

UNCLASSIFIED

AD NUMBER
AD802180
NEW LIMITATION CHANGE
TO Approved for public release, distribution unlimited
FROM Distribution authorized to U.S. Gov't. agencies and their contractors; Critical Technology; 6 Nov 1966. Other requests shall be referred to the Commanding Officer, U.S. Army Edgewood Arsenal, Attn: SMUEA-TSTI-T, Edgewood Arsenal, MD 21010.
AUTHORITY
USAEA ltr, 22 Dec 1971

THIS PAGE IS UNCLASSIFIED

Special Technical Report No. 3

802180

**EQUATIONS OF STATE OF LIQUIDS AND
CALCULATIONS OF WASTE HEAT**

Prepared for:

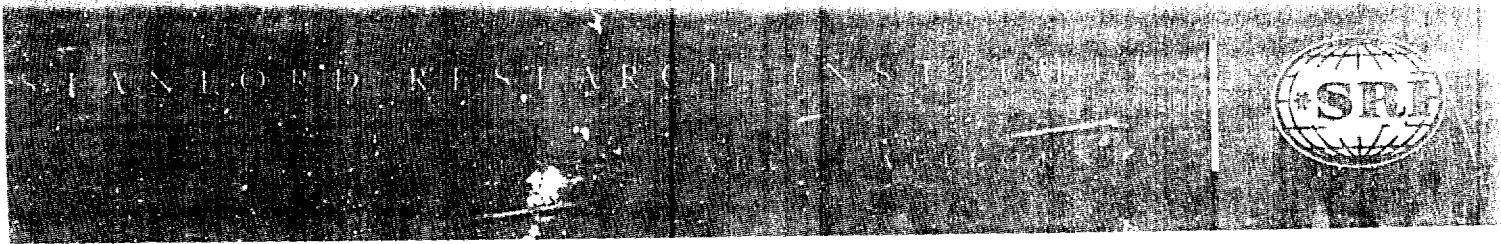
COMMANDING OFFICER
EDGEWOOD ARSENAL, MARYLAND 21010
ATTN: MR. DONALD E. BUCK
CONTRACT PROJECT OFFICER
DISSEMINATION RESEARCH DEPARTMENT
PHYSICAL RESEARCH LABORATORY

CONTRACT DA-18-035-AMC-1

STANFORD RESEARCH INSTITUT

MENLO PARK, CALIFORNIA

***SRI**



November 6, 1966

Special Technical Report No. 3

EQUATIONS OF STATE OF LIQUIDS AND CALCULATIONS OF WASTE HEAT

Prepared for:

COMMANDING OFFICER
EDGEWOOD ARSENAL, MARYLAND 21010
ATTN: MR. DONALD E. BUCK
CONTRACT PROJECT OFFICER
DISSEMINATION RESEARCH DEPARTMENT
PHYSICAL RESEARCH LABORATORY

CONTRACT DA-18-035-AMC-122(A)

By: G. E. DUVALL

SRI Project PAU-4900

Approved: MARJORIE W. EVANS, DIRECTOR
POULTER LABORATORIES

This document is subject to special export controls and each transmittal to foreign governments or foreign nationals may be made only with prior approval of the CO, U.S. Army Edgewood Arsenal, Attn: SMUEA-TSTI-T, Edgewood Arsenal, Maryland 21010

Copy No. **13**

**REPRODUCED FROM
BEST AVAILABLE COPY**

FOREWORD

The work reported herein was authorized under Task IB522301A08101, Dissemination Investigations of Liquids and Solid Agents (U). The work was started in July and completed in September 1965.

Notices

Reproduction of this document in whole or in part is prohibited except with permission of the CO, US Army Edgewood Arsenal, ATTN: SMUEA-RPR, Edgewood Arsenal, Maryland 21010; however, Defense Documentation Center is authorized to reproduce the document for United States Government purposes.

The information contained in this document has not been cleared for release to the general public.

Disclaimer

The findings in this report are not to be construed as an official Department of the Army position unless so designated by other authorized documents.

Disposition

When this report has served its purpose, DESTROY it.

PREFATORY NOTE

The casual reader may not be familiar with the term "waste heat" as used here or with the qualitative aspects of the temperature history of a material element which is shocked and then allowed to expand to ambient pressure. He can find these ideas discussed in Chapter IX of Physics and Chemistry of High Pressure, edited by R. S. Bradley and published by Academic Press, 1963, and in some of the references given there to other papers by G. E. Duvall. If he does not wish to go so far, the following description may be helpful.

The process of shock compression is necessarily dissipative, so the temperature of a material element elevated to a high pressure state by passage of a shock is necessarily higher than the initial temperature of the unshocked material. Call this elevated temperature the "shock temperature" of the material corresponding to the shock pressure P . This increase in temperature results from the dissipative forces coming into play in the shock process and also from isentropic compression, aside from any dissipation. The material element is returned to ambient pressure (whence it started before shock compression) by a rarefaction process in which dissipative forces can be neglected. The isentropic expansion cools the material to a final temperature which is lower than the shock temperature but higher than the initial temperature of the unshocked state. Call this the "final temperature" corresponding to the ambient pressure P_0 . Since the final temperature is greater than the initial temperature, and the pressures for initial and final states are the same, the passage of the shock and subsequent rarefaction have increased the specific enthalpy of the material element. This increase in enthalpy is called here the "waste heat" deposited by the shock in unit mass of the material.

ABSTRACT

Procedures for relating waste heat to entropy increases in a shock wave are described. Numerical coefficients for Mie-Gruneisen equations of state are obtained for several liquids, assuming that $(\partial P/\partial T)_V$ and C_V are constant. These equations of state are used to calculate the flow produced by a 1.6-cm-radius sphere of C-3-like explosive in a surrounding liquid. Specific entropy increase as a function of radius is included in the calculation, and this is used to determine the waste heat for a 3.85-cm-radius liquid burster. (Liquid-to-explosive mass ratio is about 10.) Calculations for glycerine, for two different water equations of state, and for ether yield total waste heats equal to $(.32 \pm .03) \times$ (explosive energy). Close agreement between calculations for two different water equations of state produces considerable confidence in the reliability of this result. On the basis of these calculations, evaporation of several liquids is estimated. If decomposition can occur or if more precise values of waste heat are needed, more exact equations of state will be required; the present calculations can be readily modified to accommodate such equations.

CONTENTS

PREFATORY NOTE	v
ABSTRACT	vii
LIST OF ILLUSTRATIONS	xi
LIST OF TABLES.	xi
I INTRODUCTION	1
II EQUATIONS OF STATE.	7
A. General	7
B. Gruneisen Equation and Specific Heat	8
C. Evaluation of $P_1(V)$	9
III COMPUTED ISOTHERMAL AND HUGONIOT CURVES	17
IV WASTE HEAT CALCULATION	25
A. Geometry	25
B. Explosive Properties	25
C. Equation of State	25
D. Waste Heat.	29
V NUMERICAL RESULTS.	37
VI CONCLUSIONS.	43
APPENDIX A WASTE HEAT IN ETHER	45

ILLUSTRATIONS

Figure 1	P-V Diagram.	2
Figure 2	Flow Chart for Waste Heat Calculation	26
Figure 3	Flow Chart for Subprogram which Calculates P, E and Other Equation of State Parameters	27
Figure 4	Computation of E, P, T, S, Using NOL Equation of State of Water and Values of $(\partial V/\partial T)_P$, C_P from Rice and Walsh (ibid.)	30
Figure 5	Flow Chart for Calculation of Waste Heat	35

TABLES

Table I	Gruneisen's Ratio Γ for Several Liquids	6
Table II	Experimental Hugoniot Curve Data for Liquids.	10
Table III	R-H Data Corrected to 20°C and Coefficients for Eq. (25)	14
Table IV	Hugoniot and Isothermal Parameters for the Materials of Table III.	19
Table V	Waste Heat and Entropy for Simple Water	38
Table VI	Waste Heat and Entropy for NOL Water	38
Table VII	Waste Heat and Entropy for Glycerine.	39
Table VIII	Distribution in J of Liquid Mass and Waste Heat.	39
Table IX	Fraction of Total Mass Evaporated by Waste Heat, M_V/M_{total}	42
Table A-1	Waste Heat and Entropy for Ether	46

I INTRODUCTION

Flash radiography of the expansion of a liquid-filled spherical burster and calculations of the kinetic energy, energy of drop formation, and energy of rupture of the plastic case indicate that a large fraction of the explosive energy--perhaps 50%--is not accounted for by these mechanisms. Part of this is dissipated in the liquid of the fill as heat because of the inherent dissipative nature of shock compression. It is the purpose of this calculation to determine what fraction of the explosive energy is dissipated in this way for a particular burster and to outline a procedure for calculating the energy so dissipated in a more general case. To this end we proceed to formulate equations of state for a number of liquids and to employ a spherical Q-code* to calculate flow produced in the liquid by detonation of the explosive and the dissipated energy.

We shall call this dissipated energy the "waste heat." An expression for it is required which can be used in the flow calculation, given a suitable equation of state. In the shock process an element of mass is compressed to a state (P_1, V_1) and then it expands along an isentrope to the initial pressure P_0 and to a volume V'_0 , greater than the initial volume V_0 (see Fig. 1). The change in enthalpy in going from the initial state (P_0, V_0) to the final state (P_0, V'_0) is simply

$$H'_0 - H_0 = \int_{T_0}^{T'_0} C_p dT = \int_{S_0}^{S'_0} T dS \quad (1)$$

* See, for example, "Computational Methods in Physics," edited by Fernbach and Alder, Vol. III, "Hydrodynamics," Academic Press, 1964.

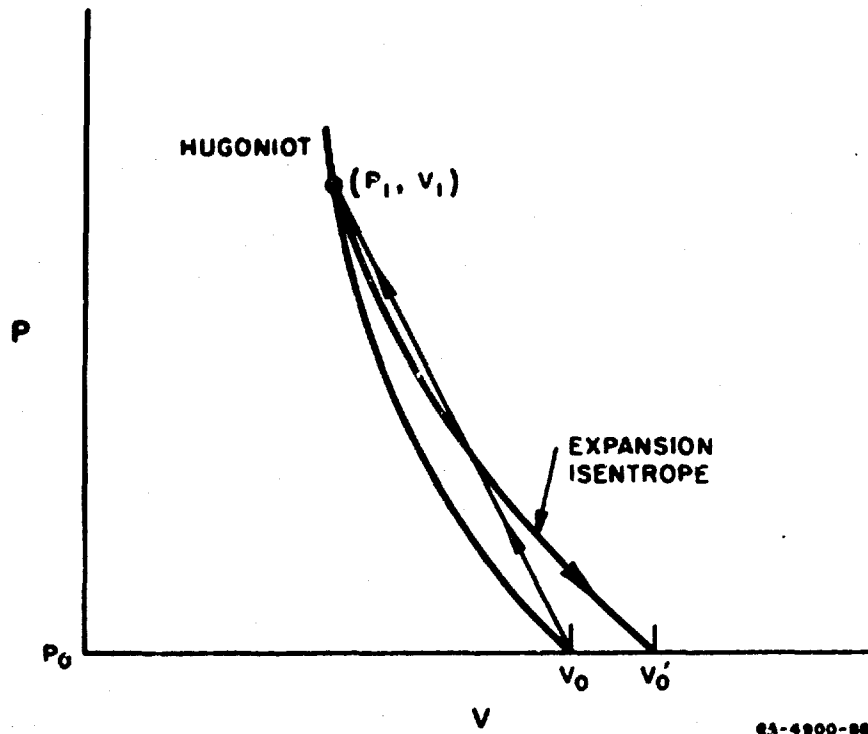


FIG. 1 P-V DIAGRAM

where T_0 and S_0 are temperature and entropy of the initial state (P_0, V_0) and (T'_0, S'_0) correspond to (P_0, V'_0) . The change in internal energy corresponding to the expansion is

$$E'_0 - E_0 = (H'_0 - H_0) - P_0(V'_0 - V_0); \quad (2)$$

$H'_0 - H_0$ is the waste heat per unit mass. Since $P_0 \approx 0$, $H'_0 - H_0 \cong E'_0 - E_0$ to an excellent approximation. In order to determine E'_0 , V'_0 , or T'_0 directly, the flow calculation must be continued until the pressure returns to P_0 , or very close to it. This is an impractical procedure with a Q-code for two reasons: first, the computing time would be very long, hence expensive. Second, the round-off errors creeping into the calculation would be apt to give serious errors in the end result.

An alternative and more practical procedure is to calculate the entropy produced by passage of the shock. Since it increases during

shock compression and remains constant in the subsequent rarefaction, it can be calculated during that part of the numerical integration where the precision is high; when it is known everywhere within the volume of interest, the waste heat can be calculated directly. We have on the isobar $P = P_0$,

$$dS = \frac{C_p dT}{T}, \quad (3)$$

and the indefinite integral gives $S(T)$. If this can be solved for $T(S)$, the solution can be substituted into the second integral in Eq. (1) and H'_0 is then given explicitly in terms of S'_0 . If Eq. (3) cannot be solved for $T(S)$, it is necessary to resort to a numerical procedure in which the second term on the right-hand side of Eq. (2) is evaluated from the integral

$$V'_0 - V_0 = \int_{T_0}^{T'_0} \left(\frac{\partial V}{\partial T} \right)_p dT, \quad (4)$$

using known values of the thermal expansion coefficient.

For the particular case $C_p = \text{constant} = C_v$ and $\left(\frac{\partial V}{\partial T} \right)_p = \text{constant}$, we have:

$$S'_0 - S_0 = C_p \ln T'_0 / T_0 \quad (5)$$

$$T'_0 = T_0 \exp[(S'_0 - S_0) / C_p]$$

$$\begin{aligned} V'_0 - V_0 &= \left(\frac{\partial V}{\partial T} \right)_p (T'_0 - T_0) \\ &= \left(\frac{\partial V}{\partial T} \right)_p T_0 \left\{ \exp[(S'_0 - S_0) / C_p] - 1 \right\} \end{aligned} \quad (6)$$

$$\begin{aligned}
E'_o - E_o &= C_p(T'_o - T_o) - P_o(V'_o - V_o) \\
&= [C_p - P_o(\frac{\partial V}{\partial T})_p] T_o \left\{ \exp[(S'_o - S_o)/C_p] - 1 \right\}
\end{aligned} \tag{7}$$

For the liquids listed in Table I, $(\frac{\partial V}{\partial T})_p < 3 \times 10^{-4} \text{ cc/g}^\circ\text{C}$ and $C_p > 8 \times 10^{-6} \text{ mbar cc/g}^\circ\text{C}$. Then since $P_o = 1 \text{ atmosphere} = 10^6 \text{ mbar}$, we have

$$\frac{P_o(\frac{\partial V}{\partial T})_p}{C_p} < 10^{-4} \tag{8}$$

Consequently, to a good approximation $E'_o - E_o = H'_o - H_o$ and, in this case,

$$E'_o - E_o = C_p T_o \left\{ \exp[(S'_o - S_o)/C_p] - 1 \right\} \tag{9}$$

Then if the liquid surrounding the explosive is partitioned into spherical shells of mass m_j , and $S'_o - S_o \equiv S_j$ is calculated for each cell, we have for the total waste heat in J cells behind the shock:

$$W = C_p T_o \sum_{j=1}^J m_j [\exp(S_j/C_p) - 1] \tag{10}$$

We shall use this expression for calculating waste heat for the present problem. The assumptions that $C_p = C_v = \text{constant}$ and that $(\frac{\partial V}{\partial T})_p = \text{constant}$ are unpalatable, but there is some reason to suppose that waste heat is quite insensitive to assumptions about specific heat anyway. Consider the following argument: For very weak shocks

$$(S'_o - S_o)/C_p \ll 1$$

and Eq. (9) becomes

$$E'_o - E_o \approx (S'_o - S_o) T_o \approx - \frac{1}{12} \left(\frac{\partial^2 P}{\partial V^2} \right)_{S_o} (V - V_o)^3$$

which is independent of C_p . For very strong shocks, energy stored elastically in the shocked material is negligible compared to the total heat stored. Then waste heat is proportional to the change in internal energy produced in the shock:

$$\text{Waste heat} = \frac{\epsilon}{2} P_H (V_0 - V)$$

where ϵ is a number which varies slowly with P_H and has magnitude approaching unity. Again the specific heats do not appear.

The numerical calculations described in this report for water with two different assumptions about C_p and C_v tend to bear out this conjecture that the assumptions made about specific heat have little effect on waste heat.

Table I
GRUNEISEN'S RATIO Γ FOR SEVERAL LIQUIDS

Liquid	V_0 Specific Volume (cc/g)*	C_p Specific Heat** (Mbar cc/g °C)	V_0/β_0 (Mbar cc/g)†	$\frac{1}{V} \left(\frac{\partial V}{\partial T} \right)_P$ Thermal Expansion Coeff. at Const. Pressure (deg. $^{-1}$)*	$b \equiv$ Γ_0/V_0 (g/cc)	Γ_0
Acetone	1.2626	2.21×10^{-5}	1.447×10^{-2}	1.487×10^{-3}	0.7717	0.9770
Benzene	1.1376	1.70×10^{-5}	1.7265×10^{-2}	1.237×10^{-3}	1.1050	1.2586
Carbon tetra- chloride	0.6270	0.84×10^{-5}	0.9025×10^{-2}	1.236×10^{-3}	2.1140	1.3234
Ethyl ether	1.4015	2.26×10^{-5}	1.012×10^{-2}	1.656×10^{-3}	0.5270	0.7404
Ethyl alcohol	1.2658	2.39×10^{-5}	1.350×10^{-2}	1.12×10^{-3}	0.5000	0.6330
Glycerine	0.7937	2.36×10^{-5}	3.625×10^{-2}	0.505×10^{-3}	0.9770	0.7767
Methanol	1.2642	2.51×10^{-5}	1.2566×10^{-2}	1.199×10^{-3}	0.4750	0.6004
Water	1.0018	4.18×10^{-5}	2.199×10^{-2}	0.207×10^{-3}	0.1070	0.1072††

* 20°C, 1 atmosphere.

** C_p at 20°C, 1 atmosphere. Assumed to be equal to C_v .

† β_0 here indicates adiabatic compressibility at 20°C, 1 atmosphere.

†† This low value of Γ_0 results primarily from a small expansion coefficient at 20°C. At 80°C α is up by a factor of nearly 6. This behavior is presumably associated with the anomalous expansion of water below 4°C.

II EQUATIONS OF STATE

A. General*

An equation of state of a nonreactive fluid is a relation between three thermodynamic variables which, given two, allows the third to be calculated. Such an equation may be incomplete, i. e., inadequate for calculation of other thermodynamic variables. For example, the ideal gas equation of state is a relation between P, V, and T, but the internal energy cannot be calculated without further information. On the other hand, a relation between E, S, and V is complete since

$$\left(\frac{\partial E}{\partial S}\right)_V = T(S, V)$$

$$\left(\frac{\partial E}{\partial V}\right)_S = -P(S, V)$$

$$H = E + PV = H(S, P)$$

$$F = E - TS = F(T, V)$$

$$G = H - TS = G(T, P)$$

In order to construct an equation of state it is necessary to fit whatever experimental data are available into a frame which is thermodynamically consistent and which does not violate our concept of what a "well-behaved" material should do.

* These remarks are suggested by conversations with Dr. Michael Cowperthwaite of Poulter Laboratories and by his memorandum: "Comments on the Calculation of Shock Temperature along Hugoniot Curves."

Available data may consist of thermal expansion coefficients vs. temperature at atmospheric pressure, sound velocity at atmospheric pressure, P-V data obtained statically under isothermal conditions, and/or shock compression data. Occasionally data on expansion coefficients at elevated temperatures and pressures are available. It is further assumed here that isotherms and adiabats of well-behaved materials satisfy the condition $(\frac{\partial P}{\partial V})_{T \text{ or } S} < 0$ everywhere and $(\frac{\partial^2 P}{\partial V^2})_{T \text{ or } S} > 0$ everywhere. We shall ignore phase changes in what follows, except for a discussion of vaporization in Section V.

B. Gruneisen Equation and Specific Heat

For the calculation of wave propagation, a (P, V, E) equation of state is adequate, and we shall assume the Mie-Gruneisen form:

$$P(V, E) = P_i(V) + \frac{\Gamma}{V} [E - E_i(V)] \quad (11)$$

where $P_i(V)$ and $E_i(V)$ are pressure and internal energy on the isotherm passing through (P_0, V_0) , and $\Gamma = \Gamma(V)$ is the Gruneisen ratio $\Gamma = \alpha V / \beta C_v$, where $\alpha = \frac{1}{V} (\frac{\partial V}{\partial T})_p$ and $\beta = -\frac{1}{V} (\frac{\partial V}{\partial P})_T$. Some values of $\Gamma_0(V_0, P_0)$ and Γ_0/V_0 are shown in Table I.

For metals, where a theory of the variation of Γ with V exists,¹ it is found that $\Gamma/V = \text{constant}$ is a fair approximation to theoretical behavior. That assumption will be made here and the ratio denoted by the symbol b . Values of the specific heat are required in order that entropy be calculable, and the simplest possible assumption is also made: $C_v = C_p = \text{constant}$. This condition violates our desire for thermodynamic consistency. The ratio C_p/C_v is given by the expression

$$\frac{C_p}{C_v} = 1 + T \frac{\Gamma}{V} (\frac{\partial V}{\partial T})_p = 1 + b V \alpha T \quad (12)$$

¹Rice, McQueen, and Walsh, Solid State Physics, Vol. 6, pp 1, ff, Seitz and Turnbull, Eds., Academic Press, 1958.

From the entries in Table I it can be found that $b V_0 T$ is as large as 0.6 at 20°C, 1 atmosphere, so that the assumption $C_v = C_p$ is not a particularly good one. However, variations in C_p as well as uncertainty about its average value over an extended range of pressures and temperatures are such that this assumption is in keeping with other uncertainties in the equation of state. We thus arrive at the following equation of state:

$$P = P_i(V) + b[E - E_i(V)] \quad (13)$$

$$E - E_i(V) = C_v(T - T_0) \quad (14)$$

The amount of time required to formulate an equation of state which is much better than that represented by Eqs. (13) and (14) would be substantial, and it is thought that the increase in accuracy thereby obtained does not now warrant the additional investment. If the results of the present calculation, concerning waste heat, temperature rise, and vaporization, point to possible serious consequences in burster performance, a more careful study may be justified.

C. Evaluation of $P_i(V)$

Since we are concerned with pressures of several kilobars or more, we can set $P_0 = 0$ without affecting results, and we do so here. The data to be used in determining $P_i(V)$ are the values of b and C_v in Table I, points on the Hugoniot (R-H) curve measured by Walsh and Rice,² (cf. Table II), and values of adiabatic compressibility obtained from sound velocities at atmospheric pressure. For points

²John M. Walsh and Melvin H. Rice, J. Chem. Phys. 26, 815-823 (1957).

Table II

EXPERIMENTAL HUGONIOT CURVE DATA FOR LIQUIDS*
 (Velocities in km/sec, pressure in kilobars, V_0 in cc/g (water data, for which actual initial temperatures were 15°C to 30°C are corrected to the uniform initial state $T_0 = 20^\circ\text{C}$, $P_0 = 1$ atmosphere)).

Liquid	T_0 (°C)	V_0	U_s	U_p	P	V/V_0
Water	20	1.0018	3.354	0.952	31.8	0.716
	20	1.0018	4.093	1.392	56.8	0.660
	20	1.0018	4.126	1.411	58.2	0.658
	20	1.0018	4.536	1.655	74.9	0.635
	20	1.0018	4.813	1.829	87.8	0.620
	20	1.0018	4.777	1.806	86.1	0.622
	20	1.0018	4.757	1.798	85.3	0.622
	20	1.0018	5.626	2.385	133.9	0.576
	20	1.0018	5.604	2.370	132.5	0.577
	20	1.0018	5.601	2.335	130.5	0.583
	20	1.0018	8.07	4.13	330.0	0.488
	20	1.0018	8.07	4.24	342.0	0.476
	20	1.0018	8.45	4.60	388.0	0.456
	20	1.0018	8.49	4.72	400.0	0.444
	20	1.0018	8.59	4.72	405.0	0.450
	20	1.0018	8.74	4.81	419.0	0.450
Mercury	25	0.0739	2.752	0.608	226.4	0.779
	17	0.0739	3.101	0.772	324.0	0.751
	24	0.0739	3.504	0.978	463.7	0.721
Acetone	26	1.274	5.37	2.510	105.8	0.533
	30	1.279	3.97	1.495	46.4	0.623
Benzene	32	1.155	5.66	2.470	121.0	0.564
	16	1.133	4.10	1.448	52.4	0.647
Bromoethane	19	0.685	4.68	2.300	157.1	0.508
	16	0.682	3.40	1.353	68.0	0.599
Carbon Disulfide	33	--	4.32	2.412	129.5	0.441
	17	--	3.37	1.415	58.5	0.580
Carbon Tetrachloride	25	0.634	4.85	2.235	171.0	0.539
	22	0.629	3.51	1.325	73.9	0.622
Ethyl Ether	32	1.433	5.40	2.550	96.1	0.528
	21	1.407	3.88	1.517	41.8	0.609

Table II (Concluded)

Liquid	T _o (°C)	V _o	U _s	U _p	P	V/V _o
Ethyl Alcohol	26	1.275	5.63	2.500	110.4	0.556
	21	1.267	4.03	1.487	47.3	0.631
Glycerine	30	0.798	6.07	2.240	170.3	0.631
	18	0.794	4.58	1.328	76.6	0.710
Hexane	32	1.499	5.54	2.590	95.7	0.533
	19	1.471	4.02	1.517	41.5	0.622
Methanol	24	1.271	5.51	2.525	109.5	0.542
	15	1.255	3.95	1.483	46.6	0.625
N-amyl Alcohol	23	1.236	5.81	2.465	115.9	0.576
	19	1.227	4.26	1.466	50.9	0.656
Toluene	4	1.138	5.73	2.412	121.5	0.579
	15	1.141	4.12	1.443	52.1	0.650
Mononitro- toluene	12	0.856	5.64	2.300	151.5	0.592
	12	0.856	4.20	1.340	65.8	0.681

*This is Table I of Reference 2.

$P_H(V)$ on the R-H curve, Eq. (13) becomes

$$P_H = P_i + b (E_H - E_i) \quad (15)$$

where

$$E_H = \frac{1}{2} P_H (V_o - V) + E_o \quad (16)$$

$$E_i = E_o + \int_{V_o}^V [T_o \left(\frac{\partial P}{\partial T}\right)_v - P_i] dV \quad (17)$$

$$= E_o + b C_v T_o (V - V_o) - \int_{V_o}^V P_i dV \quad (18)$$

Elimination of E_H and E_i from Eqs. (15), (16), and (18) yields

$$P_H = P_i + \frac{b}{2} P_H (V_o - V) - b^2 C_v T_o (V - V_o) + b \int_{V_o}^V P_i dV \quad (19)$$

Differentiation of Eq. (19) yields the following differential equation for P_i in terms of P_H and its derivatives:

$$\frac{dP_i}{dV} + b P_i = \left[1 - \frac{b}{2}(V_o - V)\right] \frac{dP_H}{dV} + \frac{b}{2} P_H + b^2 C_v T_o \quad (20)$$

The required solution of Eq. (20) is

$$P_i [(V) = \exp(-bV)] \left[f(V) - b \int_{V_o}^V f(V) dV \right] + b C_v T_o \left\{ 1 - \exp[b(V_o - V)] \right\} \quad (21)$$

where

$$f(V) = \left[1 - \frac{b}{2}(V_o - V)\right] P_H \exp(bV) \quad (22)$$

The integral in Eq. (21) is readily evaluated if $f(V)$ is fitted by a polynomial in V . A suitable expression is

$$f(V) = f(Z) = AZ + A_1 Z^2 + A_2 Z^3 \quad (23)$$

where

$$Z = 1 - V/V_0 \quad (24)$$

Substitution of Eq. (23) into Eq. (21) yields the following expression for $P_i(V)$:

$$P_i(V) = \exp(-bV) (AZ + BZ^2 + CZ^3 + DZ^4) + bC_v T_0 [1 - \exp(bV_0 Z)] \quad (25)$$

where

$$\begin{aligned} B &= A_1 + bV_0 A/2 \\ C &= A_2 + bV_0 A_1/3 \\ D &= bV_0 A_2/4 \end{aligned} \quad (26)$$

Since $f(V)$ is defined along the R-H curve, its slope at atmospheric pressure corresponds to adiabatic compressibility obtained from the sound velocity c_0 . This determines the coefficient A :

$$\begin{aligned} \left(\frac{df}{dV}\right)_{V=V_0} &= \exp(bV_0) \left(\frac{dP_H}{dV}\right)_{V_0} = -\frac{c_0^2 \exp(bV_0)}{V_0^2} = -\frac{A}{V_0} \\ A &= c_0^2 \exp(bV_0) / V_0 \end{aligned} \quad (27)$$

Values of A for several liquids are entered in Table III.

Table III

R-H DATA CORRECTED TO 20°C
AND COEFFICIENTS FOR EQ. (25)

Liquid	V/V ₀	P _H (Mbar)	A	B	C	D																																																																			
			(Mbar)																																																																						
Acetone	.5330	.1051	.03036	-.2465	1.676	.4301																																																																			
	.6230	.0458					Benzene	.6470	.0527	.05336	-.2713	2.412	.7991	.5640	.1191	Carbon Tetra- chloride	.6220	.0737	.05415	-.4949	3.121	1.110	.5390	.1699	Ethyl Alcohol	.6310	.0473	.02008	-.7433	2.965	.4943	.5560	.1100	Ethyl Ether	.6090	.0418	.01510	-.4415	1.872	.3670	.5280	.0951	Glycerine	.7100	.0766	.09914	-.4080	5.088	1.010	.6310	.1703	Methanol	.6250	.0468	.01812	-.5231	2.320	.3641	.5420	.1093	Water	.7160	.0318	.02443	-.4433	2.723	.07339	.5760	.1329	Mercury	.7790	.2256	4.432
Benzene	.6470	.0527	.05336	-.2713	2.412	.7991																																																																			
	.5640	.1191					Carbon Tetra- chloride	.6220	.0737	.05415	-.4949	3.121	1.110	.5390	.1699	Ethyl Alcohol	.6310	.0473	.02008	-.7433	2.965	.4943	.5560	.1100	Ethyl Ether	.6090	.0418	.01510	-.4415	1.872	.3670	.5280	.0951	Glycerine	.7100	.0766	.09914	-.4080	5.088	1.010	.6310	.1703	Methanol	.6250	.0468	.01812	-.5231	2.320	.3641	.5420	.1093	Water	.7160	.0318	.02443	-.4433	2.723	.07339	.5760	.1329	Mercury	.7790	.2256	4.432	.3767	53.40	40.22	.7210	.4626				
Carbon Tetra- chloride	.6220	.0737	.05415	-.4949	3.121	1.110																																																																			
	.5390	.1699					Ethyl Alcohol	.6310	.0473	.02008	-.7433	2.965	.4943	.5560	.1100	Ethyl Ether	.6090	.0418	.01510	-.4415	1.872	.3670	.5280	.0951	Glycerine	.7100	.0766	.09914	-.4080	5.088	1.010	.6310	.1703	Methanol	.6250	.0468	.01812	-.5231	2.320	.3641	.5420	.1093	Water	.7160	.0318	.02443	-.4433	2.723	.07339	.5760	.1329	Mercury	.7790	.2256	4.432	.3767	53.40	40.22	.7210	.4626													
Ethyl Alcohol	.6310	.0473	.02008	-.7433	2.965	.4943																																																																			
	.5560	.1100					Ethyl Ether	.6090	.0418	.01510	-.4415	1.872	.3670	.5280	.0951	Glycerine	.7100	.0766	.09914	-.4080	5.088	1.010	.6310	.1703	Methanol	.6250	.0468	.01812	-.5231	2.320	.3641	.5420	.1093	Water	.7160	.0318	.02443	-.4433	2.723	.07339	.5760	.1329	Mercury	.7790	.2256	4.432	.3767	53.40	40.22	.7210	.4626																						
Ethyl Ether	.6090	.0418	.01510	-.4415	1.872	.3670																																																																			
	.5280	.0951					Glycerine	.7100	.0766	.09914	-.4080	5.088	1.010	.6310	.1703	Methanol	.6250	.0468	.01812	-.5231	2.320	.3641	.5420	.1093	Water	.7160	.0318	.02443	-.4433	2.723	.07339	.5760	.1329	Mercury	.7790	.2256	4.432	.3767	53.40	40.22	.7210	.4626																															
Glycerine	.7100	.0766	.09914	-.4080	5.088	1.010																																																																			
	.6310	.1703					Methanol	.6250	.0468	.01812	-.5231	2.320	.3641	.5420	.1093	Water	.7160	.0318	.02443	-.4433	2.723	.07339	.5760	.1329	Mercury	.7790	.2256	4.432	.3767	53.40	40.22	.7210	.4626																																								
Methanol	.6250	.0468	.01812	-.5231	2.320	.3641																																																																			
	.5420	.1093					Water	.7160	.0318	.02443	-.4433	2.723	.07339	.5760	.1329	Mercury	.7790	.2256	4.432	.3767	53.40	40.22	.7210	.4626																																																	
Water	.7160	.0318	.02443	-.4433	2.723	.07339																																																																			
	.5760	.1329					Mercury	.7790	.2256	4.432	.3767	53.40	40.22	.7210	.4626																																																										
Mercury	.7790	.2256	4.432	.3767	53.40	40.22																																																																			
	.7210	.4626																																																																							

Except for mercury and water, there are but two points on the R-H curve for each liquid. These just suffice to determine the coefficients A_1 and A_2 of Eq. (23). Before this is done, the data should be corrected to a common initial temperature, since the actual temperatures vary significantly from shot to shot. This can be accomplished by finding the derivative of

$$P_H(V, V_o) = P_i(V, V_{or}) + \frac{b}{2} P_H(V_o - V) + bE_o(T_o) - bE_i(V, V_{or}) . \quad (28)$$

Here the isotherm is supposed to be a fixed curve passing through the reference volume V_{or} on which $T = T_{or}$. Then only P_H , E_o , and V_o are functions of T_o . Differentiating Eq. (28) gives the expression:

$$\left(\frac{\partial P_H}{\partial T_o}\right)_v \left[1 - \frac{b}{2}(V_o - V)\right] = \frac{bP_H}{2} \frac{dV_o}{dT_o} + b \frac{dE_o}{dT_o} = \frac{bP_H}{2} \alpha_o V_o + bC_p . \quad (29)$$

Then the required correction to P_H , in order to refer it to T_{or} , is

$$\Delta P_H = \left(\frac{\partial P_H}{\partial T_o}\right)_v (T_{or} - T_o) = \frac{b}{2} \frac{P_H \alpha_o V_o + 2C_p}{1 - \frac{b}{2}(V_o - V)} (T_{or} - T_o) . \quad (30)$$

$P_i(V, T_{or})$ was calculated for the liquids listed in Table III. Two points each were selected for water and mercury and they were treated as the others. Water was chosen because very good equations of state exist for it, and it appeared worthwhile to compare the simple equation developed here with a more elaborate equation of state developed at U.S. Naval Ordnance Laboratory. Mercury was included for comparison with other metals. Values of P_H corrected to 20°C are given in Table III.

Coefficients A_1 and A_2 of Eq. (23) can now be determined by substituting values of P_H and V/V_o from Table III into Eq. (23) and solving the resulting algebraic equations for A_1 and A_2 . These, in turn, substituted into Eqs. (26), yield the values of B, C, and D entered in Table III.

Equations (13) and (14), the data entered in Table II, Eq. (25), and the coefficients in Table III represent the required equation of state for the liquids listed in Table III.

III COMPUTED ISOTHERMAL AND HUGONIOT CURVES

Values of pressure (P_i) and energy (E_i) on the 293°K isotherm and values of pressure (P_H), energy (E_H), temperature (T_H), and entropy ($S_H - S_O$) on the R-H curve passing through $P = 0$, $T = 293^\circ\text{K}$ have been computed from Eqs. (13), (14), and (25) with the aid of the Burroughs 5500 computer. Values of these quantities as functions of specific volume are entered in Table IV for the materials listed in Table III.

Negative values of P_H , E_H , $S_H - S_O$, and P_i in Table IV are physically meaningless; they are a consequence of fitting $f(V)$ in Eq. (23) with a cubic in V . Essentially the same result would have been obtained if P_H had been fit by a cubic. The inflection point occurs between the zero-pressure point and the first shock point, and, in this region, Eq. (25) is not a good representation of the isotherm. This misrepresentation will produce some error in energy, entropy, and temperature parameters calculated at higher pressures, but, except for ethyl alcohol and ethyl ether, the error is not apt to be serious.

Negative values of E_i in Table IV may be incorrect in magnitude, but they have the right sign. This follows from Eq. (18), which is differentiated to yield the equation

$$dE_i = (-dV)(P_i - bC_vT_o)$$

Here $(-dV) > 0$, and until P_i exceeds bC_vT_o , dE_i remains negative.

On comparing P_H for water with the Walsh and Rice Hugoniot points (Table II), it is apparent that between 31 and 130 kbars the computed values of P_H are too high but do not differ from the measured

points by more than 10%. Comparison of calculated entropies and temperatures with those given by Rice and Walsh³ shows the temperature increases to be half the Rice and Walsh values, while the entropy increases are about half again as great. These differences are principally due to the high value of specific heat used here compared to that used by Walsh and Rice (1 cal/g deg compared to 0.86 at 25 kbar) and the variation in $C_p/(\partial V/\partial T)_p$ allowed.

*M. H. Rice and John M. Walsh, J. Chem. Phys. 26, 824-830 (1957).

Table IV
 HUGONIOT AND ISOTHERMAL PARAMETERS
 FOR THE MATERIALS OF TABLE III

V/V_0	V (cc/g)	P_H (Mbar)	E_H (Mbar cc/g)	T_H (°K)	$S_H - S_0$ (Mbar cc/g °C)	$P_i(v)$ (Mbar)	$E_i(v)$ (Mbar cc/g)
Acetone							
1.000	1.2660	.0000	$.00 \times 10^{-3}$	293.0	$.00 \times 10^{-6}$.0000	0.00×10^{-3}
.950	1.2027	.0004	$.01 \times 10^{-3}$	307.6	$.00 \times 10^{-6}$.0002	$-.31 \times 10^{-3}$
.900	1.1394	.0010	$.06 \times 10^{-3}$	323.2	$.01 \times 10^{-6}$.0004	$-.61 \times 10^{-3}$
.85	1.0761	.0022	$.21 \times 10^{-3}$	341.8	$.17 \times 10^{-6}$.0013	$-.87 \times 10^{-3}$
.80	1.0128	.0049	$.62 \times 10^{-3}$	368.3	$.74 \times 10^{-6}$.0036	-1.04×10^{-3}
.75	.9495	.0103	1.63×10^{-3}	411.6	2.12×10^{-6}	.0083	-1.00×10^{-3}
.70	.8862	.0196	3.72×10^{-3}	486.5	4.73×10^{-6}	.0163	$-.56 \times 10^{-3}$
.65	.8229	.0346	7.66×10^{-3}	615.5	8.85×10^{-6}	.0291	$+.53 \times 10^{-3}$
.60	.7596	.0574	14.54×10^{-3}	832.0	14.43×10^{-6}	.0482	2.63×10^{-3}
.55	.6963	.0908	25.86×10^{-3}	1183.3	21.13×10^{-6}	.0756	6.18×10^{-3}
.505	.63933	.1326	41.53×10^{-3}	1669.1	27.76×10^{-6}	.1091	11.11×10^{-3}
Benzene							
1.000	1.1390	.0000	$.00 \times 10^{-3}$	293.0	$.00 \times 10^{-6}$.0000	0.00×10^{-3}
.950	1.08205	.0007	$.02 \times 10^{-3}$	312.0	$.00 \times 10^{-6}$.0003	-0.31×10^{-3}
.900	1.0251	.0017	$.09 \times 10^{-3}$	332.9	$.03 \times 10^{-6}$.0009	-0.58×10^{-3}
.850	.96815	.0037	$.31 \times 10^{-3}$	359.1	$.25 \times 10^{-6}$.0024	$-.81 \times 10^{-3}$
.800	.9112	.0079	$.89 \times 10^{-3}$	398.4	$.94 \times 10^{-6}$.0059	$-.90 \times 10^{-3}$
.750	.85425	.0157	2.23×10^{-3}	466.0	2.54×10^{-6}	.0124	$-.71 \times 10^{-3}$
.700	.7973	.0292	4.99×10^{-3}	587.5	5.41×10^{-6}	.0237	$-.02 \times 10^{-3}$
.650	.74035	.0511	10.18×10^{-3}	804.4	9.68×10^{-6}	.0415	-1.49×10^{-3}
.600	.6834	.0848	19.33×10^{-3}	1180.6	5.12×10^{-6}	.0682	4.25×10^{-3}
.550	.62645	.1352	34.66×10^{-3}	1811.9	21.33×10^{-6}	.1067	8.85×10^{-3}
.500	.5695	.2082	59.33×10^{-3}	2839.1	27.89×10^{-6}	.1605	16.07×10^{-3}

Table IV (Continued)

V/V_0	V (cc/g)	P_H (Mbar)	E_H (Mbar cc/g)	T_H (°K)	$S_H - S_0$ (Mbar cc/g °C)	$P_i(v)$ (Mbar)	$E_i(v)$ (Mbar cc/g)
Carbon Tetrachloride							
1.0000	.6260	.0000	.00 x 10 ⁻³	293.0	.00 x 10 ⁻⁶	.0000	.00 x 10 ⁻³
.95	.5947	.0005	.01 x 10 ⁻³	313.0	.00 x 10 ⁻⁶	.0002	.16 x 10 ⁻³
.90	.5634	.0011	.04 x 10 ⁻³	334.6	.00 x 10 ⁻⁶	.0004	.31 x 10 ⁻³
.85	.5321	.0027	.13 x 10 ⁻³	361.9	.11 x 10 ⁻⁶	.0015	.45 x 10 ⁻³
.80	.5008	.0066	.41 x 10 ⁻³	404.6	.49 x 10 ⁻⁶	.0046	.53 x 10 ⁻³
.75	.4695	.0146	1.14 x 10 ⁻³	482.5	1.41 x 10 ⁻⁶	.0112	.45 x 10 ⁻³
.70	.4382	.0292	2.74 x 10 ⁻³	630.3	3.10 x 10 ⁻⁶	.0232	.10 x 10 ⁻³
.65	.4069	.0538	5.90 x 10 ⁻³	904.8	5.59 x 10 ⁻⁶	.0430	.75 x 10 ⁻³
.60	.3756	.0931	11.66 x 10 ⁻³	1396.1	8.68 x 10 ⁻⁶	.0735	2.38 x 10 ⁻³
.55	.3443	.1531	21.57 x 10 ⁻³	2241.2	12.11 x 10 ⁻⁶	.1185	5.18 x 10 ⁻³
.50	.3130	.2420	37.87 x 10 ⁻³	3645.5	15.64 x 10 ⁻⁶	.1824	9.67 x 10 ⁻³
Ethyl Alcohol							
1.00	1.2660	.0000	.00 x 10 ⁻³	293.0	.00 x 10 ⁻⁶	.0000	.00 x 10 ⁻³
.95	1.2027	-.0003	-.01 x 10 ⁻³	302.1	-.03 x 10 ⁻⁶	-.0004	-.23 x 10 ⁻³
.90	1.1394	-.0014	-.09 x 10 ⁻³	310.6	-.12 x 10 ⁻⁶	-.0016	-.51 x 10 ⁻³
.85	1.0761	-.0020	-.19 x 10 ⁻³	321.0	-.09 x 10 ⁻⁶	-.0024	-.86 x 10 ⁻³
.80	1.0128	-.0006	-.08 x 10 ⁻³	340.3	+.55 x 10 ⁻⁶	-.0012	-1.21 x 10 ⁻³
.75	.9495	+.0047	+.74 x 10 ⁻³	381.9	2.55 x 10 ⁻⁶	+.0036	-1.38 x 10 ⁻³
.70	.8862	.0162	3.08 x 10 ⁻³	466.9	6.59 x 10 ⁻⁶	.0142	-1.07 x 10 ⁻³
.65	.8229	.0366	8.11 x 10 ⁻³	626.5	12.86 x 10 ⁻⁶	.0326	+.14 x 10 ⁻³
.60	.7596	.0689	17.44 x 10 ⁻³	904.4	20.88 x 10 ⁻⁶	.0616	2.83 x 10 ⁻³
.55	.6963	.1167	33.25 x 10 ⁻³	1359.5	29.86 x 10 ⁻⁶	.1040	7.78 x 10 ⁻³
.505	.63933	.1766	55.33 x 10 ⁻³	1984.5	38.21 x 10 ⁻⁶	.1564	14.92 x 10 ⁻³

Table IV (Continued)

V/V ₀	V (cc/g)	P _H (Mbar)	E _H (Mbar cc/g)	T _H (°K)	S _H - S ₀ (Mbar cc/g °C)	P _i (v) (Mbar)	E _i (v) (Mbar cc/g)
Ethyl Ether							
1.00	1.405	.0000	.00 x 10 ⁻³	293.0	.00 x 10 ⁻⁶	.0000	.00 x 10 ⁻³
.95	1.33475	-.0001	.02 x 10 ⁻³	303.9	-.01 x 10 ⁻⁶	-.0002	-.25 x 10 ⁻³
.90	1.2645	-.0005	.04 x 10 ⁻³	314.7	-.06 x 10 ⁻⁶	-.0008	-.53 x 10 ⁻³
.85	1.19425	-.0006	.06 x 10 ⁻³	327.2	-.01 x 10 ⁻⁶	-.0010	-.84 x 10 ⁻³
.80	1.124	+.0006	.08 x 10 ⁻³	346.8	+.46 x 10 ⁻⁶	-.0000	-1.13 x 10 ⁻³
.75	1.05375	.0043	.76 x 10 ⁻³	383.1	1.88 x 10 ⁻⁶	+.0032	-1.28 x 10 ⁻³
.70	.9835	.0119	2.52 x 10 ⁻³	452.2	4.80 x 10 ⁻⁶	.0100	-1.09 x 10 ⁻³
.65	.91325	.0252	6.12 x 10 ⁻³	577.8	9.51 x 10 ⁻⁶	.0218	-.25 x 10 ⁻³
.60	.8430	.0462	12.98 x 10 ⁻³	794.0	15.87 x 10 ⁻⁶	.0402	+1.64 x 10 ⁻³
.55	.77275	.0774	24.46 x 10 ⁻³	1147.7	23.37 x 10 ⁻⁶	.0672	5.11 x 10 ⁻³
.50	.7025	.1217	42.74 x 10 ⁻³	1702.0	31.45 x 10 ⁻⁶	.1049	10.84 x 10 ⁻³
Glycerine							
1.00	.7950	.0000	.00 x 10 ⁻³	293.0	.00 x 10 ⁻⁶	.0000	.00 x 10 ⁻³
.95	.75525	.0022	.04 x 10 ⁻³	304.6	.00 x 10 ⁻⁶	.0019	-.23 x 10 ⁻³
.90	.7155	.0055	.22 x 10 ⁻³	318.0	.10 x 10 ⁻⁶	.0049	-.37 x 10 ⁻³
.85	.67575	.0123	.73 x 10 ⁻³	338.1	.63 x 10 ⁻⁶	.0112	-.33 x 10 ⁻³
.80	.6360	.0254	2.02 x 10 ⁻³	375.8	2.21 x 10 ⁻⁶	.0235	+.07 x 10 ⁻³
.75	.59625	.0484	4.81 x 10 ⁻³	449.3	5.51 x 10 ⁻⁶	.0448	1.12 x 10 ⁻³
.70	.5565	.0855	10.19 x 10 ⁻³	586.9	10.90 x 10 ⁻⁶	.0787	3.26 x 10 ⁻³
.65	.51675	.1419	19.74 x 10 ⁻³	830.2	18.16 x 10 ⁻⁶	.1295	7.06 x 10 ⁻³
.60	.4770	.2238	35.59 x 10 ⁻³	1237.2	26.66 x 10 ⁻⁶	.2020	13.30 x 10 ⁻³
.55	.43725	.3386	60.57 x 10 ⁻³	1887.3	35.71 x 10 ⁻⁶	.3019	22.95 x 10 ⁻³
.50	.3975	.4952	98.42 x 10 ⁻³	2886.7	44.82 x 10 ⁻⁶	.4354	37.21 x 10 ⁻³

Table IV (Continued)

V/V ₀	V (cc/g)	P _H (Mbar)	E _H (Mbar cc/g)	T _H (°K)	S _H - S ₀ (Mbar cc/g °C)	P _{i(v)} (Mbar)	E _{i(v)} (Mbar cc/g)
Methanol							
1.00	1.2640	.0000	.00 x 10 ⁻³	293.0	.00 x 10 ⁻⁶	.0000	.00 x 10 ⁻³
.95	1.2008	-.0001	-.00 x 10 ⁻³	301.7	-.02 x 10 ⁻⁶	-.0002	-.22 x 10 ⁻³
.90	1.1376	-.0006	-.04 x 10 ⁻³	310.3	-.07 x 10 ⁻⁶	-.0008	-.47 x 10 ⁻³
.85	1.0744	-.0006	-.06 x 10 ⁻³	320.8	+.02 x 10 ⁻⁶	-.0010	-.76 x 10 ⁻³
.80	1.0112	+.0012	+.16 x 10 ⁻³	339.0	.65 x 10 ⁻⁶	+.0007	-1.00 x 10 ⁻³
.75	.9480	.0065	1.02 x 10 ⁻³	375.3	2.45 x 10 ⁻⁶	.0055	-1.04 x 10 ⁻³
.70	.8848	.0169	3.20 x 10 ⁻³	446.1	6.03 x 10 ⁻⁶	.0150	-.65 x 10 ⁻³
.65	.8216	.0345	7.63 x 10 ⁻³	574.8	11.64 x 10 ⁻⁶	.0311	+.55 x 10 ⁻³
.60	.7584	.0618	15.62 x 10 ⁻³	794.3	19.01 x 10 ⁻⁶	.0558	3.03 x 10 ⁻³
.55	.6952	.1015	28.88 x 10 ⁻³	1148.5	27.52 x 10 ⁻⁶	.0913	7.39 x 10 ⁻³
.505	.63832	.1506	47.13 x 10 ⁻³	1629.5	35.62 x 10 ⁻⁶	.1347	13.57 x 10 ⁻³
Water							
1.00	1.0018	.0000	.00 x 10 ⁻³	293.0	.00 x 10 ⁻⁶	.0000	.00 x 10 ⁻³
.95	.95171	.0004	.01 x 10 ⁻³	294.5	-.02 x 10 ⁻⁶	.0004	-.05 x 10 ⁻³
.90	.90162	.0007	.03 x 10 ⁻³	296.0	-.02 x 10 ⁻⁶	.0007	-.09 x 10 ⁻³
.85	.85153	.0027	.20 x 10 ⁻³	299.9	+.30 x 10 ⁻⁶	.0026	-.09 x 10 ⁻³
.80	.80144	.0084	.84 x 10 ⁻³	310.6	1.54 x 10 ⁻⁶	.0083	+.10 x 10 ⁻³
.75	.75135	.0197	2.47 x 10 ⁻³	335.3	4.51 x 10 ⁻⁶	.0196	.71 x 10 ⁻³
.70	.70126	.0389	5.85 x 10 ⁻³	383.6	9.92 x 10 ⁻⁶	.0385	2.06 x 10 ⁻³
.65	.65117	.0680	11.92 x 10 ⁻³	468.2	18.02 x 10 ⁻⁶	.0672	4.59 x 10 ⁻³
.60	.60108	.1092	21.87 x 10 ⁻³	604.4	28.47 x 10 ⁻⁶	.1078	8.86 x 10 ⁻³
.55	.55099	.1647	37.13 x 10 ⁻³	810.8	40.52 x 10 ⁻⁶	.1624	15.50 x 10 ⁻³
.505	.505909	.2290	56.78 x 10 ⁻³	1074.3	52.08 x 10 ⁻⁶	.2255	24.13 x 10 ⁻³

Table IV (Concluded)

V/V_0	V (cc/g)	P_H (Mbar)	E_H (Mbar cc/g)	T_H (°K)	$S_H - S_0$ (Mbar cc/g °C)	$P_i(v)$ (Mbar)	$E_i(v)$ (Mbar cc/g)
Mercury							
1.00	.0739	.0000	.00 x 10 ⁻³	293.0	.00 x 10 ⁻⁶	.0000	.00 x 10 ⁻³
.95	.070205	.0170	.03 x 10 ⁻³	337.5	.01 x 10 ⁻⁶	.0147	-.03 x 10 ⁻³
.90	.06651	.0436	.16 x 10 ⁻³	403.7	.06 x 10 ⁻⁶	.0379	+.01 x 10 ⁻³
.85	.062815	.0897	.50 x 10 ⁻³	537.4	.27 x 10 ⁻⁶	.0771	.16 x 10 ⁻³
.80	.05912	.1729	1.28 x 10 ⁻³	852.8	.72 x 10 ⁻⁶	.1439	.50 x 10 ⁻³
.75	.055425	.3240	2.99 x 10 ⁻³	1607.1	1.41 x 10 ⁻⁶	.2561	1.16 x 10 ⁻³
.70	.05173	.5970	6.62 x 10 ⁻³	3349.1	2.24 x 10 ⁻⁶	.4391	2.37 x 10 ⁻³
.65	.048035	1.0876	14.07 x 10 ⁻³	7220.1	3.12 x 10 ⁻⁶	.7298	4.43 x 10 ⁻³
.60	.04434	1.9696	29.11 x 10 ⁻³	15581.3	4.00 x 10 ⁻⁶	1.1797	7.84 x 10 ⁻³
.55	.040645	3.5713	59.38 x 10 ⁻³	33406.1	4.87 x 10 ⁻⁶	1.8606	13.32 x 10 ⁻³
.505	.037319	6.1637	112.74 x 10 ⁻³	66347.2	5.65 x 10 ⁻⁶	2.7513	20.86 x 10 ⁻³

IV WASTE HEAT CALCULATION

The flow produced in an unbounded liquid surrounding a spherical explosive charge has been calculated numerically by direct integration of the flow equations, using a Richtmyer-von Neumann artificial viscosity to integrate through the shock front. An abbreviated flow chart showing the principal steps in the computation is given in Fig. 2. Some details of the computation are discussed in the following paragraphs. The code used in the calculation was developed by John Erkman of Poulter Laboratories.

A. Geometry

The radius of the explosive charge was taken to be 1.6 cm. Detonation was initiated at the center. The outer radius of the liquid spherical shell was taken to be 4.0 cm. The computation was stopped before the wave front reached this outer boundary, so the liquid was in effect boundless.

B. Explosive Properties

Initial density, energy of explosion, and detonation velocity were taken to be, respectively, 1.59 g/cc, 0.05136 Mbar cc/g, and 0.8163 cm/ μ sec; explosive gases were assumed to be polytropic with $\gamma = 2.736$. This loading corresponds approximately to a low-density RDX loading; it represents a total energy of 33,500 calories, compared to 32,300 for Composition B. The difference is small and in the direction to be expected when C-3 replaces Composition B.

C. Equation of State

The form of the equation of state and the parameters were discussed in Sections II and III. The computations were performed for water and for glycerine. The flow chart for the subprogram which calculates E and P is shown in Fig. 3.

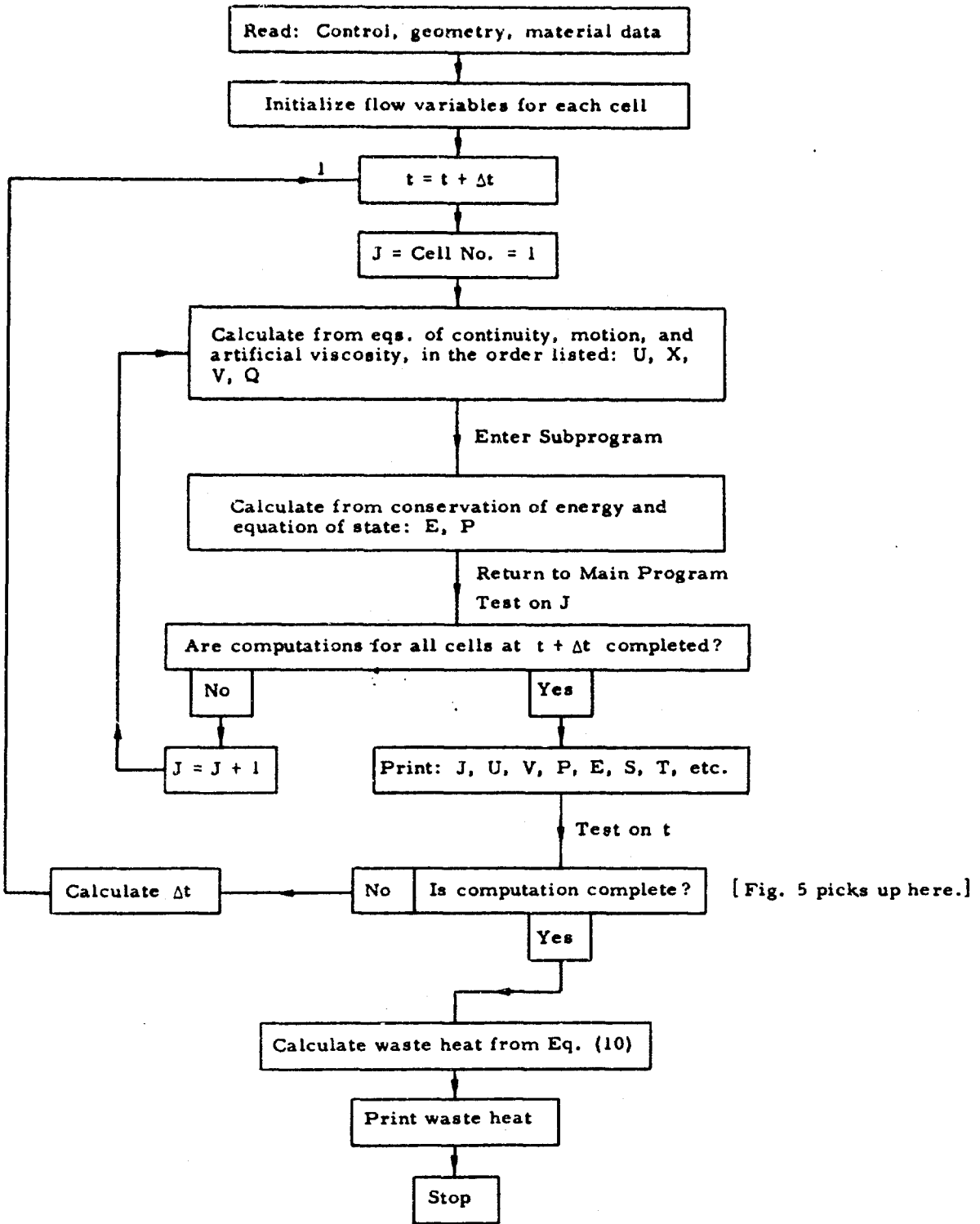


FIG. 2 FLOW CHART FOR WASTE HEAT CALCULATION

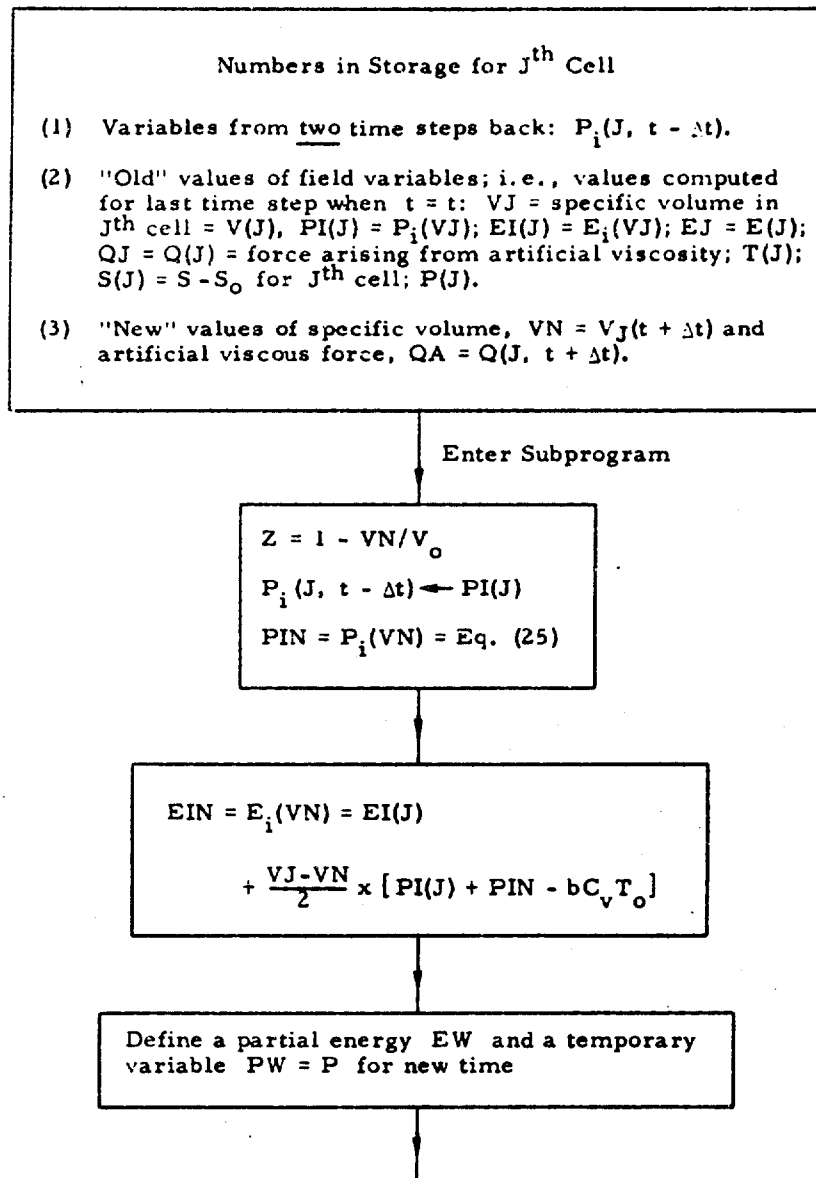


FIG. 3 FLOW CHART FOR SUBPROGRAM WHICH CALCULATES P, E AND OTHER EQUATION OF STATE PARAMETERS (see Fig. 2)

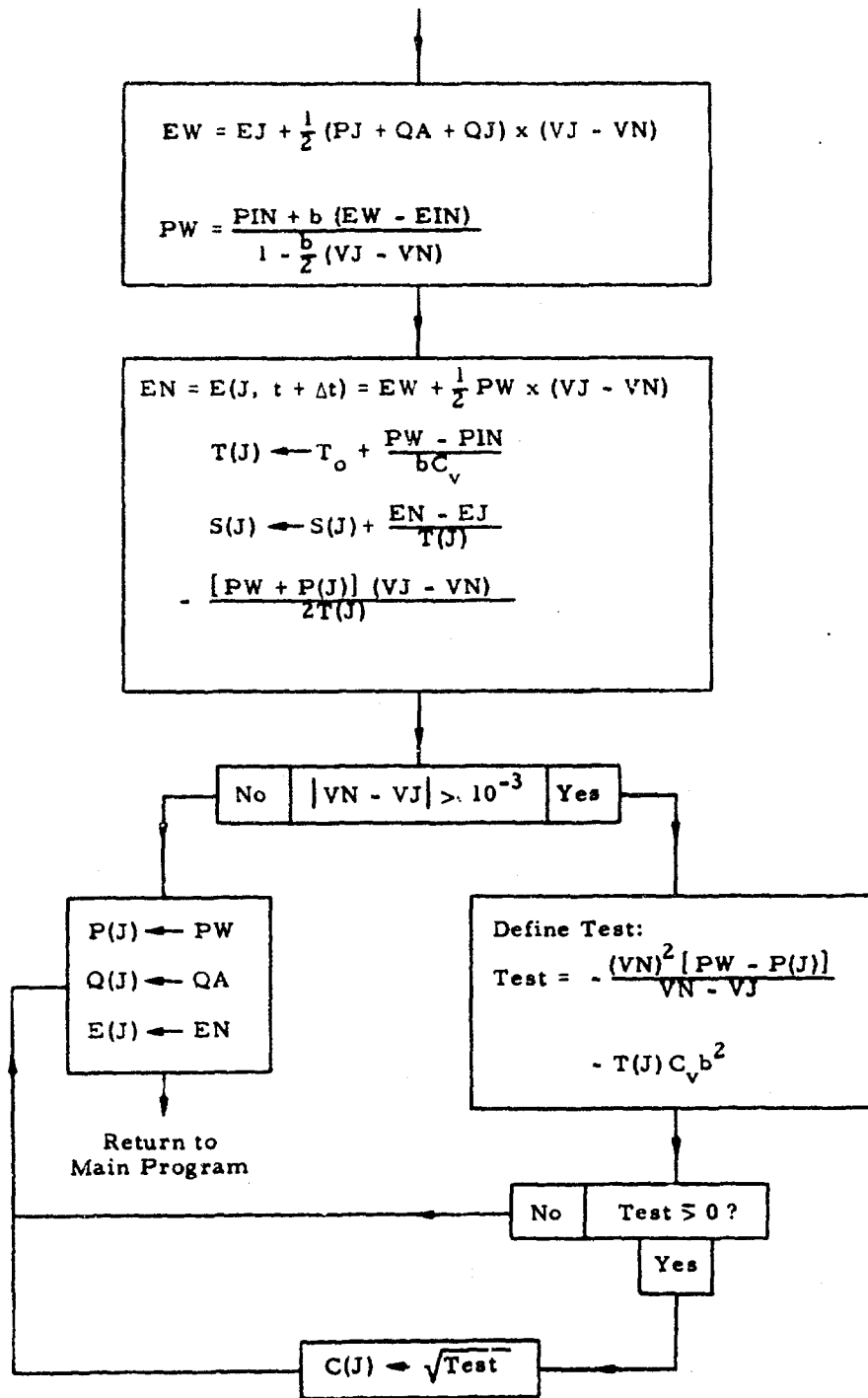


FIG. 3 Concluded

In order to check the sensitivity of the calculation to the assumptions made in the equation of state, a second calculation was made for water, using the NOL equation of state as programmed by John O. Erkman. It is believed to be an accurate P-V-E equation of state and was given to SRI by H. Sternberg of the U.S. Naval Ordnance Laboratory in Silver Spring. This equation was supplemented with specific heat and thermal expansion coefficients taken from Rice and Walsh.³ It probably comes close to being the best equation of state for water that can be constructed with presently available information. The computing procedure is quite long, but it is reproduced in Fig. 4 for reference.

D. Waste Heat

This calculation is made in the main program after the shock front has advanced to a radius equal to the outer radius of the liquid fill: 3.85 cm in the present case. At this time the shock calculation is stopped, the waste heat is calculated for each cell and summed for all cells. The flow chart for the calculation is shown in Fig. 5.

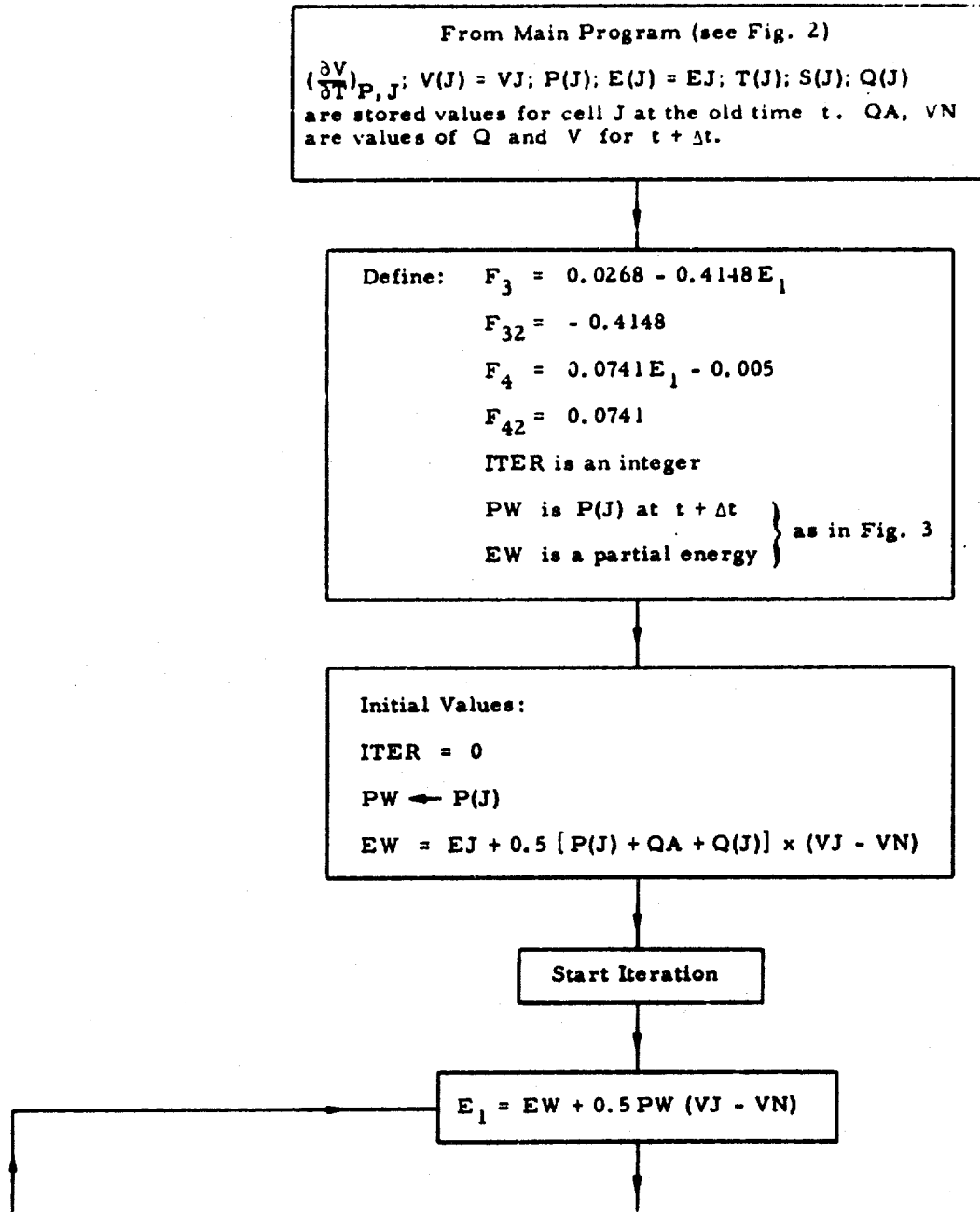


FIG. 4 COMPUTATION OF E, P, T, S, USING NOL EQUATION OF STATE OF WATER AND VALUES OF $(\partial V/\partial T)_P$, C_p FROM RICE AND WALSH (ibid.)

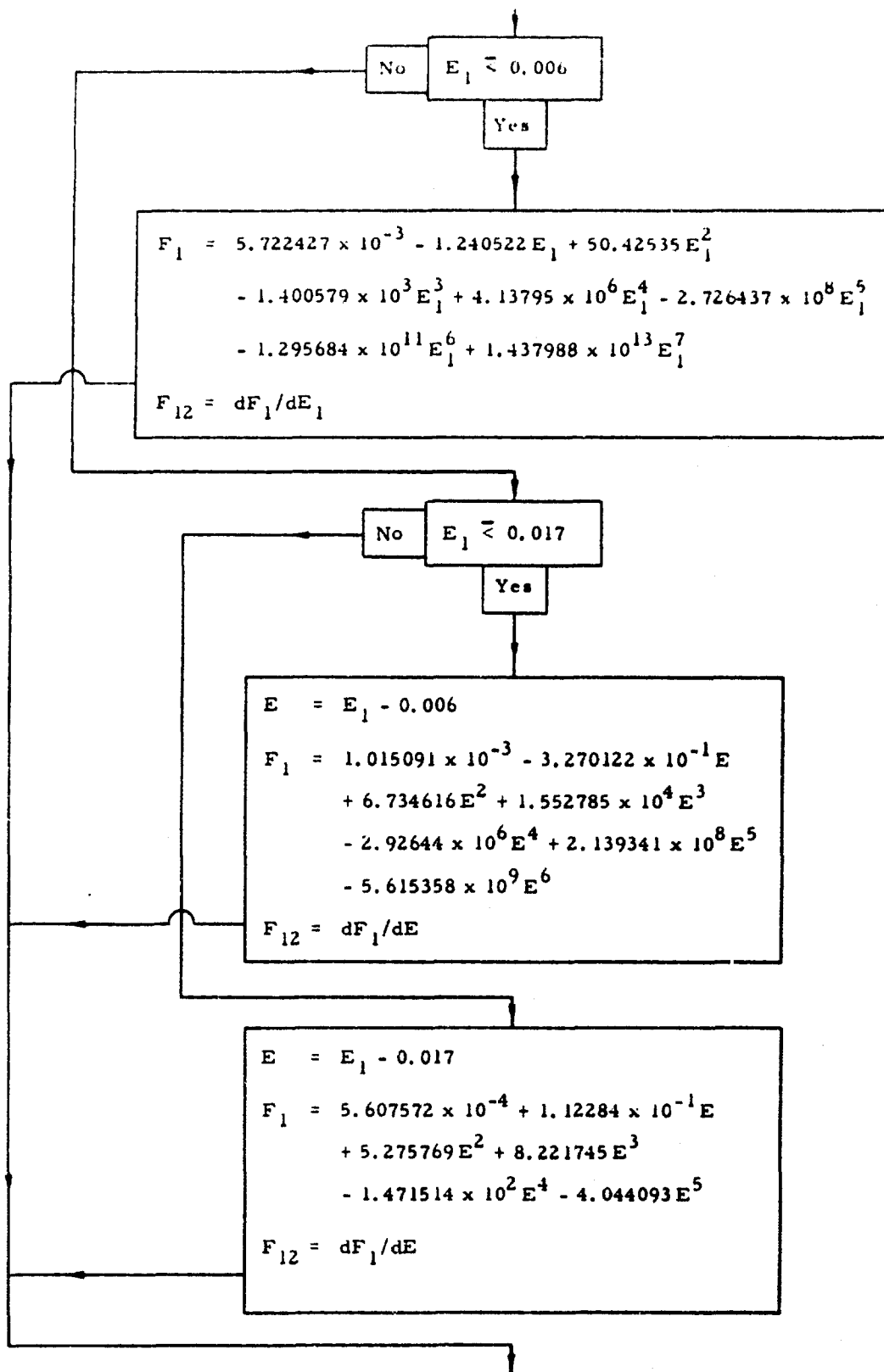


FIG. 4 Continued

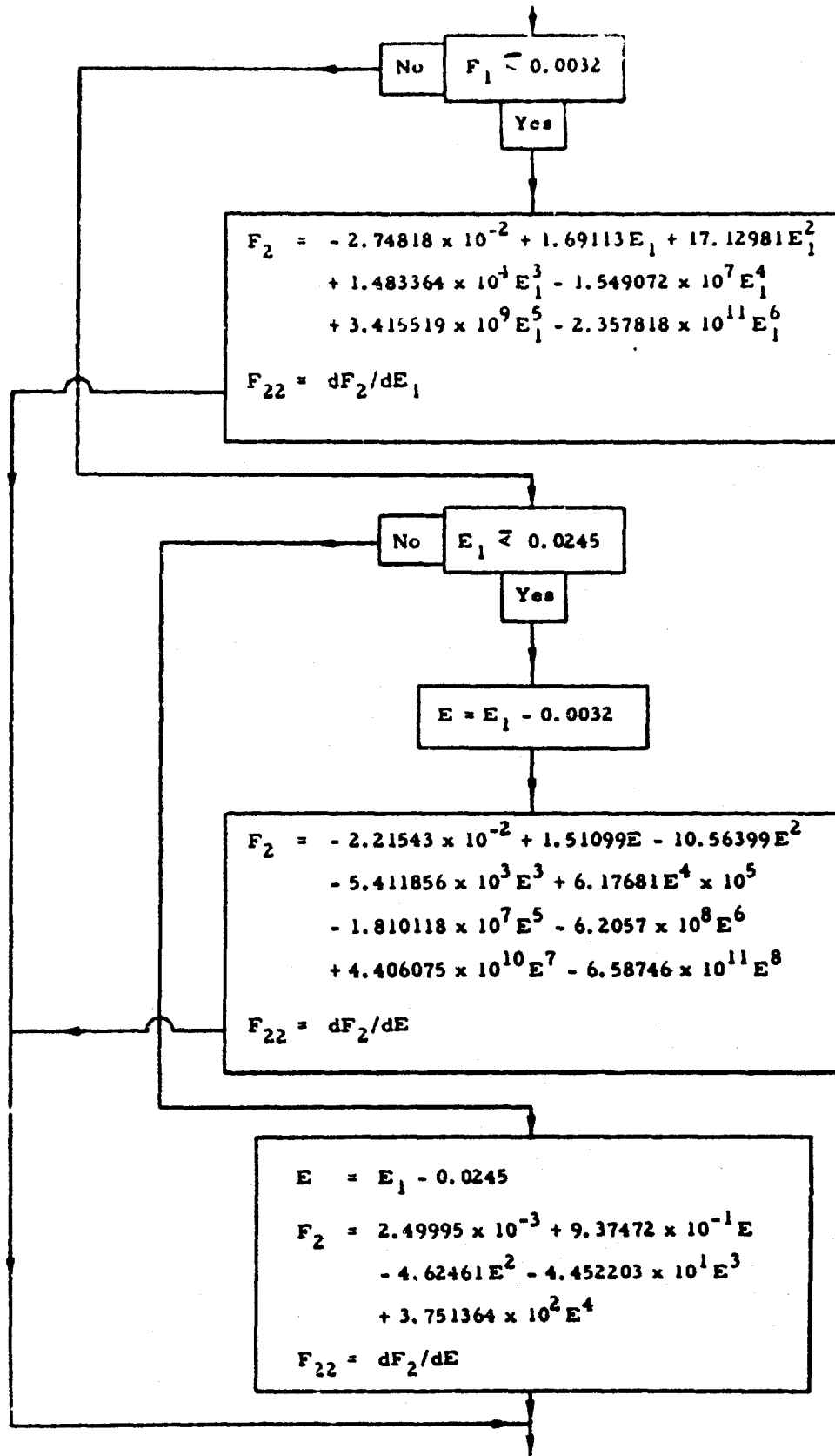


FIG. 4 Continued

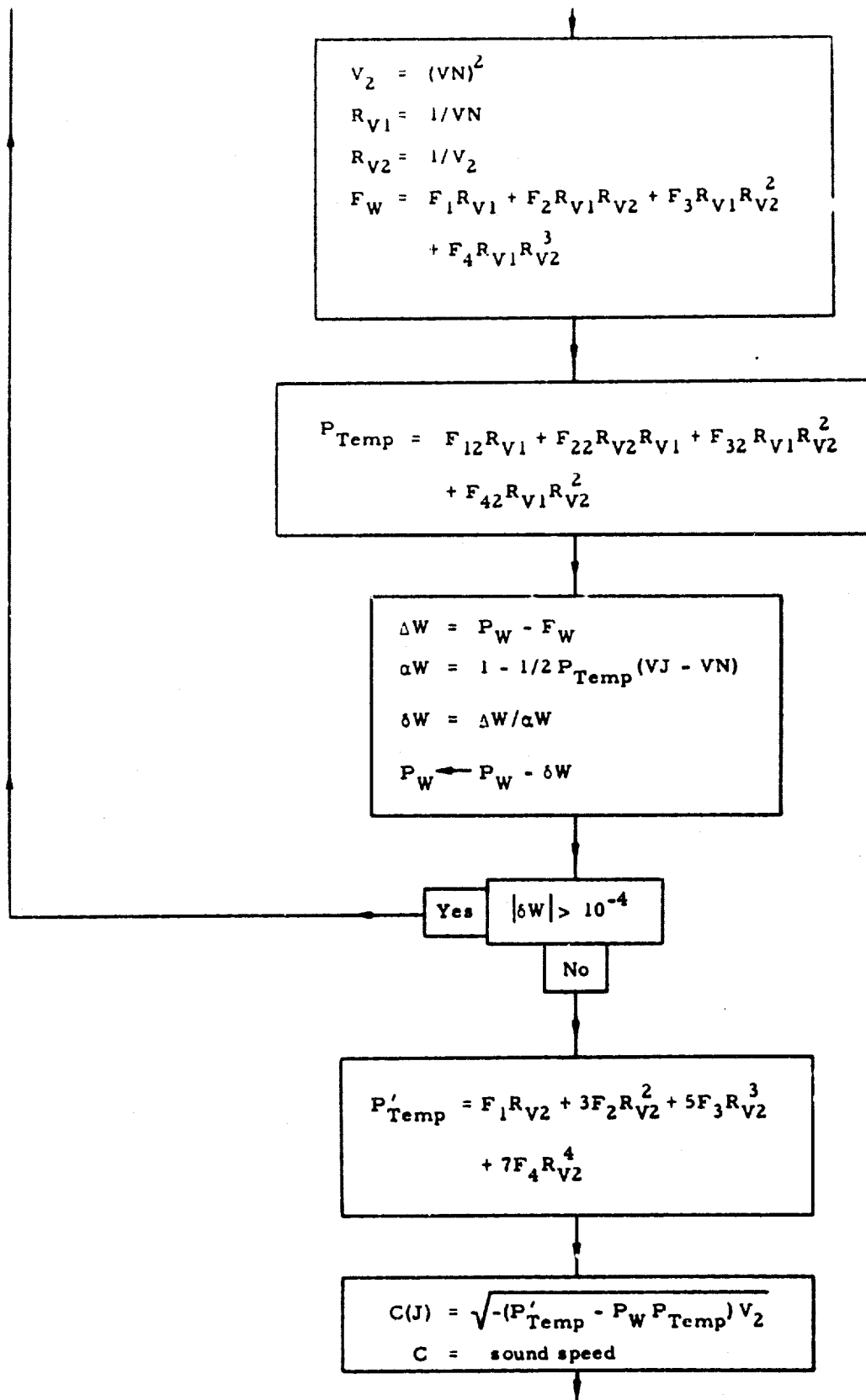


FIG. 4 Continued

$$EA = E_1$$

$$E_N = E(J) + 1/2 [P(J) + Q(J) + P_W + QA] (VJ - VN)$$

Where E_N = new value of $E(J)$.

$$\left(\frac{\partial V}{\partial T}\right)_{P,N} = \text{New value of } \left(\frac{\partial V}{\partial T}\right)_P \text{ for cell J}$$

$$= [1 - 7.4567 (P_W - 0.125) + 26.71 (P_W - 0.125)^2] \times 10^{-4}$$

$$\xi(P) = e^{2.3026 (-0.82057 + 3.0338 P_W)}$$

$$C_P = \xi(P) \left(\frac{\partial V}{\partial T}\right)_{P,N}$$

The new temp, T_N , is calculated from the equation:

$C_P dT = dH - VdP + T \left(\frac{\partial V}{\partial T}\right)_P dP$, which goes into the difference equation:

$$C_P (T_N - T_J) = 1/2 (QA + QJ) (VN - VJ) + 1/2 (T_N + T_J) \left[\left(\frac{\partial V}{\partial T}\right)_{P,N} + \left(\frac{\partial V}{\partial T}\right)_{P,J} \right] \times \frac{(P_W - P_J)}{2}$$

where $T_J = T(J)$, $P_J = P(J)$, etc. This yields

$$T_N = \left\{ C_P T_J + 1/2 (QA + QJ) (VJ - VN) + 1/4 T_J \left[\left(\frac{\partial V}{\partial T}\right)_{P,N} + \left(\frac{\partial V}{\partial T}\right)_{P,J} \right] (P_W - P_J) \right\} / C_P - 1/4 \left[\left(\frac{\partial V}{\partial T}\right)_{P,N} + \left(\frac{\partial V}{\partial T}\right)_{P,J} \right] (P_W - P_J)$$

$$S_N = \frac{S(J) + \left[E_N - E(J) - \frac{(P_W + P_J)}{2} (VJ - VN) \right]}{T_N}$$

$$P(J) \leftarrow P_W, Q(J) \leftarrow QA, \left(\frac{\partial V}{\partial T}\right)_{P,J} \leftarrow \left(\frac{\partial V}{\partial T}\right)_{P,N}$$

Return to Main Program

FIG. 4 Concluded

JSTAR is the number of a cell just ahead of the shock. Cell No. 160 lies at radius 4.0 cm. $M(J)$ is mass of J^{th} cell in grams, $WH(J)$ = waste heat per unit mass in J^{th} cell, $W(J)$ = total waste heat in all cells up to and including J . $S(J)$ = increase in entropy of J^{th} cell beyond initial value S_0 .

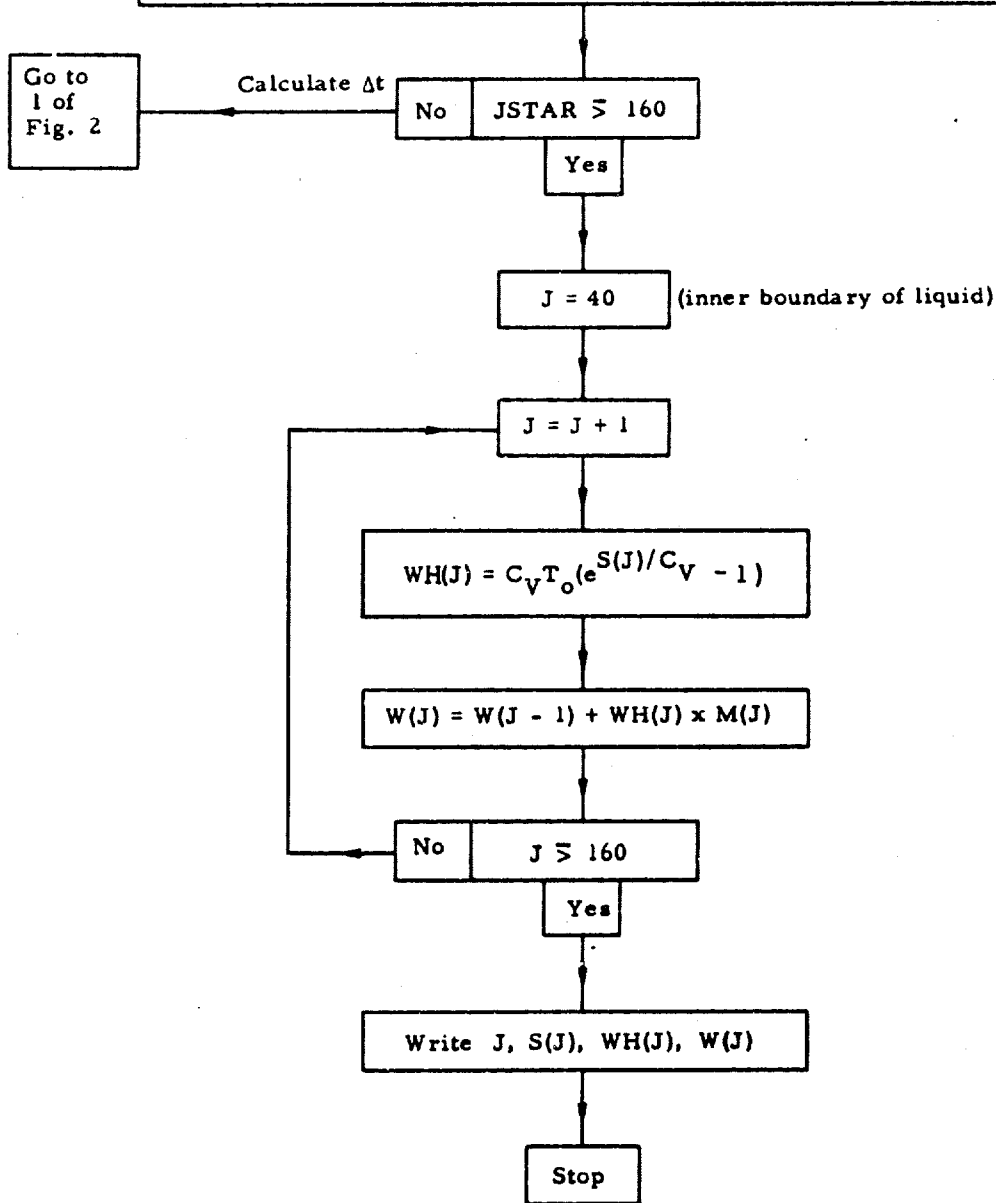


FIG. 5 FLOW CHART FOR CALCULATION OF WASTE HEAT

V NUMERICAL RESULTS

Values of $S - S_o$, W_H , and W are given in Tables V, VI, and VII for simple water, NOL water, and simple glycerine. "Simple" means with constant b and C_v as in Section II; "NOL water" means that the equation of state of Fig. 4 has been used. J is the number assigned to each cell, which consists of a spherical shell 0.02 cm thick. The initial inner radius of the J^{th} cell is

$$r_J = 1.6 + 0.02 (J - 41) \text{ cm} .$$

The mass contained in the J^{th} cell is

$$M_J = \frac{4}{3} \pi \frac{(r_J + 1)^3 - r_J^3}{1.0018} \approx \frac{4\pi r_J^2 \times 0.02}{1.0018} \text{ grams}$$

The mass of water contained within and including the J^{th} cell is

$$M_J = \frac{4\pi}{3.0054} \left\{ [1.6 + 0.02(J - 40)]^3 - (1.6)^3 \right\} \quad (31)$$

The outer boundary surface of the liquid considered in this example is at $r = 3.85$ cm, which corresponds approximately to the inner boundary of the 153rd cell. Then the fraction of total water mass contained within and including the J^{th} cell is

$$\frac{M_J}{M_{\text{total}}} = \frac{[1.6 + 0.02(J - 40)]^3 - (1.6)^3}{53}$$

Table V

WASTE HEAT AND ENTROPY FOR SIMPLE WATER

J	Entropy Change (Mbar cc/g deg)	Specific Waste Heat (Mbar cc/g)	Waste Heat Inside and Including jth Cell (Mbar cc)
41	0.000026	0.007620	0.004956
51	0.000027	0.007914	0.071979
61	0.000020	0.005861	0.133249
71	0.000015	0.004396	0.189216
81	0.000011	0.003223	0.239713
91	0.000009	0.002637	0.286267
101	0.000007	0.002051	0.328033
111	0.000005	0.001465	0.366175
121	0.000004	0.001172	0.400461
131	0.000004	0.001172	0.432881
141	0.000003	0.000879	0.460213
151	0.000002	0.000586	0.487570
153	0.000002	0.000586	0.491905

Table VI

WASTE HEAT AND ENTROPY FOR NOL WATER

J	Entropy Change (Mbar cc/g deg)	Specific Waste Heat (Mbar cc/g)	Waste Heat Inside and Including jth Cell (Mbar cc)
41	0.000021	0.008026	0.005219
51	0.000021	0.007978	0.073345
61	0.000016	0.005556	0.133261
71	0.000012	0.004069	0.186032
81	0.000009	0.003037	0.232691
91	0.000007	0.002317	0.274368
101	0.000006	0.001774	0.311459
111	0.000004	0.001379	0.344459
121	0.000004	0.001085	0.373955
131	0.000003	0.000866	0.400460
141	0.000002	0.000697	0.424317
151	0.000002	0.000566	0.445878
153	0.000002	0.000544	0.449941

Table VII

WASTE HEAT AND ENTROPY FOR GLYCERINE

J	Entropy Change (Mbar cc/g deg)	Specific Waste Heat (Mbar cc/g)	Waste Heat Inside and Including J th Cell (Mbar cc)
41	0.000014	0.005772	0.004730
51	0.000016	0.006533	0.076166
61	0.000011	0.004315	0.136227
71	0.000009	0.003050	0.186773
81	0.000007	0.002212	0.230170
91	0.000005	0.001651	0.267907
101	0.000004	0.001257	0.301107
111	0.000003	0.000972	0.330488
121	0.000002	0.000763	0.356636
131	0.000002	0.000604	0.379993
141	0.000002	0.000484	0.400910
151	0.000001	0.000392	0.419732
153	0.000001	0.000375	0.423265

Table VIII gives some values of this ratio, along with values of the fraction of total waste heat which is deposited within and including the Jth cell.

Table VIII

DISTRIBUTION IN J OF LIQUID MASS AND WASTE HEAT

J	M_J/M_{total}	Fraction of Total Waste Heat		
		Simple Water	NOL Water	Simple Glycerine
60	.09	.26	.29	.31
80	.18	.48	.51	.54
100	.335	.66	.69	.71
120	.54	.81	.83	.84
140	.71	.93	.94	.95
152-1/2	1.00	1.00	1.00	1.00

It is evident that in all three liquids the major part of the energy dissipation occurs in less than one-third of the mass. This is the kind of effect one would anticipate, since the energy dissipated in shock compression decreases rapidly with shock amplitude. The total waste heats in the three cases are:

Simple water	.493 Mbar cc
NOL water	.449 Mbar cc
Simple glycerine	.422 Mbar cc

The total energy of the explosive is 1.401 Mbar cc, so these numbers represent 35%, 32%, and 30% of the explosive energy, respectively. The insensitivity of the waste heat to the equation of state of the fill is particularly impressive; one must conclude that only the grossest features of the equation of state enter into wave propagation in spherical geometry.

Throughout this calculation the question of phase change has been ignored. As long as the pressure in the material remains above a kilobar or so, this is probably a satisfactory procedure. However, specific entropy increase in cells near the explosive is great enough that the liquid may evaporate when pressure is reduced to atmospheric, depending upon its specific and latent heats. The fraction of material so affected is estimated by locating the cell, J_B , at which the specific waste heat, $W_H(J)$, is equal to h_B , the heat required to raise unit mass to the boiling temperature from 20°C. This heat is entered in column 3 of Table IX.

The mass of liquid contained within and including J_B is denoted M_B and is calculated from Eq. (31). The heat required to boil M_B at atmospheric pressure is $(h_B + L_V)M_B$, where L_V is the latent heat of vaporization. The waste heat within and including cell J_B is denoted

by W_B . The total mass of liquid which will evaporate when the liquid expands to atmospheric pressure is $M_V = (W_B - h_B M_B) / L_V$. Except for decomposition this material will recondense after cooling by the atmosphere. It will not, however, participate in the liquid expansion process described elsewhere in this report. It will, in fact, almost certainly be augmented as a result of heating through direct contact with detonation gases. Some values of M_V / M_{total} are entered in Table IX. These have been calculated on the assumption that the distribution of waste heat for each liquid listed is the same as that calculated for NOL water, Table VI. Distributions for each liquid listed in Tables I and II can readily be calculated according to the procedures described in Section IV, but the differences between the estimate of Table IX and a more precise calculation are expected to be small. Until better equations of state are constructed, such differences are not likely to be very significant. In order to illustrate the magnitude of error associated with the estimating procedure, a flow calculation according to Section IV has been made for ether, which is likely to exhibit the largest deviation. This calculation is described in Appendix A, and the results are entered in parentheses in Table IX. Since ether is the most compressible of the liquids in Table IX, glycerine is the least compressible, and water is intermediate between them, these three materials should bracket the behavior of most liquids. Thus the values in the last column of Table IX can be taken to reasonably represent the effects of vaporization for various liquids.

The last column of Table IX suggests that experimental comparisons of distributions in ether and water, for example, would certainly indicate whether or not evaporation has a significant effect on mass distribution.

Table IX

FRACTION OF TOTAL MASS EVAPORATED BY WASTE HEAT, M_V/M_{total}

Liquid	Boiling Temp. (°C)	h_B ($\frac{\text{Mbar cc}}{\text{g}}$)	L_V ($\frac{\text{Mbar cc}}{\text{g}}$)	M_{total} (g)	J_B	W_B ($\frac{\text{Mbar cc}}{\text{g}}$)	M_B (g)	M_V (g)	$\frac{M_V}{M_{\text{total}}}$
Acetone	56.7	$.81 \times 10^{-3}$	5.22×10^{-3}	175	138	.417	136	59.	.33
Ethanol	78.3	1.39×10^{-3}	8.58×10^{-3}	175	110	.341	76	27.4	.156
Methanol	64.7	1.12×10^{-3}	11.2×10^{-3}	175	119	.368	93	23.6	.134
Benzene	80.2	1.02×10^{-3}	3.88×10^{-3}	195	124	.382	115	68.3	.287
CCl_4	76.7	$.48 \times 10^{-3}$	1.92×10^{-3}	356	153	.449	356	145.	.408
Ether	34.6	$.33 \times 10^{-3}$	3.69×10^{-3}	158	153* (153)	.449 (.4045)	158 (158)	108. (95.5)	.684 (.603)
Glycerine	290.	6.38×10^{-3}	--	280	57	.110	17	--	--
Water	100.0	3.34×10^{-3}	22.5×10^{-3}	221	78	.219.	38	4.1	.018

* Entries in parentheses are discussed in Appendix A.

VI CONCLUSIONS

The calculations presented here show that the equations of state of liquids developed in this work suffice for calculating the magnitude of energy absorbed in heating the liquid fill of a spherical burster to within about 10% of its correct value. For the particular dimensions considered here, this value is about a third of the explosive energy. The explosive is similar to C-3 and the ratio of liquid mass to explosive mass is about 10. Lower explosives would produce less heating and different explosive configurations could be expected to alter the heating effect.

The Q-code used to perform the waste heat calculations appears to be completely satisfactory for the purpose; care must be taken to insure that cell size is small enough to yield correct values of the entropy increase in shock.

If more precise values of the waste heat are required, improved equations of state will be needed. Substantial improvement over the present equations is possible, but careful thought will be required to make optimum use of available thermodynamic data. Additional Hugoniot points would be of considerable help in constructing an improved equation.

If serious decomposition of fill materials is expected to occur in the entropy ranges achieved in these calculations, the calculations should be repeated for the particular materials of interest, using the best equations of state that can be constructed. This is because specific entropy (and hence temperature) is more sensitive to thermodynamic properties than is waste heat.

Although calculations have not been made specifically for powdered solids, it is anticipated on theoretical grounds that waste heats will be as great as or greater than those calculated for liquids because of the porosity in the initial fill. Calculations for a powdered solid

can be made using initial bulk density and equation of state of the solid material.

The amount of material vaporized by passage of the shock differs markedly between water and other materials such as ether and alcohol. This suggests that comparative experiments with different materials may provide information about the importance of evaporation in dissemination by an explosive burster.

The results on evaporation also suggest that this may be a factor influencing the relative performances of bursters containing high and low explosives.

APPENDIX A
WASTE HEAT IN ETHER

The calculations described in Section IV were performed for ether after Table IX had been constructed according to the approximations described there. In order to avoid calculating negative pressures, as shown in Table IV, a set of coefficients A, B, C, D different from those in Table III was used. A_2 of Eq. (23) was set to zero, A was determined from the adiabatic sound velocity, and A_1 was determined by least squares. The following constants were obtained:

$$\begin{aligned} b &= 0.5270 \\ C_v &= 2.26 \times 10^{-5} \\ T_o &= 293^\circ\text{K} \\ V_o &= 1.405 \\ A &= 0.01511 \\ B &= 0.4428 \\ C &= 0.1079 \\ D &= 0 \end{aligned}$$

The calculation yielded the values of waste heat and entropy shown in Table A-1. The total waste heat is 0.4045 Mbar cc/g, and the mass of material vaporized is 95.5 grams, or 0.603 of the total liquid mass. These numbers are shown in parentheses in Table IX for comparison with the estimates made earlier. The mass vaporized is somewhat lower than the estimate, but the difference is not particularly significant in view of the approximations made.

Table A-1

WASTE HEAT AND ENTROPY FOR ETHER

J	Entropy Change (Mbar cc/g deg)	Specific Waste Heat (Mbar cc/g)	Waste Heat Inside and Including Jth Cell (Mbar cc)
41	0.000023	0.011758	0.005452
51	0.000020	0.009340	0.065224
61	0.000015	0.006360	0.114439
71	0.000012	0.004877	0.158461
81	0.000010	0.003717	0.198930
91	0.000008	0.002867	0.235426
101	0.000007	0.002287	0.268880
111	0.000006	0.001839	0.299810
121	0.000005	0.001484	0.328244
131	0.000004	0.001215	0.354422
141	0.000003	0.001009	0.378729
151	0.000003	0.000844	0.401349
153	0.000003	0.000814	0.405678

DISTRIBUTION

Copies 1-11 Commanding Officer, Edgewood Arsenal,
Maryland 21010
ATTN: Mr. Donald E. Buck
Contract Project Officer
Dissemination Research Department
Physical Research Laboratory

Copies 12-21 Defense Documentation Center
ATTN: TISIA-2, Cameron Station
Alexandria, Virginia

UNCLASSIFIED

Security Classification

DOCUMENT CONTROL DATA - R&D

(Security classification of title, body of abstract and indexing annotation must be entered when the overall report is classified)

1 ORIGINATING ACTIVITY (Corporate author)		2a REPORT SECURITY CLASSIFICATION	
STANFORD RESEARCH INSTITUTE Menlo Park, California 94025		UNCLASSIFIED	
		2b GROUP	
		N/A	
3 REPORT TITLE			
EQUATIONS OF STATE OF LIQUIDS AND CALCULATIONS OF WASTE HEAT			
4 DESCRIPTIVE NOTES (Type of report and inclusive dates)			
Special Technical Report - July - September 1966			
5 AUTHOR(S) (Last name, first name, initial)			
Duvall, G. E.			
6. REPORT DATE		7a. TOTAL NO. OF PAGES	7b. NO OF RLFS
July 1966		53	1
8a. CONTRACT OR GRANT NO.		8a. ORIGINATOR'S REPORT NUMBER(S)	
DA-18-035-AMC-122(A)		Report Number 3	
b. PROJECT NO.		8b. OTHER REPORT NO(S) (Any other numbers that may be assigned this report)	
c. Task No. 1B522301A08101		N/A	
d.			
10. AVAILABILITY/LIMITATION NOTICES This document is subject to special export controls and each transmittal to foreign governments or foreign nations may be made only with prior approval of the CO, US Army Edgewood Arsenal, ATTN: SMUEA-TSTI-T, Edgewood Arsenal, Maryland 21010			
11. SUPPLEMENTARY NOTES		12. SPONSORING MILITARY ACTIVITY	
Dissemination investigations of liquid and solid agents		Physical Research Laboratory RESEARCH LABORATORIES	
13. ABSTRACT Procedures for relating waste heat to entropy increases in a shock wave are described. Numerical coefficients for Mie-Gruneisen equations of state are obtained for several liquids, assuming that $(\partial P/\partial T)_V$ and C_V are constant. These equations of state are used to calculate the flow produced by a 1.6-cm-radius sphere of C-3-like explosive in a surrounding liquid. Specific entropy increase as a function of radius is included in the calculation, and this is used to determine the waste heat for a 3.85-cm-radius liquid burster. (Liquid-to-explosive mass ratio is about 10.) Calculations for glycerine, for two different water equations of state, and for ether yield total waste heats equal to $(.32 \pm .03) x$ (explosive energy). Close agreement between calculations for two different water equations of state produces considerable confidence in the reliability of this result. On the basis of these calculations, evaporation of several liquids is estimated. If decomposition can occur or if more precise values of waste heat are needed, more exact equations of state will be required; the present calculations can be readily modified to accommodate such equations.			

14	KEY WORDS	LINK A		LINK B		LINK C	
		ROLE	WT	ROLE	WT	ROLE	WT
	Waste heat, equations of state, specific entropy, liquid fills, energy absorption						