

EQUATION OF STATE OF FLUIDS. I. NITROMETHANE

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I. Introduction

The following technique is obtained from Lysne and Hardesty, J. Chem. Phys. 59, pp 6512-6523. It presupposes that the following information is available, all at ambient pressure:

1. Variation of sound velocity with temperature:

$$C_i(T_i) = a_c + b_c t_i \quad (1)$$

2. Variation of specific volume with pressure:

$$P_i = (1/V_i) = a_v - b_v t_i \quad (2)$$

3. Variation of specific heat at constant pressure:

$$C_{p_i} = a_s + b_s T_i \quad (3)$$

The linearity of these functions is not required by the computations. In the above equations, t_i is degrees celsius and T_i is degrees Kelvin. From these it is possible to construct functions for calculating entropy, S , and internal energy, e_i at ambient pressure.

$$S_i = a_s \ln(T_i/T_0) + b_s(T_i - T_0) \quad (4)$$

$$e_i = a_s(T_i - T_0) + \frac{b_s}{2} (T_i - T_0)^2 - p_i(v_i - v_{i0}) \quad (5)$$

Here T_0 is a reference temperature at which S_i and e_i vanish, p_i is ambient pressure, v_{i0} is specific volume at (P_i, T_0) .

The underlying concept is a mapping from P, V, e space to P, V, T_i space where T_i is the initial temperature of a Hugoniot Curve which goes through the point P, V, e .

Implementation of the concept requires the information contained in Eqs. 1-3 plus a Hugoniot P - V relation which includes the temperature of the reference point at ambient pressure, T_i . This may be represented by the equation

$$P = P_h(V, T_i) \quad (6)$$

The theory is developed as follows: The R-H equation is

$$e = e_i(T_i) + \frac{1}{2}(P + P_i)(V_i - V) \quad (7)$$

Differentiation gives

$$de = \frac{1}{2}(V_i - V)dP - \frac{1}{2}(P + P_i)dV + B_i dT_i \quad (8)$$

where

$$B_i = \frac{1}{2}(P + P_i) \frac{dV_i}{dT_i} + \frac{de_i}{dT_i} \quad (9)$$

Differentiation of Eq. 6 gives

$$dP = \left. \frac{\partial P}{\partial V} \right|_{T_i} dV + \left. \frac{\partial P}{\partial T_i} \right|_V dT_i \quad (10)$$

and

$$dT_i = \left. \frac{\partial T_i}{\partial P} \right|_V dP + \left. \frac{\partial T_i}{\partial V} \right|_P dV \quad (11)$$

where

$$\left. \frac{\partial T_i}{\partial V} \right|_P = - \frac{(\partial P / \partial V) T_i}{(\partial P / \partial T_i) V} \quad (12)$$

With Eqs. 8-12 it is possible to calculate the derivative of e with respect to P and V :

$$\left. \frac{\partial e}{\partial P} \right|_V = \frac{V_i - V}{2} + \frac{B_i}{(\partial P / \partial T_i)_V} \quad (13)$$

$$\left. \frac{\partial e}{\partial V} \right|_P = - \frac{P - P_i}{2} + \frac{B_i}{(\partial V / \partial T_i)_P} \quad (14)$$

The adiabatic derivative of p with respect to v can then be calculated:

$$\left. \frac{\partial P}{\partial V} \right|_S = - \frac{(\partial e / \partial V)_P + P}{(\partial e / \partial P)_V} \quad (15)$$

Also

$$\left(\frac{\partial P}{\partial T} \right)_V = \frac{C_V}{(\partial e / \partial P)_V} \quad (16)$$

Then

$$\left. \frac{\partial P}{\partial V} \right|_T = \left. \frac{\partial P}{\partial V} \right|_S + \frac{TC_V}{(\partial e / \partial P)_V^2} \quad (17)$$

The derivatives of P in Eqs. 16 and 17 represent two-thirds of what is required to calculate P , V , and T for any process described by the equation

$$de = adV + bdP \quad (18)$$

For such a process

$$\frac{dV}{dP} = \frac{\frac{1}{C_V} \left(\frac{\partial P}{\partial T} \right)_V - b}{P + a - C_V \left(\frac{\partial T}{\partial V} \right)_P} \quad (19)$$

and

$$\frac{dT}{dP} = \left. \frac{\partial T}{\partial P} \right|_V + \left. \frac{\partial T}{\partial V} \right|_P \frac{dV}{dP} \quad (20)$$

The other third of the problem is determination of C_V . C_p is assumed known on the ambient isobar and C_V can be determined there. The question is whether or not C_V can be extended into regions of high pressures. The problem is equivalent to determining the derivative of $(\partial S/\partial T)_P$ or $(\partial S/\partial T)_V$ along the curve described by Eq. 19. For example

$$\frac{d}{dP} \left(\frac{\partial S}{\partial T} \right)_P = \frac{\partial^2 S}{\partial V \partial T} + \left[\left. \frac{\partial^2 S}{\partial T^2} \right|_V + \frac{\partial^2 S}{\partial V \partial T} \left(\frac{\partial V}{\partial T} \right)_P \right] \frac{dT}{dP} \quad (21)$$

Although Lysne and Hardesty describe a numerical procedure for extending C_V to pressures above ambient, it is not clear that their scheme is theoretically sound. Without going deeply into the question, one can examine it by attempting to calculate entropy, S , on the curve given by Eq. 19. The equation for S becomes:

$$\frac{dS}{dP} = \frac{C_V}{T} \left[\left(\frac{\partial T}{\partial P} \right)_V + \left(\frac{\partial T}{\partial V} \right)_P \frac{dV}{dP} \right] + \left(\frac{\partial p}{\partial T} \right)_V \frac{dV}{dP} \quad (22)$$

Since C_V must be known in order to calculate dS/dP , the prospects for extending C_V off the ambient pressure line do not look promising. The options appear to be

1. Assume C_V or C_p constant
2. Use some kind of atomic model for cooperative vibrations, e.g., Einstein or Debye solid, and simple quantum harmonic oscillators for intramolecular vibrations.
3. Guess

II. Equations for Nitromethane

Lysne and Hardesty measured Hugoniot (U_s, U_p) values for three different initial temperatures and fitted them to a curve having the form

$$U_s(T_i) = C(T_i) \left[(SU)^2 + 2S(G+B)U + G^2 \right]^{1/2} - G \quad (1)$$

where T_i is initial temperature at ambient pressure, S and B are constants, G is a linear function of T_i , and $C(T_i)$ is sound velocity at ambient pressure P_i and temperature T_i . When Eq. 1 is combined with the jump conditions for mass and momentum, a Hugoniot P-V relation which depends on T_i is obtained:

$$P(V, T_i) = P_i + \frac{(V_i - V)c^2}{(a_1 V_i)^2} \left[2a_2^2 + 2a_2 \sqrt{a_2^2 - a_3} - a_3 \right] \quad (2)$$

where

$$a_1 = 1 - S^2(1 - V/V_i)^2 \quad (3)$$

$$a_2 = 1 + \frac{S(B+G)}{C} (1 - V/V_i) - G/C \quad (4)$$

$$a_3 = a_1(1 - 2G/C) \quad (5)$$

Values of the parameters given by Lysne and Hardesty are

$$S = 1.68 \quad (6)$$

$$B = 0.0262 \text{ cm}/\mu\text{sec} \quad (7)$$

$$G(T_i) = 0.1 - 2.7 \times 10^{-4}(T_i - 273), \text{ cm}/\mu\text{sec} \quad (8)$$

$$C(T_i) = 0.1417 - 4.28 \times 10^{-4}(T_i - 273), \text{ cm}/\mu\text{sec} \quad (9)$$

$$1/V_i = 1.5392 - 1.4 \times 10^{-3} T_i, \text{ g/cc} \quad (10)$$

$$C_p(T_i) = 1.55 \times 10^{-5} + 6.17 \times 10^{-9} T_i, \text{ Mbarcc/g}^\circ\text{K} \quad (11)$$

From these the internal energy can be calculated:

$$e_i(T_i) = 1.55 \times 10^{-5} (T_i - 244.2) + 3.085 \times 10^{-9} (T_i - 244.2)^2 - P_i (V_i - V_{i0}), \text{ Mbarcc/g} \quad (12)$$

where $V_{i0} = 0.83520 \text{ cc/g}$

Derivatives of V_i and e_i are required:

$$\frac{dV_i}{dT_i} = 1.4 \times 10^{-3} V_i^2 \quad (13)$$

$$\begin{aligned} \frac{de_i}{dT_i} &= 1.55 \times 10^{-5} + 6.17 \times 10^{-9} (T_i - 244.2) \\ &\quad - 1.4 \times 10^{-3} P_i V_i^2 \end{aligned} \quad (14)$$

Equation 2 reduces to a familiar result for small values of $\eta \equiv 1 - V/V_i$:

$$\begin{aligned} P - P_i &= \frac{c^2 \eta}{V_i} \left(1 - \frac{S(G+B)}{c} \eta \right)^{-2} \\ &= \frac{\eta c^2}{V_i} \left[1 + \frac{2S(G+B)}{G} \eta + 0(\eta^2) \right] \end{aligned} \quad (15)$$

From Eq. 15 limiting values of derivatives are obtained as $\eta \rightarrow 0$:

$$\left. \frac{\partial P}{\partial T_i} \right|_V = 1.4 \times 10^{-3} C^2(T_i) \quad (16)$$

$$\left. \frac{\partial P}{\partial V} \right|_{T_i} = -(C(T_i)/V_i)^2 \quad (17)$$

Specific heat is approximated by the equations

$$C_V(T, T_i) = C_{Vi}(T_i) + (C_{VA} - C_{Vi})[1 - \exp[-(T - T_i)/R(T_i)]] \quad (18)$$

where

$$\begin{aligned} C_{Vi}(T_i) &= 1.16 \times 10^{-5} + 2.320 \times 10^{-9}(T_i - 244.2) \\ &\quad + 5.9925 \times 10^{-11}(T_i - 244.2)^2 \end{aligned} \quad (19)$$

$$\begin{aligned} C_{VA}(T_i) &= 1.80 \times 10^{-5} + 2.07 \times 10^{-8}(T_i - 244.2) \\ &\quad - 4.041 \times 10^{-11}(T_i - 244.2)^2 \end{aligned} \quad (20)$$

$$R(T_i) = 130 + 0.38316(T_i - 244.2) + 4.4409 \times 10^{-4}(T_i - 244.2)^2 \quad (21)$$

III. Computational Procedures and Program

The program listed in Appendix A consists of a principal subroutine, EOSNTR, to be called from MAIN and secondary subroutines called from EOSNTR. It is written explicitly for Hugoniot P,V,T calculations, but it can easily be modified for other applications. Variables transferred from MAIN are PO, VO, TO, the reference state into which the shock is running,

- P The incremented value of pressure for which new values of P and T will be calculated
- V,T The "old" values of specific volume and temperature
- DP The pressure increment
- MM A control index which provides for initializing procedures in EOSNTR.

Variables transferred to MAIN from EOSNTR are DV and DT, the calculated increments in V and T.

The program is separated into BLOCKS; their functions are described below.

Block 1

Values of P_i and T_i are set. DELTI and DELV are increments in T_i and V used to estimate $(\partial P / \partial T_i)_V$ and $(\partial P / \partial V)_{T_i}$. V_i is computed for the initial T_i . T_i , V_i and P_i are restricted to the subroutine.

Block 2

Pressure corresponding to the transferred values of V is calculated. This should differ insignificantly from the transferred value of P. The calculated value is stored as P1 and used as the base for estimating derivatives.

P2 is centered between P and P + DP; it is used for calculating some derivatives.

Block 3

Specific heat at constant volume is calculated for the old values of T_i and T from Eqs. II.18 to II.21.

Block 4

$(\partial P/\partial T_i)_V$ is estimated as the difference ratio

$$\frac{P(V, T_i + dT_i) - P(V, T_i)}{dT_i} = \text{DPHDTI}$$

Block 5

$(\partial P/\partial V)_{T_i}$ is estimated as the ratio

$$\frac{P(V + dV, T_i) - P(V, T_i)}{dV} = \text{DPHDV}$$

Block 6

$$\text{DVDTI} = (\partial V/\partial T_i)_P = - (\partial P_H/\partial T_i)_V / (\partial P_H/\partial V)_{T_i}$$

Block 7

$$dV_i/dT_i = \text{DVIDTI}$$

and

$$de_i/dT_i = \text{DEIDTI}$$

are calculated from Eqs. II.13 and II.14.

Block 8

$BI = B_i$ is calculated from Eq. I.9.

$DEDPV = (\partial e / \partial P)_V$ is calculated from Eq. I.13, and

$DPDVS = (\partial P / \partial V)_S$ is calculated from Eq. I.15.

Block 9

$DPDVT = (\partial P / \partial V)_T$ is calculated from Eq. I.17.

$DPDTV = (\partial P / \partial T)_V$ is calculated from Eq. I.16.

$DVDTP = (\partial V / \partial T)_P = - (\partial P / \partial T)_V / (\partial P / \partial V)_T$

Block 10

DV is calculated from Eq. 11.19 with

$$a = - (P + P_0)/2; \quad b = (V_0 - V)/2$$

where

$$P_0 \equiv P_0; \quad T_0 \equiv T_0$$

DT is calculated from Eq. II.20.

VT and TT are temporary storage for the "new" values of V and T.

Block 11

The Hugoniot P-V equation, Eq. II.2 is solved for the "new" value of T_i which corresponds to the new P and V. New values of T_i and V_i are stored.

A listing of output for the principal Hugoniot centered at 293°K is given in Appendix B.

APPENDIX A

PROGRAM LISTING OF EOSNTR

(Statements 0.01 to 0.17 comprise a calling program for the computation shown in Appendix B)

```

0.005 $JOB
0.01 PI=1.02E-6
0.02 TI=293.
0.03 VI=VOL(TI)
0.04 P=PI
0.05 T=TI
0.06 V=VI
0.07 MM=1
0.08 DP=1.E-3
0.09 DG 2 J=1,100
0.1 P=P+DP
0.11 CALL EDSNTR(PI,VI,TI,MM,P,V,T,DP,DV,DT)
0.12 V=V+DV
0.13 T=T+DT
0.14 WRITE(6,*)'P=',P,'V=',V,'T=',T
0.15 2 CONTINUE
0.16 STOP
0.17 END
1.1 SUBROUTINE EDSNTR(PD,VD,TD,MM,P,V,T,DP,DV,DT)
1.2 IF(MM.EQ.2)GO TO 1
1.3 PI = 1.02E-6
1.4 TI = 293.
1.5 DELTI = 1.
1.6 DELV = -00.001
1.7 MM=2
1.8 1 VI = 1./(1.5392 - 1.4E-3 * TI)
2. P1=PH(TI,VI,V)
3. P2=(P1+P)/2.
40. CV = SPHT(T,TI)
50. TIX = TI + DELTI
60. VIX=VOL(TIX)
70. PX = PH(TIX, VIX, V)
76.5 AA=ABS(V-VI)
76.6 IF(AA.LT.1.0E-5)GO TO 100
80. DPHDTI = (PX-P1)/DELTI
81. GO TO 101
82. 100 DPHDTI=1.4E-3*(1.417-4.28E-3*(TI-273.))**2 * 1.0E-2
83. 101 CONTINUE
100. VX = V + DELV
110. PX = PH(TI, VI, VX)
120. DPHDV = (PX - P1)/DELV
130. DVDTI=-DPHDTI/DPHDV
140. DVIDTI = 1.4E-3*(VI**2)
160. DEIDTI = 1.55 E-5 + 6.17E-9 * (TI - 244.2)
170. DEIDTI = DEIDTI - PI * 1.4E-3 *(VI**2)
180. BI = 0.5 * (P2 + PI) * DVIDTI + DEIDTI
190. DEDPV = (VI-V)/2. + BI/DPHDTI
200. DDPVS = - ((P2 - PI)/2. + BI / DVDTI)/DEDPV
210. DDPVT = DDPVS + CV * T/(DEDPV**2)
219. DPDTV = CV/DEDPV
220. DVDTP = - DDPVT/DPDVT
230. DV = DP * (2. * CV - (VD - V) * DPDTV)
240. DV = DV/((P - PD) * DPDTV + 2. * CV * DDPVS)
250. VT = V + DV
270. DT = DP/DPDTV + DV/DVDTP
TT = T + DT
290. TIO = TI
300. TI = TXI(P, VT, TIO, VI, PI)
310. VI=VOL(TI)
317. RETURN
318. END
320. C
330. C

```

```

350. C
360. C
370. DTI = 20.0
380. TI = TIO
380.1 VIO=VOL(TIO)
380.2 PX1=PH(TIO,VIO,V)
380.3 TI=TIQ+DTI
380.4 VI=VOL(TI)
380.5 PX2=PH(TI,VI,V)
380.6 TI=TI-DTI
380.7 IF(ABS(PX1-P).LE.1.0E-8)GO TO 8
380.8 IF(PX1.LT.P)GO TO 10
380.9 IF(PX1.LT.PX2)GO TO 12
391. GO TO 14
391.1 10 IF(PX1.LT.PX2)GO TO 14
391.2 12 DTI=-DTI
391.3 14 CONTINUE
390. 1 TI = TI + DTI
398. VI=VOL(TI)
400. PX = PH(TI, VI, V)
410. Y = P - PX
420. A = ABS(Y)
430. IF(A.LE.1.0E-5) GO TO 8
440. S=(P-PX)/(PX-PX1)
441. IF(S.GT.0.)GO TO 1
442. TI=TI-DTI
450. DTI = DTI/2.
460. GO TO 1
490. 8 TXI = TI
500. RETURN
510. END

```

```

520. C
530. C
540. C
550. FUNCTION PH(TI, VI, V)
555. PI=1.02E-6
560. S = 1.68
570. A1 = 1. - S*S*(1. - V/VI)**2
580. B = .262E-1
590. C =(1.417 - 4.280E-3*(TI - 273.)) * 1.0E-1
600. G = (1.0 - .0027*(TI - 273.))*1.0E-1
610. A2 = 1. + S*B*(1. - V/VI)/C + G*S*(1. - V/VI)/C - G/C
620. A3 = A1 * (1. - 2.*G/C)
630. F1 = 2.* A2*A2 + 2.*A2*SQRT(A2*A2 - A3) - A3
640. PH = PI + (VI - V) * C*C * F1/(A1*A1*VI*VI)
640.5 C PH IN MEGABARS
650. RETURN
660. END

```

```

670. C
680. C
690. C
700. FUNCTION SPHT(T, TI)
710. C
720. C CV IN MGCC/GRAM DEGREE K
730. C
740. Y = T - TI
750. X = TI - 244.2
760. CVA = 1.8E-5 + 2.07E-8 * X - 4.041E-11 * X*X
770. R = 130. + .38316 * X + 4.4906E-4 * X*X
780. CVI = 1.16E-5 + 2.32E-9 * X + 5.9925E-11 * X*X
790. SPHT = (CVI + (CVA - CVI) * (1. - EXP(-Y/R)))
800. RETURN
810. END
812. FUNCTION VOL(TI)
817.

```

815. END

816. \$DATA

APPENDIX B

816. \$DATA

P=	0.1001020E-02	V=	0.8409356E 00	T=	0.3113760E 03
P=	0.2001020E-02	V=	0.8117852E 00	T=	0.3257495E 03
P=	0.3001020E-02	V=	0.7897956E 00	T=	0.3380842E 03
P=	0.4001018E-02	V=	0.7720530E 00	T=	0.3491594E 03
P=	0.5001016E-02	V=	0.7571608E 00	T=	0.3594094E 03
P=	0.6001014E-02	V=	0.7443338E 00	T=	0.3690410E 03
P=	0.7001013E-02	V=	0.7330675E 00	T=	0.3782341E 03
P=	0.8001011E-02	V=	0.7230299E 00	T=	0.3871123E 03
P=	0.9001009E-02	V=	0.7139879E 00	T=	0.3957324E 03
P=	0.1000101E-01	V=	0.7057657E 00	T=	0.4041619E 03
P=	0.1100101E-01	V=	0.6982334E 00	T=	0.4124365E 03
P=	0.1200100E-01	V=	0.6912875E 00	T=	0.4205903E 03
P=	0.1300100E-01	V=	0.6848508E 00	T=	0.4286521E 03
P=	0.1400100E-01	V=	0.6788540E 00	T=	0.4366345E 03
P=	0.1500100E-01	V=	0.6732467E 00	T=	0.4445706E 03
P=	0.1600100E-01	V=	0.6679858E 00	T=	0.4524590E 03
P=	0.1700100E-01	V=	0.6630311E 00	T=	0.4603242E 03
P=	0.1800099E-01	V=	0.6583529E 00	T=	0.4681638E 03
P=	0.1900099E-01	V=	0.6539228E 00	T=	0.4759905E 03
P=	0.2000099E-01	V=	0.6497189E 00	T=	0.4838120E 03
P=	0.2100099E-01	V=	0.6457214E 00	T=	0.4916318E 03
P=	0.2200099E-01	V=	0.6419120E 00	T=	0.4994558E 03
P=	0.2300099E-01	V=	0.6382750E 00	T=	0.5072856E 03
P=	0.2400098E-01	V=	0.6347971E 00	T=	0.5151289E 03
P=	0.2500098E-01	V=	0.6314665E 00	T=	0.5229875E 03
P=	0.2600098E-01	V=	0.6282722E 00	T=	0.5308618E 03
P=	0.2700098E-01	V=	0.6252056E 00	T=	0.5387551E 03
P=	0.2800098E-01	V=	0.6222568E 00	T=	0.5466707E 03
P=	0.2900098E-01	V=	0.6194179E 00	T=	0.5546052E 03
P=	0.3000097E-01	V=	0.6166820E 00	T=	0.5625657E 03
P=	0.3100097E-01	V=	0.6140436E 00	T=	0.5705510E 03
P=	0.3200097E-01	V=	0.6114954E 00	T=	0.5785603E 03
P=	0.3300097E-01	V=	0.6090326E 00	T=	0.5865940E 03
P=	0.3400097E-01	V=	0.6066499E 00	T=	0.5946536E 03
P=	0.3500096E-01	V=	0.6043438E 00	T=	0.6027419E 03
P=	0.3600096E-01	V=	0.6021088E 00	T=	0.6108569E 03
P=	0.3700096E-01	V=	0.5999416E 00	T=	0.6189976E 03
P=	0.3800096E-01	V=	0.5978386E 00	T=	0.6271675E 03
P=	0.3900096E-01	V=	0.5957972E 00	T=	0.6353665E 03
P=	0.4000096E-01	V=	0.5938137E 00	T=	0.6435945E 03
P=	0.4100095E-01	V=	0.5918856E 00	T=	0.6518503E 03
P=	0.4200095E-01	V=	0.5900099E 00	T=	0.6601348E 03
P=	0.4300095E-01	V=	0.5881843E 00	T=	0.6684497E 03
P=	0.4400095E-01	V=	0.5864068E 00	T=	0.6767922E 03
P=	0.4500095E-01	V=	0.5846747E 00	T=	0.6851655E 03
P=	0.4600095E-01	V=	0.5829865E 00	T=	0.6935659E 03
P=	0.4700094E-01	V=	0.5813403E 00	T=	0.7019963E 03
P=	0.4800094E-01	V=	0.5797337E 00	T=	0.7104558E 03
P=	0.4900094E-01	V=	0.5781660E 00	T=	0.7189453E 03
P=	0.5000094E-01	V=	0.5766349E 00	T=	0.7274631E 03
P=	0.5100094E-01	V=	0.5751390E 00	T=	0.7360085E 03
P=	0.5200094E-01	V=	0.5736771E 00	T=	0.7445815E 03
P=	0.5300093E-01	V=	0.5722479E 00	T=	0.7531831E 03
P=	0.5400093E-01	V=	0.5708500E 00	T=	0.7618147E 03
P=	0.5500093E-01	V=	0.5694824E 00	T=	0.7704746E 03
P=	0.5600093E-01	V=	0.5681438E 00	T=	0.7791589E 03
P=	0.5700093E-01	V=	0.5668334E 00	T=	0.7878718E 03
P=	0.5800093E-01	V=	0.5655500E 00	T=	0.7966140E 03
P=	0.5900092E-01	V=	0.5642927E 00	T=	0.8053828E 03
P=	0.6000092E-01	V=	0.5630601E 00	T=	0.8141782E 03
P=	0.6100092E-01	V=	0.5618522E 00	T=	0.8230007E 03
P=	0.6200092E-01	V=	0.5606673E 00	T=	0.8318481E 03

F=	0.6500089E-01	V=	0.5572469E 00	T=	0.8585542E 03
F=	0.6600088E-01	V=	0.5561492E 00	T=	0.8675093E 03
F=	0.6700087E-01	V=	0.5550714E 00	T=	0.8764873E 03
F=	0.6800085E-01	V=	0.5540128E 00	T=	0.8854912E 03
F=	0.6900084E-01	V=	0.5529730E 00	T=	0.8945208E 03
F=	0.7000083E-01	V=	0.5519515E 00	T=	0.9035757E 03
F=	0.7100081E-01	V=	0.5509474E 00	T=	0.9126541E 03
F=	0.7200080E-01	V=	0.5499605E 00	T=	0.9217561E 03
F=	0.7300079E-01	V=	0.5489902E 00	T=	0.9308828E 03
F=	0.7400078E-01	V=	0.5480359E 00	T=	0.9400334E 03
F=	0.7500076E-01	V=	0.5470976E 00	T=	0.9492083E 03
F=	0.7600075E-01	V=	0.5461742E 00	T=	0.9584053E 03
F=	0.7700074E-01	V=	0.5452657E 00	T=	0.9676255E 03
F=	0.7800072E-01	V=	0.5443715E 00	T=	0.9768689E 03
F=	0.7900071E-01	V=	0.5434913E 00	T=	0.9861362E 03
F=	0.8000070E-01	V=	0.5426248E 00	T=	0.9954253E 03
F=	0.8100069E-01	V=	0.5417719E 00	T=	0.1004737E 04
F=	0.8200067E-01	V=	0.5409317E 00	T=	0.1014072E 04
F=	0.8300066E-01	V=	0.5401043E 00	T=	0.1023428E 04
F=	0.8400065E-01	V=	0.5392891E 00	T=	0.1032805E 04
F=	0.8500063E-01	V=	0.5384858E 00	T=	0.1042205E 04
F=	0.8600062E-01	V=	0.5376942E 00	T=	0.1051625E 04
F=	0.8700061E-01	V=	0.5369139E 00	T=	0.1061067E 04
F=	0.8800060E-01	V=	0.5361448E 00	T=	0.1070528E 04
F=	0.8900058E-01	V=	0.5353867E 00	T=	0.1080013E 04
F=	0.9000057E-01	V=	0.5346391E 00	T=	0.1089517E 04
F=	0.9100056E-01	V=	0.5339019E 00	T=	0.1099042E 04
F=	0.9200054E-01	V=	0.5331745E 00	T=	0.1108586E 04
F=	0.9300053E-01	V=	0.5324571E 00	T=	0.1118151E 04
F=	0.9400052E-01	V=	0.5317492E 00	T=	0.1127735E 04
F=	0.9500051E-01	V=	0.5310508E 00	T=	0.1137338E 04
F=	0.9600049E-01	V=	0.5303616E 00	T=	0.1146961E 04
F=	0.9700048E-01	V=	0.5296814E 00	T=	0.1156603E 04
F=	0.9800047E-01	V=	0.5290099E 00	T=	0.1166264E 04
F=	0.9900045E-01	V=	0.5283470E 00	T=	0.1175943E 04
F=	0.1000004E 00	V=	0.5276926E 00	T=	0.1185642E 04

STATEMENTS EXECUTED= 30452
 COREUSAGE= 59388 BYTES, CODE= 5872 BYTES, ARRAY AREA= 28 BYTES, TOTAL AREA
 EXTENSIONS= NUMBER OF ERRORS= 0, NUMBER OF WARNINGS= 0, NUMBE
 COMPILE TIME= 82 0.27 SEC, EXECUTION TIME= 14.50.48 THURSDA

APPROXIMATIONS TO THE HUGONIOT P-V CURVE OF FUSED QUARTZ

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1. The Hugoniot U_S , U_P relation has the form

$$U_S = a + bu + cu^2 + du^3 \quad (1)$$

Then

$$P = \rho_0 au + \rho_0 bu^2 + \rho_0 cu^3 + \rho_0 du^4 \quad (2)$$

A direct relation between P and V is desired. There are various measures of V in common use; two are

$$\eta = 1 - V/V_0 \quad (3)$$

$$x = (V_0/V) - 1 \quad (4)$$

A form frequently used is

$$P = \alpha x + \beta x^2 + \gamma x^3 + \delta x^4 \quad (5)$$

The jump condition for mass conservation can be written as

$$\frac{U_S}{U} = \frac{1}{\eta} = \frac{x+1}{x} \quad (6)$$

The coefficients of x in Eq. (5) can be obtained in several ways:

- a) Use equations (1), (2), and (6) to calculate P and x , with U as a parameter. Fit the resulting values to Eq. (5) by least squares. This is the simplest

procedure, but care must be taken to insure that the resulting curve goes through $P = 0$, $x = 0$. This can be done by weighting the $(0,0)$ point very heavily.

b) If a suitable least squares program is not available, a fairly good determination of the coefficients can be made graphically through successive approximations, i.e. if (y,x) are the given values, proceed as follows:

- i) plot y vs x and draw a straight line through the data. This gives

$$y_1 = \alpha x \quad (7)$$

- ii) plot $y - y_1$ vs x^2 and again draw a straight line. The result is

$$y_2 = y_1 + \beta x^2 \quad (8)$$

etc.

This procedure works well for a parabola. Increasing care is required as higher order terms are introduced.

c) The coefficients in (5) may be determined analytically. With $P' \equiv dP/du$ and $u' \equiv du/dx$, the coefficients in (5) are

$$\alpha = \left. \frac{dp}{dx} \right|_{x=0} = (P'U')_{u=0} \quad (9.1)$$

$$\beta = \left. \frac{1}{2} \frac{d^2 p}{dx^2} \right|_{x=0} = \frac{1}{2} (P''U'^2 + P'U'')_{u=0} \quad (9.2)$$

$$\gamma = \left. \frac{1}{6} \frac{d^3 p}{dx^3} \right|_{x=0} = \frac{1}{6} (P'''U'^3 + 3P''U'U'' + P'U''')_{u=0} \quad (9.3)$$

$$\delta = \left. \frac{1}{24} \frac{d^4 p}{dx^4} \right|_{x=0} = \frac{1}{24} (P^{iv}U'^4 + 6P'''U'^2U'' + 3P''U''^2 + 4P''U'U''' + P'U^{iv})_{u=0} \quad (9.4)$$

With P given by Eq. (2),

$$P'_0 = \rho_0 a, \quad P''_0 = 2\rho_0 b, \quad P'''_0 = 6\rho_0 c, \quad P^{iv}_0 = 24\rho_0 d, \quad (10)$$

where

$$P'_0 = (P')_{u=0}, \quad \text{etc.}$$

Values of U'_0 , U''_0 , etc. are obtained by successive differentiations of the mass jump condition, as in Appendix A. With U_S given by Eq. (1), these are

$$U'_0 = a \quad U''_0 = 2a(b - 1) \quad (11.1)$$

$$U'''_0 = 6a[(b - 1)^2 + ac] \quad (11.2)$$

$$U^{iv}_0 = 24a[(b - 1)^3 + 3ac(b - 1) + a^2 d] \quad (11.3)$$

Substitution of Eqs. (10) and (11) into Eq. (9) gives

$$\alpha = \rho_0 a^2 \quad (12.1)$$

$$\beta = \rho_0 a^2 (2b - 1) \quad (12.2)$$

$$\gamma = \rho_0 a^2 [(b - 1)^2 + 2b(b - 1) + 2ac] \quad (12.3)$$

$$\begin{aligned} \delta = \rho_0 a^2 [(b - 1)^3 + 3b(b - 1)^2 \\ + 6ac(b - 1) + 2abc + 2a^2d] \quad (12.4) \end{aligned}$$

Determination of the coefficients of a power series in this fashion is often less satisfactory than least square fitting or alternative analytic methods. In this case the function fits very well near $x = 0 = u$, but falls off toward the upper range of validity of Eq. (2). This is shown in the following table, where coefficients for fused quartz have been used.

TABLE I

Analytical Fit to $P(x)$ for Eqs. (1)-(6) for Fused Quartz

$$\begin{aligned}
 a &= 0.59755 & b &= -3.3398 & c &= 45.132 & d &= -188.88 & \rho_0 &= 2.204 \\
 \alpha &= 0.786973 & \beta &= -6.04364 & \gamma &= 80.0818 & \delta &= -1013.38
 \end{aligned}$$

U cm/ μ sec	U_S cm/ μ sec	x	P_1 kbar	P_2 kbar
.001	0.59426	0.168561×10^{-2}	1.30973	1.30973
.01	0.56848	1.79058×10^{-2}	12.5292	12.5092
.02	0.54730	3.79293×10^{-2}	24.1247	23.4272
.03	0.532875	5.96569×10^{-2}	35.2336	29.6064
.04	0.52408	8.26308×10^{-2}	46.2029	21.7012

P_1 is calculated using Eqs. (1), (2), (4), and (6).

P_2 is calculated from Eqs. (5) and (12).

The above constants give P in megabars with U_p and U_s in cm/ μ sec,
 ρ_0 in g/cc.

2. When U_S and U_P are linearly related, the relation between P and X or P and η can be obtained exactly from Eq (6).

$$U_S = \frac{U}{\eta} = a + bu \quad (13.1)$$

$$u = \frac{a\eta}{1 - b\eta} \quad (13.2)$$

$$\begin{aligned} P &= \rho_o U_S U = \frac{\rho_o u^2}{\eta} \\ &= \frac{\rho_o a^2 \eta}{(1 - b\eta)^2} \end{aligned} \quad (14)$$

Let U_S deviate from linear dependence on U , say

$$U_S = a + bu + \psi(u) \quad (15)$$

Let

$$u = u_o + u_1 \quad (16)$$

where

$$u_o = \frac{a\eta}{1 - b\eta} \quad (17)$$

Then

$$P = \frac{\rho_o u^2}{\eta} = \frac{\rho_o}{\eta} (u_o^2 + 2u_o u_1 + u_1^2) \quad (18)$$

and

$$U_S = a + bu_o + bu_1 + \psi(u_o + u_1) = \frac{u_o + u_1}{\eta} \quad (19)$$

Because of Eqs. (13) and (19),

$$\frac{u_1}{\eta} = bu_1 + \psi(u_0) + \left. \frac{d\psi}{du} \right|_{u_0} u_1 + \dots \quad (20)$$

$$u_1 = \frac{u_0 \psi(u_0)}{a - u_0 (d\psi/du)_0} \quad (21)$$

Substituting this into Eq. (18) and retaining only terms of first order in u_1 gives

$$P = \frac{\rho_0 u_0^2}{\eta} + \frac{2\rho_0 u_0^2 \psi(u_0)}{\eta [a - u_0 (d\psi/du)_0]} \quad (22)$$

where

$$\frac{\rho_0 u_0^2}{\eta} = \frac{\rho_0 a^2 \eta}{(1 - b\eta)^2} \quad (23)$$

Eq. (23) represents a perturbation of the Hugoniot P-V curve from its normal form corresponding to a linear U_S - U_P relation. Again, taking fused quartz as an example

$$\psi(u) = cu^2 + du^3$$

$$(d\psi/du)_{u=u_0} = 2cu_0 + 3du_0^2$$

Then Eq. (22) becomes

$$P_2 = \frac{\rho_0 a^2 \eta}{(1 - b\eta)^2} + \frac{2\rho_0 u_0^4 (c + du_0)}{\eta (a - 2cu_0^2 - 3du_0^3)} \equiv P_2^{(0)} + P_2^{(1)} \quad (24)$$

TABLE II

Perturbation Hugoniot for Fused Quartz
 Same Constants as Table I. P_1 from Table I

x	P_1	$P_2^{()}$	$P_2^{()}$	P_2
0.168561×10^{-2}	1.30973	1.30953	1.97×10^{-4}	1.30973
1.79058×10^{-2}	12.5292	12.3497	0.17873	12.5285
3.79293×10^{-2}	24.1247	22.8425	1.2639	24.1064
5.96569×10^{-2}	35.2336	31.3909	3.7223	35.1132
8.26308×10^{-2}	46.2029	38.1415	7.62715	45.7687

This simple calculation produces a remarkably good fit, as seen in Table II. Even at 46 kbar the error is only slightly greater than one percent.

3. Modified Series Expansion

The success of the perturbation calculation described in the preceding section suggests a series expansion in the parameter

$$y = a\eta/(1 - b\eta) \quad (25)$$

With U_S given by Eq. (1), the mass jump condition, Eq. (6), becomes

$$(1 + z)q = z(A + Bq + Cq^2 + Dq^3) \quad (26)$$

where

$$z = by/a, \quad q = au, \quad A = a^2/b, \quad B = 1, \quad C = c/ab, \quad D = d/a^2b$$

Hugoniot pressure is now expressed as

$$P = \alpha'y + \beta'y^2 + \gamma'y^3 + \delta'y^4 \quad (27)$$

The coefficients α' , β' , γ' , δ' , are determined in the same manner as α , β , γ , δ in Section 2. The derivatives of q with respect to z are obtained from Eq. (26) in the manner described in Appendix A. The derivative of U with respect to y are obtained by a simple transformation. With

$u'_0 \equiv (du/dy)_{y=0}$, we have

$$u'_0 = 1, \quad u''_0 = 0, \quad u'''_0 = 6c/a, \quad u^{iv}_0 = 24d/a \quad (28)$$

The coefficients in Eq. (27) are

$$\alpha' = \rho_0 a, \quad \beta' = \rho_0 b, \quad \gamma' = 2\rho_0 c, \quad \delta' = 2\rho_0 (d + bc/a) \quad (29)$$

Pressures in fused quartz calculated from the same values of x used in Tables I and II are given in Table III. The result is considerably better than that obtained from expansion in x (p_2 of Table I), but not quite as good as obtained from perturbation calculation of Table II.

TABLE III

Hugoniot pressures calculated from Eqs. (27) and (29), kbars.

Pressures in kilobars. $p_2^{(1)} \rightarrow p_2^{(4)}$ are the contributions of

individual terms in Eq. (22). P_1 from Table I.

x	$p_2^{(1)}$	$p_2^{(2)}$	$p_2^{(3)}$	$p_2^{(4)}$	P_2	P_1
0.168561 E-2	1.31689	-7.4×10^{-3}	2.0×10^{-4}	-3×10^{-6}	1.30973	1.30973
1.79058 E-2	13.0753	-0.7255	0.1947	-3.2×10^{-2}	12.5128	12.5292
3.79293 E-2	25.630	-2.787	1.466	-0.467	23.842	24.1247
5.769 E-2	37.293	-5.902	4.517	-2.092	33.8157	35.2336
8.26308 E-2	47.864	-9.723	9.55	-3.392	44.299	46.2029

APPENDIX A

APPENDIX A

Derivatives of Particle Velocity

The mass jump condition is

$$(1 + x)u = xU_S \quad (1)$$

where $x = (V_0/V) - 1$. Denote dU_S/du by U'_S , du/dx by U' . Eq. (1) gives by successive differentiation,

$$u + (1 + x)u' = U_S + xU'_S u' \quad (2)$$

$$2u' + (1 + x)u'' = 2U'_S u' + x(U''_S u'^2 + U'_S u'') \quad (3)$$

$$3u'' + (1 + x)u''' = 3U''_S u'^2 + 3U'_S u'' + x(U'''_S u'^3 + 3U''_S u' u'' + U'_S u''') \quad (4)$$

$$= A + xB$$

where

$$A = 3U''_S u'^2 + 3U'_S u''$$

$$B = U'''_S u'^3 + 3U''_S u' u'' + U'_S u'''$$

Continuing,

$$(1 + x)u^{iv} + 4u''' = A' + B + xB'$$

$$A' = 3U'''_S u'^3 + 9U''_S u' u'' + 3U'_S u'''$$

So,

$$(1 + x)u^{iv} + 4u''' = 3U'''_S u'^3 + 9U''_S u' u'' + 3U'_S u'''$$

$$+ U'''_S u'^3 + 3U''_S u' u'' + U'_S u''' + xB'$$

$$(1 + x)u^{iv} + 4u''' = 4U_S''' u'^3 + 12U_S'' u' u'' + 4U_S' u''' + xB' \quad (5)$$

Values of the derivatives are required at $x = 0$ where $u = 0$. Denote these by subscript "0". Then,

$$\text{from (2)} \quad u'_0 = U_{S0} \quad (6)$$

$$\text{from (3)} \quad u''_0 = 2U_{S0}' u'_0 - 2u'_0 = 2u'_0 (U_{S0}' - 1) \quad (7)$$

$$\text{from (4)} \quad u'''_0 = 3U_{S0}'' u'^2_0 + 3u''_0 (U_{S0}' - 1) \quad (8)$$

$$\text{from (5)} \quad u^{iv}_0 = 4U_{S0}''' u'^3_0 + 12U_{S0}'' u'_0 u''_0 + 4u'''_0 (U_{S0}' - 1) \quad (9)$$

With $U_S = a + bu + cu^2 + du^3$, $U_{S0} = a$, $U'_{S0} = b$, $U''_{S0} = 2c$, $U'''_{S0} = 6d$,

$$\text{Then, } \left. \begin{aligned} U'_0 &= a, & U''_0 &= 2a(b - 1), & u'''_0 &= 6a(b - 1)^2 + 6a^2c, \\ U^{iv}_0 &= 24a[(b - 1)^3 + 3ac(b - 1) + a^2d] \end{aligned} \right\} \quad (10)$$