] \right\}} \left(\frac{M_X}{M_{WY}} \right) \quad (14)$$

and

$$A'_{WY} = \frac{\left(\frac{1}{2} \right) \left[-(1+f) + \sqrt{(1+f)^2 + 4f \left(\frac{\pi}{K} \right)} \right]}{f \left\{ \left(\frac{\pi}{K} \right) - \left(\frac{1}{2} \right) \left[-(1+f) + \sqrt{(1+f)^2 + 4f \left(\frac{\pi}{K} \right)} \right] \right\}} \left(\frac{M_X}{M_{WY}} \right) \quad (15)$$

Then:

$$\frac{A'_{WY}}{A_{WY}} = \frac{\left(\frac{1}{2} \right) \left[-(1+f) + \sqrt{(1+f)^2 + 4f \left(\frac{\pi}{K} \right)} \right]}{\left[-1 + \sqrt{1 + \left(\frac{\pi}{K} \right)} \right]} \times \frac{\left\{ \left(\frac{\pi}{K} \right) - \left[-1 + \sqrt{1 + \left(\frac{\pi}{K} \right)} \right] \right\}}{f \left\{ \left(\frac{\pi}{K} \right) - \left(\frac{1}{2} \right) \left[-(1+f) + \sqrt{(1+f)^2 + 4f \left(\frac{\pi}{K} \right)} \right] \right\}} \quad (16)$$

Given $\left(\frac{\pi}{K} \right)$, one can plot $\frac{A'_{WY}}{A_{WY}}$ vs. f .

$$\text{At } f \approx 1, \frac{A'_{wy}}{A_{wy}} \approx 1 \quad (17)$$

$$\text{At } f \approx 0, \frac{A'_{wy}}{A_{wy}} \approx \frac{\left(\frac{M_x}{M_{wy}}\right)}{A_{wy}} \quad (18)$$

$$\left[\text{or } A'_{wy} \approx \frac{M_x}{M_{wy}} \right] \quad (19)$$

$$\text{In range } f = 0 \text{ to } f = 1, \frac{A'_{wy}}{A_{wy}} > 1 \quad (20)$$

c. For mixtures of WY + W, or WY + XY in feed:

(This case not derived.)

Case III: Decrease in gaseous moles.



Assume: X/c is essentially non-volatile.

Gaseous component Z is inert.

a. For pure Y feed:

$$p_Y = \left(\frac{-1 + \sqrt{1 + 4K\pi}}{2K} \right) \quad (2)$$

$$p_{XY_2} = \pi - \left(\frac{-1 + \sqrt{1 + 4K\pi}}{2K} \right) \quad (3)$$

and $A_Y = \left(\frac{1 + 2K\pi - \sqrt{1 + 4K\pi}}{1 + 4K\pi - \sqrt{1 + 4K\pi}} \right) \left(\frac{M_X}{M_Y} \right) \quad (4)$

b. For mixture of Y and Z in feed:

$$[1 \text{ mole feed} = f \text{ moles } Y + (1-f) \text{ moles } Z] \quad (5)$$

$$p_Y = \frac{-1 + \sqrt{1 + 4f(2-f)K\pi}}{2(2-f)K} \quad (6)$$

$$p_{XY_2} = \frac{[1 + 2f(2-f)K\pi] - \sqrt{1 + 4f(2-f)K\pi}}{2(2-f)^2 K} \quad (7)$$

$$p_Z = (1-f) \left\{ \frac{[1 + 4(2-f)K\pi] - \sqrt{1 + 4f(2-f)K\pi}}{2(2-f)^2 K} \right\} \quad (8)$$

and $A_{Y+Z} = \left\{ \frac{[1 + 2f(2-f)K\pi] - \sqrt{1 + 4f(2-f)K\pi}}{[1 + 4(2-f)K\pi] - \sqrt{1 + 4f(2-f)K\pi}} \right\} \left[\frac{M_X}{fM_Y + (1-f)M_Z} \right] \quad (9)$

or

$$A_{Y+Z} = \left[\frac{f M_Y}{f M_Y + (1-f) M_Z} \right] A'_Y \quad (10)$$

or

$$A_{Y+Z} = \left(\frac{\text{weight Y in feed}}{\text{total weight feed}} \right) A'_Y \quad (11)$$

where

$$A'_Y = \left[\frac{[1 + 2f(2-f)K\pi] - \sqrt{1 + 4f(2-f)K\pi}}{f\{[1 + 4(2-f)K\pi] - \sqrt{1 + 4f(2-f)K\pi}\}} \right] \left(\frac{M_X}{M_Y} \right) \quad (12)$$

$$\text{But } A'_Y \neq A_Y \quad (13)$$

$$\frac{A'_Y}{A_Y} = \left\{ \frac{[1 + 2f(2-f)K\pi] - \sqrt{1 + 4f(2-f)K\pi}}{[1 + 2K\pi] - \sqrt{1 + 4K\pi}} \right\}$$

$$\times \left[\frac{[1 + 4K\pi] - \sqrt{1 + 4K\pi}}{f\{[1 + 4(2-f)K\pi] - \sqrt{1 + 4f(2-f)K\pi}\}} \right] \quad (14)$$

Given $K\pi$, one can plot $\frac{A'_Y}{A_Y}$ vs. f .

$$\text{At } f \approx 1, \frac{A'_Y}{A_Y} \approx 1 \quad (15)$$

$$\text{At } f \approx 0, \frac{A'_Y}{A_Y} \approx 0 \quad (16)$$

$$[\text{or } A'_Y \approx 0] \quad (17)$$

$$\text{In range } f = 0 \text{ to } f = 1, \frac{A'_Y}{A_Y} < 1 \quad (18)$$

c. For mixture of Y and XY_2 in feed:

(This case not derived.)

Case IV: Inert gas feed; simple decomposition of ablator.



Assume Z_1 and Z_2 are inert.

a. Feed composition: 1 mole feed = f moles Z_1 and $(1-f)$ moles Z_2 . (2)

$$p_X = K \quad (3)$$

$$p_{Z_1} = f(\pi - K) \quad (4)$$

$$p_{Z_2} = (1-f)(\pi - K) \quad (5)$$

$$A_{Z_1+Z_2} = \frac{KM_X}{(\pi - K)[fM_{Z_1} + (1-f)M_{Z_2}]} \quad (6)$$

But $A_{Z_1} = \left(\frac{K}{\pi - K}\right)\left(\frac{M_X}{M_{Z_1}}\right) \quad (7)$

$$A_{Z_2} = \left(\frac{K}{\pi - K}\right)\frac{M_X}{M_{Z_2}} \quad (8)$$

Thus $A_{Z_1+Z_2} = \frac{A_{Z_1}A_{Z_2}}{fA_{Z_2} + (1-f)A_{Z_1}} \quad (9)$
or

$$A_{Z_1+Z_2} = A_{Z_1}\left(\frac{\text{weight } Z_1 \text{ in feed}}{\text{total weight feed}}\right) + A_{Z_2}\left(\frac{\text{weight } Z_2 \text{ in feed}}{\text{total weight feed}}\right) \quad (10)$$

The additivity rule applies in this case, even though there is a change in gaseous moles.

b. Feed composition: $X + \text{inert}$.

(This case not derived.)

3.4.2 COMMENTS

It is seen that the simple additivity rule applies only for reactions involving zero mole change, or for ablator decomposition reactions with inert diluents. For reactions involving an increase in gaseous moles, equilibrium ablation, as would be expected, is enhanced by either a drop in total pressure or dilution with inerts; exactly the reverse is true for reactions in which net gaseous moles disappear. As part of Case I, it is also shown that dilution with an ablation product species reverses the corrosion equilibria, yielding lower isothermal saturation numbers than dilution with a comparable amount of inerts. The same should hold true for the other three cases as well.

Within certain limitations, the method may be extended to cover other situations as well. For reactions having mole changes such as $2 \rightarrow 3$, $1 \rightarrow 3$, or $1 \rightarrow 4$, rigorous mathematical treatment becomes unwieldy, since a third-or-higher order algebraic equation must be solved. It is obvious, from extension of Case I, that the "additivity" rule still applies to two or more independent ablation reactions, if the mole change is zero for each. If the mole changes are not zero, the problem of two independent reactions is much more complex. Fortunately, one ablation equilibrium usually predominates over the others in mixtures of practical interest.

3.5 EXAMPLES

Two examples are provided to illustrate the application of the method, and to point out some calculational details not apparent from the preceding discussion. The first system involves BOF as the major corrodant, while in the second case, H_2 is the principal reacting species. In both examples the ablator is graphite (C/c).

Example 1: $T_c = 3865^\circ\text{K}$, $P_c = 500$ psia, C-H-N-O-F-B propellant.

The computer-derived equilibrium composition of the free stream at the given temperature and pressure was recalculated in terms of the minimum number of stable species required to make up the system at these conditions. Since the isothermal saturation number "A" is fixed by overall equilibrium rather than by reaction rates, this simplification appears a valid means of eliminating minor or uncertain species from consideration. For the system under consideration, the composition was most conveniently expressed in terms of the following: BF, BOF, CO, HF, H_2 , N_2 .

	Composition		A_{1000} Isothermal Saturation Number at 1000 psia
	Gm-moles 100 gms	Gms 100 gms	
BF	0.050	1.49	0*
BOF	0.872	39.93	0.27
CO	1.286	36.02	0.0035
HF	0.021	0.42	0.17
H_2	0.088	0.18	5.0
N_2	0.784	21.96	0.072

* Estimated from "A's" of BF_3 and BF_2 .

On preliminary examination, the major corrodant species is seen to be BOF, based on both its "A" value at 1000 psia, and upon its large weight fraction. (H_2 has a much higher value of "A", but based upon its very small weight fraction, should not be a significant reactant.) The ablation reaction of BOF with graphite is:



This equation fits the form of Case II:



in which X is C, W is BF, and Y is O. The equilibrium constant, " K_1 ", may be obtained from the JANAF thermochemical data tables, or, as an alternative, evaluated from the computed "A" value for BOF at 3865°K. In order to allow for the effects of minor side reactions, the latter is preferable:

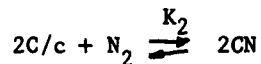
$$0.27 \approx \frac{-1 + \sqrt{1 + \left(\frac{68.0}{K_1}\right)}}{\left(\frac{68.0}{K_1}\right) - \left[-1 + \sqrt{1 + \left(\frac{68.0}{K_1}\right)}\right]} \left(\frac{12.01}{45.82}\right) \quad (\text{Eq. II-4})$$

from which $K_1 \approx \infty$; i.e., the ablation reaction goes essentially to completion.

Knowing that the "A" value for BOF is determined by stoichiometry rather than by equilibrium, the approach must be modified as follows:

- (1) The value $A = 0.27$ for BOF at 3865°K can be assumed constant, irrespective of the total pressure or the dilution.
- (2) The influence of the large CO concentration on the BOF ablation reaction can be neglected.
- (3) Since the BOF stoichiometry is fixed, some other species can be considered as a major corrodant.

The next most corrosive species is seen to be N_2 , by virtue of the reaction:



The equation also fits the form of Case II:



in which X is 2C, W is CN, and Y is $C^{-1}N$.

As before, the equilibrium constant, " K_2 ", may be evaluated from the computed value of "A" at 3865°K and 1000 psia:

$$0.072 = \frac{-1 + \sqrt{1 + \left(\frac{68.0}{K_2}\right)}}{\left(\frac{68.0}{K_2}\right) - \left[-1 + \sqrt{1 + \left(\frac{68.0}{K_2}\right)}\right]} \left(\frac{24.02}{28.02}\right) \quad (\text{Eq. II-4})$$

from which $K_2 \cong 0.49$. At 500 psia pressure and 3865°K, the "A" value for pure N_2 attacking graphite would be:

$$A_{500} \cong \frac{-1 + \sqrt{1 + \left(\frac{34.0}{0.49}\right)}}{\left(\frac{34.0}{0.49}\right) - \left[-1 + \sqrt{1 + \left(\frac{34.0}{0.49}\right)}\right]} \left(\frac{24.02}{28.02}\right) = 0.102^* \quad (\text{Eq. II-4})$$

(*This computation shows how the method can be used to compute total pressure effects but is not otherwise used in the material which follows.)

In the given mixture, the mole fraction of N_2 is 0.252. Accordingly, the "effective" isothermal saturation number of N_2 in the mixture may be derived:

$$A'_{500} \cong \frac{\frac{1}{2} \left[-1.252 + \sqrt{(1.252)^2 + (4)(0.252)\left(\frac{34.0}{0.49}\right)} \right]}{0.252 \left\{ \left(\frac{34.0}{0.49}\right) - \frac{1}{2} \left[-1.252 + \sqrt{(1.252)^2 + (4)(0.252)\left(\frac{34.0}{0.49}\right)} \right] \right\}} \left(\frac{24.02}{28.02}\right) = 0.217 \quad (\text{Eq. II-15})$$

Neglecting effects of pressure and dilution upon the ablation equilibria for the minor corrodant species, the overall "A" value for the combustion mixture at 3865°K and 500 psia can be estimated:

$$A \cong \left[(1.49)(0) + (39.93)(0.27) + (36.02)(0.0035) + (0.42)(0.17) + (0.18)(5.0) + (21.96)(0.217) \right] \div 100 = 0.166$$

This compares to an "A" value of 0.168 determined rigorously, using an IBM 7090 computer.

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Example 2: $T_c = 2793^\circ\text{K}$, $P_c = 1000$ psia, B-N-H propellant

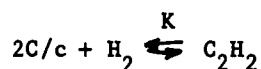
As in Example 1, the computed equilibrium composition was recalculated in terms of the minimum number of stable species. For the system under consideration, the composition was expressed in terms of H_2 , N_2 , and BN/c:

	Composition		A_{1000} , Isothermal Saturation Number at 1000 psia
	Gm-moles	Gms	
	100 gms	100 gms	
H_2	6.609	13.32	0.44
N_2	0.165	4.62	0.0009
BN/c	3.305	82.06	0*

(*Assumed non-reactive.)

Since BN/c was considered inert, calculations were based only on the gas phase.

The major corrodant species is seen to be H_2 . At this temperature and pressure, the primary ablation reaction of H_2 with graphite is:



This equation fits the form of Case I:



in which X is 2C and Y is H_2 .

Because the reaction involves no change in gaseous moles, dilution effects can be neglected.

The isothermal saturation number of only the gas phase may be estimated:

$$A_{\text{gas}} \cong \frac{(13.32)(0.44) + (4.62)(0.0009)}{(13.32) + (4.62)} = 0.327$$

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Based upon the total combustion mixture, the isothermal saturation number would be predicted as:

$$A \cong \frac{(13.32)(0.44) + (4.62)(0.0009) + (82.06)(0)}{100} = 0.059$$

This compares to an "A" value of 0.079 determined rigorously, using an IBM 7090 computer. In this instance, the method does not give as good an estimate of "A", as desired.

By inspection of the computed equilibrium composition of the combustion mixture after saturation with graphite, the reason for the discrepancy between predicted and computed "A" values was uncovered. A major product of the ablation process was found to be gaseous HCN, which obviously was not taken into account in the individual "A" values of H_2 and N_2 with C/c considered separately. Owing to a three-way chemical interaction between two combustion species and the ablator, the prediction approach breaks down in this case.

SECTION 4

PLANS FOR FUTURE WORK

It is contemplated that future effort under this contract will be devoted to the following:

- (1) Detailed study of HfN, the highest melting nitride, in equilibrium with various "pure" gases.
- (2) Interpretation of computer results to compare suitability of various materials in various atmospheres, considering melting points and density effects. The degree of cooling $\left[(T_{\text{free stream}} - T_{\text{wall}}) / B \right]$ per unit of wall material evaporated or in other fashion will be considered.
- (3) Comparison of various materials for real propellants.
- (4) Comparison of theoretical corrosion rate predictions against measured values for real propellants or pure gases.

Certain other areas such as solid (or liquid)-solid reactions, effects of uncertainties in thermodynamic data, further mixture and pressure effects, and a general study of other types of materials will be carried out as time permits.

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APPENDIX

ERRATA IN PREVIOUS REPORTS

A number of significant errors or omissions in presentation have been noted in the three previous quarterlies issued under this contract, as follows:

First Quarterly (15 September, 1962)

- p. 16 -- N_x^c should be defined as moles of nozzle material as condensed phase per 100 grams of equilibrium mixture, including condensed phase.
p. 17 and Figures 1-8 -- the pressure used in these calculations was 1000 psia.

Second Quarterly (15 December, 1962) - Volume I

- p. 66 -- ΔH_{f298}^o for $WF_5(g)$ should be listed as -384 kcal/mole.

Third Quarterly (15 March, 1963)

- p. 4 -- Brackets should surround the terms following T, as

$$\left[H_T - H_{298} - Cp_{298} (T-298) \right]$$

- p. 6 -- The symbol identification code should read

o Southern Research
□ Mezaki
x K. K. Kelley

- p. 33 -- The title for Figure 9 should have the words "at 1000 psia" added.

- p. 36 -- The title of the referenced publication should read

"Thermodynamic Properties of Inorganic Substances, V. High Temperature Heat Contents of Fifteen Refractory Borides."