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Calculation of Hugoniot Values from Atomic Properties

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Calculation of Hugoniot Values from Atomic Properties

Abstract

A relatively simple equation is presented for use in calculating the Hugoniot values of any condensed element from its atomic weight, atomic radius, and density. Calculations from the equation are compared with data for many elements, and a discussion of the development and utility of the equation is included. The equation also appears to be useful for the gaseous elements when they are in condensed phases.

Introduction

Considerable equipment and instrumentation are required to measure accurately the velocity of a shock produced in a condensed material by a high-velocity impacting plate, and it would be very useful to have a simple calculational method to obtain reasonably accurate Hugoniot values. The basic description of this shock phenomenon for a material initially at rest is given by the relationship

$$(P - P_0) = \rho U_s U_p \quad (1)$$

in which, with three variables (pressure P , shock velocity U_s , and particle velocity U_p), two are measured to allow calculation of the third.^{1,2} The initial density is ρ .

In molecular dynamics studies³⁻⁶ of the effects of shock waves in condensed substances, a Hugoniot "experiment" was conducted on the computer.⁴ A flying plate was propelled mathematically with increasing velocity increments into an acceptor material; the velocity of the induced shock wave was then calculated. Comparison of these results in simulated organic substances with data for organic plastics and explosives (see Fig. 1) showed a very good correlation, which was corroborated in an independent study.⁷ Extrapolation of the calculated values to $P = 0$ gave a good approximation of representative sonic velocities c .

Subsequently, calculations of $U_s = f(P)$ in materials with properties representative of aluminum, iron, and tungsten were completed,⁸ and with a reasonable normalization they matched well the Hugoniot data for these materials over a range of P of about 40-460 GPa, as shown in Table 1 and Fig. 2.

Figure 1. Comparison of computer-calculated Hugoniot curves with experimental data for organic plastics and high explosives.

Figure 2. Computer-calculated Hugoniot curves for tungsten, lead, and aluminum.

Table 1. Computer calculated Hugoniot results for Fe.

	Experimental		Calculated		Max. error	Min. error
	U_p (km/s)	U_s (km/s) ^a	P (GPa)	U_s		
1		5.404	42.5	5.826	± 0.65	± 0.32
3		8.74	206.0	8.74 ^b	± 1.46	± 0.73
5		11.812	464.0	10.502	± 2.12	± 1.05

$$^a U_s = 3.635 + 1.802 U_p - 0.0333 U_p^2$$

^b Adjusted.

The maximum and minimum errors are based on the possible errors in the calculation time where the maximum error is $\pm 1 \times 10^{-14}$ and the minimum error is $\pm 0.5 \times 10^{-14}$.

Calculations and Discussion

Derivation of the Equations

The foregoing results suggested that satisfactory Hugoniot values should be calculable from a few basic atomic properties, and a simple equation based on these properties and an exponential $f(P)$ was found that provided a good approximation of these values for the ten diverse elements in Table 2. At $P > 40$ GPa, particularly, the values were given precisely over large ranges of P . Again, at $P = 0$ the sonic velocities were approximated.

This equation,

$$U_s = f(P)(r_A/\omega_A)^{1/4} \rho^{-0.1} \quad (2)$$

where

$$f(P) = (0.42P + 10.3P^{1/2} + 12) \quad (3)$$

works well for the elements we reviewed in Groups IB, IIB, IVB, VB, VIB, IIA, and VIII. Here r_A

is atomic radius and ω_A is atomic weight as taken from a periodic table.⁹ The results indicate that Eq. (2) may also provide satisfactory values for VIIb elements and first-order values or better for any condensed element. Representative calculated and experimental results are compared in Table 2, and values for beryllium, nickel, and gold are plotted in Fig. 3.

The $f(P)$ curve of Eq. (3) is given in Fig. 4. It is empirically derived from an experimental data set,¹⁰ but it could be calculated from a selected Morse (or similar) potential equation. The point of this discussion is that the primary properties that determine the shock values for all elements in this study are simply the atomic weight, the atomic radius, and the initial density. One simple $f(P)$ equation serves well for the 22 elements of Tables 2 and 3.

A small change in the lower segment of the $f(P)$ curve, also shown in Fig. 4, improves the fit

Table 2. U_s values in mm/ μ s calculated for ten elements with Eq. (2) and compared with experimental data.

Element	20 GPa		60 GPa		160 GPa	
	Data	Calc.	Data	Calc.	Data	Calc.
Beryllium	9.50	9.32	11.2	11.3	15.0	14.4
Titanium	5.57	6.01	6.80	7.29	9.15	9.26
Iron	5.00	5.27	5.90	6.38	8.00	8.11
Nickel	5.27	5.12	6.20	6.20	8.05	7.88
Silver	4.15	4.49	5.10	5.44	6.70	6.91
Tantalum	3.86	3.80	4.46	4.60	5.54	5.85
Tungsten	4.31	3.68	4.76	4.46	5.90	5.66
Platinum	3.88	3.57	4.60	4.33	5.73	5.50
Gold	3.58	3.65	4.20	4.42	5.40	5.61
Uranium	3.00	3.43	3.80	4.16	—	5.28

Figure 3. U_s vs P curves for beryllium, nickel, and gold calculated with Eq. (2).

Figure 4. The $f(P)$ curve of Eq. (3) with the small change noted at the low end from Eq. (4).

Table 3. Comparison of the sonic velocities extrapolated from the data in Ref. 11 and those calculated for the elements in this study by setting $P = 0$ in Eq. (2) and making the correction for relative electron density where appropriate.

Element	Sonic velocities (mm/ μ s)		
	Data extrapolation	Measured	Calculated ($P = 0$)
Lithium ^a	4.65	—	7.12 4.40 ^b
Beryllium	8.00	12.9	6.70
Carbon	—	—	5.81
Nitrogen ^a	—	1.50	5.02
Oxygen ^a	—	2.00	4.67
Sodium ^a	2.63	—	5.22 3.23 ^b
Magnesium ^a	4.49	5.77	5.75
Aluminum	5.04	6.42	5.21
Potassium ^a	1.97	—	4.88 3.02 ^b
Titanium	5.22 (4.88)	—	4.32
Iron	3.57	5.85	3.78
Nickel	4.60	—	3.68
Copper	3.94	4.88	3.63
Zinc	3.01	—	3.76
Silver	3.23	3.65	3.22
Tantalum	3.41	—	2.73
Tungsten	4.03	5.22	2.64
Platinum	3.60	3.26	2.57
Gold	3.06	3.24	2.62
Lead ^a	2.05	—	2.31 1.43 ^b
Bismuth ^a	1.83	—	2.32 1.44 ^b
Uranium	2.49	2.47	2.47

^a Corrected by the factor for low relative electron density.

^b Using the $f(P)$ from Eq. (6).

for some of the elements in Groups IIA, IIIA, IB, and IIB. The equation for this segment is

$$f(P) = (12.4P - 0.37P^{1/2} + 12) \quad (4)$$

A comparison of shock values for magnesium, aluminum, copper, and zinc calculated with $f(P)$ of Eq. (4) is made in Table 4, and the values for magnesium, aluminum, and copper are plotted in Fig. 5.

U_s is a relatively weak function of P , as had been observed earlier.¹¹ The general shape of the $f(P)$ curve from Eq. (3) (see Fig. 4) compares favorably with that seen at the sonic, thermal, and shock "barriers," as shown in Fig. 6.¹¹ Also, from the Hugoniot data for one element near the center of the periodic table, such as iron or nickel, an $f(P)$ curve can be derived to use with all the element groups reviewed herein.

Correction for Large Atomic Volume

The only elements in the list of 22 discussed here for which the calculated values vary (high) more than about 8% at lower pressures (<40 GPa) are the ones with very large atomic volumes. More precisely, these are the elements with very small average electron densities (atomic number/atomic volume) relative to their neighbors in the center of their atomic table rows. Specifically, these are the Group IA elements listed (lithium, potassium, sodium), lead and bismuth, and the liquefied gases, N_2 and O_2 . Zinc was a little low in relative electron density, and it had calculated values of U_s that were a little high.

It is simple to correct for this factor, because for all of these elements the calculated U_s values are a factor of about 1.15 high at 10 GPa and nearly correct at 70 GPa. A linear empirical correction based on Eq. (5) brings the values for these

Figure 5. Comparison of shock velocities calculated with Eq. (2) and the $f(P)$ of Eq. (4) with data for magnesium, aluminum, and copper.

elements into closer agreement with the data at <60 GPa:

$$k = 0.4P + 0.8 \quad (5)$$

Here k is the U_s correction factor, and P is the pressure in Mb. Table 5 compares the Group IA and the lead and bismuth values before and after correction. Comparison curves for lithium and potassium are given in Fig. 7 and for lead and bismuth in Fig. 8. These are some of the elements for which one would expect the shock velocity to be most difficult to calculate by this method, yet the results are reasonable.

Table 4. Comparison of Hugoniot values calculated with Eq. (2) with $f(P)$ of Eq. (4), for $P = 10$ to 160 GPa.

Element	P (GPa)											
	10		20		40		60		100		160	
	Data ^a	Calc. ^a	Data	Calc.	Data	Calc.	Data	Calc.	Data	Calc.	Data	Calc.
Magnesium	6.37	6.29	6.97	6.86	8.17	8.02	9.25	9.17	11.1	10.9	13.3	12.3
Aluminum	5.80	5.70	6.50	6.22	7.26	7.27	8.53	8.32	10.0	9.88	11.7	11.2
Copper	4.27	3.97	4.55	4.33	5.17	5.06	5.70	5.79	6.52	6.88	7.50	7.78
Zinc	3.74	4.11	4.10	4.49	4.82	5.24	5.55	5.99	6.50	7.12	7.72	8.05

^a All U_s values are given as mm/μs.

Figure 6. Representation of the sonic, thermal, and shock "barriers" as related to sonic flow, hyper-sonic flow, and detonation velocities.

Figure 7. Comparison of Hugoniot curves calculated with Eq. (2) using the correction for relative electron density with data for lithium and potassium.

Table 5. Comparison of the data, the calculated U_s values, and the corrected values for the elements with large atomic volumes.

Element	20			40			60		
	Data ^a	Calc. ^a	Corr. ^a	Data	Calc.	Corr.	Data	Calc.	Corr.
Lithium	9.00	10.5	9.05	11.7	12.3	11.2	13.5	14.0	13.5
Sodium	6.50	7.70	6.64	8.60	9.00	8.20	10.3	10.3	9.90
Potassium	6.26	7.20	6.21	8.23	8.41	7.65	9.83	9.62	9.25
Lead	2.93	3.40	2.93	3.54	3.98	3.62	3.78	4.55	4.40
Bismuth	2.76	3.42	2.95	3.60	4.00	3.64	4.25	4.58	4.40

^a All U_s values are given as mm/μs.

Figure 8. Comparison of Hugoniot calculated with Eq. (2) using the correction for relative electron density with data for lead and bismuth.

An alternative method that can improve still further the data fit for the elements with relatively small average electron densities, particularly at lower pressures (<40 GPa), is to select one element in a group as the $f(P)$ model for that group.

Equation (6) is derived from averaged values of these low electron density elements. Table 6 shows representative shock velocity values for lithium, sodium, potassium, lead, and bismuth based on this equation:

$$f(P) = (3.7P + 12.1P^{1/2} + 6) \quad (6)$$

The values for lithium, sodium, and bismuth are plotted in Fig. 9.

It appears that at the lower shock pressures (<60 GPa) the interatomic potentials on these

larger atoms induce the atoms to move more rapidly under shock loading without deforming too much and without absorbing too much energy. However, at the higher pressures these relatively weak interatomic repulsive forces are rapidly overcome, and the higher repulsive forces of the inner core electrons become dominant, so that the electron density correction is unnecessary.

All of these second-order effects resulting from electronic structure appear to become less important with increasing pressure, and when $P > 60$ GPa the shock velocity curves become more nearly parallel and in some cases even tend to coalesce.

Our molecular dynamics calculations indicate that many chemical bonds would be broken by shock waves of high intensity. The experimental

Table 6. Comparison of the data and the calculated values of U_s using Eq. (6) for the elements with large atomic volumes.

Element	P (GPa)									
	10		20		40		60		100	
	Data ^a	Calc. ^a	Data	Calc.	Data	Calc.	Data	Calc.	Data	Calc.
Lithium	7.40	7.47	9.00	8.89	11.7	11.1	13.5	12.9	15.5	16.0
Sodium	4.95	5.49	6.50	6.52	8.60	8.14	10.3	9.46	12.7	11.7
Potassium	4.70	5.13	6.26	6.10	8.23	7.60	9.83	8.84	12.5	11.0
Lead	2.50	2.43	2.93	2.89	3.54	3.60	3.78	4.18	4.80	5.18
Bismuth	2.20	2.44	2.76	2.90	3.60	3.62	4.25	4.21	—	5.21

^a All U_s values are given as mm/μs.

Figure 9. Comparison of Hugoniot curves calculated with Eq. (2) and the $f(P)$ given as Eq. (6).

work of Graham¹² with shocked plastics, Dremin and Breusov¹³ with many organics, the experimental¹⁴ and theoretical studies¹⁵ of Dodson et al., and the spectroscopic investigation of shock-induced reactivity in nitromethane by Granholm and Duval¹⁶ and in benzene by Holmes et al.¹⁷ add validity to this view of significant chemical bond fracture in highly shocked materials. This could be a factor in the similarity and order in the Hugoniot of the elements at very high shock pressures, because the electronic bonding forces would become less significant.

Correlation with Sonic Velocities

An assemblage of Hugoniot curves where U_s is given as a $f(P)$ (see Fig. 10) shows that the curves cross each other, cross the $P = 0$ axis at different points (as they should, because the $P = 0$ value should denote the approximate sonic velocity), and yet they all begin to rise quite sharply near 40 GPa. As discussed above, the MD calculations gave good values for the sonic velocities of the organic-like lattices, and with general Eqs. (2) and (3), the sonic velocities were approximated for most of the 22 elements considered. However, the sonic velocities for the Group IA

Figure 10. Hugoniot curves prepared from data given in Ref. 9.

elements calculated with Eq. (6) are much closer to the data.¹⁰

The data curves for liquid N_2 and O_2 show shock velocities substantially lower at the lower shock pressures (< 20 GPa) than those calculated by Eq. (2), and the measured sonic velocities are very low—1.5 mm/μs for N_2 and 2.0 for O_2 . Because the initial vibrational velocities of the N_2 and O_2 atoms at 75K and 77K, respectively, where the sonic velocities were measured, would have been much slower than at standard temperature, this should provide a partial explanation for this deviation.

Table 3 compares the calculated sonic velocities [obtained from Eq. (2) with the appropriate $f(P)$ equation by setting $P = 0$] and measured (as extrapolated from the U_s data)¹⁰ sonic velocities of the 22 elements included in this study. The correlation is a good indication of this fundamental relationship between r_A , ω_A , ρ , and U_s , because P is not a factor here.

Shock Velocity Variations with Density

It has been observed in Teflon¹⁰ that an increase in density gives a lower U_s at constant T for a given P (see Fig. 11). Using Eq. (2) to calculate the effect of density changes in Teflon, the results fit quite well with the data, as shown in Table 7 and Fig. 11.

Figure 11. Teflon Hugoniot at densities of 0.78, 0.98, and 2.17 g/cm³ compared with the calculation of density change from 2.17 to 0.98 using Eq. (2).

The equations thus show the opposing effects of density change from porosity and from heavier particles due to larger ω_A , as seen in experiment.

Shock Velocities in Compounds and Mixtures

It is possible that Hugoniot plots for compounds and some mixtures may be calculable

Figure 12. U_s vs P curves for nitromethane and ethanol compared with Hugoniot for C, N₂, and O₂.

when averaged atomic radii, atomic weights, and densities are considered. Obviously, the structure and extent of voids and the effects of other complicating factors such as the extent of heterogeneity, new crystalline forms, coordination bonding, etc., must be analyzed. However, as illustrated in Fig. 12, the Hugoniot for both nitromethane and ethanol fall near the curves for C, N₂, and O₂ (see Table 8). Ethanol, with the lower density and higher atomic fraction of H, has the higher shock velocity for a given P , as we would anticipate from this analysis. There is some evidence that explosives with higher atomic fractions of hydrogen have higher than expected (from a thermodynamic perspective) detonation velocities, i.e., some mac° from mixtures containing hydrazines and hydrazine compounds.

Table 7. Comparison of shock data and calculated values for the shock velocities in Teflon of different densities.

Shock velocity	Density [g/cm ³]			
	2.17	Data ^a 0.98	0.78	Calculated ^b 0.98
2	2.40	2.20	2.80	2.60
6	3.20	3.32	3.72	3.47
10	3.80	4.10	4.42	4.22
20	5.00	5.50	6.00	5.45
30	5.85	—	7.20	6.33
40	6.60	—	—	7.15

^a All U_s values are given in mm/μs.

^b The calculated values are derived by making a density correction to the data at a density of 2.17 g/cm³ with the use of Eq. (2).

Table 8. Comparison of data and calculated shock velocity values for liquid N₂ and O₂.

Element	P (GPa)							
	10 ^a		20 ^a		40		60	
	Data ^b	Calc. ^b	Data	Calc.	Data	Calc.	Data	Calc.
N ₂	5.20	5.66	6.80	6.36	9.05	8.65	10.0	9.89
O ₂	4.42	5.27	5.78	5.92	7.72	8.04	9.16	9.20

^a The U_s values ≤ 20 GPa are corrected for the low relative electron density.

^b All U_s values are given in mm/ μ s.

Table 9. Summary of equations.

Equation No.	Equation	Use
2	$U_s = f(P) (r_A/\omega_A)^{1/4} \rho^{-0.1}$	Basic equation
3	$f(P) = (0.42P + 10.3P^{1/2} + 12)$	General $f(P)$ for all elements shown
4	$f(P) = (12.4P - 0.37P^{1/2} + 12)$	Better fit for few elements at low P
6	$f(P) = (3.7P + 12.1P^{1/2} + 6)$	Better fit to sound velocity c for elements with larger r_A

Comments

Many methods of Hugoniot calculations based on electron band theory^{18,19} and different empirical or semiempirical analyses have been developed. However, the simplicity and apparent wide applicability of the method presented here have some appeal.

With Eq. (2) and the small corrections for $f(P)$ and relative electron densities given in Eqs. (4)–(6)

(see Table 9), the U_s calculations for 22 elements covering the range from lithium to platinum in density, from nickel to potassium in atomic radius, and from 6 rows and 12 element groups in the periodic table can be well correlated to the data. The majority of the values up to 900 GPa are less than 8% different from the data, and most are within the experimental error.

Conclusions

We conclude that the method and equations given can be used to calculate to a substantial accuracy the U_s vs P (Hugoniot) values for all of the condensed elements, including the liquefied gases. Some of the electronic and structural fea-

tures of the elements appear to have decreasing contributions to the shock velocity values as the shock pressures reach higher levels, particularly above 60 GPa.

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