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Computations on Internal Blast From Titanium-Cased Charges in Air

by

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for the
Research Department

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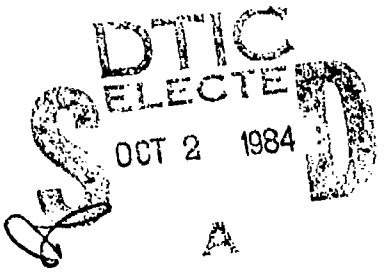

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FOREWORD

This report documents extension of the continuing research effort on internal blast at the Naval Weapons Center to include addition of titanium as the active metal. Work was performed during the period 1982-1984.

This effort was supported by the Naval Air Systems Command (NAVAIR) and was executed by the Naval Weapons Center under the Surface/Aerospace Weaponry Technology Block Program under AIRTASK A32-320J/008B/3F32-300-000 (Appropriation 1721319.41AJ). This airtask provides for continued exploratory development in the air-to-air and air-to-surface mission areas. Mr. H. B. Benefiel, AIR-320E, is the cognizant NAVAIR technology administrator.

This report has been reviewed for technical accuracy by K. J. Graham.

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(U) *Computations on Internal Blast From Titanium-Cased Charges in Air*, by Richard A. Reinhardt, Naval Postgraduate School. China Lake, Calif., Naval Weapons Center, July 1984. 44 pp. (NWC TP 6544, publication UNCLASSIFIED.)

(U) This report documents the results of adiabatic internal explosions in systems containing a variety of C–H–N–O fuels in air with the addition of titanium as the active metal. For all of the systems studied, the following were found: adiabatic temperature, overpressure, and yield of each product in terms of moles and as partial pressures for the gaseous products.

CONTENTS

INTRODUCTION

Calculations have been reported from the Naval Postgraduate School for the results of adiabatic internal explosions in systems containing a variety of C–H–N–O fuels in air with or without the addition of the active metals magnesium or aluminum.[1-7] The present study reflects the extension of the studies to titanium as the active metal.

As before, metal and fuel are considered introduced into a constant volume of 1 m^3, initially at 25°C. Products are assumed distributed evenly throughout the volume. The process is treated as adiabatic, and the ideal-gas approximation is assumed to hold.

The fuels considered are listed in Table 1, along with a few pertinent properties. Oxygen balance is computed, on a mass-percent basis, as the excess (deficiency, when negative) of oxygen in the fuel relative to the production of water, carbon monoxide, and elemental nitrogen.

In all the following, the symbol C will represent the charge, or mass of fuel, per cubic meter of air and M, the mass of metal (titanium) per cubic meter. Charge-to-metal (C/M) ratios and total concentrations ($C + M$, in kilograms per cubic meter) were varied over the range 0.1 to 10 for each.

In several of the tables, a code is used to indicate the condensed phases present: L = liquid oxide solution; C = TiC; N = TiN; G = graphite; A = Ti_3O_5; B = TiO_2.

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[1] Naval Weapons Center. *Peak Overpressures for Internal Blast*, by G. F. Kinney, R. G. S. Sewell, and K. J. Graham. China Lake, Calif., NWC, June 1979. (NWC TP 6087, publication UNCLASSIFIED.)

[2] Naval Weapons Center. *Reactive Metals in Internal Explosions: The Combustion of Magnesium in Air*, by R. A. Reinhardt. China Lake, Calif., NWC, February 1978. (NWC TM 3429, publication UNCLASSIFIED.)

[3] Naval Weapons Center. *Adiabatic Computation of Internal Blast for Magnesium-Cased Charges in Air*, by R. A. Reinhardt. China Lake, Calif., NWC, April 1979. (NWC TM 3820, GIDEP E202-1481, publication UNCLASSIFIED.)

[4] Naval Weapons Center. *Adiabatic Computation of Internal Blast for Aluminum-Cased Charges in Air*, by R. A. Reinhardt and A. K. McDonald. China Lake, Calif., NWC, January 1982. (NWC TP 6287, publication UNCLASSIFIED.)

[5] Naval Weapons Center. *A Working Model for the System Alumina-Magnesia*, by R. A. Reinhardt. China Lake, Calif., NWC, May 1983. (NWC TP 6433, GIDEP E392-0754, publication UNCLASSIFIED.)

[6] Naval Weapons Center. *Computer Program for Internal Aluminum-Fuel-Air Explosions*, by R. A. Reinhardt. China Lake, Calif., NWC, May 1983. (NWC TP 6449, GIDEP E413-0319, publication UNCLASSIFIED.)

[7] Naval Postgraduate School. *Internal Explosions of Reactive Aluminum with a PBX in Air*, by R. A. Reinhardt. Monterey, Calif., NPS, August 1983. (NPS-61-83-011-PR, publication UNCLASSIFIED.)

TABLE 1. Properties of the Fuels.

Designation	Name and chemical formula	$\Delta U_{f,298}$, kJ/mole	Oxygen balance, to CO + H_2O, %
PETN	Pentaerythritol tetranitrate, $C_5H_8N_4O_{12}$	−489.8	+15
NC	Nitrocellulose, 13.3% N; $C_6H_7N_{2.5}O_{10}$	−812.9	+3
HMX	sym-Cyclotetramethylene-tetranitramine, $C_4H_8N_8O_8$	+77.4	0
Pentolite	50% PETN, 50% TNT; $C_{6.16}H_{6.25}N_{3.41}O_{8.5}$	−97.9	−5
Comp B	65% RDX, 35% TNT; $C_{1.96}H_{2.53}N_{2.22}O_{2.68}$	+11.47	−9
TNT	2,4,6-Trinitrotoluene, $C_7H_5N_3O_6$	+30.7	−25
N_2H_4	Hydrazine	−165.0	−100
C_2H_4O	Ethylene oxide	−47.29	−109
Carbon	Graphite	0	−133
C_6H_{14}	Hexane	+100.31	−242

Internal energies of formation are per mole of formula indicated.
Data were taken or computed from Ref. 1.

BASIS OF CALCULATIONS

As is pointed out in Ref. 4, the adiabatic restriction requires that a temperature be found such that the sums of the internal energies of the equilibrium mixture of products at that temperature must equal the initial internal energy of formation of the chosen fuel. The pressure is then computed from the ideal gas law, taking into account the total number of moles of gas present at equilibrium at the temperature. The overpressure is found by subtracting 1 bar.

As before,[4] thermochemical data are represented by the five-parameter expression

$$U = B_1 + B_2T + B_3T^2 + B_4 lnT + B_5/T$$

where T is the Kelvin temperature. In Table 2 are listed the internal energy parameters for the 25 gaseous and 15 condensed-phase species considered. Those for titanium species were

TABLE 2. Internal Energies of Combustion Products.
Expressed as a function of $\tau = T/1000$ (in kilokelvins);
values given in joules/mole: $U(T) = B_1 + B_2\tau + B_3\tau^2 + B_4 \ln\tau + B_5/\tau$

Substance	B_1	B_2	B_3	B_4	B_5
Ti	310931	11660	75	1364	664
TiO	264015	30151	272	-2961	1040
TiO_2	-55866	60797	-355	-22628	-4116
Ti^+	1029558	29682	-252	-49343	-43618
Ar	-3718	12473	0	0	0
CO	-84115	31136	-25	-6218	24
CO_2	-361013	56789	67	-9201	1764
H	213029	12473	0	0	0
OH	166505	34786	-88	-20093	-7842
H_2	136535	32890	313	-21058	-9413
H_2O	50545	63224	-395	-45949	-16417
NO	105501	30619	10	-4353	631
N_2	38785	31651	-61	-7831	-657
O	214445	9604	298	4428	2050
O_2	32105	29476	662	-6265	-2102
TiC (l)	-617142	62760	0	0	0
TiC (s)	-762144	27917	6225	14807	3981
Ti (l)	-465953	35564	0	0	0
Ti (s)	-695970	-10976	8134	35009	11727
C (s)	-40329	22904	320	10	0
CN^-	102390	31551	-69	29	0
CN	691554	38828	740	-37192	-24658
C_2H	758476	66613	239	-43882	-20692
C_2N	538335	54371	-15	-1052	2404
HCN	284944	62760	-302	-26216	-5947
HNCO	36816	83592	-474	-28281	-4750
HCO	90276	56166	-353	-19233	-2345
CH_2O	54534	85563	-609	-32362	-1612
C_2H_2	474890	92019	-27	-42593	-10539
C_3	906056	48907	282	-16185	-3220
TiO (l)	-1040198	66944	0	0	0
TiO (s)	-1011246	56480	4163	0	0
Ti_2O_3 (l)	-1942190	156900	0	0	0
Ti_2O_3 (s)	-2041671	145104	2725	-30	4248
Ti_3O_5 (l)	-2875209	234304	0	0	0
Ti_3O_5 (s)	-2963674	174570	16844	266	123
TiO_2 (l)	-1395260	87864	0	0	0
TiO_2 (s)	-1436271	62766	5687	159	1079
TiN (l)	-770564	62760	0	0	0
TiN (s)	-847427	38404	5099	4361	812

Substances are gaseous unless otherwise specified.

calculated from data in the JANAF tables,[8] recomputing the data so as to accommodate the universal choice of titanium vapor as the reference state. Parameters for the other species are taken from Ref. 4.

EQUILIBRIUM CONSIDERATIONS

THE SYSTEM TITANIUM-OXYGEN

Unlike magnesium and aluminum, the metals studied earlier, titanium forms a number of solid oxides. The compounds TiO, Ti_2O_3 and TiO_2 are well known, and their formation accords with the solution chemistry of this transition metal. The phase diagram of the system Ti–O is reasonably well established up to the melting point.[9,10] Maxima in melting point appear to correspond to Ti_2O, Ti_2O_3, Ti_3O_5 and TiO_2. TiO appears to melt incongruently. There is extensive solid-solution formation and considerable temperature-dependent polymorphic transition. Oxygen is soluble in titanium metal to the extent of about 25 atom-percent, yielding solid solutions which show metallic conductance. In general, the lower oxides are all nonstoichiometric and show semiconductor properties.

The phase diagram gives no direct evidence regarding the liquid phase, but the appearance is not inconsistent with that of a system with no discontinuities in the liquid phase.

For these reasons, it has been assumed in the present study that the liquid phase in the system Ti–O is continuous; that is, that there is complete miscibility from the metal to the composition TiO_2. This liquid is assumed to be an ideal solution of the liquids Ti, TiO, Ti_2O_3, Ti_3O_5 and TiO_2. Ti_2O was not included since no thermochemical or equilibrium data appear to be available for it.

The complexities of the solid phases have been ignored in the present study. Only a small number of points were at temperatures below the melting-point curve; most of these were for oxygen-rich systems in which solid TiO_2 formed or for carbon-rich systems in which TiC but no oxide at all resulted. Pure solid phases were assumed in those few cases where solid Ti_3O_5, alone or with TiO_2, appeared.

In the computer program the presence of "liquid oxide" (that is, the liquid solution of oxygen in titanium) required in part that the temperature be above 2143 K (the melting point of TiO_2 and the highest temperature on the melting-point curve). This criterion was adopted for the sake of simplicity, and proved satisfactory in all but a handful of cases where a liquid was obtained, but below 2143 K. These points were recomputed, now waiving the temperature requirement for liquid oxide. It was found that this change made very little difference (at most a few tenths of a bar) in the computed pressure.

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[8] National Bureau of Standards. *JANAF Thermochemical Tables*, 2nd edition, by D. R. Stull and H. Prophet. Washington, D.C., NBS, June 1971.

[9] R. C. DeVries and R. Roy, *Am. Ceramic Soc. Bull.*, Vol. 33 (1954), pp. 370-72.

[10] P. G. Wahlbeck and P. W. Gilles, *J. Am. Ceramic Soc.*, Vol. 49 (1966), pp. 180-83.

A set of calculations was carried out for the system TNT–Ti–air using the quite different (and less reasonable) assumption that the liquid oxide phases were completely immiscible with one another and with the liquid metal. Results were appreciably different, as to both adiabatic temperatures and pressures found. The pressures tended to be higher (by up to 12%) even though the temperatures were lower. This result was in accord with the reduction in fugacities accompanying solution formation.

It should be remarked that it was assumed that TiC, TiN and graphite, when present, existed as pure phases.

EQUILIBRIUM DATA

As in the previous study,[4] equilibrium constants of formation were fitted to the four-parameter equation:

$$log_{10} K = A_1 + A_2/(A_3 + T) + A_4 T$$

In Table 3 are listed the equilibrium constant parameters for all the species considered (except for the elements in the reference states, for which all the parameters are zero). Those for the titanium species were computed from the JANAF tables,[8] with the data below 3591 K (the normal boiling point for titanium) recomputed to take into account the choice of titanium vapor as the reference state. (This choice was made to avoid the discontinuities that would otherwise occur at the melting and boiling temperatures of titanium.) Parameters for the other species are taken from Ref. 4.

In application, each K_p (expressed in partial pressures) is first converted to a K_n (in terms of mole numbers). Then for any species the number of moles is given as a known function of K_n and the "master variables": $X = \sqrt{O_2}$; $Y = \sqrt{H_2}$; $Z = \sqrt{N_2}$; Ti; and Acc, which is the activity of carbon (standard state, graphite). (Formulas in the last sentence refer to number of moles.)

EQUILIBRIUM CALCULATIONS

For argon, the mole number is always 0.4036, the number of moles in 1 m^3 of air at 298 K, 1 bar. For each of the five remaining elements, a material balance equation may be written representing conservation of the number of moles of atoms of each element. The mole number of each of the chemical species present is a function of those of the elements in standard states and the activity of carbon; hence, five simultaneous equations in five unknowns (the five "master variables" referred to earlier) are obtained.

In actuality the maximum number of unknowns to be considered is four, since $Y = \sqrt{H_2}$ can always be found in closed form as a function of the others. Considering also the phase rule restriction, the number of variables to be solved for is four less the number of condensed phases. The Newton-Raphson method, as described in Ref. 4, is then used to solve this set of simultaneous nonlinear equations.

TABLE 3. Equilibrium Constants of Formation of Products.
(Base 10 logarithm of the formation constant of the indicated substance, expressed as a function of $\tau = T/1000$ (in kilokelvins): $\log_{10} K = A_1 + A_2/(A_3 + \tau) + A_4\tau$)

Substance	A_1	A_2	A_3	A_4
TiO	-2.256	23.248	-0.018	-0.133
TiO_2	-7.510	37.603	-0.008	-0.067
Ti^+	4.082	-39.359	0.079	0.027
CO	4.593	6.108	0.030	-0.067
CO_2	0.087	20.642	0.001	-0.024
H	3.132	-12.016	0.019	0.015
OH	0.769	-1.969	-0.016	-0.015
H_2O	-3.056	13.305	0.014	-0.005
NO	0.710	-4.300	0.008	-0.009
O	3.497	-13.439	0.010	0.006
TiC (l)	-6.352	29.181	-0.002	0.019
TiC (s)	-8.124	33.929	-0.003	0.118
Ti (l)	-6.033	21.383	-0.060	-0.006
Ti (s)	-7.550	24.361	0.000	0.165
CN^-	0.826	0.005	-2.418	0.047
CN	5.092	-22.218	-0.012	-0.016
C_2H	6.529	-24.269	-0.012	-0.043
C_2N	7.060	-29.343	-0.000	-0.066
HCN	1.607	-6.807	-0.012	-0.008
HNCO	-25.740	96.491	2.563	2.862
HCO	2.221	1.209	0.219	-0.060
CH_2O	-2.036	6.770	0.018	-0.016
C_2H_2	2.655	-11.332	-0.016	0.000
C_3	10.850	-41.395	-0.016	-0.186
TiO (l)	-8.512	44.816	-0.050	0.052
TiO (s)	11.560	50.682	-0.009	0.348
Ti_2O_3 (l)	-22.269	112.701	-0.054	0.030
Ti_2O_3 (s)	-28.610	126.047	-0.007	0.607
Ti_3O_5 (l)	-36.762	182.554	-0.039	0.085
Ti_3O_5 (s)	-45.523	200.007	-0.003	0.984
TiO_2 (l)	-13.912	66.399	-0.042	0.042
TiO_2 (s)	-17.167	73.460	-0.003	0.290
TiN (l)	-5.271	20.076	-0.672	-0.437
TiN (s)	-12.371	41.581	-0.007	0.196

Substances are gaseous unless otherwise specified.

An initial approximation scheme is available wherein it is assumed that oxygen is taken up in the order CO, TiO_x, H_2O, CO_2. With insufficient oxygen to proceed beyond TiO, TiN is assumed. With excess carbon, TiC or C (solid) is assumed. Based on these assumptions, initial values of all the master variables can be found and the computation may be started. After the first computation in a series it is a matter of operator choice whether to repeat the initial approximation or to use the values of the master variables from the last run.

In any case, after convergence of the Newton's method of calculation, tests are performed for the presence or absence of each condensed phase. If a change from those assumed has occurred the computation is rerun. This procedure continues until all the tests are satisfied and no change in condensed phases is predicted. Further detail on the computational method with a copy of the computer program is given in Appendixes A and B to this report.

RESULTS

For all the systems studied the following were found: adiabatic temperature, overpressure, and yield of each product in terms of moles and also as partial pressures for the gaseous products. Total concentration (metal plus fuel) was varied regularly over the range 0.1 to 10 kg/m^3 and the fuel-to-metal ratio likewise was varied over the range 0.1 to 10.

In Table 4 the following data are given for titanium plus air (in the absence of fuel): overpressures (bars), adiabatic temperatures (K), and product yields, expressed as mole-percent for the gases and total mole number for condensed phases. The composition of the liquid oxide phase is given as x in the empirical formula TiO_x (x ranging from 0 to 2).

TABLE 4. Combustion of Pure Titanium in Air: Overpressure, Adiabatic Temperature, and Product Yield.

Property/ system	Concentration, kg/m^3						
	0.1	0.2	0.4	1.0	2.0	4.0	10.0
Overpressure, bars	7.3	9.7	11.7	14.3	18.4	26.3	49.8
Temperature, K	2602	3423	4024	4338	4393	4542	4869
Mole-%:							
Ar	1.05	1.08	1.07	0.95	0.76	0.56	0.32
Ti		...	0.01	7.22	30.08	50.59	72.46
TiO		0.12	4.86	17.42	9.85	5.22	2.15
TiO_2		0.01	0.08	...	...	...	...
NO	2.47	5.05	4.09	0.05	0.01	...	...
N_2	80.84	81.46	81.12	74.26	59.59	43.63	25.06
O	0.32	3.64	6.54	0.10	0.01	0.01	...
O_2	15.31	8.64	2.23	...	...	...	...
Liquid oxide:							
Moles	2.04	2.77	4.55	10.40	20.55	43.2	115.0
x in TiO_x	1.99	1.79	1.40	0.91	0.57	0.31	0.12

Table 5 gives overpressures in bars, with the temperature in parentheses, for the titanium-air-fuel mixtures. Each portion of the table is devoted to a particular fuel, and the fuels are arranged in decreasing order of oxygen balance, starting with the most oxygen-rich, PETN, and ending with the most oxygen-deficient, hexane. In each case, $C + M$ represents the total concentration in kilogram/meter^3, and C/M represents the mass ratio of fuel to metal. For each table entry a code indicates the condensed phases present; this code, described earlier, is also explained as a footnote to the table.

TABLE 5. Overpressure (in bars), Adiabatic Temperature (in K) (in parentheses), and Condensed Phases for the Combustion of Titanium With Fuels in Air.

$C + M$	C/M						
	0.1	0.2	0.4	1.0	2.0	4.0	10.0
a. Fuel: PETN.							
0.1	7.1 (2496) L	6.8 (2403) L	6.4 (2249) L	5.8 (2004) B	5.1 (1743) B	4.4 (1527) B	3.8 (1344) B
0.2	9.6 (3314) L	9.5 (3228) L	9.3 (3095) L	8.9 (2832) L	8.2 (2564) L	7.5 (2286) L	6.7 (2041) B
0.4	11.9 (3947) L	12.1 (3874) L	12.2 (3739) L	12.1 (3450) L	11.8 (3209) L	11.5 (2995) L	11.0 (2776) L
1.0	15.4 (4363) L	16.3 (4335) L	17.5 (4253) L	19.1 (4033) L	19.6 (3788) L	19.6 (3554) L	19.4 (3349) L
2.0	20.7 (4438) L	22.6 (4486) L	25.6 (4549) L	29.7 (4349) L	31.6 (4107) L	32.3 (3861) L	32.4 (3635) L
4.0	31.3 (4586) L	35.3 (4639) L	41.7 (4743) L	51.4 (4674) L	55.8 (4390) L	57.7 (4116) L	58.3 (3865) L
10.0	63.2 (4913) L	74.4 (4970) L	91.9 (5098) L	121.0 (5177) L	132.1 (4773) L	136.4 (4426) L	138.0 (4127) L

L = liquid oxide, B = TiO_2 (s).

TABLE 5. (Contd.).

$C+M$	C/M						
	0.1	0.2	0.4	1.0	2.0	4.0	10.0
b. Fuel: Nitrocellulose.							
0.1	7.1 (2508) L	6.9 (2427) L	6.6 (2294) L	6.1 (2089) B	5.4 (1863) B	4.9 (1676) B	4.4 (1520) B
0.2	9.6 (3322) L	9.5 (3244) L	9.4 (3125) L	9.1 (2903) L	8.7 (2696) L	8.2 (2488) L	7.6 (2285) L
0.4	11.9 (3949) L	12.1 (3880) L	12.3 (3756) L	12.3 (3497) L	12.2 (3289) L	12.0 (3118) L	11.8 (2965) L
1.0	15.4 (4347) L	16.4 (4324) L	17.7 (4246) L	19.4 (4045) L	20.2 (3829) L	20.4 (3625) L	20.4 (3451) L
2.0	20.8 (4408) L	22.8 (4428) L	25.8 (4467) L	30.3 (4339) L	32.5 (4120) L	33.6 (3902) L	34.0 (3703) L
4.0	31.3 (4550) L	35.4 (4568) L	41.8 (4610) L	52.9 (4649) L	57.8 (4389) L	60.2 (4137) L	61.2 (3908) L
10.0	63.0 (4870) L	73.9 (4884) L	91.2 (4922) L	122.9 (5040) L	137.9 (4775) L	143.0 (4436) L	145.2 (4150) L
c. Fuel: HMX.							
0.1	7.0 (2492) L	6.8 (2396) L	6.4 (2235) L	5.7 (1977) B	4.9 (1706) B	4.3 (1481) B	3.6 (1290) B
0.2	9.6 (3311) L	9.5 (3222) L	9.3 (3084) L	8.8 (2808) L	8.1 (2519) L	7.3 (2218) L	6.5 (1956) B
0.4	11.9 (3944) L	12.1 (3869) L	12.2 (3731) L	12.1 (3431) L	11.8 (3175) L	11.4 (2943) L	10.7 (2697) L
1.0	15.4 (4340) L	16.3 (4313) L	17.6 (4225) L	19.1 (3999) L	19.6 (3744) L	19.5 (3491) L	19.2 (3267) L
2.0	20.8 (4396) L	22.7 (4406) L	25.7 (4429) L	29.9 (4287) L	31.7 (4032) L	32.2 (3765) L	32.0 (3514) L
4.0	31.2 (4536) L	35.2 (4540) L	41.4 (4560) L	52.1 (4579) L	56.2 (4285) L	57.5 (3979) L	57.4 (3691) L
10.0	62.8 (4852) L	73.3 (4849) L	89.9 (4857) L	119.9 (4910) L	133.7 (4639) L	135.7 (4236) L	135.0 (3879) L

L = liquid oxide, B = TiO_2 (s).

TABLE 5. (Contd.).

C + M	C/M						
	0.1	0.2	0.4	1.0	2.0	4.0	10.0
d. Fuel: Pentolite.							
0.1	7.1 (2510) L	6.9 (2431) L	6.6 (2301) L	6.1 (2102) B	5.5 (1881) B	5.0 (1698) B	4.5 (1545) B
0.2	9.6 (3324) L	9.5 (3247) L	9.4 (3130) L	9.1 (2914) L	8.7 (2715) L	8.3 (2517) L	7.7 (2323) L
0.4	11.9 (3951) L	12.1 (3883) L	12.3 (3762) L	12.3 (3505) L	12.2 (3297) L	12.1 (3130) L	11.8 (2983) L
1.0	15.4 (4334) L	16.4 (4313) L	17.6 (4236) L	19.4 (4037) L	20.1 (3822) L	20.3 (3613) L	20.3 (3432) L
2.0	20.7 (4385) L	22.6 (4384) L	25.6 (4389) L	30.3 (4311) L	32.5 (4091) L	33.4 (3863) L	33.6 (3647) L
4.0	31.1 (4523) L	35.0 (4514) L	41.1 (4508) L	52.0 (4517) L	57.8 (4343) L	59.8 (4071) L	60.3 (3811) L
10.0	62.3 (4839) L	72.4 (4822) L	88.3 (4800) L	117.3 (4778) L	137.8 (4710) L	142.1 (4345) L	142.1 (4000) L
e. Fuel: Comp B.							
0.1	7.1 (2503) L	6.9 (2418) L	6.5 (2277) L	6.0 (2056) B	5.3 (1817) B	4.7 (1618) B	4.2 (1452) B
0.2	9.6 (3319) L	9.5 (3238) L	9.4 (3113) L	9.0 (2876) L	8.5 (2648) L	7.9 (2414) L	7.3 (2188) L
0.4	11.9 (3948) L	12.1 (3877) L	12.3 (3750) L	12.3 (3477) L	12.1 (3252) L	11.8 (3065) L	11.5 (2893) L
1.0	15.5 (4326) L	16.4 (4302) L	17.7 (4220) L	19.3 (4009) L	20.0 (3776) L	20.0 (3546) L	19.9 (3344) L
2.0	20.8 (4373) L	22.7 (4362) L	25.6 (4350) L	30.3 (4270) L	32.2 (4029) L	32.8 (3771) L	32.7 (3520) L
4.0	31.1 (4509) L	35.0 (4488) L	40.9 (4460) L	51.4 (4421) L	57.4 (4264) L	58.6 (3949) L	58.2 (3632) L
10.0	62.2 (4822) L	72.2 (4791) L	87.5 (4743) L	114.9 (4655) L	135.4 (4567) L	139.0 (4187) L	135.6 (3756) L

L = liquid oxide, B = TiO_2 (s).

TABLE 5. (Contd.).

C + M	C/M						
	0.1	0.2	0.4	1.0	2.0	4.0	10.0
f. Fuel: TNT.							
0.1	7.1 (2524) L	7.0 (2459) L	6.7 (2352) L	6.2 (2147) L	5.9 (2013) B	5.5 (1862) B	5.1 (1736) B
0.2	9.6 (3334) L	9.6 (3265) L	9.5 (3163) L	9.3 (2982) L	9.1 (2832) L	8.9 (2695) L	8.6 (2565) L
0.4	12.0 (3954) L	12.2 (3891) L	12.4 (3780) L	12.6 (3547) L	12.5 (3355) L	12.4 (3205) L	12.3 (3082) L
1.0	15.5 (4298) L	16.4 (4264) L	17.8 (4195) L	19.6 (3995) L	20.4 (3776) L	20 5 (3537) L	20.2 (3292) L
2.0	20.7 (4331) L	22.5 (4281) L	25.2 (4201) L	29.5 (4037) L	32.3 (3874) L	33.3 (3641) L	31.8 (3252) L
4.0	30 8 (4463) L	34.3 (4404) CL	39.4 (4352) CL	48.1 (4194) CL	53.6 (3979) CL	56.1 (3682) CL	54.8 (3259) CL
10.0	60.7 (4812) CL	69.2 (4791) CL	82.7 (4732) CL	106 0 (4531) CL	120 7 (4244) CL	126.2 (3833) CL	122.3 (3286) CL
g. Fuel: Hydrazine.							
0.1	7 2 (2510) L	7 1 (2437) L	6.9 (2320) L	6.6 (2143) B	6 1 (1961) B	5.8 (1809) B	5.4 (1684) B
0.2	9 7 (3303) L	9.8 (3227) L	9.9 (3118) L	10.0 (2921) L	9 9 (2 750) L	9.7 (2589) L	9 4 (2436) L
0 4	12 3 (3899) L	12 7 (3805) L	13.3 (3659) L	14 0 (3386) L	14 2 (3141) L	14 0 (2895) L	13 5 (2644) L
1.0	17.0 (4277) L	18.8 (4146) L	21.2 (3983) L	23.4 (3555) L	22.8 (3005) L	20.8 (2457) L	18 3 (1979) A
2.0	23 4 (4252) L	27 0 (4152) L	32 0 (3991) L	39.0 (3626) L	39.1 (3042) L	29 9 (2047) A	28.2 (1739) AB
4.0	36.2 (4373) L	43.3 (4248) L	53.4 (4104) NL	68.0 (3735) NL	70.9 (3101) NL	55 3 (2062) NL	43.7 (1443) AB
10.0	75.6 (4650) L	93.8 (4482) L	119.9 (4374) NL	157.9 (3927) NL	165 0 (3148) NL	130.3 (2068) NL	93.1 (1291) AN

L = liquid oxide, A = Ti_3O_5 (s), B = TiO_2 (s), C = TiC, N = TiN

TABLE 5. (Contd.).

C + M	C/M						
	0.1	0.2	0.4	1.0	2.0	4.0	10.0
h. Fuel: Ethylene oxide.							
0.1	7.3 (2580) L	7.4 (2568) L	7.5 (2551) L	7.6 (2523) L	7.8 (2502) L	7.9 (2487) L	7.9 (2475) L
0.2	9.8 (3354) L	10.0 (3314) L	10.2 (3261) L	10.6 (3175) L	10.9 (3103) L	11.1 (3034) L	11.2 (2963) L
0.4	12.3 (3929) L	12.8 (3857) L	13.4 (3743) L	14.3 (3502) L	14.5 (3246) L	14.2 (2975) L	13.7 (2711) L
1.0	16.6 (4194) L	18.2 (4083) L	20.3 (3903) L	22.7 (3551) CL	23.5 (3220) CLN	22.4 (2760) CN	18.9 (2164) CG
2.0	22.6 (4207) L	25.4 (4085) CL	29.3 (3984) CL	35.0 (3676) CL	37.3 (3252) CL	32.9 (2578) CG	29.6 (2133) CG
4.0	34.1 (4374) CL	39.6 (4318) CL	47.9 (4204) CL	59.9 (3820) CL	62.6 (3268) C	57.0 (2612) CG	51.1 (2115) CG
10.0	68.9 (4741) CL	83.3 (4676) CL	105.1 (4535) CL	136.2 (4022) CL	136.8 (3259) C	129.8 (2648) CG	115.8 (2107) CG
i. Fuel: Carbon.							
0.1	7.4 (2616) L	7.5 (2627) L	7.6 (2643) L	7.8 (2667) L	7.9 (2678) L	8.0 (2678) L	8.1 (2671) L
0.2	9.8 (3404) L	9.9 (3386) L	10.0 (3350) L	10.2 (3241) L	9.9 (3038) L	9.0 (2657) L	7.8 (2260) L
0.4	12.1 (3979) L	12.3 (3929) L	12.6 (3792) L	12.1 (3336) N	10.5 (2821) CG	8.4 (2305) CG	7.0 (1960) GN
1.0	15.2 (4067) L	15.3 (3908) CL	15.2 (3804) CL	13.8 (3588) CG	11.2 (3010) CG	8.0 (2221) CG	5.8 (1709) GN
2.0	19.2 (4168) CL	19.1 (4126) CL	20.0 (4473) C	15.0 (3788) CG	11.7 (3128) CG	7.8 (2170) CG	5.1 (1558) GN
4.0	26.5 (4414) CL	26.1 (4375) CL	24.5 (4716) C	16.4 (3962) CG	12.1 (3212) CG	7.7 (2135) CG	3.5 (1421) AGN
10.0	48.2 (4792) CL	47.8 (5133) C	36.4 (5014) C	18.9 (4165) CG	12.3 (3276) CG	7.6 (2110) CG	2.4 (1365) AGN

L = liquid oxide, C = TiC, G = graphite, N = TiN, A = Ti_3O_5 (s)

TABLE 5. (Contd.).

C + M	C/M						
	0.1	0.2	0.4	1.0	2.0	4.0	10.0
j. Fuel: Hexane.							
0.1	7.6 (2650) L	7.8 (2691) L	8.2 (2749) L	8.9 (2824) L	9.3 (2850) L	9.6 (2833) L	9.6 (2771) L
0.2	10.1 (3387) L	10.4 (3373) L	10.9 (3336) L	11.4 (3127) L	11.0 (2757) L	10.1 (2391) L	9.3 (2082) L
0.4	12.7 (3902) L	13.4 (3794) L	14.4 (3572) L	14.7 (3037) LN	12.7 (2359) CN	10.8 (1925) GN	9.1 (1552) GN
1.0	17.4 (4005) L	18.9 (3805) CLN	20.8 (3629) CLN	20.2 (2826) C	17.7 (2184) CG	15.3 (1760) GN	12.6 (1377) ABG
2.0	23.6 (4075) CL	26.6 (3972) CL	30.7 (3740) CL	30.5 (2891) CG	27.3 (2162) CG	23.3 (1674) GN	19.2 (1297) BG
4.0	35.8 (4293) CL	42.3 (4177) CL	52.2 (4042) C	51.3 (2951) CG	46.5 (2151) CG	39.4 (1622) GN	31.9 (1205) BG
10.0	73.4 (4623) CL	90.2 (4481) CL	111.5 (4276) C	113.7 (3009) CG	104.3 (2146) CG	88.2 (1586) GN	64.2 (1025) BGN

L = liquid oxide, A = Ti_3O_5 (s), B = Ti_3O_5 (s), C = TiC, G = graphite, N = TiN

In Table 6 is given the set of product yields for TNT-titanium-air at $C/M = 1.0$, chosen as representative. Mole-percent in the vapor is given for each species that reaches at least 0.1% at some point. Numbers of moles of condensed phases are also given. As with Table 4, the composition of the liquid oxide phase is given as x in the empirical formula TiO_x.

Product-yield data are available for all the systems run but have not been included in this report due to the bulk of data involved. They are available from the author.

DISCUSSION

Figure 1 shows the effect of total concentration ($C + M$) on adiabatic temperature for pure titanium in air as well as for two representative C/M ratios for the oxygen-deficient hexane and the oxygen-rich nitrocellulose.

TABLE 6. Combustion of TNT-Titanium in Air at C/M = 1.0: Overpressure, Adiabatic Temperature, and Product Yields.

Property/ system	$C + M$, kg/m^3						
	0.1	0.2	0.4	1.0	2.0	4.0	10.0
Overpressure, bars	5.2	9.3	12.5	19.6	29.5	48.1	106.0
Temperature, K	2147	2982	3547	3995	4037	4194	4531
Mole %:							
Ar	0.99	0.97	0.88	0.65	0.44	0.29	0.14
Tl	...	...	...	0.03	4.47	6.80	7.84
TiO	...	...	0.31	4.35	3.22	2.41	2.57
TiO_2	...	...	0.02	0.02	...	...	...
Tl^+	..	..	..	...	..	0.01	0.01
CO	0.01	1.82	9.79	24.20	33.46	37.91	40.95
CO_2	3.78	5.58	3.62	0.62	..	...	..
H	..	0.14	1.53	7.02	8.55	10.01	12.30
OH	0.08	1.02	2.19	0.91	0.01	...	0.01
H_2	..	0.09	0.74	4.03	7.65	10.06	12.22
H_2O	1.31	1.97	2.19	0.87	0.01	0.01	0.01
NO	0.99	3.08	3.14	0.62		...	...
N_2	77.86	75.58	69.80	55.73	41.72	31.12	21.69
O	0.03	0.98	2.66	0.89		..	..
O_2	14.94	8.78	3.13	0.08	..		..
CN^-	...	...	...	...	...	0.01	0.01
CN	..	..	...	..	0.09	0.25	0.46
C_2H	..	...	...	...	0.01	0.06	0.20
C_2N	...	...	...	...	...	0.02	0.06
HCN	..	...	...	..	0.34	0.97	1.52
HNCO		...	...	.			0.01
HCO	.	..	...	0.01	0.01	0.03	0.06
C_2H_2	.	...	..	...		0.03	0.11
Liquid oxide.							
Moles	1.04	1.70	2.58	6.48	13.88	22.60	45.39
x in TiO_x	2.00	1.94	1.69	1.18	0.72	0.57	0.56
Moles TiC (l)	..	...	...	...		6.17	29.86

The behavior of the pure metal is quite unlike that previously seen for aluminum (where a maximum in T versus $C + M$ occurred at approximately the Al_2O_3 stoichiometry; see Ref. 4). With titanium there is a steady increase in temperature with concentration, the result of the existence of a number of oxides, the formation of each being an exothermic process. Again, whereas aluminum showed formation of AlN at high concentrations, TiN does not form here as a product owing to the lesser high-temperature stability of TiN. The

curves for the explosive (relatively oxygen-rich) fuels are very similar to those for the metal alone.

With the oxygen-deficient fuels, first TiN and then TiC and graphite appear as products in the carbon-rich region. These tend to cause a falling off of temperature, as is seen in the case of hexane in Figure 1.

Figure 2 shows the strong effect of total concentration on overpressure. Nitrocellulose has been chosen as representative; all the fuels (except carbon) show a similar pattern. The large increase in number of moles of gaseous products combined with a much less profound change in temperature (Figure 1) is responsible for the monotonic increase in pressure.

The effect of C/M on temperature is shown in Figure 3. In general, titanium has a higher heating value than any of the fuels used; hence, there is a generally observed decrease in temperature as titanium is replaced by fuel. At high concentrations with oxygen-rich fuels, the oxygen supplied by the fuel causes the temperature to rise at first, resulting in a shallow maximum in the curve. The considerable break downward in the curves for hexane again corresponds to the production of TiC and graphite.

Commonly, overpressure increases with C/M, as seen in Figure 4, owing to the increase in number of moles of gases ($CO + H_2$) as titanium is replaced by fuel. The maximum seen with hexane reflects the sharp drop in temperature, referred to above.

The nature of the fuel has little effect on the adiabatic temperature for the oxygen-rich fuels. For the oxygen-deficient fuels there is a general increase in temperature as the oxygen balance increases (becomes less negative), as is shown in Figure 5, presumably due to relieving the oxygen lack. Pressure is surprisingly insensitive to the nature of the fuel, except for the case of carbon which shows higher temperatures and markedly lower pressures as a result of a much smaller quantity of gaseous product than with the hydrogen-containing fuels. Carbon also shows a very different set of products from those represented in Table 6. With carbon at high concentrations are seen large amounts of CN, C_2N and C_3 and even several tenths mole-percent of the ions as a result of the high temperatures experienced, combined with the absence of hydrogen.

APPROXIMATIONS

Athow has examined[11] the ideal-gas approximation for computation on internal explosions in the presence of the reactive metal aluminum. In those systems it appears that the only gas below its critical temperature is aluminum vapor; and for aluminum[7] the reduced pressure can be seen not to exceed 10^{-4} and the reduced volume not to be less than 200 so that no appreciable deviation from ideality should occur. It is anticipated that the same conclusions can be made regarding the titanium systems, although no estimates of the critical properties have been made and thus no estimates of errors attempted.

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[11] L. K. Athow, "Real Gas Considerations for Determining Physical and Thermodynamic Properties of Gases Involved in the Prediction of the Effects of Internal Explosions." M. S. Thesis, Naval Postgraduate School, Monterey, Calif., June 1982.

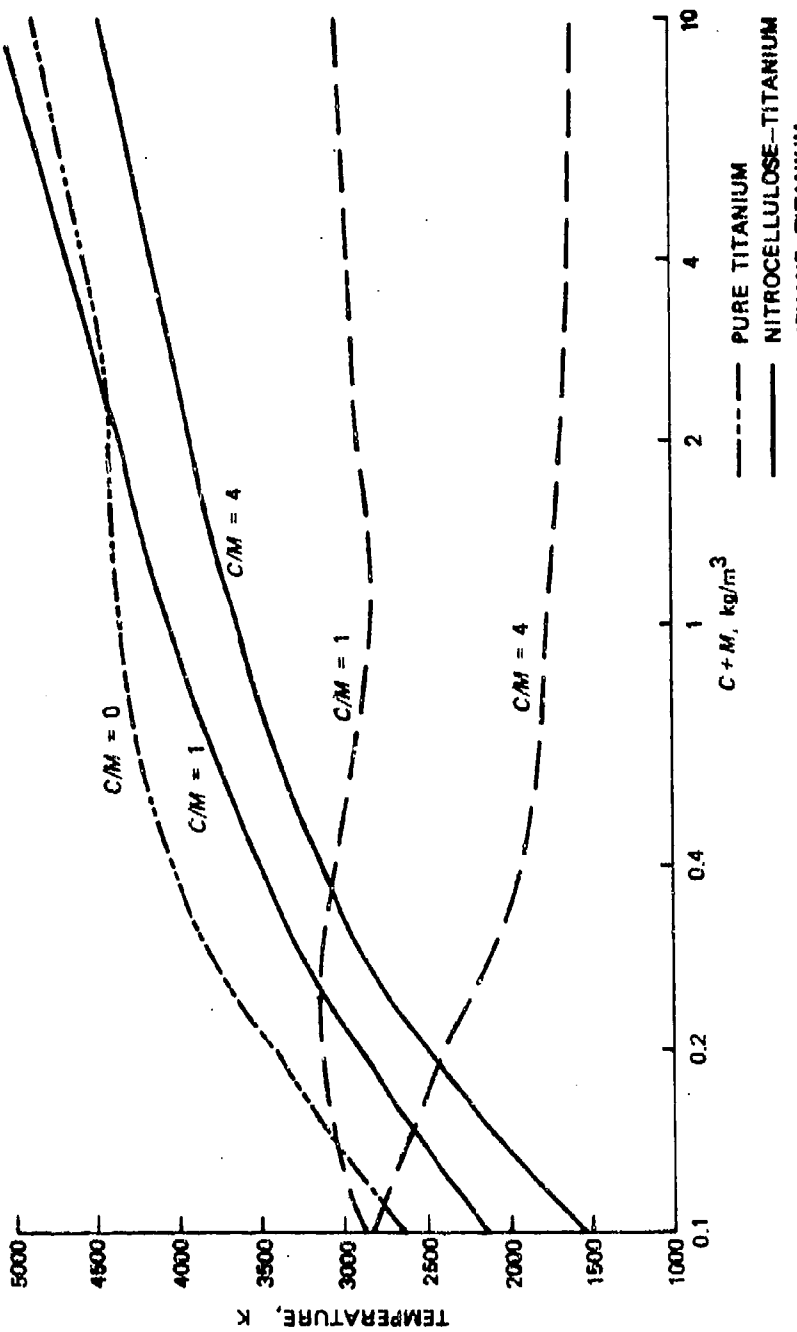

FIGURE 1. Adiabatic Temperature vs. Total Concentration for Pure Titanium; for Nitrocellulose-Titanium; and for Hexane-Titanium in Air.

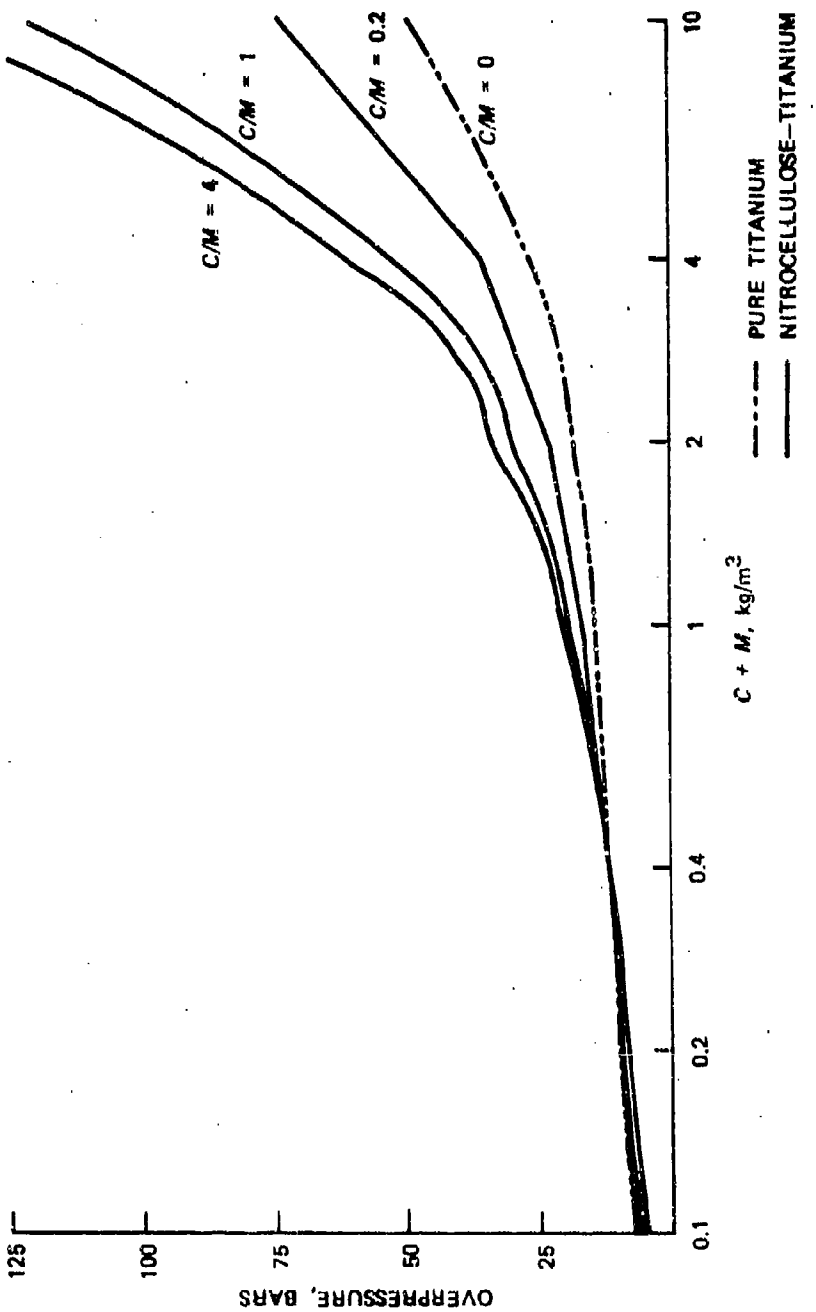

FIGURE 2. Overpressure vs. Total Concentration for Pure Titanium and for Nitrocellulose-Titanium in Air.

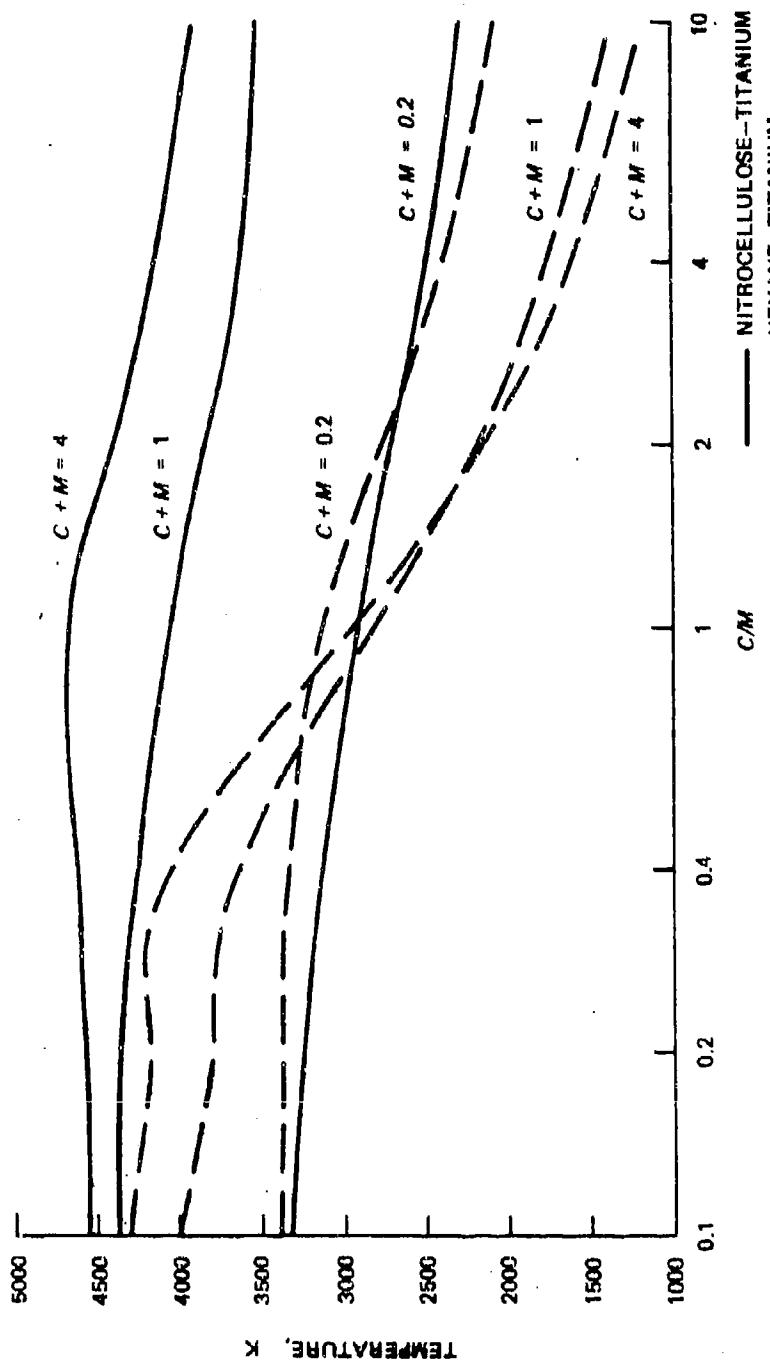

FIGURE 3. Adiabatic Temperature vs. Charge-to-Metal Ratio for Nitrocellulose and Hexane with Titanium in Air.

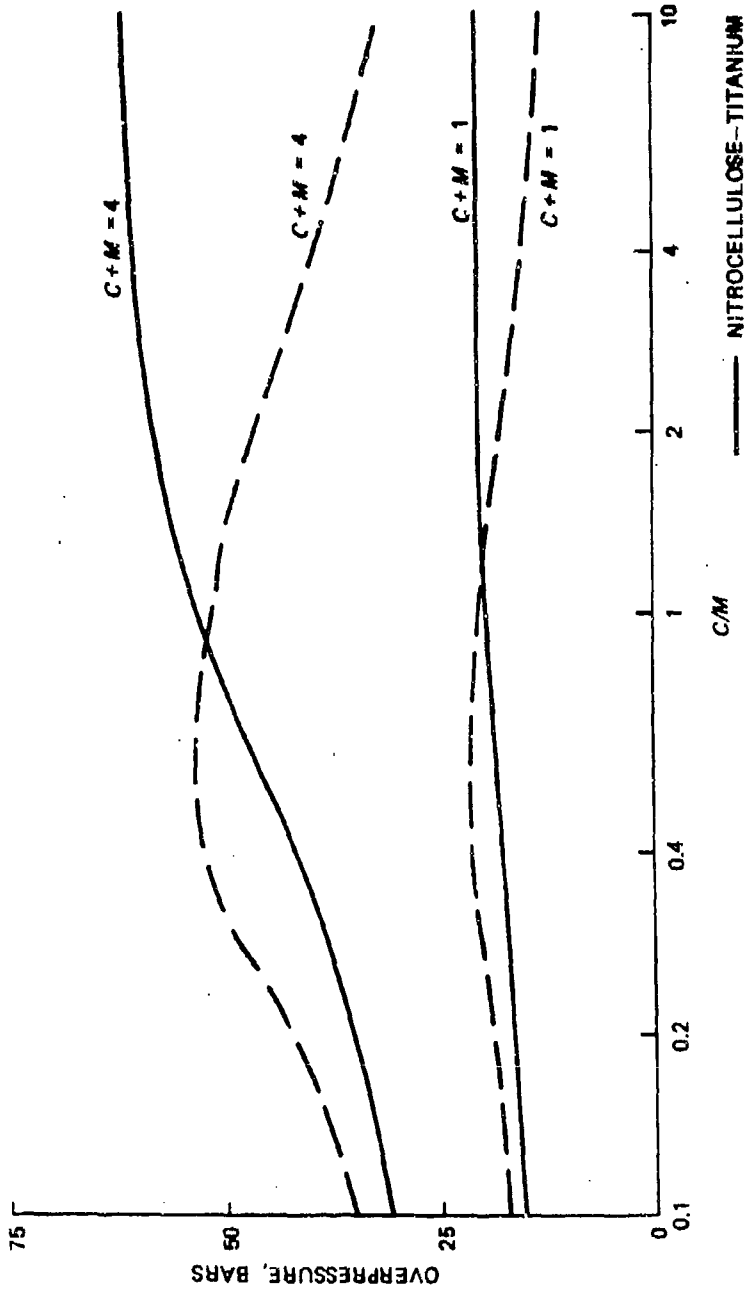

FIGURE 4. Overpressure vs. Charge-to-Metal Ratio for Nitrocellulose and Hexane with Titanium in Air.

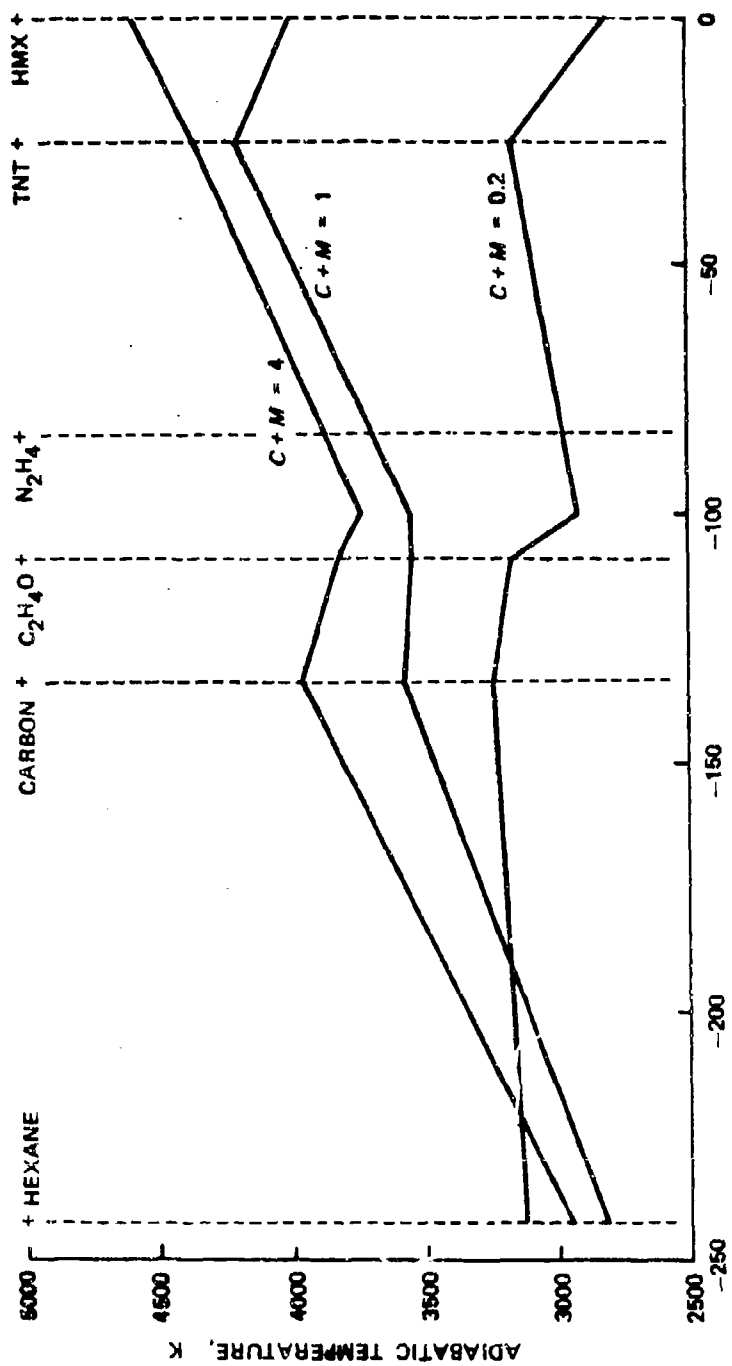

FIGURE 5. Adiabatic Temperature vs. Oxygen Balance for the Combustion of Six Fuels at C/M = 1.0 in the Presence of Titanium and Air.

It was pointed out by Smith[12] that radiation effects should be negligible when detonation takes place. When the combustion is a deflagration, however, the adiabatic assumption is expected to be less reliable. A comparison of the experimental data on dust explosions reported by the Bureau of Mines[13] would seem to show that the computed results from the present report may be high by a factor of about two. It has, however, been pointed out by Baker *et al.*[14] that the Hartmann apparatus used by the Bureau of Mines investigators seriously underestimates the maximum overpressures to be expected. On this basis it is anticipated that the adiabatic results will show much less extreme negative departures from realistic maximum overpressures.

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[12] D. E. Smith, "Attenuation Effects of Thermal Radiation on Internal Blast Overpressure." M. S. Thesis, Naval Postgraduate School, Monterey, Calif., December 1979.

[13] Bureau of Mines. *Explosibility of Metal Powders*, by M. Jacobson, A. R. Cooper and J. Nagy. U.S. Department of Interior, Washington, D.C., 1964. (RI 6516, publication UNCLASSIFIED.)

[14] W. E. Baker, P. A. Cox, P. S. Westine, J. J. Kulesz, and R. A. Strehlow. *Explosion Hazards and Evaluation*. Amsterdam, Elsevier, 1982, pp. 260-61.

Appendix A
DESCRIPTION OF THE COMPUTER PROGRAM

The program itself, which is listed in Appendix B, is written for the HP 9845A computer. Various sections are referred to by their labels.

MAIN PROGRAM

Input Section

Fuel (accessible from line 1900). Enter formula and internal energy of formation. Computes formula mass; allows for zero C or H or no fuel. Resets flags.

Conc (accessible from line 1870). Resets counters. Enter $C + M$ (total concentration in kg/m^3) and then C/M, as asked for.

Temp (for entering total temperature manually). May be accessed by use of special function key k4. After at least two trials, **Temp** may be bypassed and interpolation used to find the new temperature. Pressing k5, so that At$ = "Y", after two iterations allows for automatic interpolation. If needed, the automatic interpolation may be stopped by pressing PAUSE, then k5 (which returns At$ to "N"), and finally k4 for manual setting of temperature.

Computation Section

Calc calls up the computational subroutines **Eq**, **Tical**, and **Ex**.

Eq is a subroutine of the main program to evaluate equilibrium constants of formation of each of the 40 chemical species. K_p is first computed from the stored parameters and then converted to K_n (expressed in mole numbers). K_p or K_n is defined as the ratio of the activity of the species to the product of the activities of C, Ti vapor, H_2, N_2, and O_2, each raised to the appropriate power. For Ti_2O_3 and Ti_3O_5, $\sqrt{K_n}$ is computed so as to avoid overflow at lower temperatures. For condensed phases, the standard state is the pure phase; for K_n, the standard state for gases is 1 mole (in 1 m^3).

Tical is the master subroutine which carries out equilibrium and energy calculations. Results are displayed as "dU" (net) and "T high" or "T low"; dU = 0 is desired for convergence. A new temperature approximation is performed automatically by interpolation, based on the previous T and dU values; or else it is entered manually with k4. A more detailed description of **Tical** will be found below.

Output

At **Ex**, results of the calculations are printed: temperature, overpressure, mole numbers of all products and the diagnostic features described under DIAGNOSTICS, below. Options are allowed at this point for changing *C/M*, *C + M* or for a new fuel.

SUBROUTINE TICAL

Tical is the major computational subroutine whose task is to find the numbers of moles of the products present at equilibrium at the selected temperature. The conditions to be satisfied (other than for the trivial case of argon) are the atom balances in C, H, N, O, and Ti and the establishment of chemical equilibrium between each compound and its component elements in their reference states.

The master variables (all in mole numbers) are $X = \sqrt{O_2}$, $Y = \sqrt{H_2}$, $Z = \sqrt{N_2}$, Acc = activity of carbon (standard state = graphite), and Ti = Ti metal vapor. Of these, Y is always computed in closed form; from one to four of the remaining are found as unknown parameters in the subroutine **Newt** by using the Newton-Raphson method. The actual number of unknowns is equal to four, reduced by the number of condensed phases present. Possible condensed phases are: Ti (solid), TiO (solid), Ti_2O_3 (solid), Ti_3O_5 (solid), TiO_2 (solid), liquid oxide solution (designated Lox in the program), C (solid), TiC (solid or liquid), TiN (solid or liquid). The presence of each condensed phase is indicated by a flag, to be set as described under **Flags**.

Based on the values of the master variables and the equilibrium constant of formation, the mole number of each species is computed. Then the material balance in the elements O, N, C, and Ti is written in terms of these mole numbers. When liquid oxide is present, the stoichiometric condition is that the sum of the activities (that is, mole-fractions) of the components of the solution should add to unity; this condition replaces the atom balance in titanium for this case. There thus results a set of up to four simultaneous nonlinear equations; this set is the basis of the Newton-Raphson scheme to find the unknown parameters.

At the conclusion of an iteration, the newly generated values of the master variables are used to repeat the calculations. In favorable situations, each iteration results in improvement (although temporary divergence sometimes occurs). Iteration is repeated until the stoichiometric errors are less than one part in ten thousand.

Newt solves the set of simultaneous nonlinear equations needed to find the master variables. The Newton-Raphson method is used. In this subroutine it is necessary to find a number of derivatives numerically by observing the effect of a fractional change in each variable. This fractional change is set initially at 0.1. It is found that divergences which would otherwise occur when the errors are large can be averted by altering this fractional change to 0.5. This is accomplished by the use of special function key k8, when the computer is in a pause mode or is waiting for input. Depressing k8 a second time will change the fraction back to 0.1. The fractional errors in the stoichiometric conditions may be observed by the use of k1 (TRACE VARIABLES Yn(*)/EXECUTE) after which will be displayed Y(1),

Y(2), etc., which are these fractional errors. The display of these will remain on the screen if PRT ALL is locked down.

Approx: To begin the calculation an initial approximation of the master variables is needed. In this approximation an arbitrary hierarchy of oxygen and nitrogen uptake is assumed. Oxygen is assumed to be taken up in the order CO, titanium oxides, H_2O, CO_2. If there is insufficient oxygen to form TiO, then TiN is assumed to be present. With excess C, C (solid) or TiC are assumed.

It has been found that **Approx** gives quite satisfactory values of the master variables at temperatures below about 3000 K; at higher temperatures the initial approximation may be in considerable error. After each entry into **Temp** the question is asked, "Do you want 'Approx'?". The default condition (obtained by pressing CONT) is "Y" for a new concentration (*C/M* or *C + M*) and "N" otherwise.

Flags sets the flags for condensed phases and gives the values of the temporary variables used in **Newt**. The criteria for the presence of a condensed phase are that the quantity of the phase, if previously computed, be nonnegative and that the formation constant be satisfied or exceeded. In the case of liquid oxide, the formation-constant requirement is replaced by the requirement that the temperature be above the melting-point curve (T = 2143 is used for simplicity; see text for discussion of this point) and that the sum of the activities of the components of the solution be no less than unity.

Two important indexes are set by **Flags**. Iiflag gives the number of metal-plus-oxide phases (no greater than two); for liquid oxide solution, Iiflag = 1 except that, when TiC, C (solid), and liquid oxide are all present, Iiflag = 0. The index Ii gives the number of unknowns to be sought in **Newt**. Finally **Flags** gives initial values of the variables to be used in **Newt**.

Fx gives the fitting functions for **Newt**. There are three branches, depending on the value of Iiflag. Certain of the master variables are computed in **Fx**. After **Diff** is called, the current mole numbers of all species are generated. The subroutine returns to **Newt** the variable Fx, which is the fractional error in the stoichiometry in whichever element **Newt** is considering at the time.

Diff first computes those master variables which were not found in **Fx**. Then **Spec** and **Oxides** are called to compute the mole numbers of all species, and finally the errors in stoichiometry for all elements (and the sum of activities when liquid oxide is present) are computed.

Spec computes the mole numbers of all gaseous species, given the current values of X, Z, Acc, and Ti. $Y = \sqrt{H_2}$ is computed in closed form in **Spec**; it is needed for computations on hydrogen-containing species. For each species the appropriate formation equilibrium constant is used.

Oxides computes the mole numbers of condensed metal and oxide phases. For two such phases (Iiflag = 2) the atom balance conditions for titanium and oxygen are used; for Iiflag = 1, only the titanium balance is used; for Iiflag = 0 the oxygen balance is used.

Nwl serves to route the computation to the proper portions of **Tical**. On first entry, the flags will have been set and control is sent to **Newt**; except, if Ii = 0, provision exists for a closed-form solution. In either case, **Flags** is called again. If any flag has changed, the computation must be repeated for the new set of condensed phases; otherwise preparation is made for exit from **Tical** at the line **Energy**.

Energy computes from the stored parameters the molar internal energy of each component and then the total change in internal energy (dU) from the starting materials, taking into account the mole numbers of each species present. If the system is at the melting point of any of the condensed phases present, the amounts of solid and liquid are computed from the energy balance, using the known energy of fusion. Control is then returned to the main program.

DIAGNOSTICS

Sum1 is called at the end of each run to report the following items: (1) a check on the material balance of each element; (2) the activity of carbon (Acc) and the sum of the activities of the components of the liquid oxide solution; (3) a comparison of the computed amounts with the equilibrium constants of formation for each condensed phase; and (4) the activities (mole-fractions) of each component in the liquid oxide solution.

Sum is called whenever special function key k0 has been depressed once. At each emergence from **Newt** the mole numbers of all species are presented in condensed form: this is followed by **Sum1**, the output of which has been just described. These checks are of particular interest in troubleshooting. Depressing k0 a second time will cancel calling up **Sum**.

Depressing k1 will cause execution of TRACE VARIABLES Yn(*). Then during each iteration in **Newt** the relative error functions used to test convergence will be displayed. Each Yn(*) must drop below 0.0001 for convergence. This feature may be turned off by executing NORMAL.

Appendix B
PROGRAM LISTING FOR "TIF4"

```
10   ! FILE NAME "TIF4" 22 Feb 84  :  Ti + air + fuel; continuous liquid phase
20   ! Adiabatic overpressure calculation (constant volume)
30   !
40        OPTION BASE 1
50        OVERLAP
60        ASSIGN @3 TO "THTI"
70        READ @3,1
80        DIM Xn(50),Yn(50),Xt(50),Delx(50),D(50,5),In(50,5),Hold(50),Ns(2),Xf(50)
90        DIM N(50),Ax(50,6),K(50),Bw(50,5),Fe0(50)[81],P(50),MaWt(9),U(50)
100       INTEGER Cflag,Tinflag,Ticflag
110       INTEGER G(50),I,J,K,I1,Nw,Cw,Nwct,In,Flag0,Flag1,Flag2,Flag3,Flag4
120       INTEGER I1,Idf,Idfuel,Check,F80,F10,F20,F30,F40,C0,Tin0,Tic0
130       MAT G=CON                                          !
140       G(5)=G(13)=G(14)=G(28)=0                           Index for gases
150       FOR I=19 TO 23
160         G(I)=0
170         NEXT I
180       FOR I=35 TO 50
190         G(I)=0
200         NEXT I
210       READ @3;Ax(*),Bw(*),Fe0(*)
220       LOAD KEY "INEX"
230       DISP "FOR ALL N(I) PRESS K0;     FOR TRACE VARIABLES Yn(#): K1"
240                 !
250       PAUSE
260         DEF FNQd(A,B,C)=(-B+SQR(B^2-4*A*C))/2/A
270         DEF FNSti=Ti1+Ti2+Ti3+Tip !                      Sum gaseous Ti atoms
280         DEF FNSo=Tio+Co+Oh+H2o+No+O+Hnco+Hco+Ch2o+2*(Co2+O2+Tio2)
290                 !                                        Sum gaseous O atoms
300         DEF FNOa=Noa-FNSo !                              Sum condensed O
310         DEF FNTsum=Ti1+2*Ti2+2*Ti3+Ti4!                  Sum Ti oxides
320                 !
330       C_M=0
340       Cpm=.1!                                            Default total mass is 0.1 kg/cu m.
350       V=1 !                                              Default final volume is 1.0 cu m.
360       Pw$="V"!                                           Default mode is constant volume
370       Cpm=C_M=.1 !                                       Initial nominal values
380       Eps=1E-4 !                                         Fractional error for convergence
390       Dlt=.1 !                                           Fractional change in variable to compute derivative
400       !                                                  Dlt may be changed to or from .5 by Key K8
410                 !
420  Fuel:  INPUT "Name of compound",M$
430       DISP "Formula, as atoms per mole of C, H, N, O in order";
440       DISP "use k7 for TNT"
450       INPUT Ac,Ah,An,Aox
460       Act=N(21)=N(22)=Tic=N(19)=N(20)=Tin=N(43)=N(44)=Cr=N(23)=Cw=0
470       Cw=Nw=Flag0=Flag1=Flag2=Flag3=Flag4=Cflag=Tinflag=Ticflag=0
480       !                                                  Flags and condensed phases reset for new fuel
490       IF Ac=0 THEN Ac=1E-10
500       IF Ah=0 THEN Ah=1E-10 !                            Provide for fuel with no C or no H
510       DISP "Internal energy of formation, J/mole";
520       DISP "use SHIFT k7 (=k23) for TNT"
530       INPUT Um
540       Fms=Ac@12.0115+Ah@1.008+An@14.0067+Aox@15.999!     Formula mass, g/mole
550                 !
560  Conc:  OUTPUT 16;"Nominal C+H = ",Cpm
570       IF Fms=0 THEN Fms=1E-10
580       INPUT "Total concentration, kg/cu m of air, C+H",Cpm
590       OUTPUT 16;"Nominal C/H =",C_M
600       INPUT "Ratio of fuel to metal, C/H",C_M
610       PRINTER IS 7,1
620       PRINT "Total conc = ";Cpm
630       Mti=Cpm/(1+C_M)!                                   Total mass of titanium
640       Mf=Cpm-Mti !                                       Mass of fuel
650       Cw=Nw=0 !                                          Counter for iterations and criterion for "Approx"
660       Anp=PROUND(An,-3)
670       Acp=PROUND(Ac,-3)
680       Ahp=PROUND(Ah,-3)
690       Aop=PROUND(Aox,-3)
700  Vp:  Pw$="V"
710       V=1
720  Conc1:       PRINT USING Inc;Mti,Mf,M$,Acp,Ahp,Anp,Aop,C_M
730  Inc:IMAGE /,/,2DZ.3D" kg of Ti",2X,2DZ.3D" kg of ",K,"  C",K," H",K," N",K," O",K2X"C/H= ",3DZ.3D/
740       Nti=Mti/7.8479!                                    Moles of Ti
750  !
```

```
760 Exit:   Mols=MAX(1000*Mf/Fms,1E-10)
770         Fms=PROUND(Fms,-3)
780         Mo=PROUND(Mols,5)
790         Mt=PROUND(Mtl,5)
800         PRINT Mt;" moles of Ti"
810         PRINT "Formula mass of fuel is";Fms;"g/mole.  present are ";Mo;"moles"
820         PRINT "VOLUME = ";V;" cu m"
830 Conca:        N(6)=.4836 !                                  Argon
840         Nc=Ac*Mols
850         Nh=Ah*Mols
860         Nn=An*Mols+62.96 !                                  Includes moles of N atoms from air
870         Nga=Aga*Mols+16.951!                                  "   "  "  O   "  "  "
880         Lf=1 !                                              Default value. TiC and graphite not both present.
890         U0=0 !                                              Resets internal energy
900         Ti=U1=0 !                                           For temperature interpolation
910         At$="N" !                                           Default manual temperature setting
920         IF At$()"Y" THEN Temp
930         T=2500 !                                            For automatic temperature setting
940         GOTO Temp1
950
960 Temp:   IF Flag0 THEN DISP "Tm=1933 ";
970         IF Flag1 THEN DISP "Tm=2023 ";
980         IF Flag2 THEN DISP "Tm=2113 ";
990         IF Flag3 THEN DISP "Tm=2947 ";
1000        IF Flag4 THEN DISP "Tm=3143 ";
1010        IF Ticflag THEN DISP "Tm=3290 ";
1020        IF Tinflag THEN DISP "Tm=3220 ";
1030        !                                                   Preceding give melting points of condensed phases
1040        INPUT "Approximate temperature ",T
1050        INPUT "Do you want 'Approx'?(Y/N)",T$
1060        !                                                   Default: "Y" for new concentration; "N" otherwise
1070        !                                                   "Approx" is generally desirable below 3000 K, but not above.
1080        IF UPC$(T$)="Y" THEN Nu=0
1090        IF UPC$(T$)="N" THEN Nu=1
1100        T$=" "
1110        !
1120 Temp1: !
1130 Calc:        GOSUB Eq !                                    Computes equilibrium constants at T
1140        DISP "T = ";T;
1150        GOSUB Tical !                                       Subroutine calculates mole numbers and residual Delta U.
1160        D$=" T high  "
1170        IF Du<0 THEN D$=" T low  "
1180        DISP D$
1190        FIXED 0
1200        PRINT "T = ";T;" K","DelU = ";Du;" J" LIN(2)
1210        DISP "T = ";T;" K","DelU = ";Du;" J"!
1220        DISP D$
1230        STANDARD
1240        IF Du=0 THEN Ex
1250        T2=T1
1260        U2=U1
1270        T1=T
1280        U1=Du
1290        IF T2()0 THEN Temp2
1300        IF At$()"Y" THEN Temp
1310        T=3500-500*SGN(Du)
1320        GOTO Temp1
1330 Temp2:       IF ABS(Du)<1000 THEN Ex
1340     IF At$="Y" THEN Into!                                  Ati reset with key K5
1350        DISP "To exit, press K2;  manual temperature: K4!";
1360        DISP " Interpolate: CONT"
1370        PAUSE
1380 Intp:  T=T2-U2*(T2-T1)/(U2-U1)!                            Linear interpolation
1390        GoTO Calc
1400 !
1410 Ex:    Nsum=Nt=0
1420        FOR I=1 TO 44
1430          Nt=Nt+N(I)!                                       Total moles of products
1440          Nsum=Nsum+G(I)*N(I) !                             Moles of gas
1450          NEXT I
1460 Conc3:Ng=Nsum !                                           Moles of gas
1470        Mass=(Nt*4+Mf*1.1692)*1000!                        Total mass in grams
1480        Masg=Mass-59.91*Tic-47.9*Mnt-63.9*Ti1-142.8*Ti2
1490        Masg=Masg-223.7*Ti3-79.9*Ti4-61.91*Tin-12.011*Gr
1500        !                                                   Mass of gas
```

```
1520        M_g=Mass/Ng !                                   Avge molar mass of gases
1530        M_t=Mass/Nt !                                   Avge molar mass of all products
1540        PRINT USING Incon;T
1550 Incon:     IMAGE /"T = ",4D.D,"K"
1560        FIXED 3
1570        PRINT "Avg Molar mass(gases) = ";M_g;" g/mol";
1580        PRINT SPA(2);"Avg Molar mass(total) = ";M_t;" g/mol";
1590        PRINT SPA(5);Ng;" moles of GAS ";Nt;" moles TOTAL";LIN(1)
1600        P=8.3143E-5*Ng*T/V !                            nRT/V, VALUE IN BARS
1610        PRINT LIN(1);"Overpressure = ";P-1;" bars";LIN(2)
1620        STANDARD
1630        PRINT "Species";SPA(8);"Moles";SPA(8);"Mole %";SPA(4);"Part. pres.";
1640        PRINT SPA(4);"LGT(K)";SPA(6);"LGT(P)";LIN(1)
1650        !                                               Final output
1660        FOR I=1 TO 34
1670          IF G(I)=0 THEN Conc5
1680          IF N(I)<=0 THEN N(I)=1E-90
1690          PRINT USING Incon3;Fo$(I),N(I),100*N(I)/Ng,N(I)*P/Ng,LGT(N(I)/Ng),LGT(N(I)*P/Ng)
1700 Incon3:        IMAGE 9A,5X,Z.3DE,5X,2D.4D,5X,3D.4D,5X,MDZ.3D,5X,MDZ.3D
1710 Conc5:NEXT I
1720 Incon1:        IMAGE 9A,5X,Z.3DE,5X,Z.3DE,"moles"
1730        FOR I=19 TO 23
1740          IF N(I)=0 THEN Conc6
1750          PRINT USING Incon1;Fo$(I),N(I)
1760 Conc6: NEXT I
1770        FOR I=35 TO 44
1780          IF N(I)=0 THEN Conc7
1790          PRINT USING Incon1;Fo$(I),N(I)
1800 Conc7:     NEXT I
1810 Comp1: GOSUB Sum1
1820        PRINT USING Inc;Mt1,MF,N$,Acp,Ahp,Anp,Aap,C_m
1830        PRINT USING Inc2;T,P-1,V
1840 Inc2:      IMAGE "T = ",4D.D,"   Overpressure = ",3D.3D," bars",  "   Volume = ",3D.3D," cu m"
1850        PRINT LIN(4)
1860        BEEP
1870        LINPUT "DO YOU WISH TO RUN ANOTHER CONCENTRATION (Y/N)?",C$
1880        PRINT PAGE
1890        IF C$="Y" THEN Conc
1900        INPUT "Another fuel? (Y/N)",Cf$
1910        IF UPC$(Cf$)="Y" THEN Fuel
1920        OUTPUT 16;"END OF ROUTINE"
1930        STOP !
1940 ! ************************************************************************
1950 Eq:        ! COMPUTES Kn FROM LGT(Kp) PARAMETERS    ************************
1960 ! ************************************************************************
1970        V_rt=12180@V/T  ! V/RT FOR CONST VOL = V CU M.
1980        FOR I=1 TO 50
1990          Lgk=Ak(I,1)+Ak(I,2)/(T+Ak(I,3))+Ak(I,4)@T
2000          Lgk=Lgk+Ak(I,6)@LGT(V_rt)                 ! Conversion from Kp to Kn
2010          IF (I=36) AND (I<41) THEN Lgk=Lgk/2
2020          !                                         Use SQR(K) for T1203 and T1305 to avoid overflow
2030          IF I=43 THEN Lgk=MIN(Lgk,99)
2040          K(I)=10^Lgk
2050          NEXT I
2060          K1c=K(19)!                                 For T1C
2070          IF T<3290 THEN K1c=K(20)
2080          K1=K(21)!                                 For condensed metal
2090          IF T<1933 THEN K1=K(22)
2100          K1=K(35)!                                 For T1O
2110          IF T<2823 THEN K1=K(36)
2120          K2=K(37)!                                 For T1203
2130          IF T<2112 THEN K2=K(38)
2140          K3=K(39)!                                 For T1305
2150          IF T<2047 THEN K3=K(40)
2160          K4=K(41)!                                 For T1O2
2170          IF T<2143 THEN K4=K(42)
2180          K1n=K(43)!                                For T1N
2190          IF T<3220 THEN K1n=K(44)
2200          K843=(K3/K4)^4/K1/K4
2210          K832=K2/K1@(K2/K3@K2@(K2/K3))^3
2220          K831=K1@(K1/K1)@(K1/K1)@(K1/K3)@K1/K3
2230          !                                         These last 3 used for Lox calcn.
2240          RETURN !
```

```
2250 ! ************************************************************************
2260 Tical:     PRINT LIN(2) ! ***************************************************
2270 !   WILL FIND ALL MOLE NUMBERS AND THEN COMPUTE ENERGY BALANCE.
2280 ! ************************************************************************
2290      Cu=0 !                                                  Counts iterations
2300      IF Nw THEN Nwl
2310      Ncc=Nc
2320      Nnc=Nn
2330 ! ************************************************************************
2340 Approx: !  (Based mostly on condensed phases)    ************************
2350 ! ************************************************************************
2360      FOR I=1 TO 48
2370        N(I)=0
2380      NEXT I
2390      Ar=N(6)=.4036
2400      Flag0=Flag1=Flag2=Flag3=Flag4=Tinflag=Ticflag=Lexflag=0
2410      Z=SQR(Nn/2) !                                           Applies when Tinflag=0
2420      IF Nea)Nc THEN Apex
2430      Co=Nea !                                                No oxides
2440      Ticflag=1
2450      IF Nti)Ncc-Nea THEN Appn
2460      Cflag=1 !                                               Graphite present, no metal.
2470      Acc=1
2480      X=Co/Acc/K(7)
2490      Ti=N(1)=1/Acc/Kt1c
2500      GOTO Appx
2510           !
2520 Appn:Flag0=1 !                                               Metal present, no graphite
2530      Ti=1/Kt1
2540      Acc=1/Ti/Kt1c
2550      X=Co/X/K(7)
2560      GOTO Appx
2570           !
2580 Apex:Co=Ncc !                                                Metal oxides present
2590      IF Nti(Nea-Ncc THEN App1
2600      Flag1=1 !                                               Excess Ti: Ti>TiO
2610      Tinflag=1
2620      Ext1=Nti-Nea-Ncc-Nn !                                   The excess of Ti(c) over N
2630      IF Ext1)0 THEN App2
2640      IF Ktin/K1*K2/K1*K2/K1)1 THEN App1a
2650      Z=SQR(-Ext1/2) !                                        N is in excess: TiN + TiO
2660      Ti=N(1)=1/Ktin/Z
2670           !
2680 App3:X=1/K1/Ti
2690      GOTO Appx
2700           !
2710 App2:Flag0=1       !                                         Ti(c) is in excess over N
2720      Ti=MIN(Ext1,1/Kti)
2730      Z=1/Ktin/Ti
2740      GOTO App3
2750           !
2760 App1:IF Nti(2*(Nea-Ncc)/3 THEN App4
2770      X=K1*K1/K2/K2     !                                     TiO   Ti2O3 region
2780      Flag1=Flag2=1
2790      Ti=1/K1/X
2800      IF Ktin/K1*K2/K1*K2/K1(1 THEN Appx
2810      Tinflag=1
2820      Z=1/Ktin/Ti !                                           TiN + 2 oxides
2830      IF Nti-2*(Nea-Ncc)/3)Nn THEN Appx
2840      IF 6*LOG(K3)+LOG(Ktin))10*LOG(K2) THEN App4a
2850           !
2860 App1a:Z=SQR((Nn-Nti+2*(Nea-Ncc)/3)/2)!                       TiN + Ti2O3
2870      Ti=1/Ktin/Z
2880      X=(1/K2/Ti)^(2/3)
2890      GOTO Appx
2900           !
```

```
2910 App4: IF Nti(.6*(Noa-Ncc) THEN App5
2920       X=(K2/K3)^4*K2*K2   !                          Ti203 - Ti305 region
2930       Flag2=Flag3=1
2940       Ti=1/K2/X/SQR(X)
2950       IF 6*LOG(K3)+LOG(Ktin)(18*LOG(K2) THEN Appx
2960       Tinflag=1
2970       Z=1/Ktin/Ti  !                                 TiN + 2 oxides
2980       IF Nti-3*(Noa-Ncc)/5>Nn THEN Appx
2990         !
3000 App4a:Z=SQR((Nn-Nti+3*(Noa-Ncc)/5)/2)!               TiN + Ti305
3010       Ti=1/Ktin/Z
3020       X=(1/K3/Ti/SQR(Ti))^.4
3030       GOTO Appr
3040         !
3050 App5:IF Nti((Noa-Ncc)/2 THEN App6
3060       Flag3=Flag4=1 !                                Ti305 - Ti02 region
3070       X=K3/K4/K4/K4*K3
3080         !
3090 App7:Ti=1/K4/X/X
3100         !
3110 Appx:Acc=Co/X/K(7)!                                  Exit from "Approx"
3120       At3=Ti^3*X^5*K3*K3 !                           (initial approx.)
3130       GOSUB Oxides
3140       GOSUB Flags
3150       GOTO Nwi
3160         !
3170 App6:Flag4=1 !                                       Ti02 + H20
3180       IF Noa)Nc+2*Nti+Nh/2 THEN Appc
3190       H2o=Noa-(Nc+2*Nti) !                           H2 - H20 mixture
3200       H2=Nh/2-H2o
3210       X=H2o/H2/K(12)
3220       GOTO App7
3230         !
3240 Appc:IF Noa)2*(Nc+Nti)+Nh/2 THEN Appo
3250       Co2=Noa-Nc-2*Nti-Nh/2 !                        CO - CO2 mixture
3260       Co=Ncc-Co2
3270       X=K(7)*Co2/Co/K(8)
3280       GOTO App7
3290         !
3300 Appo:Co2=Nc !                                        Excess 02
3310       02=Noa/2-(Ncc+Nti)-Nh/4
3320       X=SQR(02)
3330       Co=K(7)*Co2/X/K(8)
3340       GOTO App7
3350 ! ************************************************************************
3360 ! *              Set-up for Newton's method calculation                  *
3370 ! ************************************************************************
3380 Nwi:  !
3390       Nw=Nw+1 !                                      Controls entry into "Approx"
3400       IF Ii THEN Nw3
3410       PRINT "Closed-form calculation"!               "Newt" not used in this case
3420       GOSUB Fi2
3430       GOSUB Prtflg
3440       GOSUB Dspflg
3450       IF Check THEN GOSUB Sum
3460       GOTO Nw2
3470 Nw3:  GOSUB Newt
3480 Nw2:  GOSUB Flags
3490         IF (Tinflag()Tin0) OR (Flag0()F00) OR (Flagi()F10) THEN Nwi
3500         IF (Flag2()F20) OR (Flag3()F30) OR (Flag4()F40) THEN Nwi
3510         IF (Ticflag()Tic0) OR (Cflag()C0) THEN Nwi
3520         IF (Loxflag=Lox0) AND (Lflag=L0) THEN Energy
3530         !                                            If any flag changes, iterations are repeated.
3540       GOTO Nwi !
```

```
3550 !     ************************
3560 !     *   PRINT FLAG STATUS   *
3570 !     ************************
3580 Prtflg:IF Tinflag THEN PRINT " TiN";
3590       IF Ticflag THEN PRINT " TiC";
3600       IF Cflag AND (Ac)1E-10) THEN PRINT " Gr";
3610       IF Lexflag OR Lflag THEN PRINT " Lex";"(";LF;")";
3620       IF Flag0 THEN PRINT " Mat";
3630       IF Flag1 THEN PRINT " Ti0";
3640       IF Flag2 THEN PRINT " Ti2D3";
3650       IF Flag3 THEN PRINT " Ti3D5";
3660       IF Flag4 THEN PRINT " Ti02";
3670       PRINT TAB(1)
3680       RETURN
3690 ! ************************************************************************
3700 !          DISPLAY FLAG STATUS
3710 ! ************************************************************************
3720 Dspflg: DISP TAB(1)   !                                    Display flag status
3730       DISP "NEWTON'S CALC., ";SPA(5);
3740       IF Tinflag THEN DISP " TiN";
3750       IF Ticflag THEN DISP " TiC";
3760       IF Cflag AND (Ac)1E-10) THEN DISP " Gr";
3770       IF Lexflag OR Lflag THEN DISP " Lex";"(";LF;")";
3780       IF Flag0 THEN DISP " Mat";
3790       IF Flag1 THEN DISP " Ti0";
3800       IF Flag2 THEN DISP " Ti2D3";
3810       IF Flag3 THEN DISP " Ti3D5";
3820       IF Flag4 THEN DISP " Ti02";
3830       RETURN
3840 ! ************************************************************************
3850 Newt:         !  A NEWTON'S METHOD FOR UP TO FIVE SIMULTANEOUS NON-LINEAR EQNS
3860 ! ************************************************************************
3870       REDIM Xn(I1),Yn(I1),Xt(I1),Delx(I1),D(I1,I1),In(I1,I1)
3880       GOSUB Dspflg
3890 Newt0:Cv=0   !                                             Counter for Newton's method iterations
3900       Nwct=Nwct+1!                                         Counts entries into Newt
3910 Newt3:        MAT Xt=Xn
3920       PRINTER IS 7,1
3930       Cv=Cv+1
3940       FOR I=1 TO I1
3950         K=I
3960         GOSUB Fx
3970         Yn(I)=Fx
3980         FOR J=1 TO I1
3990           K=J
4000           Xt(J)=(1-Dlt)*Xn(J)!                           Dlt=.1 by default: may be reset to .5 by KB
4010           GOSUB Fx
4020           D(I,J)=-(Fx-Yn(I))/Xn(J)/Dlt!                  Partial of Yn(i) wrt Xn(j)
4030           Xt(J)=Xn(J)
4040           NEXT J
4050         NEXT I
4060       IF DET(D)<>0 THEN Newt1
4070                    !
4080       PRINT "MATRIX SINGULAR"
4090       DISP "MATRIX SINGULAR"
4100       PRINTER IS 0
4110       PRINT LIN(1),"D Matrix:"
4120       MAT PRINT D
4130       PRINT LIN(1)
4140       GOSUB Sum
4150       STOP
4160                !
4170 Newt1:MAT In=INV(D)
4180       MAT Delx=In*Yn
4190       MAT Xn=Xn-Delx
4200 Newt4:FOR I=1 TO I1
4210         IF Xn(I))=0 THEN Newt2
4220         Xn(I)=(Xn(I)+Delx(I))/2!                         If (= 0, use 1/2 previous value
4230 Newt2:  NEXT I
4240       FOR I=1 TO I1
4250         IF ABS(Yn(I)))Eps THEN Newt3
4260         GOSUB Fx
4270         NEXT I
4280         PRINT Cv;" ITERATIONS FOR  ";I1;" VARIABLES; ";
4290         GOSUB Prtflg
4300         PRINTER IS 7,1
4310         IF Check=0 THEN RETURN
4320         GOSUB Sum !                                      Diagnostics given when Check=0 (given by key K0)
4330 Retn: RETURN !
```

```
4340 ! ##########################################################################
4350 Flags:! ##########   Sets flags, Ii, initial values for Newt  ##############
4360 ! ##########################################################################
4370 !                                                  Sets flags for condensed phases.
4380 !                                                    Formation constants must be exceeded
4390 !                                                    and amount of phase not negative
4400          !
4410      Tin0=Tinflag !                                To save old values
4420      Lf0=Lflag
4430      Lox0=Loxflag
4440      F00=Flag0
4450      F10=Flag1
4460      F20=Flag2
4470      F30=Flag3
4480      F40=Flag4
4490      Tic0=Ticflag
4500      C0=Cflag
4510      Cflag=MIN(1,INT(Acc))*(Gr>0)
4520      IF Gr<0 THEN Gr=0
4530      IF Ac=1E-10 THEN Cflag=1 !                    For fuels with no carbon
4540      Ticflag=(Ti*Acc*Ktic)^1-1E-5)*(Tic>0)*(Ac>1E-10)
4550      IF Tic<0 THEN Tic=0
4560      Lf=NOT (Ticflag AND Cflag)!                   Lf=1 unless TiC and graphite both present
4570      Tinflag=(Ti^2*Ktin)^1-1E-5)*(Tin>0)
4580      IF Tin<0 THEN Tin=0
4590      Flag0=(Ti*Kt1)^1-1E-5)*(Met>0)
4600      IF Met<0 THEN Met=0
4610      Flag1=(Ti*X*X*K1)^1-1E-5)*(Ti1>0)
4620      IF Ti1<0 THEN Ti1=0
4630      Flag2=(Ti*X*SQR(X)*K2)^1-1E-5)*(Ti2>0)
4640      IF Ti2<0 THEN Ti2=0
4650      Flag3=(Ti*SQR(Ti)*X*X*SQR(X)*K3)^1-1E-5)*(Ti3>0)
4660      IF Ti3<0 THEN Ti3=0
4670      Flag4=(Ti*X*X*K4)^1-1E-5)*(Ti4>0)
4680      IF Ti4<0 THEN Ti4=0
4690      GOSUB Act
4700      Loxflag=(T>2143) AND (Lox>0) AND (Atsum>1-Eps)
4710      !                                             For Lox: Sum of activities of liquid oxides + metal )>1
4720      !                                             and T ) melt. pt. of TiO2
4730      IF Lox<0 THEN Lox=0
4740      IF Loxflag THEN Flag0=Flag1=Flag2=Flag3=Flag4=0
4750      Lflag=Loxflag AND Lf
4760      IF Lflag THEN Loxflag=0!                      Lflag for Lox except Loxflag used when
4770      !                                                both TiC and graphite also present.
4780      Tcon=Nti-FNSti-Tin !                          Condensed Ti, except for TiN
4790      Ocon=Noa-FNSo  !                              Condensed O
4800      IF NOT (Cflag AND Flag1) THEN Flag0
4810      Cflag=(Ncc>MIN(Tcon,Ocon)/3)  !               Gr + Ti1  => TiC + Ti2
4820      Flag1=1-Cflag
4830      Flag2=Ticflag=1
4840 Flag0:IF NOT (Ticflag AND Flag3) THEN Flag0
4850      Flag2=Cflag=1 !                               TiC + Ti3  =>  C + Ti2
4860      Flag3=(Tcon>10*Ncc)
4870      Ticflag=1-Flag3
4880 Flag0:IF NOT (Ticflag AND Flag4) THEN Flag0
4890      Flag2=Cflag=1 !                               TiC + Ti4  =>  C + Ti2
4900      Ticflag=(2*Ocon/3<Tcon)
4910      Flag4=1-Ticflag
4920 Flag0:IF (Ticflag=0) OR (Flag0>0) OR (Cflag=0) OR (Ac=1E-10) THEN Iiset
4930      Flag0=(Nti-FNSti)<Ncc)!                       With  TiC, either Met or Gr, not both
4940      Cflag=1-Flag0
4950          !
4960 Iiset:Iiflag=Flag0+Flag1+Flag2+Flag3+Flag4+Lflag !   Iiflag can be 0, 1, or 2.
4970 !                                                      Iiflag = 1 for Lflag but 0 for Loxflag
4980      IF Iiflag>2 THEN Flag1
4990      Ii=4-Iiflag-Tinflag-Ticflag-Cflag!            Number of variables in "Newt"
5000      IF Ii=0 THEN RETURN
5010      REDIM Xn(Ii)
5020      !                                             Following sets values of variables in "Newt"
5030      IF NOT Tinflag THEN Xn(Ii)=Z
5040      IF NOT Tinflag AND NOT Cflag AND NOT Ticflag THEN Xn(Ii-1)=Acc
5050      IF Tinflag AND NOT Cflag AND NOT Ticflag THEN Xn(Ii)=Acc
5060      IF Iiflag<2 THEN Xn(1)=X
5070      IF (Iiflag=1) AND Tinflag AND NOT Flag0 AND NOT Loxflag AND NOT Lflag THEN Xn(1)=Ti
5080      IF (Iiflag=0) AND NOT (Cflag AND Ticflag) THEN Xn(2)=Ti
5090      RETURN
5100 !                                                  The variables are X (if no more than one oxide or metal),
5110 !                                                  Ti (if no oxide or metal) and Z (if TiN is absent).
5120 !                                                  Exception: When TiN and one solid oxide, but no metal or liquid oxide
5130 !                                                  present  then Ti (and not X) is first variable.
```

```
5140 Flag1:Tcon=Nti-FNSti-Tin-Tic !                    The case of Iiflag)2, which is disallowed
5150       IF Iiflag=4 THEN F14
5160       IF NOT Flag0 AND NOT Flag1 THEN F13a
5170       IF NOT Flag0 AND NOT Flag4 THEN F13b
5180       IF NOT Flag3 AND NOT Flag4 THEN F13c
5190       IF Ocon)Tcon THEN F1a  !                    The case of Iiflag=5
5200       Flag0=Flag1=1
5210       Flag2=Flag3=Flag4=0
5220       GOTO Iset
5230 F1a:  Flag0=0
5240       GOTO F14a
5250 F14:  !                                           For Iiflag =4
5260       IF NOT Flag0 THEN F14a
5270 F13c: !                                           Flags 0,1,2
5280       Flag2=(Ocon)Tcon)
5290       Flag0=NOT Flag2
5300       GOTO Iset
5310 F13b: !                                           Flags 1,2,3
5320       Flag0=Flag4=0
5330       Flag3=(Ocon)1.6*Tcon)
5340       Flag1=NOT Flag3
5350       GOTO Iset
5360 F14a: !                                           Iiflag = 4, Flag0 = 0
5370       IF Ocon(=1.5*Tcon THEN F13b
5380       Flag1=0
5390 F13a: !                                           Flags 2,3,4
5400       Flag4=(Ocon)5*Tcon/3)
5410       Flag2=NOT Flag4
5420       GOTO Iset
5430 ! ##########################################################################
5440 Fx:! #########  Fitting functions for Newton's method calc.  ###############
5450 ! ##########################################################################
5460 !                                                 "Fx" computes errors in stoichiometric conditions for
5470 !                                                 exisiting values of variables.
5480 !                                                 Finds appropriate values of master variables
5490 !                                                 Calls on "Spec" to compute moles of all species
5500 !                                                 Xt(j) is used, since both original value of variable
5510 !                                                 and value changed by Dlt are employed.
5520       IF NOT Iinflag THEN Z=Xt(Ii)
5530       IF NOT Iinflag AND NOT Cflag AND NOT Iicflag THEN Acc=Xt(Ii-1)
5540       IF Iinflag AND NOT Cflag AND NOT Iicflag THEN Acc=Xt(Ii)
5550        ON Iiflag+1 GOTO Fx0,Fx1,Fx2
5560          !
5570 Fout:GOSUB Diff !                                 Exit routine for "Fx"
5580 !                                                 Following are stoichiometric conditions to use in "Newt"
5590       IF (I=1) AND (Iiflag(2) THEN Fx=Do/Noo
5600       IF (I=1) AND (Iiflag=1) AND Iinflag AND NOT Lflag AND NOT Flag0 THEN Fx=Dti/N*i
5610       IF Loxflag AND ((I=2) OR (I=1) AND Cflag AND Iicflag) THEN Fx=Atsum-1
5620       IF (I=2) AND NOT Iiflag AND NOT Lflag THEN Fx=Dti/Nti
5630       IF NOT Iinflag AND (I=Ii) THEN Fx=Deln/Nn
5640       IF NOT Iinflag AND NOT Cflag AND NOT Iicflag AND (I=Ii-1) THEN Fx=Delc/Nc
5650       IF Iinflag AND NOT Cflag AND NOT Iicflag AND (I=Ii) THEN Fx=Delc/Nc
5660          !                                        The stoichiometric tests correspond with the variables.
5670       RETURN !                                    Returns to "Newt" (or to "Nw" for Ii=0)
5680              !
5690 Fx0:  X=Xt(1)!                                    For Iiflag=0
5700       IF NOT (Cflag AND Iicflag) THEN Ti=N(1)=Xt(2)
5710       IF Cflag AND Iicflag THEN Ti=N(1)=1/Ktic
5720       IF NOT Loxflag THEN Fout
5730       GOSUB Act
5740       GOTO Fout
5750 ! ##########################################################################
5760 Act:! ##########  Gives activities in liquid oxide  ##########################
5770 ! ##########################################################################
5780       At0=Kti*Ti!                                 Activity of metal in liquid oxide
5790 !                                                 Following are activities of oxides in liquid oxide
5800       At1=K1*Ti*X
5810       At2=Ti*Ti*X**X**X**K2*K2
5820       At3=Ti*Ti*Ti*X**X**X**X**K3*K3*(Lflag(2)
5830       At4=K4*Ti*X**X
5840       Atsum=At0+At1+At2+At3+At4
5850       RETURN
5860 ! ##########################################################################
```

```
5870 Fxi:!                                                  For Iiflag =1
5880        IF Tinflag AND NOT Flag0 AND NOT Lflag THEN Fxia
5890        X=Xt(i)
5900        IF NOT Lflag THEN Fxib
5910        !                                               For Lflag=1, solves a cubic to find Ti = f(X)
5920        !                                               Must satisfy sum of activities = 1
5930        A3=-1/K3/K3/X/X/X/X/X
5940        A2=-(Kti+K1*X+K4*X*X)*A3
5950        A1=-X*X*X*K2*K2*A3 !                            Coeff. of cubic (Unit coeff. for cubic term.)
5960        Ar=(3*A2-A1*A1)/3
5970        Br=(2*A1*A1*A1-9*A1*A2)/27+A3 !                 Reduced cubic. lacks quadratric.
5980        Dc=Br*Br/4+Ar*Ar*Ar/27 !                        Discriminant of the cubic
5990        IF Dc<=0 THEN Fxic
6000        R1=-Br/2+SQR(Dc)
6010        R1=SGN(R1)*(SGN(R1)*R1)^(1/3) !                 Avoids cube roots of negative no.
6020        R2=-Br/2-SQR(Dc)
6030        R2=SGN(R2)*(SGN(R2)*R2)^(1/3)
6040        Xr=R1+R2 !                                      The only real root of the reduced eqn.
6050        Ti=N(i)*Xr-A1/3
6060        IF Ti>0 THEN Fxut
6070 Fxic.  IF Lflag THEN Ti=N(i)=FNBd(X*X*X*K2*K2,Kti+K1*X+K4*X*X,-1)
6080 !                                                      In case cubic had negative root
6090        Lf=2
6100        GOTO Fxut
6110 Fxib:  !
6120        IF Flag0 THEN Ti=N(i)=1/Kti
6130        IF Flag1 THEN Ti=N(i)=1/K1/X
6140        IF Flag2 THEN Ti=N(i)=1/K2/X/SQR(X)
6150        IF Flag3 THEN Ti=N(i)=(1/K3/X/X/SQR(X))^(2/3)
6160        IF Flag4 THEN Ti=N(i)=1/K4/X/X
6170        IF NOT (Cflag AND Ticflag) THEN Fxut
6180        Z=Xt(i)!                                        Case of TiC + graphite + Ti2O3
6190        Ti=N(i)=1/Ktic
6200        X=(1/K2/Ti)^(2/3)
6210        GOTO Fxut
6220 Fxia:  Ti=N(i)=Xt(i)  !                                For TiN + ore oxide
6230        IF Flag1 THEN X=1/K1/Ti
6240        IF Flag2 THEN X=((1/K2/Ti)^(2/3)
6250        IF Flag3 THEN X=(1/K3/Ti/SQR(Ti))^.4
6260        IF Flag4 THEN X=SQR(1/K4/Ti)
6270        GOTO Fxut
6280        !
6290 Fx2:   IF NOT (Flag0 AND Flag1) THEN Fx2a
6300        Ti=N(i)=1/Kti !                                 Ti - TiO region
6310        X=1/Ti/K1
6320        GOTO Fxut
6330 Fx2a:  IF NOT (Flag1 AND Flag2) THEN Fx2b
6340        X=K1/K2*K1/K2 !                                 TiO - Ti2O3 region
6350        Ti=N(i)=1/K1/X
6360        GOTO Fxut
6370 Fx2b:  IF NOT (Flag2 AND Flag3) THEN Fx2c
6380        X=(K2/K3)^4*K2*K2   !                           Ti2O3 - Ti3O5 region
6390        Ti=N(i)=1/K2/X/SQR(X)
6400        GOTO Fxut
6410 Fx2c:  IF NOT (Flag3 AND Flag4) THEN Fx2d
6420        X=K3/K4/K4/K4*K3
6430        Ti=N(i)=1/K4/X/X
6440        GOTO Fxut
6450 Fx2d:  IF NOT (Flag2 AND Flag4) THEN Fx2e
6460        X=K2/K4*K2/K4
6470        Ti=N(i)=1/K4/X/X
6480        GOTO Fxut
6490 Fx2e:  IF Cflag AND Flag1 AND NOT Ticflag THEN Alert2
6500        Ti=1/Ktic
6510        X=1/K1/Ti
6520        GOTO Fxut !
```

```
6530 ! ##########################################################################
6540 !  ####  Diff:  Calculates error functions for C, O, N, Mg and Al  ##########
6550 ! ##########################################################################
6560 Diff:
6570       IF Tinflag THEN Z=1/Ti/Ktin
6580       IF Ticflag THEN Acc=1/Ti/Ktic
6590       GOSUB Spec
6600       Tin=(Nnc-No-2*N2)*Tinflag
6610       Tic=(Ncc-Co-Co2)*Ticflag!                          Nnc and Ncc are corrected moles of N or C
6620       !                                                  atoms  as given in "Spec"
6630       N(44)=Tin*(T(3220.
6640       N(43)=Tin-N(44)
6650       N(20)=Tic*(T(3290)
6660       N(19)=Tic-N(20)
6670       GOSUB Oxides ! GIVES OXIDES AND METALS
6680       Dti=Nti-FNSti-Tin-Tic-Met-FNIsum
6690       Do=Noo-FNSo-Ti1-3*Ti2-5*Ti3-2*Ti4
6700       Deln=Nnc-No-2*N2-Tin
6710       IF Dflag AND Ticflag THEN Tic=Dti+Tic
6720       Delc=Ncc-Co-Co2-Tic
6730       Gr=N(23)=Delc*Dflag*(Ac)1E-10)
6740       RETURN
6750       !
6760 ! ##########################################################################
6770 ! ################  Computes moles of all gaseous species  ##################
6780 ! ##########################################################################
6790 Spec: !                                                  Input: X  Ti, Z. Acc
6800        O2=N(18)=X^2
6810       O=N(17)=K(17)*X
6820       Tio=N(2)=K(2)*Ti*X
6830       Tio2=N(3)=K(3)*T:*X*X
6840 Nit:  !
6850       N2=N(16)=Z^2
6860       No=N(15)=K(15)*X*Z
6870       Mgov=N(42)=K(42)*Mgv*X
6880 Car:  IF Dflag=1 THEN Acc=1
6890       IF Ac=1E-10 THEN Acc=1E-30 !                       For fuels with no carbon
6900       Co=N(7)=K(7)*Acc*Y
6910       Co2=N(8)=K(8)*Acc*X*X
6920       Mh=K(9)+K(10)*X+Acc*(K(29)*Z+K(30)*Z*X+K(31)*X*X+K(32)*Acc*Acc
6930       !                                                  Coefficient of monohydrogen species
6940       Dh=1+K(12/*X+K(32)*Acc*Y+K(33)*Acc*Acc !           Coefficient of dihydrogen species
6950       Y=FNQd(2*Dh,Mh,-Nh)
6960       H=N(9)=K(9)*Y
6970       Oh=N(10)=K(10)*X*Y
6980       H2=N(11)=Y*Y
6990       H2o=N(12)=K(12)*X*Y*Y
7000       Hcn=N(29)=K(29)*Acc*Y*Z
7010       Hncc=N(30)=K(30)*Acc*X*Y*Z
7020       Hco=N(31)=K(31)*Acc*X*Y
7030       Ch2o=N(32)=K(32)*Acc*X*Y*Y
7040       C2h2=N(33)=K(33)*Acc*Acc*Y*Y
7050       Tio=N(4)=Cnn=N(24)=SQR(K(4)*K(24)*Ti*Acc*Z)
7060       Cn=N(25)=K(25)*Acc*Z
7070       C2n=N(26)=K(26)*Acc*Acc*Y
7080       C2n=N(27)=K(27)*Acc*Acc*Z
7090       C3=N(34)=K(34)*Acc*Acc*Acc
7100       Ncc=Nc-Hcn-Hnco-Hco-Ch2o-Cn-Cnn-2*(C2h2+C2h+C2n+3*C3
7110       !                                                  Corrected moles of C atoms
7120       Nnc=No-Hcn-Hnco-Cn-C2n-Cnn  !                      Corrected moles of N atoms
7130       IF Nnc<0 THEN Nnc=1E-50
7140       RETURN !
```

```
7150 ! ********************************************************************
7160 ! ********** Moles of metals and oxides ******************************
7170 ! ********************************************************************
7180 Oxides: FOR In=19 TO 22
7190           N(In)=0
7200           NEXT In
7210         FOR In=35 TO 44
7220           N(In)=0
7230           NEXT In
7240         Met=Ti1=Ti2=Ti3=Ti4=0
7250         !                                          Preceding prevents carryover of old values
7260         IF NOT Iiflag AND NOT Loxflag THEN RETURN
7270         Tcon=Nti-FNSfi-Tin-Tic !                   Condensed Ti + oxides
7280         Ocon=Nou-FNSo  !                           Condensed O
7290         IF Loxflag OR Lflag THEN Oxlox
7300         IF Iiflag=1 THEN Ox1
7310         !                                          Following for two oxides or metal + one oxide
7320         IF NOT (Flag0 AND Flag1) THEN Oxb
7330         Ti1=Ocon
7340         Met=Tcon-Ti1
7350         GOTO Ox2
7360              !
7370 Oxb:    IF NOT (Flag1 AND Flag2) THEN Oxc
7380         Ti2=Ocon-Tcon
7390         Ti1=Tcon-2*Ti2
7400         GOTO Ox2
7410              !
7420 Oxc:    IF NOT (Flag2 AND Flag3) THEN Oxd
7430         Ti3=2*Ocon-3*Tcon
7440         Ti2=(Tcon-3*Ti3)/2
7450         GOTO Ox2
7460              !
7470 Oxd:    IF NOT (Flag3 AND Flag4) THEN Oxe
7480         Ti3=2*Tcon-Ocon
7490         Ti4=Tcon-3*Ti3
7500         GOTO Ox2
7510              !
7520 Oxe:    IF NOT Flag2 AND Flag4 THEN Alert2
7530         Ti2=2*Tcon-Ocon
7540         Ti4=Tcon-2*Ti2
7550         GOTO Ox2
7560 Ox1:    IF Tinflag THEN Oxtin
7570         IF Flag0 THEN Met=Tcon !                   For Iiflag =1, no liquid oxide
7580         IF Flag1 THEN Ti1=Tcon
7590         IF Flag2 THEN Ti2=Tcon/2
7600         IF Flag3 THEN Ti3=Tcon/3
7610         IF Flag4 THEN Ti4=Tcon
7620         GOTO Ox2
7630              !
7640 Oxtin:  IF Flag0 THEN Met=Tcon-Nnc+No+2*N2  !      Routine for TiN + one oxide.  This line is not bal in N.
7650         IF Flag1 THEN Ti1=Ocon
7660         IF Flag2 THEN Ti2=Ocon/3
7670         IF Flag3 THEN Ti3=Ocon/5
7680         IF Flag4 THEN Ti4=Ocon/2
7690         GOTO Ox2
7700              !
7710 Oxlox:  Sumox=Tcon/(1+At2+2*At3)!                  Liquid oxide present
7720         IF Cflag AND Ticflag THEN Sumox=Ocon/(1+2*At2+4*At3+At4)
7730              !                                     For this case use O rather than Ti balance
7740         GOSUB Act
7750         Met=At0*Sumox
7760         Ti1=At1*Sumox
7770         Ti2=At2*Sumox
7780         Ti3=At3*Sumox
7790         Ti4=At4*Sumox
7800         Lox=Met+Ti1+Ti2+Ti3+Ti4!                   Moles of liquid oxide
7810              !
7820 Ox2:    N(22)=Met*(T(1933)
7830         N(21)=Met-N(22)
7840         N(36)=Ti1*(T(2823)
7850         N(35)=Ti1-N(36)
7860         N(38)=Ti2*(T(2112)
7870         N(37)=Ti2-N(38)
7880         N(40)=Ti3*(T(2647)
7890         N(39)=Ti3-N(40)
7900         N(42)=Ti4*(T(2143)
7910         N(41)=Ti4-N(42)
7920         RETURN !
```

```
7930 ! ##########################################################################
7940 ! ############     Energy: Computes Delta U     ############################
7950 ! ##########################################################################
7960 Energy:Du=-U0
7970        FOR I=1 TO 44
7980          U(I)=Bu(I,1)+Bu(I,2)*T+Bu(I,3)*T*T+Bu(I,5)/T+Bu(I,4)*LOG(T)
7990          !                                          Molar internal energy of each species
8000          Du=Du+U(I)*N(I)!                           Sums total internal energy
8010          NEXT I
8020          IF Du<=0 THEN RETURN
8030          IF Flag0 AND (T=1933) THEN En0
8040          IF Ticflag AND (T=3298) THEN Entic
8050          IF Flag1 AND (T=2023) THEN En1
8060          IF Flag2 AND (T=2112) THEN En2
8070          IF Flag3 AND (T=2047) THEN En3
8080          IF Flag4 AND (T=2143) THEN En4
8090          IF Tinflag AND (T=3220) THEN Entin
8100          RETURN !                                   Return from "Tical" to main program
8110 !                                                   In the following, 2 phases of the substance are present.
8120 !                                                   Solid is given by dU divided by energy of fusion.
8130 Entic:   N(20)=Du/71145 !                           Solid TiC
8140          N(19)=MAX(0,Tic-N(20)) !                   Liquid TiC
8150          Du=Du*(N(19)=0)
8160          IF N(19) THEN RETURN
8170          N(20)=Tic
8180          GOTO Enbeep
8190 En0:     N(22)=Du/18623 !                           Solid Ti
8200          N(21)=MAX(0,Met-N(22)) !                   Liquid Ti
8210          Du=Du*(N(21)=0)
8220          IF N(21) THEN RETURN
8230          N(22)=Met
8240          GOTO Enbeep
8250 Entin:   N(44)=Du/66960 !                           Solid TiN
8260          N(43)=MAX(0,Tin-N(44)) !                   Liquid TiN
8270          Du=Du*(N(43)=0)
8280          IF N(43) THEN RETURN
8290          N(44)=Tin
8300          GOTO Enbeep
8310 En1:     N(36)=Du/54405 !                           Solid TiO
8320          N(35)=MAX(0,Ti1-N(36)) !                   Liquid TiO
8330          Du=Du*(N(35)=0)
8340          IF N(35) THEN RETURN
8350          N(36)=Ti1
8360          GOTO Enbeep
8370 En2      N(38)=Du/110484 !                          Solid Ti2O3
8380          N(37)=MAX(0,Ti2-N(38)) !                   Liquid Ti2O3
8390          Du=Du*(N(37)=0)
8400          IF N(37) THEN RETURN
8410          N(38)=Ti2
8420          GOTO Enbeep
8430 En3:     N(40)=Du/138105 !                          Solid Ti3O5
8440          N(39)=MAX(0,Ti3-N(40)) !Liquid Ti3O5
8450          Du=Du*(N(39)=0)
8460          IF N(39) THEN RETURN
8470          N(40)=Ti3
8480          GOTO Enbeep
8490 En4:     N(42)=Du/85960 !                           Solid TiO2
8500          N(41)=MAX(0,Ti4-N(42)) !                   Liquid TiO2
8510          Du=Du*(N(41)=0)
8520          IF N(41) THEN RETURN
8530          N(42)=Ti4
8540                !
8550 Enbeep:  BEEP
8560          DISP "Select a lower temperature"
8570          RETURN !
```

```
8580 ! ##########################################################################
8590 ! ##################    Diagnostics    ###################################
8600 ! ##########################################################################
8610 Alert2:   !                                          Improper oxides present
8620       PRINT "Error in OXIDES"
8630       GOSUB Sum
8640       STOP
8650       GOTO Temp
8660       !
8670       !
8680 Sum:       PRINTER IS 7,1!                           If activated by K1, prints after each iteration
8690        GOSUB Spec
8700        GOSUB Prtflg
8710       PRINT LIN(1),"T = ",T,LIN(1)
8720             I=1
8730          PRINT USING Imsum;Fo$(I),N(I),Fo$(I+1),N(I+1),Fo$(I+2),N(I+2),Fo$(I+3),N(I+3)
8740            I=6
8750          PRINT USING Imsum;Fo$(I),N(I),Fo$(I+1),N(I+1),Fo$(I+2),N(I+2),Fo$(I+3),N(I+3)
8760          I=10
8770          PRINT USING Imsum;Fo$(I),N(I),Fo$(I+1),N(I+1),Fo$(I+2),N(I+2),Fo$(I+3),N(I+3)
8780          I=15
8790          PRINT USING Imsum;Fo$(I),N(I),Fo$(I+1),N(I+1),Fo$(I+2),N(I+2),Fo$(I+3),N(I+3)
8800          I=24
8810          PRINT USING Imsum;Fo$(I),N(I),Fo$(I+1),N(I+1),Fo$(I+2),N(I+2),Fo$(I+3),N(I+3)
8820          I=29
8830          PRINT USING Imsum;Fo$(I),N(I),Fo$(I+1),N(I+1),Fo$(I+2),N(I+2),Fo$(I+3),N(I+3)
8840          I=33
8850          PRINT USING Imsum;Fo$(I),N(I),Fo$(I+1),N(I+1)
8860          PRINT USING Imsum;"TiC",Tic,"Met",Met,"TiO",Ti1,"Ti203",Ti2
8870          PRINT USING Imsum;"Ti305",Ti3,"TiO2",Ti4,"TiN",Tin,"Gr",Gr
8880 Imsum:       IMAGE 3(8A,MZ.DDDE,3X)
8890 Sum1:        Sum=FNSti+Tin+Tic+Met+FNTsum!             Appears in final output
8900       PRINT LIN(1),"Ti BALANCE ",Mti,Sum
8910       Sum=FNSo+Ti1+3*Ti2+5*Ti3+2*Ti4
8920       PRINT "O BALANCE ",Noo,Sum
8930       Sum=Tin+2*N2+No+Hcn+Hnco+Cn+C2n+Cnn
8940       PRINT "N BALANCE ",Mn,Sum
8950       Sum=Nc+Ncc+Co+Co2+Tic+Gr
8960       PRINT "C balance",Mc,Sum
8970       Sum=Mh*Y+2*Dh*Y*Y
8980       PRINT "H balance",Mh,Sum
8990       PRINT USING "K,K";"Acc= ",Acc
9000       PRINT USING "K,K,//";"Atsum = ",Atsum
9010       PRINT LIN(2);TAB(20);"Test for equilibrium",LIN(1)
9020       PRINT SPA(1),"K";TAB(10);"Numeric";TAB(30);
9030       PRINT "Functional((=Numeric)",LIN(1)
9040       FLOAT 7
9050       IF NOT Loxflag AND NOT Lflag THEN At0=At1=At2=At3=A*4=1
9060       PRINT "Ti(g)";TAB(10),At0/Kt1;TAB(30),Ti
9070       PRINT "TiO";TAB(10),At1/K1;TAB(30),Ti*X
9080       PRINT "Ti2O3",TAB(10),SQR(At2)/K2;TAB(30),Ti*X*SQR(X)
9090       PRINT "Ti3O5";TAB(10),SQR(At3)/K3;TAB(30),Ti*X*X*SQR(Ti*X)
9100       PRINT "TiO2";TAB(10),At4/K4;TAB(30),Ti*O2
9110       PRINT "TiN";TAB(10),1/Ktin;TAB(30),Ti*Z
9120       PRINT "TiC";TAB(10),1/Ktic;TAB(30),Ti*Acc
9130       IF Loxflag OR Lflag THEN PRINT LIN(1)
9140       IF Loxflag OR Lflag THEN PRINT USING Imsum;"a(Met)",At0,"a(TiO)",At1,"a(Ti2O3)",At2
9150       IF Loxflag OR Lflag THEN PRINT USING Imsum;"a(Ti3O5)",At3,"a(TiO2)",At4
9160       !                                              Activities in liquid oxide
9170       STANDARD
9180       PRINTER IS 7,1
9190       RETURN !
```

```
9200 ! ##########################################################################
9210 ! ################  Species, codes, and flags  ##############################
9220 ! ##########################################################################
9230 !                              CODE     FLAG       FORMATION CONST
9240 !
9250 ! 1  Ti                       Ti
9260 ! 2  TiO
9270 ! 3  TiO2
9280 ! 4  Ti+
9290 ! 5        (not used)
9300 ! 6  Ar
9310 ! 7  CO
9320 ! 8  CO2
9330 ! 9  H
9340 ! 10  OH
9350 ! 11  H2
9360 ! 12  H2O
9370 ! 13      (not used)
9380 ! 14      (not used)
9390 ! 15  NO
9400 ! 16  N2
9410 ! 17  O
9420 ! 18  O2
9430 ! 19  TiC(l)                   Tic      Ticflag        Ktic
9440 ! 20  TiC(s)                   Tic      Ticflag        Ktic
9450 ! 21  Ti(l)                    Met      Flag0          Kti
9460 ! 22  Ti(s)                    Met      Flag0          Kti
9470 ! 23  C(s)                     Gr       Cflag
9480 ! 24  CN-
9490 ! 25  CN
9500 ! 26  C2H
9510 ! 27  C2N
9520 ! 28      (not used)
9530 ! 29  HCN
9540 ! 30  HNCO
9550 ! 31  HCO
9560 ! 32  CH2O
9570 ! 33  C2H2
9580 ! 34  C3
9590 ! 35  TiO(l)                   Ti1      Flag1          K1
9600 ! 36  TiO(s)                   Ti1      Flag1          K1
9610 ! 37  Ti2O3(l)                 Ti2      Flag2          K2=SQR(Kn)
9620 ! 38  Ti2O3(s)                 Ti2      Flag2          K2=SQR(Kn)
9630 ! 39  Ti3O5(l)                 Ti3      Flag3          K3=SQR(Kn)
9640 ! 40  Ti3O5(s)                 Ti3      Flag3          K3=SQR(KN)
9650 ! 41  TiO2(l)                  Ti4      Flag4          K4
9660 ! 42  TiO2(s)                  Ti4      Flag4          K4
9670 ! 43  TiN(l)                   Tin      Tinflag        Ktin
9680 ! 44  TiN(s)                   Tin      Tinflag        Ktin
9690 !
9700 !
9710 !      Loxflag or Lflag indicates presence of continuous liquid phase
9720 !      At0, At1, At2, At3, At4 for activity (ideal solution)
9730 !      of Met, TiO, Ti2O3, Ti3O5, TiO2
9740 !      Acc = activity of carbon
9750 !      X = SQR(O2)
9760 !      Y = SQR(H2)
9770 !      Z = SQR(N2)
9780 !
9790 !   Variables used in Newton's method calculation:
9800 !           No metal or oxide          X,Ti
9810 !           One oxide only/metal only  Y (Ti if TiN + 1 solid oxide, no metal)
9820 !           Two oxides/Metal + 1 oxide -
9830 !      In all cases, Z and Acc are the last two variables when appropriate
9840 END
```

```
KEY 0
   Check=(Check+8)
  -Execute

KEY 1
   TRACE VARIABLES Yn(8)
  -Execute

KEY 2
   CONT Ex
  -Execute

KEY15
  -Clear line
   SCRATCH

KEY 4
   CONT Temp
  -Execute

KEY 5
   A$="Y"
  -Execute

KEY 6
    TRACE PAUSE 5
  -Execute

KEY 7
    7,5,3,6
  -Continue

KEY 8
    Dlt=.48(Dlt=.1)+.1
  -Execute

KEY 9
  -Clear line
   LOAD

KEY10
  -Clear line
   SAVE

KEY11
  -Clear line
   STORE

KEY12
  -Clear line
   EDIT

KEY13
  -Clear line
   EDIT LINE

KEY14
  -Clear line
   LIST

KEY15
  -Clear line
   SCRATCH

KEY23
    -11750
  -Continue
```

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