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CALCULATION OF ROCKET PERFORMANCE PARAMETERS BASED ON THE EQUILIBRIUM COMPOSITION OF THE COMBUSTION PRODUCTS

by KLAUS W. GROSS
Propulsion and Vehicle Engineering Laboratory

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ABSTRACT

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The theory is developed and essential equations are derived for calculating frozen and shifting equilibrium compositions of the combustion products of a rocket engine. The equilibrium composition of the combustion products is used as a basis for rocket performance calculations. The physical equations of a computer program and pertinent flow charts are also presented to enable individual programming.

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Klaus W. Gross

PROPULSION AND VEHICLE ENGINEERING LABORATORY
RESEARCH AND DEVELOPMENT OPERATIONS

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DEFINITION OF SYMBOLS

Symbol	Definition	Units
A	Multiple of mass considered,	(-)
	Area	in^2
C	Specific heat	$\frac{cal}{mole^0K}$
E	Energy	$\frac{cal}{g}$
F	Any function	(-)
G	Gibb's function	cal
H	Enthalpy	cal
I	Impulse	sec
K	Equilibrium constant	(-)
L	Atomic weight	(-)
M	Molecular weight	$\frac{g}{mole}$
Ma	Mach number	(-)
N	Multiple of mole numbers (A · n = N	mole
P	Pressure	atm
Q	Heat energy	cal
R	Specific gas constant	$\frac{cal}{g^0K}$
$\overline{R}$	Universal gas constant, 1.98726	$\frac{cal}{mole^0K}$
S	Entropy	$\frac{cal}{^0K}$

DEFINITION OF SYMBOLS (Cont'd)

Symbol	Definition	Units
T	Temperature	^{0}K
U	Internal energy	cal
V	Volume	ft^3
W	Work energy	cal
X	Element	(-)
Y	Element	(-)
Z	Element	(-)
a	Number of gram atoms of element Z	$\frac{g}{mole}$
b	Number of gram atoms of element Y	$\frac{g}{mole}$
c	Number of gram atoms of element X	$\frac{g}{mole}$
	Concentration	$\frac{mole}{ft^3}$
	Specific heat per unit mass	$\frac{cal}{g^{0}K}$
d	Differential	(-)
e	Euler number, 2.7182818	(-)
g	Gibb's function per unit mass	$\frac{cal}{g}$
g_o	Gravitational constant, 32.1740	$\frac{ft}{sec^2}$
h	Enthalpy per unit mass	$\frac{cal}{g}$

DEFINITION OF SYMBOLS (Cont'd)

Symbol	Definition	Units
m	Mass, slope of a curve	g
n	Mole number	mole
q	Heat energy per unit mass	$\frac{cal}{g}$
s	Entropy per unit mass	$\frac{cal}{g^{0}K}$
u	Internal energy per unit mass	$\frac{cal}{g}$
v	Specific volume	$\frac{ft^3}{lb}$
w	Flow velocity	$\frac{ft}{sec}$
x	Variable	(-)
y	Variable	(-)
z	Geodetic height	ft
	Variable	(-)
α	Angle	o
γ	Specific heat ratio	(-)
δ	Difference	(-)
Δ	Difference	(-)
∂	Partial differential	(-)
ϵ	Expansion ratio	(-)
ζ	Number of oxidizer atoms	(-)

DIFINITION OF SYMBOLS (Cont'd)

Symbol	Definition	Units
μ	Mixture ratio	(-)
ν	Valence	(-)
ξ	Number of fuel atoms	(-)
ρ	Density	$\frac{\text{lb sec}^2}{\text{ft}^4}$
ϕ	Stochiometric mixture ratio	(-)

SUBSCRIPTS

a	Number of gram atoms of element Z	$\frac{\text{g}}{\text{mole}}$
b	Number of gram atoms of element Y	$\frac{\text{g}}{\text{mole}}$
c	Number of gram atoms of element X	$\frac{\text{g}}{\text{mole}}$
ch	Chamber	(-)
Des	Desired	(-)
equ	Equilibrium	(-)
F	Fuel	(-)
f	Formation	(-)
g	Gas	(-)
i	Pertaining to the i^{th} element or compound	(-)
K	Kinetic	(-)
ℓ	Liquid	(-)

DEFINITION OF SYMBOLS (Cont'd)

Symbol	Definition	Units
max	Maximum	(-)
O	Oxidizer	(-)
P	Potential, at constant pressure	(-)
ref	Reference	(-)
s	At constant entropy, sound	(-)
sp	Specific	(-)
st	Stagnation	(-)
stat	Static	(-)
T	At temperature T	(-)
t	Throat	(-)
tot	Total	(-)
v	At constant volume	(-)
vap	Vapor, vaporizing process	(-)
X	Element	(-)
Y	Element	(-)
Z	Element	(-)
o	Correct solution	(-)
∞	Any location in the flow	(-)

DEFINITION OF SYMBOLS (Cont'd)

SUPERSCRIPTS

Symbol	Definition	Units
o	At reference level of one atmosphere	(-)
-	Molar quantity	(-)
·, ··	Derivatives	(-)

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CALCULATION OF ROCKET PERFORMANCE PARAMETERS BASED ON THE EQUILIBRIUM COMPOSITION OF THE COMBUSTION PRODUCTS

By Klaus W. Gross

George C. Marshall Space Flight Center

SUMMARY

The theory and development of equations are presented for calculating the composition of combustion products for frozen and shifting equilibrium, and a combination of both, based on a chosen temperature limit. The equilibrium compositions of combustion products are used to calculate rocket performance parameters based on a one-dimensional flow model.

Furthermore, a technique is described for determining the maximum specific impulse for a constant chamber pressure. A procedure is also included for establishing the optimum chamber pressure and propellant mixture ratio for use when the thrust level of a specific rocket engine is uprated.

INTRODUCTION

Theoretical equations are developed for the solution of equilibrium compositions of combustion products obtained in liquid propellant rocket motors by minimizing the Gibbs function. Subsequently, the more important rocket performance parameters can be calculated, such as: characteristic velocity, specific impulse, thrust coefficient, temperature, expansion ratio, thrust, flow rate, stochiometric mixture ratio, molecular weight of the combustion products, isentropic exponent, local velocity, local speed of sound, specific heats at constant pressure and volume, specific gas constant of the combustion products, and local static pressure. The indicated performance parameters can be determined for desired local static pressures and expansion ratios.

A maximum specific impulse calculation routine for constant chamber pressure is presented as well as an optimum chamber pressure and mixture ratio calculation to obtain a desired thrust level. The thermodynamic properties, entropy, enthalpy and specific heat at a pressure of one atmosphere are determined from polynomials for a temperature range from $298.15^{0}K$ to $5000^{0}K$.

The calculation procedure is limited as to number of elements taking part in the combustion and formed combustion compounds. However, space is provided to include or exchange additional elements and compounds. The basic program uses only a portion of available computer storage space. This allows the combination of this procedure with other programs. Many programs have been written that solve for equilibrium compositions automatically. This program uses mainly the approach of Gordan et al. (Ref. 1). However, changes have been made, and additional computation procedures are provided.

Grateful acknowledgement is given Mr. Richard Lewis of General Electric Company assigned to MSFC Computation Laboratory. Without his proficiency in mathematics and machine techniques this effort might well have been far less productive.

CONSERVATION OF ENERGY

Energy exists in various forms, e.g., kinetic energy, potential energy, electrical energy, chemical energy, heat energy, etc. Experience has shown that in a closed system the sum of all energies does not change with time. An addition of heat energy (ΔQ) to a system can cause change in all existing energies.

$$\Delta Q = \Delta U + \Delta W + \Delta E_P + \Delta E_K + \Sigma \Delta E \qquad (1)$$

The energy differences between state 1 and 2 per unit mass can be expressed as follows:

1. Internal energy $\frac{\Delta U}{m} = u_2 - u_1$
2. Work energy $\frac{\Delta W}{m} = P_2 v_2 - P_1 v_1$

   P is the pressure and v the specific volume
3. Potential energy $\frac{\Delta E_P}{m} = z_2 - z_1$

   z is the geodetic height
4. Kinetic energy $\frac{\Delta E_K}{m} = \frac{w_2{}^2 - w_1{}^2}{2g_0}$

   w is the flow velocity and g_o is the gravitational constant.

Neglecting the other forms of energy, the first law of thermodynamics reads

$$q_2 - q_1 = u_2 - u_1 + \frac{w_2{}^2 - w_1{}^2}{2g_0} + z_2 - z_1 + P_2 v_2 - P_1 v_1 \qquad (2)$$

CONSTANT ENTHALPY PROCESS

The enthalpy per unit mass(h) is defined as the sum of the internal energy per unit mass (u), plus the product P · v, the work energy required to transport the masses. This amount of work, however, no longer exists in the considered mass, but has been transferred to the surroundings.

With $$h = u + Pv \tag{3}$$

$$q_2 - q_1 = h_2 - h_1 + \frac{w_2^2 - w_1^2}{2g_0} + z_2 - z_1 \tag{4}$$

The combustion process in a rocket combustion chamber can be assumed to be adiabatic, which means no heat will be added or taken out of the system and $q_1 - q_2 = 0$. The injection velocity of the propellants and also the velocities of the formed combustion products in the combustion chamber are relatively small and can be neglected. Therefore,

$$\frac{w_2^2 - w_1^2}{2g_0} = 0$$

Futhermore, the potential energy difference can be neglected. For a comubstion chamber with a flow in the vertical direction, the difference in height between the inlet and outlet cross sectional areas is small, and for a horizontal chamber the height differences between the centers of geometry of the two areas is zero. Therefore,

$$z_2 - z_1 = 0$$

This leaves only the two enthalpy terms before and after the combustion, and they are equal,

$$h_1 = h_2 \tag{5}$$

$$u_1 + P_1 v_1 = u_2 + P_2 v_2$$

ENTROPY

The entropy change of an ideal gas can be developed from the second law of thermodynamics,

$$T\,ds = dh - v\,dP \qquad (6)$$

The enthalpy change (dh) can also be expressed by

$$dh = c_p\,dT$$

Applying the ideal gas equation

$$Pv = RT \qquad (7)$$

we obtain

$$ds = c_P \frac{dT}{T} - R\frac{dP}{P} \qquad (8)$$

Considering an isothermal process with dT = 0 and integrating the equation yields

$$s_2 - s_1 = -R(\ln P_2 - \ln P_1) \qquad (9)$$

The third law of thermodynamics states: The entropy of matter is equal to zero for 0^oK. Therefore, the entropy represents absolute values when this point is used as a reference level. Furthermore, if a pressure reference of one atmosphere is selected, we obtain

$$s_2 - s_1 = R \ln P_2$$

Entropy of a gas per unit mass can now be calculated for a certain temperature and pressure

$$s_T = s_T{}^0 - R \ln P \qquad (10)$$

The Gibbs - Dalton law indicates that the entropy of a nonreactive mixture of ideal gases is equal to the sum of the entropy values of the individual constituents, considering their quantities present. Since most thermodynamic tables list the molar entropy of a species, the total entropy of a mixture can be calculated when the individual mole numbers of the compounds are known:

$$s = \sum_i n_i (s_T)_i \qquad (11)$$

CONSTANT ENTROPY PROCESS

The expansion of the combustion products through a De Laval nozzle occurs very rapidly and almost without friction losses or heat exchange with the surroundings. This is nearly equivalent to a reversible adiabatic process. Therefore, the total entropy of the gas mixture will hardly change during the expansion process, and the assumption of a constant entropy process is justified.

$$s = s_{ch} \qquad (12)$$

Knowing the static pressure at a specific location downstream, the properties of the fluid can be determined if the chamber properties are known.

MAXIMUM WORK AND EQUILIBRIUM

Work can be obtained from a system as long as the pressure and temperature are not in equilibrium with the surroundings (potential, kinetic and other energy forms shall be neglected). Considering the system and the surroundings as a unit that cannot receive or lose heat energy, the whole work energy is supplied by the difference between internal energy before (U') and after (U'') the change of state. The internal energies of the unit before and after the process are composed of the internal energies of the system and the surrounding,

$$U' = U_1 + U_{01}$$

$$U'' = U_2 + U_{02}$$

where the subscript zero (o) indicates the surrounding.

Considering that the pressure and temperature of the surrounding do not vary, then the surroundings change from the initial to the final state by a constant pressure and constant temperature process. At the same time, however, the volume of the system changes, and the work done on the surroundings at constant pressure amounts to

$$P_0(V_1 - V_2)$$

Furthermore heat energy ($Q_o = T_o \Delta S_o$) is transferred to the surrounding without changing its temperature T_o. The change of internal energy in the surrounding amounts to

$$U_{02} - U_{01} = T_0 \Delta S_0 + P_0(V_2 - V_1)$$

where $\Delta S_0 = S_{0_2} - S_{0_1}$ indicates the entropy change of the surrounding. The total entropy change equals

$$\Delta S_0 + S_2 - S_1 \geq 0$$

The work that can be obtained from this unit is

$$W \leq U_1 + U_{01} - (U_2 + U_{02})$$

$$W \leq U_1 - U_2 + (U_{01} - U_{02})$$

$$W \leq U_1 - U_2 - T_0 \Delta S_0 + P_0(V_1 - V_2)$$

If the process is completely reversible, the maximum work will be obtained

$$W_{max} = U_1 - U_2 - T_0(S_1 - S_2) + P_0(V_1 - V_2) \tag{13}$$

Using the following definitions for enthalpy

$$H = U + PV \tag{14}$$

and the Gibbs function

$$G = H - TS \tag{15}$$

the work equation reduces to $W_{max} = H_1 - H_2 - T_0(S_1 - S_2)$

$$W_{max} = G_1 - G_2 \tag{16}$$

This equation states an important fact: During such a process, only the change of (G) can be converted into work energy while the amount $T_0 \; (S_1 - S_2)$ is carried away as heat.

When the state of a system approaches equilibrium, the maximum work gradually diminishes and is finally zero.

$$W_{max} = 0 = \Delta G \quad \text{(at equilibrium)}$$

For a closed system undergoing a chemical reaction, an equilibrium state is achieved when the summation of the Gibb's functions for all present compounds equals zero.

EQUILIBRIUM CONSTANT

The Gibbs function, or free energy function, is the basis for the equilibrium therory. The differentiated Gibbs function yields

$$dG = dH - S\,dT - T\,dS \tag{17}$$

or

$$dG = dU + P\,dV + V\,dP - S\,dT - T\,dS$$

In a reversible process, with only expansion work involved, the first law of thermodynamics yields

$$dQ = T\,dS = dU + P\,dV$$

Substituting dU in the prior equation gives

$$dG = V\,dP - S\,dT \tag{18}$$

For an isothermal process $dT = 0$ and the equation reduces to

$$dG = V\,dP$$

With the ideal gas law

$$PV = n\overline{R}T$$

we find

$$dG = \frac{n\overline{R}T}{P}\,dP$$

The integration between two states results in

$$G_2 - G_1 = n\overline{R}T \ln\frac{P_2}{P_1}$$

or on a mole basis

$$\overline{G}_2 - \overline{G}_1 = \overline{R}T \ln\frac{P_2}{P_1} \tag{19}$$

This equation can be interpreted as: The maximum work that can be obtained in a reversible constant temperature process, going from one state with a pressure P_1 to a second state with pressure P_2, is equal to the Gibbs function difference.

Assuming that the Gibbs function (G^o) at one atmosphere and all temperatures are known, the Gibbs function at any other pressure is

$$\overline{G} = \overline{G}^0 + \overline{R}T \ln P \qquad (20)$$

Formerly it was believed that the reactants in a thermochemical reaction were completely consumed to form the products. But developments in chemistry have shown that the reactants never disappear. After initiation of the reaction, the concentration of the reactants decreases while the concentration of the formed products increases correspondingly until equilibrium is reached. Guldberg and Waage stated a relationship between the concentrations and reaction rates: The rate of reaction is proportional to the active concentration of the constituents.

Consider the following chemical reaction

$$aA + bB \rightleftharpoons cC + dD$$

where A and B are the reactants, C and D the products, and a, b, c, d the corresponding mole numbers. After starting the reaction, more and more products will be formed from the continuously decreasing reactants. During this process the Gibbs function of each species will change

$$\overline{G} = \overline{G}^0 + \overline{R}T \ln P$$

until a condition is reached in which the same amount of products are formed from the reactants as reactants are formed from the products. This is the equilibrium condition. It was established earlier that no work can be produced from a system when it is in equilibrium with it's surroundings. In the above reaction, the surrounding of the reactants is all the products. Therefore, the difference between the Gibbs function of the products and the reactants must be zero at this condition.

$$\Delta G = 0 = c\overline{G}_C + d\overline{G}_D - (a\overline{G}_A + b\overline{G}_B)$$

Applying equation 20 yields

$$0 = c\overline{G}_C{}^0 + d\overline{G}_D{}^0 - (a\overline{G}_A{}^0 + b\overline{G}_B{}^0) + \overline{R}T(\ln P_C{}^c + \ln P_D{}^d - \ln P_A{}^a - \ln P_B{}^b)$$

Expressing

$$\Delta\overline{G}^0 = c\overline{G}_C{}^0 + d\overline{G}_D{}^0 - a\overline{G}_A{}^0 - b\overline{G}_B{}^0$$

results in (21)

$$0 = \Delta\overline{G}^0 + \overline{R}T\ln\frac{P_C{}^c P_D{}^d}{P_A{}^a P_B{}^b}$$

In this equation the following expression is called the equilibrium constant.

$$K_P = \frac{P_C{}^c P_D{}^d}{P_A{}^a P_B{}^b} \qquad (22)$$

Since the Gibbs function G is a function of temperature only, K_P is independent of pressure and dependent only on temperature. However, this does not necessarily mean that the concentrations of the reacting components remain the same when the pressure is increased. Since the chosen standard condition for the pressure was one atmosphere, the equilibrium constant K_P is dependent on the units for pressure. The subscript P has been chosen to indicate this.

Pressure has an influence on the chemical equilibrium only when a reaction occurs with a change in mole numbers or when the gases at high pressures cannot be considered ideal. Le Chatelier and Braun discovered the principle: If a factor influencing the equilibrium changes, an effect is produced that tends to reduce the action caused by the change.

CONDENSED PHASES

A pure substance is defined as having an invariable chemical composition for all states of aggregation: solid, liquid and vapor. Single-phase or multiple-phase conditions are considered to be in an equilibrium state. A pure substance will have, in general, the following pressure-temperature and temperature-entropy diagrams (Ref. FIG. 1 and 2).

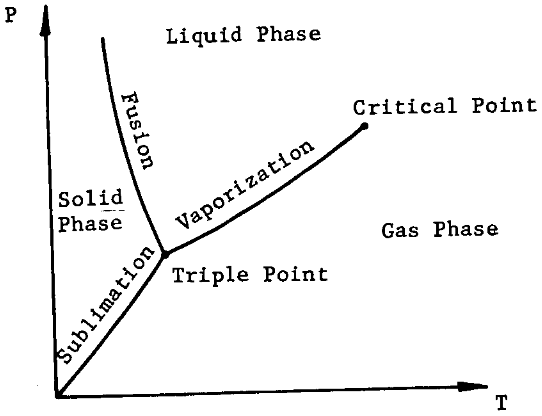

FIGURE 1. GENERAL PRESSURE-TEMPERATURE DIAGRAM FOR DIFFERENT STATES OF AGGREGATION

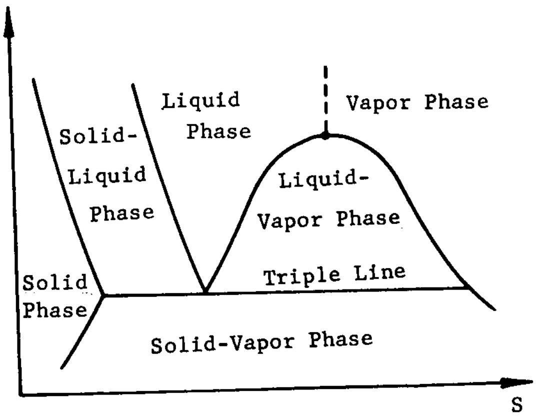

FIGURE 2. GENERAL TEMPERATURE-ENTROPY DIAGRAM FOR DIFFERENT STATES OF AGGREGATION

During a melting (fusion), sublimation and vaporization process, the corresponding two-phase conditions are in equilibrium: solid-liquid, solid-vapor, liquid-vapor. All three states of aggregation are possible only at the triple point.

In this report condensed and gaseous compounds are treated independently, and are expressed by the application of separate equilibrium equations. The vapor pressure is associated with the gaseous compound only and is zero for the condensed phase. Therefore, the vapor-condensed phase equilibrium is included in this procedure. Solid-liquid equilibrium states are treated in Reference 2.

A reversible isothermal constant pressure process converting liquid into vapor can be performed at the equilibrium pressure. The entropy change during the vaporization is

$$\Delta S_{vap} = \frac{\Delta H_{vap}}{T}$$

The change in the Gibbs function is zero because

$$\Delta G_{vap} = \Delta H_{vap} - T\,\Delta S_{vap} = 0$$

This can be generalized for any kind of transition between two phases of a pure substance, such as solid-vapor or solid-liquid. A pure substance is assumed to keep the same thermodynamic properties despite the presence of the same matter in another state of aggregation or another substance.

As shown in equation 18, the Gibbs function for a reversible isothermal process is

$$dG = V\,dP$$

Performing a vaporization process of a substance, the change in the Gibbs Function is

$$\Delta G_{vap} = \int \Delta V\, dP = \int_{P_{vap}}^{P_\ell} (V_{vap} - V_\ell) dP$$

The volume of a liquid can usually be neglected when compared with the volume of the vapor. If, furthermore, the vapor behaves like an ideal gas, the equation reduces to

$$\Delta G = \int V_{vap}\, dP = \int \frac{n\,\overline{R}T}{P}\, dP = n\,\overline{R}T\, \ln \frac{P_\ell}{P_{vap}}$$

For a unit mole, the equation reduces to

$$\Delta\overline{G} = \overline{R}T \ln \frac{P_\ell}{P_{vap}} \qquad (23)$$

In equilibrium, the Gibbs function equals zero. This is only possible when the pressure of the liquid is the same as the vapor pressure

$$P_\ell = P_{vap} = P_{equ}$$

Neglecting any effect of the applied pressure on the vapor, which is compatible with the assumption that V_ℓ is negligible, and treating the vapor like a pure substance, the vapor pressure remains a function of temperature only. The Gibbs function changes to

$$\Delta\overline{G}_{vap} = - \overline{R}T \ln P_{equ} \qquad (24)$$

Comparison with equation 23 shows that the equilibrium constant is equal to the vapor pressure. The pressure of the condensed phase has no effect on the equilibrium constant.

Example:

$$H_2O_{(\ell)} \rightleftharpoons H_2O_{(vap)} \qquad T = 298\ ^\circ K$$

$$\Delta\overline{G}_{vap} = -\ \overline{R}T \ln K_P = -\overline{R}T \ln P_{equ}$$

$$\ln K_P = -\frac{\Delta\overline{G}}{\overline{R}T} = -\ \frac{\Delta\overline{H} - T\Delta\overline{S}}{\overline{R}T} = -\ \frac{\Delta\overline{H}}{\overline{R}T} + \frac{\Delta\overline{S}}{\overline{R}}$$

$$= \left(\frac{n_{vap}\overline{H}_{vap} - n_\ell\,\overline{H}_\ell}{\overline{R}T}\right)_{H_2O} - \left(\frac{n_{vap}\overline{S}_{vap} - n_\ell\,\overline{S}_\ell}{\overline{R}}\right)_{H_2O}$$

$\Delta\overline{H}$ = 10520 cal mole, is the latent heat

$\Delta\overline{S}$ = 28.393 cal mole $^\circ$K

$$\overline{R} = 1.987\ \frac{\text{cal}}{\text{mole}\ ^\circ\text{K}}$$

$$\ln K_P = -\ \frac{10520}{1.987 \times 298} + \frac{28.393}{1.987}$$

$$K_P = 0.03125 \text{ atm}$$

This result is equal to the vapor pressure at T = 298°K.

SPECIFIC HEAT AT CONSTANT PRESSURE

The specific heat at constant pressure is defined as the amount of heat added to a specified amount of matter to increase the temperature by one degree while the pressure is kept constant.

$$C_P = \frac{\Delta Q}{\Delta T}$$

Expressing ΔQ by the first law of thermodyamics

$$\Delta Q = \Delta U + P\Delta V$$

yields

$$C_P = \frac{\Delta U + P\Delta V}{\Delta T}$$

Applying the definition of enthalpy

$$\Delta H = \Delta U + P\Delta V$$

we obtain

$$C_P = \frac{\Delta H}{\Delta T} \qquad (25)$$

SPECIFIC GAS CONSTANT

The equation of state for an ideal gas is

$$Pv = RT$$

At constant temperature and pressure, one mole of two different gases may be described as

$$Pv_1 M_1 = M_1 R_1 T$$

$$Pv_2 M_2 = M_2 R_2 T$$

Avogadro's law states that the mole volumina ($v \cdot M$) of different gases are the same when the temperatures and pressures are equal.

$$v_1 M_1 = v_2 M_2 \tag{26}$$

or

$$M_1 R_1 = M_2 R_2 = MR = \overline{R} \tag{27}$$

$\overline{R}$ is called the universal gas constant.

For a mixture of ideal gases enclosed in a volume (V), the total pressure is equal to the summation of the partial pressures of all constituents when the temperature is homogeneous.

$$P_{tot} = \sum_i P_i \tag{28}$$

Replacing the pressures by the corresponding term of the general gas equation, the specific gas constant of the mixture can be calculated.

$$\frac{M_{tot} R_{tot} T}{V} = \sum_i \frac{M_i R_i T}{V}$$

$$R_{tot} = \frac{\sum_i M_i R_i}{M_{tot}} \tag{29}$$

Since the mass is equal to the product of the mole number and the molecular weight,

$$m = nM \tag{30}$$

the specific gas constant can also be determined without knowing the specific gas constant of each constituent.

$$R_{tot} = \frac{\sum_i n_i M_i R_i}{m_{tot}}$$

$$\overline{R} = M_i R_i \tag{31}$$

$$R_{tot} = \overline{R}\frac{\sum_i n_i}{m_{tot}} = \overline{R}\frac{\sum_i n_i}{\Sigma n_i M_i}$$

If a condensed phase is existent, its share is only considered in the total mass, not in the total mole number, because we neglected the volume as previously indicated.

DALTON'S LAW

Dalton's law states that the total pressure of a gas mixture is composed of the partial pressure of the individual components.

$$P_{tot} = \sum_i P_i$$

Hereby, a gaseous constituent fills the whole volume and behaves as if the other gases were not present. When the temperature of all the gases is the same,

$$P_1 V = m_1 R_1 T$$

$$P_2 V = m_2 R_2 T$$

or

$$\frac{P_1}{P_2} = \frac{m_1 R_1}{m_2 R_2}$$

Since the mass equals the mole number times the molecular weight, we obtain

$$m = nM$$

$$\frac{P_1}{P_2} = \frac{n_1 M_1 R_1}{n_2 M_2 R_2}$$

Using the relationship between the specific gas constant and the universal gas constant

$$\overline{R} = MR$$

$$\frac{P_1}{P_2} = \frac{n_1}{n_2}$$

or

$$\frac{P}{P_{tot}} = \frac{n}{n_{tot}}$$

The pressures can also be expressed by the general gas equation

$$P = \frac{n\overline{R}T}{V}$$

Defining the concentration to be

$$c = \frac{n}{V}$$

we obtain

$$P = c\overline{R}T \tag{32}$$

This relationship can be used to express the equilibrium constants by concentrations or mole numbers.

HEAT OF FORMATION

When a compound is formed from reactants, the heat liberated or induced is called heat of formation and represents an enthalpy change during the reaction.

Mostly, thermodynamic processes occur in fixed nonreactive gas mixtures. In this case, use can be made of the existing thermodynamic property tables for the given substances, since only changes in state of these substances must be considered. The enthalpy tables are based on a reference level that is arbitrary since only enthalpy changes are significant.

When a chemical reaction takes place, this concept is not adequate. Compounds may change or new ones may be formed from the reactants. When an energy balance is made between the reactants and reaction products, a common reference level has to be established. Since reactants and reaction products are composed of the same elements, the enthalpy reference level for the elements is arbitrarily chosen to be zero at standard conditions (1 atm pressure and 298.15°K). The enthalpy of formation determines the enthalpy level of a specific compound at standard conditions with respect to the chosen reference level. If the heat of formations are summed for the reactants and products separately, their difference indicates how much energy is liberated or has to be induced during a chemical reaction.

In case of a combustion reaction, the energy difference is available to heat the combustion products from standard conditions to a higher temperature.

STOCHIOMETRY

By definition a stochiometric mixture ratio corresponds to complete combustion, the formation of saturated molecules in the combustion product. A method to solve this problem is based on the principles of oxidation and reduction.

Definitions:

Oxidation occurs when electrons are lost.

Reduction occurs when electrons are gained.

The loss of electrons is represented by a postive valence; the gain of electrons is represented by a negative valence. The valence, therefore, determines the degree of combining power of an element or a radical.

General rules (Ref. 7 and 8)

1. Free elements have no valences.
2. Hydrogen in combination always has a positive valence.
3. Oxygen in combination has two negative valences.
4. The sum of the valences in any compound equals zero.

In an oxidation-reduction reaction, the total increase of positive valences equals the total increase in negative valences.

Example: Formation of water

$$H_2 + \frac{1}{2} O_2 \rightarrow H_2 O$$

including the valences

$$H_2{}^0 + \frac{1}{2} O_2{}^0 \rightarrow H_2{}^{+2} O^{-2}$$

In this reaction, all compounds have a total valence of zero; however, in H_2O, the valence of hydrogen is (+2) and the valence for oxygen is (-2). Hydrogen, therefore, has encountered a loss of electrons (oxidation), and oxygen, an increase of electrons (reduction).

The atoms of the various elements differ in their combining capacities and, therefore, have different valences. To determine the stochiometric mixture ratio for a combustion process from the reactants, it is assumed that in all formed compounds, the elements possess a valence that is the most common.

element	valence
C	+4
F	-1
H	+1
HE	0
N	0
O	-2

If a reaction takes place between oxygen and hydrogen and the products formed possess the most common valences of these two elements, we can transfer the valences to the reactants, because all products are composed of the reactants.

$$H_{\xi_F}^{\nu_F} + C_{\zeta_\theta}^{\nu_\theta} \rightarrow \text{Products}$$

ν = valence

ξ = atomic number of an element in the fuel

ζ = atomic number of an element in the oxidizer

M= molecular weight

In one gram of hydrogen there are $\nu_F \frac{\xi_F}{M_F}$ valences.

In one gram of oxygen there are $\nu_\theta \frac{\zeta_\theta}{M_\theta}$ valences.

Since the valences of oxidizer and fuel in a stochiometric combustion must be equal, we can form a ratio of the two values, including a proportionality factor, so that this ratio equals one.

$$1 = \frac{\nu_\theta \zeta_\theta M_F}{-(\nu_F \xi_F M_\theta)} \cdot \phi_s$$

The minus sign makes the ratio independent of the sign.

Solving for the stochimetric mixture ratio (ϕs), we obtain

$$\phi_s = \frac{\nu_F \xi_F M_\theta}{\cdot\, \nu_\theta \zeta_\theta M_F}$$

When each reactant is composed of more elements, as in C_2H_2, the equation must read:

$$\phi_s = - \frac{(\sum_i \nu_i \xi_i)_F M_\theta}{(\sum_j \nu_j \zeta_j)_\theta M_F} \tag{33}$$

If one of the propellants is a mixture of two or more compounds, as $O_2 + F_2$, the summation of the parenthetical terms must consider the percentage quantities of each compound.

COMBUSTION AND EXPANSION PROCESS IN A ROCKET ENGINE

Most liquid propellant rocket engines use two propellants, a fuel and an oxidizer. Each propellant, is forced into the combustion chamber by a pump or by a high-pressure system. Nozzle walls consist of many small tubes brazed together, and are regeneratively cooled by one of the propellants, recovering most of the transferred heat energy and feeding it back into the combustion chamber. Another important device, the injector plate, consists of a series of small orifices that mix the fuel and oxidizer in the forward end of the combustion chamber. The quality of mixing influences the space occupied by the combustion reaction and, therefore, is important in determining combustion chamber length. Combustion stability is also affected by the quality of the mixture.

Cryogenic propellants usually are injected at the boiling point, unless one of the propellants is a mixture (for example with the oxidizer liquid fluorine - liquid oxygen, the injection temperature is the fluorine boiling point and the liquid oxygen is undercooled). Storable propellants are normally injected at ambient temperatures.

The isenthalpic reaction of the fuel and oxidizer liberates heat and produces combustion products that dissociate and recombine. When the mean composition of these products stabilizes (that is, the rates of recombination and dissociation are equal), a state of equilibrium is reached. The potential energy of the combustion products is isentropically converted into kinetic energy when expanded through the nozzle. A choked condition develops at the throat when the following equation is satisfied:

$$\frac{P_t}{P_{ch}} = \left(\frac{2}{\gamma + 1}\right)^{\frac{\gamma}{\gamma - 1}} \tag{34}$$

At this point, the velocity of the gas particles equals the local speed of sound. Since this velocity can only exist in the throat area, the mass flowrate can be calculated.

The combustion of the reactants does not occur instantaneously in a specified area in the combustion chamber but rather in some portion of the chamber. During this period, the quantity of gases formed progresses; this naturally requires an increase in velocity. The velocity increase calls for a drop in static pressure according to Bernoulli's equation for compressible flow (Ref. 9).

$$P_{st} - P_{\infty} = w_{\infty}^2 \frac{\rho_{\infty}}{2}\left(1 + \frac{Ma_{\infty}^2}{4}\right) \tag{35}$$

(The equation is only valid in the range of Ma = 0 to Ma = 0.9)

The continuing combustion, therefore, releases energy at constantly falling pressure levels. The total energy released during the reaction is a fixed value, but the availability of this energy varies. The combustion occurring in a finite length causes a pressure loss and an increase in entropy.

With rising temperatures, the reaction rates of dissociation and recombination increase. Therefore, at high temperatures a change of state of a system reaches equilibrium quickly; however, at low temperatures more time is needed to reach equilibrium.

During the expansion process, the combustion products change state continuously. When the reaction rates are so fast that a chemical and thermal equilibrium is maintained at any point, the condition is that of shifting equilibrium. If the reaction rates are slow, freezing almost any dissociation or recombination during the expansion process, the condition is frozen equilibrium.

THEORETICAL COMBUSTION AND EXPANSION MODEL

The following assumptions are made:

1. Propellants are injected at boiling conditions or at ambient temperature. Injection velocity is negligible.

2. Combustion occurs instantly in an isenthalpic process at combustion chamber end stagnation pressure and a predetermined mixture ratio.

3. The expansion process is isentropic and follows either frozen or shifting equilibrium conditions by minimizing the Gibbs function.

4. All gases behave according to the ideal gas law.

5. Condensed phases and the corresponding gas phase possess the vapor pressure.

6. The occupied volume of a condensed phase is negligible.

7. No heat transfer occurs through the nozzle wall.

8. Thermodynamic and performance parameters are uniform in a cross-sectional area of the nozzle.

9. The velocity of the gas and condensed products are the same and are parallel to the nozzle axis (one dimensional).

10. No boundary layer influence is considered.

11. The performance parameters are a function of expansion ratio, but are independent of nozzle wall contour.

12. There is no jet separation from the wall towards the nozzle exit.

DEVELOPMENT OF THE EQUATIONS USED IN THE COMBUSTION AND EXPANSION CALCULATION

In a combustion process at constant pressure, compounds formed from the reactants can be represented by the following equation

$$N_F (Z_{aF} Y_{bF} X_{cF} \dots) + N_\theta (Z_{a\theta} Y_{b0} X_{c0} \dots) = \tag{36}$$

$$\sum_{i=1}^{100} n_i (Z_{ai} Y_{bi} X_{ci} \dots) + \sum_{i=101}^{110} n_i (Z_{ai} Y_{bi} X_{ci} \dots) + \sum_{i=111}^{115} n_i (Z_{ai} Y_{bi} X_{ci} \dots)$$

where

$\sum_{i=1}^{100} n_i (Z_{ai} Y_{bi} X_{ci} \dots)$ represent the gaseous compounds

$\sum_{i=101}^{110} n_i (Z_{ai} Y_{bi} X_{ci} \dots)$ represent the gaseous elements

$\sum_{i=111}^{115} n_i (Z_{ai} Y_{bi} X_{ci} \dots)$ represent the condensed products

All equations involve the mole numbers and the partial pressures. To simplify the problem, the chemical reaction equation is multiplied by a factor (A), which makes both the mole number and the partial pressure of each compound numerically equal.

$$A[N_F(Z_{aF}Y_{bF}X_{cF}\ldots) + N_0(Z_{a0}Y_{b0}X_{c0}\ldots)] \doteq \quad (37)$$

$$\sum_{i=1}^{100} N_i(Z_{ai}Y_{bi}X_{ci}\ldots) + \sum_{i=101}^{110} N_i(Z_{ai}Y_{bi}X_{ci}\ldots) + \sum_{i=111}^{115} N_i(Z_{ai}Y_{bi}X_{ci}\ldots)$$

$$A\,n_i = N_i$$

The equilibrium state can be determined by the following equations.

1. Chemical equilibrium equations

Consider that each reaction product is formed from gaseous atoms.

$$a_i Z + b_i Y + c_i X = Z_{ai}Y_{bi}X_{ci}$$

The equilibrium condition for these reactions follows from equation 21

$$\Delta\overline{G}_i = \Delta\overline{G}_i^0 + \overline{R}T(\ln P_i - a_i \ln P_Z - b_i \ln P_Y - c_i \ln P_X - \ldots) \quad (38)$$

ΔG_i must equal zero at equilibrium. For any other condition close to equilibrium, ΔG_i will be a small number δ_i so that

$$\delta_i = \left(\frac{\Delta\overline{G}^0}{\overline{R}T}\right)_i + \ln P_i - a_i \ln P_Z - b_i \ln P_Y - c_i \ln P_X - \ldots \quad (39)$$

For condensed products, the ln P_i terms are zero because they have no influence on the equilibrium constants.

$$\delta_i = \left(\frac{\Delta\overline{G}^0}{\overline{R}T}\right)_i - a_i \ln P_Z - b_i \ln P_Y - c_i \ln P_X - \ldots \quad (40)$$

2. Mass balance equations

The total mass does not change in a reaction; also, the masses of the individual elements stay the same.

$$a_{tot} = \frac{1}{A} \sum_{i=1}^{115} a_i N_i$$

$$b_{tot} = \frac{1}{A} \sum_{i=1}^{115} b_i N_i \qquad (41)$$

$$c_{tot} = \frac{1}{A} \sum_{i=1}^{115} c_i N_i$$

These masses must be equal to the masses of the elements in the reactants.

3. Pressure equation

In a constant pressure reaction, the total pressure remains the same. Due to Dalton's law, the summation of the partial pressures of all compounds in the reaction product must be equal to this pressure

$$P = \sum_{i=1}^{110} P_i \qquad (42)$$

4. Constant enthalpy equation.

As was mentioned in the section "Equilibrium Constant", the enthalpy of the reactants must equal the enthalpy of the combustion products. The enthalpy of reactants is equal to the heat of formation plus the heat energy required to go from the reference level to the injection conditions.

$$HO = \sum_F (\overline{H}_f + \int_{T_{ref}}^{T} \overline{C}_P{}^0\, dT)_F N_F + \sum_\theta (\overline{H}_f + \int_{T_{ref}}^{T} \overline{C}_P{}^0\, dT)_\theta N_\theta \qquad (43)$$

The enthalpy of the combustion products is equal to the sum of the individual enthalpies of the formed compounds.

$$H = \frac{1}{A} \sum_i (\overline{H}_T{}^0)_i N_i \qquad (44)$$

Note: The heat of formation is already included in the $\overline{H}_T{}^O$ terms.

5. Constant entropy equation.

The entropy of the combustion products is given by the following equation as developed in the section "Entropy".

For gaseous compounds

$$S_T = \frac{1}{A} \sum_i [(\overline{S}_T{}^0)_i - \overline{R} \ln P_i] N_i \qquad (45)$$

For condensed products

$$S_T = \frac{1}{A} \sum_i (\overline{S}_T{}^0)_i N_i \qquad (46)$$

To determine the equilibrium condition for the combustion process at constant pressure, the equilibrium, mass balance, pressure, and enthalpy equations must be solved simultaneously. During the expansion process, the same equations are considered to determine equilibrium conditions except the enthalpy equation is replaced by the entropy equation.

Both sets of simultaneous equations are non-linear. The Newton-Raphson method is applied to obtain a solution using a finite difference approximation to the total differential.

NEWTON-RAPHSON METHOD

Consider two nonlinear simultaneous equations in x and y in the following form

$$F_1 = F_1(x, y) = 0$$

$$F_2 = F_2(x, y) = 0$$

When $\bar{x}$ and $\bar{y}$ are the solutions there exists a difference for any other estimate of x_i and y_i so that

$$F_1(\bar{x}, \bar{y}) - F_1(x_i, y_i) = \Delta F_1 \neq 0$$

$$F_2(\bar{x}, \bar{y}) - F_2(x_i, y_i) = \Delta F_2 \neq 0$$

The definition of the difference is arbitrary (as far as signs are concerned), but when it is once established, the proper correction equations must be set up.

The total differentials of the given functions are

$$dF_1 = \frac{\partial F_1}{\partial x} dx + \frac{\partial F_1}{\partial y} dy$$

$$dF_2 = \frac{\partial F_2}{\partial x} dx + \frac{\partial F_2}{\partial y} dy$$

Going to finite differences, the equations change to

$$\Delta F_1 = \left(\frac{\partial F_1}{\partial x}\right) \Delta x + \left(\frac{\partial F_1}{\partial y}\right) \Delta y$$

$$\Delta F_2 = \left(\frac{\partial F_2}{\partial x}\right) \Delta x + \left(\frac{\partial F_2}{\partial x}\right) \Delta y \tag{47}$$

These equations are linear in Δx and Δy when numerically solved at the point x_i and y_i. Because of the transition from the total differential to the finite difference form, the equations are only approximate. Therefore, the correction variables are

$$x_{i+1} = x_i + \Delta x \tag{48}$$

$$y_{i+1} = y_i + \Delta y$$

x_{i+1} and y_{i+1} approaching $\overline{x}$ and $\overline{y}$.

Using the following mathematical concept

$$\frac{d \ln x}{dx} = \frac{1}{x}$$

or in finite difference form

$$\frac{\Delta \ln x}{\Delta x} \simeq \frac{1}{x}$$

$$\Delta x \simeq x \Delta \ln x \tag{49}$$

the total differentials can be rewritten.

$$\Delta F_1 = \left(\frac{\partial F_1}{\partial x}\right) x \Delta \ln x + \left(\frac{\partial F_1}{\partial y}\right) y \Delta \ln y \tag{50}$$

$$\Delta F_2 = \left(\frac{\partial F_2}{\partial x}\right) x \Delta \ln x + \left(\frac{\partial F_2}{\partial y}\right) y \Delta \ln y$$

According to these equations, the set of nonlinear simultaneous equations is transformed into a set of linear simultaneous equations. The corresponding correction equations are

$$\ln x_{i+1} = \ln x_i + \Delta \ln x \tag{51}$$

$$\ln y_{i+1} = \ln y_i + \Delta \ln y$$

This procedure is used to solve for the equilibrium condition in the combustion and expansion process.

RESULT OF EQUATIONS LINEARIZED BY THE NEWTON-RAPHSON METHOD

The final equations, as used in the equilibrium calculation solving for $N_i = P_i$, T, A, are presented below. A matrix can be constructed as shown on page 34 (FIG. 3). The equations are derived in Appendix B.

Equilibrium equation for gaseous compounds

$$\Delta F = \Delta \ln P_i - a_i \Delta \ln P_Z - b_i \Delta \ln P_Y - c_i \Delta \ln P_X - \ldots - \left(\frac{\Delta \bar{H}_T{}^0}{\bar{R}T}\right)_i \Delta \ln T \qquad (52)$$

Equilibrium equation for condensed phases

$$\Delta F = - a_i \Delta \ln P_Z - b_i \Delta \ln P_Y - c_i \Delta \ln P_X - \ldots - \left(\frac{\Delta \bar{H}_T{}^0}{\bar{R}T}\right)_i \Delta \ln T \qquad (53)$$

Mass balance equations

$$\Delta F_a = -\frac{1}{A}\sum_{i=1}^{115} a_i N_i \Delta \ln A + \frac{1}{A}\sum_{i=1}^{115} a_i N_i \Delta \ln N_i \qquad (54)$$

Total pressure equation

$$\Delta F_P = \sum_{i=1}^{110} P_i \Delta \ln P_i \qquad (55)$$

Enthalpy equation

$$\begin{aligned}\Delta F_H = &- \frac{1}{A}\sum_{i=1}^{115} (\overline{H}_T{}^0)_i N_i \Delta\ln A + \frac{1}{A}\sum_{i=1}^{115} (\overline{H}_T{}^0)_i N_i \Delta\ln N_i \\ &+ T \sum_{i=1}^{115} (\overline{C}_P{}^0)_i N_i \Delta\ln T\end{aligned} \tag{56}$$

Entropy equation

a) for gaseous products

$$\begin{aligned}\Delta F_S = &- \frac{1}{A}\sum_{i=1}^{110} [(\overline{S}_T{}^0)_i - \overline{R}\ln P_i] N_i \Delta\ln A \\ &+ \frac{1}{A}\left[\sum_{i=1}^{110} (\overline{S}_T{}^0)_i N_i \Delta\ln N_i - \sum_{i=1}^{110} \overline{R} N_i \ln P_i \Delta\ln N_i\right. \\ &\left. - \sum_{i=1}^{110} \overline{R} N_i \Delta\ln P_i\right] + \frac{1}{A}\sum_{i=1}^{110} (\overline{C}_P{}^0)_i N_i \Delta\ln T\end{aligned} \tag{57}$$

b) for condensed phases

$$\begin{aligned}\Delta F_S = &- \frac{1}{A}\sum_{i=111}^{115} (\overline{S}_T{}^0)_i N_i \Delta\ln A + \frac{1}{A}\sum_{i=111}^{115} (\overline{S}_T{}^0)_i N_i \Delta\ln N_i \\ &+ \frac{1}{A}\sum_{i=111}^{115} (\overline{C}_P{}^0)_i N_i \Delta\ln T\end{aligned} \tag{58}$$

Combining both equations yields

$$\begin{aligned}\Delta F_S = &\frac{1}{A}\left[\sum_{i=1}^{115} (\overline{S}_T{}^0)_i N_i \Delta\ln N_i - \sum_{i=1}^{110} \overline{R} N_i \ln P_i \Delta\ln N_i - \sum_{i=1}^{110} \overline{R} N_i \Delta\ln P_i\right] \\ &+ \frac{1}{A}\sum_{i=1}^{115} (\overline{C}_P{}^0)_i N_i \Delta\ln T - \frac{1}{A}\left[\sum_{i=1}^{115} (\overline{S}_T{}^0)_i N_i - \sum_{i=1}^{110} \overline{R} N_i \ln P_i\right] \Delta\ln A\end{aligned}$$

$$\begin{aligned}\Delta F_S = &\frac{1}{A}\left[\sum_{i=1}^{115} (\overline{S}_T{}^0)_i - \sum_{i=1}^{110} \overline{R}(\ln P_i + 1)\right] N_i \Delta\ln P_i + \frac{1}{A}\sum_{i=1}^{115} (\overline{C}_P{}^0)_i N_i \Delta\ln T \\ &- \frac{1}{A}\left[\sum_{i=1}^{115} (\overline{S}_T{}^0)_i N_i - \sum_{i=1}^{110} \overline{R} N_i \ln P_i\right] \Delta\ln A\end{aligned}$$

Type of Equation	Gaseous Molecules			Gaseous Atoms			Condensed Phases					
	$\Delta \ln P_1$	$\Delta \ln P_2$	....	$\Delta \ln P_Z$	$\Delta \ln P_Y$	....	$\Delta \ln P_{111}$	$\Delta \ln P_{112}$	....	$- \Delta \ln A$	$\Delta \ln T$	constant
Equilibrium Equation 52	1	0	0	$-a_1$	$-b_1$	....	0	0	0	0	$-\left(\frac{\Delta \bar{H}_T^0}{\bar{R}T}\right)_1$	$-F_1$
	0	1	0	$-a_2$	$-b_2$	....	0	0	0	0	$-\left(\frac{\Delta \bar{H}_T^0}{\bar{R}T}\right)_2$	$-F_2$
	0	0	....	....	....	....	0	0	0	0	....	....
Mass Balance Equation 54	$a_1 N_1$	$a_2 N_2$	....	$a_{101} N_{101}$	0	0	$a_{111} N_{111}$	$a_{112} N_{112}$	....	$\sum_{i=1}^{115} a_i N_i$	0	$A \cdot \Delta F_a$
	$b_1 N_1$	$b_2 N_2$	....	0	$b_{102} N_{102}$	0	$b_{111} N_{111}$	$b_{112} N_{112}$	....	$\sum_{i=1}^{115} b_i N_i$	0	$A \cdot \Delta F_b$
	....	....	....	0	0	....	....	....	....	....	0	....
Condensed Phase Equilibrium Equation 53	0	0	0	$-a_{111}$	$-b_{111}$	....	0	0	0	0	$-\left(\frac{\Delta \bar{H}_T^0}{\bar{R}T}\right)_{111}$	$-F_{111}$
	0	0	0	$-a_{112}$	$-b_{112}$	....	0	0	0	0	$-\left(\frac{\Delta \bar{H}_T^0}{\bar{R}T}\right)_{112}$	$-F_{112}$
	0	0	0	....	....	....	0	0	0	0	....	....
Total Pressure Equation 55	P_1	P_2	....	P_{101}	P_{102}	....	0	0	0	0	0	ΔF_P
Enthalpy Equation 56	$(\bar{H}_T^0)_1 N_1$	$(\bar{H}_T^0)_2 N_2$	....	$(\bar{H}_T^0)_{101} N_{101}$	$(\bar{H}_T^0)_{102} N_{102}$	....	$(\bar{H}_T^0)_{111} N_{111}$	$(\bar{H}_T^0)_{112} N_{112}$	....	$\sum_{i=1}^{115} (\bar{H}_T^0)_i N_i$	$T \cdot \sum_{i=1}^{115} (\bar{C}_P^0)_i N_i$	$A \cdot \Delta F_H$
Entropy Equations 57 and 58	$S_1^* N_1$	$S_2^* N_2$	....	$S_{101}^* N_{101}$	$S_{102}^* N_{102}$	....	$S_{111}^{**} N_{111}$	$S_{112}^{**} N_{112}$	....	S^{***}	$\sum_{i=1}^{115} (\bar{C}_P^0)_i N_i$	$A \cdot \Delta F_S$

$S_i^* = [(\bar{S}_T^0)_i - \bar{R}(\ln P_i + 1)]$

$S_i^{**} = (\bar{S}_T^0)_i$

$$S^{***} = \left[\sum_{i=1}^{115} (\bar{S}_T^0)_i N_i - \sum_{i=1}^{110} \bar{R} \cdot N_i \ln P_i\right]$$

FIGURE 3. ORIGINAL COEFFICIENT MATRIX FOR THE SET OF SIMULTANEOUS EQUATIONS SOLVING FOR Ni, A, AND T

Type of Equation	Gaseous Atoms			Condensed Phases					
	$\Delta \ln P_Z$	$\Delta \ln P_Y$	....	$\Delta \ln P_{111}$	$\Delta \ln P_{112}$	....	$-\Delta \ln A$	$\Delta \ln T$	constant r
Mass Balance	$\sum_{i=1}^{110} a_i^2 N_i$	$\sum_{i=1}^{110} a_i b_i N_i$	....	$a_{111} N_{111}$	$a_{112} N_{112}$	....	$\sum_{i=1}^{115} a_i N_i$	$\sum_{i=1}^{110} a_i N_i \left(\frac{\Delta \bar{H}_T^0}{RT}\right)_i \circledast$	$A \cdot \Delta F_a + \sum_{i=1}^{110} F_i a_i N_i \quad +$
	$\sum_{i=1}^{110} a_i b_i N_i$	$\sum_{i=1}^{110} b_i^2 N_i$	....	$b_{111} N_{111}$	$b_{112} N_{112}$	....	$\sum_{i=1}^{115} b_i N_i$	$\sum_{i=1}^{110} b_i N_i \left(\frac{\Delta \bar{H}_T^0}{RT}\right)_i \circledast$	$A \cdot \Delta F_b + \sum_{i=1}^{110} F_i b_i N_i \quad +$
	....	....	....	....	....	....	....	....	....
Condensed Phase	$-a_{111}$	$-b_{111}$	....	0	0	0	0	$-\left(\frac{\Delta \bar{H}_T^0}{RT}\right)_{111}$	$-F_{111}$
	$-a_{112}$	$-b_{112}$	....	0	0	0	0	$-\left(\frac{\Delta \bar{H}_T^0}{RT}\right)_{112}$	$-F_{112}$
	....	....	....	0	0	0	0	....	....
Total Pressure	$\sum_{i=1}^{110} a_i P_i$	$\sum_{i=1}^{110} b_i P_i$	....	0	0	0	0	$\sum_{i=1}^{110} P_i \left(\frac{\Delta \bar{H}_T^0}{RT}\right)_i \circledast$	$\Delta F_P + \sum_{i=1}^{110} F_i P_i \quad +$
Enthalpy	$\sum_{i=1}^{110} (\bar{H}_T^0)_i a_i N_i$	$\sum_{i=1}^{110} (\bar{H}_T^0)_i b_i N_i$	....	$(\bar{H}_T^0)_{111} N_{111}$	$(\bar{H}_T^0)_{112} N_{112}$	....	$\sum_{i=1}^{115} (\bar{H}_T^0)_i N_i$	$T \cdot \sum_{i=1}^{115} (\bar{C}_P^0)_i N_i + \sum_{i=1}^{110} (\bar{H}_T^0)_i \left(\frac{\Delta \bar{H}_T^0}{RT}\right)_i N_i \circledast$	$A \cdot \Delta F_H + \sum_{i=1}^{110} F_i (\bar{H}_T^0)_i N_i \quad +$
Entropy	$\sum_{i=1}^{110} a_i S_i^* N_i$	$\sum_{i=1}^{110} b_i S_i^* N_i$	....	$S_{111}^{**} N_{111}$	$S_{112}^{**} N_{112}$	....	S^{***}	$\sum_{i=1}^{115} (\bar{C}_P^0)_i N_i + \sum_{i=1}^{110} S_i^* N_i \left(\frac{\Delta \bar{H}_T^0}{RT}\right)_i \circledast$	$A \cdot \Delta F_S + \sum_{i=1}^{110} F_i S_i^* N_i \quad +$

The summations were generalized considering either all gaseous products $\left(\sum_{i=1}^{110}\right)$ or all combustion products.

It shall be pointed out that: (a) In all terms marked with an $\circledast$ the $(\Delta \bar{H}_T^0)_i$ for the gaseous elements is zero

(b) In all terms marked with a (+) the F_i for all gaseous elements is zero.

$S_i^* = \left[(\bar{S}_T^0)_i - \bar{R}(\ln P_i + 1)\right]$

$S_i^{**} = (\bar{\bar{S}}_T^0)_i$

$S^{***} = \left[\sum_{i=1}^{115} (\bar{S}_T^0)_i N_i - \sum_{i=1}^{115} \bar{R} \cdot N_i \ln P_i\right]$

FIGURE 4. REDUCED AUGMENTED MATRIX USED TO SOLVE FOR Ni, A, AND T SIMULTANEOUSLY

DERIVATION OF THE MOLAR SPECIFIC HEAT AT CONSTANT PRESSURE

By definition:

$$A\,dH = N\overline{C}_P\,dT$$

$$\frac{A}{N}\frac{dH}{dT} = \overline{C}_P \tag{59}$$

The total enthalpy of the product is equal to the summation of the proper enthalpy portions of the compounds.

$$H = \frac{1}{A}\sum_{i=1}^{115} (\overline{H}_T{}^0)_i N_i \tag{60}$$

The enthalpy is a function of:

$$H = F(A,\ N,\ \overline{H}_T{}^0) \tag{61}$$

At first, the enthalpy equation is differentiated with respect to T in order to obtain an expression for the $\overline{C}_P$ equation.

1. In the case of shifting equilibrium, we obtain:

$$dH = \frac{\partial H}{\partial N_i}\,dN_i + \frac{\partial H}{\partial(\overline{H}_T{}^0)}\,d\,(\overline{H}_T{}^0)_i + \frac{\partial H}{\partial A}\,dA$$

The individual partial derivatives are

$$\frac{\partial H}{\partial N_i} = \frac{\partial}{\partial N_i}\left(\frac{1}{A}\sum_{i=1}^{115} (\overline{H}_T{}^0)_i N_i\right) = \frac{1}{A}\sum_{i=1}^{115} (\overline{H}_T{}^0)_i$$

$$\frac{\partial H}{\partial(\overline{H}_T{}^0)_i} = \frac{\partial}{\partial(\overline{H}_T{}^0)_i}\left(\frac{1}{A}\sum_{i=1}^{115} (\overline{H}_T{}^0)_i N_i\right) = \frac{1}{A}\sum_{i=1}^{115} N_i$$

$$\frac{\partial H}{\partial A} = \frac{\partial}{\partial A}\left(\frac{1}{A}\sum_{i=1}^{115} (\overline{H}_T{}^0)_i N_i\right) = -\frac{1}{A^2}\sum_{i=1}^{115} (\overline{H}_T{}^0)_i N_i$$

Substituting the proper terms and dividing by dT yields.

$$dH = \frac{1}{A}\sum_{i=1}^{115} (\overline{H}_T{}^0)_i\, dN_i + \frac{1}{A}\sum_{i=1}^{115} N_i\, d(\overline{H}_T{}^0)_i - \frac{1}{A^2}\sum_{i=1}^{115} (\overline{H}_T{}^0)_i N_i\, dA$$

$$\frac{dH}{dT} = \frac{1}{A}\sum_{i=1}^{115} (\overline{H}_T{}^0)_i \frac{dN_i}{dT} + \frac{1}{A}\sum_{i=1}^{115} N_i \frac{d(\overline{H}_T{}^0)_i}{dT} - \frac{1}{A^2}\sum_{i=1}^{115} (\overline{H}_T{}^0)_i N_i \frac{dA}{dT}$$

According to the mathematical concept

$$\frac{d\ln x}{dx} = \frac{1}{x}$$

and with

$$\frac{d(\overline{H}_T{}^0)_i}{dT} = \frac{d}{dT}\left(\int \overline{C}_P{}^0\, dT\right)_i = (\overline{C}_P{}^0)_i$$

we obtain:

$$\frac{dH}{dT} = \frac{1}{A}\sum_{i=1}^{115} (\overline{H}_T{}^0)_i \frac{N_i}{T}\frac{d\ln N_i}{d\ln T} + \frac{1}{A}\sum_{i=1}^{115} (\overline{C}_P{}^0)_i N_i - \frac{1}{AT}\sum_{i=1}^{115} (\overline{H}_T{}^0)_i N_i \frac{d\ln A}{d\ln T}$$

$$\frac{dH}{dT} = \frac{1}{AT}\left[\sum_{i=1}^{115} (\overline{H}_T{}^0)_i N_i \frac{d\ln N_i}{d\ln T} + T\sum_{i=1}^{115} (\overline{C}_P{}^0)_i N_i - \sum_{i=1}^{115} (\overline{H}_T{}^0)_i N_i \frac{d\ln A}{d\ln T}\right]$$

The molar specific heat at constant pressure is now

$$\overline{C}_P = \frac{A}{\sum_{i=1}^{115} N_i}\left(\frac{dH}{dT}\right) = \frac{1}{T\sum_{i=1}^{115} N_i}\left[\sum_{i=1}^{115} (\overline{H}_T{}^0)_i N_i \frac{d\ln N_i}{d\ln T} + T\sum_{i=1}^{115} (\overline{C}_P{}^0)_i N_i \right.$$

$$\left. - \sum_{i=1}^{115} (\overline{H}_T{}^0)_i N_i \frac{d\ln A}{d\ln T}\right]$$

Since $N_i = P_i$, the term $\frac{d \ln N_i}{d \ln T} = \frac{d \ln P_i}{d \ln T}$ can be replaced by the corresponding expression obtained from the equilibrium equation 52.

$$\left(\frac{\Delta\bar{G}_T{}^0}{\bar{R}T}\right)_i + \ln P_i - (a_i \ln P_Z + b_i \ln P_Y + c_i \ln P_X + \ldots) = 0$$

$$\frac{d\ln P_i}{d\ln T} = a_i \frac{d\ln P_Z}{d\ln T} + b_i \frac{d\ln P_Y}{d\ln T} + c_i \frac{d\ln P_X}{d\ln T} + \left(\frac{\Delta\bar{H}_T{}^0}{\bar{R}T}\right)$$

The molar specific heat at constant pressure finally results in

$$\bar{C}_P = \frac{1}{T\sum\limits_{i=1}^{115} N_i}\left\{\sum_{i=1}^{115} (\bar{H}_T{}^0)_i N_i \left[a_i \frac{d\ln P_Z}{d\ln T} + b_i \frac{d\ln P_Y}{d\ln T} + c_i \frac{d\ln P_X}{d\ln T} + \ldots + \left(\frac{\Delta\bar{H}_T{}^0}{\bar{R}T}\right)_i\right] + \sum_{i=111}^{115} (\bar{H}_T{}^0)_i N_i \frac{d\ln N_i}{d\ln T} + T\sum_{i=1}^{115} (\bar{C}_P{}^0)_i N_i - \sum_{i=1}^{115} (\bar{H}_T{}^0)_i N_i \frac{d\ln A}{d\ln T}\right\} \tag{62}$$

2. For frozen equilibrium N_i and A, are no longer functions of temperature. Therefore, equation 62 reduces to

$$\bar{C}_P = \frac{1}{T\sum\limits_{i=1}^{115} N_i}\left[T\sum_{i=1}^{115} (\bar{C}_P{}^0)_i N_i\right]$$

$$\bar{C}_P = \frac{\sum\limits_{i=1}^{115} (\bar{C}_P{}^0)_i N_i}{\sum\limits_{i=1}^{115} N_i} \tag{63}$$

DERIVATION OF THE MOLAR SPECIFIC HEAT AT CONSTANT VOLUME

Applying equations 156 and 157 to equation 118 in Appendix B yields the following equation for C_v

$$C_v = C_P \frac{\left(\frac{\partial v}{\partial P}\right)_s}{\left(\frac{\partial v}{\partial P}\right)_T} \tag{64}$$

Take the difference of the specific heats from equations 156 and 157

$$C_P - C_v = T\left[\left(\frac{\partial s}{\partial T}\right)_P - \left(\frac{\partial s}{\partial T}\right)_v\right] \tag{65}$$

The derivatives are calculated from the property equations:

Combining both equations 140 and 141 yields

$$dT\left[\left(\frac{\partial s}{\partial T}\right)_P - \left(\frac{\partial s}{\partial T}\right)_v\right] = \left(\frac{\partial s}{\partial v}\right)_T dv - \left(\frac{\partial s}{\partial P}\right)_T dP$$

Comparing this with equation 65 shows

$$\frac{dT}{T}(C_P - C_v) = \left(\frac{\partial s}{\partial v}\right)_T dv - \left(\frac{\partial s}{\partial P}\right)_T dP \tag{66}$$

Applying equations 144, 146, 147, 149, 152, 153, results in

$$dT = \frac{T}{C_P - C_v}\left(\frac{\partial P}{\partial T}\right)_v dv + \frac{T}{C_P - C_v}\left(\frac{\partial v}{\partial T}\right)_P dP$$

Comparison of the coefficients with equations 142 yields

$$\left(\frac{\partial T}{\partial v}\right)_P = \frac{T}{C_P - C_v}\left(\frac{\partial P}{\partial T}\right)_v$$

$$\left(\frac{\partial T}{\partial P}\right)_v = \frac{T}{C_P - C_v}\left(\frac{\partial v}{\partial T}\right)_P$$

Both equations have the same result

$$C_P - C_v = T\left(\frac{\partial v}{\partial T}\right)_P\left(\frac{\partial P}{\partial T}\right)_v$$

Substituting $\left(\frac{\partial P}{\partial T}\right)_v$ from equation 118 gives

$$C_P - C_v = - T\left(\frac{\partial v}{\partial T}\right)_P^2\left(\frac{\partial P}{\partial v}\right)_T \tag{67}$$

In the following section expressions are developed for $\left(\frac{\partial v}{\partial T}\right)_P$ and $\left(\frac{\partial P}{\partial v}\right)_T$. Starting with the equation of state for an ideal gas

$$MPv = \overline{R}T$$

taking the logarithm, forming the differential, and dividing by dlnT yields

$$\frac{d\ln M}{d\ln T} + \frac{d\ln P}{d\ln T} + \frac{d\ln v}{d\ln T} = \frac{d\ln \overline{R}}{d\ln T} + \frac{d\ln T}{d\ln T}$$

Since

$$\frac{d\ln \overline{R}}{d\ln T} = 0$$

$$\frac{d\ln T}{d\ln T} = 1$$

It follows that for a constant pressure process

$$\left(\frac{d\ln v}{d\ln T}\right)_P = 1 - \left(\frac{d\ln M}{d\ln T}\right)_P$$

or

$$\left(\frac{dv}{dT}\right)_P = \frac{v}{T}\left[1 - \frac{d\ln M}{d\ln T}\right]_P \tag{68}$$

Beginning again with the general gas equation, taking the logarithm, forming the differential, and dividing by dln P yields

$$\frac{d\ln M}{d\ln P} + \frac{d\ln P}{d\ln P} + \frac{d\ln v}{d\ln P} = \frac{d\ln \overline{R}}{d\ln P} + \frac{d\ln T}{d\ln P}$$

with

$$\frac{d\ln \overline{R}}{d\ln P} = 0$$

$$\frac{d\ln P}{d\ln P} = 1$$

For a constant temperature process

$$\left(\frac{d\ln v}{d\ln P}\right)_T = -1 - \left(\frac{d\ln M}{d\ln P}\right)_T$$

or

$$\left(\frac{dv}{dP}\right)_T = -\frac{v}{P}\left[1 + \frac{d\ln M}{d\ln P}\right]_T \tag{69}$$

Solving equation 67 for C_V and substituting equations 68 and 69 for the corresponding terms results in

$$C_V = C_P - \frac{vP}{T}\frac{\left[1 - \frac{d\ln M}{d\ln T}\right]_P^2}{\left[1 + \frac{d\ln M}{d\ln P}\right]_T} \tag{70}$$

Changing over to molar specific heats according to

$$\overline{C}_V = MC_V$$

$$\overline{C}_P = MC_P \tag{71}$$

and using equation 70, we finally obtain

$$\overline{C}_V = \overline{C}_P - \overline{R}\frac{\left[1 - \frac{d\ln M}{d\ln T}\right]_P^2}{\left[1 + \frac{d\ln M}{d\ln P}\right]_T} \tag{72}$$

RESULTS OF EQUATIONS LINEARIZED BY THE NEWTON-RAPHSON METHOD TO SOLVE FOR THE PARTIAL DERIVATIVES AT CONSTANT PRESSURE AND TEMPERATURE

As shown in Appendix A, the equation of state can be expressed by

$$F = F(P, v, T) = 0$$

$$-1 = \left(\frac{\partial v}{\partial T}\right)_P \left(\frac{\partial P}{\partial v}\right)_T \left(\frac{\partial T}{\partial P}\right)_v$$

Since any other property can be expressed by the three properties, P, v, T, any other partial derivative can be expressed by the three partial derivatives.

In this report, the following first partial derivatives are used

$$\left(\frac{\partial H}{\partial T}\right)_P$$

$$\left(\frac{d \ln M}{d \ln T}\right)_P$$

$$\left(\frac{d \ln M}{d \ln P}\right)_T$$

This leads to the determination of the specific heat at constant pressure C_P and constant volume C_V. These terms can be expressed by the quantities

$$\left(\frac{\partial \ln P_Z}{\partial \ln T}\right)_P, \quad \left(\frac{\partial \ln P_Y}{\partial \ln T}\right)_P, \quad \left(\frac{\partial \ln P_X}{\partial \ln T}\right)_P, \ldots$$

$$\left(\frac{\partial \ln P_Z}{\partial \ln A}\right)_T, \quad \left(\frac{\partial \ln P_Y}{\partial \ln A}\right)_T, \quad \left(\frac{\partial \ln P_X}{\partial \ln A}\right)_T, \ldots$$

$$\left(\frac{\partial \ln A}{\partial \ln T}\right)_P$$

To solve for the partial derivatives, a set of equations must be solved simultaneously. The soultions of the equations, which are derived in Appendix C, are given below:

1. The derivatives at constant pressure can be obtained from the following equations:

a. Equilibrium equation for gaseous compounds

$$0 = -\left(\frac{\Delta H_T{}^0}{\bar{R}T}\right)_i + \frac{d\ln P_i}{d\ln T} - a_i\frac{d\ln P_Z}{d\ln T} - b_i\frac{d\ln P_Y}{d\ln T} - c_i\frac{d\ln P_X}{d\ln T} - \ldots \tag{73}$$

b. Equilibrium equations for condensed phases

$$0 = -\left(\frac{\Delta \bar{H}_T{}^0}{\bar{R}T}\right)_i - a_i\frac{d\ln P_Z}{d\ln T} - b_i\frac{d\ln P_Y}{d\ln T} - c_i\frac{d\ln P_X}{d\ln T} - \ldots \tag{74}$$

c. Mass balance equation

$$0 = -\sum_{i=1}^{115} a_i N_i \frac{d\ln A}{d\ln T} + \sum_{i=1}^{115} a_i N_i \frac{d\ln N_i}{d\ln T} \tag{75}$$

d. Total pressure equation

$$0 = \sum_{i=1}^{110} P_i \frac{d\ln P_i}{d\ln T} \tag{76}$$

This simultaneous set of equations can be simplified when the equilibrium equations for gaseous compounds is solved for $\frac{d\ \ln\ P_i}{d\ \ln\ T}$ and the result is substituted in the mass balance equation for $\frac{d\ \ln\ N_i}{d\ \ln\ T}$

This yields

$$0 = -\sum_{i=1}^{115} a_i N_i \frac{d\ln A}{d\ln T} + \sum_{i=1}^{110} a_i N_i \left[a_i\frac{d\ln P_Z}{d\ln T} + b_i\frac{d\ln P_Y}{d\ln T} + c_i\frac{d\ln P_X}{d\ln T} + \ldots + \left(\frac{\Delta \bar{H}_T{}^0}{\bar{R}T}\right)_i\right] + \sum_{i=1}^{115} a_i N_i \frac{d\ln N_i}{d\ln T} \tag{77}$$

In writing a coefficient matrix for these equations, using equations 77, 74, 76, the system is incorporated in the reduced augmented matrix solving for the mole numbers.

2. The derivatives at constant temperature can be obtained form the following equations:

a. Equilibrium equations for gaseous compounds

$$0 = \frac{d \ln P_i}{d \ln A} - a_i \frac{d \ln P_Z}{d \ln A} - b_i \frac{d \ln P_Y}{d \ln A} - c_i \frac{d \ln P_X}{d \ln A} - \dots \tag{78}$$

b. Equilibrium equations for condensed phases

$$0 = - a_i \frac{d \ln P_Z}{d \ln A} - b_i \frac{d \ln P_Y}{d \ln A} - c_i \frac{d \ln P_X}{d \ln A} \tag{79}$$

c. Mass balance equations

$$0 = - a_0 A + \sum_{i=1}^{115} a_i N_i \frac{d \ln P_i}{d \ln A} \tag{80}$$

This simultaneous set of equations can be simplified by replacing the term $\frac{d \ln P_i}{d \ln A}$ with the proper expression from the equilibrium equation. The result is

$$0 = - a_0 A + \sum_{i=1}^{110} a_i N_i \left[a_i \frac{d \ln P_Z}{d \ln A} + b_i \frac{d \ln P_Y}{d \ln A} + c_i \frac{d \ln P_X}{d \ln A} + \dots \right] + \sum_{i=1}^{115} a_i N_i \frac{d \ln P_i}{d \ln A} \tag{81}$$

The coefficient matrix for this simultaneous set, using equations 79, 81, is also incorporated in the reduced matrix.

The relationship between $\left(\frac{d \ln M}{d \ln T}\right)_P$ and $\left(\frac{d \ln M}{d \ln P}\right)_T$ is derived in Appendix D.

ISENTROPIC EXPONENT

Speed of sound is by definition

$$w_s = \sqrt{\left(\frac{\partial P}{\partial \rho}\right)_s} \tag{82}$$

Using the adiabatic relationship for a perfect gas,

$$Pv^{\gamma} = P \frac{1}{\rho^{\gamma}} = \text{const} \tag{83}$$

taking the logarithm

$$\ln P - \gamma \ln \rho = \text{const}$$

and forming the differential yields

$$d \ln P - \gamma d \ln \rho = 0$$

$$\gamma = \frac{d \ln P}{d \ln \rho} = \frac{\rho \, dP}{P \, d\rho} \tag{84}$$

With the relationship

$$\rho = \frac{1}{v}$$

we obtain

$$\ln \rho = \ln 1 - \ln v \qquad \ln 1 = 0$$

$$d \ln \rho = - d \ln v$$

$$\frac{d\rho}{\rho} = - \frac{dv}{v}$$

such that

$$\gamma = - \frac{v \, dP}{P \, dv}$$

Setting both terms for γ equal to each other and solving for $\frac{dP}{d\rho}$ yields

$$\frac{dP}{d\rho} = - \frac{P v \, dP}{\rho P \, dv}$$

Substituting this in equation 82 gives

$$w_s = \sqrt{- \frac{Pv}{\rho P} \left(\frac{dP}{dv} \right)_s} = \sqrt{- \frac{v}{P} \left(\frac{dP}{dv} \right)_s RT} \tag{85}$$

The specific heat ratio is by definition

$$\gamma = \frac{C_P}{C_v}$$

from equation 64, it follows that

$$\frac{C_P}{C_v} = \left(\frac{\partial v}{\partial P}\right)_T \left(\frac{\partial P}{\partial v}\right)_s$$

Applying equation 69 results in

$$\gamma = -\frac{v}{P}\left[1 + \frac{d\ln M}{d\ln P}\right]_T \left(\frac{\partial P}{\partial v}\right)_s$$

with $$\gamma = \left[1 + \frac{d\ln M}{d\ln P}\right]_T \gamma_s \qquad (86)$$

$$\gamma_s = -\frac{v}{P}\left(\frac{\partial P}{\partial v}\right)_s$$

This expression appears in the equation for the speed of sound. Replacing $\left(\frac{\partial P}{\partial v}\right)_s$ by equation 64 results in

$$\gamma_s = -\frac{v}{P}\left[\frac{C_P}{C_v\left(\frac{\partial v}{\partial P}\right)_T}\right]$$

Considering furthermore equations 67, 68, 69 gives

$$\gamma_s = -\frac{v}{P}\left[\frac{C_P}{\left[C_P + T\left(\frac{\partial v}{\partial T}\right)_P^2 \left(\frac{\partial P}{\partial v}\right)_T\right]\left(\frac{\partial v}{\partial P}\right)_T}\right]$$

$$\gamma_s = -\frac{v}{P}\left[\frac{C_P}{-\frac{C_P v}{P}\left[1 + \frac{d\ln M}{d\ln P}\right]_T + \frac{Tv^2}{T^2}\left[1 - \frac{d\ln M}{d\ln T}\right]_P}\right]$$

Applying the general gas equation and going over to molar specific heats finally yields

$$\gamma_s = \frac{\overline{C}_P}{\overline{C}_P\left[1 + \frac{d\ln M}{d\ln P}\right]_T - \overline{R}\left[1 - \frac{d\ln M}{d\ln T}\right]_P^2} \qquad (87)$$

The thermodynamec properties per mole of the individual combustion products used in the calculation procedure are the specific heat at constant pressure $\bar{C}^{o}_{P}$, the enthalpy $\bar{H}^{o}_{T}$ and the entropy $\bar{S}^{o}_{T}$. These properties are correlated by the following definitions:

$$\overline{C}_P{}^0 = F(T)$$

$$\overline{H}_T{}^0 = \int \overline{C}_P{}^0 \, dT$$

$$\overline{S}^0 = \int \frac{\overline{C}_P{}^0}{T} \, dT$$

When the $\bar{C}_P$ values are represented by the following polynomial

$$\overline{C}_P{}^0 = a + bT + cT^2 + dT^3 + eT^4 \tag{88}$$

in which a, b, c, d, e are constant values, the enthalpy and entropy equations yield correspondingly

$$\overline{H}_T{}^0 = aT + \frac{b}{2} T^2 + \frac{c}{3} T^3 + \frac{d}{4} T^4 + \frac{e}{5} T^5 + \text{const} \tag{89}$$

$$\overline{S}_T{}^0 = a \ln T + bT + \frac{c}{2} T^2 + \frac{d}{3} T^3 + \frac{e}{4} T^4 + \text{const} \tag{90}$$

The enthalpy function must include the reference enthalpy $\bar{H}^{o}_{298.15}$ at 298.15 K. In most cases, the properties are tabulated as a function of temperature at atmospheric pressure. To minimize the errors that show up if each polynomial is developed individually, all three polynomials are developed simultaneously by the least-squares method. This is advantageous because all corresponding coefficients have the same value, and it saves storage space in a computer. One polynomial does not cover the total range from 300 to 5000°K with sufficient accuracy; therefore, two ranges were considered, one from 300 to 1000°K, and another from 1000 to 5000°K. In this case, however, a constraint must be placed on the development of the polynomials so that at 1000°K the intersection point of the two corresponding polynomials have the same value (but not the same tangent).

The equations in the calculation procedures use the properties

$$\frac{\bar{C}_P^0}{\bar{\bar{R}}}, \qquad \frac{\bar{S}_T^0}{\bar{\bar{R}}}, \qquad \frac{\bar{H}_T^0}{\bar{\bar{R}}T}$$

and the polynomials were developed as

$$\frac{\bar{C}_P^0}{\bar{\bar{R}}} = A + BT + CT^2 + DT^3 + ET^4 \tag{91}$$

$$\frac{\bar{H}_T^0}{\bar{\bar{R}}T} = A + \frac{BT}{2} + \frac{CT^2}{3} + \frac{DT^3}{4} + \frac{ET^4}{5} + \frac{F}{T} \tag{92}$$

$$\frac{\bar{S}_T^0}{\bar{\bar{R}}} = A \ln T + BT + \frac{CT^2}{2} + \frac{DT^3}{3} + \frac{ET^4}{4} + G \tag{93}$$

The polynomial coefficients A, B, C, D, E, F, for various compounds and elements have been published in Ref. 3.

THROAT AREA CONDITION

Knowledge of flow and thermodynamic properties of the combustion products in the throat area is necessary to determine performance parameters for a rocket engine; for example, characteristic velocity, flow rate, expansion ratio, thrust, etc. The approach to compute the throat condition is iterative and is based on the criterion that the flow velocity is equal to the speed of sound

$$w = w_s \qquad \mathrm{Ma} = \frac{w}{w_s} = 1 \tag{94}$$

With known chamber data, a first approximation of pressure in the throat region can be made according to the thermodynamic equation derived for ideal gases and constant isentropic exponent.

$$P_t = P_{ch}\left[\frac{2}{\gamma_s + 1}\right]^{\left(\frac{\gamma_s}{\gamma_s - 1}\right)} \tag{95}$$

The corresponding temperature is

$$T_t = T_{ch}\left[\frac{2}{\gamma_s + 1}\right] \tag{96}$$

The velocity and the speed of sound must be calculated for this condition considering a constant entropy expansion process. If the results do not satisfy the criterion $w = w_s$ a new approximation of the pressure will be performed using the following concept.

Every thermodynamic property can be determined when two other properties are known.

Choosing

$$h = F(P, s)$$

which reduces to

$$h = F(P)$$

for a constant entropy process. From experience it is known that there is a logarithmic relationship between the pressure and the enthalpy. Differentiating with respect to ln P results in

$$dh = \left(\frac{\partial h}{\partial \ln P}\right)_s d \ln P$$

or considering finite differences

$$\Delta h = \left(\frac{\partial h}{\partial \ln P}\right)_s \Delta \ln P$$

During an isentropic process the total energy cannot change. However, as long as the proper static pressure in the throat area has not been found, the difference between the chamber enthalpy and the total enthalpy for the throat region is not zero.

$$\Delta h = h_{ch} - h$$

Applying the mathematical relationship

$$\Delta \ln P = \frac{\Delta P}{P} = \frac{P_{k+1} - P_k}{P_k}$$

with k indicating the previous calculation of the static pressure, we obtain

$$h_{ch} - h = \left(\frac{\partial h}{\partial \ln P}\right)_s \frac{P_{k+1} - P_k}{P_k}$$

Solving for P_{k+1} yields

$$P_{k+1} = P_k \left[1 + \frac{h_{ch} - h}{\left(\frac{\partial h}{\partial \ln P}\right)_s}\right] \tag{97}$$

The total enthalpy in the nozzle is composed of a static and a dynamic portion

$$h = h_{stat} + h_{dyn} \tag{98}$$

$$h = h_{stat} + \frac{w^2}{2g_0}$$

Multiplying and dividing the dynamic term by w_s^2 and the molecular weight gives

$$h = h_{stat} + \frac{Ma^2 w_s^2 M}{2g_0 M}$$

Expressing the speed of sound w_s by the following thermodynamic relationship

$$w_s = \sqrt{g_0 \gamma_s RT}$$

results in

$$h = h_{stat} + \frac{Ma^2}{2M} \gamma_s \overline{R}T$$

This equation must be differentiated with respect to ln P to adapt it to equation 97.

$$\left(\frac{\partial h}{\partial \ln P}\right)_s = \left(\frac{\partial h_{stat}}{\partial \ln P}\right)_s + \frac{Ma^2}{2} \gamma_s \overline{R} \left(\frac{\partial \left(\frac{T}{M}\right)}{\partial \ln P}\right)_s \tag{99}$$

Considering the Mach-number and the specific heat ratio as independent of the pressure, the derivative of the dynamic term is derived. From the ideal gas law the following expressions are developed

$$PvM = \overline{R}T$$

$$v = \frac{1}{\rho}$$

$$\left[\frac{\partial\left(\frac{T}{M}\right)}{\partial P}\right]_s = \frac{1}{\overline{R}}\left[\frac{\partial\left(\frac{P}{\rho}\right)}{\partial P}\right]_s = \frac{1}{\overline{R}}\left[\frac{\rho - P\frac{\partial \rho}{\partial P}}{\rho^2}\right]_s = \frac{1}{\overline{R}\rho}\left[1 - \frac{P\,\partial\rho}{\rho\,\partial P}\right]_s$$

Applying equation 84

$$\left(\frac{\partial \ln \rho}{\partial \ln P}\right)_s = \frac{1}{\gamma_s}$$

results in

$$\left[\frac{\partial\left(\frac{T}{M}\right)}{\partial P}\right]_s = \frac{1}{\overline{R}\rho}\left[\frac{\gamma_s - 1}{\gamma_s}\right]$$

Next, the static enthalpy derivative is determined. The first law of thermodynamics states:

$$h_{stat} = u + Pv$$

$$\left(\frac{\partial h_{stat}}{\partial P}\right)_s = \frac{1}{\rho}$$

or

$$\left(\frac{\partial h_{stat}}{\partial \ln P}\right)_s = \frac{P}{\rho}$$

Substituting the corresponding terms into equation 99 yields

$$\left(\frac{\partial h}{\partial \ln P}\right)_s = \left[1 + \frac{Ma^2}{2}(\gamma_s - 1)\right]\frac{P}{\rho} \qquad (100)$$

Applying the ideal gas law yields

$$\frac{PM}{\rho} = \overline{R}T$$

$$\left(\frac{\partial h}{\partial \ln P}\right)_s = \frac{\overline{R}T}{M}\left[1 + \frac{Ma^2}{2}(\gamma_s - 1)\right] \qquad (101)$$

At the throat area, the Mach-number equals one. Therefore, the last equation reduces to

$$\left(\frac{\partial h}{\partial \ln P}\right)_s = \frac{\overline{R}T}{2M}(\gamma_s - 1) \qquad (102)$$

With this expression, the following approximations for the static pressure at the throat area can be made.

$$P_{k+1} = P_k\left(1 + \frac{h_{ch} - \left[h_{stat} + \frac{\gamma_s \overline{R}T}{2M}\right]}{\frac{\overline{R}T}{2M}\left[\gamma_s + 1\right]}\right) \tag{103}$$

EXIT AREA CONDITION

To determine the condition at a given expansion ratio ϵ, the computation is similar to that used for the throat condition. At first, a proper static pressure must be estimated for the expansion ratio being investigated. An equation from Ref. 4 serves as a basis for considering the flow of an ideal gas through an isentropic nozzle.

$$\varepsilon = \left(\frac{\gamma_s + 1}{2}\right)^{\frac{1}{\gamma_s - 1}} \left(\frac{P}{P_{ch}}\right)^{\frac{1}{\gamma_s}} \sqrt{\frac{\gamma_s + 1}{\gamma_s - 1}\left[1 - \left(\frac{P}{P_{ch}}\right)^{\frac{\gamma_s - 1}{\gamma_s}}\right]} \tag{104}$$

Since the exit static pressure cannot be determined implicity from this equation, the following procedure was applied:

1. For any combination of the pressure ratios $\frac{P}{P_{ch}} = 0.1; 0.01; 0.001; 0.0001; 0.00001$, and specific heat ratios $\gamma_s = 1.10, 1.15, 1.20, 1.25, 1.30, 1.35, 1.40$, the expansion ratio was calculated.
2. Plotting the data $\frac{P}{P_{ch}}$ versus $\frac{A}{A_T}$ for constant specific heat ratios on log - graph paper indicates a fairly linear relationship.

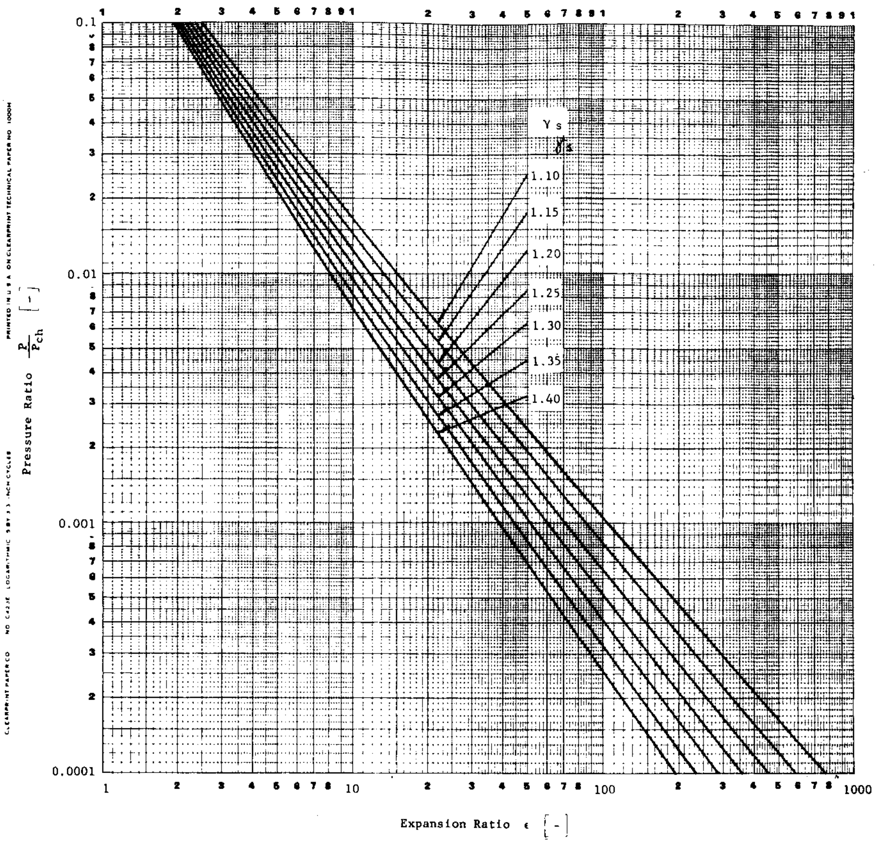

FIGURE 5. PRESSURE RATIO VERSUS EXPANSION RATIO FOR CONSTANT SPECIFIC HEAT RATIOS

3. A range of 3 to 100 for the expansion ratio of all specific heat ratios (γ_s) was taken into account.

4. Because of the linear relationship of a constant specific heat ratio curve, an equation of the following straight line equation can be written for each case.

$$y_{\gamma s} = mx_{\gamma s} + b$$

or if log-scales are used

$$\left(\ln\frac{P}{P_{ch}}\right)_{\gamma_s} = \frac{\left(\ln\frac{P}{P_{ch}}\right)_1 - \left(\ln\frac{P}{P_{ch}}\right)_2}{\left(\ln\frac{A}{A_t}\right)_1 - \left(\ln\frac{A}{A_t}\right)_2}\left(\ln\frac{A}{A_t}\right)_{\gamma_s} + \ln c$$

5. The slope of each constant γ-line can be calculated from the end points.

6. Knowing the slope and considering one point on the corresponding γ_s-line, the term ln c can be computed.

7. Plotting the different slopes (m) and constants (ln c) as a function of the specific heat ratios (γ_s), a linear relationship was again found so that a straight line equation could be written for either case.

$$m - m_{\gamma_{s1}} = \frac{m_{\gamma_{s1}} - m_{\gamma_{s2}}}{\gamma_{s1} - \gamma_{s2}} (\gamma_s - \gamma_{s1})$$

$$\ln c - \ln c_{\gamma_{s1}} = \frac{\ln c_{\gamma_{s1}} - \ln c_{\gamma_{s2}}}{\gamma_{s1} - \gamma_{s2}} (\gamma_s - \gamma_{s1})$$

8. A general equation can be developed that represents the family of curves

$$y = m(\gamma_s)x + b(\gamma_s)$$

$$\ln \frac{P}{P_{ch}} = \left[\left(\frac{m_{\gamma_{s1}} - m_{\gamma_{s2}}}{\gamma_{s1} - \gamma_{s2}}\right)(\gamma_s - \gamma_{s1}) + m_{\gamma_{s1}}\right] \ln \frac{A}{A_t}$$
$$+ \left[\left(\frac{\ln c_{\gamma_{s1}} - \ln c_{\gamma_{s2}}}{\gamma_{s1} - \gamma_{s2}}\right)(\gamma_s - \gamma_{s1}) + \ln c_{\gamma_{s1}}\right]$$

or

$$\frac{P}{P_{ch}} = e \left[\left(\frac{m_{\gamma_{s1}} - m_{\gamma_{s2}}}{\gamma_{s1} \quad \gamma_{s2}}\right)(\gamma_s - \gamma_{s1}) + m_{\gamma_{s1}}\right] \ln \frac{A}{A_t}$$
$$+ \left[\left(\frac{\ln c_{\gamma_{s1}} - \ln c_{\gamma_{s2}}}{\gamma_{s1} - \gamma_{s2}}\right)(\gamma_s - \gamma_{s1}) + \ln c_{\gamma_{s1}}\right] \qquad (105)$$

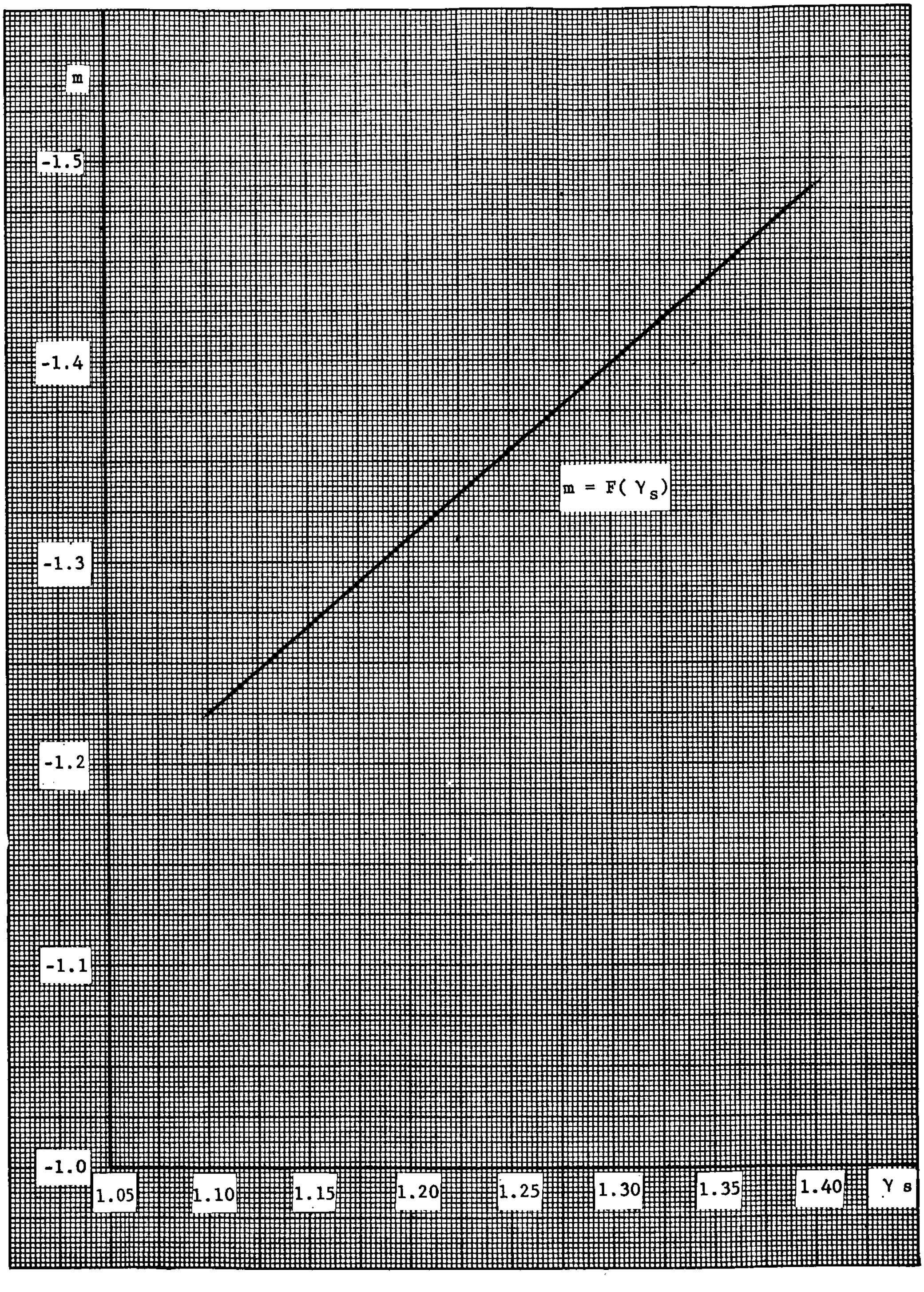

FIGURE 6. SLOPE OF CONSTANT γ_S LINES VERSUS SPECIFIC HEAT RATIO

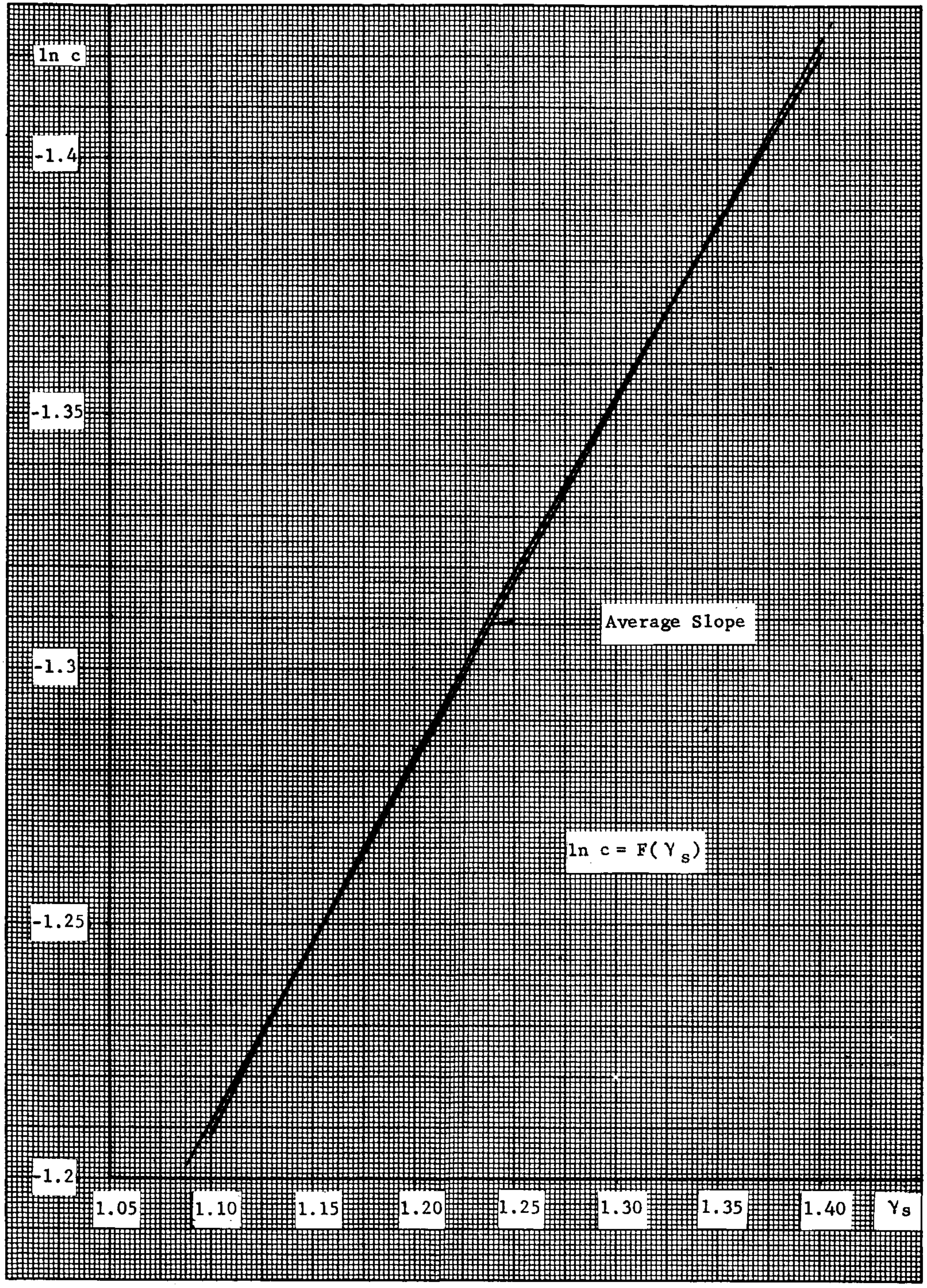

FIGURE 7. ORDINATE SECTION OF CONSTANT γ_s LINES VERSUS SPECIFIC HEAT RATIO

9. Using real values from Figures 5, 6, 7, the equation reads

$$\frac{P}{P_{ch}} = e^{-[(0.867\gamma_s + 0.27165)\ln\frac{A}{A_t} + (0.699228\gamma_s + 0.442199)]} \tag{106}$$

10. From this equation an approximation of the static pressure (P) at a desired expansion ratio can be made.

With the approximation of the static pressure in the exit area, the desired expansion ratio (ϵ) will not be obtained the first time. Consecutive approximations of the static pressure can be calculated from the generally developed equation 97 by introduction of an expansion ratio relationship.

The total enthalpy does not change during the expansion process, and equation 98 can be expressed by the expansion ratio (ϵ).

Since the mass flow rate through the throat section is equal to the mass flow rate through every other cross sectional area, the following equations result:

$$A_t \rho_t w_t = A \rho w \tag{107}$$

$$\varepsilon = \frac{A}{A_t} = \frac{w_t \rho_t}{w \rho} \tag{108}$$

$$\frac{w}{w_t} = \frac{\rho_t}{\rho_\epsilon}$$

Expressing furthermore the speed of sound in the throat area by

$$w_s = \sqrt{g_0 \gamma_{s,\,t} R_t T_t}$$

equation 98 finally yields

$$h = h_{stat} + \frac{\rho_t^2 \gamma_{s,\,t} R_t T_t}{2\varepsilon^2 \rho^2}$$

Applying this result to equation 98 yields the partial derivative shown below:

$$\left(\frac{\partial h}{\partial \ln P}\right)_s = \left(\frac{\partial h_{stat}}{\partial \ln P}\right)_s + \frac{\rho_t^2 \gamma_{s,\,t} R_t T_t}{2\varepsilon^2}\left(\frac{\partial\left(\frac{1}{\rho^2}\right)}{\partial \ln P}\right)_s \qquad (109)$$

According to equation 100 we obtain

$$\left(\frac{\partial h_{stat}}{\partial \ln P}\right)_s = \frac{P}{\rho}$$

Furthermore

$$\left(\frac{\partial\left(\frac{1}{\rho^2}\right)}{\partial \ln P}\right)_s = P\left(\frac{\partial\left(\frac{1}{\rho^2}\right)}{\partial P}\right)_s = -\frac{2P}{\rho^3}\left(\frac{\partial \rho}{\partial P}\right)_s = -\frac{2P}{\rho^2 \rho}\left(\frac{\partial \rho}{\partial P}\right)_s = -\frac{2}{\rho^2}\left(\frac{\partial \ln \rho}{\partial \ln P}\right)_s = -\frac{2}{\rho^2 \gamma_s}$$

Using the general gas equation, we obtain

$$\left(\frac{\partial h}{\partial \ln P}\right)_s = RT\left[1 - \frac{P_t^2 \gamma_{s,\,t} RT}{P^2 \gamma_s R_t T_t \varepsilon^2}\right] \qquad (110)$$

Substituting the proper terms in equation 97 finally results in

$$P_{k+1} = P_k\left[1 + \frac{h_{ch} - \left(h_{stat} + \frac{P_t^2 R^2 T^2 \gamma_{s,\,t}}{P^2 R_t T_t 2\varepsilon^2}\right)}{RT\left(1 - \frac{P_t^2 RT \gamma_{s,\,t}}{P^2 R_t T_t \gamma_s \varepsilon^2}\right)}\right] \qquad (111)$$

MAXIMUM SPECIFIC IMPULSE

Optimum rocket engine performance is achieved when the mixture ratio provides the maximum specific impulse. The theoretical performance calculation in this report includes an option to determine optimum mixture ratio for a constant combustion chamber pressure. The following computation procedure is used. Initially, a mixture ratio is assumed, and the corresponding specific impulse is determined. The mixture ratio is then increased twice by a chosen increment, and the pertinent specific impulse values are calculated. These three points in an I_{sp} - μ - diagram are the basis for the extrapolation routine explained below.

The specific impulse as a function of mixture ratio for a constant chamber pressure can be represented by an equation

$$I_{sp} = F(\mu)_{P_{ch}}$$

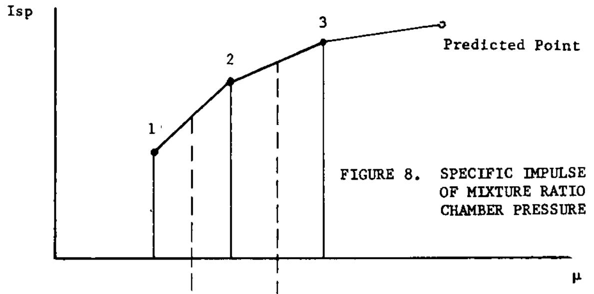

FIGURE 8. SPECIFIC IMPULSE AS A FUNCTION OF MIXTURE RATIO FOR CONSTANT CHAMBER PRESSURE

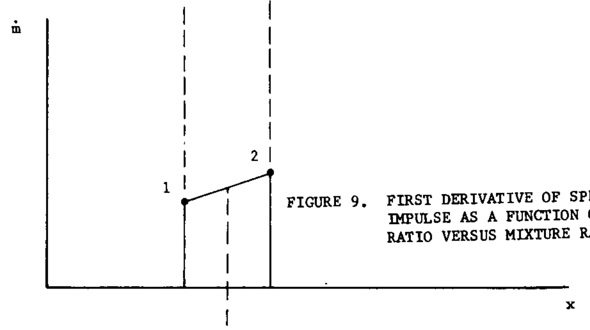

FIGURE 9. FIRST DERIVATIVE OF SPECIFIC IMPULSE AS A FUNCTION OF MIXTURE RATIO VERSUS MIXTURE RATIO

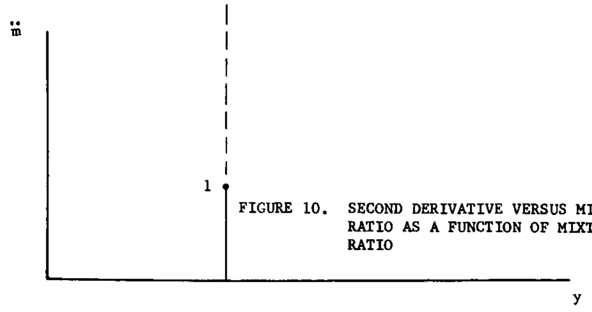

FIGURE 10. SECOND DERIVATIVE VERSUS MIXTURE RATIO AS A FUNCTION OF MIXTURE RATIO

Based on the known three points, a mean slope can be determined between two points

$$\dot{m}_1 = \frac{I_{sp1} - I_{sp2}}{\mu_1 - \mu_2}$$

$$\dot{m}_2 = \frac{I_{sp2} - I_{sp3}}{\mu_2 - \mu_3}$$

which also holds true for the mean mixture ratios

$$x_1 = \frac{\mu_1 + \mu_2}{2}$$

$$x_2 = \frac{\mu_2 + \mu_3}{2}$$

The terms $\dot{m}_1$ and $\dot{m}_2$ can be understood as the first derivative of the original function. A second derivative can be developed by taking into account the change of the slopes $\dot{m}$

$$\ddot{m}_1 = \frac{\dot{m}_1 - \dot{m}_2}{x_1 - x_2}$$

at a mean mixture ratio of

$$y = \frac{x_1 + x_2}{2}$$

Since the specific impulse as a function of mixture ratio is represented by a curve that resembles an inverse parabola, the first derivative can be assumed to have a constant slope. Therefore, the equation of a straight line for the first derivative yields:

$$\dot{m} - \dot{m}_2 = \frac{\dot{m}_1 - \dot{m}_2}{x_1 - x_2} (x - x_2)$$

Considering the second derivative, this equation changes to

$$\dot{m} - \dot{m}_2 = \ddot{m}_1 (x - x_2)$$

The condition for the maximum specific impulse requires

$$\dot{m} = 0$$

leaving

$$- \dot{m}_2 = \ddot{m}_1 (x - x_2)$$

The three originally calculated points are used to compute $\dot{m}_2$, $\ddot{m}_1$, and x_2. A new approximation for the mixture ratio μ can be obtained by solving the latter equation for x.

$$x = \frac{\ddot{m}_1 x_2 - \dot{m}_2}{\ddot{m}_1} \qquad (112)$$

At the point of maximum specific impulse, a secant changes into a tangent; the difference between two consecutive x-values approaches zero, or

$$x = \mu$$

This approach exactly determines the maximum for a parabolic curve when three points are known. Since the Isp-μ curve is not an exact parabola, the predicted maximum is not identical with the real one. However, with every new calculation point a new set of three points is available to predict a new and better point. This approach physically moves an inverse parabola along the line $Isp = F(\mu)_{P_{ch}}$ for a constant chamber pressure until its maximum converges into the real maximum.

In the calculation procedure presented in Appendix G, it is assumed that a maximum specific impulse is obtained when

$$\tan\alpha = \frac{I_{sp1} - I_{sp2}}{\mu_1 - \mu_2} \leq 0.01$$

To avoid any point of inversion, the mixture ratio determined for the maximum specific impulse is changed by $\Delta\mu = 0.001$ to the other side of the maximum to determine whether the specific impulse in this location is smaller than the previous one.

THRUST LEVEL UPRATING

When the thrust of an engine is uprated without changing its geometry, the new operating parameters, mixture ratio and chamber pressure, can be calculated in a separate option using the calculation program described in Appendix G.

The thrust increase can be invoked by changing the chamber pressure without varying the mixture ratio. In this case a new chamber pressure can be determined under the assumption that the chamber pressure is directly proportional to the thrust

$$\frac{P_{ch2}}{P_{ch1}} = \frac{F_{Des}}{F_1} \tag{113}$$

The thrust value (F_2) (calculated using the program) belonging to the new chamber pressure (P_{ch_2}) must be compared with the desired thrust (F_{Des}). If both values do not fall within a certain extablished tolerance, a new chamber pressure (P_{ch_2}) will be determined by applying a straight line extrapolation.

$$P_{ch2} = P_{ch2} + \frac{P_{ch2} - P_{ch1}}{F_2 - F_1} (F_{Des} - F_2) \qquad (114)$$

This procedure must be repeated until the desired thrust value is obtained (within a certain tolerance).

Figure 11 indicates that lines for constant chamber pressure, representing the relationship between specific impulse and mixture ratio, show a shift in maximum specific impulses to higher mixture ratios with increasing chamber pressure.

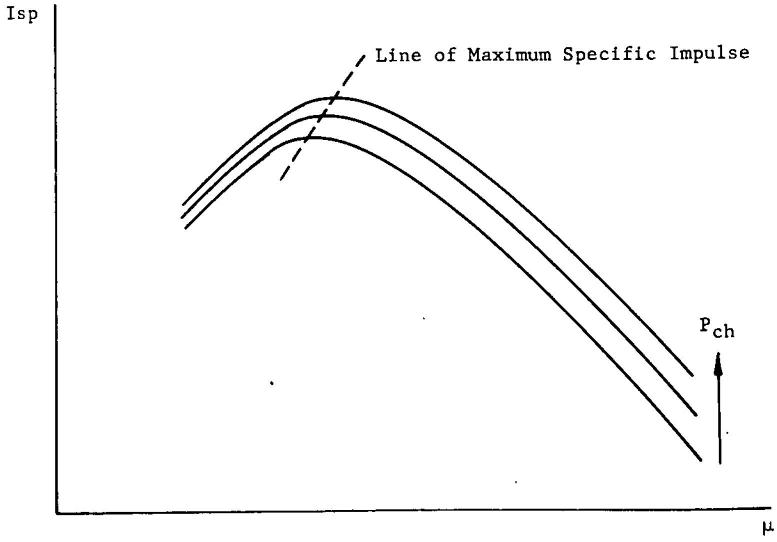

FIGURE 11. SHIFT OF MAXIMUM SPECIFIC IMPULSE AS A FUNCTION OF CHAMBER PRESSURE AND MIXTURE RATIO

For uprated engines a mixture ratio shift should also be taken into account to obtain high performance.

One method is to determine the chamber pressure so that the desired thrust level is obtained, and the specific impulse is a maximum. This option is included in the computer program by combination of the maximum specific impulse and the constant mixture ratio uprating procedure.

A second method considers that most rocket engines operate by some percent off the optimum mixture ratio, which yields maximum Isp. Since the mixture ratio of a rocket engine shifts during flight because of acceleration, propellant column height above pump inlet, density change of the propellants as a function of temperature, and many other reasons, it is preferred to stay on the side of the maximum impulse that shows the smaller slope. This allows a greater variation in mixture ratio for the same Isp tolerance, compared to the other side having a steeper slope.

The calculation proceeds as follows:

At first the combustion chamber at its original performance level is considered. Then for the same chamber pressure, the mixture ratio is determined that will yield maximum specific impulse. The difference between these mixture ratios is expressed as a percentage, and the sign indicates on which side of the optimum μ-value the combustion chamber is presently operating. Next the chamber pressure is varied, and the new point of maximum Isp, with the corresponding optimum mixture ratio is calculated. Deviating from this optimum mixture ratio value by the initially calculated per cent value, an uprated mixture ratio is found, with which the desired thrust level and the calculated level must be compared. If the thrust level difference does not satisfy a chosen tolerance, the whole procedure must be repeated.

COMBINATION OF SHIFTING AND FROZEN EQUILIBRIUM

As stated in Reference 10, dissociation is becoming more and more pronounced when the temperature rises above 1500°K. In the exit area of rocket engines, the static temperature is normally below this value. A real expansion process does not follow either the shifting or frozen equilibrium assumption, but occurs somewhere between these two cases. To calculate data that are close to real values, a combination of both concepts was considered in the calculation program and can be used if desired. The calculation starts with shifting equilibrium and switches to frozen equilibrium when the static temperature of the exhaust products falls below $T = 1500$°K.

PARAMETERS

Thermodynamic and rocket performance parameters are calculated according to the generally indicated procedures in text books (Ref. 4). The equations used in the computation process presented are indicated in Appendix G.

TOLERANCES

When a combustion-expansion process is calculated, an inaccuracy of the results develops because of the influence of the two main factors. First, the thermodynamic data, entropy, enthalpy, and specific heat at constant pressure, vary with different sources. Data for the heat of formation show discrepancies that are caused by the way they were obtained (calculated, measured, determined under the assumption of certain molecular structures). In forming polynomials for these properties as a function of temperature, an additional inaccuracy develops depending on the type of polynomial and the temperature range covered.

Secondly, the calculation procedure does not produce exact answers. Numerical solutions and iteration procedures can only yield answers within a certain tolerance. This refers especially to the determination of the mole numbers, temperature, enthalpy, entropy and in particular to the throat and exit area conditions on which all the rocket performance parameters are dependent.

A theoretical error analysis for the complete calculation procedure is not favourable because of the complexity of the program.

Usually the following tolerances resulted in a better accuracy than required (compare Reference 1).

With the nomenclature of Appendix B we apply to:

1. Equilibrium equations

$$\left|\Delta F_i\right| < 5 \times 10^{-6}$$

2. Mass balance equations

$$\left|1 - \frac{F_a}{a_o}\right| < 5 \times 10^{-7}$$

$$\left|1 - \frac{F_b}{b_o}\right| < 5 \times 10^{-7} \qquad \text{etc.}$$

3. Pressure equation

$$\left|1 - \frac{F_P}{PO}\right| < 5 \times 10^{-7}$$

4. Enthalpy equation

$$\left|1 - \frac{F_H}{HO}\right| < 5 \times 10^{-7}$$

5. Entropy equation

$$\left|1 - \frac{F_s}{SO}\right| < 5 \times 10^{-7}$$

6. Tolerance for the throat area condition

$$\left|1 - \frac{w}{w_s}\right| < 2 \times 10^{-4}$$

7. Tolerance for the exit condition

$$\left|1 - \frac{\epsilon}{\epsilon_{Des}}\right| < 1 \times 10^{-3}$$

These tolerances are too stringent in some cases and must be relaxed to obtain a solution. When a sequence of calculations is performed over a range of chamber pressures and mixture ratios, the tolerances must be relaxed so that the most critical case will pass.

During the iterations solving for mole numbers and temperature, the calculated new approximations sometimes lead to a divergence and failure in the computations. This occurs occasionally when the first assumptions of the mole numbers were not close enough, and the corrections caused divergence or an underflow in the electronic computer. To avoid such breakdowns, the following procedures were applied:

1. If the mole numbers are corrected and become so small that the computer assigns them equal to zero, these terms shall be reset to a small value (1×10^{-35}).

2. If the corrections become greater than 10, they are to be divided into 10. All corrections shall then be multiplied by the maximum absolute value obtained.

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APPENDIX A

THERMODYNAMIC RELATIONS

Each property of state can be expressed by two other properties of state. From the relationship $F(P, v, T) = 0$ an important equation is derived.

$$v = F(P, T)$$
$$T = F(P, v)$$

$$dv = \left(\frac{\partial v}{\partial T}\right)_P dT + \left(\frac{\partial v}{\partial P}\right)_T dP \qquad (116)$$

$$dT = \left(\frac{\partial T}{\partial P}\right)_v dP + \left(\frac{\partial T}{\partial v}\right)_P dv \qquad (117)$$

Replacing dv in one of the equations and rearranging the terms yields

$$-1 = \left(\frac{\partial v}{\partial T}\right)_P \left(\frac{\partial P}{\partial v}\right)_T \left(\frac{\partial T}{\partial P}\right)_v \qquad (118)$$

A similar expression will be developed from the relationships

$$T = F(u, v) \qquad (119)$$
$$u = F(T, v) \qquad (120)$$

$$dT = \left(\frac{\partial T}{\partial u}\right)_v du + \left(\frac{\partial T}{\partial v}\right)_u dv \qquad (121)$$

$$du = \left(\frac{\partial u}{\partial T}\right)_v dT + \left(\frac{\partial u}{\partial v}\right)_T dv \qquad (122)$$

Substituting du in one of the equations and rearranging gives

$$-1 = \left(\frac{\partial T}{\partial u}\right)_v \left(\frac{\partial u}{\partial T}\right)_u \left(\frac{\partial u}{\partial v}\right)_T \qquad (123)$$

The first law of thermodynamics is represented by the equation

$$dq = du + Pdv \tag{124}$$

The second law of thermodynamics reads

$$dq = Tds \tag{125}$$

Introducing the definition of enthalpy

$$h = u + Pv \tag{126}$$

Helmholtz function

$$a = u - Ts \tag{127}$$

Gibbs function

$$g = h - Ts \tag{128}$$

their differentials are

$$dh = du + Pdv + vdP \tag{129}$$

$$da = du - Tds - sdT \tag{130}$$

$$dg = dh - Tds - sdT \tag{131}$$

Application of the corresponding equations representing the first and second law of thermodynamics yields

$$dh = Tds + Pdv \tag{132}$$

$$da = -Pdv - sdT \tag{133}$$

$$dg = vdP - sdT \tag{134}$$

Futhermore, the following relations hold true

$$a = F(v, T)$$

$$g = F(P, T)$$

$$u = F(s, v)$$

$$h = F(s, P)$$

$$s = F(T, P)$$

$$s = F(T, v)$$

$$T = F(v, P) \tag{135}$$

Their derivatives are

$$da = \left(\frac{\partial a}{\partial v}\right)_T dv + \left(\frac{\partial a}{\partial T}\right)_v dT \tag{136}$$

$$dg = \left(\frac{\partial g}{\partial P}\right)_T dP + \left(\frac{\partial g}{\partial T}\right)_P dT \tag{137}$$

$$du = \left(\frac{\partial u}{\partial s}\right)_v ds + \left(\frac{\partial u}{\partial v}\right)_s dv \tag{138}$$

$$dh = \left(\frac{\partial h}{\partial s}\right)_P ds + \left(\frac{\partial h}{\partial P}\right)_s dP \tag{139}$$

$$ds = \left(\frac{\partial s}{\partial T}\right)_P dT + \left(\frac{\partial s}{\partial P}\right)_T dP \tag{140}$$

$$ds = \left(\frac{\partial s}{\partial T}\right)_v dT + \left(\frac{\partial s}{\partial v}\right)_T dv \tag{141}$$

$$dT = \left(\frac{\partial T}{\partial v}\right)_P dv + \left(\frac{\partial T}{\partial P}\right)_v dP \tag{142}$$

Comparing the equivalent terms in the corresponding equations

$$\left(\frac{\partial u}{\partial s}\right)_v = T \tag{143}$$

$$\left(\frac{\partial u}{\partial v}\right)_s = -P \tag{144}$$

$$\left(\frac{\partial h}{\partial s}\right)_P = T \tag{145}$$

$$\left(\frac{\partial g}{\partial P}\right)_T = v \tag{146}$$

$$\left(\frac{\partial g}{\partial T}\right)_P = -s \tag{147}$$

$$\left(\frac{\partial h}{\partial P}\right)_s = v \tag{148}$$

$$\left(\frac{\partial a}{\partial T}\right)_v = -s \tag{149}$$

All of the above equations involve properties and are exact differentials. Since properties are independent of a path, the following mathematical concept applies.

$$dz = Adx + Bdy$$

$$\left(\frac{\partial A}{\partial y}\right)_x = \left(\frac{\partial B}{\partial x}\right)_y$$

This results in the subsequent relationships

$$\left(\frac{\partial T}{\partial v}\right)_s = -\left(\frac{\partial P}{\partial s}\right)_v \tag{150}$$

$$\left(\frac{\partial T}{\partial P}\right)_s = \left(\frac{\partial v}{\partial s}\right)_P \tag{151}$$

$$\left(\frac{\partial P}{\partial T}\right)_v = \left(\frac{\partial s}{\partial v}\right)_T \tag{152}$$

$$\left(\frac{\partial v}{\partial T}\right)_P = -\left(\frac{\partial s}{\partial P}\right)_T \tag{153}$$

The specific heats are, by definition

$$C_v = \left(\frac{\partial u}{\partial T}\right)_v \tag{154}$$

$$C_P = \left(\frac{\partial h}{\partial T}\right)_P \tag{155}$$

Expanding these two equations indicates

$$C_v = \left(\frac{\partial u}{\partial s}\right)_v \left(\frac{\partial s}{\partial T}\right)_v$$

$$C_P = \left(\frac{\partial h}{\partial s}\right)_P \left(\frac{\partial s}{\partial T}\right)_P$$

Applying equations (143) and 145) and expanding the terms

$$C_v = T \left(\frac{\partial s}{\partial T}\right)_v \quad T \left(\frac{\partial s}{\partial P}\right)_v \left(\frac{\partial P}{\partial T}\right)_v$$

$$C_P = T \left(\frac{\partial s}{\partial T}\right)_P \quad T \left(\frac{\partial s}{\partial v}\right)_P \left(\frac{\partial v}{\partial T}\right)_P$$

Substitution of terms from equation (150) and (151) yields

$$\left(\frac{\partial P}{\partial T}\right)_v = -\frac{C_v}{T}\left(\frac{\partial T}{\partial v}\right)_s \tag{156}$$

$$\left(\frac{\partial v}{\partial T}\right)_P = \frac{C_P}{T}\left(\frac{\partial T}{\partial P}\right)_s \tag{157}$$

APPENDIX B

APPLICATION OF NEWTON-RAPHSON METHOD TO SOLVE FOR MOLE NUMBERS AND TEMPERATURE

This appendix applies the Newton-Raphson method to equations 39, 40, 41, 42, 44, 45, and 46 to linearize the original non-linear equations that are used to solve for the mole numbers, N_i, and the temperature, T.

1. Equilibrium equation

$$F_i = 0 = \left(\frac{\Delta \bar{G}_T{}^0}{\bar{R}T}\right)_i + \ln P_i - a_i \ln P_z - b_i \ln P_y - c_i \ln P_x \ldots. \tag{158}$$

$\Delta F_i = 0 - F_i$ for the right solution $F_i = 0$, otherwise F_i has a value

$$\Delta F_i = \frac{\partial F_i}{\partial A}\Delta A + \frac{\partial F_i}{\partial P_i}\Delta P_i + \frac{\partial F_i}{\partial T}\Delta T$$

$$\frac{\partial F_i}{\partial A} = 0$$

$$\frac{\partial F_i}{\partial P_i} = \frac{1}{P_i}; \quad \frac{\partial F_i}{\partial P_z} = -\frac{a_i}{P_z}; \quad \frac{\partial F_i}{\partial P_y} = -\frac{b_i}{P_y}; \quad \frac{\partial F_i}{\partial P_x} = -\frac{c_i}{P_x}$$

$$\frac{\partial F_i}{\partial T} = \frac{\partial}{\partial T}\left(\frac{\Delta \bar{G}_T{}^0}{\bar{R}T}\right)_i = \frac{\partial}{\partial T}\left(\frac{\Delta \bar{H}_T{}^0 - \Delta T\bar{S}^0}{\bar{R}T}\right)_i = \left(-\frac{\Delta \bar{H}_T{}^0}{\bar{R}T^2}\right)_i$$

$$\Delta F_i = \frac{1}{P_i}\Delta P_i - \frac{a_i}{P_z}\Delta P_z - \frac{b_i}{P_y}\Delta P_y - \frac{c_i}{P_x}\Delta P_x - \ldots. - \left(\frac{\Delta \bar{H}_T{}^0}{\bar{R}T^2}\right)_i \Delta T$$

$$\Delta F_i = \Delta \ln P_i - a_i \Delta \ln P_z - b_i \Delta \ln P_y - c_i \Delta \ln P_x - \ldots. - \left(\frac{\Delta \bar{H}_T{}^0}{\bar{R}T}\right)_i \Delta \ln T \tag{159}$$

When a condensed product is formed, the partial pressure must be neglected due to the section entitled "condensed phases." The equilibrium equation for condensed phases yields:

$$\Delta F_i = -a_i \Delta \ln P_z - b_i \Delta \ln P_y - c_i \Delta \ln P_x - \ldots. - \left(\frac{\Delta \bar{H}_T{}^0}{\bar{R}T}\right)_i \Delta \ln T \tag{160}$$

2. Mass balance equation for element Z

$$F_a = a_{tot} = \frac{1}{A}\sum_{i=1}^{115} a_i N_i \tag{161}$$

$a_{tot} = a_o$ for the correct solution

$$\Delta F_a = a_o - \frac{1}{A} \sum_{i=1}^{115} a_i N_i$$

$$\Delta F_a = \frac{\partial F_a}{\partial A} \Delta A + \frac{\partial F_a}{\partial N_i} \Delta N_i + \frac{\partial F_a}{\partial T} \Delta T$$

$$\frac{\partial F_a}{\partial A} = -\frac{1}{A^2} \sum_{i=1}^{115} a_i N_i$$

$$\frac{\partial F_a}{\partial P_i} = \frac{\partial F_a}{\partial N_i} = \frac{1}{A} \sum_{i=1}^{115} a_i$$

$$\frac{\partial F_a}{\partial T} = 0$$

$$\Delta F_a = -\left(\frac{1}{A^2} \sum_{i=1}^{115} a_i N_i\right) \Delta A + \left(\frac{1}{A} \sum_{i=1}^{115} a_i\right) \Delta N_i$$

$$\Delta F_a = -\frac{1}{A} \sum_{i=1}^{115} a_i N_i \,\Delta \ln A + \frac{1}{A} \sum_{i=1}^{115} a_i N_i \,\Delta \ln N_i \qquad (162)$$

3. Pressure equation

$$F_P = P = \sum_{i=1}^{110} P_i \qquad (163)$$

$P = P_o$ for the correct solution

$$\Delta F_P = P_o - \sum_{i=1}^{110} P_i$$

$$\Delta F_P = \frac{\partial F_P}{\partial A} \Delta A + \frac{\partial F_P}{\partial P_i} \Delta P_i + \frac{\partial F_P}{\partial T} \Delta T$$

$$\frac{\partial F_P}{\partial A} = 0$$

$$\frac{\partial F_P}{\partial P_i} = \sum_{i=1}^{110} 1$$

$$\frac{\partial F_P}{\partial T} = 0$$

$$\Delta F_P = \sum_{i=1}^{110} 1 \; \Delta P_i = \sum_{i=1}^{110} P_i \, \Delta \ln P_i \qquad (164)$$

The summation of partial pressures can only be performed for the gaseous products because the partial pressures for condensed phases have to be neglected.

4. Enthalpy equation

$$F_H = H = \frac{1}{A} \sum_{i=1}^{115} (\bar{H}_T^{\,0}) N_i \qquad (165)$$

$H = H_o$ for the correct solution

$$\Delta F_H = H_o - \frac{1}{A} \sum_{i=1}^{115} (\bar{H}_T^{\,0})_i N_i$$

$$\Delta F_H = \frac{\partial F_H}{\partial A} \Delta A + \frac{\partial F_H}{O N_i} \Delta N_i + \frac{\partial F_H}{\partial T} \Delta T$$

$$\frac{\partial F_H}{\partial A} = - \frac{1}{A^2} \sum_{i=1}^{115} (\bar{H}_T^{\,0})_i N_i$$

$$\frac{\partial F_H}{\partial P} = \frac{\partial F_H}{\partial N} = \frac{1}{A} \sum_{i=1}^{115} (\bar{H}_T{}^0)_i$$

$$\frac{\partial F_H}{\partial T} = \frac{\partial}{\partial T} \sum_{i=1}^{115} (\bar{H}_T{}^0)_i N_i = \frac{\partial}{\partial T} \sum_{i=1}^{115} \left(\int \bar{C}_P{}^0 \, dT \right)_i N_i = \sum_{i=1}^{115} (\qquad)_i N_i$$

$$\Delta F_H = - \frac{1}{A^2} \sum_{i=1}^{115} (\bar{H}_T{}^0)_i N_i \, \Delta A + \frac{1}{A} \sum_{i=1}^{115} (\bar{H}_T{}^0)_i \Delta N_i$$

$$+ \sum_{i=1}^{115} (\bar{C}_P{}^0)_i N_i \, \Delta T$$

$$\Delta F_H = - \frac{1}{A} \sum_{i=1}^{115} (\bar{H}_T{}^0)_i N_i \, \Delta \ln A + \frac{1}{A} \sum_{i=1}^{115} (\bar{H}_T{}^0)_i N_i \, \Delta \ln N_i$$

$$+ T \sum_{i=1}^{115} (\bar{C}_P{}^0)_i N_i \, \Delta \ln T \qquad (166)$$

5. Entropy equation for gaseous products

$$F_S = S = \frac{1}{A} \sum_{i=1}^{110} [(\bar{S}_T{}^0)_i - \bar{R} \ln P_i] N_i \qquad (167)$$

S = SO for the correct solution

$$\Delta F_S = SO - \frac{1}{A} \sum_{i=1}^{110} [(\bar{S}_T{}^0)_i - \bar{R} \ln P_i] N_i$$

$$\Delta F_S = \frac{\partial F_S}{\partial A} \Delta A + \frac{\partial F_S}{\partial P_i} \Delta P_i + \frac{\partial F_S}{\partial T} \Delta T$$

$$\frac{\partial F_S}{\partial A} = -\frac{1}{A^2} \sum_{i=1}^{110} \left[(\bar{S}_T{}^0)_i - \bar{R} \ln P_i \right] N_i$$

$$\frac{\partial F_S}{\partial P_i} = \frac{\partial F_S}{\partial N_i} = \frac{1}{A} \sum_{i=1}^{110} (\bar{S}_T{}^0)_i - \left[\frac{1}{A} \left(\sum_{i=1}^{110} \bar{R} \ln P_i + N_i \sum_{i=1}^{110} \bar{R} \frac{1}{P_i} \right) \right]$$

$$\frac{\partial F_S}{\partial T} = \frac{\partial}{\partial T} \left(\frac{1}{A} \sum_{i=1}^{110} N_i \int \left(\frac{\bar{C}_P{}^0}{T} \right)_i \partial T \right) = \frac{1}{A} \sum_{i=1}^{110} N_i \left(\frac{\bar{C}_P{}^0}{T} \right)_i$$

$$\Delta F_S = -\frac{1}{A^2} \sum_{i=1}^{110} \left[(\bar{S}_T{}^0)_i - \bar{R} \ln P_i \right] N_i \, \Delta A + \frac{1}{A} \left[\sum_{i=1}^{110} (\bar{S}_T{}^0)_i \, \Delta N_i - \sum_{i=1}^{110} \bar{R} \ln P_i \, \Delta N_i - \sum_{i=1}^{110} N_i \frac{\bar{R}}{P_i} \Delta P_i \right] + \frac{1}{A} \sum_{i=1}^{110} N_i \left(\frac{\bar{C}_P{}^0}{T} \right)_i \Delta T$$

$$\Delta F_S = -\frac{1}{A} \sum_{i=1}^{110} \left[(\bar{S}_T{}^0)_i - \bar{R} \ln P_i \right] N_i \, \Delta \ln A + \frac{1}{A} \left[\sum_{i=1}^{110} (\bar{S}_T{}^0)_i N_i \, \Delta \ln N_i - \sum_{i=1}^{110} \bar{R} N_i \ln P_i \, \Delta \ln N_i - \sum_{i=1}^{110} \bar{R} N_i \, \Delta \ln P_i \right] + \frac{1}{A} \sum_{i=1}^{110} N_i (\bar{C}_P{}^0)_i \, \Delta \ln T \qquad (168)$$

For condensed phases, the partial pressures must be neglected. The entropy equation is then

$$S = \frac{1}{A} \sum_{i=111}^{115} (\bar{S}_T{}^0)_i N_i \qquad (169)$$

Applying the Newton-Raphson method, we finally obtain:

$$\Delta F_S = \frac{1}{A} \sum_{i=111}^{115} N_i (\bar{C}_P{}^0)_i \Delta \ln T + \frac{1}{A} \sum_{i=111}^{115} N_i (\bar{S}_T{}^0)_i \Delta \ln N_i - \frac{1}{A} \sum_{i=111}^{115} (\bar{S}_T{}^0)_i N_i \Delta \ln A \tag{170}$$

APPENDIX C

APPLICATION OF NEWTON-RAPHSON METHOD TO SOLVE PARTIAL DERIVATIVES FOR CONSTANT PRESSURE AND TEMPERATURE

This appendix applies the Newton-Raphson method to equations 39, 40, 41, 42, 44, 45 and 46 to linearize them so that the partial derivatives for constant pressure and temperature can be solved easily.

Derivatives at Constant Pressure

1. Equilibrium equations considering gaseous compounds expressed by partial derivatives at constant pressure:

$$0 = \left(\frac{\Delta\overline{G}_T{}^0}{\overline{R}T}\right)_i + \ln P_i - a_i \ln P_z - b_i \ln P_y - c_i \ln P_x - \dots \qquad (171)$$

$$0 = d\left(\frac{\Delta\overline{G}_T{}^0}{\overline{R}T}\right)_i + d\ln P_i - a_i\, d\ln P_z - b_i\, d\ln P_y - c_i\, d\ln P_x - \dots$$

$$0 = \frac{d\left(\frac{\Delta\overline{G}_T{}^0}{\overline{R}T}\right)_i}{d\ln T} + \frac{d\ln P_i}{d\ln T} - a_i \frac{d\ln P_z}{d\ln T} - b_i \frac{d\ln P_y}{d\ln T} - c_i \frac{d\ln P_x}{d\ln T} - \dots$$

$$\frac{d}{d\ln T}\left(\frac{\Delta\overline{G}_T{}^0}{\overline{R}T}\right)_i = \frac{d}{\frac{dT}{T}}\left(\frac{\Delta\overline{G}_T{}^0}{\overline{R}T}\right) = T\frac{d}{dT}\left(\frac{\Delta\overline{H}_T{}^0 - \Delta T\overline{S}^0}{\overline{R}T}\right)_i$$

$$= T\frac{d}{dT}\left(\frac{\Delta\overline{H}_T{}^0}{\overline{R}T}\right)_i = T\left(\frac{\Delta\overline{H}_T{}^0}{\overline{R}T}\right)(-1)\,T^{-2} = -\left(\frac{\Delta\overline{H}_T{}^0}{\overline{R}T}\right)_i$$

$$0 = -\left(\frac{\Delta\overline{H}_T{}^0}{\overline{R}T}\right)_i + \frac{d\ln P_i}{d\ln T} - a_i \frac{d\ln P_z}{d\ln T} - b_i \frac{d\ln P_y}{d\ln T} - c_i \frac{d\ln P_x}{d\ln T} - \dots \qquad (172)$$

2. For condensed phases the equation is identical except that the term

$$\frac{d\ln P_i}{d\ln T} = 0$$

$$0 = -\left(\frac{\Delta\overline{H}_T{}^0}{\overline{R}T}\right)_i - a_i \frac{d\ln P_z}{d\ln T} - b_i \frac{d\ln P_y}{d\ln T} - c_i \frac{d\ln P_x}{d\ln T} - \dots \qquad (173)$$

3. Mass balance equation expressed by partial derivatives at constant pressure:

$$a_o = \frac{1}{A}\sum_{i=1}^{115} a_i N_i \qquad (174)$$

$$0 = -a_o A + \sum_{i=1}^{115} a_i N_i$$

$$0 = -a_o dA - A \cancelto{0}{da_o} + \sum_{i=1}^{115} a_i dN_i + \sum_{i=1}^{115} \cancelto{0}{N_i da_i}.$$

da_o and da_i cannot change since mass is constant.

$$0 = -a_o A \, d\ln A \, \ldots. + \sum_{i=1}^{115} a_i N_i \, d\ln N_i$$

$$0 = -a_o A \frac{d\ln A}{d\ln T} \ldots. + \sum_{i=1}^{115} a_i N_i \frac{d\ln N_i}{d\ln T}$$

or

$$0 = -\sum_{i=1}^{115} a_i N_i \, d\ln A + \sum_{i=1}^{115} a_i N_i \, d\ln N_i$$

$$0 = -\sum_{i=1}^{115} a_i N_i \frac{d\ln A}{d\ln T} + \sum_{i=1}^{115} a_i N_i \frac{d\ln N_i}{d\ln T} \tag{175}$$

4. Total pressure equation expressed by partial derivatives at constant pressure:

$$P = \sum_{i=1}^{110} P_i \tag{176}$$

$$\frac{\partial P}{\partial P} dP = \frac{\partial \sum_{i=1}^{110} P_i}{\partial P_i} dP_i$$

Applying the mathematical concept

$$\frac{d\ln x}{dx} = \frac{1}{x}$$

or

$$dx = x \, d \ln x$$

we obtain

$$\sum_{i=1}^{110} P_i \, d \ln P_i = P \, d \ln P$$

at constant total pressure the d ln P term is equal to zero.

$$P \, d \ln P = 0$$

Dividing the equation by d ln T it follows

$$0 = \sum_{i=1}^{110} P_i \frac{d \ln P_i}{d \ln T} \tag{177}$$

Derivatives at Constant Temperature

5. Equilibrium equations expressed by partial derivatives at constant temperature:

$$0 = \left(\frac{\Delta \overline{G}_T{}^0}{\overline{R}T}\right)_i + \ln P_i - a_i \ln P_z - b_i \ln P_y - c_i \ln P_x - \ldots . \tag{178}$$

$$0 = d\left(\frac{\Delta \overline{G}_T{}^0}{\overline{R}T}\right)_i + d \ln P_i - a_i \, d \ln P_z - b_i \, d \ln P_y - c_i \, d \ln P_x - \ldots .$$

$$0 = \frac{d\left(\frac{\Delta \overline{G}_T{}^0}{\overline{R}T}\right)_i}{d \ln A} + \frac{d \ln P_i}{d \ln A} - a_i \frac{d \ln P_z}{d \ln A} - b_i \frac{d \ln P_y}{d \ln A} - c_i \frac{d \ln P_x}{d \ln A}$$

$$- \frac{d\left(\frac{\Delta \overline{G}_T{}^0}{\overline{R}T}\right)_i}{d \ln A} = 0$$

$$\left(\left(\frac{\Delta \overline{G}_T{}^0}{\overline{R}T}\right)_i \text{ is only a function of temperature}\right)$$

$$0 = \frac{d \ln P_i}{d \ln A} - a_i \frac{d \ln P_z}{d \ln A} - b_i \frac{d \ln P_y}{d \ln A} - c_i \frac{d \ln P_x}{d \ln A} \tag{179}$$

6. Mass balance equations expressed by partial derivatives at constant temperature:

$$A\, a_o = \sum_{i=1}^{115} a_i N_i \tag{180}$$

$$0 = -A\, a_o + \sum_{i=1}^{115} a_i N_i \ .$$

Since $N_i = P_i$ we obtain

$$A \frac{\partial a_o}{\partial a_o} da_o + a_o \frac{\partial A}{\partial A} dA = \sum_{i=1}^{115} a_i \frac{\partial N_i}{\partial N_i} dP_i + \sum_{i=1}^{115} N_i \frac{\partial a_i}{\partial a_i} da_i \ .$$

Because of the constancy of elements

$$da_o = 0$$

$$da_i = 0 \ .$$

Dividing the equation by d ln A and applying the following mathematical concept

$$\frac{d \ln x}{dx} = \frac{1}{x}$$

or

$$dx = x\, d \ln x$$

the result is

$$0 = -a_o A \frac{d \ln A}{d \ln A} + \sum_{i=1}^{115} a_i N_i \frac{d \ln P_i}{d \ln A}$$

$$0 = -a_o A + \sum_{i=1}^{115} a_i N_i \frac{d \ln P_i}{d \ln A} \tag{181}$$

APPENDIX D

DERIVATION OF THE CHANGE IN MOLECULAR WEIGHT AS A FUNCTION OF PRESSURE AND TEMPERATURE

Performing a mass balance due to the reaction equation.

$$A[N_F(Z_{aF}, Y_{bF}, X_{cF}, \ldots) + N\ (Z_{a\theta}, Y_{b\theta}, X_{c\theta}, \ldots)]$$

$$= \Sigma N_i(Z_{ai}, Y_{bi}, X_{ci} \ldots) \tag{182}$$

we find for each element

$$A(N_F a_F + N_\theta a_\theta) L_Z = \Sigma N_i a_i L_Z \tag{183}$$

$$A(N_F b_F + N_\theta b_\theta) L_Y = \Sigma N_i b_i L_Y$$

$$A(N_F c_F + N_\theta c_\theta) L_X = \Sigma N_i c_i L_X$$

$$A[N_F(a_F L_Z + b_F L_Y + c_F L_X + \ldots) + N_\theta (a_\theta L_Z + b_\theta L_Y + c_\theta L_X$$

$$+ \ldots)] = \Sigma N_i (a_i L_Z + b_i L_Y + c_i L_X + \ldots) .$$

In general the molecular weight is defined as

$$M_i = a_i L_Z + b_i L_Y + c_i L_X + \ldots \quad . \tag{184}$$

In a reaction process, the mole numbers and the molecular weights of the reactants are known. This means the relative mass is a constant. The mass balance equation reads now

$$A\ m_r = \sum_{i=1}^{115} N_i M_i \quad .$$

Very often the mole numbers of the reactants are determined so that the total mass of the reactants is equal to one. In this case, $m_r = 1$.

An average molecular weight can be defined for a mixture as

$$NM = \sum_{i=1}^{115} N_i M_i$$

$$M = \frac{\sum_{i=1}^{115} N_i M_i}{N} \quad .$$

With $N = \sum_{i=1}^{110} N_i = \sum_{i=1}^{110} P_i = P$ (neglecting the volume of the condensed products) and the total mass of the products equal to the total mass of the reactants, we obtain

$$M = \frac{A\, m_r}{P} \quad . \tag{185}$$

Rewriting this equation in a logarithmic form and differentiating with respect to ln T results in

$$\frac{d \ln M}{d \ln T} = \frac{d \ln A}{d \ln T} + \frac{d \ln m_r}{d \ln T} - \frac{d \ln P}{d \ln T} \quad .$$

Since the mass, m_r, will not change,

$$\frac{d \ln m_r}{d \ln T} = 0 \quad .$$

For a constant pressure process, P does not change and

$$\frac{d \ln P}{d \ln T} = 0 \quad .$$

Finally we obtain

$$\left(\frac{d \ln M}{d \ln T}\right)_P = \left(\frac{d \ln A}{d \ln T}\right)_P \quad . \tag{186}$$

Starting again from equation (185) in logarithmic form but now differentiating with respect to ln P yields

$$\frac{d \ln M}{d \ln P} = \frac{d \ln A}{d \ln P} + \frac{d \ln m_r}{d \ln P} - \frac{d \ln P}{d \ln P} \quad .$$

Due to the constancy of mass

$$\frac{d \ln m_r}{d \ln P} = 0 \ .$$

The final result is

$$\frac{d \ln M}{d \ln P} = \frac{d \ln A}{d \ln P} - 1$$

and can also be applied to a constant temperature process

$$\left(\frac{d \ln M}{d \ln P}\right)_T = \left(\frac{d \ln A}{d \ln P}\right)_T - 1$$

APPENDIX E

CONSTANTS AND CONVERSION FACTORS

R	$\left[\frac{\text{cal}}{\text{mole}^{\circ}\text{K}}\right]$	1.98726	Universal gas constant
E	$\left[\text{—}\right]$	2.7182818285	Euler number
KE	$\left[\frac{\text{ft}}{\text{sec}^2}\right]$	32.1740	Gravitational constant at sea level
1 Kcal	$\equiv$	3087.16928168	ft/lb
1 Kg	$\equiv$	2.2046	lb
1 atm	$\equiv$	14.696	$\frac{\text{lb}}{\text{in}^2}$

APPENDIX F

NOMENCLATURE FOR CALCULATION PROGRAM

A	[g]	Multiplier in reaction equation to make the partial pressures and mole numbers numerically equal
ACC	[in^2]	Injector plate area
AISP	[sec]	Local specific impulse
AISPX AISPY AISPZ	[sec]	Previous values of AISP during iteration for maximum specific impulse at constant chamber pressure
AISPM	[sec]	Maximum specific impulse
AISPRA	[sec]	Real specific impulse at predetermined altitude
AISPRV	[sec]	Real vacuum specific impulse
ALPHA	[—]	Mole per cent value of oxidizer A in a mixture
AMNF	[mole]	Mole number of the fuel, determined as one (1)
AMNFS	[mole]	Mole number of the fuel to yield a molecular weight of one (1) for the propellants
AMNΘ	[mole]	Mole number of the oxidizer to satisfy the required mixture ratio of the propellants by weight
AMNΘS	[mole]	Mole number of the oxidizer to yield a molecular weight of one (1) for the propellants, considering also the desired mixture ratio by weight
AMNR$_i$	[—]	Mole ratios of the combustion products
AMRW	[—]	Mixture ratio by weight
AMRWD	[—]	Chosen mixture ratio increment for iteration on maximum specific impulse at constant chamber pressure

AMRWL	[—]	Original mixture ratio by weight to determine the PERCT value for thrust level uprating
AMRWM	[—]	Optimum mixture ratio by weight yielding maximum specific impulse for considered chamber pressure
AMRWS	[—]	Stoichiometric mixture ratio
AMRWX AMRWY AMRWZ	[—]	Previous values of AMRW during iteration for maximum specific impulse at constant chamber pressure
AMW	$\left[\frac{g}{mole}\right]$	Average molecular weight per mole of gaseous products
AMWP	[g]	Relative mass of propellants for the required mixture ratio
AMWR	[—]	Relative mass of the reaction products defined as one (1)
ANA ANB AND ANG	$\left[\frac{g}{mole}\right]$	Number of Nitrogen gram atoms in oxidizer A and B, and Fuel G and D
AN_i	$\left[\frac{g}{mole}\right]$	Number of gram atoms in the combustion products
AS	$[in^2]$	Throat area
ATWC ATWF ATWH ATWHE ATWN ATWO ATWU ATWX ATWY ATWZ	[—]	Atomic weight of Carbon, Fluorine, Hydrogen, Helium, Nitrogen, Oxygen, with U, X, Y, Z as available spaces for other elements
BETA	[—]	Mole per cent value of oxidizer B in a mixture
C_i	$\left[\frac{g}{mole}\right]$	Number of carbon gram atoms in the combustion products
C*	$\left[\frac{ft}{sec}\right]$	Characteristic velocity

CA CB CD CG	$\left[\frac{\text{g}}{\text{mole}}\right]$	Number of carbon gram atoms in oxidizer A and B, and fuel G and D
CF	[—]	Local thrust coefficient
CFA	[—]	Thrust coefficient at predetermined altit
CFRA	[—]	Real thrust coefficient at predetermined altitude
CFRV	[—]	Real vacuum thrust coefficient
CFV	[—]	Vacuum thrust coefficient
CK_1		Conversion factor
CK_2		Conversion factor
CK_3		Conversion factor
CK_4		Conversion factor
CN_i	[mole]	Mole numbers of the combustion products
CNS	[mole]	Summation of the mole numbers of the combustion products
CNSMCP	[mole]	Summation of the mole numbers of the gaseous combustion products only
CONVER	[—]	Error left in the iteration process due to the approximated values
CP_i	$\left[\frac{\text{cal}}{\text{mole}^\circ\text{K}}\right]$	Specific heat at constant pressure of the individual combustion products
CPP	$\left[\frac{\text{cal}}{\text{mole}^\circ\text{K}}\right]$	Specific heat at constant pressure considering all combustion products
C*R	$\left[\frac{\text{ft.}}{\text{sec}}\right]$	Real characteristic velocity
CRS	[—]	Local isentropic exponent
CRSS	[—]	Isentropic exponent in the throat area
CVV	$\left[\frac{\text{cal}}{\text{mole}^\circ\text{K}}\right]$	Specific heat at constant volume considering all combustion products
DELTA	[—]	Mole per cent value of fuel D in a mixture

DH_i	[—]	Enthalpy difference between the combustion products and the elements from which they are formed. All values divided by $R \cdot T$
DlnA	[—]	Finite difference of the logarithm of the reaction equation multiplier.
$DlnP_i$	[—]	Finite differences of the natural logarithm of the partial pressures (mole mumbers)
DPA	[—]	Change of molecular weight as a function of temperature at constant pressure
DPM	[—]	Change of molecular weight as a function of temperature at constant pressure
DPP_i	[—]	Partial derivatives $\left(\frac{\partial \ln P_i}{\partial \ln T}\right)_P$ at constant pressure
DQ_i	[—]	Constant term in the equilibrium equation
DTM	[—]	Change of molecular weight as a function of pressure at constant temperature
DTP_i	[—]	Partial derviatives $\left(\frac{\partial \ln P_i}{\partial \ln A}\right)_T$ at constant temperature
E	[—]	Euler number (2.7182818285)
EQUIVR	[—]	Equivalence ratio; mixture ratio divided by the stoichiometric mixture ratio
ETAC*	[—]	Correction coefficient for the characteristic velocity
ETACFV	[—]	Correction coefficient for the vacuum thrust coefficient
ETAW	[—]	Correction coefficient for the mass flow rate.
EXPR	[—]	Expansion ratio
EXPRL	[—]	Required expansion ratio
F_i	$\left[\frac{g}{mole}\right]$	Number of fluorine gram atoms in the combustion products

FA FB FD FG	$\left[\frac{\text{g}}{\text{mole}}\right]$	Number of fluorine gram atoms in oxidizer A and B and fuel D and G .
FL	[lb]	Desired thrust level
FROZ	[—]	Switch constant for frozen equilibrium
FT	[lb]	Local theoretical thrust
FTA	[lb]	Theoretical thrust at predetermined altitude
FTRA	[lb]	Real thrust at predetermined altitude
FTRV	[lb]	Real vacuum thrust
FTV	[lb]	Theoretical vacuum thrust
FX FY	[lb]	Previous values for FTRA during iteration for desired thrust level
GAMMA	[—]	Mole per cent value of fuel G in a mixture
H	[cal]	Enthalpy of all combustion products
H_i	$\left[\frac{\text{g}}{\text{mole}}\right]$	Number of hydrogen gram atoms in the combustion products
HA HB HD HG	$\left[\frac{\text{g}}{\text{mole}}\right]$	Number of hydrogen gram atoms in oxidizer A and B, and fuel D and G
HE_i	$\left[\frac{\text{g}}{\text{mole}}\right]$	Number of helium gram atoms in the combustion products
HEA HEB HED HEG	$\left[\frac{\text{g}}{\text{mole}}\right]$	Number of helium gram atoms in oxidizer A and B, and fuel D and G
HO	$\left[\frac{\text{cal}}{\text{g}}\right]$	Enthalpy of the propellants
HT_i	$\left[\frac{\text{cal}}{\text{mole}}\right]$	Molar enthalpy of the combustion products
HTFD HTFG	$\left[\frac{\text{cal}}{\text{mole}}\right]$	Enthalpy of fuel D and G at normal boiling point or at $T = 298.15^{\circ}$ K

HTΘA HTΘB	$\left[\frac{\text{cal}}{\text{mole}}\right]$	Enthalpy of oxidizer A and B at normal boiling point or at T = 298.15° K
IA	[—]	Switch constant for throat area calculation
IB	[—]	Switch constant within the throat area calculation
IC	[—]	Switch constant considering either calculation at a required expansion ratio or many local conditions downstream of the chamber
ID	[—]	Switch constant considering static pressures in a chosen range
IE	[—]	Switch constant considering static pressures in a chosen range
IF	[—]	Switch constant considering static pressures in a chosen range
IG	[—]	Switch constant considering the calculation of a desired thrust level
IH	[—]	Switch constant considering the calculation of a maximum specific impulse
II	[—]	Switch constant within the calculation routine for maximum specific impulse
IJ	[—]	Switch constant within the calculation routine for maximum specific impulse
IK	[—]	Switch constant considering the difference between an optimum and required mixture ratio
IL	[—]	Switch constant considering a combination of a desired thrust level and a maximum specific impulse
IM	[—]	Switch constant within the desired thrust level calculation routine
K	[—]	Test constants
KE	$\left[\frac{\text{ft}}{\text{sec}^2}\right]$	Gravitational constant at sea level, 32.174
KF	$\left[\frac{\text{g}}{\text{mole}}\right]$	Molecular weight of fuel
KΘ	$\left[\frac{\text{g}}{\text{mole}}\right]$	Molecular weight of oxidizer

$KK1_i$ $KK2_i$ $KK3_i$ $KK4_i$ $KK5_i$ $KK6_i$ $KK7_i$	$\left[— \right]$	Polynomial coefficients for calculation of enthalpy, entropy, and specific heat at constant pressure
θ_i	$\left[\frac{g}{mole}\right]$	Number of oxygen gram atoms in the combustion products
θA θB θD θG	$\left[\frac{g}{mole}\right]$	Number of oxygen gram atoms in oxidizer A and B, and fuel D and G
P	$[atm]$	Local static pressure of all combustion products
P_i	$[atm]$	Local partial pressures of the individual combustion products
PC	$[atm]$	combustion chamber end stagnation pressure
PAM	$[atm]$	Ambient pressure at considered altitude
PCM	$[atm]$	Optimum combustion chamber end stagnation pressure which belongs to a required thrust level yielding maximum specific impulse
PERCT	$\left[— \right]$	Percent value considering the deviation in mixture ratio off the optimum value yielding maximum specific impulse
PO	$[atm]$	Predetermined local static pressure of the combustion products
PS	$[atm]$	Static pressure of the combustion products in the throat area
PSUM	$[atm]$	Local static pressure of all combustion products
PX PY	$[atm]$	Previous values for PC during iteration on desired thrust level
R	$\left[\frac{cal}{mole\ ^{o}K}\right]$	Universal gas constant 1.98726
RS	$\left[\frac{cal}{g \cdot {}^{o}K}\right]$	Specific gas constant for all combustion products

RSS	$\left[\frac{cal}{g \cdot {}^{o}K}\right]$	Specific gas constant for all combustion products in the throat area.
S	$\left[\frac{cal}{g\,{}^{o}K}\right]$	Entropy of all combustion products
SHIFT	$\left[\text{—}\right]$	Switch constant considering shifting equilibrium calculation
SO	$\left[\frac{cal}{g\,{}^{o}K}\right]$	Calculated entropy value which is considered in the isentropic expansion process
ST_i	$\left[\frac{cal}{mole\ {}^{o}K}\right]$	Molar entropy of the combustion products
T	$\left[{}^{o}K\right]$	Temperature
TL	$\left[{}^{o}K\right]$	Temperature limit counsidering the transition from shifting to frozen equilibrium calculation procedure
TC	$\left[{}^{o}K\right]$	Theoretical combustion chamber temperature
TS	$\left[{}^{o}K\right]$	Theoretical static temperature in the throat area
Tang α	$\left[\text{—}\right]$	Slope of the secant for maximum specific impulse calculation.
U_i	$\left[\frac{g}{mole}\right]$	Number of gram atoms for an element (to be determined) in the combustion products
UA UB UD UG	$\left[\frac{g}{mole}\right]$	Number of gram atoms for an element (to be determined) in oxidizer A and B, and fuel D and G
V	$\left[\frac{ft}{sec}\right]$	Local velocity
VC	$\left[\text{—}\right]$	Most common valence of carbon
VF		Fluorine
VH		Hydrogen
VHE		Helium
VN		Nitrogen
VO		Oxygen
VU		Element to be determined
VX		Element to be determined
VY		Element to be determined
VZ		Element to be determined
VS	$\left[\frac{ft}{sec}\right]$	Local speed of sound

VSS	$\left[\frac{ft}{sec}\right]$	Speed of sound in the throat area
W	$\left[\frac{lb}{sec}\right]$	Theoretical weight flow rate
WR	$\left[\frac{lb}{sec}\right]$	Real weight flow rate
X_i	$\left[\frac{g}{mole}\right]$	Number of gram atoms for an element (to be considered) in the combustion products
XA XB XD XG	$\left[\frac{g}{mole}\right]$	Number of gram atoms for an element (to be considered) in oxidizer A and B and fuel D and G
Y_i	$\left[\frac{g}{mole}\right]$	Number of gram atoms for an element (to be considered) in the combustion products
YA YB YD YG	$\left[\frac{g}{mole}\right]$	Number of gram atoms for an element (to be considered) in oxidizer A and B and fuel D and G
Z_i	$\left[\frac{g}{mole}\right]$	Number of gram atoms for an element (to be considered) in the combustion products
ZA ZB ZD ZG	$\left[\frac{g}{mole}\right]$	Number of gram atoms of an element (to be considered) in oxidizer A and B and fuel D and G
0C 0F 0H 0HE 0N 0θ 0U 0X 0Y 0Z	[—]	Number of gram atoms yielding a relative mass of one (1) for the propellants considering carbon, fluorine, hydrogen, helium, nitrogen, oxygen, and elements to be determined (U, X, Y, Z)
1C 1F 1H 1HE 1N 1θ 1U 1X 1Y 1Z	[—]	Number of gram atoms yielding a relative mass of one (1) for the combustion products, considering carbon, fluorine, hydrogen, helium, nitrogen, oxygen and elements to be determined (U, X, Y, Z)

APPENDIX G

CALCULATION PROGRAM

In this section the complete calculation procedure is documented. Input data, determination of chemical elements and compounds, equations, tests, option to solve for various desired conditions and output data are listed. The simplified flow chart in Appendix H shows the arrangement of all equations and tests.

The computer listing and pertinent flow charts are available and can be obtained on request from the author.

INPUT DATA

Oxidizer:
Fuel:
Frozen Equilibrium ☐ IFE = 1 IFETL = 0
Shifting Equilibrium ☐ IFE = 0 IFETL = 0
Combination of Shifting and Frozen Equilibrium ☐ IFE = 0 IFETL = 1
Number of Atoms in One Mole of:

Oxidizer A	Oxidizer B	Fuel G	Fuel D
CA =	CB =	CG =	CD =
FA =	FB =	FG =	FD =
HA =	HB =	HG =	HD =
HEA =	HEB =	HEG =	HED =
ANA =	ANB =	ANG =	AND =
θA =	θB =	θG =	θD =
UA =	UB =	UG =	UD =
XA =	XB =	XG =	XD =
YA =	YB =	YG =	YD =
ZA =	ZB =	ZG =	ZD =

ALPHA = [-] (mole per cent of Oxidizer A)
BETA = [-] (mole per cent of Oxidizer B)
GAMMA = [-] (mole per cent of Fuel G)
DELTA = [-] (mole per cent of Fuel D)

AMNF = 1 [-] (mole number of fuel defined as one)
AMRW = [-] (mixture ratio)
AMRWD = [-] (mixture ratio increment for max I_{sp} calculation)
AMRWL = [-] (mixture ratio to determine deviation from optimum m[illegible]ure ratio, in. %)
AMWR = 1 [-] (relative mass of reactants, defined as one)
A = [g] (assumed multiplier for reaction equation)
AS = [in^2] (throat area)
ACC = [in^2] (injector plate area)

ETACFV = [-](correction coefficient for CFV, or 1)
ETAC* = [-](correction coefficient for C*, or 1)
ETAW = [-](correction coefficient for W, or 1)
EXPRL = [-](desired expansion ratio)
FL = [lb](desired thrust level at altitude)

HT0A = [cal/mole](injection enthalpy of Oxidizer A at normal boiling point or 298.16 °K)
HT0B = [cal/mole](injection enthalpy of Oxidizer B at normal boiling point or 298.16 °K)
HTFG = [cal/mole](injection enthalpy of Fuel G at normal boiling point or 298.16 °K)
HTFD = [cal/mole](injection enthalpy of Fuel D at normal boiling point or 298.16 °K)

NEACS = [-](total number of combustion products)
NATS = [-](total number of gaseous atoms)
NCPDS = [-](total number of gaseous compounds)
NCPS = [-](total number of condensed phases)
NAT(I) = [-](elements considered, 1 - 10)
NEAC(I) = [-](identified number of combustion products, 1 - 115)

PAM = [atm](ambient pressure)
PO = [atm](combustion chamber end stagnation pressure)

T = [°K](assumed combustion chamber temperature)
TL = [°K](assumed temperature limit to switch from shifting to frozen equilibrium)

Assumed Partial Pressures of the Considered Combustion Products [atm]:

P = P = P = P = P =
P = P = P = P = P =
P = P = P = P = P =
P = P = P = P = P =
P = P = P = P = P =

Polynomial Coefficients to Calculate Thermodynamic Properties for the Considered Combustion Products:

I	KK1	KK2	KK3	KK4	KK5	KK6	KK7

IC = [-] (if 0, chamber, throat and exit conditions are calculated;
if 1, chamber, throat, intermediate and exit conditions are calculated)

IG = [-] (if 0, calculation on a desired thrust level is not performed;
if 1, iteration towards a desired thrust level for constant mixture ratio but changing chamber pressure)

IH = [-] (if 0, calculation on max ISP is not performed; with IG = 0
if 1, iteration towards max ISP at constant chamber pressure but varying mixture ratio with IG = 0)

IL = [-] (if 0, only max ISP calculation is performed with IG = 0 and IH = 1
if 1, iteration on desired thrust level with an ISP by PERCT off the maximum value considering a change in chamber pressure and mixture ratio, with IG = 0 and IH = 1)

PRINT IN FRONT OF THE OUTPUT

Propellant Combination:
Frozen or Shifting Equilibrium:
Compounds Used in the Combustion Process:
Elements Used in the Combustion Process:
Condensed Phase Used in the Combustion Process:

Input Data:

ALPHA	BETA	GAMMA	DELTA	AMRW
AMNF	PAM	AS	EXPRL	ETACFV
ETAC*	ETAW	HTθA	HTθB	HTFG
HTFD	PO	TL	AMWR	T
A	R	AKE	AMRWD	AMRWL
FL	ACC			

Switch Constants:

IC	IG	IH	IL

Constants:

$K1 = 0.1049466 \times 10^{-1}$, $K2 = 0.14696 \times 10^{2}$, $K3 = 0.3742099 \times 10^{2}$, $K4 = 0.5292127 \times 10^{2}$

Number of Atoms in the Oxidizer and Fuel Presently Used:

CA	CB	CG	CD
FA	FB	FG	FD
HA	HB	HG	HD
HEA	HEB	HEG	HED
ANA	ANB	ANG	AND
θA	θB	θG	θD
UA	UB	UG	UD
XA	XB	XG	XD
YA	YB	YG	YD
ZA	ZB	ZG	ZD

Atomic Weights of the Elements:

ATWC = 0.12011 x 10^2
ATWF = 0.19000 x 10^2
ATWH = 0.10080 x 10
ATWHE = 0.40030 x 10
ATWN = 0.14008 x 10^2
ATWθ = 0.16000 x 10^2
ATWU =
ATWX =
ATWY =
ATWZ =

Most Common Valences of the Elements:

VC = 4
VF = -1
VH = 1
VHE = 0
VN = 0
Vθ = -2
VU =
VX =
VY =
VZ =

PRINT AT EVERY CALCULATION POINT

AISP	AISPRA	AISPRV	AMNθ	AMRWS
AMW	C*	C*R	CF	CFA
CFV	CFRA	CFRV	CθNVER	CPP
CRS	CVV	EQUIVR	EXPR	FT
FTA	FTV	FTRA	FTRV	H
HO	PO	RS	S	SO
T	V	VS	W	WR
C*MRW				

Mole Ratios

Partial Pressures

COMBUSTION PRODUCTS

Elements Considered in Reaction Processes:

Number:	1	2	3	4	5	6	7	8	9	10
Element:	C	F	H	HE	AN	θ	U	X	Y	Z
Name:	Carbon	Fluorine	Hydrogen	Helium	Nitrogen	Oxygen				

Combustion Products are Composed of these Elements:

Gaseous Compounds

Number:	1	2	3	4	5	6	7	8	9
Formula:	CF	$CFH\theta$	CFH_3	CFN	CF_2	CF_2H_2	$CF_2\theta$	CF_3	CF_3H
Number:	10	11	12	13	14	15	16	17	18
Formula:	CF_4	CH	CHN	$CHN\theta$	$CH\theta$	CH_2	$CH_2\theta$	CH_3	CH_4
Number:	19	20	21	22	23	24	25	26	27
Formula:	CN	$C\theta$	$C\theta_2$	C_2	C_2F_2	C_2F_4	C_2H	C_2H_2	C_2H_4
Number:	28	29	30	31	32	33	34	35	36
Formula:	$C_2H_4\theta$	C_2H_6	C_2N_2	C_3	C_3H_4	C_3H_6	C_3H_8	$C_3\theta_2$	C_4
Number:	37	38	39	40	41	42	43	44	45
Formula:	C_4H_2	C_4H_6	C_4H_8	C_4H_{10}	C_4N_2	C_5	C_5H_8	C_6H_6	C_6H_6
Number:	46	47	48	49	50	51	52	53	54
Formula:	C_6H_{12}	C_8H_{10}	C_8H_{14}	$C_{12.5}H_{24.4125}$	FH	$FH\theta$	$F\theta$	FN	$FN\theta$
Number:	55	56	57	58	59	60	61	62	63
Formula:	F_2	F_2N	F_2N_2	F_3N	F_4N_2	HN	$HN\theta$	$H\theta$	H_2
Number:	64	65	66	67	68	69	70	71	72
Formula:	H_2N	$H_2\theta$	H_3N	H_4N_2	$N\theta$	$N\theta_2$	N_2	$N_2\theta_3$	$N_2\theta_4$

Number:	73	74	75	76	77	78	79	80	81
Formula:	$N_2\theta_5$	θ_2	θ_3						
Number:	82	83	84	85	86	87	88	89	90
Formula:									
Number:	91	92	93	94	95	96	97	98	99
Formula:									
Number:	100								
Formula:									

Gaseous Elements

Number:	101	102	103	104	105	106	107	108	109
Formula:	C	F	H	HE	AN	θ	U	X	Y
Number:	110								
Formula:	Z								

Condensed Phases

Number:	111	112	113	114	115
Formula:	C				

The vacant spaces in this table are available for additional elements, compounds, and condensed phases.

Limits of the matrix are presently:
30 gaseous compounds
10 gaseous elements
5 condensed phases

1. Molecular Weight of Oxidizer [g/mole]

2. Molecular Weight of Fuel [g/mole]

3. Mole Number of Oxidizer to Satisfy Desired Mixture Ratio [mole]
4. Relative Weight of Propellants for the Required Mixture Ratio [g]
5. Number of Gram Atoms Yielding a Relative Weight of One for the Propellants [-]

$$\begin{aligned}\mathrm{K\theta} = {} & \mathrm{ALPHA(CA \cdot ATWC + FA \cdot ATWF + HA \cdot ATWH + HEA \cdot ATWHE} \\ & \mathrm{+ ANA \cdot ATWN + \theta A \cdot ATW\theta + UA \cdot ATWU + XA \cdot ATWX + YA \cdot ATWY} \\ & \mathrm{+ ZA \cdot ATWZ) + BETA(CB \cdot ATWC + FB \cdot ATWF + HB \cdot ATWH} \\ & \mathrm{+ HEB \cdot ATWTHE + ANB \cdot ATWN + \theta B \cdot ATW\theta + UB \cdot ATWU} \\ & \mathrm{+ XB \cdot ATWX + YB \cdot ATWY + ZB \cdot ATWZ)}\end{aligned}$$

$$\begin{aligned}\mathrm{KF} = {} & \mathrm{GAMMA(CG \cdot ATWC + FG \cdot ATWF + HG \cdot ATWH + HEG \cdot ATWHE} \\ & \mathrm{+ ANG \cdot ATWN + \theta G \cdot ATW\theta + UG \cdot ATWU + XG \cdot ATWX + YG \cdot ATWY} \\ & \mathrm{+ ZG \cdot ATWZ) + DELTA(CD \cdot ATWC + FD \cdot ATWF + HD \cdot ATWH} \\ & \mathrm{+ HED \cdot ATWHE + AND \cdot ATWN + \theta D \cdot ATW\theta + UD \cdot ATWU + XD \cdot ATWX} \\ & \mathrm{+ YD \cdot ATWY + ZD \cdot ATWZ)}\end{aligned}$$

$$\mathrm{AMN\theta} = \frac{\mathrm{AMRW \cdot AMNF \cdot KF}}{\mathrm{K\theta}}$$

$$\mathrm{AMWP = AMNF \cdot KF + AMN\theta \cdot K\theta}$$

$$\mathrm{OC} = \frac{\mathrm{AMN\theta(ALPHA \cdot CA + BETA \cdot CB) + AMNF(GAMMA \cdot CG + DELTA \cdot CD)}}{\mathrm{AMWP}}$$

$$\mathrm{OF} = \frac{\mathrm{AMN\theta(ALPHA \cdot FA + BETA \cdot FB) + AMNF(GAMMA \cdot FG + DELTA \cdot FD)}}{\mathrm{AMWP}}$$

$$\mathrm{OH} = \frac{\mathrm{AMN\theta(ALPHA \cdot HA + BETA \cdot HB) + AMNF(GAMMA \cdot HG + DELTA \cdot HD)}}{\mathrm{AMWP}}$$

$$\mathrm{OHE} = \frac{\mathrm{AMN\theta(ALPHA \cdot HEA + BETA \cdot HEB) + AMNF(GAMMA \cdot HEG + DELTA \cdot HED)}}{\mathrm{AMWP}}$$

$$\mathrm{ON} = \frac{\mathrm{AMN\theta(ALPHA \cdot ANA + BETA \cdot ANB) + AMNF(GAMMA \cdot ANG + DELTA \cdot AND)}}{\mathrm{AMWP}}$$

$$\mathrm{O\theta} = \frac{\mathrm{AMN\theta(ALPHA \cdot \theta A + BETA \cdot \theta B) + AMNF(GAMMA \cdot \theta G + DELTA \cdot \theta D)}}{\mathrm{AMWP}}$$

$$\mathrm{OU} = \frac{\mathrm{AMN\theta(ALPHA \cdot UA + BETA \cdot UB) + AMNF(GAMMA \cdot UG + DELTA \cdot UD)}}{\mathrm{AMWP}}$$

$$\mathrm{OX} = \frac{\mathrm{AMN\theta(ALPHA \cdot XA + BETA \cdot XB) + AMNF(GAMMA \cdot XG + DELTA \cdot XD)}}{\mathrm{AMWP}}$$

6. Mole Number of Oxidizer to Yield Molecular Weight of One for Propellants [mole/g]

7. Mole Number of Fuel to Yield Molecular Weight of One for Propellants [mole/g]

8. Stochiometric Mixture Ratio [-]

9. Equivalence Ratio [-]

10. Enthalpy of Propellants [cal/g]

11. Test on T for Proper Selection of Temperature Ranges for Entropy, Enthalpy and Specific Heat Polynomials.

12. Local Enthalpy of the Combustion Compounds [cal/mole]
    i = 1 - 115

13. Local Specific Heat at Constant Pressure of the Combustion Compounds [cal/mole °K] i = 1 - 115

14. Local Entropy of the Combustion Compounds [cal/mole °K]
    i = 1 - 115

15. Test Whether Shifting or Frozen Equilibrium is Invoked

$$OY = \frac{AMN\theta(ALPHA \cdot YA + BETA \cdot YB) + AMNF(GAMMA \cdot YG + DELTA \cdot YD)}{AMWP}$$

$$OZ = \frac{AMN\theta(ALPHA \cdot ZA + BETA \cdot ZB) + AMNF(GAMMA \cdot ZG + DELTA \cdot ZD)}{AMWP}$$

$$AMN\theta S = \frac{AMN\theta}{AMWP}$$

$$AMNFS = \frac{AMNF}{AMWP}$$

$$\begin{aligned} AMRWS = {} & (GAMMA\,[CG \cdot VC + FG \cdot VF + HG \cdot VH + HEG \cdot VHE + ANG \cdot VN \\ & + \theta G \cdot V\theta + UG \cdot VU + XG \cdot VX + YG \cdot VY + ZG \cdot VZ] \\ & + DELTA\ [CD \cdot VC + FD \cdot VF + HD \cdot VH + HED \cdot VHE + AND \cdot VN \\ & + \theta D \cdot V\theta + UD \cdot VU + XD \cdot VX + YD \cdot VY + ZD \cdot VZ]) \cdot K\theta / \\ & -(ALPHA\,[CA \cdot VC + FA \cdot VF + HA \cdot VH + HEA \cdot VHE + ANA \cdot VN \\ & + \theta A \cdot V\theta + UA \cdot VU + XA \cdot VX + YA \cdot VY + ZA \cdot VZ] \\ & + BETA\,[CB \cdot VC + FB \cdot VF + HB \cdot VH + HEB \cdot VHE + ANB \cdot VN \\ & + \theta B \cdot V\theta + UB \cdot VU + XB \cdot VX + YB \cdot VY + ZB \cdot VZ]) \cdot KF \end{aligned}$$

$$EQUIVR = \frac{AMRW}{AMRWS}$$

$$\begin{aligned} HO = {} & AMN\theta S(HT\theta A \cdot ALPHA + HT\theta B \cdot BETA) + AMNFS\ (HTFG \cdot GAMMA \\ & + HTFD \cdot DELTA) \end{aligned}$$

$$HT_i = RT \cdot \left(KK1_i + KK2_i \frac{T}{2} + KK3_i \frac{T^2}{3} + KK4_i \frac{T^3}{4} + KK5_i \frac{T^4}{5} + KK6_i \frac{1}{T}\right)$$

$$CP_i = R \cdot (KK1_i + KK2_i T + KK3_i T^2 + KK4_i T^3 + KK5_i T^4)$$

$$ST_i = R(KK1_i \ln T + KK2_i T + KK3_i \frac{T^2}{2} + KK4_i \frac{T^3}{3} + KK5_i \frac{T^4}{4} + KK7_i)$$

If FROZ = 1 Skip to Step 20
If SHIFT = 1 Continue

16. Simultaneous Set of Equations Solving for A, T, P_i

a. Equilibrium Equations [-]
Gaseous Products: i = 1 to 100
Condensed Products: i = 111 to 115, in this case $\ln P_i = 0$
The term of the left-hand side of this equation is equal to $-DQ_i$ and approaches zero for a solution.
The positive parenthetical term on the right hand side of the equilibrium equation, not multiplied by D ln T, is abbreviated by DH_i

$$-\Bigg\{\left(\frac{HT}{R\cdot T}\right)_i - C_i\left(\frac{HT}{R\cdot T}\right)_{101} - F_i\left(\frac{HT}{R\cdot T}\right)_{102} - H_i\left(\frac{HT}{R\cdot T}\right)_{103} - HE_i\left(\frac{HT}{R\cdot T}\right)_{104}$$

$$- AN_i\left(\frac{HT}{R\cdot T}\right)_{105} - \theta_i\left(\frac{HT}{R\cdot T}\right)_{106} - U_i\left(\frac{HT}{R\cdot T}\right)_{107} - X_i\left(\frac{HT}{R\cdot T}\right)_{108} - Y_i\left(\frac{HT}{R\cdot T}\right)_{109}$$

$$- Z_i\left(\frac{HT}{R\cdot T}\right)_{110} - \left(\frac{ST}{R}\right)_i + \ln P_i + C_i\left[\left(\frac{ST}{R}\right)_{101} - \ln P101\right] + F_i\left[\left(\frac{ST}{R}\right)_{102} - \ln P102\right]$$

$$+ H_i\left[\left(\frac{ST}{R}\right)_{103} - \ln P103\right] + HE_i\left[\left(\frac{ST}{R}\right)_{104} - \ln P104\right] + AN_i\left[\left(\frac{ST}{R}\right)_{105} - \ln P105\right]$$

$$+ \theta_i\left[\left(\frac{ST}{R}\right)_{106} - \ln P106\right] + U_i\left[\left(\frac{ST}{R}\right)_{107} - \ln P107\right] + X_i\left[\left(\frac{ST}{R}\right)_{108} - \ln P108\right]$$

$$+ Y_i\left[\left(\frac{ST}{R}\right)_{109} - \ln P109\right] + Z_i\left[\left(\frac{ST}{R}\right)_{110} - \ln P110\right]\Bigg\} = D\ln P_i - C_i D\ln P101$$

$$- F_i D\ln P102 - H_i D\ln P103 - HE_i D\ln P104 - AN_i D\ln P105 - \theta_i D\ln P106$$

$$- U_i D\ln P107 - X_i D\ln P108 - Y_i D\ln P109 - Z_i D\ln P110 - \Bigg[\left(\frac{HT}{R\cdot T}\right)_i$$

$$- C_i\left(\frac{HT}{R\cdot T}\right)_{101} - F_i\left(\frac{HT}{R\cdot T}\right)_{102} - H_i\left(\frac{HT}{R\cdot T}\right)_{103} - HE_i\left(\frac{HT}{R\cdot T}\right)_{104} - AN_i\left(\frac{HT}{R\cdot T}\right)_{105}$$

$$- \theta_i\left(\frac{HT}{R\cdot T}\right)_{106} - U_i\left(\frac{HT}{R\cdot T}\right)_{107} - X_i\left(\frac{HT}{R\cdot T}\right)_{108} - Y_i\left(\frac{HT}{R\cdot T}\right)_{109} - Z_i\left(\frac{HT}{R\cdot T}\right)_{110}\Bigg] D\ln T$$

b. Mass Balance Equations [-]

c. Total Pressure Equation [atm or mole]
The partial pressures and mole numbers are equivalent with the application of A.

$$A \cdot \left(OC - \frac{1}{A} \sum_{i=1}^{115} C_i \cdot P_i\right) = -\left(\sum_{i=1}^{115} C_i \cdot P_i\right) \cdot D \ln A + \sum_{i=1}^{115} C_i \cdot P_i \cdot D \ln P_i$$

$$A \cdot \left(OF - \frac{1}{A} \sum_{i=1}^{115} F_i \cdot P_i\right) = -\left(\sum_{i=1}^{115} F_i \cdot P_i\right) \cdot D \ln A + \sum_{i=1}^{115} F_i \cdot P_i \cdot D \ln P_i$$

$$A \cdot \left(OH - \frac{1}{A} \sum_{i=1}^{115} H_i \cdot P_i\right) = -\left(\sum_{i=1}^{115} H_i \cdot P_i\right) \cdot D \ln A + \sum_{i=1}^{115} H_i \cdot P_i \cdot D \ln P_i$$

$$A \cdot \left(OHE - \frac{1}{A} \sum_{i=1}^{115} HE_i \cdot P_i\right) = -\left(\sum_{i=1}^{115} HE_i \cdot P_i\right) \cdot D \ln A + \sum_{i=1}^{115} HE_i \cdot P_i \cdot D \ln P_i$$

$$A \cdot \left(ON - \frac{1}{A} \sum_{i=1}^{115} AN_i \cdot P_i\right) = -\left(\sum_{i=1}^{115} AN_i \cdot P_i\right) \cdot D \ln A + \sum_{i=1}^{115} AN_i \cdot P_i \cdot D \ln P_i$$

$$A \cdot \left(O\theta - \frac{1}{A} \sum_{i=1}^{115} \theta_i \cdot P_i\right) = -\left(\sum_{i=1}^{115} \theta_i \cdot P_i\right) \cdot D \ln A + \sum_{i=1}^{115} \theta_i \cdot P_i \cdot D \ln P_i$$

$$A \cdot \left(OU - \frac{1}{A} \sum_{i=1}^{115} U_i \cdot P_i\right) = -\left(\sum_{i=1}^{115} U_i \cdot P_i\right) \cdot D \ln A + \sum_{i=1}^{115} U_i \cdot P_i \cdot D \ln P_i$$

$$A \cdot \left(OX - \frac{1}{A} \sum_{i=1}^{115} X_i \cdot P_i\right) = -\left(\sum_{i=1}^{115} X_i \cdot P_i\right) \cdot D \ln A + \sum_{i=1}^{115} X_i \cdot P_i \cdot D \ln P_i$$

$$A \cdot \left(OY - \frac{1}{A} \sum_{i=1}^{115} Y_i \cdot P_i\right) = -\left(\sum_{i=1}^{115} Y_i \cdot P_i\right) \cdot D \ln A + \sum_{i=1}^{115} Y_i \cdot P_i \cdot D \ln P_i$$

$$A \cdot \left(OZ - \frac{1}{A} \sum_{i=1}^{115} Z_i \cdot P_i\right) = -\left(\sum_{i=1}^{115} Z_i \cdot P_i\right) \cdot D \ln A + \sum_{i=1}^{115} Z_i \cdot P_i \cdot D \ln P_i$$

$$PO - \sum_{i=1}^{110} P_i = \sum_{i=1}^{110} P_i \cdot D \ln P_i$$

d. Enthalpy Equation [cal]
Replace enthalpy by entropy equation (16e) when step 44 has been passed the first time.

e. Entropy Equation [cal/°K]
Use step 16d during the first calculation until step 44 is passed.

17. Test on Tolerances

During the first calculation loop $\left|1 - \frac{S}{SO}\right|$ must be by-passed.

During all consecutive calculation loops $\left|1 - \frac{H}{HO}\right|$ must be by-passed.

P, H, S, IC, IF, IH, IHE, IN, Iθ, IU, IX, IY, IZ, are the constants, calculated during the iterations in the simultaneous set of equations solving for A, T, and P_i (see step 16b, 16c, 16d, 16e), which have approximately the same value as PO, HO, SO, OC, OF, OH, OHE, ON, Oθ, OU, OX, OY, OZ.

$$A \cdot \left[HO - \frac{1}{A} \cdot R \cdot T \cdot \sum_{i=1}^{115} \left(\frac{HT}{R \cdot T} \right)_i \cdot P_i \right] = - \left[R \cdot T \cdot \sum_{i=1}^{115} \left(\frac{HT}{R \cdot T} \right)_i \cdot P_i \right] \cdot D \ln A$$

$$+ \sum_{i=1}^{115} \left(\frac{HT}{R \cdot T} \right)_i \cdot P_i \cdot R \cdot T \cdot D \ln P_i + \left[R \cdot T \cdot \sum_{i=1}^{115} \left(\frac{CP}{R} \right)_i \cdot P_i \right] \cdot D \ln T$$

$$A \cdot \left\{ SO - \frac{1}{A} \cdot R \cdot \sum_{i=1}^{110} \left[\left(\frac{ST}{R} \right)_i \cdot P_i - P_i \cdot \ln P_i \right] - \frac{1}{A} \cdot R \cdot \sum_{i=111}^{115} \left[\left(\frac{ST}{R} \right)_i \cdot P_i \right] \right\}$$

$$= + R \left[\sum_{i=1}^{115} \left(\frac{CP}{R} \right)_i \cdot P_i \right] D \ln T - \sum_{i=1}^{110} R \cdot \left[P_i (1 + \ln P_i) - \left(\frac{ST}{R} \right)_i \cdot P_i \right] \cdot D \ln P_i$$

$$+ \sum_{i=111}^{115} R \left[\left(\frac{ST}{R} \right)_i \cdot P_i \right] \cdot D \ln P_i - R \cdot \sum_{i=1}^{110} \left[\left(\frac{ST}{R} \right)_i \cdot P_i - P_i \cdot \ln P_i \right] \cdot D \ln A$$

$$- R \cdot \sum_{i=111}^{115} \left(\frac{ST}{R} \right)_i \cdot P_i \cdot D \ln A$$

$\left| 1 - \frac{P}{PO} \right| < 5 \times 10^{-7}$ Continue otherwise go to step 18

$\left| 1 - \frac{H}{HO} \right| < 5 \times 10^{-7}$ Continue otherwise go to step 18

$\left| 1 - \frac{S}{SO} \right| < 5 \times 10^{-7}$ Continue otherwise go to step 18

$\left| 1 - \frac{1C}{OC} \right| < 5 \times 10^{-7}$ Continue otherwise go to step 18

$\left| 1 - \frac{1F}{OF} \right| < 5 \times 10^{-7}$ Continue otherwise go to step 18

$\left| 1 - \frac{1H}{OH} \right| < 5 \times 10^{-7}$ Continue otherwise go to step 18

$\left| 1 - \frac{1HE}{OHE} \right| < 5 \times 10^{-7}$ Continue otherwise go to step 18

$\left| 1 - \frac{1N}{ON} \right| < 5 \times 10^{-7}$ Continue otherwise go to step 18

DQ_i is the constant in the equilibrium equation which approaches zero.

18. New Estimates for Simultaneous Set of Equations

i = 1 to 115

If any $|D \ln \ldots| > 10$ calculate $\frac{10}{|D \ln \ldots|_{max}}$ and multiply all D ln... values by this factor

19. Test on Condensation Products

$\left| 1 - \frac{1\theta}{O\theta} \right| < 5 \times 10^{-7}$ Continue otherwise go to step 18

$\left| 1 - \frac{1U}{OU} \right| < 5 \times 10^{-7}$ Continue otherwise go to step 18

$\left| 1 - \frac{1X}{OX} \right| < 5 \times 10^{-7}$ Continue otherwise go to step 18

$\left| 1 - \frac{1Y}{OY} \right| < 5 \times 10^{-7}$ Continue otherwise go to step 18

$\left| 1 - \frac{1Z}{OZ} \right| < 5 \times 10^{-7}$ Continue otherwise go to step 18

$\left| DQ_i \right| < 5 \times 10^{-6}$ Skip to step 19 otherwise go to step 18

$\ln P_i = \ln P_i + D \ln P_i$ Determine P_i and test: If $P_i = 0$ set $P_i = 1 \times 10^{-35}$

$\ln A = \ln A + D \ln A$ Determine A

$\ln T = \ln T + D \ln T$ Determine T

Return to step 11

If $-\left(\frac{HT}{R \cdot T}\right)_{101} + \left(\frac{ST}{R}\right)_{101} + \left(\frac{HT}{R \cdot T}\right)_{111} - \left(\frac{ST}{R}\right)_{111} - \ln P101 \leq 0$

call for No. 111 and continue

If $-\left(\frac{HT}{R \cdot T}\right)_{i} + \left(\frac{ST}{R}\right)_{i} + \left(\frac{HT}{R \cdot T}\right)_{112} - \left(\frac{ST}{R}\right)_{112} - \ln P_i \leq 0$

call for No. 112 and continue

If $-\left(\frac{HT}{R \cdot T}\right)_{i} + \left(\frac{ST}{R}\right)_{i} + \left(\frac{HT}{R \cdot T}\right)_{113} - \left(\frac{ST}{R}\right)_{113} - \ln P_i \leq 0$

call for No. 113 and continue

If $-\left(\frac{HT}{R \cdot T}\right)_{i} + \left(\frac{ST}{R}\right)_{i} + \left(\frac{HT}{R \cdot T}\right)_{114} - \left(\frac{ST}{R}\right)_{114} - \ln P_i \leq 0$

call for No. 114 and continue

If $-\left(\frac{HT}{R \cdot T}\right)_{i} + \left(\frac{ST}{R}\right)_{i} + \left(\frac{HT}{R \cdot T}\right)_{115} - \left(\frac{ST}{R}\right)_{115} - \ln P_i \leq 0$

call for No. 115 and return to step 11

If all values are > 0 go to step 27.

20. Entropy of the Combustion Products [cal/g °K]

21. Test on Tolerance for Constant Entropy Process at Frozen Equilibrium Condition

22. New Estimates on Temperature for Constant Entropy Process at Frozen Equilibrium Condition

23. Partial Pressures of the Combustion Products for Frozen Equilibrium $i = 1$ to 110

24. Sum of the Partial Pressures for all Gaseous Combustion Products [atm]

25. Simultaneous Set of Equations Solving for Derivatives DPP (P = Constant)

    a. Mass Balance Equations
    For definition of DH_i see equation 16a

$$S = \left[R \cdot \sum_{i=1}^{115} \left(\frac{ST}{R}\right)_i \cdot CN_i - R \cdot \sum_{i=1}^{110} CN_i \cdot \ln \frac{CN_i \cdot PO}{CNSMCP} \right] \cdot \frac{1}{A}$$

If $\left| 1 - \frac{S}{SO} \right| < 5 \times 10^{-7}$ skip to step 23 otherwise continue

$$D \ln T = \frac{(SO - S)}{\frac{R}{A} \sum_{i=1}^{115} CN_i \left(\frac{CP}{R}\right)_i}$$

$\ln T = \ln T + D \ln T$

determine T and return to step 11

$$P_i = \frac{CN_i \cdot PO}{CNSMCP}$$

$$PSUM = \sum_{i=1}^{110} P_i$$

$$0 = \sum_{i=1}^{110} C_i \cdot P_i [C_i \cdot DPP101 + F_i \cdot DPP102 + H_i \cdot DPP103 + HE_i \cdot DPP104$$

$$+ AN_i \cdot DPP105 + \theta_i \cdot DPP106 + U_i \cdot DPP107 + X_i \cdot DPP108 + Y_i \cdot DPP109$$

$$+ Z_i \cdot DPP110 + DH_i] + \sum_{i=111}^{115} C_i \cdot P_i \cdot DPP_i - A \cdot 1C \cdot DPA$$

$$0 = \sum_{i=1}^{110} F_i \cdot P_i [C_i \cdot DPP101 + F_i \cdot DPP102 + H_i \cdot DPP103 + HE_i \cdot DPP104$$

$$+ AN_i \cdot DPP105 + \theta_i \cdot DPP106 + U_i \cdot DPP107 + X_i \cdot DPP108 + Y_i \cdot DPP109$$

$$+ Z_i \cdot DPP110 + DH_i] + \sum_{i=111}^{115} F_i \cdot P_i \cdot DPP_i - A \cdot 1F \cdot DPA$$

$$0 = \sum_{i=1}^{110} H_i \cdot P_i [C_i \cdot DPP101 + F_i \cdot DPP102 + H_i \cdot DPP103 + HE_i \cdot DPP104$$

$$+ AN_i \cdot DPP105 + \theta_i \cdot DPP106 + U_i \cdot DPP107 + X_i \cdot DPP108 + Y_i \cdot DPP109$$

$$+ Z_i \cdot DPP110 + DH_i] + \sum_{i=111}^{115} H_i \cdot P_i \cdot DPP_i - A \cdot 1H \cdot DPA$$

$$0 = \sum_{i=1}^{110} HE_i \cdot P_i [C_i \cdot DPP101 + F_i \cdot DPP102 + H_i \cdot DPP103 + HE_i \cdot DPP104$$

$$+ AN_i \cdot DPP105 + \theta_i \cdot DPP106 + U_i \cdot DPP107 + X_i \cdot DPP108 + Y_i \cdot DPP109$$

$$+ Z_i \cdot DPP110 + DH_i] + \sum_{i=111}^{115} HE_i \cdot P_i \cdot DPP_i - A \cdot 1HE \cdot DPA$$

$$0 = \sum_{i=1}^{110} AN_i \cdot P_i [C_i \cdot DPP101 + F_i \cdot DPP102 + H_i \cdot DPP103 + HE_i \cdot DPP104$$

$$+ AN_i \cdot DPP105 + \theta_i \cdot DPP106 + U_i \cdot DPP107 + X_i \cdot DPP108 + Y_i \cdot DPP109$$

$$+ Z_i \cdot DPP110 + DH_i] + \sum_{i=111}^{115} AN_i \cdot P_i \cdot DPP_i - A \cdot 1N \cdot DPA$$

$$0 = \sum_{i=1}^{110} \theta_i \cdot P_i [C_i \cdot DPP101 + F_i \cdot DPP102 + H_i \cdot DPP103 + HE_i \cdot DPP104$$

$$+ AN_i \cdot DPP105 + \theta_i \cdot DPP106 + U_i \cdot DPP107 + X_i \cdot DPP108 + Y_i \cdot DPP109$$

$$+ Z_i \cdot DPP110 + DH_i] + \sum_{i=111}^{115} \theta_i \cdot P_i \cdot DPP_i - A \cdot 1\theta \cdot DPA$$

$$0 = \sum_{i=1}^{110} U_i \cdot P_i [C_i \cdot DPP101 + F_i \cdot DPP102 + H_i \cdot DPP103 + HE_i \cdot DPP104$$

$$+ AN_i \cdot DPP105 + \theta_i \cdot DPP106 + U_i \cdot DPP107 + X_i \cdot DPP108 + Y_i \cdot DPP109$$

$$+ Z_i \cdot DPP110 + DH_i] + \sum_{i=111}^{115} U_i \cdot P_i \cdot DPP_i - A \cdot 1U \cdot DPA$$

25 a. (Continued)

Equilibrium Equation for Condensed Products
$i = 111$ to 115

Total Pressure Equation

$$0 = \sum_{i=1}^{110} X_i \cdot P_i [C_i \cdot DPP101 + F_i \cdot DPP102 + H_i \cdot DPP103 + HE_i \cdot DPP104$$

$$+ AN_i \cdot DPP105 + \theta_i \cdot DPP106 + U_i \cdot DPP107 + X_i \cdot DPP108 + Y_i \cdot DPP109$$

$$+ Z_i \cdot DPP110 + DH_i] + \sum_{i=111}^{115} X_i \cdot P_i \cdot DPP_i - A \cdot 1X \cdot DPA$$

$$0 = \sum_{i=1}^{110} Y_i \cdot P_i [C_i \cdot DPP101 + F_i \cdot DPP102 + H_i \cdot DPP103 + HE_i \cdot DPP104$$

$$+ AN_i \cdot DPP105 + \theta_i \cdot DPP106 + U_i \cdot DPP107 + X_i \cdot DPP108 + Y_i \cdot DPP109$$

$$+ Z_i \cdot DPP110 + DH_i] + \sum_{i=111}^{115} Y_i \cdot P_i \cdot DPP_i - A \cdot 1Y \cdot DPA$$

$$0 = \sum_{i=1}^{110} Z_i \cdot P_i [C_i \cdot DPP101 + F_i \cdot DPP102 + H_i \cdot DPP103 + HE_i \cdot DPP104$$

$$+ AN_i \cdot DPP105 + \theta_i \cdot DPP106 + U_i \cdot DPP107 + X_i \cdot DPP108 + Y_i \cdot DPP109$$

$$+ Z_i \cdot DPP110 + DH_i] + \sum_{i=111}^{115} Z_i \cdot P_i \cdot DPP_i - A \cdot 1Z \cdot DPA$$

$$0 = C_i \cdot DPP101 + F_i \cdot DPP102 + H_i \cdot DPP103 + HE_i \cdot DPP104 + AN_i \cdot DPP105$$

$$+ \theta_i \cdot DPP106 + U_i \cdot DPP107 + X_i \cdot DPP108 + Y_i \cdot DPP109 + Z_i \cdot DPP110 + DH_i$$

$$0 = \sum_{i=1}^{110} P_i [C_i \cdot DPP101 + F_i \cdot DPP102 + H_i \cdot DPP103 + HE_i \cdot DPP104$$

$$+ AN_i \cdot DPP105 + \theta_i \cdot DPP106 + U_i \cdot DPP107 + X_i \cdot DPP108 + Y_i \cdot DPP109$$

$$+ Z_i \cdot DPP110 + DH_i]$$

b. Derivatives for the Gaseous Combustion Products
Equilibrium Equation for Gaseous Compounds
$i = 1$ to 100
For definition of DH_i see equation 16a

26. Simultaneous Set of Equations Solving for Derivatives DTP_i (T = Constant)

a. Mass Balance Equations

$$DPP_i = C_i \cdot DPP101 + F_i \cdot DPP102 + H_i \cdot DPP103 + HE_i \cdot DPP104 + AN_i \cdot DPP105$$

$$+ \theta_i \cdot DPP106 + U_i \cdot DPP107 + X_i \cdot DPP108 + Y_i \cdot DPP109 + Z_i \cdot DPP110$$

$$+ DH_i$$

$$O = - \sum_{i=1}^{115} C_i \cdot P_i + \sum_{i=1}^{110} C_i \cdot P_i [C_i \cdot DTP101 + F_i \cdot DTP102 + H_i \cdot DTP103$$

$$+ HE_i \cdot DTP104 + AN_i \cdot DTP105 + \theta_i \cdot DTP106 + U_i \cdot DTP107 + X_i \cdot DTP108$$

$$+ Y_i \cdot DTP109 + Z_i \cdot DTP110] + \sum_{i=111}^{115} C_i \cdot P_i \cdot DTP_i$$

$$O = - \sum_{i=1}^{115} F_i \cdot P_i + \sum_{i=1}^{110} F_i \cdot P_i [C_i \cdot DTP101 + F_i \cdot DFP102 + H_i \cdot DTP103$$

$$+ HE_i \cdot DTP104 + AN_i \cdot DTP105 + \theta_i \cdot DTP106 + U_i \cdot DTP107 + X_i \cdot DTP108$$

$$+ Y_i \cdot DTP109 + Z_i \cdot DTP110] + \sum_{i=111}^{115} F_i \cdot P_i \cdot DTP_i$$

$$O = - \sum_{i=1}^{115} H_i \cdot P_i + \sum_{i=1}^{110} H_i \cdot P_i [C_i \cdot DTP101 + F_i \cdot DTP102 + H_i \cdot DTP103$$

$$+ HE_i \cdot DTP104 + AN_i \cdot DTP105 + \theta_i \cdot DTP106 + U_i \cdot DTP107 + X_i \cdot DTP108$$

$$+ Y_i \cdot DTP109 + Z_i \cdot DTP110] + \sum_{i=111}^{115} H_i \cdot DTP_i$$

$$O = - \sum_{i=1}^{115} HE_i \cdot P_i + \sum_{i=1}^{110} HE_i \cdot P_i [C_i \cdot DTP101 + F_i \cdot DTP102 + H_i \cdot DTP103$$

$$+ HE_i \cdot DTP104 + AN_i \cdot DTP105 + \theta_i \cdot DTP106 + U_i \cdot DTP107 + X_i \cdot DTP108$$

$$+ Y_i \cdot DTP109 + Z_i \cdot DTP110] + \sum_{i=111}^{115} HE_i \cdot DTP_i$$

$$O = -\sum_{i=1}^{115} AN_i \cdot P_i + \sum_{i=1}^{110} AN_i \cdot P_i[C_i \cdot DTP101 + F_i \cdot DTP102 + H_i \cdot DTP103$$

$$+ HE_i \cdot DTP104 + AN_i \cdot DTP105 + \theta_i \cdot DTP106 + U_i \cdot DTP107 + X_i \cdot DTP108$$

$$+ Y_i \cdot DTP109 + Z_i \cdot DTP110] + \sum_{i=111}^{115} AN_i \cdot DTP_i$$

$$O = -\sum_{i=1}^{115} \theta_i \cdot P_i + \sum_{i=1}^{110} \theta_i \cdot P_i[C_i \cdot DTP101 + F_i \cdot DTP102 + H_i \cdot DTP103$$

$$+ HE_i \cdot DTP104 + AN_i \cdot DTP105 + \theta_i \cdot DTP106 + U_i \cdot DTP107 + X_i \cdot DTP108$$

$$+ Y_i \cdot DTP109 + Z_i \cdot DTP110] + \sum_{i=111}^{115} \theta_i \cdot DTP_i$$

$$O = -\sum_{i=1}^{115} U_i \cdot P_i + \sum_{i=1}^{110} U_i \cdot P_i[C_i \cdot DTP101 + F_i \cdot DTP102 + H_i \cdot DTP103$$

$$+ HE_i \cdot DTP104 + AN_i \cdot DTP105 + \theta_i \cdot DTP106 + U_i \cdot DTP107 + X_i \cdot DTP108$$

$$+ Y_i \cdot DTP109 + Z_i \cdot DTP110] + \sum_{i=111}^{115} U_i \cdot DTP_i$$

$$O = -\sum_{i=1}^{115} X_i \cdot P_i + \sum_{i=1}^{110} X_i \cdot P_i[C_i \cdot DTP101 + F_i \cdot DTP102 + H_i \cdot DTP103$$

$$+ HE_i \cdot DTP104 + AN_i \cdot DTP105 + \theta_i \cdot DTP106 + U_i \cdot DTP107 + X_i \cdot DTP108$$

$$+ Y_i \cdot DTP109 + Z_i \cdot DTP110] + \sum_{i=111}^{115} X_i \cdot DTP_i$$

$$O = -\sum_{i=1}^{115} Y_i \cdot P_i + \sum_{i=1}^{110} Y_i \cdot P_i[C_i \cdot DTP101 + F_i \cdot DTP102 + H_i \cdot DTP103$$

$$+ HE_i \cdot DTP104 + AN_i \cdot DTP105 + \theta_i \cdot DTP106 + U_i \cdot DTP107 + X_i \cdot DTP108$$

$$+ Y_i \cdot DTP109 + Z_i \cdot DTP110] + \sum_{i=111}^{115} Y_i \cdot DTP_i$$

26 a. (Continued)

Equilibrium Equation for Condensed Products
$i = 111$ to 115

b. Derivatives for the Gaseous Combustion Products
Equilibrium Equation for Gaseous Compounds
$i = 1$ to 100

27. Separation of Mole Numbers and Partial Pressures Which Will be Used for Further Calculations [mole]
$i = 1$ to 115

28. Total Mole Number of the Combustion Product [mole]

Total Mole Number of the Combustion Product Minus the Condensed Phases [mole]

29. Test on Desired Calculation Procedure During Expansion

30. Test

$$O = -\sum_{i=1}^{115} Z_i \cdot P_i + \sum_{i=1}^{110} Z_i \cdot P_i [C_i \cdot DTP101 + F_i \cdot DTP102 + H_i \cdot DTP103$$

$$+ HE_i \cdot DTP104 + AN_i \cdot DTP105 + \theta_i \cdot DTP106 + U_i \cdot DTP107 + X_i \cdot DTP108$$

$$+ Y_i \cdot DTP109 + Z_i \cdot DTP110] + \sum_{i=111}^{115} Z_i \cdot DTP_i$$

$$O = C_i \cdot DTP101 + F_i \cdot DTP102 + H_i \cdot DTP103 + HE_i \cdot DTP104 + AN_i \cdot DTP105$$

$$+ \theta_i \cdot DTP106 + U_i \cdot DTP107 + X_i \cdot DTP108 + Y_i \cdot DTP109 + Z_i \cdot DTP110$$

$$DTP_i = C_i \cdot DTP101 + F_i \cdot DTP102 + H_i \cdot DTP103 + HE_i \cdot DTP104 + AN_i \cdot DTP105$$

$$+ \theta_i \cdot DTP106 + U_i \cdot DTP107 + X_i \cdot DTP108 + Y_i \cdot DTP109 + Z_i \cdot DTP110$$

$$CN_i = P_i$$

$$CNS = \sum_{i=1}^{115} CN_i$$

$$CNSMCP = \sum_{i=1}^{110} CN_i$$

(a) If shifting equilibrium calculation is desired set SHIFT = 1 and replace enthalpy equation in simultaneous set of equations by entropy equation

(b) If frozen equilibrium calculation is desired set FROZ = 1

(c) If combination of shifting and frozen equilibrium is desired test

If $T > TL$ set SHIFT = 1

If $T \leq TL$ set FROZ = 1

If SHIFT = 1 go to step 25

If FROZ = 1 go to step 31

31. For Frozen Equilibrium the Mole Numbers do not Change

32. Specific Heat at Constant Pressure for Frozen Equilibrium [cal/mole °K]

33. Enthalpy of the Gaseous Combustion Products for Frozen Equilibrium [cal/g]

34. Change of Molecular Weight as a Function of Temperature at Constant Pressure for Shifting Equilibrium [-]

35. Change of Molecular Weight as a Function of Pressure at Constant Temperature for Shifting Equilibrium [-]

Coefficients of Derivative Compare with Pressure Row in the Matrix

Set DPM = 0

DTM = 0

$$CPP = \frac{\sum_{i=1}^{115} CN_i \cdot CP_i}{\sum_{i=1}^{110} CN_i}$$

$$H = \left[\sum_{i=1}^{115} CN_i \cdot HT_i \right] \cdot \frac{1}{A}$$ and skip to step 37

DPM = DPA

$$DTM = \frac{P}{\sum_{i=1}^{110} P_i \left[C_i \cdot DTP101 + F_i \cdot DTP102 + H_i \cdot DTP103 + HE_i \cdot DTP104 + AN_i \cdot DTP105 + \theta_i \cdot DTP106 + U_i \cdot DTP107 + X_i \cdot DTP108 + Y_i \cdot DTP109 + Z_i \cdot DTP110 \right]} - 1$$

36. Specific Heat at Constant Pressure for Shifting Equilibrium [cal/mole °K]
Coefficients compare with enthalpy row in the matrix

37. Specific Heat at Constant Volume [cal/mole °K]

38. Specific Heat Ratio at Constant Entropy [-]

39. Mole Ratios of the Combustion Products [-]
i = 1 to 115

40. Average Molecular Weight Per Mole of Gaseous Products [g/mole]
The volume of the condensed phases is considered negligible compared to the gaseous compounds.

$$
\begin{aligned}
CPP = \frac{1}{\sum\limits_{i=1}^{110} CN_i \cdot T} \Bigg\{ & - R \cdot T \cdot \sum_{i=1}^{115} \left(\frac{HT}{R \cdot T}\right)_i P_i \cdot DPA + R \cdot T \cdot \sum_{i=1}^{115} \left(\frac{CP}{R}\right)_i \cdot CN_i \\
& + R \cdot T \Bigg[\sum_{i=1}^{110} \left(\frac{HT}{R \cdot T}\right)_i \cdot CN_i \cdot C_i \cdot DPP101 + \sum_{i=1}^{110} \left(\frac{HT}{R \cdot T}\right)_i \cdot CN_i \cdot F_i \cdot DPP102 \\
& + \sum_{i=1}^{110} \left(\frac{HT}{R \cdot T}\right)_i \cdot CN_i \cdot H_i \cdot DPP103 + \sum_{i=1}^{110} \left(\frac{HT}{R \cdot T}\right)_i \cdot CN_i \cdot HE_i \cdot DPP104 \\
& + \sum_{i=1}^{110} \left(\frac{HT}{R \cdot T}\right)_i \cdot CN_i \cdot AN_i \cdot DPP105 + \sum_{i=1}^{110} \left(\frac{HT}{R \cdot T}\right)_i \cdot CN_i \cdot \theta_i \cdot DPP106 \\
& + \sum_{i=1}^{110} \left(\frac{HT}{R \cdot T}\right)_i \cdot CN_i \cdot U_i \cdot DPP107 + \sum_{i=1}^{110} \left(\frac{HT}{R \cdot T}\right)_i \cdot CN_i \cdot X_i \cdot DPP108 \\
& + \sum_{i=1}^{110} \left(\frac{HT}{R \cdot T}\right)_i \cdot CN_i \cdot Y_i \cdot DPP109 + \sum_{i=1}^{110} \left(\frac{HT}{R \cdot T}\right)_i \cdot CN_i \cdot Z_i \cdot DPP110 \\
& + \sum_{i=111}^{115} \left(\frac{HT}{R \cdot T}\right)_i \cdot CN_i \cdot DPP_i + \sum_{i=1}^{110} \left(\frac{HT}{R \cdot T}\right)_i \cdot CN_i \cdot DH_i \Bigg] \Bigg\}
\end{aligned}
$$

$$CVV = CPP - R \cdot \frac{(1 - DPM)^2}{(1 + DTM)}$$

$$CRS = \frac{\dfrac{CPP}{R}}{\dfrac{CPP}{R}\,[1 + DTM] - [1 - DPM]^2}$$

$$AMNR_i = \frac{CN_i}{\sum\limits_{i=1}^{115} CN_i}$$

$$AMW = \frac{A}{\sum\limits_{i=1}^{110} CN_i} \cdot AMWR$$

41. Convergence

Delete $\left(1 - \frac{S}{SO}\right)^2$ during the first calculation loop

Delete $\left(1 - \frac{H}{HO}\right)^2$ during the following calculation loops

42. Specific Gas Constant [cal/g°K]

$R = 1.98726$ [cal/mole°K]

43. Local Speed of Sound [ft/sec]

$CK_3 = 37.42098622$

44. Local Velocity [ft/sec]

$CK_4 = 52.92126623$

$\frac{1}{A} \cdot \sum_{i=1}^{115} HT_i \cdot CN_i$ from simultaneous set for shifting equilibrium

$\frac{1}{A} \cdot \sum_{i=1}^{115} HT_i \cdot CN_i$ from step 33 for frozen equilibrium

45. Local Specific Impulse [sec]

$KE = 32.1740$ [ft/sec^2]

46. Test

a. For chamber calculation determine the expansion ratio

b. For throat area calculation set

c. For all consecutive calculation loops

$$\mathrm{CONVER} = \left(1 - \frac{\sum_{i=1}^{110} P_i}{PO}\right)^2 + \left(1 - \frac{S}{SO}\right)^2 + \left(1 - \frac{H}{HO}\right)^2 + \left(1 - \frac{1C}{OC}\right)^2 + \left(1 - \frac{1F}{OF}\right)^2$$

$$+ \left(1 - \frac{1H}{OH}\right)^2 + \left(1 - \frac{1HE}{OHE}\right)^2 + \left(1 - \frac{1N}{ON}\right)^2 + \left(1 - \frac{1\theta}{O\theta}\right)^2 + \left(1 - \frac{1U}{OU}\right)^2$$

$$+ \left(1 - \frac{1X}{OX}\right)^2 + \left(1 - \frac{1Y}{OY}\right)^2 + \left(1 - \frac{1Z}{OZ}\right)^2 + \sum_{i=1}^{100} DQ_i^2 + \sum_{i=110}^{115} DQ_i^2$$

$$RS = \frac{R}{AMW}$$

$$VS = CK_3\sqrt{CRS \cdot RS \cdot T \cdot KE}$$

$$V = CK_4\sqrt{\left(HO - \frac{1}{A}\sum_{i=1}^{115} HT_i \cdot CN_i\right) \cdot KE}$$

$$AISP = \frac{V}{KE}$$

$EXPR = \dfrac{ACC}{AS}$ and skip to step 64

$PS = PO$ $TS = T$ $RSS = RS$

$VSS = VS$ $CRSS = CRS$ and go to step 47

go to step 47

47. Local Expansion Ratio [-]

48. Weight Flow Rate [lb/sec]
    $CK_1 = 0.01049466$

49. Characteristic Velocity [ft/sec]
    $CK_2 = 14.696$ [lb/in^2 atm]

50. Local Thrust Coefficient [-]

51. Local Thrust [lb]
    $CK_2 = 14.696$

52. Thrust at Altitude [lb]
    $CK_2 = 14.696$

53. Thrust at Vacuum [lb]
    $CK_2 = 14.696$

54. Thrust Coefficient at Altitude [-]
    $CK_2 = 14.696$

55. Thrust Coefficient at Vacuum [-]
    $CK_2 = 14.696$

56. Real Thrust Coefficient at Altitude [-]

57. Real Thrust Coefficient at Vacuum [-]

58. Real Thrust at Altitude [lb]
    $CK_2 = 14.696$

59. Real Thrust at Vacuum [lb]
    $CK_2 = 14.696$

$$EXPR = \frac{RS \cdot T \cdot VSS \cdot PS}{V \cdot PO \cdot RSS \cdot TS}$$

$$W = \frac{PO \cdot V \cdot AS \cdot EXPR \cdot CK_1}{RS \cdot T}$$

$$C^* = \frac{PC \cdot AS \cdot KE \cdot CK_2}{W}$$

$$CF = \frac{AISP \cdot KE}{C^*}$$

$$FT = AS \cdot PC \cdot CF \cdot CK_2$$

$$FTA = FT - EXPR \cdot AS \cdot (PAM - PO) \cdot CK_2$$

$$FTV = FT + EXPR \cdot AS \cdot PO \cdot CK_2$$

$$CFA = \frac{FTA}{AS \cdot PC \cdot CK_2}$$

$$CFV = \frac{FTV}{AS \cdot PC \cdot CK_2}$$

$$CFRA = ETACFV \cdot CFV - EXPR \cdot \frac{PAM}{PC}$$

$$CFRV = ETACFV \cdot CFV$$

$$FTRA = CFRA \cdot AS \cdot PC \cdot CK_2$$

$$FTRV = CFRV \cdot AS \cdot PC \cdot CK_2$$

60. Real Weight Flow Rate [lb/sec]

61. Real Characteristic Velocity [ft/sec]

62. Real Specific Impulse at Altitude [sec]

63. Real Specific Impulse at Vacuum [sec]

64. a. Calculate X value for plotting purpose

b. Store:

Options

65. Test: If IA = 0 conditions in the throat area are calculated
If IA = 1 conditions except the throat area are calculated

66. Test: If IB = 0 print the results of the previous calculation and determine the approximate throat parameters

If IB = 1

$WR = ETAW \cdot W$

$C^*R = ETAC^* \cdot C^*$

$$AISPRA = \frac{FTRA}{WR}$$

$$AISPRV = \frac{FTRV}{WR}$$

If $V < VS$ calculate $X = EXPR - 1$

If $V \geq VS$ calculate $X = -(EXPR - 1)$

During the first calculation loop set: $TC = T$

$SO = S$

During every calculation loop store the results as indicated on page 107 for printing purpose

If $IA = 0$ skip to step 66

If $IA = 1$ go to step 69

If $IB = 0$ PRINT, then calculate

$$PO = PC \left[\frac{2}{CRS + 1}\right]^{\left(\frac{CRS}{CRS - 1}\right)}$$

$$T = TC\left[\frac{2}{CRS + 1}\right]$$

Set $IB = 1$ and return to step 11

If $IB = 1$ go to step 67

67. Test on Local Velocity and Speed of Sound

68. Test: IC is an Input Parameter Indicating

a. IC = 0 only chamber, throat and exit conditions are considered

b. IC = 1 intermediate locations between chamber, throat and exit area are considered

69. Test: Determination of whether the point of calculation is upstream or downstream of the throat area

If $\left| 1 - \frac{V}{VS} \right| \geq 0.2 \times 10^{-4}$ calculate

$$PO = PO\left[1 + \frac{HO - \left(H + \frac{CRS \cdot R \cdot T}{2 \cdot AMW}\right)}{\frac{R \cdot T}{2 \cdot AMW}(CRS + 1)}\right]$$

and return to step 11

If $\left| 1 - \frac{V}{VS} \right| < 0.2 \times 10^{-4}$

Set: IB = 0

IA = 1

PRINT

and go to step 68

If IC = 0 calculate

$$PO = PC \cdot E^{-[(0.867 \cdot CRS + 0.272) \ln EXPRL + (0.699 \cdot CRS + 0.442)]}$$

and return to step 11

If IC = 1 calculate

PO = PC - 10

and return to step 11

If IC = 0 test

If VS ≥ V skip to equation PO in step 70

If VS < V go to step 70

If IC = 1 skip to step 71

70. Test on Required Expansion Ratio

71. Test on Expansion Ratio

The test on VS and V shall avoid an iteration on an expansion ratio in the subsonic range

72. Test to Define Assumed Static Pressure Differences for Various Ranges during the Expansion Process

73. Static Pressure in the Nozzle Between Chamber Pressure and 1 atm

If $\left| 1 - \frac{EXPR}{EXPRL} \right| > 1 \times 10^{-3}$ calculate

$$PO = PO \left[1 + \frac{HO - \left(H + \frac{PS^2 \cdot CRSS \cdot RS^2 \cdot T^2}{RSS \cdot TS \cdot 2 \cdot PO^2 \cdot EXPRL^2} \right)}{RS \cdot T \left(1 - \frac{CRSS \cdot PS^2 \cdot RS \cdot T}{CRS \cdot PO^2 \cdot RSS \cdot TS \cdot EXPRL^2} \right)} \right]$$

and return to step 11

If $\left| 1 - \frac{EXPR}{EXPRL} \right| \leq 1 \times 10^{-3}$

set IA = 0

PRINT

and go to new input reading

If EXPR $\geq$ EXPRL

Test: If VS > V

PRINT

and go to step 72

If VS < V continue

$$PO = PO \left[1 + \frac{HO - \left(H + \frac{PS^2 \cdot CRSS \cdot RS^2 \cdot T^2}{RSS \cdot TS \cdot 2 \cdot EXPRL^2 \cdot PO^2} \right)}{RS \cdot T \left(1 - \frac{CRSS \cdot PS^2 \cdot RS \cdot T}{CRS \cdot PO^2 \cdot RSS \cdot TS \cdot EXPRL^2} \right)} \right]$$

set IC = 0

and return to step 11

If EXPR < EXPRL

PRINT

and go to step 72.a.

(a) If ID = 1 skip to step 79 otherwise continue

(b) If IE = 1 skip to step 77 otherwise continue

(c) If IF = 1 skip to step 75 otherwise go to step 73

PO = PO - 10

74. Test

75. Static Pressure in the Nozzle Between 1 atm and 0.2 atm

76. Test

77. Static Pressure in the Nozzle Between 0.2 atm and 0.1 atm

78. Test

79. Static Pressure Between 0.1 atm and 0.02 atm

80. Test

81. Test: If IG = 0 maximum specific impulse can be calculated
If IG = 1 desired thrust level for a fixed mixture ratio is calculated

```
If PO > 1
return to step 11
If PO ≤ 1
set PO = 1
IF = 1
return to step 11

PO = PO - 0.2

If PO = 0.2
set IE = 1        PO = 0.3
IF = 0
return to step 11

PO = PO - 0.1

If PO = 0.1
set ID = 1
    IE = 0
return to step 11

PO = PO - 0.02

If PO < 0.02
set IA = 0
    ID = 0
go to new input reading

If  IG = 0    go to step 82
If  IG = 1    skip to step 103
```

82. Test: If IH = 0 no maximum specific impulse is considered
If IH = 1 maximum specific impulse is calculated for a constant chamber pressure and varying mixture ratio (exit pressure equals ambient pressure)

83. Test: During two calculation loops II = 0, afterwards II = 1

84. New Mixture Ratio for the Approach of Maximum Specific Impulse
AMRWD is Loaded, but an Assumed Value

85.

86. Determination of the Slope for a Tangent through Two Consecutive Points on the Specific Impulse Versus Mixture Ratio Curve

87. Test: Calculation for maximum specific impulse
Check whether maximum has been obtained

88. Test: Slope of tangent is not small enough K = 0.001
Slope of tangent is within required tolerance K = 0.001

89. New Mixture Ratio for the Approach Towards Maximum Specific Impulse

If IH = 0 go to new input reading

If IH = 1 set: AISPZ = AISPY AMRWZ = AMRWY

AISPY = AISPX AMRWY = AMRWX

AISPX = AISP AMRWX = AMRW

and go to step 83

If II = 0 go to step 84

If II = 1 skip to step 86

AMRW = AMRW + AMRWD

Set PO = PC

II = 1 after second calculation loop and return to step 3

$$\tan \alpha = \frac{AISPX - AISPY}{AMRWX - AMRWY}$$

If IJ = 0 go to step 88

If IJ = 1 skip to step 93

If $\tan \alpha \leq |K|$ skip to step 90

If $\tan \alpha > |K|$ go to step 89

$$AMRW = \frac{AMRWY + AMRWX}{2} - \frac{\dfrac{AISPY - AISPX}{AMRWY - AMRWX}}{\dfrac{\dfrac{AISPZ - AISPY}{AMRWZ - AMRWY} - \dfrac{AISPY - AISPX}{AMRWY - AMRWX}}{\dfrac{AMRWZ - AMRWX}{2}}}$$

set PO = PC

and return to step 3

90. Store Maximum Values for Constant Chamber Pressure

91. New Mixture Ratio to Check on the Obtained Maximum Specific Impulse Value $K = 0.001$

92.

93. Test: Maximum Specific Impulse is Obtained

Maximum Specific Impulse is not Within the Required Tolerance

94. Repeat Iteration Using the Mixture Ratio Calculated in Step 91

95. Print the Maximum Values Stored in Step 90

96. Initialize

97. Test: Determine the derivation of the loaded mixture ratio from the one for maximum specific impulse during the first calculation loop

Consecutive Passes

98. Calculate the Deviation of the Original Loaded Mixture Ratio from the One for Maximum Specific Impulse at Loaded Chamber Pressure. Sign is Important for Step 101

AISPM = AISP

AMRWM = AMRW

PCM = PC

$$AMRW = AMRWM + \frac{\tan \alpha}{|\tan \alpha|} \cdot K$$

Set IJ = 1 PO = PC and return to step 3

If $\tan \alpha$ changes sign and

If AISPM > AISP go to step 95

If $\tan \alpha$ does not change signs or

If AISPM $\leq$ AISP go to step 94

Set IJ = 0 PO = PC and return to step 89

PRINT [maximum values for constant chamber pressure]

Set II = 0

IJ = 0

If IK = 0 go to step 98

If IK = 1 skip to step 100

$$PERCT = \frac{AMRWM - AMRWL}{AMRWM}$$

99. Set

100. Test: If IL = 0 no further calculation for desired thrust level is considered

If IL = 1 calculation for a desired thrust level deviating in mixture ratio by PERCT from the one for maximum specific impulse

101. Calculate Mixture Ratio Which Deviates by PERCT from the One for Maximum Specific Impulse at Presently Considered Chamber Pressure

102. Set Switch to Avoid Maximum Specific Impulse Calculation for the Following Calculation Pass

103. Test: Desired thrust level has been obtained
K = 0.001

Desired thrust level has not been obtained

104. Test: First calculation loop
Consecutive passes

105. Set

```
IK = 1

If IL = 0   go to new input reading

If IL = 1   go to step 101

AMRW = AMRWM - AMRWM · PERCT

Set IG = 1
PO = PC
and return to step 3

If $\left|1 - \frac{FTRA}{FL}\right| \le K$
set IG = 0
    IK = 0
    IM = 0
PRINT
and go to new input reading
If $\left|1 - \frac{FTRA}{FL}\right| > K$
go to step 104

If  IM = 0   go to step 105
If  IM = 1   skip to step 108

Set:  PX = PC
      FX = FTRA
```

106. Calculate New Combustion Chamber End Stagnation Pressure (First Calculation Loop)

107. Set

108. Set

109. Calculate New Combustion Chamber End Stagnation Pressure (Consecutive Passes)

110. Set

111. Test: If maximum specific impulse values are considered set IG = 0

If constant mixture ratio is considered set IG = 1

$$PC = PC \frac{FL}{FTRA}$$

$PO = PC$

$IM = 1$

and skip to step 111

$PY = PX \qquad FY = FX$

$PX = PC \qquad FX = FTRA$

$$PC = PX + \frac{PX - PY}{FX - FY} \cdot (FL - FX)$$

$PO = PC$

If $IH = 1$ set $IG = 0$ and return to step 3

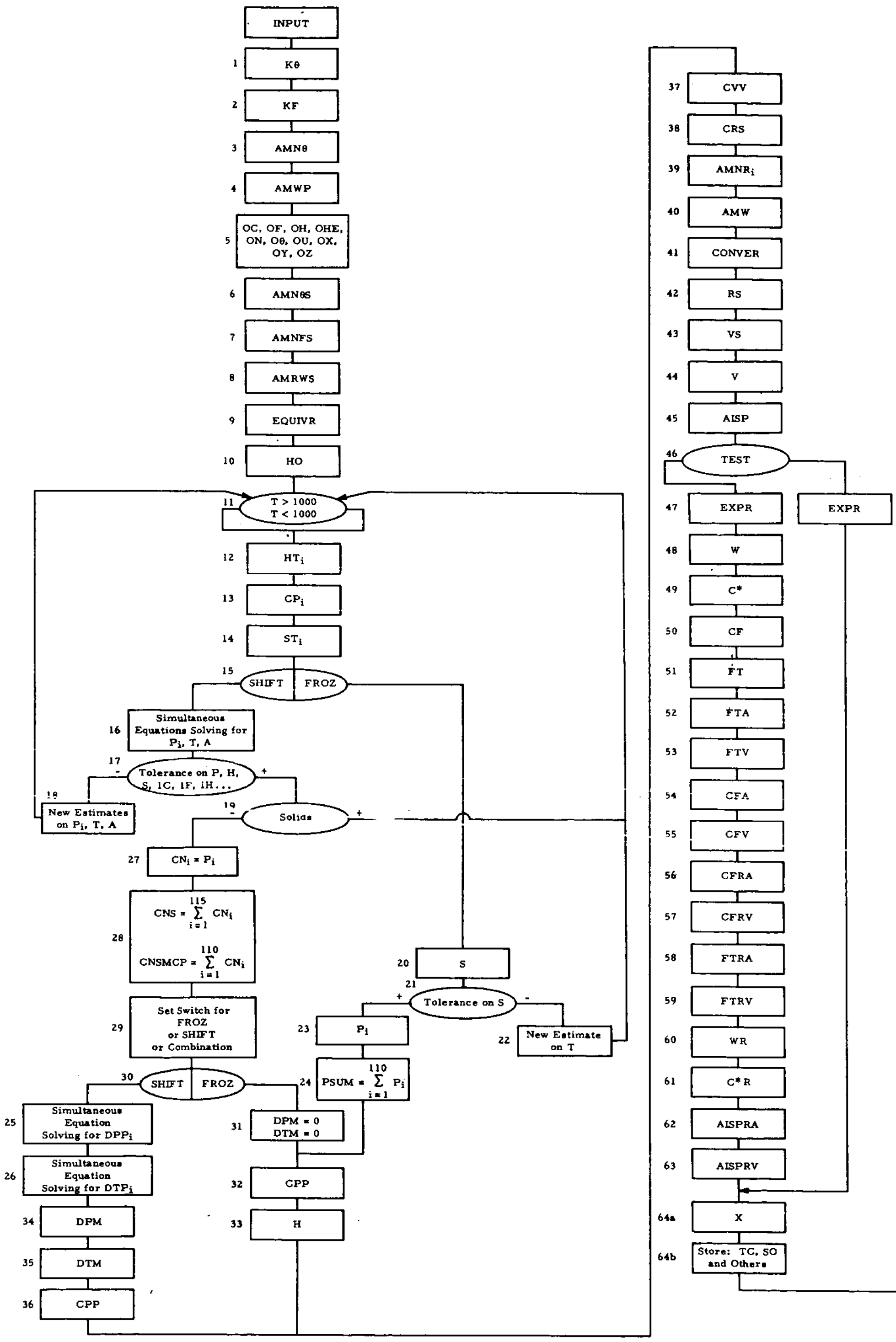
If $IH = 0$ set $IG = 1$ and return to step 3

APPENDIX H

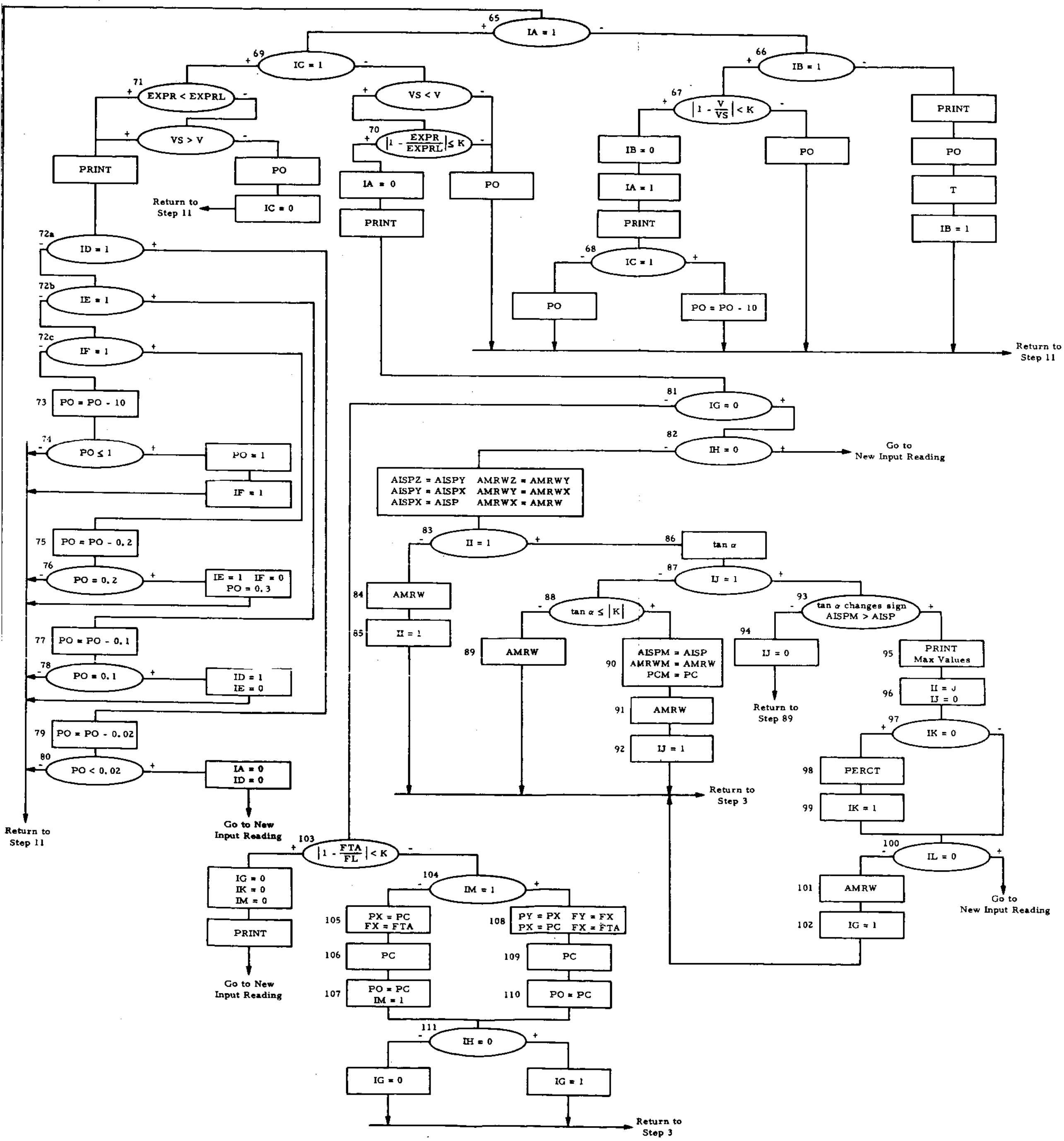
ENGINEERING FLOW CHART
FOR THE
CALCULATION PROGRAM

The symbol in each box refers to the proper equation or test in Appendix G

FLOW DIAGRAM O



F GENERAL COMBUSTION PROGRAM



August 27, 1965 APPROVAL TM X- 53334

CALCULATION OF ROCKET PERFORMANCE PARAMETERS BASED ON THE EQUILIBRIUM COMPOSITION OF THE COMBUSTION PRODUCTS

By Klaus W. Gross

The information in this report has been reviewed for security classification. Review of any information concerning Department of Defense or Atomic Energy Commission programs has been made by the MSFC Security Classification Officer. This report, in its entirety, has been determined to be unclassified.

This document has also been reviewed and approved for technical accuracy.

Klaus W. Gross
KLAUS W. GROSS
Simulation Unit

B.K. Heusinger
B. K. HEUSINGER
Chief, Propulsion Evaluation Branch

H G Paul
H. G. PAUL
Chief, Propulsion Division

Emil A. Hellebrand
for F. B. CLINE
Director, Propulsion and Vehicle Engineering Laboratory

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Lewis Research Center
21000 Brookpark Road
Cleveland 35, Ohio Dr. Sanford Gordon

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College of Engineering
Auburn, Alabama

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Rocketdyne
Division of North American Aviation, Inc.
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Canoga Park, California 91304

Mr. Robert O. Chase
TRW Systems
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