

SATURN HISTORY DOCUMENT
University of Alabama Research Institute
History of Science & Technology Group

Date 3-01-67 Doc. No. -----

#3-67-101

CLEARED
FOR OPEN RELEASE

25 MAY 1967 16

DIRECTORATE FOR POLITICAL AND SECURITY AFFAIRS (DASD-PA)
DEPARTMENT OF DEFENSE

*Theoretical Liquid Propellant
Performance Calculations*

[LIQUID PROPELLANT

ROCKET TECHNOLOGY]

BY

GOERGE MISKO

March 1967

X1.14

NOT ALL HERE

~~ENJOY~~

3076

PREFACE

The purpose of these writings is to compile in one volume the basic elements of thermodynamics and gas dynamics which are useful in the evaluation of thrust chamber performance. It is presumed that the reader will have had an elementary course in thermodynamics and gas dynamics. The discussion of topics useful in evaluating thrust chamber performance is, of necessity, limited to those physical effects amenable to numerical analysis. No effort has been made to discuss those other areas that are as yet in the research stage of development.

The author would like to take this opportunity to express his gratitude to Mr. G. S. Gill for many stimulating discussions on this subject. Thanks are due to Mr. D. J. Kuyper for permission to utilize his discussion on elastic-plastic strain and its application to nozzle throat area change. Finally, the author wishes to express his gratitude to his wife, Alice, who typed the bulk of the manuscript.

G. M.

Dec. 27, 1966

CONTENTS

PART I

THERMODYNAMICS

CHAPTER I.	THE FIRST LAW OF THERMODYNAMICS.....	2
CHAPTER II.	THE SECOND LAW OF THERMODYNAMICS.....	14
CHAPTER III.	CHEMICAL EQUILIBRIUM CRITERIA.....	22

PART II

GAS DYNAMICS

CHAPTER IV.	ONE-DIMENSIONAL GAS DYNAMICS.....	34
CHAPTER V.	THEORETICAL PROPELLANT PERFORMANCE CALCULATIONS.....	44
CHAPTER VI.	GENERALIZED ONE-DIMENSIONAL FLOW.....	66

PART III

THE REAL THRUST CHAMBER

CHAPTER VII.	STAGNATION PRESSURE LOSS AND INCOMPLETE COMBUSTION.....	86
CHAPTER VIII.	HEAT TRANSFER.....	132
CHAPTER IX.	FRICTION.....	155
CHAPTER X.	FLOW IN AXIALLY-SYMMETRIC NOZZLES.....	171
CHAPTER XI.	ANALYSIS OF EXPERIMENTAL DATA.....	184

PART I

THERMODYNAMICS

CHAPTER I

THE FIRST LAW OF THERMODYNAMICS

The first law of thermodynamics is nothing more than a statement of the ^{serv}conservation of energy. For a closed system, the first law is expressed mathematically as follows:

$$dq = du + dw \quad (1)$$

where:

dq = the heat transferred across the boundaries of the system

du = the change in internal energy of the system

dw = the work done on, or by, the system.

We use the bar on the differentials, dq and dw , to indicate that these differentials are not exact; i.e., these quantities depend upon the path. The unbarred differential, du , indicates a quantity that is an exact differential; i.e., a quantity dependent only on the initial and final state of the system irrespective of the path followed in going between the initial and final state.

The power of thermodynamics lies in the logical structure of the subject and the extensive use of exact differentials in the mathematical formulation. This shall be illustrated by various examples in the following discussion.

EXPANSION WORK

An explicit expression for the work of expansion may be

obtained by considering a piston acted upon by a constant pressure P , see Figure 1.

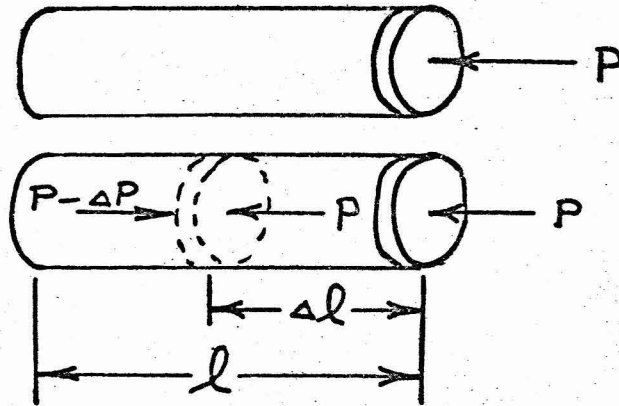


Figure 1. Schematic for Development of Expansion Work

The pressure resisting the motion of the piston is infinitesimally different from the external pressure P . The external pressure acts over an area A so that the force on the piston is

$$F = PA \quad (2)$$

and the work in moving the piston a distance Δl is

$$\Delta W = F \Delta l = PA \Delta l \quad (3)$$

But the volume displaced is

$$\Delta V = A \Delta l \quad (4)$$

so that

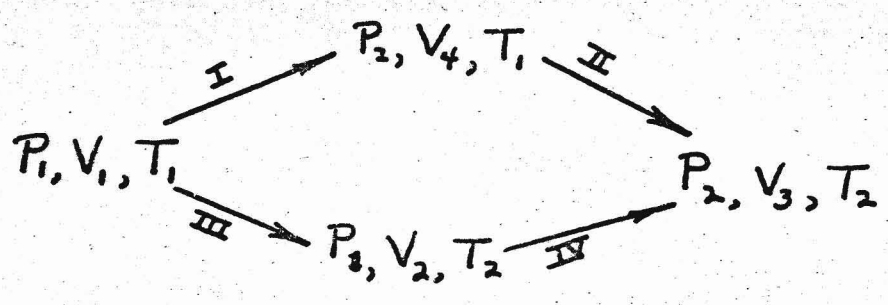
$$\Delta W = P \Delta V \quad (5)$$

or in the limit

$$dW = PdV \quad (6)$$

DEMONSTRATION THAT WORK DEPENDS ON PATH

Consider the following two different paths between an initial and final state



Assume that an ideal gas is acted on so that the equation of state is

$$PV = RT$$

The work of expansion is

$$W = \int P dV$$

Now

$$W_I = \int P dV = RT_1 \int_{V_1}^{V_4} \frac{dV}{V} = RT_1 \ln \frac{V_4}{V_1} \tag{7}$$

$$W_{II} = \int_{V_4}^{V_3} P dV = P(V_3 - V_4) \tag{8}$$

$$W_{III} = \int_{V_1}^{V_2} P dV = P(V_2 - V_1) \tag{9}$$

$$W_{IV} = \int P dV = RT_2 \int_{V_2}^{V_3} \frac{dV}{V} = RT_2 \ln \frac{V_3}{V_2} \tag{10}$$

In general, the work along path I-II will be different from the work along path III-IV; i.e.,

$$W_I + W_{II} \neq W_{III} + W_{IV} \tag{11}$$

REVERSIBLE ADIABATIC PROCESS

An adiabatic process is defined as a change from an initial to a final state such that no heat is transferred across the

boundaries of the system; thus, we have

$$dq = 0 \quad (12)$$

and the first law becomes

$$du + dw = 0 \quad (13)$$

Considering only reversible expansion work yields

$$dw = PdV \quad (14)$$

where:

P = pressure in system

V = volume of the system

The use of equation (14) implies a reversible process since the system pressure must be everywhere the same and the changes in pressure must be sufficiently small so that no pressure gradients are generated. If pressure gradients were included, a spatial coordinate would be required in equation (14) to describe such a gradient. Substitution of eq. (14) into eq. (13) yields

$$du + PdV = 0 \quad (15)$$

Assume that the internal energy U is a function of volume and temperature only, then

$$u = u(V, T) \quad (16)$$

and

$$du = \left(\frac{\partial u}{\partial V}\right)_T dV + \left(\frac{\partial u}{\partial T}\right)_V dT \quad (17)$$

for an ideal gas

$$\left(\frac{\partial u}{\partial V}\right)_T = 0 \quad (18)$$

so that eq. (17) becomes

$$du = \left(\frac{\partial u}{\partial T}\right)_V dT \quad (19)$$

and consequently eq. (15) becomes

$$\left(\frac{\partial u}{\partial T}\right)_V dT + PdV = 0 \quad (20)$$

The heat capacity is by definition the amount of heat added to, or taken from, the system per degree of temperature change. According to the first law

$$dq = du + PdV \quad (21)$$

and for a constant volume process eq. (21) becomes

$$dq = du \quad (22)$$

but

$$du = \left(\frac{\partial u}{\partial T}\right)_V dT \quad (23)$$

so that eq. (22) may be written

$$dq = \left(\frac{\partial u}{\partial T}\right)_V dT \quad (24)$$

Replacing the derivatives in eq. (24) with finite differences yields

$$\Delta q = \left(\frac{\partial u}{\partial T}\right)_V \Delta T \quad (25)$$

or

$$\frac{\Delta q}{\Delta T} = \left(\frac{\partial u}{\partial T}\right)_V \quad (26)$$

Taking the limit of left-hand side of eq. (26) yields

$$\lim_{\Delta T \rightarrow 0} \frac{\Delta q}{\Delta T} = \frac{dq}{dT} \equiv C \quad (27)$$

where: C = heat capacity

Combining eqs. (20), (26), and (27) yields

$$C_V dT + PdV = 0 \quad (28)$$

The ideal gas equation of state per mole is

$$PV = RT \quad (29)$$

where R = universal gas constant

T = absolute temperature of the system

and substitution of eq. (29) into eq. (28) results in

$$C_V dT + RT \frac{dV}{V} = 0 \quad (30)$$

Dividing through by T and integrating leads to

$$\int_{T_1}^{T_2} C_V \frac{dT}{T} = -R \int_{V_1}^{V_2} \frac{dV}{V} \quad (31)$$

Assuming C_V is a constant permits explicit integration of eq. (31) to obtain the result

$$C_V \ln \frac{T_2}{T_1} = -R \ln \frac{V_2}{V_1} \quad (32)$$

or

$$\left(\frac{T_2}{T_1}\right)^{C_V} = \left(\frac{V_1}{V_2}\right)^R \quad (33)$$

or after suitable algebraic manipulation

$$\frac{P_2}{P_1} = \left(\frac{P_2}{P_1}\right)^{\frac{R}{k}} \quad (34)$$

where:

$$\frac{R}{k} = \text{specific heat ratio}$$

Equation (34) has been derived subject to the following assumptions: (1) the system is enclosed with perfectly insulating walls, (2) the only work done by the system is expansion work, (3) the process is reversible, (4) the system contains an ideal gas, and (5) the constant volume heat capacity is a constant.

ENTHALPY

A quantity of considerable use in chemical thermodynamics and gas dynamics is the enthalpy. By definition the enthalpy is the sum

of the internal energy and pressure-volume product of the system. Mathematically this becomes

$$H = U + PV \quad (35)$$

Taking differentials of both sides of eq. (35) results in the following

$$dH = dU + PdV + VdP \quad (36)$$

and utilizing eq. (21) reduces eq. (36) to

$$dH = dq + VdP \quad (37)$$

Constant Pressure Heat Capacity

For a constant pressure process, eq. (37) becomes

$$dH = dq \quad (38)$$

or in terms of finite differences

$$\Delta H = \Delta q \quad (39)$$

Dividing both sides of eq. (39) by ΔT and taking the limit yields

$$\lim_{\Delta T \rightarrow 0} \frac{\Delta H}{\Delta T} = \lim_{\Delta T \rightarrow 0} \frac{\Delta q}{\Delta T} \quad (40)$$

or

$$\left(\frac{\partial H}{\partial T}\right)_P = \left(\frac{\partial q}{\partial T}\right)_P = C_P \quad (41)$$

Equation (41) is the defining relationship for the constant pressure heat capacity.

THERMOCHEMISTRY

We shall consider the problem of calculating the heat of chemical reaction at constant pressure. This is of immediate importance since, in general, rocket combustion chamber processes occur at what constitutes constant pressure conditions. The first law of thermodynamics for a finite process is

$$\Delta q = \Delta U + P\Delta V \tag{42}$$

From eq. (35), we obtain for a finite process

$$\Delta H = \Delta U + P\Delta V + V\Delta P \tag{43}$$

and combination of eqs. (42) and (43) yields

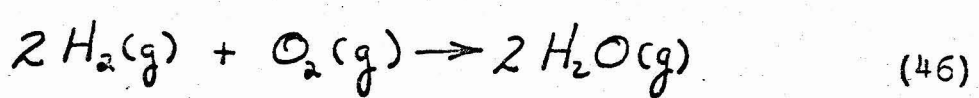
$$\Delta H = \Delta q + V\Delta P \tag{44}$$

For a constant pressure process, eq. (44) becomes

$$\Delta H_P = \Delta q_P \tag{45}$$

where the subscript P is used to denote a constant pressure process. Thus, it has been shown that the problem of computing constant pressure heats of reaction is one of computing changes in enthalpy.

The heat of reaction is simply calculated by using standard heats of formation which are nothing more than the enthalpy change required to form that species from the elements in their standard state at constant temperature. For example, consider the formation of water by the chemical combination of molecular hydrogen and molecular oxygen



The heat of reaction is the enthalpy difference between the final state and the initial state or

$$\Delta H = 2[\Delta H_f^\circ(H_2O)] - 2[\Delta H_f^\circ(H_2)] - [\Delta H_f^\circ(O_2)] \tag{47}$$

where: $\Delta H_f^\circ(\dots)$ = standard heat of formation for the chemical species in parentheses

Using the heats of formation in Table I in eq. (47) yields

$$\Delta H = (2)(-57.7979) = -115.5958 \text{ kcal} \tag{48}$$

TABLE 1. STANDARD HEATS OF FORMATION OF SELECTED SUBSTANCES AT 298.16°K

10.

SUBSTANCE	ΔH_f° kcal/mole	SUBSTANCE	ΔH_f° kcal/mole
O(g)	59.159	NO ₂ (g)	8.091
O ₂ (g)	0.000	NO ₃ (g)	13.0
O ₃ (g)	34.0	N ₂ O(g)	19.49
H(g)	52.089	N ₂ O ₃ (g)	20.0
H ₂ (g)	0.000	N ₂ O ₄ (g)	2.309
OH(g)	10.06	N ₂ O ₅ (g)	3.6
H ₂ O(g)	-57.7979	N ₂ O ₅ (c)	-10.0
H ₂ O(l)	-68.3174	NH ₃ (g)	-11.04
H ₂ O ₂ (g)	-31.83	N ₂ H ₄ (l)	12.05
H ₂ O ₂ (l)	-44.84	N ₂ H ₄ · H ₂ O(l)	-57.95
F(g)	19.45	HNO ₃ (l)	-41.404
F ₂ (g)	0.000	HNO ₃ · H ₂ O(l)	-112.960
F ₂ O(g)	5.5	NF ₃ (g)	-27.2
HF(g)	-64.2	C(g)	171.698
Cl(g)	29.012	C(c, diamond)	0.4532
Cl ₂ (g)	0.000	C(c, graphite)	0.0000
HCl(g)	-22.063	CO(g)	-26.4157
Cl ₂ O ₇ (g)	63.4	CO ₂ (g)	-94.0518
ClF(g)	-25.7	CH ₄ (g)	-17.889
Br(g)	26.71	CF ₄ (g)	-162.5
Br ₂ (g)	7.34	B(c)	0.000
HBr(g)	-8.66	B(g)	95.3
I(g)	25.482	B ₂ (g)	105.7
I ₂ (g)	14.876	B ₂ H ₆ (g)	-33
I ₂ (c)	0.000	B ₅ H ₉ (l)	-17
HI(g)	6.20	BO(g)	-56.5
N(g)	112.75	B ₂ O ₃ (c)	-342.76
N ₂ (g)	0.000	BF ₃ (g)	-285.8
NO(g)	21.600		

where the minus sign indicates heat release; i.e., an exothermic reaction.

EFFECT OF TEMPERATURE ON THE HEAT OF REACTION

The effect of temperature on the heat of reaction may be shown in a very simple manner. Consider the general reaction



for which the heat of reaction is

$$\Delta H = H_B - H_A \quad (50)$$

where

H_B = enthalpy of the products

H_A = enthalpy of the reactants.

Differentiate eq. (50) with respect to temperature at constant pressure and it is seen that

$$\left[\frac{\partial(\Delta H)}{\partial T} \right]_P = \left(\frac{\partial H_B}{\partial T} \right)_P - \left(\frac{\partial H_A}{\partial T} \right)_P \quad (51)$$

But according to eq. (41), we may write eq. (51) in the following equivalent form

$$\left[\frac{\partial(\Delta H)}{\partial T} \right]_P = (C_P)_B - (C_P)_A \quad (52)$$

or

$$\left[\frac{\partial(\Delta H)}{\partial T} \right]_P = \Delta C_P \quad (53)$$

Integration of eq. (53) yields the Kirchoff equation

$$\Delta H_2 - \Delta H_1 = \int_{T_1}^{T_2} \Delta C_P dT \quad (54)$$

where:

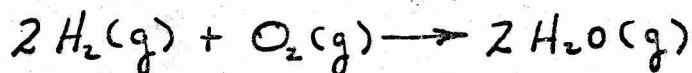
ΔH_2 = heat of reaction at temperature

ΔH_1 = heat of reaction at temperature

Equation (44) may be used to evaluate the heat of reaction at a temperature T_2 if the heat of reaction is known at temperature T_1 and

if the variation of heat capacity with temperature is known for the products and reactants.

Consider the reaction



and calculate the heat of reaction at 120°C . The heat of reaction at 25°C was previously shown to be 115,596 cal. Now

$$\Delta H_{373} = \Delta H_{298} + \int_{298}^{373} \Delta C_p dT$$

$$C_p(\text{H}_2) = 6.62 + 0.81 \times 10^{-3} T$$

$$C_p(\text{O}_2) = 6.76 + 0.606 \times 10^{-3} T + 0.13 \times 10^{-6} T^2$$

$$C_p(\text{H}_2\text{O}) = 7.00 + 2.77 \times 10^{-3} T$$

$$\Delta H_{373} = \Delta H_{298} + \int_{298}^{373} (2)(7.00 + 2.77 \times 10^{-3} T) dT$$

$$- \int_{298}^{373} [(2)(6.62 + 0.81 \times 10^{-3} T) + (6.76 + 0.606 \times 10^{-3} T + 0.13 \times 10^{-6} T^2)] dT$$

$$\Delta H_{373} = -115,850 \text{ cal.}$$

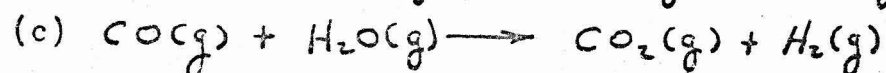
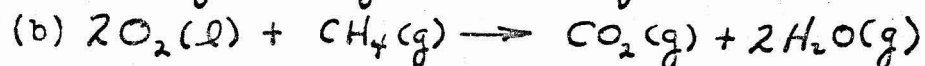
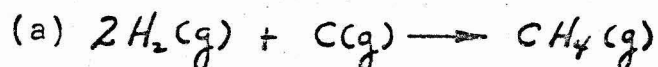
Thus, it is seen that more heat is released at the higher reaction temperature.

PROBLEMS

1. Develop expressions for the work of expansion under the conditions of: (a) constant pressure, (b) constant temperature, (c) constant volume, and (d) reversible adiabatic process.

Assume the fluid is an ideal gas.

2. Calculate the heat of reaction for the following



3. Calculate the work required to compress one mole of ideal gas from one atm to 200 atm at 298.16°K.

4. The van der Waal's equation of state is

$$\left(P + \frac{a}{V^2}\right)(V - b) = RT$$

where a and b are constants. Show that for a van der Waal's gas, the isothermal, reversible work of expansion for one mole is given by

$$W = RT \ln \frac{V_2 - b}{V_1 - b} - a \left(\frac{1}{V_1} - \frac{1}{V_2} \right)$$

where V_1 is the initial volume and V_2 is the final volume.

CHAPTER II

THE SECOND LAW OF THERMODYNAMICS

The first law of thermodynamics is only concerned with the problem of making an energy balance. In one sense, the first law may be looked upon as an accountant that keeps track of where energy goes and how much goes there. However, the first law places no restrictions upon energy transfer so that utilization of the first law by itself could result in the interesting situation wherein heat would be transferred from a system at low temperature to a system at a higher temperature. The second law of thermodynamics plays the part of a manager who makes policy so that limits are set up and, for example, heat transfer is permitted to take place only from a high temperature to a lower temperature. Like the first law, the second law is an empiricism and is justified by the fact that all experience has been in accord with this law.

The second law of thermodynamics introduces the concept of entropy. According to the second law, all entropy changes must be zero or positive. Specifically, the entropy change during a reversible process is zero and during a natural or spontaneous process is positive; i.e.,

$$\begin{aligned} dS &= 0, & \text{for a reversible process} \\ dS &> 0, & \text{for a natural or spontaneous process} \end{aligned} \quad (1)$$

Entropy, S , is defined as the ratio of the heat change within the system divided by the absolute temperature of the system

$$dS \geq \frac{dq}{T} \quad (2)$$

and it should be noted that dS is a perfect differential. This is extremely valuable when making computations of entropy changes since we may compute the entropy change between any two states by following a hypothetical reversible process and thereby obtain the irreversible entropy change. We shall now consider the calculation of entropy changes for various physical processes.

CHANGE OF PHASE

Since a change of phase occurs at constant temperature and the change of phase is a reversible process, eq. (2) may be used to evaluate the entropy change. Thus

$$dS_{(\text{phase change})} = \frac{dq}{T} \quad (3)$$

or

$$\Delta S = \frac{l}{T} \quad (4)$$

where: l = latent heat of phase transition

ENTROPY CHANGES FOR AN IDEAL GAS

Combining the first and second laws of thermodynamics yields the following very useful relation

$$TdS = du + PdV \quad (5)$$

$$dS = C_V \frac{dT}{T} + R \frac{dV}{V} \quad (6)$$

Integrating eq. (6) yields

$$\Delta S = C_V \ln \frac{T_2}{T_1} + R \ln \frac{V_2}{V_1} \quad (7)$$

From eq. (7) it follows that the entropy change during the isothermal expansion of an ideal gas is given by

$$\Delta S = R \ln \frac{V_2}{V_1} \quad (8)$$

For a change of temperature at constant volume, the entropy increase of an ideal gas is found to be

$$\Delta S = C_V \ln \frac{T_2}{T_1} \quad (9)$$

In a reversible, adiabatic process, the entropy change is zero and thus eq. (6) becomes

$$C_V \frac{dT}{T} + R \frac{dV}{V} = 0 \quad (10)$$

which is identical to the equation used in Chapter I to derive the characteristic expression for a reversible, adiabatic process.

ENTROPY OF MIXING

Consider n_1 moles of an ideal gas at volume V_1 and n_2 moles of an ideal gas at volume V_2 . The two volumes of gas are both at temperature T and pressure P . If these two volumes are mixed together, the final volume V will be

$$V = V_1 + V_2 \quad (11)$$

and the total number of moles n will be

$$n = n_1 + n_2 \quad (12)$$

For an isothermal process, the entropy increase is given by eq. (8) which we apply to each constituent

$$\Delta S_1 = n_1 R \ln \frac{V}{V_1} \quad (13)$$

and

$$\Delta S_2 = n_2 R \ln \frac{V}{V_2} \quad (14)$$

The total entropy change is

$$\Delta S = \Delta S_1 + \Delta S_2 \quad (15)$$

or

$$\Delta S = n_1 R \ln \frac{V}{V_1} + n_2 R \ln \frac{V}{V_2} \quad (16)$$

By definition, the mole fraction of a given component is the number of moles of that component divided by the total number of moles in the mixture, so that

$$X_1 = \frac{n_1}{n} \quad (17)$$

$$X_2 = \frac{n_2}{n} \quad (18)$$

where

X_1 = mole fraction of component gas 1

X_2 = mole fraction of component gas 2

At constant pressure and temperature, the ideal gas law yields the result that

$$X_1 = \frac{V_1}{V} \quad (19)$$

and

$$X_2 = \frac{V_2}{V} \quad (20)$$

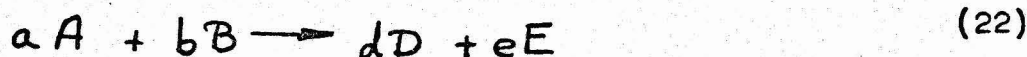
Using eqs. (19) and (20) in eq. (16) yields

$$\Delta S(\text{mixing}) = -n_1 R \ln X_1 - n_2 R \ln X_2 \quad (21)$$

ENTROPY CHANGE AND CHEMICAL REACTION

The entropy change for a chemical reaction is calculated in the same manner as the enthalpy change. Since the entropy is a path independent quantity, the entropy change is simply the entropy difference between the final and initial states.

Consider the general reaction



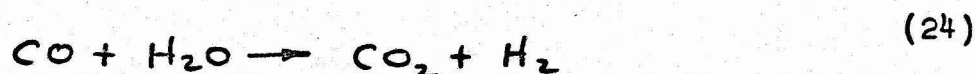
and the entropy change is

$$\begin{aligned} \Delta S(\text{reaction}) = & dS_T^\circ(D) + eS_T^\circ(E) \\ & - aS_T^\circ(A) - bS_T^\circ(B) \end{aligned} \quad (23)$$

where:

$S_T^\circ(\dots)$ = standard entropy at temperature T
of chemical species in parenthesis

For example, the entropy change for the water gas reaction is



$$\Delta S_{298}(\text{reaction}) = 51.06 + 31.21 - 47.30 - 45.11 = -10.14 \text{ cal/deg.}$$

A tabulation of molar entropies for some selected compounds is given in Table 2.

TABLE 2a

MOLAR ENTROPIES (cal/mole-°K)

T (°K)	O ₂ (g)	H ₂ (g)	N ₂ (g)	O (g)	H (g)	N (g)	C (c, graphite)
298.16	49.00	31.21	45.77	38.47	27.39	36.61	1.361
300	49.05	31.25	45.81	38.50	27.42	36.65	1.374
400	51.09	33.25	47.82	39.99	28.85	38.07	2.081
500	52.72	34.81	49.39	41.13	29.96	39.18	2.788
600	54.10	36.08	50.69	42.05	30.87	40.09	3.474
700	55.30	37.17	51.81	42.83	31.63	40.85	4.127
800	56.36	38.11	52.80	43.50	32.30	41.52	4.740
900	57.32	38.95	53.69	44.09	32.88	42.10	5.314
1000	58.19	39.70	54.51	44.62	33.40	42.63	5.846
1100	58.99	40.40	55.26	45.09	33.88	43.10	6.342
1200	59.73	41.04	55.95	45.53	34.31	43.53	6.807
1300	60.42	41.63	56.61	45.93	34.71	43.93	7.247
1400	61.06	42.19	57.22	46.30	35.08	44.30	7.663
1500	61.66	42.72	57.79	46.64	35.42	44.64	8.057
1600	62.23	43.22	58.33	46.96	35.74	44.96	8.43
1700	62.76	43.70	58.84	47.27	36.04	45.26	8.79
1800	63.27	44.15	59.32	47.55	36.32	45.55	9.13
1900	63.75	44.59	59.79	47.82	36.59	45.82	9.45
2000	64.21	45.01	60.23	48.07	36.84	46.07	9.76
2100	64.66	45.41	60.65	48.32	37.09	46.31	10.05
2200	65.08	45.79	61.05	48.55	37.32	46.54	10.34
2300	65.49	46.16	61.44	48.77	37.54	46.76	10.61
2400	65.88	46.52	61.81	48.98	37.75	46.98	10.88
2500	66.26	46.87	62.16	49.19	37.96	47.18	11.13
2750	67.15	47.69	63.00	49.66	38.43	47.65	11.73
3000	67.98	48.45	63.77	50.10	38.86	48.09	12.29
3250	68.74	49.16	64.48	50.50	39.26	48.49	12.80
3500	69.46	49.82	65.14	50.87	39.63	48.87	13.29
3750	70.14	50.44	65.76	51.22	39.97	49.22	13.74
4000	70.78	51.03	66.34	51.55	40.29	49.55	14.18
4250	71.38	51.59	66.88	51.86	40.59	49.87	
4500	71.96	52.12	67.40	52.15	40.88	50.18	
4750	72.50	52.62	67.89	52.43	41.15	50.47	
5000	73.02	53.10	68.35	52.69	41.40	50.76	

TABLE 2b

MOLAR ENTROPIES (cal/mole-°K)

T (°K)	Cl ₂ (g)	Cl (g)	HCl (g)	F ₂ (g)	F (g)	HF (g)
298.16	53.29	39.46	44.62	48.51	37.93	41.53
300	53.34	39.49	44.66	48.55	37.97	41.57
400	55.72	41.01	46.66	50.76	39.52	43.57
500	57.63	42.22	48.22	52.56	40.71	45.13
600	59.21	43.21	49.51	54.08	41.66	46.40
700	60.56	44.05	50.60	55.39	42.46	47.48
800	61.74	44.77	51.57	56.27	43.15	48.42
900	62.79	45.41	52.43	57.57	43.76	49.25
1000	63.74	45.97	53.22	58.50	44.29	50.01
1100	64.59	46.47	53.95	59.35	44.78	50.70
1200	65.38	46.93	54.62	60.13	45.22	51.34
1300	66.10	47.35	55.26	60.85	45.62	51.94
1400	66.77	47.74	55.85	61.52	45.99	52.50
1500	67.39	48.09	56.41	62.15	46.34	52.93
1600	68.03	48.43	56.81	62.74	46.66	53.52
1700	68.58	48.74	57.31	63.30	46.97	54.00
1800	69.10	49.03	57.79	63.82	47.26	54.45
1900	69.59	49.31	58.24	64.32	47.53	54.89
2000	70.06	49.57	58.67	64.79	47.78	55.30
2100	70.51	49.82	59.09	65.25	48.03	55.68
2200	70.94	50.06	59.49	65.68	48.26	56.08
2300	71.35	50.28	59.87	66.09	48.48	56.45
2400	71.74	50.50	60.24	66.50	48.69	56.81
2500	72.12	50.70	60.60	66.87	48.90	57.15
2750		51.18				
3000	73.82	51.62	62.20	68.60	49.81	58.71
3250		52.03				
3500	75.27	52.40	63.58			
3750		52.74				
4000	76.52	53.07	64.77	71.36	51.24	61.24
4250		53.37				
4500	77.63	53.66	65.84			
4750						
5000	78.63	54.18	66.80	73.54	52.35	63.26

MOLAR ENTROPIES (cal/mole-°K)

T (°K)	OH (g)	NO (g)	C (g)	CO (g)	CO ₂ (g)	H ₂ O (g)	CH ₄ (g)
298.16	43.89	50.34	37.76	47.30	51.06	45.11	44.50
300	43.93	50.38	37.79	47.34	51.12	45.15	44.55
400	45.98	52.44	39.22	49.35	53.82	47.49	47.17
500	47.55	54.05	40.33	50.93	56.11	49.34	49.48
600	48.84	55.39	41.24	52.24	58.11	50.90	51.64
700	49.93	56.56	42.01	53.37	59.90	52.27	53.68
800	50.88	57.59	42.67	54.38	61.51	53.49	55.61
900	51.72	58.52	43.26	55.29	62.98	54.60	57.45
1000	52.49	59.37	43.78	56.12	64.33	55.62	59.21
1100	53.19	60.15	44.25	56.88	65.58	56.56	60.89
1200	53.85	60.87	44.68	57.59	66.75	57.45	62.50
1300	54.46	61.54	45.08	58.24	67.84	58.29	64.04
1400	55.03	62.17	45.45	58.86	68.86	59.08	65.51
1500	55.57	62.76	45.79	59.44	69.82	59.83	66.93
1600	56.08	63.32	46.12	59.98	70.72	60.55	
1700	56.56	63.84	46.42	60.50	71.58	61.24	
1800	57.03	64.33	46.70	60.99	72.40	61.90	
1900	57.07	64.80	46.97	61.45	73.17	62.53	
2000	57.89	65.25	47.23	61.90	73.92	63.14	
2100	58.30	65.68	47.47	62.32	74.63	63.72	
2200	58.66	66.09	47.71	62.77	75.31	64.29	
2300	59.07	66.49	47.93	63.11	75.96	64.83	
2400	59.43	66.86	48.15	63.49	76.59	65.36	
2500	59.78	67.23	48.35	64.85	77.20	65.86	
2750	60.61	68.08	48.84	63.69	78.62	67.07	
3000	61.37	68.86	49.29	65.46	79.92	68.19	
3250	62.09	69.58	49.70	66.17	81.14	69.23	
3500	62.75	70.25	50.09	66.84	82.27	70.22	
3750	63.38	70.87	50.45	67.46	83.33	71.15	
4000	63.97	71.46	50.80	68.04	84.32	72.04	
4250	64.53	72.01	51.12	68.59	85.26	72.86	
4500	65.06	72.54	51.43	69.10	86.15	73.63	
4750	65.57	73.03	51.73	69.59	86.99	74.37	
5000	66.05	73.50	52.00	70.06	87.80	75.08	

PROBLEMS

1. Solid mercury melts at -38.9°C with the absorption of 560 cal per mole. Calculate the entropy change.
2. A mole of supercooled water freezes at -10°C . The heat capacity of liquid water is 1.0 cal per degree and that of ice is 0.5 cal per degree over the range. The crystallization of liquid water at 0°C evolves 80 cal per mole. Calculate the entropy change for the process.
3. A thermostat was maintained at a temperature of 96.9°C . The air in the room was at 26.9°C . During a certain length of time 1000 cal of heat leaked through the thermostat insulation into the room.
 - (a) What was the entropy change of the thermostat?
 - (b) What was the entropy change of the air in the room?
 - (c) Was the process reversible or irreversible?
4. One mole of steam is compressed reversibly to liquid water at the boiling point 100°C . Heat of vaporization of water at 100°C and 760 mm is 539.7 cal per gram. Calculate:

$$\begin{array}{l} \left. \begin{array}{l} \text{(a)} \\ \text{(b)} \\ \text{(c)} \\ \text{(d)} \\ \text{(e)} \end{array} \right\} \begin{array}{l} w \\ q \\ \Delta H \\ \Delta U \\ \Delta S \end{array} \end{array}$$

5. Starting with the combined form of the first and second laws, show that

$$PV^{\gamma} = \text{constant.}$$

List all assumptions made in the argument.

CHAPTER III
CHEMICAL EQUILIBRIUM CRITERIA

Equilibrium criteria are easily developed from the Gibbs free energy and the Helmholtz free energy. By definition, the Gibbs free energy is

$$G = H - TS = U + PV - TS \quad (1)$$

and the Helmholtz free energy is

$$A = U - TS \quad (2)$$

Taking differentials of eqs. (1) and (2), and using the combined form of the first and second laws leads to

$$dG = VdP - SdT \quad (3)$$

and

$$dA = -PdV - SdT \quad (4)$$

Equations (3) and (4) apply to thermodynamic systems which are subjected to pressure-volume work.

It is convenient to view the free energies in terms of the useful work done on, or by, the system other than pressure-volume work. To do this, we write the first law as follows

$$dq = du + PdV + d\phi \quad (5)$$

where $d\phi$ is work other than pressure-volume work. Combining eq. (5) with the second law yields

$$TdS = du + PdV - d\phi \quad (6)$$

But

$$TdS = dH - VdP - d\phi \quad (7)$$

and

$$dG = dH - TdS - SdT \quad (8)$$

Combination of eqs. (7) and (8) yields

$$dG = VdP - SdT + d\phi \quad (9)$$

or

$$d\phi = dG - VdP + SdT \quad (10)$$

At constant temperature and constant pressure

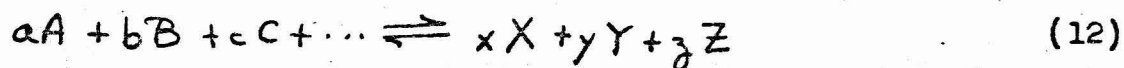
$$d\phi = dG \quad (11)$$

so that the useful work other than pressure-volume work is equal to the change in Gibbs free energy.

The condition when no useful work is done other than pressure volume work is the equilibrium condition. Thus, at equilibrium, the change in Gibbs free energy is zero.

EQUILIBRIUM CONSTANT

For the purposes of this discussion, the equilibrium constant will be defined for the special case of an ideal gas. We consider the following general reaction



where the reactants and products are ideal gases. The equilibrium constant for the reaction of eq. (12) is

$$K_p = \frac{p_X^x p_Y^y p_Z^z \dots}{p_A^a p_B^b p_C^c \dots} \quad (13)$$

where the p_β^α is the partial pressure of species β raised to the power α . The quantity α is numerically equal to the molar coefficients in the reaction of eq. (12). Equation (13) can be recast into another useful form by noting that the partial pressure of an ideal gas is equal to the product of the mole fraction and pressure of the system; i.e.,

$$p = xP \quad (14)$$

where:

p = partial pressure

x = mole fraction

P = system pressure.

Introduction of eq. (14) into eq. (13) yields

$$K_x = \frac{X_x^x X_y^y X_z^z \dots}{X_A^a X_B^b X_C^c \dots} P^{(x+y+z \dots)/(a+b+c \dots)} \quad (15)$$

EQUILIBRIUM CONSTANT AND GIBBS FREE ENERGY

For a system participating in a reversible isothermal process with pressure-volume work only, the change in Gibbs free energy is

$$dG = VdP \quad (16)$$

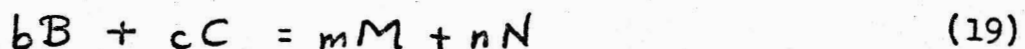
In the case of an ideal gas, eq. (16) becomes

$$dG = RT \frac{dP}{P} \quad (17)$$

and upon integration of eq. (17), we obtain

$$\Delta G = RT \ln \frac{P_2}{P_1} \quad (18)$$

Now consider the general reaction



The change in free energy for the reaction of eq. (19) is

$$\Delta G = mG_M + nG_N - bG_B - cG_C \quad (20)$$

Suppose this reaction takes place under two different sets of conditions. Call the two set of reaction conditions Δ and e .

For the Δ states, we have

$$\Delta G^\Delta = m(G_M)^\Delta + n(G_N)^\Delta - b(G_B)^\Delta - c(G_C)^\Delta \quad (21)$$

and for the e states, we have

$$\Delta G^e = m(G_M)^e + n(G_N)^e - b(G_B)^e - c(G_C)^e \quad (22)$$

Subtracting eq. (22) from eq. (21) yields

$$\begin{aligned} \Delta G^\Delta - \Delta G^e &= m(G_M^\Delta - G_M^e) + n(G_N^\Delta - G_N^e) \\ &\quad - b(G_B^\Delta - G_B^e) - c(G_C^\Delta - G_C^e) \end{aligned} \quad (23)$$

But according to eq. (18)

$$G_M^s - G_M^e = RT \ln \frac{P_M^s}{P_M^e} \quad (24)$$

and

$$m(G_M^s - G_M^e) = RT \ln \left(\frac{P_M^s}{P_M^e} \right)^m \quad (25)$$

Similar relations hold for the other constituents. Substitution of eq. (25) and its counterparts into eq. (23) yields

$$\begin{aligned} \Delta G^s - \Delta G^e = & RT \ln \left(\frac{P_M^s}{P_M^e} \right)^m + RT \ln \left(\frac{P_N^s}{P_N^e} \right)^n \\ & - RT \ln \left(\frac{P_B^s}{P_B^e} \right)^b - RT \ln \left(\frac{P_C^s}{P_C^e} \right)^c \end{aligned} \quad (26)$$

Rearranging eq. (26) to bring together terms relating to the same state yields

$$\Delta G^s - \Delta G^e = RT \ln \frac{(P_M^s)^m (P_N^s)^n}{(P_B^s)^b (P_C^s)^c} - RT \ln \frac{(P_M^e)^m (P_N^e)^n}{(P_B^e)^b (P_C^e)^c} \quad (27)$$

or

$$\Delta G^s - \Delta G^e = RT \ln K^s - RT \ln K^e \quad (28)$$

Now we identify the state s as the reference state in which the ideal gas has a pressure of unity, so that

$$K^s = 1 \text{ and } \ln K^s = 0 \quad (29)$$

then

$$\Delta G^s = \Delta G^0 \quad (30)$$

Further, we identify the state e as the equilibrium state and

then

$$K^e = K_p \quad (31)$$

and

$$\Delta G^e = 0 \quad (32)$$

since the change in Gibbs free energy is zero for an equilibrium process. Thus, eq. (28) becomes

$$\Delta G^0 = -RT \ln K_p \quad (33)$$

EFFECT OF TEMPERATURE ON EQUILIBRIUM CONSTANT

Rearrange eq. (33) to the following:

$$\ln K_p = -\Delta G^\circ / RT \quad (34)$$

and differentiate eq. (34) with respect to temperature

$$\frac{d(\ln K_p)}{dT} = -\frac{1}{R} \frac{d(\Delta G^\circ / T)}{dT} \quad (35)$$

Differentiation of G/T at constant pressure gives

$$\frac{d(G/T)}{dT} = \frac{T \frac{dG}{dT} - G}{T^2} \quad (36)$$

But

$$\left(\frac{\partial G}{\partial T}\right)_P = -S \quad (37)$$

therefore eq. (36) becomes

$$\frac{d(G/T)}{dT} = \frac{-TS + G}{T^2} = -\frac{H}{T^2} \quad (38)$$

So that eq. (35) becomes

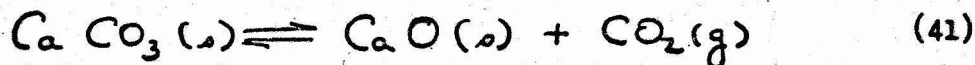
$$\frac{d(\ln K_p)}{dT} = \frac{\Delta H^\circ}{RT^2} \quad (39)$$

or

$$\ln \frac{K_{p_2}}{K_{p_1}} = \int_{T_1}^{T_2} \frac{\Delta H^\circ}{RT^2} dT \quad (40)$$

HETEROGENEOUS EQUILIBRIA

When the species participating in an equilibrium exist in more than one phase, the equilibrium is said to be heterogeneous. For example, suppose calcium carbonate is heated in a closed space; it undergoes dissociation and the equilibrium is



The equilibrium constant is

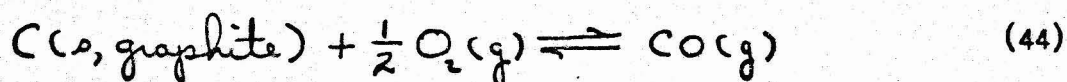
$$K_p = \frac{P_{\text{CaO}(s)} P_{\text{CO}_2(g)}}{P_{\text{CaCO}_3(s)}} \quad (42)$$

but since the partial pressures of the solid species are independent of the quantity of solid present and furthermore are constants, eq. (42) may be written

$$K_p = P_{\text{CO}_2(g)} \quad (43)$$

In this case, the equilibrium constant is equal to the partial pressure of the carbon dioxide formed which is the dissociation pressure for calcium carbonate.

An equilibrium of more immediate concern is



The equilibrium constant for the latter equilibrium is

$$K_p = \frac{P_{\text{CO}(g)}}{P_{\text{C}(s, \text{graphite})} P_{\text{O}_2(g)}^{1/2}} \quad (45)$$

or

$$K_p = \frac{P_{\text{CO}(g)}}{P_{\text{O}_2(g)}^{1/2}} \quad (46)$$

where the argument given above was used to eliminate the partial pressure of solid graphite. This argument can be put on a rigorous basis by use of the fugacity concept and will not be discussed here.

COMBINATION OF EQUILIBRIUM CONSTANTS

It has been pointed out that the internal energy, entropy, enthalpy, Gibbs free energy, and Helmholtz free energy are perfect differentials. This property which implies an independence of the path followed between any two states permits the development of some practically useful relationships. In particular, we shall be concerned here with the problem of evaluating equilibrium constants for a given equilibrium by use of tables of equilibrium constants.

First, we note that the change in Gibbs free energy for the reaction



is given by

$$\begin{aligned} \Delta G^\circ &= d \Delta G_f^\circ(D) + e \Delta G_f^\circ(E) \\ &\quad - a \Delta G_f^\circ(A) - b \Delta G_f^\circ(B) \end{aligned} \quad (48)$$

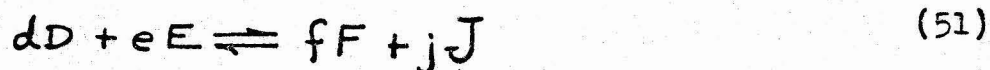
The equilibrium constant for eq. (47) is

$$\Delta G^\circ = -RT \ln K_p \quad (48)$$

or

$$\ln K_p = - \frac{\Delta G^\circ(47)}{RT} \quad (50)$$

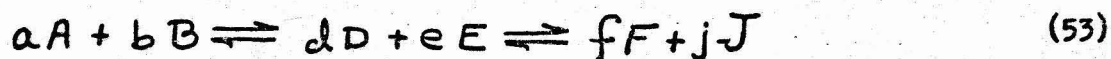
Consider the additional chemical equilibrium



and then

$$\ln K_p = - \frac{\Delta G^\circ(51)}{RT} \quad (52)$$

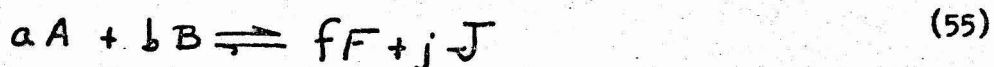
The net change in Gibbs free energy for the transformation



is

$$\Delta G^\circ(53) = \Delta G^\circ(47) + \Delta G^\circ(51) \quad (54)$$

and the equilibrium constant for the overall transformation



is

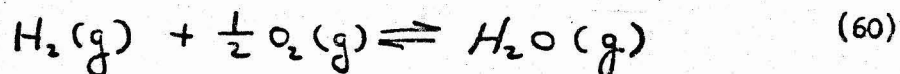
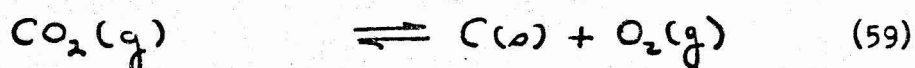
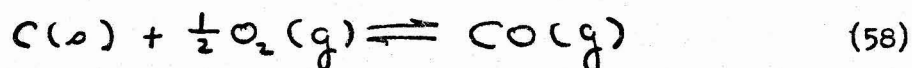
$$\ln K_P + \ln K_P = - \left[\frac{\Delta G^\circ(47) + \Delta G^\circ(51)}{RT} \right] \quad (56)$$

or

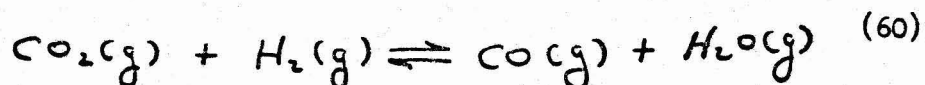
$$\ln K_P = - \frac{\Delta G^\circ(53)}{RT} \quad (57)$$

Thus, if an equilibrium may be represented as the sum or difference of two or more equilibria, the equilibrium constant for the resultant is the product or quotient of the equilibrium constants for the equilibria whose sum or difference is the desired result.

This will now be illustrated with an example. Consider the following equilibria



The algebraic sum of eqs. (58), (59), and (60) is



and

$$K_P = \frac{K_{P,4} K_{P,9}}{K_{P,10}} \quad (62)$$

where $K_{P,4}$, $K_{P,9}$, and $K_{P,10}$ were taken from Table 3.

TABLE 3a

EQUILIBRIUM CONSTANTS*

T (°K)	$K_{P,1}$	$K_{P,2}$	$K_{P,3}$	$K_{P,4}$	$K_{P,5}$
298.16	4.8978 E-41	2.4831 E-36	2.8340 E-7	1.1143 E 40	1.9187 E-60
300	9.0157 E-41	4.2560 E-36	3.1311 E-7	6.1235 E 39	4.6559 E-60
400	5.5335 E-30	1.3459 E-26	2.1419 E-5	1.7418 E 29	1.8323 E-44
500	1.7140 E-23	6.9984 E-21	2.6984 E-4	7.6913 E 22	4.3351 E-35
600	3.7239 E-19	4.6452 E-17	1.4555 E-3	4.2954 E 18	7.8886 E-29
700	4.7315 E-16	2.5351 E-14	4.8362 E-3	3.8282 E 15	2.3768 E 24
800	1.0162 E-13	2.9040 E-12	1.1869 E-2	1.9454 E 13	5.4828 E-21
900	6.6681 E-12	1.1700 E-10	2.3757 E-2	3.1405 E 11	2.2856 E-18
1000	1.9055 E-10	2.2693 E-9	4.1295 E-2	1.1482 E 10	2.8708 E-16
1100	2.9703 E-9	2.5852 E-8	6.4834 E-2	7.6015 E 8	1.5066 E-14
1200	2.9390 E-8	1.9715 E-7	9.4287 E-2	7.8759 E 7	4.0926 E-13
1300	2.0469 E-7	1.1052 E-6	1.2900 E-1	1.1497 E 7	6.7143 E-12
1400	1.0824 E-6	4.8596 E-6	1.6889 E-1	2.2060 E 6	7.4131 E-11
1500	4.5973 E-6	1.7575 E-5	2.1324 E-1	5.2541 E 5	5.9402 E-10
1600	1.6315 E-5	5.4300 E-5	2.6104 E-1	1.4955 E 5	3.6787 E-9
1700	4.9911 E-5	1.4710 E-4	3.1180 E-1	4.9204 E 4	1.8420 E-8
1800	1.3493 E-4	3.5752 E-4	3.6495 E-1	1.8302 E 4	7.7215 E-8
1900	3.2885 E-4	7.9232 E-4	4.2004 E-1	7.5422 E 3	2.7861 E-7
2000	7.3350 E-4	1.6233 E-3	4.7664 E-1	3.3931 E 3	8.8491 E-7
2100	1.5174 E-3	3.1110 E-3	5.3394 E-1	1.6458 E 3	2.5194 E-6
2200	2.9383 E-3	5.6247 E-3	5.9208 E-1	8.5212 E 2	6.5283 E-6
2300	5.3753 E-3	9.6627 E-3	6.5041 E-1	4.6677 E 2	1.5585 E-5
2400	9.3821 E-3	1.5874 E-2	7.0871 E-1	2.6847 E 2	3.4610 E-5
2500	1.5574 E-2	2.5090 E-2	7.6648 E-1	1.6127 E 2	7.2161 E-5
2750	4.7424 E-2	6.8250 E-2	9.0910 E-1	5.3272 E 1	3.5917 E-4
3000	1.2010 E-1	1.5762 E-1	1.0478	2.0999 E 1	1.3515 E-3
3250	2.6381 E-1	3.2048 E-1	1.1788	9.5786	4.2678 E-3
3500	5.1807 E-1	5.8993 E-1	1.3046	4.9295	1.1311 E-2
3750	9.3022 E-1	1.000	1.4218	2.7498	2.6363 E-2
4000	1.5528	1.5933	1.5315	1.6623	5.5361 E-2
4250	2.4416	2.4010	1.6351	1.0568	1.0668 E-1
4500	3.6521	3.4602	1.7322	7.0307 E-1	1.9134 E-1
4750	5.2349	4.8029	1.8229	4.9181 E-1	3.2321 E-1
5000	7.2395	6.4506	1.9067	3.5465 E-1	5.1874 E-1

* See Table 3c for definition of symbols

TABLE 3b

EQUILIBRIUM CONSTANTS*

T (°K)	$K_{P,6}$	$K_{P,7}$	$K_{P,8}$
298.16	6.5013 E-16	1.0169 E 24	1.2331 E 69
300	8.1283 E-16	8.4723 E 23	4.6559 E 68
400	6.9823 E-12	1.3397 E 19	3.4356 E 51
500	1.6055 E-9	1.7865 E 16	1.8113 E 41
600	6.0353 E-8	2.1677 E 14	2.5177 E 34
700	8.0612 E-7	9.2258 E 12	3.1842 E 29
800	5.6234 E-6	8.5507 E 11	6.7143 E 25
900	2.5486 E-5	1.3366 E 11	9.2470 E 22
1000	8.5487 E-5	3.0061 E 10	4.7534 E 20
1100	2.3020 E-4	8.8004 E 9	6.3387 E 18
1200	5.2590 E-4	3.1499 E 9	1.7378 E 17
1300	1.0554 E-3	1.3110 E 9	8.2414 E 15
1400	1.9178 E-3	6.1660 E 8	6.0534 E 14
1500	3.2255 E-3	3.1945 E 8	6.2951 E 13
1600	5.0781 E-3	1.7960 E 8	8.6896 E 12
1700	7.5770 E-3	1.0708 E 8	1.5031 E 12
1800	1.0817 E-2	6.7422 E 7	3.1623 E 11
1900	1.4873 E-2	4.4586 E 7	7.8524 E 10
2000	1.9815 E-2	3.0641 E 7	2.2387 E 10
2100	2.5674 E-2	2.1827 E 7	7.2028 E 9
2200	3.2516 E-2	1.5389 E 7	2.5498 E 9
2300	4.0346 E-2	1.1943 E 7	9.9426 E 8
2400	4.9125 E-2	9.1348 E 6	4.1850 E 8
2500	5.8878 E-2	7.1532 E 6	1.8915 E 8
2750	8.7466 E-2	4.5426 E 6	3.3083 E 7
3000	1.2148 E-1	2.6182 E 6	7.7108 E 6
3250	1.6040 E-1	1.7527 E 6	2.2527 E 6
3500	2.0334 E-1	1.1844 E 6	7.8109 E 5
3750	2.4939 E-1	9.1496 E 5	3.1275 E 5
4000	2.9793 E-1	6.9375 E 5	1.3880 E 5
4250	3.4839 E-1		
4500	4.0085 E-1		
4750	4.5188 E-1		
5000	5.0405 E-1		

* See Table 3c for definitions of symbols

TABLE 3c

EQUILIBRIUM CONSTANTS

$$K_{P,1} = \frac{P_{O_2}}{P_{O_2}^{1/2}}$$

$$K_{P,2} = \frac{P_H}{P_{H_2}^{1/2}}$$

$$K_{P,3} = \frac{P_{OH}}{P_{O_2}^{1/2} P_{H_2}^{1/2}}$$

$$K_{P,4} = \frac{P_{H_2O}}{P_{H_2} P_{O_2}^{1/2}}$$

$$K_{P,5} = \frac{P_N}{P_{N_2}^{1/2}}$$

$$K_{P,6} = \frac{P_{NO}}{P_{N_2}^{1/2} P_{O_2}^{1/2}}$$

$$K_{P,7} = \frac{P_{CO}}{P_{O_2}^{1/2}}$$

and

$$K_{P,7} = \frac{P_{CO}}{P_C(c, \text{graphite}) P_{O_2}^{1/2}}$$

$$K_{P,8} = \frac{P_{CO_2}}{P_{O_2}}$$

and

$$K_{P,8} = \frac{P_{CO_2}}{P_C(c, \text{graphite}) P_{O_2}}$$

PART II

GAS DYNAMICS

CHAPTER IV

CONSERVATION LAWS IN ONE-DIMENSIONAL GASDYNAMICS

The correct starting point for solving any problem in gasdynamics is the formulation of the three conservation laws; i.e., continuity, energy, and momentum. Our purposes here will be adequately served by considering the one-dimensional, steady flow of a compressible fluid. The consideration of one-dimensional flow principles is necessary before a clear understanding of theoretical thrust chamber performance may be achieved.

THE CONTINUITY EQUATION

The continuity equation is an expression for conservation of mass. At any two sections in steady flow field, the mass flows are the same and may be expressed as

$$\rho_1 u_1 A_1 = \rho_2 u_2 A_2 \quad (1)$$

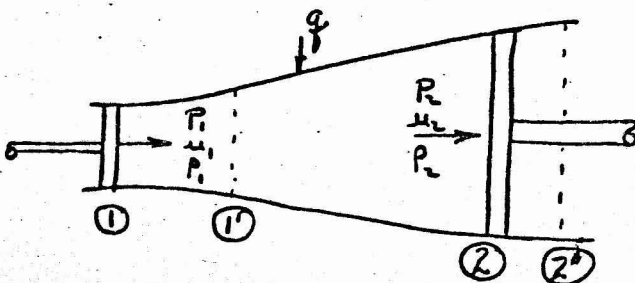
or

$$\dot{m} = \rho u A \quad (2)$$

where ρ_i = density at point i
 u_i = velocity at point i
 A_i = streamtube area at point i
 \dot{m} = mass flowrate

THE ENERGY EQUATION

Select for the system a definite portion of fluid as shown in Fig. / .



The energy equation is simply the appropriate form of the first law of thermodynamics for the system under study. According to the first law

$$q + \text{work done on the system} = \text{increase in energy} \quad (3)$$

The volume displaced in moving the piston from position 1 to 1' is v_1 and from position 2 to 2' is v_2 . The work done is

$$\text{Work} = P_1 v_1 - P_2 v_2 \quad (4)$$

The energy in the system consists of two parts: (1) the internal energy and (2) the kinetic energy. Thus, the increase in energy due to the fore-mentioned displacements is

$$\text{Increase in energy} = (e_2 + \frac{1}{2} u_2^2) - (e_1 + \frac{1}{2} u_1^2) \quad (5)$$

Combining eqs. (3), (4), and (5) yields the energy equation for steady flow

$$q + P_1 v_1 - P_2 v_2 = (e_2 + \frac{1}{2} u_2^2) - (e_1 + \frac{1}{2} u_1^2) \quad (6)$$

which upon introduction of the enthalpy becomes

$$q = h_2 - h_1 + \frac{1}{2} u_2^2 - \frac{1}{2} u_1^2 \quad (7)$$

THE MOMENTUM EQUATION

In this section, Newton's second law of motion will be applied to a fluid element. The Eulerian viewpoint will be used; i.e., the fluid particle will be followed as it passes through a tube and thereby meets varying conditions.

The acceleration of a particle is

$$a_x = \frac{\partial u}{\partial t} + u \frac{\partial u}{\partial x} \quad (8)$$

where a_x = acceleration component in the X direction

u = velocity in the X direction

t = time

Next we compute the force acting on the fluid element and for this consider the fluid element in Fig. 2. Let forces acting to the right be positive and forces

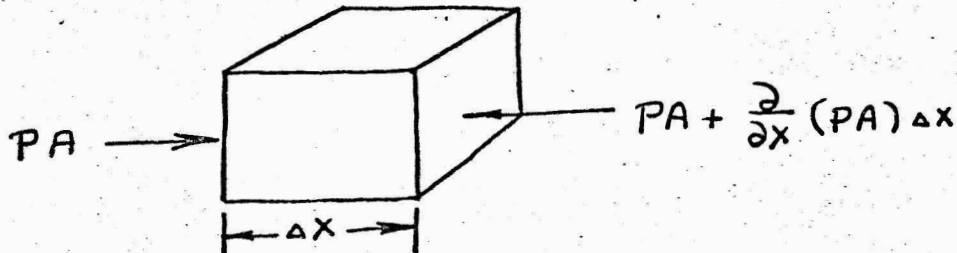


FIGURE 2. PRESSURE ACTING ON FLUID PARTICLE

acting to the left be negative so that the resultant force is

$$F_x = PA - PA - \frac{\partial}{\partial x} (PA) \Delta x \quad (9)$$

or

$$F_x = - \frac{\partial P}{\partial x} (A \Delta x) \quad (10)$$

Dividing eq. (10) by the volume $A \Delta x$ and the mass per unit volume yields the force per unit mass

$$f_x = - \frac{1}{\rho} \frac{\partial P}{\partial x} \quad (11)$$

according to Newton's second law, we may set eq. (8) equal to eq. (11) to obtain

$$\frac{\partial u}{\partial t} + u \frac{\partial u}{\partial x} = - \frac{1}{\rho} \frac{\partial P}{\partial x} \quad (12)$$

which is Euler's equation.

For steady flow

$$\frac{\partial u}{\partial t} = 0 \quad (13)$$

and eq. (12) becomes

$$u \, du + \frac{1}{\rho} \, dP = 0 \quad (14)$$

or in integral form

$$\frac{u^2}{2} + \int \frac{dP}{\rho} = \text{constant} \quad (15)$$

INTEGRATED MOMENTUM EQUATION FOR ISENTROPIC FLOW

It was shown in Chapter I that the relationship between pressure and density for a reversible, adiabatic process is

$$\frac{P}{\rho^k} = \text{constant} \quad (16)$$

Differentiating eq. (16) yields

$$dP = c k \rho^{k-1} \, d\rho \quad (17)$$

Substituting eq. (17) into eq. (14) and integrating yields

$$\frac{u_2^2 - u_1^2}{2} = \frac{k}{k-1} \left[\frac{P_1}{\rho_1} - \frac{P_2}{\rho_2} \right] \quad (18)$$

Equation (18) is completely general and may be applied to variable area flow.

OTHER FORMS OF THE MOMENTUM EQUATION

Two cases of practical interest are incompressible and constant area flow.

For incompressible, the density is constant and integration of the momentum equation yields

$$\frac{u_2^2 - u_1^2}{2} = \frac{1}{\rho} (P_1 - P_2) \quad (19)$$

In the constant area case, we substitute the continuity equation into eq.

(14) and then integration yields

$$u_2 - u_1 = \frac{A}{w} (P_1 - P_2) \quad (20)$$

ISENTROPIC ENERGY EQUATION

The energy equation for isentropic flow has the form

$$h_2 + \frac{1}{2} u_2^2 = h_1 + \frac{1}{2} u_1^2 \quad (21)$$

or in differential form

$$dh + u du = 0 \quad (22)$$

Setting $dh = C_p dT$ in eq. (22) yields

$$C_p dT + u du = 0 \quad (23)$$

which may be integrated to yield

$$C_p T_2 + \frac{1}{2} u_2^2 = C_p T_1 + \frac{1}{2} u_1^2 \quad (24)$$

COMPRESSIBLE NOZZLE FLOW

In this section, we shall develop the one-dimensional theory for compressible, isentropic flow through a channel of various cross-sectional area. For this purpose, the flow system will be taken to be a converging-diverging nozzle attached to an infinite reservoir as shown in Fig. 3.

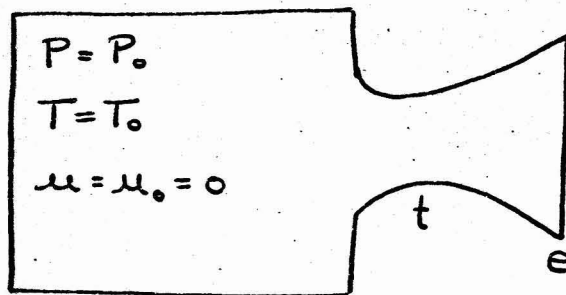


FIGURE 3. SCHEMATIC DIAGRAM FOR VARIABLE AREA FLOW SYSTEM

The isentropic energy equation for this system is eq. (21) which becomes

$$h_o = h_i + \frac{1}{2} u_i^2 \quad (25)$$

or

$$h_o - h_i = \frac{1}{2} u_i^2 \quad (26)$$

where the subscript i refers to any point in the flow field downstream from the reservoir. According to eq. (26) the velocity at any point in the nozzle is proportional to the enthalpy drop between the reservoir and the point of interest. Specifically, the velocity at the nozzle exit is given by

$$u_e = \sqrt{\frac{h_o - h_e}{2}} \quad (27)$$

Equation (27) will be useful after the expression for thrust due to nozzle flow is developed.

Another useful expression for velocity in the case of isentropic flow may be obtained by using eq. (24) in the following form

$$C_p (T_2 - T_1) + \frac{1}{2} (u_2^2 - u_1^2) = 0 \quad (28)$$

Using the ideal gas equation of state in eq. (28) yields

$$\frac{C_p}{R} \left(\frac{P_2}{P_2} - \frac{P_1}{P_1} \right) + \frac{1}{2} (u_2^2 - u_1^2) = 0 \quad (29)$$

but

$$\frac{C_p}{R} = \frac{\gamma}{\gamma - 1} \quad (30)$$

so that eq. (29) becomes

$$\frac{\gamma}{\gamma - 1} \left(\frac{P_2}{P_2} - \frac{P_1}{P_1} \right) + \frac{1}{2} (u_2^2 - u_1^2) = 0 \quad (31)$$

Setting u_1 equal to zero and making appropriate changes in the subscripts yields

$$\frac{\gamma}{\gamma - 1} \left(\frac{P_e}{P_e} - \frac{P_o}{P_o} \right) + \frac{u_2^2}{2} = 0 \quad (32)$$

ONE-DIMENSIONAL VARIABLE AREA FLOW

In this section, differential equations describing reversible, adiabatic flow of an ideal gas in a channel of variable cross-sectional area will be developed. The starting point is the continuity equation

$$\dot{m} = \rho u A \quad (33)$$

which may be differentiated to yield

$$\frac{d\rho}{\rho} + \frac{du}{u} + \frac{dA}{A} = 0 \quad (34)$$

Also, we differentiate the isentropic relation; i.e.,

$$\frac{P}{\rho^k} = c \quad (35)$$

thus

$$\frac{dP}{P} - k \frac{d\rho}{\rho} = 0 \quad (36)$$

and finally we shall require the differential form of the momentum equation

$$u du + \frac{1}{\rho} dP = 0 \quad (37)$$

Combining eqs. (36) and (37) yields

$$\frac{du}{u} = - \frac{kP}{\rho u^2} \frac{d\rho}{\rho} \quad (38)$$

and then combining eqs. (34) and (38) yields

$$\frac{du}{u} = - \frac{1}{\left(\frac{\rho u^2}{kP} - 1\right) A} dA \quad (39)$$

The Mach number is given by

$$M = \frac{u}{a} = \frac{u}{\sqrt{\frac{kP}{\rho}}} \quad (40)$$

or

$$M^2 = \frac{u^2 \rho}{kP} \quad (41)$$

Using eq. (41) in eq. (39) finally yields

$$\frac{du}{u} = -\frac{1}{(1-M^2)} \frac{dA}{A} \quad (42)$$

Area is always greater than zero while the Mach number is always greater than or equal to zero. Velocity must be different from zero for eq. (42) to have meaning. Therefore, if

$$M < 1, \quad dA < 0, \quad du > 0 \quad (43)$$

that is to say the velocity increases in subsonic flow in a channel of decreasing area; and if

$$M > 1, \quad dA < 0, \quad du < 0 \quad (44)$$

so that it is seen that for supersonic flow in a channel of decreasing area the velocity decreases.

Utilization of eqs. (34), (36), (37), and (41) leads to the following differential equations for one-dimensional, isentropic flow of an ideal gas

$$\frac{dM}{M} = -\frac{2 + (k-1)M^2}{2(1-M^2)} \frac{dA}{A} \quad (45)$$

$$\frac{dp}{p} = \frac{M^2}{1-M^2} \frac{dA}{A} \quad (46)$$

$$\frac{dP}{P} = \frac{kM^2}{1-M^2} \frac{dA}{A} \quad (47)$$

$$\frac{dT}{T} = \frac{(k-1)M^2}{1-M^2} \frac{dA}{A} \quad (48)$$

FLOWRATE THROUGH A NOZZLE

In this section, we shall develop the relationships for mass flowrate of an ideal gas flowing through a converging-diverging nozzle in a reversible adiabatic manner. The system and nomenclature shown in Figure 3 will be used. We rewrite eq. (32) as follows:

$$u = \sqrt{\frac{2R}{R-1} \left(\frac{P_0}{\rho_0} - \frac{P}{\rho} \right)} \quad (49)$$

or

$$u = \sqrt{\frac{2R}{R-1} \frac{P_0}{\rho_0} \left[1 - \frac{P}{P_0} \frac{\rho_0}{\rho} \right]} \quad (50)$$

and upon introduction of the isentropic relation eq. (50) becomes

$$u = \sqrt{\frac{2R}{R-1} \frac{P_0}{\rho_0} \left[1 - \left(\frac{P}{P_0} \right)^{(R-1)/R} \right]} \quad (51)$$

where the variable without a subscript refers to any point in the stream.

Combining the continuity equation with eq. (51) yields

$$\dot{m} = \rho A \sqrt{\frac{2R}{R-1} \frac{P_0}{\rho_0} \left[1 - \left(\frac{P}{P_0} \right)^{(R-1)/R} \right]} \quad (52)$$

Using the isentropic relation to eliminate ρ from eq. (52) yields

$$G = \frac{\dot{m}}{A} = \rho_0 \sqrt{\frac{2R}{R-1} T_0 \left[\left(\frac{P}{P_0} \right)^{2/R} - \left(\frac{P}{P_0} \right)^{(R+1)/R} \right]} \quad (53)$$

The maximum flowrate will be achieved when G is a maximum and the condition for maximum flowrate is obtained by differentiating eq. (53) with respect to P/P_0 and setting the derivative equal to zero. This gives the so-called critical-pressure ratio

$$\left(\frac{P}{P_0} \right)_c = \left(\frac{2}{R+1} \right)^{R/(R+1)} \quad (54)$$

PROBLEMS

1. Following the method outlined in developing eq. (53), develop an expression for flowrate through a nozzle in which the entrance velocity is sufficiently greater than zero and, therefore, not neglected.
2. Using the result of Problem 1, develop the expression for the critical pressure and show that this expression reduces to eq. (54) when the area of the nozzle entrance becomes very large.
3. Prepare a table showing how velocity, density, pressure, and temperature vary in a converging channel and in a diverging channel for both subsonic and supersonic flow.

CHAPTER V

THEORETICAL PROPELLANT PERFORMANCE CALCULATION

Calculation of theoretical performance parameters is accomplished by the straightforward application of thermodynamic and fluid dynamic principles. In this chapter, the methods used to calculate combustion temperature, specific impulse, thrust coefficient, and characteristic velocity will be discussed. In particular, theoretical propellant performance calculation techniques for constant composition flow, shifting equilibrium flow, and kinetic flow will be discussed. No effort will be made to deal with the techniques for generation of the basic thermodynamic data needed since this would be beyond the scope of this discussion nor will any effort be made to discuss numerical methods and digital computer programming techniques that are used in the machine calculations.

ASSUMPTIONS

There are seven assumptions upon which theoretical propellant performance calculations are based. These are:

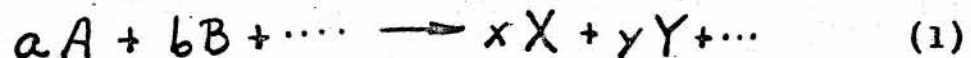
1. Thermodynamic equilibrium is reached in the combustion chamber after adiabatic reaction.
2. Expansion through the nozzle is isentropic.
3. Products of combustion behave as ideal gases.
4. The expansion process involved the one-dimensional flow of inviscid ideal gases.
5. The velocity of the gases at the nozzle entrance is zero; i.e., the combustion chamber is an infinite reservoir.

6. The propellants are chemically pure.
7. Initial propellant temperature is room temperature for storeable propellants and the boiling temperature at one atmosphere pressure for cryogenics.

CONSTANT COMPOSITION FLOW

The first step in a performance calculation is to calculate the adiabatic flame temperature. From a conceptual point of view, the reaction is presumed to take place at constant temperature. Since rocket propellant reactions are exothermic, this process will be accompanied by a heat release. The heat released, heat of reaction, is then presumed to heat the products to some temperature above the initial temperature. The steps in the calculation are outlined below.

Consider a generalized reaction



The heat of reaction is given by

$$Q = (x \Delta H_f^\circ(X) + y \Delta H_f^\circ(Y) + \dots) - (a \Delta H_f^\circ(A) + b \Delta H_f^\circ(B) + \dots) \quad (2)$$

This heat of reaction, Q , is absorbed by the products thereby increasing the temperature of the products to the combustion temperature. Analytically this becomes

$$Q = x \Delta H_{T_i}^{T_c}(X) + y \Delta H_{T_i}^{T_c}(Y) + \dots \quad (3)$$

where the upper limit T_c is the combustion temperature.

A first guess for the flame temperature is made and the change in enthalpy for the products is computed and compared with the heat of reaction Q , if

$$Q > \Delta H_{T_c}^{T_c}(\text{products}) \quad (3a)$$

T_c is too small, and if

$$Q < \Delta H_{T_c}^{T_c}(\text{products}) \quad (3b)$$

T_c is too large. Such an iterative technique will converge to the combustion temperature very quickly.

However, the products and the number of moles of each product is not arbitrary but must be obtained from chemical equilibrium and conservation of mass considerations. Various of the products will be connected by equilibrium expressions of the form



The equilibrium constant for equation (4) is by definition

$$K_p = \frac{p_Y}{p_X} \quad (5)$$

where p_i = partial pressure of the i th species.

$$\sigma = \sum_{j=1}^n a_{ij} n_j, \quad i = 1, 2, \dots, N \quad (6)$$

The result is a set of non-linear simultaneous algebraic equations for the composition consisting of m equilibrium expressions and n mass conservation expressions.

In summary, the steps to be followed when calculating the combustion temperature are:

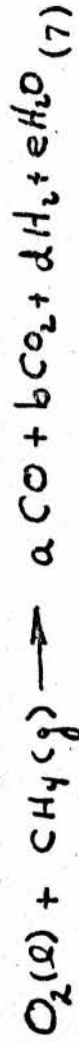
1. Assume a value for the combustion temperature.
2. Obtain the necessary equilibrium constants from tables or calculate using the Gibbs Free Energy as discussed in Chapter III.
3. Solve the $m+n$ set of simultaneous equations given by equations (5) and (6).
4. Compute the heat of reaction from equation (2).
5. Compute Q according to equation (3)
6. Test according to equations (3a) and (3b) to determine the next guess for T_c then repeat from step 2.

At this point a pair of examples will serve to clarify the procedure outlined above.

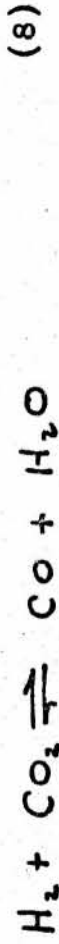
ADIABATIC FLAME TEMPERATURE CALCULATION FOR A LOW TEMPERATURE

C, H, O SYSTEM.

Consider the reaction of liquid oxygen with methane to produce combustion products



The coefficients a , b , d , and e in eq. (7) are used to indicate that these quantities are to be determined in the process of calculating the adiabatic flame temperature. The counterparts to eqs. (4), (5) and (6) are



$$K_p = \frac{p_{CO} p_{H_2O}}{p_{H_2} p_{CO_2}} \quad (9)$$

$$\sum C = n_{CO_2} + n_{CO} = C \quad (10a)$$

$$\sum H = 2n_{H_2} + 2n_{H_2O} = H \quad (10b)$$

$$\sum O = 2n_{CO_2} + n_{CO} + n_{H_2O} = O \quad (10c)$$

where eqs. (10a), (10b), and (10c) correspond to eq. (6).

The total quantity of carbon, hydrogen and oxygen is fixed by the quantity of liquid oxygen and methane while the value of the equilibrium constant, K_p is fixed by the combustion temperature. Thus, eqs. (9) and (10) constitute a set of four simultaneous equations for the four unknowns n_{H_2} , n_{CO_2} , n_{CO} and n_{H_2O} .

It is not convenient to use eq. (9) in the form given so the following substitution is made

$$pV = nRT \quad (11)$$

or

$$p = \frac{nRT}{V} \quad (12)$$

and eq. (9) becomes

$$K_n = \frac{n_{CO} n_{H_2O}}{n_{H_2} n_{CO_2}} \quad (13)$$

Elimination of n_{CO_2} , n_{H_2O} and n_{H_2} from eqs. (10) and (13) yields

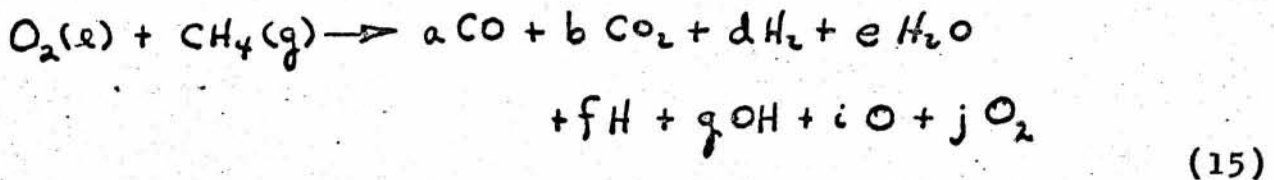
$$(3 - 3K_n)n_{CO}^2 + \left\{ \left(C - \frac{H}{2} + O \right) K_n + (2C - O) \right\} n_{CO} + \left(\frac{HC}{2} - OC + 2C^2 \right) K_n = 0 \quad (14)$$

which is a quadratic equation for N_{co} . No difficulty should be encountered with the notation in eq. (14) since it is clear that the symbols C, H, and O refer to the gram-atoms of carbon, hydrogen, and oxygen in the propellant system.

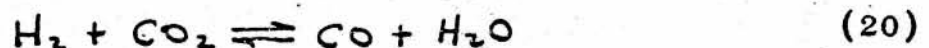
This particular approach is valid when the anticipated temperature is sufficiently low to justify neglecting molecular dissociation. That is to say, the approach presented above is useful for low or high mixture ratios.

ADIABATIC FLAME TEMPERATURE CALCULATION FOR A HIGH TEMPERATURE C, H, O SYSTEM.

Once again let us consider the propellant system - liquid oxygen and gaseous methane. In this case, the mixture ratio will be such that dissociation must be taken into account. The overall reaction is



The equilibria for this system are



and the mass balance expressions are

$$\sum C = n_{co} + n_{co_2} \quad (21)$$

$$\sum H = 2n_{H_2} + 2n_{H_2O} + n_H + n_{OH} \quad (22)$$

$$\sum O = n_{CO} + 2n_{CO_2} + n_{H_2O} + n_{OH} + n_O + 2n_{O_2} \quad (23)$$

In terms of equilibrium constants eqs. (16), (17), (18), (19) and (20) become

$$K_{P,1} = \frac{P_O}{P_{O_2}^{1/2}} \quad (24)$$

$$K_{P,2} = \frac{P_H}{P_{H_2}^{1/2}} \quad (25)$$

$$K_{P,3} = \frac{P_{OH}}{P_{O_2}^{1/2} P_{H_2}^{1/2}} \quad (26)$$

$$K_{P,4} = \frac{P_{H_2O}}{P_{H_2} P_{O_2}^{1/2}} \quad (27)$$

$$K_P = \frac{P_{CO} P_{H_2O}}{P_{H_2} P_{CO_2}} \quad (28)$$

Equations (21), (22), and (23) may be expressed in terms of partial pressures by noting that

$$X_i = \frac{n_i}{n_T} \quad (29)$$

and

$$p_i = X_i P \quad (30)$$

so that

$$n_i = \frac{n_T}{P} p_i \quad (31)$$

where

X_i = mole fraction of species i

n_i = moles of species i

n_T = total number of moles

P = system pressure

p_i = partial pressure of species i

Substituting eq. (31) into eqs. (21), (22), and (23) yields

$$\frac{P}{n_T} \sum C = p_{CO} + p_{CO_2} = \frac{P_C}{n_T} \quad (32)$$

$$\frac{P}{n_T} \sum H = 2p_{H_2} + 2p_{H_2O} + p_H + p_{OH} = \frac{P_H}{n_T} \quad (33)$$

$$\frac{P}{n_T} \sum O = p_{CO} + 2p_{CO_2} + p_{H_2O} + p_{OH} + p_O + 2p_{O_2} = \frac{P_O}{n_T} \quad (34)$$

and thus eqs. (24), (25), (26), (27), (28), (32), (33), and (34) constitute a set of eight simultaneous equations in eight unknowns. Solving this set of simultaneous equations for p_{H_2} yields

$$K_p = \left\{ \left(\frac{P_H}{n_T} - P_{H_2} - \frac{P_{H_2}^{1/2} K_{P,2}}{2} - \frac{K_{P,3} \left[\frac{P_H}{n_T} - P_{H_2} - \frac{P_{H_2}^{1/2} K_{P,2}}{2} \right]}{[2 P_{H_2}^{1/2} K_{P,4} + K_{P,3}]} \right) \left(2 \frac{P_C}{n_T} - \frac{P_O}{n_T} + \frac{P_H}{n_T} - P_{H_2} \right) \right.$$

$$- \frac{P_{H_2}^{1/2} K_{P,2}}{2} + \frac{K_{P,3} \left[\frac{P_H}{n_T} - P_{H_2} - \frac{P_{H_2}^{1/2} K_{P,2}}{2} \right]}{[2 P_{H_2}^{1/2} K_{P,4} + K_{P,3}]} + \frac{K_{P,3} \left[\frac{P_H}{n_T} - P_{H_2} - \frac{P_{H_2}^{1/2} K_{P,2}}{2} \right] K_{P,1}}{[2 P_{H_2}^{1/2} K_{P,4} + K_{P,3}] P_{H_2}^{1/2} K_{P,3}}$$

$$+ 2 \left(\frac{2 \left[\frac{P_H}{n_T} - P_{H_2} - \frac{P_{H_2}^{1/2} K_{P,2}}{2} \right]^2}{[2 P_{H_2}^{1/2} K_{P,4} + K_{P,3}] P_{H_2}^{1/2}} \right) \left\{ P_{H_2} \left[\frac{P_O}{n_T} - \frac{P_C}{n_T} - \frac{P_H}{n_T} + P_{H_2} \right] \right.$$

$$+ \frac{P_{H_2}^{1/2} K_{P,2}}{2} - \frac{K_{P,3} \left[\frac{P_H}{n_T} - P_{H_2} - \frac{P_{H_2}^{1/2} K_{P,2}}{2} \right]}{[2 P_{H_2}^{1/2} K_{P,4} + K_{P,3}]} - \frac{K_{P,1} \left[\frac{P_H}{n_T} - P_{H_2} - \frac{P_{H_2}^{1/2} K_{P,2}}{2} \right]}{P_{H_2}^{1/2} [2 P_{H_2}^{1/2} K_{P,4} + K_{P,3}]}$$

$$- 2 \left(\frac{2 \left[\frac{P_H}{n_T} - P_{H_2} - \frac{P_{H_2}^{1/2} K_{P,2}}{2} \right]^2}{P_{H_2}^{1/2} [2 P_{H_2}^{1/2} K_{P,4} + K_{P,3}]} \right) \left. \right\}$$

(35)

Strictly speaking, eq. (35) has two unknowns which are the partial pressure of molecular hydrogen and the total number of moles. This presents no great difficulty since the first estimate for the total number of moles may be made by using the total number of moles of propellant. The second iteration will use the total number of moles from the first iteration and so on. Using eq. (35) with eqs. (24), (25), (26), (27), (28), (32), (33), and (34), and the conditions given by eqs. (3a) and (3b), it is possible to calculate the adiabatic flame temperature. Once the flame temperature has been calculated the remaining parts of the performance calculation are quite easy to accomplish.

CONTINUATION OF PERFORMANCE CALCULATION FOR CONSTANT COMPOSITION NOZZLE FLOW

It was assumed that the flow process would be isentropic and therefore, the next step is to calculate the chamber entropy. For this calculation, an effective molecular weight of the combustion products is needed. This is calculated using

$$\bar{M} = \sum X_i M_i \quad (36)$$

The chamber entropy is computed from the relation

$$S_c = \left[\sum n_j (S_T^0)_j - \frac{R}{M\bar{P}} \sum p_j \ln p_j \right] \quad (37)$$

We calculate the nozzle exit temperature subject to the condition that the flow is isentropic. Equation (37) may be written

$$S_e = \left[\sum n_j (S_T^0)_j - \frac{R}{M\bar{P}} \sum p_j \ln p_j \right] \quad (38)$$

Again an iterative technique is used to obtain the exit temperature. Assume an exit temperature and an exit pressure and substitute in equation (38) along with the moles n , calculated previously. When S_e is equal to S_c , the exit temperature for frozen flow is obtained.

The exit enthalpy is given by

$$H_e = \sum n_j (\Delta H_{T_i}^{T_e})_j \quad (39)$$

and we note that the chamber enthalpy was given by

$$H_c = \sum n_j (\Delta H_{T_i}^{T_c})_j \quad (40)$$

Conservation of energy requires that

$$H_c + \frac{V_c^2}{2gJ} = H_e + \frac{V_e^2}{2gJ} \quad (41)$$

or

$$V_e = \sqrt{2gJ(H_c - H_e)} \quad (42)$$

Where use has been made of the assumption that gas velocity in the combustion chamber is zero. Velocity is connected to thrust through Newton's second law of motion

$$F = \frac{\dot{w} V_e}{g} \quad (43)$$

and thus combination of equations (42) and (43) yields

$$I_s = \sqrt{\frac{2J}{g} (H_c - H_e)} \quad (44)$$

CHARACTERISTIC VELOCITY

The characteristic velocity is defined by

$$C^* = \frac{(P_c)_0 A_t g}{\dot{w}} \quad (45)$$

which may be written on the following approximate form

$$C^* = \sqrt{\frac{gRT_c}{\bar{M}} \left[\frac{1}{k} \left(\frac{k+1}{2} \right)^{(k+1)/(k-1)} \right]} \quad (46)$$

Equation (45) is useful in the treatment of experimental data but not very convenient for theoretical calculations. On the other hand, equation (46) has been used quite extensively for theoretical purposes and is useful for demonstrating the dependence of characteristic velocity on combustion temperature, average molecular weight of the gases, and specific heat ratio. However, equation (46) is an approximation since the development of this equation involves the assumption that the specific heat ratio is independent of temperature or that a suitable average value may be assigned to the ratio of specific heat.

An average value for the specific heat ratio may be obtained from the chamber and exit conditions.

By definition

$$C_P = \left(\frac{\partial H}{\partial T} \right)_P \quad (47)$$

or

$$\bar{C}_P = \left(\frac{\Delta H}{\Delta T} \right)_P = \frac{H_c - H_e}{T_c - T_e} \quad (48)$$

Finally

$$\bar{R} = \frac{\bar{C}_P}{\bar{C}_V} = \frac{\bar{C}_P}{\bar{C}_P - R} \quad (49)$$

The average value for the specific heat ratio may be used in eq. (46) to obtain a reasonably good estimate for the characteristic velocity.

The difficulties associated with equation (46) are circumvented in the Rocketdyne N-element propellant performance program by combining equation (45) with the continuity equation to yield

$$C^* = \frac{(P_c)_0 g}{(\rho V)_t} \quad (50)$$

The ρV product is a maximum at the nozzle throat, and this criterion is used to determine throat conditions and characteristic velocity. This is accomplished by assuming various values for nozzle pressure and calculating the temperature and composition as dictated by the isentropic flow requirement. Gas density

is obtained from the ideal gas equation of state. Calculation of stream properties for several different nozzle pressures is accomplished by using an iterative technique to converge on the nozzle throat flow field property values.

THRUST COEFFICIENT

The simplest technique for calculating a theoretical value for the nozzle thrust coefficient is to use theoretical values for the specific impulse and characteristic velocity. It is easily shown that

$$I_s = \frac{C^* C_F}{g} \quad (51)$$

and rearrangement yields

$$C_F = \frac{g I_s}{C^*} \quad (52)$$

This latter formula is currently used in the Rocketdyne N-element theoretical propellant performance calculation program. The often quoted expression for thrust coefficient

$$C_F = \sqrt{\left(\frac{2R^2}{R-1}\right) \left(\frac{2}{R+1}\right)^{(R+1)/(R-1)} \left[1 - \left(\frac{P_e}{P_c}\right)^{(R-1)/R}\right]} \quad (53)$$

poses the same problems and has the same limitations as eq. (46). However, if eq. (53) is used, the proper value for the specific heat ratio is obtained from eqs. (48) and (49).

SHIFTING EQUILIBRIUM CALCULATION TECHNIQUE

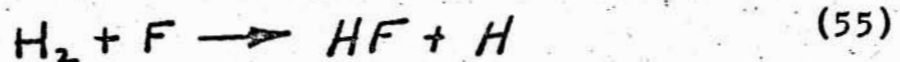
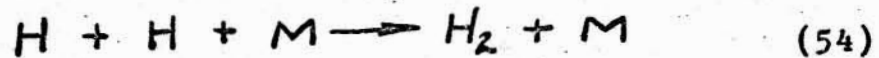
The adiabatic flame temperature, or chamber temperature, is calculated as described above for the constant composition flow. In the shifting equilibrium calculation, nozzle flow field properties are calculated at a number of points between the chamber and the nozzle exit. The shifting equilibrium calculation is comprised of a series of entropy balance determinations.

A value for the chamber entropy is calculated using eq. (37). A value for the nozzle pressure is selected and then eqs. (5), (6), and (38) are used to determine the temperature and composition subject to the condition that the entropy remain constant. Hand calculations would be quite laborious so that the practical method for making a shifting equilibrium calculation requires the use of a digital computer.

It should be pointed out that the frozen composition calculation implicitly assumes that chemical reaction rates are zero and the shifting equilibrium calculation assumes that chemical reaction rates are infinitely fast. Therefore, a third method of theoretical performance calculation is the so-called kinetic performance wherein measured chemical reaction rates are used in the chemical composition calculation.

KINETIC PERFORMANCE

On the basis of physical grounds, it is clear that the assumption of zero chemical reaction rate or infinite chemical reaction rate is not realistic but rather constitutes a pair of limiting assumptions. A more realistic calculation of propellant performance would include chemical reaction rate data for those reactions that constitute the rate limiting steps. This means that the slowest reactions would be represented by reaction rate expressions and the fastest reactions would be treated as having achieved chemical equilibrium instantaneously. For example, the formation of hydrogen fluoride from hydrogen and fluorine may be represented as follows:



Eq. (56) is the sum of eqs. (54) and (53) with eq. (54) proceeding at a rate that is orders of magnitude less than the rate for eq. (55). Therefore, the rate of formation of HF is controlled by the slow step - eq. (54).

In general the reactions that will constitute rate controlling steps in nozzle flow problems are recombination reactions. The recombination of hydrogen atoms to form hydrogen molecules, of hydrogen and oxygen atoms to form water, and of fluorine atoms to form fluorine molecules are typical. These reactions are important in nozzle flow because the recombination is inversely proportional to the

temperature so that as the temperature decreases during nozzle flow the rate of recombination increases.

The kinetic performance calculation begins as described above for the frozen and shifting composition calculations. A difference appears in the nozzle flow calculation where the flow field composition is determined by a combination of chemical kinetics and mass conservation considerations. The reaction kinetic equations may be represented in a general way by a reaction expression

$$\sum_{j=1}^{N_r} \left[\sum_i A'_{ij} M_i \frac{R_{fj}}{R_{bj}} \sum_i A''_{ij} M_i \right] \quad (57)$$

where:

N_r = total number of reactions

A'_{ij}, A''_{ij} = stoichiometric coefficients of the i^{th} species in the j^{th} reaction

R_{fj}, R_{bj} = specific reaction rates of the forward and backward chemical changes in the j^{th} reaction of the chemical system

M_i = concentration of the i^{th} specie

Rates of change of the concentrations of the species are determined by

$$\left[\frac{\partial (M_i)}{\partial T} \right]_{\rho} = \sum_{j=1}^{N_r} (A''_{ij} - A'_{ij}) \left\{ R_{fj} \prod_{k=1}^n [M_k]^{A'_{kj}} - R_{bj} \prod_{k=1}^n [M_k]^{A''_{kj}} \right\} \quad (58)$$

where:

n = total number of chemical species

Since we have introduced time into the formulation by use of reaction rate expressions, the residence time of the various chemical species in different parts of the nozzle is required. This is best obtained by using the actual nozzle contour and a calculated flow velocity profile to determine the residence time. It is seen that as a result of the effort to achieve a more realistic prediction of propellant performance some of the generality of the frozen and shifting composition calculation has been lost. This is the result of the kinetic calculations dependence on the real nozzle contour. The method of performing such a calculation will now be illustrated by considering a case wherein one chemical reaction takes place.

We shall consider the flow of nitrogen gas with a small amount of nitrogen dioxide. Reservoir conditions are such that nitrogen and nitrogen dioxide are the only species present. During flow as the nozzle temperature decreases the nitrogen dioxide recombines to form nitrogen tetroxide as per



As in any flow problem, the formulation begins by writing the three conservation expressions in the form proper to the problem. The differential form of the continuity equation is

$$\frac{dA}{A} + \frac{d\rho}{\rho} + \frac{dw}{w} = 0 \quad (60)$$

and the momentum equation may be written

$$-\rho w dw = dP \quad (61)$$

We apply the first law of thermodynamics to a unit mass of the mixture

$$du + P dw = 0 \quad (62)$$

With the enthalpy per unit mass defined by

$$h = u + Pw \quad (63)$$

we differentiate eq. (63) and insert the result in eq. (62) to obtain

$$dh - w dP = 0 \quad (64)$$

Combining eqs. (61) and (64) gives

$$dh + w dw = 0 \quad (65)$$

or

$$d\left(h + \frac{w^2}{2}\right) = 0 \quad (66)$$

The enthalpy h of eq. (66) is determined by

$$h = \omega_{N_2} h_{N_2} + \omega_{NO_2} h_{NO_2} + \omega_{N_2O_4} h_{N_2O_4} \quad (67)$$

Next, we note that the heat of formation of N_2O_4 is the difference of the molar enthalpies of the two reacting species

$$\Delta H_{N_2O_4} = 2H_{NO_2} - H_{N_2O_4} \quad (68)$$

Defining $h_i = H_i/\mu_i$ where μ_i is the molecular weight of the i^{th} species, we find from eq. (68)

$$h_{N_2O_4} = h_{NO_2} - \Delta h_{N_2O_4} \quad (69)$$

since $\mu_{N_2O_4} = 2\mu_{NO_2}$. Introducing eq. (69) into eq. (67) yields

$$h = \omega_{N_2} h_{N_2} + \omega_{NO_2} h_{NO_2} + \omega_{N_2O_4} h_{NO_2} - \omega_{N_2O_4} \Delta h_{N_2O_4} \quad (70)$$

where the ω_i is mass fraction of the i^{th} species.

It was initially stated that we would assume the reservoir conditions to be such that the N_2O_4 is fully dissociated and therefore $(\omega_{NO_2})_0$ is known so that we may write

$$\omega_{N_2O_4} = (\omega_{NO_2})_0 - \omega_{NO_2} \quad (71)$$

Inserting eq. (71) into eq. (70) yields

$$h = \omega_{N_2} h_{N_2} + (\omega_{NO_2})_0 h_{NO_2} - \omega_{N_2O_4} \Delta h_{N_2O_4} \quad (72)$$

and the energy eq. (66) becomes

$$d\left[\omega_{N_2} h_{N_2} + (\omega_{NO_2})_0 h_{NO_2} - \omega_{N_2O_4} \Delta h_{N_2O_4} + \frac{u^2}{2}\right] = 0 \quad (73)$$

The ideal gas equation of state for the mixture is given by

$$P = \frac{R}{\mu} \rho T \quad (74)$$

where

$$\frac{1}{\mu} = \frac{\omega_{N_2}}{\mu_{N_2}} + \frac{\omega_{NO_2}}{\mu_{NO_2}} + \frac{\omega_{N_2O_4}}{\mu_{N_2O_4}} \quad (75)$$

The mass fraction of the nitrogen is given by

$$\omega_{N_2} = 1 - (\omega_{NO_2})_0 \quad (76)$$

With eqs. (71), (75) and (76) the equation of state becomes

$$P = \rho RT \left[\frac{1 - (\omega_{NO_2})_0}{\mu_{N_2}} + \frac{(\omega_{NO_2})_0 - \omega_{N_2O_4}}{\mu_{NO_2}} + \frac{\omega_{N_2O_4}}{\mu_{N_2O_4}} \right] \quad (77)$$

A complete description of the flow process is obtained by adding the reaction rate equation

$$\frac{d\omega_{NO_2}}{dt} = w \frac{d\omega_{NO_2}}{dx} = \frac{\omega_{N_2} \rho}{\mu_{N_2}} \left[k_D \omega_{N_2O_4} - 2k_R \omega_{NO_2}^2 \frac{\rho}{\mu_{NO_2}} \right] \quad (78)$$

The constant of integration for the continuity equation is the mass flow so that

$$\dot{m} = \rho A w \quad (79)$$

The integrational constant for the energy equation, eq. (73), may be evaluated in the reservoir where $\omega_{N_2O_4} \approx 0$ and $w \approx 0$ and eq. (72) becomes

$$h_0 = (\omega_{N_2} h_{N_2})_0 + (\omega_{NO_2} h_{NO_2})_0 \quad (80)$$

Integration of eq. (73) with eq. (80) yield

$$\begin{aligned} \omega_{N_2} h_{N_2} + (\omega_{NO_2})_0 h_{NO_2} - \omega_{N_2O_4} h_{N_2O_4} + \frac{w^2}{2} \\ = (\omega_{N_2} h_{N_2})_0 + (\omega_{NO_2} h_{NO_2})_0 \end{aligned} \quad (81)$$

We now have five equations, eq. (79), (61), (81), (77), and (78) with the five unknowns P , ρ , T , w and $\omega_{N_2O_4}$. The numerical procedure involves an iteration process in which the composition of the mixture is estimated and then corrected.

The simultaneous solution of equations (79), (61), (81), (77), and (78) is realized by including the constraint of isentropic flow. This limitation is required for achievement of a unique solution to the forementioned set of simultaneous equations. In effect, the isentropic condition implies that at any point in the flow a complete reversal of the process may be achieved by an infinitesimal change in the flow field properties.

BRAY ANALYSIS

The Bray analysis is a technique for estimating kinetic performance without the arduous detail described above. K. N. C. Bray, an English aerodynamicist, first suggested that the analysis of hypersonic wind tunnel flow could be achieved by assuming the complete chemical equilibrium holds until a point in the flow field is reached where the chemical kinetic rate of recombination is equal to the rate of recombination calculated from the thermodynamics of the flow and thereafter constant composition flow prevails. Such an analysis is mechanically less complex than the kinetic analysis and the former yields results that are in good agreement with the latter. As in the kinetic analysis, the Bray analysis utilizes a nozzle geometry and thereby loses some of the generality of the shifting and frozen imposition flow analysis.

The simultaneous solution of equations (79), (61), (81), (77), and (78) is realized by including the constraint of isentropic flow. This limitation is required for achievement of a unique solution to the forementioned set of simultaneous equations. In effect, the isentropic condition implies that at any point in the flow a complete reversal of the process may be achieved by an infinitesimal change in the flow field properties.

BRAY ANALYSIS

The Bray analysis is a technique for estimating kinetic performance without the arduous detail described above. K. N. C. Bray, an English aerodynamicist, first suggested that the analysis of hypersonic wind tunnel flow could be achieved by assuming the complete chemical equilibrium holds until a point in the flow field is reached where the chemical kinetic rate of recombination is equal to the rate of recombination calculated from the thermodynamics of the flow and thereafter constant composition flow prevails. Such an analysis is mechanically less complex than the kinetic analysis and the former yields results that are in good agreement with the latter. As in the kinetic analysis, the Bray analysis utilizes a nozzle geometry and thereby loses some of the generality of the shifting and frozen imposition flow analysis.

CHAPTER VI

GENERALIZED ONE-DIMENSIONAL FLOW

As in previous chapters, the emphasis is on steady flow in the one-dimensional regime and the fluid is assumed to obey the ideal gas equation of state

$$P = \rho RT/W \quad (1)$$

where:

P = pressure

ρ = density

R = universal gas constant

T = absolute temperature

W = molecular weight

The assumption of one-dimensional flow is justified largely by the great simplifications it makes possible. It follows then that changes in the stream properties are continuous, changes in the stream properties normal to the direction of flow are negligible, and the effect of turbulence is small.

ENERGY EQUATION

We shall consider the steady flow of fluid through the control surface shown in Figure 1.

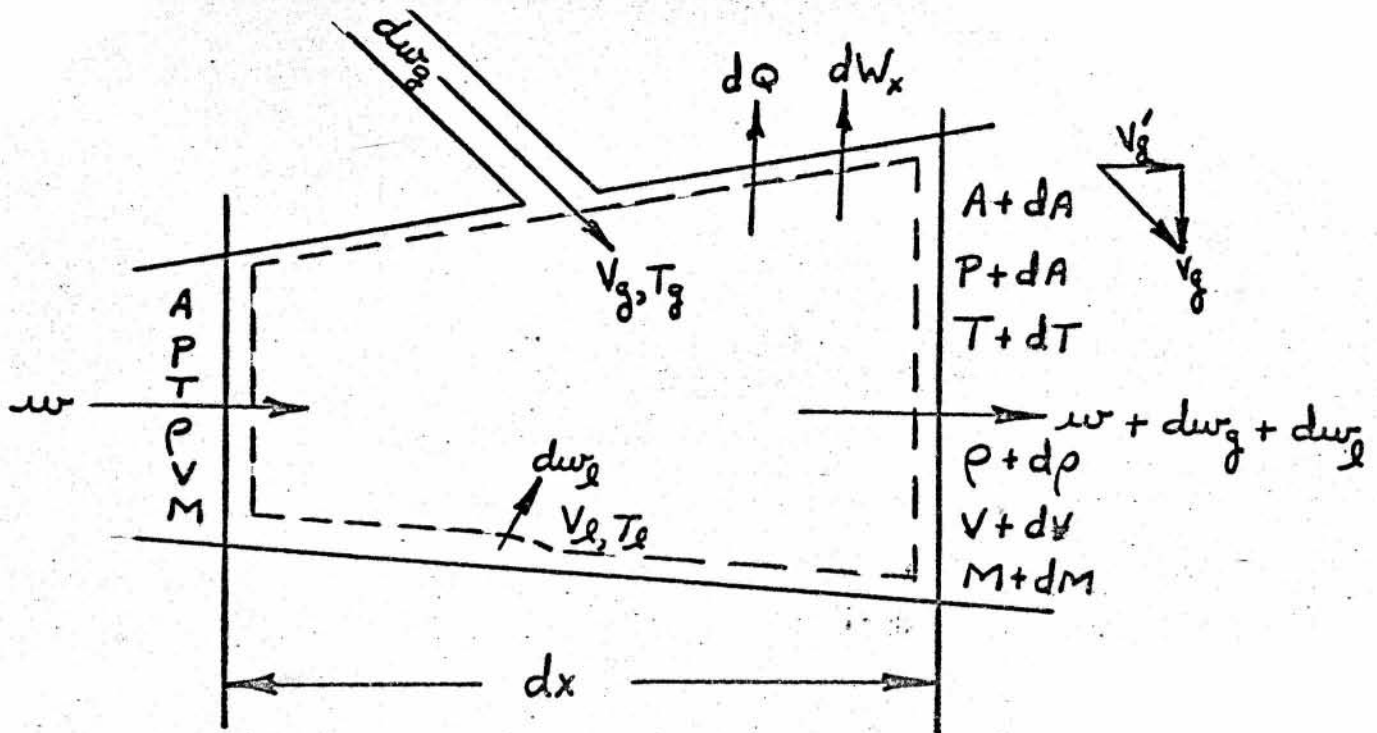


Figure 1. Control Surface for Analysis of Continuous Change

The various terms in Figure 1 are defined as follows:

- A = cross-sectional area
- M = Mach number
- P = static pressure
- Q = heat transfer to stream from external sources, per unit mass of stream
- T = absolute temperature
- V = stream velocity
- w = mass rate of flow of stream
- dw_g = mass rate of flow of injected gas
- dw_e = mass rate of flow of evaporated gas
- W_x = work delivered by stream to surroundings, per unit mass of stream

- ρ = mass density of stream
 $()_g$ = refers to injected gas
 $()_l$ = refers to injected fluid which changes phase

In this model, the liquid stream is considered to be external to the system. Only the liquid crossing the control surface boundary and evaporating within the control surface is taken into account in evaluating the flux of enthalpy. Changes in the temperature of the liquid traveling along with the stream are then taken to be the result of external heat exchange to or from the main stream. This implies that the liquid crossing the boundary is saturated and at the temperature of the gas stream. The liquid passes out of the control surface in the form of vapor and it has achieved thermal equilibrium with the main stream; i.e., the temperature of the vapor is equal to the mainstream temperature.

The sum of the heat added to the stream and the work done by the stream on external bodies is equal to the increase of stream enthalpy, kinetic energy, and potential energy. By convention the heat added to the system is positive and the work done on the surroundings is negative; thus, the energy equation for steady flow becomes

$$\begin{aligned}
 w(dQ - dW_x) &= w(h + dh) + (h_g)_T dw_g + (h_l)_T dw_l \\
 -w h - (h_g)_{T_g} dw_g - (h_l)_{T_l} dw_l &+ (w + dw_g + dw_l) \left(\frac{V^2}{2} + d\frac{V^2}{2} \right) \\
 -w \frac{V^2}{2} - \frac{V_g^2}{2} dw_g - \frac{V_l^2}{2} dw_l &+ (w + dw_g + dw_l) (z + dz) \quad (2) \\
 -w z - z_g dw_g - z_l dw_l &
 \end{aligned}$$

The elevation z_g is taken at the height where h_g and V_g are measured and similarly for z_e . Symbols $(h_g)_T$ and $(h_g)_{T_g}$ denote the enthalpies of the injected gas dw_g at temperature T and at temperature T_g at which dw_g crosses the control surface, respectively. Also, the symbol $(h_e)_T$ denotes the enthalpy of the evaporated liquid at temperature T , and $(h_e)_{T_e}$ denotes the enthalpy of evaporating liquid as it crosses the control surface at temperature T .

We rearrange eq. (2) into the following form

$$\begin{aligned} d\phi - dw_x = & dh + d\frac{V^2}{2} + dz \\ & + [(h_g)_T - (h_g)_{T_g} + \frac{V^2 - V_g^2}{2} + z - z_g] \frac{dw_g}{w} \\ & + [(h_e)_T - (h_e)_{T_e} + \frac{V^2 - V_e^2}{2} + z - z_e] \frac{dw_e}{w} \end{aligned} \quad (3)$$

Further simplification of the energy equation is possible by noting that the enthalpy change of the main gas stream is the sum of changes due to chemical reaction and to temperature change; thus

$$dh = -dh_{pr} + c_p dT \quad (4)$$

where dh_{pr} is the enthalpy increase at temperature T and pressure P due to chemical reaction; i.e., for a change from reactants to products. This is the heat of reaction,

but this heat of reaction is computed per unit mass of total gas stream.

Also, we write

$$(h_g)_T - \left[(h_g)_{T_0g} + \frac{V_g^2}{2} \right] = (h_g)_T - h_{0g} = C_{Pg} (T - T_{0g}) \quad (5)$$

and

$$C_{Pg} = \int_{T_{0g}}^{T_g} \frac{C_{Pg} dT}{(T - T_{0g})} \quad (6)$$

where h_{0g} is the stagnation enthalpy of the injected gas stream and T_{0g} is its stagnation temperature. Finally, we note that

$$(h_x)_T - (h_x)_{T_e} = h_{fg} \quad (7)$$

where h_{fg} is the latent heat of evaporation of the injected liquid at the temperature T.

Inserting Eqs. (4), (5), and (7) into eq. (3) yields the final form of the energy equation

$$dQ - dW_x + dH = \bar{C}_p dT + d\left(\frac{V^2}{2}\right) + dz \quad (8)$$

where

$$dH = dh_{pr} - \left[C_{Pg} (T - T_{0g}) + \frac{V^2}{2} + (z - z_0) \right] \frac{dW_x}{W} \\ - \left[h_{fg} + \frac{V^2 - V_e^2}{2} + (z - z_e) \right] \frac{dW_e}{W} \quad (9)$$

Hereafter, we shall assume that there are no differences in elevation and thus the z terms will not appear in the subsequent discussion.

MOMENTUM EQUATION

To obtain the momentum equation, we apply Newton's second law of motion to the control volume. The net force acting on the system is equated to the increase of momentum flux of the streams flowing through the control surface. Consider forces acting in the direction of flow as positive. In addition, it is assumed that the injected gas and liquid streams are at the control surface pressure as they cross the boundary and the angle of divergence of the walls is small. The momentum equation becomes

$$PA + PdA - (P+dP)(A+dA) - \tau_w dA_w - dX$$

$$= (\rho + d\rho_g + d\rho_l)(V+dV) - V'_g d\rho_g - V'_l d\rho_l - \rho V$$
(10)

where τ_w represents the frictional shearing stress acting on the wall area dA_w ; dX is the sum of (a) the drag of bodies immersed in the stream within the control surface boundaries, and (b) the component of body or gravity forces acting on the fluid within the control surface in the direction opposite to the velocity vector. The velocity V'_g is the forward component of the velocity V_g with which the injected gas $d\rho_g$ crosses the control surface and similarly for V'_l .

The wall shearing force is related to the friction factor f , through the definition

$$\tau_w = f \rho V^2 / 2 \quad (11)$$

It is convenient to define the following quantities

$$y_g = V_g' / V \quad \text{and} \quad y_e = V_e' / V \quad (12)$$

From the definition of the hydraulic diameter D , we obtain

$$\frac{dA_w}{A} = \frac{4 dx}{D} \quad (13)$$

Substituting eqs. (11), (12), and (13) into eq. (10), and noting that

$$\rho V^2 = \mathcal{R} P M^2$$

we obtain the final form of the momentum equation

$$\begin{aligned} \frac{dP}{P} + \frac{\mathcal{R} M^2}{2} \frac{dV^2}{V^2} + \frac{\mathcal{R} M^2}{2} \left(4f \frac{dx}{D} + \frac{dX}{\frac{1}{2} \mathcal{R} P A M^2} \right) \\ + \mathcal{R} M^2 (1 - y) \frac{dw}{w} = 0 \end{aligned} \quad (14)$$

where

$$(1 - y) \frac{dw}{w} = (1 - y_g) \frac{dw_g}{w} + (1 - y_e) \frac{dw_e}{w} \quad (15)$$

$$\frac{dw}{w} = \frac{dw_g}{w} + \frac{dw_e}{w} \quad (16)$$

$$y \frac{dw}{w} = y_g \frac{dw_g}{w} + y_e \frac{dw_e}{w} \quad (17)$$

FLOW WITH CONTINUOUS CHANGES FOR VARIABLE MOLECULAR WEIGHT AND SPECIFIC HEAT

In addition to the equations for energy and momentum, several other differential expressions are required for an efficient formulation. The equation of state, eq. (1), may be differentiated logarithmically to obtain

$$\frac{dP}{P} = \frac{d\rho}{\rho} + \frac{dT}{T} - \frac{dW}{W} \quad (18)$$

From the definition of Mach number and the relation for sound velocity in a perfect gas, we get

$$c^2 = \frac{R}{k} RT / W \quad (19)$$

and

$$M^2 = V^2 / c^2 = V^2 W / \frac{R}{k} RT \quad (20)$$

where:

c = sound velocity

k = specific heat ratio

The latter expressions lead to

$$\frac{dc}{c} = \frac{1}{2} \left(\frac{dR}{R} + \frac{dT}{T} - \frac{dW}{W} \right) \quad (21)$$

and

$$\frac{dM^2}{M^2} = \frac{dV^2}{V^2} + \frac{dW}{W} - \frac{dR}{R} - \frac{dT}{T} \quad (22)$$

From the continuity equation, we obtain

$$w = \rho AV \quad (23)$$

and

$$\frac{dw}{w} = \frac{d\rho}{\rho} + \frac{dA}{A} + \frac{dV}{V} \quad (24)$$

it should be noted that dw denotes the total increase of mass flow in the main stream and includes both injected gas and evaporated gas; that is

$$dw = dw_e + dw_g \quad (25)$$

Furthermore if vapor is condensed, the term dw_e is negative and we also note that dA refers to the change in cross-sectional area occupied by the main stream excluding the cross-sectional area of the injected stream before mixing. In addition, it is assumed that the injected streams are perfectly mixed and diffused at the downstream boundary of the control surface.

A quantity called the impulse function is defined such that the change in the function represents the total force exerted by the solid boundaries on the stream. Thus

$$F = PA + \rho AV^2 = PA(1 + \bar{R}M^2) \quad (26)$$

or

$$\frac{dF}{F} = \frac{dA}{A} + \frac{dP}{P} + \frac{\bar{R}M^2}{1 + \bar{R}M^2} \frac{dM^2}{M^2} + \frac{\bar{R}M^2}{1 + \bar{R}M^2} \frac{d\bar{R}}{\bar{R}} \quad (27)$$

As in all aerothermodynamic flows, the entropy is required to complete the formulation. For a perfect gas, the entropy change is

$$\frac{ds}{c_p} = \frac{dT}{T} - \frac{\bar{r}-1}{\bar{r}} \frac{dP}{P} \quad (28)$$

and for the main stream plus injected gas and liquid, the entropy change is given by

$$\frac{dS}{C_p} = \frac{ds}{C_p} + (s-s_g) \frac{dw_g}{w} + (s-s_e) \frac{dw_e}{w} \quad (29)$$

Among the seven relations given by Equations (18), (21) or (22), (24), (8), (14), (27), (28) or (29), we find thirteen variables. Consequently, six variables may be chosen as independent and seven as dependent. The independent variables are chosen to be those quantities whose values are most easily controlled in a practical problem, and each of the dependent variables is expressed in terms of the independent ones. For example, we may show that

$$\begin{aligned} \frac{dM^2}{M^2} = & - \frac{2(1 + \frac{k-1}{2} M^2)}{1-M^2} \frac{dA}{A} + \frac{1+kM^2}{1-M^2} \frac{dQ - dW + dH}{C_p T} \\ & + \left[\frac{kM^2(1 + \frac{k-1}{2} M^2)}{1-M^2} 4f \frac{dx}{D} + \frac{dX}{\frac{1}{2} k P A M^2} - 2y \frac{dw}{w} \right] \\ & + \frac{2(1+kM^2)(1 + \frac{k-1}{2} M^2)}{1-M^2} \frac{dw}{w} - \frac{1+kM^2}{1-M^2} \frac{dW}{W} - \frac{dk}{k} \end{aligned} \quad (30)$$

The coefficients of the independent variables are called influence coefficients and are functions of k and M only. A complete list of the influence coefficients is presented in Table I. Some general aspects of flow may be obtained from the influence coefficients without recourse to any numerical analysis. It will be observed that almost all of the influence coefficients in Table I have the term $1-M^2$ in the denominator; thus, these terms are undefined \times

TABLE I. INFLUENCE COEFFICIENTS: VARIABLE SPECIFIC HEAT AND MOLECULAR WEIGHT

	$\frac{dA}{A}$	$\frac{dQ-dW_x+dH}{C_p T}$	$4f \frac{dx}{D} + \frac{dx}{\frac{1}{2} R P A M^2} - 24 \frac{d\mu}{\mu}$	$\frac{d\mu}{\mu}$	$\frac{dW}{W}$	$\frac{dR}{R}$
$\frac{dM^2}{M^2}$	$-\frac{2(1+\frac{R-1}{2}M^2)}{1-M^2}$	$\frac{1+RM^2}{1-M^2}$	$\frac{RM^2(1+\frac{R-1}{2}M^2)}{1-M^2}$	$\frac{2(1+RM^2)(1+\frac{R-1}{2}M^2)}{1-M^2}$	$-\frac{1+RM^2}{1-M^2}$	-1
$\frac{dV}{V}$	$-\frac{1}{1-M^2}$	$\frac{1}{1-M^2}$	$\frac{RM^2}{2(1-M^2)}$	$\frac{1+RM^2}{1-M^2}$	$-\frac{1}{1-M^2}$	0
$\frac{dc}{c}$	$\frac{\frac{R-1}{2}M^2}{1-M^2}$	$\frac{1-RM^2}{2(1-M^2)}$	$-\frac{R(R-1)M^2}{4(1-M^2)}$	$-\frac{\frac{R-1}{2}M^2(1+RM^2)}{1-M^2}$	$\frac{RM^2-1}{2(1-M^2)}$	$\frac{1}{2}$
$\frac{dT}{T}$	$\frac{(R-1)M^2}{1-M^2}$	$\frac{1-RM^2}{1-M^2}$	$-\frac{R(R-1)M^2}{2(1-M^2)}$	$-\frac{(R-1)M^2(1+RM^2)}{1-M^2}$	$\frac{(R-1)M^2}{1-M^2}$	0
$\frac{dp}{p}$	$\frac{M^2}{1-M^2}$	$-\frac{1}{1-M^2}$	$-\frac{RM^2}{2(1-M^2)}$	$-\frac{(R+1)M^2}{1-M^2}$	$\frac{1}{1-M^2}$	0
$\frac{dP}{P}$	$\frac{RM^2}{1-M^2}$	$-\frac{RM^2}{1-M^2}$	$-\frac{RM^2[1+(R-1)M^2]}{2(1-M^2)}$	$-\frac{2RM^2(1+\frac{R-1}{2}M^2)}{1-M^2}$	$\frac{RM^2}{1-M^2}$	0
$\frac{dF}{F}$	$\frac{1}{1+RM^2}$	0	$-\frac{RM^2}{2(1+RM^2)}$	0	0	0
$\frac{ds}{C_p}$	0	1	$\frac{(R-1)M^2}{2}$	$(R-1)M^2$	0	0

at the sonic point; i.e., at $M=1$. Furthermore, the sign of the terms that are undefined at Mach one change in going from subsonic to supersonic flow conditions. In subsonic flow the term $1-M^2$ is positive and in supersonic flow this term is negative. This indicates that the effect of the variables controlled by the influence coefficient are of opposite sign in the two flow regimes.

By considering the influence coefficients in Table I, it is easily shown that:

1. An increase in area tends to reduce M in subsonic flow and to increase it in supersonic flow
2. Heating or combustion tends to increase M at subsonic speeds and to decrease M at supersonic speeds
3. The effect of friction, or drag of internal bodies, acts to increase M at subsonic speeds and to decrease M at supersonic speeds
4. An increase in mass flow tends to increase M at subsonic speeds and to decrease M at supersonic speeds
5. If the molecular weight is increased, the Mach number tends to drop for subsonic flow and to rise for supersonic flow

6. Finally, an increase in the isentropic exponent k always tends to reduce M , for either subsonic or supersonic speeds.

The analysis of the influence coefficients could be continued for the other dependent variables, V, C, T, ρ, P, F and S , to obtain a list of reactions to changes in area, heat transfer, etc.

FLOW WITH CONTINUOUS CHANGES FOR CONSTANT MOLECULAR WEIGHT AND SPECIFIC HEAT

Many problems may be adequately analyzed by assuming that molecular weight and specific heat are constant. The assumptions used here are the same as in the preceding section except for the additional constraints that $dW = dC_p = dR = 0$.

Two quantities, in addition to those already introduced, are useful here; namely, the stagnation temperature and stagnation pressure. The stagnation temperature (or pressure) is the temperature (or pressure) which the stream assumes if it were brought to rest isentropically.

These two quantities are given by the following expressions

$$T_0 = T + \frac{V^2}{2C_p} = T \left(1 + \frac{k-1}{2} M^2 \right) \quad (31)$$

and

$$P_0 = P \left(1 + \frac{k-1}{2} M^2 \right)^{k/(k-1)} \quad (32)$$

In differential form, eqs. (31) and (32) become

$$\frac{dT_0}{T_0} = \frac{dT}{T} + \frac{\frac{k-1}{2} M^2}{1 + \frac{k-1}{2} M^2} \frac{dM^2}{M^2} \quad (33)$$

$$\frac{dP_0}{P_0} = \frac{dP}{P} + \frac{\frac{kM^2}{2}}{1 + \frac{k-1}{2} M^2} \frac{dM^2}{M^2} \quad (34)$$

Also, the energy equation becomes

$$dQ - dW_x + dH = C_p dT + d \frac{V^2}{2} = C_p dT_0 \quad (35)$$

Finally, the entropy change is related to the stagnation temperature and pressure through

$$\frac{dS}{C_p} = \frac{dT_0}{T_0} - \frac{k-1}{k} \frac{dP_0}{P_0} \quad (36)$$

As before, the equations are combined to yield nine equations containing six independent variables. The influence coefficients for these cases are presented in Table II.

Analysis of the influence coefficients in Table II leads to some useful qualitative results regarding the stagnation pressure. These results are:

1. Changes in area have no effect on stagnation pressure.
2. An increase in stagnation temperature always tends to reduce P_0 , be the speed subsonic or supersonic. Thus, the stagnation pressure loss in combustion chambers can never be entirely eliminated.

TABLE 2. INFLUENCE COEFFICIENTS: CONSTANT SPECIFIC HEAT AND MOLECULAR WEIGHT

	$\frac{dA}{A}$	$\frac{dT_0}{T_0}$	$f \frac{dx}{D} + \frac{dX}{\frac{1}{2} R P A M^2} - 2y \frac{dw}{w}$	$\frac{dw}{w}$
$\frac{dM^2}{M^2}$	$-\frac{2(1 + \frac{R-1}{2} M^2)}{1-M^2}$	$\frac{(1+R M^2)(1 + \frac{R-1}{2} M^2)}{1-M^2}$	$\frac{R M^2(1 + \frac{R-1}{2} M^2)}{1-M^2}$	$\frac{2(1+R M^2)(1 + \frac{R-1}{2} M^2)}{1-M^2}$
$\frac{dV}{V}$	$-\frac{1}{1-M^2}$	$\frac{1 + \frac{R-1}{2} M^2}{1-M^2}$	$\frac{R M^2}{2(1-M^2)}$	$\frac{1+R M^2}{1-M^2}$
$\frac{dc}{c}$	$\frac{\frac{R-1}{2} M^2}{1-M^2}$	$\frac{\frac{1-R M^2}{2}(1 + \frac{R-1}{2} M^2)}{1-M^2}$	$-\frac{R(R-1) M^4}{4(1-M^2)}$	$-\frac{\frac{R-1}{2} M^2(1+R M^2)}{1-M^2}$
$\frac{dT}{T}$	$\frac{(R-1) M^2}{1-M^2}$	$\frac{(1-R M^2)(1 + \frac{R-1}{2} M^2)}{1-M^2}$	$-\frac{R(R-1) M^4}{2(1-M^2)}$	$-\frac{(R-1) M^2(1+R M^2)}{1-M^2}$
$\frac{dp}{p}$	$\frac{M^2}{1-M^2}$	$-\frac{1 + \frac{R-1}{2} M^2}{1-M^2}$	$-\frac{R M^2}{2(1-M^2)}$	$-\frac{(R+1) M^2}{1-M^2}$
$\frac{dP}{P}$	$\frac{R M^2}{1-M^2}$	$-\frac{R M^2(1 + \frac{R-1}{2} M^2)}{1-M^2}$	$-\frac{R M^2 [1 + (R-1) M^2]}{2(1-M^2)}$	$-\frac{2R M^2(1 + \frac{R-1}{2} M^2)}{1-M^2}$
$\frac{dP_0}{P_0}$	0	$-\frac{R M^2}{2}$	$-\frac{R M^2}{2}$	$-R M^2$
$\frac{dF}{F}$	$\frac{1}{1+R M^2}$	0	$-\frac{R M^2}{2(1+R M^2)}$	0
$\frac{ds}{c_p}$	0	$1 + \frac{R-1}{2} M^2$	$\frac{(R-1) M^2}{2}$	$(R-1) M^2$

3. Friction and drag always act to reduce P_0 for both subsonic and supersonic flow.
4. Gas injection tends to decrease P_0 if $y < 0$; i.e., if the gas is injected with a forward velocity less than that of the main stream; while the stagnation pressure tends to be increased when gas is injected with a forward velocity greater than that of the main stream.

SIMPLE TYPES OF FLOW

We shall define a simple type of flow as one in which all but the independent differentials in Table 2 are zero. Analytical relations may easily be obtained for the several simple types of flow. For example, consider a simple area change. Using the first influence coefficient in Table 2, we find

$$\int_{A^*}^A \frac{dA}{A} = - \int_1^M \frac{(1-M^2) dM^2}{2M^2 (1 + \frac{\gamma-1}{2} M^2)} \quad (37)$$

or

$$\frac{A}{A^*} = \frac{1}{M} \sqrt{\left[\frac{2(1 + \frac{\gamma-1}{2} M^2)}{\gamma+1} \right]^{(\gamma+1)/(\gamma-1)}} \quad (38)$$

Equation (38) is the well-known formula giving the ratio of local area to throat area as a function of the local Mach number for an isentropic process.

TABLE 3. FORMULAS FOR SIMPLE TYPES OF ONE-DIMENSIONAL FLOW: CONSTANT SPECIFIC HEAT AND MOLECULAR WEIGHT

	Area Change Only $dT_0=0$ $f=0$ $dw=0$	Change in T_0 only $dA=0$ $f=0$ $dw=0$	Friction Only $dA=0$ $dT_0=0$ $dw=0$	Gas Injection Only $y=0$ $dA=0$ $dT_0=0, f=0$	Gas Injection Only $y=1$ $dA=0$ $dT_0=0, f=0$
$\frac{A}{A^*}$	$\frac{1}{M} \left[\frac{2(1 + \frac{R-1}{2} M^2)}{R+1} \right]^{\frac{R+1}{2(R-1)}}$	1	1	1	1
$\frac{T_0}{T^*}$	1	$\frac{2(R+1)M^2(1 + \frac{R-1}{2} M^2)}{(1 + RM^2)^2}$	1	1	1
$4f \frac{L_{max}}{D}$	0	0	$\frac{1-M^2}{RM^2} + \frac{R+1}{2R} \ln \frac{(R+1)M^2}{2(1 + \frac{R-1}{2} M^2)}$	0	0
$\frac{w}{w^*}$	1	1	1	$\frac{M \sqrt{2(R+1)(1 + \frac{R-1}{2} M^2)}}{1 + RM^2}$	$M \left[\frac{R+1}{2(1 + \frac{R-1}{2} M^2)} \right]^{\frac{R+1}{2(R-1)}}$
$\frac{V}{V^*}$	$M \sqrt{\frac{R+1}{2(1 + \frac{R-1}{2} M^2)}}$	$\frac{(R+1)M^2}{1 + RM^2}$	$M \sqrt{\frac{R+1}{2(1 + \frac{R-1}{2} M^2)}}$	$M \sqrt{\frac{R+1}{2(1 + \frac{R-1}{2} M^2)}}$	$M \sqrt{\frac{R+1}{2(1 + \frac{R-1}{2} M^2)}}$
$\frac{T}{T^*} = \left(\frac{C}{C^*}\right)^2$	$\frac{R+1}{2(1 + \frac{R-1}{2} M^2)}$	$\frac{(R+1)(M^2)}{(1 + RM^2)^2}$	$\frac{R+1}{2(1 + \frac{R-1}{2} M^2)}$	$\frac{R+1}{2(1 + \frac{R-1}{2} M^2)}$	$\frac{R+1}{2(1 + \frac{R-1}{2} M^2)}$
$\frac{P}{P^*}$	$\left[\frac{R+1}{2(1 + \frac{R-1}{2} M^2)} \right]^{\frac{1}{R-1}}$	$\frac{1 + RM^2}{(R+1)M^2}$	$\frac{1}{M} \sqrt{\frac{2(1 + \frac{R-1}{2} M^2)}{R+1}}$	$\frac{2(1 + \frac{R-1}{2} M^2)}{1 + RM^2}$	$\left[\frac{R+1}{2(1 + \frac{R-1}{2} M^2)} \right]^{R/(R-1)}$
$\frac{P}{P^*}$	$\left[\frac{R+1}{2(1 + \frac{R-1}{2} M^2)} \right]^{R/(R-1)}$	$\frac{R+1}{1 + RM^2}$	$\frac{1}{M} \sqrt{\frac{R+1}{2(1 + \frac{R-1}{2} M^2)}}$	$\frac{R+1}{1 + RM^2}$	$\left[\frac{R+1}{2(1 + \frac{R-1}{2} M^2)} \right]^{R/(R-1)}$
$\frac{P_0}{P_0^*}$	1	$\frac{R+1}{1 + RM^2} \left[\frac{2(1 + \frac{R-1}{2} M^2)}{R+1} \right]^{\frac{R}{R-1}}$	$\frac{1}{M} \left[\frac{2(1 + \frac{R-1}{2} M^2)}{R+1} \right]^{\frac{R+1}{2(R-1)}}$	$\frac{R+1}{1 + RM^2} \left[\frac{2(1 + \frac{R-1}{2} M^2)}{R+1} \right]^{\frac{R}{R-1}}$	1
$\frac{F}{F^*}$	$\frac{1 + RM^2}{M \sqrt{2(R+1)(1 + \frac{R-1}{2} M^2)}}$	1	$\frac{1 + RM^2}{M \sqrt{2(R+1)(1 + \frac{R-1}{2} M^2)}}$	1	$\frac{1 + RM^2}{R+1} \left[\frac{R+1}{2(1 + \frac{R-1}{2} M^2)} \right]^{\frac{R}{R-1}}$
$\frac{S-S^*}{C_p}$	0	$\ln M^2 \left(\frac{R+1}{1 + RM^2} \right)^{\frac{R+1}{R}}$	$\ln M^2 \left[\frac{R+1}{2(1 + \frac{R-1}{2} M^2)} \right]^{\frac{R+1}{2R}}$	$\ln \frac{R+1}{2(1 + \frac{R-1}{2} M^2)} \left(\frac{1 + RM^2}{R+1} \right)^{\frac{R-1}{R}}$	0