A THERMOCHEMICAL MODEL FOR SHOCK-INDUCED CHEMICAL REACTIONS IN POROUS SOLIDS: ANALOGS AND CONTRASTS TO DETONATION

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There is a class of non-explosive energetic materials ("ballotechnics"), that undergo rapid shock-induced chemical reactions, but whose products contain no vapor that can cause a rapid expansion upon pressure release. The present paper presents a thermochemical model describing such reactions in terms analogous to detonation. By contrast, however, the chemical energy in ballotechnics is converted mostly to heat rather than work by the shock wave, and an unsupported reaction wave will decay. In the absence of volatiles, there are no large increases in pressure, specific volume, or particle velocity associated with ballotechnic reactions. Thus, experimental methods normally applied to high explosives are insensitive, and time-resolved temperature measurements are the most appropriate. The pressure-volume-velocity relationships are strongly dependent on small amounts of volatiles (such as water) when present, but the shock temperature is not. Thermochemically, the possiblity of a true detonation in a volatile-bearing ballotechnic powder cannot be precluded. By the same arguments, geochemical detonations in volatile-saturated, supercooled magmas are possible.

INTRODUCTION

There have been a number of efforts to study the problem of shock-initiation of chemical reactions in non-explosive porous solids. Graham[1] has recently pointed out that such reactions are fundamentally different from either high explosive detonations or pyrotechnic reactions. He has applied the term "ballotechnics" to this class of materials, whose controlling features seem to be shock-induced mixing, shock activation, configuration change and heating.[2]

The experimental work to date has been dominated by studies aimed at understanding shock-induced chemical synthesis by examination of samples recovered from exposure to explosive loading.[3,4] Such recovery experiments have provided evidence for the uniqueness of the shock environment in its ability to mix and activate substituents, initiating reactions at a rate commensurate with that of shock wave propagation. Hugoniot measurements on lead nitrate/aluminum mixtures,[5] and tin/sulfur mixtures,[6] have demonstrated that shock-initiated reactions occur at a rapid enough rate to affect the pressure-volume state behind the shock wave in those mixtures. However, those experiments have the drawback that they are relatively insensitive to the amount of reaction, and are highly sensitive to small quantities of volatile impurities, as will be shown in the present paper.

Radiation pyrometry has been used to measure the shock temperatures of nickel/aluminum mixtures[7] and iron oxide/aluminum (thermite) mixtures,[8] providing evidence that shock-induced exothermic reactions occur in less than 100 ns in those materials. The model presented in this paper will demonstrate that, in contrast to the Hugoniot measurements, shock temperature measurements are very sensitive to chemical reactions and insensitive to volatile impurities.

There have been several efforts at modelling shock-initiated chemical reactions in non-explosive energetic materials.[9-12] These models have all considered the kinetics of the reactions, making various assumptions as to the controlling factors. The model presented here is an attempt to develop a description based only on thermochemistry and shock wave physics, ignoring kinetic aspects entirely. The present model assumes only that the reaction proceeds rapidly enough that an equilibrium state can be defined behind the shock wave; a possibility suggested by the experiments mentioned above. It is intended to provide a conceptual framework to which the more advanced models can be related, and is an approach similar to the earliest descriptions of detonations without regard for chemical mechanisms.

MIXING MODEL

If we consider a heterogeneous mixture of reactants A_i and products B_i, we can write an equation for a shock-induced chemical reaction as:

$$\sum_i n_{ai}A_i \rightarrow \sum_i n_{bi}B_i \qquad (1)$$

where n_{ai} and n_{bi} are the number of moles of reactant i and product i, respectively. The specific volume of a multi-component system with a uniform stress distribution is given by:

$$V = \sum_i n_i M_i V_i \qquad (2)$$

where M_i and V_i are the relative molecular mass and specific volume of component i, respectively.

To determine the specific volume dependence on pressure (P_S) at constant entropy, we can use Bridgman's quadratic equation:[13]

$$V/V_0 = 1 - (P_S/K_{0S}) + \tfrac{1}{2}(1+K'_{0S})(P_S/K_{0S})^2 \qquad (3)$$

where V_0 is the specific volume at standard conditions, K_{0S} is the isentropic bulk modulus, and K'_{0S} is its first pressure derivative. This quadratic equation is only accurate for pressures at which the strain is very small (less than a few percent), so the present calculations are limited to pressures of less than 10 GPa. A higher-order finite strain theory can be used to describe isentopes at higher pressures, but would introduce unnecessary complications into the mixture theory in the pressure range of interest here.

Summing eq. (3) for a multi-component system in eq. (2) results in a Reuss average composite bulk modulus and its pressure derivative in terms of those parameters for the individual components:

$$K_{0S} = [\sum_i (v_i/K_{0Si})]^{-1} \qquad (4)$$

$$K'_{0S} = K^2_{0S}\{\sum_i [v_i(1+K'_{0Si})/K^2_{0Si}]\} - 1 \qquad (5)$$

where v_i is the initial volume fraction of component i.

HUGONIOT CALCULATIONS

For a porous, reactive material, the Rankine-Hugoniot equation relating the specific internal energy on the Hugoniot (E_H) to that of the initial state (E_0) can be written:

$$E_H - E_0 = -Q + \tfrac{1}{2} P_H (V_{00} - V) \qquad (6)$$

where V_{00} is the initial (porous) volume, (P_H, V) is the pressure-volume state on the Hugoniot, and Q is the heat of reaction. The energy along the principal isentrope of a porous, zero-strength solid is given by

$$E_S - E_0 = \int_{V_0}^{V} P_S \, dV \ . \qquad (7)$$

Combining eqs. (6) and (7) together with the Mie-Gruneisen approximation

$$E_H - E_S = (V/\gamma)(P_H - P_S) \qquad (8)$$

gives an equation for the Hugoniot:

$$P_H(V) = \left(Q + \int_{V_0}^{V} P_S \, dV + \left[\frac{V}{\gamma}\right] P_S \right) \Bigg/ \left(\left[\frac{V}{\gamma}\right] - \tfrac{1}{2}(V_{00} - V) \right) . \qquad (9)$$

The theoretical Hugoniot of the reactants can be determined by setting Q to zero and inverting eq. (3) with parameters taken from (4) and (5) from the known material properties of the components, and inserting into (9). The product Hugoniot is determined in the same way, with Q equal to the appropriate heat of reaction.

THERMITE HUGONIOTS

For thermite, eq. (1) can be written:

$$Fe_2O_3 + 2Al \rightarrow Al_2O_3 + Fe \qquad (10)$$

The elastic constants have been calculated[14] using eqs. (4) and (5) with ultrasonic data for hematite, aluminum and alumina, and shock wave data for liquid iron (since the products are in the liquid state). A Gruneisen parameter was also determined for each mixture from a mass-fraction-weighted average of the experimental values for the components.[14] This method has been shown to be innacurate,[15] but is a reasonable approximation for the present calculations. These calculated parameters for the thermite reactants and products are listed in Table 1.

TABLE 1. THERMITE EQUATION OF STATE PARAMETERS

Parameter	Reactants	Products
Initial Density (ρ_0, g/cm^3)	4.249	4.154
Initial Specific Volume (V_0, cm^3/g)	0.2353	0.241

Zero Pressure Bulk Modulus (K_{0S}, GPa)	122	197
Pressure Derivative of K_{0S} (K'_{0S})	6.65	5.2
Zero Pressure Gruneisen Parameter (γ_0)	2.08	1.7

Because the thermite product Hugoniot is at high temperature, the reference isentrope P_S used in eq. (9) was centered on the liquid side of the melting point of alumina at 1 atmosphere and 2312 K. This requires that the heat of reaction used in eq. (9) be reduced by the enthalpy required to heat the product mixture from standard conditions to 2312 K, including melting and other phase transformations.[14] This calculation results in $Q = -1.9\times10^6$ J/kg. The calculated isentropes and families of porous Hugoniots for thermite reactants and products are plotted in Figs. 1 and 2, respectively.

FIGURE 1. CALCULATED REACTANT ISENTROPE AND FAMILY OF CALCULATED REACTANT HUGONIOTS FOR POROUS THERMITE CENTERED ON STANDARD CONDITIONS.

FIGURE 2. CALCULATED PRODUCT REFERENCE ISENTROPE AND FAMILY OF CALCULATED PRODUCT HUGONIOTS FOR POROUS THERMITE CENTERED ON STANDARD CONDITIONS PLUS HEAT OF REACTION.

To make comparisons to experimental shock wave data, a more useful way to represent the Hugoniots is in the pressure-particle velocity plane. The Rankine-Hugoniot equations can be used to write the particle velocity (u) in terms of P and V:

$$u = \sqrt{P(V_{00}-V)} \qquad (11)$$

This equation was used to transform the reactant and product Hugoniots for 50% porous thermite to the P-u plane. Fig. 3 shows that the pressure on the product Hugoniot is about 10% greater than that on the reactant Hugoniot at a given particle velocity. Similarly, the particle velocity is about 5% greater on the reactant Hugoniot compared to that on the product Hugoniot at the same shock pressure. This observation implies that experimental attempts to measure the reaction by performing Hugoniot measurements are bound to be complicated by the large uncertaities that are inherent for porous solids. Similarly, the time-resolved particle velocity measurements often applied to high explosives will also be insensitive to shock-initiated reactions in ballotechnics.

FIGURE 3. CALCULATED REACTANT AND PRODUCT HUGONIOTS FOR 50% POROUS THERMITE.

"HEAT DETONATIONS"

For reaction rates that are finite but rapid enough to go to completion, the shock wave will first achieve a state on the reactant Hugoniot. After the reaction goes to completion, the state behind the shock wave must lie on the product Hugoniot. It is well known[16] that a steady wave can only reach states intersected by the Rayleigh line, as illustrated in Fig. 4 for a shock wave propagating into 50% porous thermite. Since the product Hugoniot is steeper than the Rayleigh line at all possible points of intersection, an unsupported reaction wave will always decay.[14]

FIGURE 4. CALCULATED REACTANT AND PRODUCT HUGONIOTS FOR 50% POROUS THERMITE AND RAYLEIGH LINE WHICH DEFINES STATES CONNECTED BY STEADY REACTION WAVE.

Such shock-induced reactions are not detonations in the conventional sense, because the products are not in the vapor phase and high pressures cannot be sustained upon expansion. However, examination of Fig. 4 demonstrates that this type of reaction is the thermochemical equivalent of an overdriven detonation. The term "heat detonation" can be used to make the important distinction between these shock-initiated reactions, which rely on processes proceeding at the rate of the shock wave, and gasless combustion, which are controlled by the thermal and mass transport properties of the reacting material.[17]

HEATING EFFICIENCY

One way to make a comparison between heat detonations and explosive detonations is to define a quantity called the "heating efficiency". The work efficiency has been used to describe the net amount of energy that can ideally be converted to work from the heat of reaction of a detonating explosive.[18] If Q is the heat of reaction, and V_f is the final specific volume of the reaction products after complete isentropic release, then the work efficiency is defined as

$$w = \left(\int_{V}^{V_f} P_S dV - V_0 P_H u/U \right)/Q. \qquad (12)$$

By analogy, we can define the heating efficiency as the fraction of the heat of reaction that ideally remains in the reactants after they have isentropically released to zero pressure (h-l-w). In Table 2, the calculated work and heat efficiencies for two explosives[18] are compared to those for 50% porous thermite. The >100% heat efficiency for the thermite indicates that some of the work associated with shock compression is converted to heat along with all of the chemical energy.

TABLE 2. WORK AND HEAT EFFICIENCIES

	RDX[18]	$2Al/NH_4NO_3$[18]	$2Al/Fe_2O_3$
Work Efficiency (%)	98	75	< 0
Heat Efficiency (%)	2	25	> 100
Postshock Temperature (K)	374	1694	4600

SHOCK TEMPERATURES

The temperatures along an isentrope are determined by integrating the differential equation:

$$TdS = C_V dT + \left(\frac{\partial P}{\partial T}\right)_V TdV \qquad (13)$$

with $dS=0$. For an isentrope centered on a reference state with temperature T_{ref} and volume V_{ref}, the temperature is

$$T_S = T_{ref} \exp\left[\int_V^{V_{ref}} \frac{\gamma}{V} dv\right] \qquad (14)$$

The temperature on the Hugoniot can be found by integrating eq. (13) and $dE=TdS-PdV$ setting $dV=0$:

$$\int_{T_S}^{T_H} C_V dT = \frac{V}{\gamma}(P_H - P_S) \qquad (15)$$

These equations can be solved in simple form for the shock temperature if C_V and γ/V are both assumed to be constant:

$$T_H = \frac{1}{C_V}\frac{V_0}{\gamma_0}(P_H - P_S) + T_{ref} \exp\left[\frac{\gamma_0}{V_0}(V_{ref} - V)\right] \qquad (16)$$

Postshock temperatures can be determined from the equation:

$$T_f = T_H \exp[\frac{\gamma_0}{V_0}(V-V_f)] \qquad (17)$$

Fig. 5 depicts calculated temperatures for both reactant and product of 50% porous thermite.

FIGURE 5. CALCULATED TEMPERATURES FOR REACTANT AND PRODUCT HUGONIOTS OF 50% POROUS THERMITE.

Time-resolved shock temperature measurements have recently been performed on porous thermite mixtures.[14] The results for two experiments are listed in Table 3. The measured temperatures are much higher that those calculated for the reactants, but are also significantly less than those calculated for the products, implying that the reaction was not complete. A first-order estimate of the amount of reaction can be made by linearly interpolating between the two temperature calculations. A more accurate determination of the amount of reaction would require that phase transitions and variable specific heats are taken into account, an effort beyond the scope of the present paper.

TABLE 3. SHOCK TEMPERATURES IN POROUS THERMITE

Experiment #	2274	2279
Porosity (%)	48	49
P_H (GPa)	4.4-4.7	3.9-4.1
Measured T_H (K)	3000-3300	2800-2900
Reactant T_H (K)	980	910
Product T_H (K)	4270	4200
Percent Reacted (%)	61-70	58-61

EFFECT OF VOLATILES

Thus far all calculations have been based on the assumption that there are no volatile impurities in the mixed powders. Since many of the reactive powders that have been examined experimentally have small grain sizes (approximately 1 μm), and consequently large specific surface areas (about 10^4 cm^2/g for smooth spherical particles), the possibility of a significant amount of surface-adsorbed water and other volatile impurities cannot be ignored. A monolayer of water adsorbed on such a powder (about 10^{15} molecules/cm^2) amounts to about 0.1% of the mass. Significant surface roughness or grain aspect ratios will give rise to even greater surface areas and amounts of impurities.

When the mass of a volatile impurity is a small fraction of the total mass, the resulting Hugoniot can be calculated by determining a first-order correction to the Hugoniot of the pure powder. The family of equations of state of the mixture for various impurity mass fractions (m) can be expressed as the specific volume as a function of the intrinsic variables and of m:

$$V(P,T,m) = V^{o}(P,T) + m[V'(P,T) - V^{o}(P,T)] \qquad (18)$$

where V^{o} and V' are the specific volumes of the pure phase and the impurity, respectively. The family of Hugoniots can be written similarly:

$$V_{H}(P,m) = V^{o}(P,T_{H}) + m[V'(P,T_{H}) - V^{o}(P,T_{H})] \qquad (19)$$

where the shock temperature depends on m. The partial derivative can be written as

$$\left(\frac{\partial V}{\partial m}\right)_{P} = \left(\frac{\partial V^{o}}{\partial T_{H}}\right)_{P}\left(\frac{\partial T_{H}}{\partial m}\right)_{P} + V'(P,T_{H}) - V^{o}(P,T_{H})$$

$$+ \text{ higher order terms } O(m) \qquad (20)$$

This derivative can be inserted into the first order expansion

$$V_{H}(P,m) = V^{o}(P) + m\left(\frac{\partial V}{\partial m}\right)_{P} \qquad (21)$$

to get the correction to the mixed Hugoniot. The following approximation can be made:

$$m\left(\frac{\partial T_{H}}{\partial m}\right)_{P} \simeq T_{H}^{o} - T_{H} = \Delta H/C_{V} \simeq mQ/C_{V} \qquad (22)$$

where T_{H}^{o} is the shock temperature of the pure mixture, Q is the heat of reaction, and C_{V} is the specific heat of the total mixture (including the impurity), which can be approximated by that for the pure mixture for small m.

We can also make the approximation:

$$\left(\frac{\partial V^{o}}{\partial T_{H}}\right)_{P} = V\alpha = \gamma C_{V}/K_{T} \simeq \gamma C_{V}/K_{S} \simeq \gamma C_{V}/(K_{0S}+PK'_{0S}) \qquad (23)$$

and for $V' >> V^{o}$ we can write

$$V_{H}(P,m) \simeq (1-m)V_{H}^{o}(P) +$$

$$m[Q\gamma/(K_{0S}+PK'_{0S}) + V'(P,T_{H})] \qquad (24)$$

Eq. (24) can be solved for water-bearing thermite by using the previously-determined thermite Hugoniots for $V_{H}^{o}(P)$ and the Bakanova et. al[19] equation of state of water for $V'(P,T_{H})$, which is a fit to porous ice Hugoniot data with final (P,T) states in the same range as those of interest here.

The resulting family of Hugoniots is plotted in Figs. 6 and 7.

FIGURE 6. FAMILY OF HUGONIOTS FOR 50% POROUS THERMITE CONTAINING VARIOUS AMOUNTS OF WATER.

FIGURE 7. PRESSURE-PARTICLE VELOCITY DIAGRAMS FOR WATER-BEARING POROUS THERMITE HUGONIOTS IN FIGURE 6.

From Fig. 6 it can be seen that, for certain combinations of initial porosity and volatile mass fraction, a Rayleigh line can be found that is tangent to the product Hugoniot. This fact indicates that a sustained detonation is thermochemically possible under those circumstances. As shown earlier for porous dry thermite, the shock-induced reaction can be described as an overdriven detonation that will decay when unsupported, because the product Hugoniot is always steeper than the Rayleigh line. By contrast, the Rayleigh line is steeper than the water-bearing thermite product Hugoniot below a given pressure. If this pressure is greater than that required for rapid shock-induced release of chemical energy, the sustained detonation will take place.

The purpose of Fig. 7 is to show that measurements in the P-u plane are highly sensitive to volatile content, and attempts to determine amounts of reaction from pressure or particle velocity measurments are subject to very large errors unless the volatile content is precisely known. On the other hand, the temperature is influenced by the impurity, to first order, only to the extent that the heat of reaction is reduced by an amount proportional to the mass fraction, as noted in eq. (22). Thus, only shock temperature measurements can provide an accurate determination of the amount of reaction that takes place under shock loading.

GEOCHEMICAL DETONATIONS

The observation of rapid shock-induced solid state chemical reactions, combined with the fact that small amounts of water or other volatiles can control the ability of a reactive mixture to detonate, has important implications for earth science. Kuznetsov[20] outlined a set of criteria required for a detonation to take place due to a single-component phase transformation. These same criteria are met by a supercooled, volatile-saturated magma.

The possibility of volcanic detonations has been invoked throughout history to explain structures now known to be impact craters.[21] Once the importance of hypervelocity impact was recognized, arguments invoking natural detonations have been dismissed, and volcanic eruptions are now considered to be decompression events in all cases. However, there is still significant conroversy surrounding the origin of certain cryptoexplosion structures on earth, and explanations based on internally-generated shock waves remain in the literature.[22] A small number of workers believe that the shock features in quartz found at the Cretaceous-Tertiary boundary are volanically-generated,[23] and it has even been suggested that the May, 1980 eruption of Mt. St. Helens was triggered by a natural detonation.[24] These hypotheses have largely been ignored because a reasonable physicochemical mechanism for volcanically-generated shock waves has never been proposed.

To determine whether such a detonation is thermochemically possible, the product Hugoniot for a supercooled, water-saturated magma was calculated in a manner similar to that for the thermite. For simplicity, the magma was taken to consist of pure albite ($NaAlSi_3O_8$). The extensive thermodynamic data on the albite-water system at high temperatures and pressures were used.[25-27] The product Hugoniot for water-saturated albite melt initially at $P=0.1$ GPa and $T=873$ K is plotted in Fig. 8. If a Chapman-Jouget detonation takes place, the peak pressure is only about 0.6 GPa. Since the product Hugoniot is dominated by the equation of state of water, it is unlikely that significantly higher shock pressures could be attained with more realistic melt compositions. The calculated detonation pressure is also not a strong function of the initial state.

FIGURE 8. CALCULATED HUGONIOTS FOR REACTANT AND PRODUCT OF WATER-SATURATED UNDERCOOLED ALBITE MELT. RAYLEIGH LINE INDICATES STEADY CHAPMAN-JOUGET DETONATION.

According to these calculations, the pressures required to generate planar features diagnostic of shock deformation in quartz (10 GPa)[28] cannot be reached in a geochemical detonation, so an internal cause for the Cretaceous-Tertiary event can be eliminated. On the other hand, such detonations cannot be precluded on the basis of thermochemistry, and the implications for cryptoexplosion structures and explosive volcanism cannot immediately be dismissed.

SUMMARY

A thermochemical model has been applied to shock-induced chemical reactions in porous solids. When the products consist of condensed phases only, the reaction front is thermochemically identical to an overdriven detonation. To distinguish this type of reaction from a conventional explosive detonation, the term "heat detonation" has been applied. This term is also descriptive in the sense that the chemical energy is converted mostly to heat rather than work, as is the case for detonations in explosives. The "heat efficiency" was defined by analogy to work efficiency in an attempt to quantify this difference.

Conventional Hugoniot, pressure and particle velocity measurements are insensitive to shock-induced chemical reactions when the products do not include vapor phases. The experimental technique most sensitive to such reactions is the measurement of shock temperature. The addition of a volatile impurity has a disproportionately large effect on the Hugoniot, but a small effect on the temperature, so Hugoniot, pressure and particle velocity measurements are subject to impurity-induced errors, whereas temperature measurements are not. Moreover, a sustained detonation can become thermochemically possible when reactive powders contain a volatile component. The same type of mixing model that allows for detonations in volatile-bearing reactive powders predicts the possibility of geochemical detonations in volatile-saturated supercooled silicate melts. This latter possability has significant implications in earth science.

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REFERENCES

1. Graham, R.A., Ballotechnic Materials, Sandia Report SAND88-1055, Aug 1988, Sandia National Laboratories, Albuquerque, New Mexico.

2. Graham, R.A., "Shock Compression of Solids as a Physical-Chemical-Mechanical Process", in Shock Waves in Condensed Matter--1987, Monterey, California, 20-23 July 1987, 11-18.

3. Graham, R.A., Morosin B., Venturini E.L., Boslough, M.B., Carr, M.J. and Williamson, D.L., "Chemical Synthesis Under High Pressure Shock Loading", in Shock Waves in Condensed

Matter, Spokane, Washington, 22-25 July 1985, 693-711.

4. Graham, R.A., Morosin, B., Venturini, E.L. and Carr, M.J., "Materials Modification and Synthesis under High Pressure Shock Compression", Ann. Rev. Mater. Sci., Vol. 16, 1986, p.315.

5. Kovalenko, A.N. and Ivanov, "Physicochemical Transformations of Lead Nitrate in Mixtures with Aluminum Under the Effect of Shocks", Combustion, Explosion and Shock Waves, Vol. 19, 1981, p. 481.

6. Batsanov, S.S., Doronin G.S., Klochdov, S.V. and Teut, A.I., "Synthesis Reactions Behind Shock Fronts", Combustion, Explosion and Shock Waves, Vol. 22, 1986, p. 765.

7. Boslough, M.B. and Graham R.A., "Submicrosecond Shock-Induced Chemical Reactions in Solids: First Real-Time Observations", Chem. Phys. Lett., Vol. 121, No. 4,5, 1985, p. 446.

8. Hornig, H., Kury, J., Simpson, R., Helm, F. and von Holle, W., "Shock Ignition of Pyrotechnic Heat Powders", in Proceedings of the Eleventh International Pyrotechnics Seminar, Vail, Colorado, 7-11 July, 1986, pp. 699-719.

9. Maiden, D.E. and Nutt, G.L., "A Hot-Spot Model for Calculating the Threshold for Shock Initiation of Pyrotechnic Mixtures", in Proceedings of the Eleventh International Pyrotechnics Seminar, Vail, Colorado, 7-11 July, 1986, pp. 813-826.

10. Enikolopyan, N.S., Khzardzhyan A.A., Gasparyan E.E. and Vol'eva, V.B. "Kinetics of Explosive Chemical Reactions in Solids", Academy Nauk, USSR, Procs. Phys. Chem., Vol. 294, 1987, p. 567.

11. Horie, Y. and Kipp, M.E., "Modeling of Shock-Induced Chemical Reactions in Powder Mixtures", J. Appl. Phys., Vol. 63, 1988, p. 5718.

12. Taylor, P.A., Boslough, M.B. and Horie, Y., "Modeling of Shock-Induced Chemistry in Nickel-Aluminum Systems", in Shock Waves in Condensed Matter--1987, Monterey, California, 20-23 July 1987, 395-398.

13. Anderson, O.L., "The Use of Ultrasonic Measurements Under Modest Pressure to Estimate Compression at High Pressure", J. Phys. Chem. Solids, Vol. 27, 1966, p. 547.

14. Boslough, M.B., "A Thermochemical Model for Shock-Induced Reactions (Heat Detonations) in Solids", *J. Chem. Phys.*, 1989, submitted.

15. Duvall, G.E. and Taylor S.M., "Shock Parameters in a Two Component Mixture", *J. Composite Materials*, Vol. 5, 1971, p. 130.

16. Courant, R. and Friedrichs, K.O., *Supersonic Flow and Shock Waves*, Springer-Verlog, New York, New York, 1976, pp. 204-232.

17. Merzhanov, A. "Theory of Gasless Combustion", *Archives of Combustion Processes*, Vol. 5, 1974, p. xx.

18. Fickett, W. and Davis, W.C., *Detonation*, University of California Press, Berkeley, California, 1979, pp. 35-39.

19. Bakanova, A.A., Zubarev, V.N., Sutulov, Yu.N. and Trunin, R.F., "Thermodynamic Properties of Water at High Pressures and Temperatures", *Sov. Phys.-JETP*, Vol. 41, 1976, p. 544.

20. Kuznetsov, N.M., "Detonation and Gas-Dynamic Discontinuities in Phase Transitions of Metastable Substances", *Sov. Phys.-JETP*, Vol. 22, 1966, p. 1047.

21. Melosh, H.J., *Impact Cratering a Geologic Process*, Oxford University Press, New York, New York, 1989, pp. 3-13.

22. Lilly, P.A., "Shock Metamorphism in the Vredefort Collar: Evidence for Internal Shock Sources", *J. Geophys. Res.*, Vol. 86, No. B11, 1981, p. 10689.

23. Carter, N.L., Officer, C.B., Chesner, C.A. and Rose, W.I., "Dynamic Deformation of Volcanic Ejecta from the Toba Caldera: Possible Relevance to Cretaceous/Tertiary Boundary Phenomena", *Geology*, Vol. 14, 1986, p. 380.

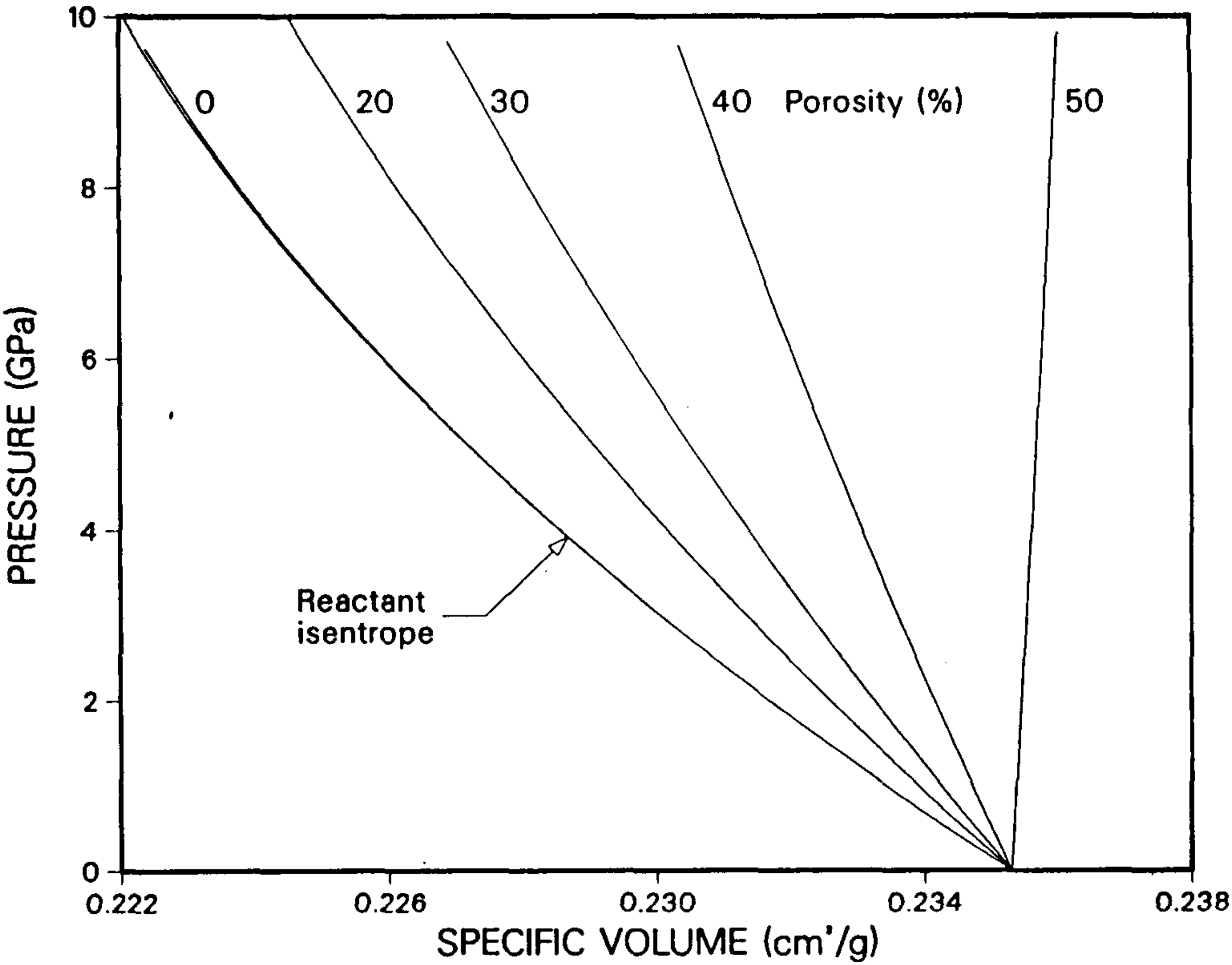
24. Rice, A., "Shocked Minerals at the K/T Boundary: Explosive Volcanism as a Source", *Phys. Earth Planet. Interiors*, Vol. 48, 1987, p. 167.

25. Burnham, C.W., Holloway, J.R. and Davis, N.F., *Thermodyamic Properties of Water to 1,000 °C and 10,000 Bars*, Geological Society of America, Boulder, Colorado, 1969, 96 pp.

26. Burnham, C.W. and Davis, N.F., "The Role of H_2O in Silicate Melts I. P-V-T Relations in the System $NaAlSi_3O_8$-H_2O to 10 Kilobars and 1000°C", *Am. J. Sci.*, Vol. 270, 1971, p. 54.

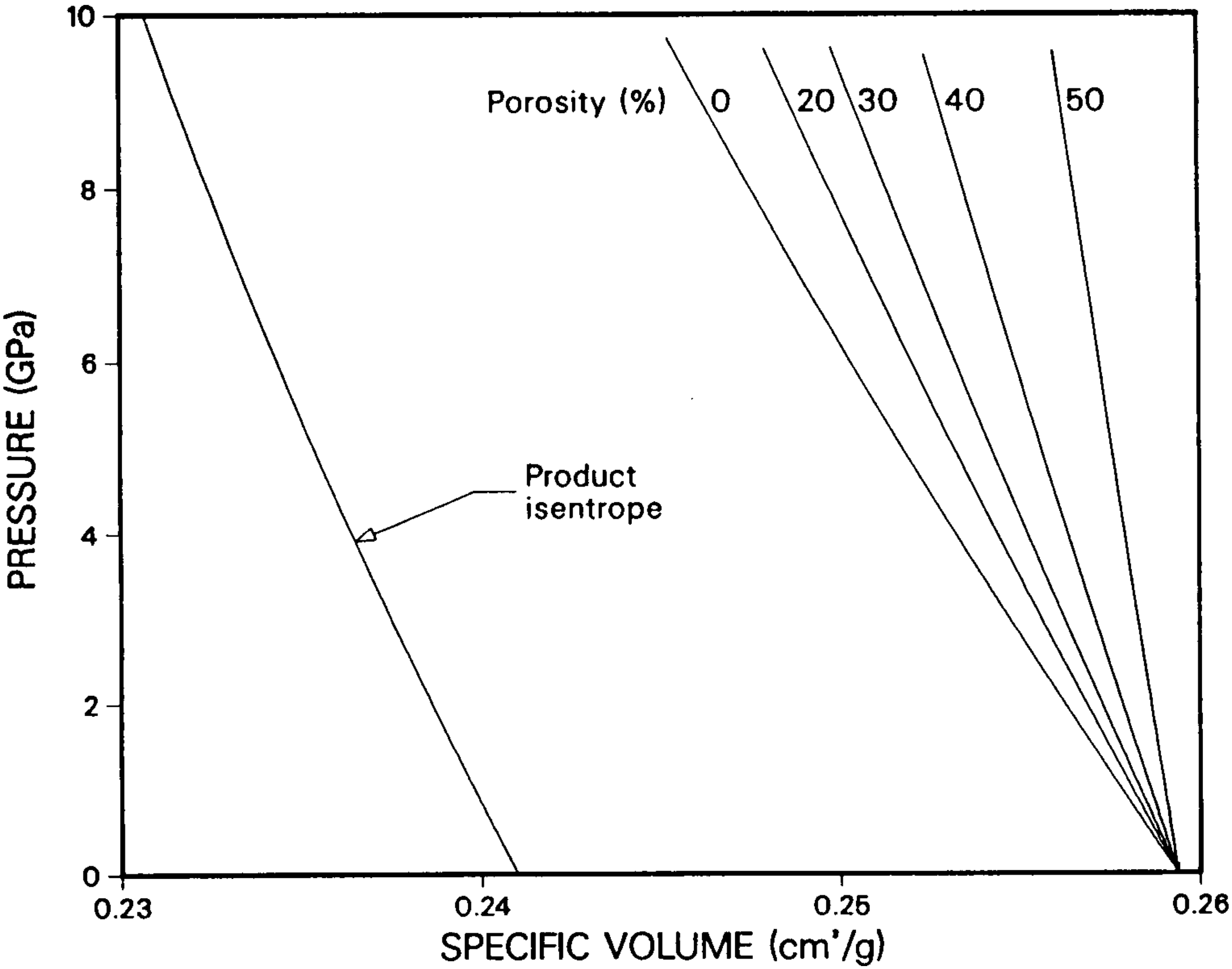
27. Burnham, C.W. and Davis, N.F., "The Role of H_2O in Silicate Melts II. Thermodynamic and Phase Relations in the System $NaAlSi_3O_8$-H_2O to 10 Kilobars , 700° to $1100^\circ C$", Am. J. Sci., Vol. 274, 1974, p. 902.

28. Horz, F., "Statistical Measurements of Deformation Structures and Refractive Indices in Experimentally Shock Loaded Quartz", in Shock Metamorphism of Natural Materials, Mono Book Corp., Baltimore, Maryland, pp.243-253.



10
8
6
4
2
0
PRESSURE (GPa)
0.222
0.226
0.230
0.234
0.238
SPECIFIC VOLUME (cm³/g)
0
20
30
40
Porosity (%)
50
Reactant isentrope

Fig. 1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2
0
PRESSURE (GPa)
0.23
0.24
0.25
0.26
SPECIFIC VOLUME (cm³/g)
Porosity (%)
0
20
30
40
50
Product isentrope

Fig. 2

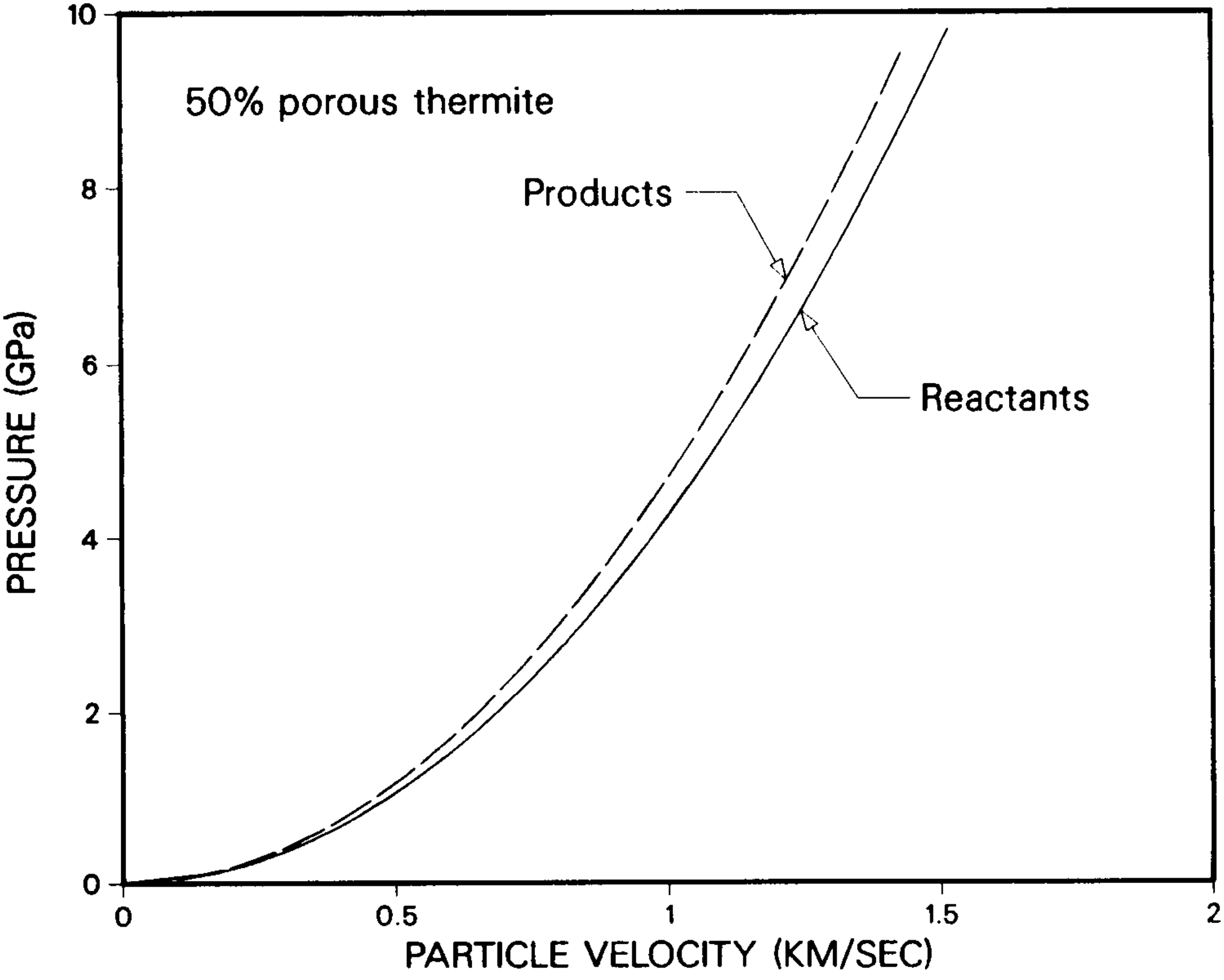

50% porous thermite
Products
Reactants
10
8
6
4
2
0
PRESSURE (GPa)
0
0.5
1
1.5
2
PARTICLE VELOCITY (KM/SEC)

Fig. 3

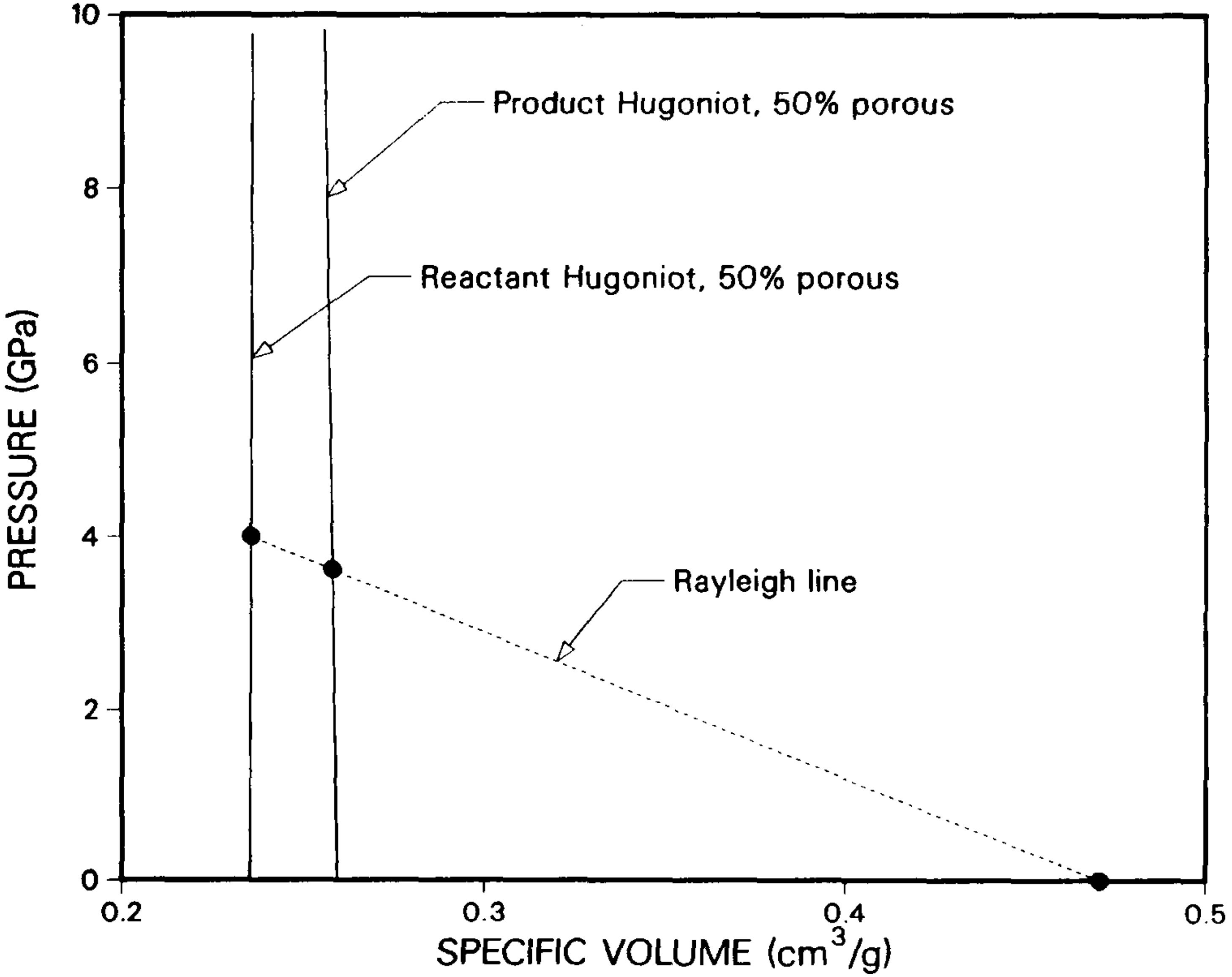

10
8
6
4
2
0
PRESSURE (GPa)
0.2
0.3
0.4
0.5
SPECIFIC VOLUME (cm^3/g)
Product Hugoniot, 50% porous
Reactant Hugoniot, 50% porous
Rayleigh line

Fig 4

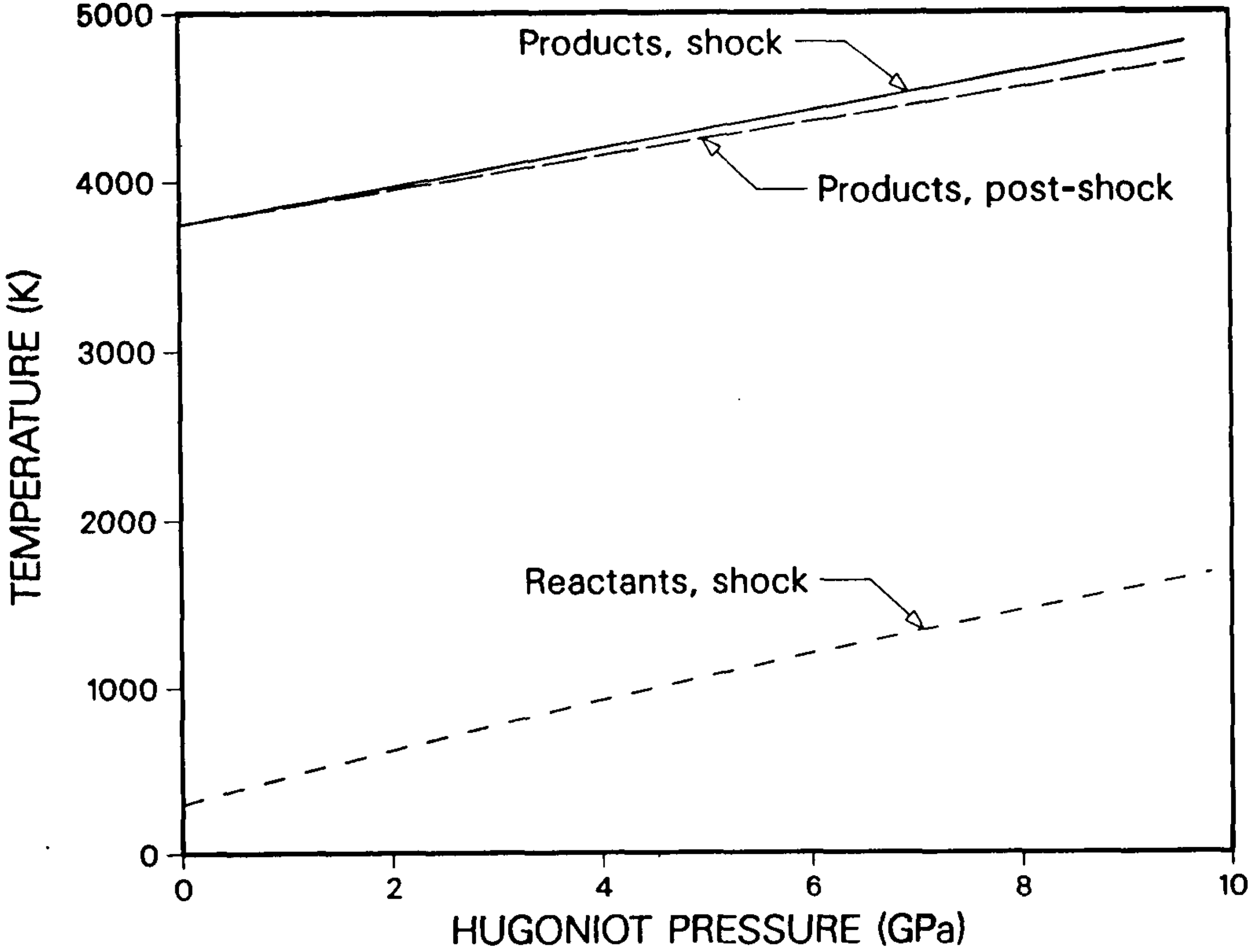

5000
4000
3000
2000
1000
0
TEMPERATURE (K)
0
2
4
6
8
10
HUGONIOT PRESSURE (GPa)
Products, shock
Products, post-shock
Reactants, shock

Fig.5

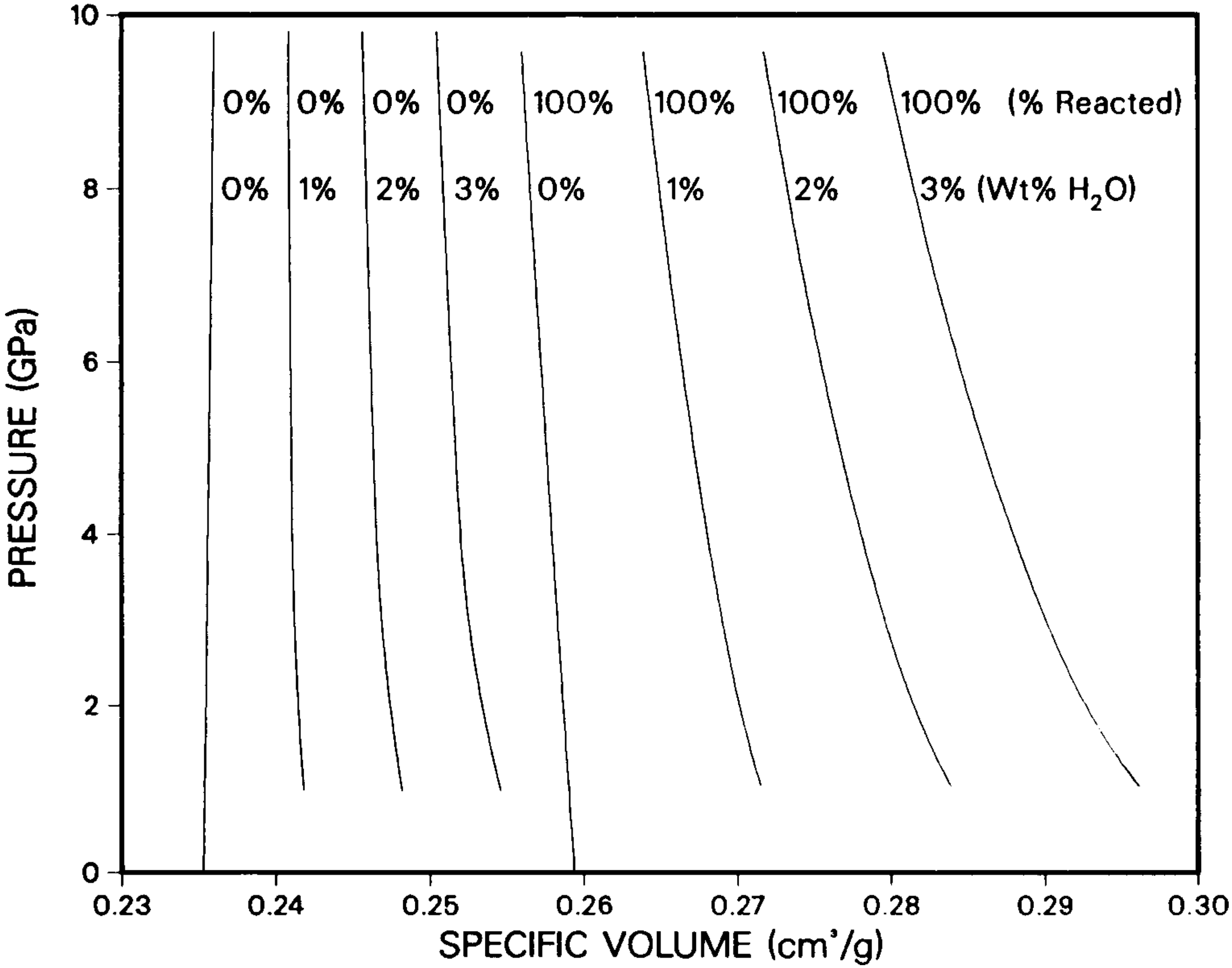

0%
0%
0%
0%
100%
100%
100%
100% (% Reacted)
0%
1%
2%
3%
0%
1%
2%
3% (Wt% H_2O)
PRESSURE (GPa)
0
2
4
6
8
10
0.23
0.24
0.25
0.26
0.27
0.28
0.29
0.30
SPECIFIC VOLUME (cm^3/g)

Fig. 6

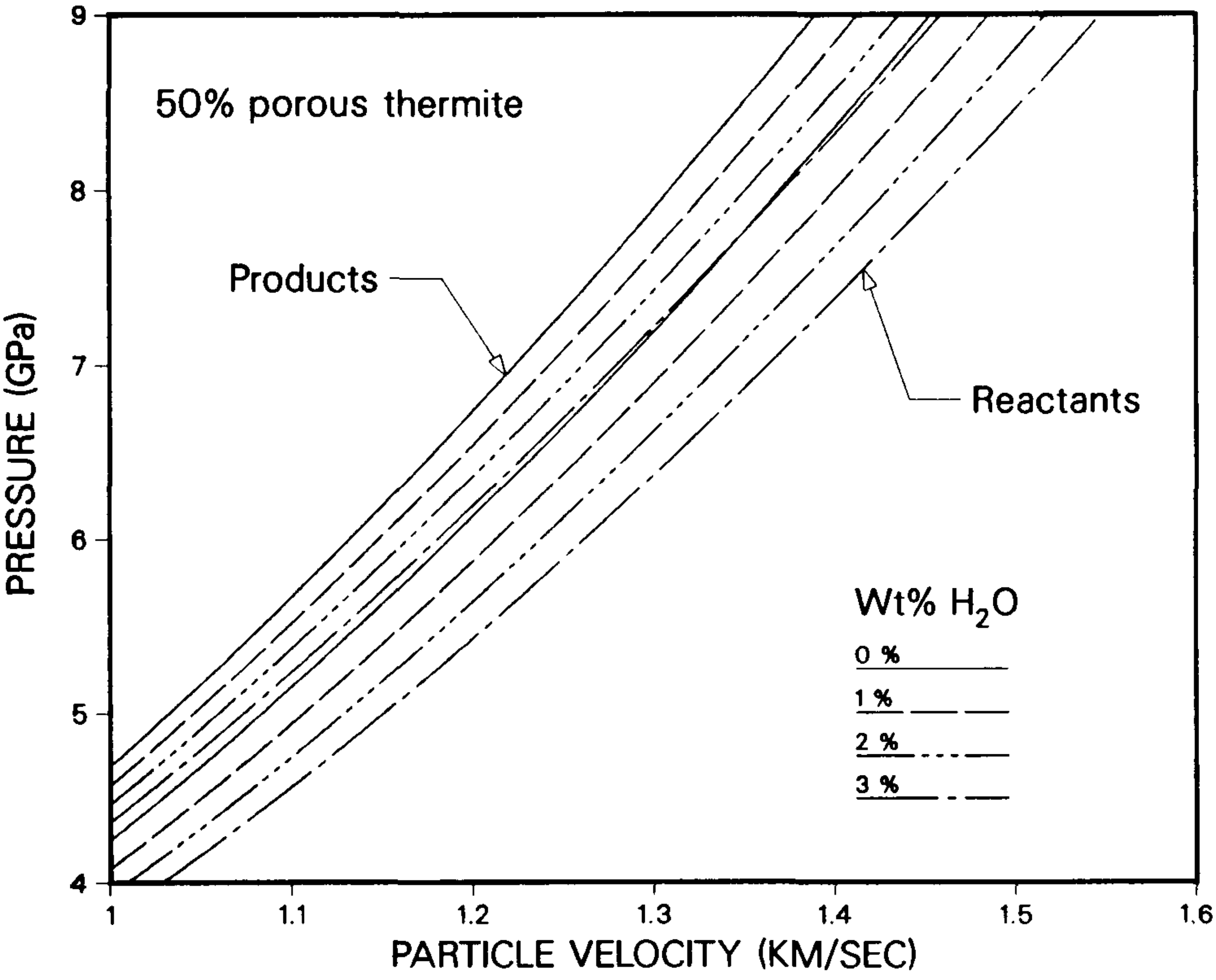
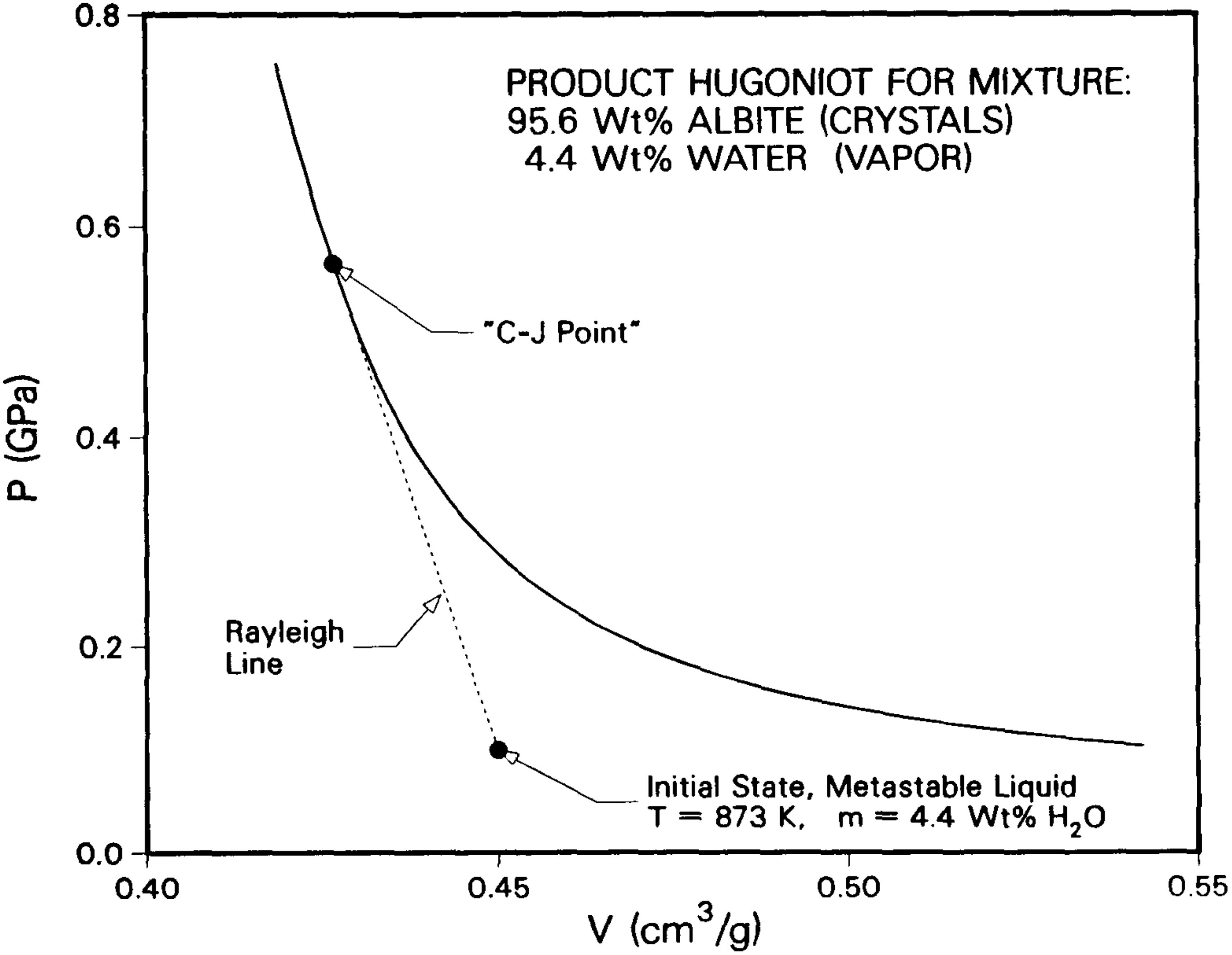

50% porous thermite
Products
Reactants
Wt% H_2O
0 %
1 %
2 %
3 %
PRESSURE (GPa)
9
8
7
6
5
4
1
1.1
1.2
1.3
1.4
1.5
1.6
PARTICLE VELOCITY (KM/SEC)

Fig. 7



PRODUCT HUGONIOT FOR MIXTURE:
95.6 Wt% ALBITE (CRYSTALS)
4.4 Wt% WATER (VAPOR)
"C-J Point"
Rayleigh Line
Initial State, Metastable Liquid
T = 873 K, m = 4.4 Wt% H_2O
P (GPa)
0.8
0.6
0.4
0.2
0.0
0.40
0.45
0.50
0.55
V (cm^3/g)

Fig. 8