

Improved relationships for the thermodynamic properties of carbon phases at detonation conditions

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Abstract. Accurate volumetric and heat capacity relationships have been developed for graphite and diamond carbon forms for use with the Jaguar thermochemical equilibrium program for the calculation of the detonation properties of explosives. Available experimental thermodynamic properties and Hugoniot values have been analyzed to establish the equations of state for the carbon phases. The diamond-graphite transition curve results from the equality of the chemical potentials of the phases. The resulting relationships are utilized to examine the actual phase behaviour of carbon under shock conditions. The existence of metastable carbon states is established by analyses of Hugoniot data for hydrocarbons and explosives at elevated temperatures and pressures. The accuracy of the resulting relationships is demonstrated by comparisons for several properties, including the Hugoniot behaviour of oxygen-deficient explosives at overdriven conditions.

1. Introduction

Accurate relationships for the thermodynamic properties of carbon phases at elevated temperatures and pressures are necessary to establish the phase boundaries for the equilibrium phases. These relationships are also required for the reliable calculation of the detonation properties of explosives and other molecules with a thermochemical equilibrium program such as Jaguar [1]. In this study equation of state and heat capacity relationships have been established for carbon graphite and diamond phases from available information for the thermodynamic properties of the solid forms. The metastable behavior of diamond and graphite phases has also been investigated from Hugoniot data of hydrocarbons and explosives and incorporated in the thermochemical equilibrium procedures.

2. Model for each carbon phase

The reference state heat capacity for each phase is represented by the following polynomial form:

$$\frac{C_{pi}^o}{R} = \sum_{j=0}^2 e_{ij} \theta^j + \sum_{j=1}^3 f_{ij} \theta^{(-j)} \quad (1)$$

where $\theta = T \text{ (K)}/1000$. For graphite the coefficients of equation (1) were established from the tabulated NIST-JANAF values for temperatures to 6000 K [2]. For diamond the data of Victor [3] for temperatures to 1200 K were utilized, and the heat capacities were assumed to be the same as for diamond at higher temperatures, as suggested by Gustafson [4]. The resulting coefficients of equation 1 for each phase are included in table 1.



The equations of state for the molar volumes of the phases use a temperature- dependent Murnaghan form,

$$V_i(P, T) = V_{0i}(T) \left(1 + \frac{n_i}{B_{0i}(T)} P \right)^{-1/n_i} \quad (2)$$

where the reference volume at approximately zero pressure is represented as

$$V_{0i} = a_i + b_i T + c_i T^2 \quad (3)$$

Gustafson [4] utilized similar relationships for the equation of state of carbon phases, with the bulk modulus at the reference pressure, B_{0i} , independent of temperature. Fried and Howard [5] developed temperature- dependent Murnaghan relationships of an alternate form for carbon phases at elevated temperatures and pressures. Recently, Day [6] studied the carbon graphite-diamond transition curve with equations of state of the form of equation (2). As suggested by Day, the temperature dependences of B_{0i} are represented in this study as approximate linear relationships,

$$B_{0i}(T) = B_{00i} + d_i(T - 298.15) \quad (4)$$

The coefficients of equation (3) were established from the experimental volumetric data of Touloukian and Buyco [7] for temperatures to 3500 K for graphite and to 1660 K for diamond. The resulting extrapolated volumes for diamond at elevated temperatures are consistent with recent theoretical calculations [8]. The values of B_{0i} (298.15) and n_i result from the diamond anvil volumetric data at elevated pressures of Hanfland [9] for graphite and of Occelli [10] for diamond. The values of d_i of equation (4) were estimated by Day [6] from available experimental and theoretical information of the temperature dependences of the reference state bulk modulus for the carbon phases. It can be seen from figures 1 and 2 that the volumes calculated by the approach of this study at elevated pressures have a considerably weaker temperature dependence for graphite than for diamond. As shown in figure 2, the resulting pressure dependence of the volume of diamond at 298 K is consistent with that from the study of Fujushia et al [11]. The values of the parameters of equations (2) –(4) utilized in this study are presented in table 2.

Table 1. Coefficients of equation (1).

	GRAPHITE	DIAMOND
ei0	3.85651	3.62608
ei1	-0.1469	-0.06740
ei2	0.02411	0.015408
fi1	-1.3320	-1.08028
fi2	0.17653	0.034447
fi3	-7.973E-3	9.6127E-3

Table 2. Coefficients of equations (2) - (4).

	GRAPHITE	DIAMOND
ai (cm ³ /mol)	5.2606	3.4063
bi (cm ³ /mol)	1.1745E-4	2.9648E-5
ci (cm ³ /mol)	1.9121E-8	6.5010E-9
di (GPa/K)	-0.007	-0.03
B _{00i} (GPa)	33.8	446
ni	8.9	3.2

3. Diamond-graphite transition curve

The chemical potential of potential of each phase is calculated from the heat capacity and volumetric relationships of this study through the equation

$$\mu_i(P, T) = \mu_i^0(T) + \int_{P^0}^P V_i(T, P) dP|_T \quad (5)$$

The equilibrium diamond-graphite pressure variation with temperature determined by the equality of the chemical potentials for each phase is shown in figure 3. The diamond - graphite transition curve

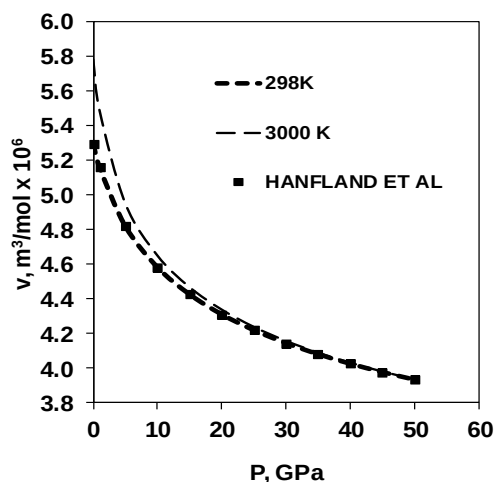


Figure 1. Graphite volumes.

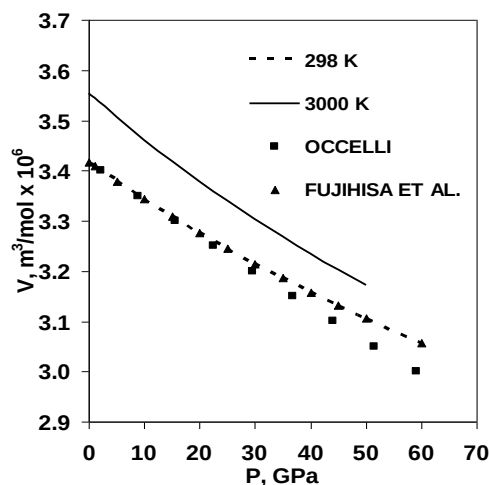


Figure 2. Diamond volumes.

obtained in this study is consistent with the experimental data of Kennedy and Kennedy [12] and with the calculated values of Berman [13]. It can be seen from figure 3 that the phase boundary points resulting from the carbon relationships of Day [6] are somewhat higher at elevated temperatures.

At elevated temperatures (4600–4800 K) diamond and graphite melt to form liquid carbon phases, and the relationship of figure 3 terminates in this range by intersection with the melting pressure-temperature boundary curve [5]. Only meager experimental information are available for the thermodynamic properties of liquid forms of carbon, and the thermodynamic relationships for these phases have not been considered in the present study.

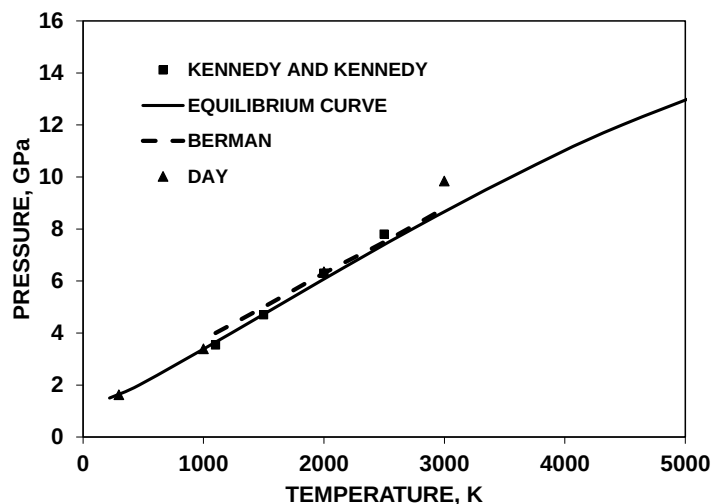


Figure 3. Graphite-diamond transition curve.

4. Hydrocarbon Hugoniot values

The new graphite and diamond thermodynamic relationships were tested with Hugoniot data for several hydrocarbons and hydrocarbon polymers. In figure 4 the results of Jaguar thermochemical calculations for high density polyethylene, which dissociates to methane, hydrogen, and carbon at elevated pressures, are compared with experimental values [14,15] for pressures to 70 GPa. Diamond is indicated to be the appropriate carbon phase for the entire range by the minimization of the Gibbs free energy of the gaseous and solid products. The calculated Hugoniot conditions are seen to be in good agreement with the experimental values for pressures above 20 GPa. At lower pressures calculations with graphite exhibit larger deviations, indicating that polyethylene is not disassociated.

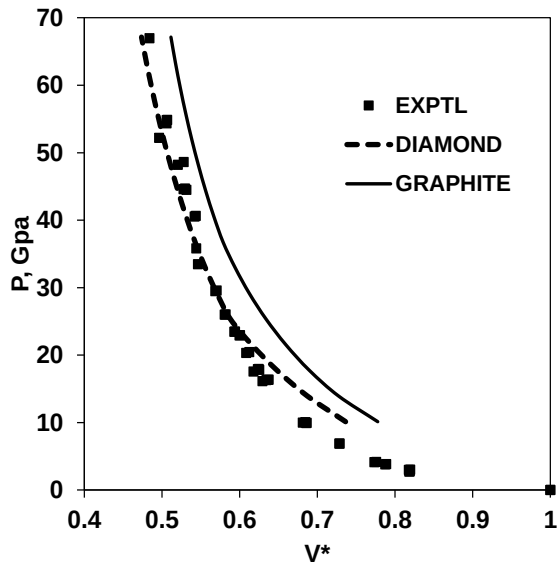


Figure 4. Polyethylene Hugoniot values.

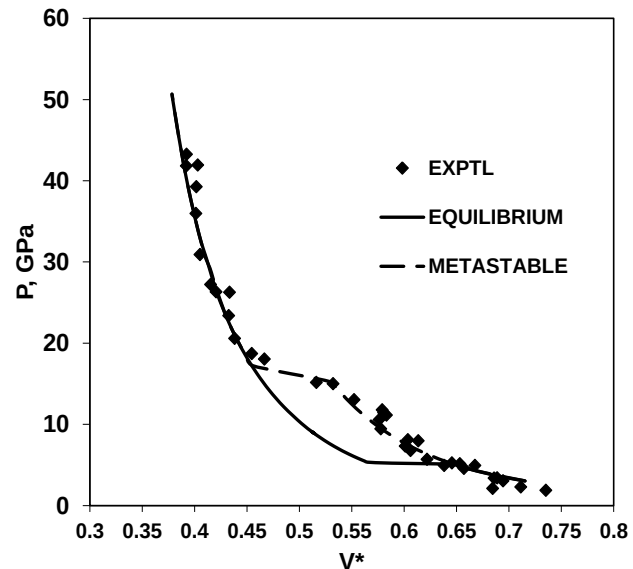


Figure 5. Benzene Hugoniot values.

In figure 5, comparisons of calculated and experimental Hugoniot values [15] are presented for benzene which also dissociates into methane, hydrogen, and carbon at elevated pressures. With the Jaguar procedures and the equilibrium phase transitions exhibited in figure 3, carbon transforms from graphite to diamond at about 5 GPa. However, the actual transition indicated by a sharp break in the experimental data is the range 18-20 GPa along the Hugoniot curve.

5. Metastable carbon states

It is known that at shock conditions carbon exhibits metastable behavior, so that equilibrium phase transitions are not usually attained [16,17]. The study of Viecelli et al [18] indicated that substantial transformations of the carbon phase boundaries occur due to the formation of nanometer size carbon particles in the shock products. Corrections to the bulk Gibbs free energy were provided for diamond, graphite, and liquid carbon phases based on estimates for the particle surface energy for each phase. For several carbon property models [5,19] modified phase boundaries were calculated which indicate considerable expansions of the graphite region at low temperatures and of the liquid region at elevated temperatures.

In this study in order to account for non-equilibrium carbon phase behavior, the following modified phase transition relationship has been developed based on Hugoniot data for explosives and explosive products, including benzene, carbon monoxide, and methane:

$$P = 1.3616 + 0.65763T - 1.6415 \times 10^{-5} T^2 \quad (6)$$

where P is in GPa and T in Kelvin. The enhanced graphite region resulting from Equation 6 is shown in figure 6. The actual diamond and graphite regions may be reduced further by the formation of metastable liquid phases below the graphite and diamond melting temperatures.

Jaguar calculations of the benzene Hugoniot curve utilizing equation (6) for the modified carbon phase transitions are included in figure 5. It can be seen that good agreement with the experimental values is obtained with this procedure for the entire pressure range, involving calculations with the graphite relationships to about 18 GPa and with the diamond relationships above about 20 GPa. Temperatures as high as 5600 K are attained at the highest pressures, but reasonable results for these conditions are indicated with the present procedures.

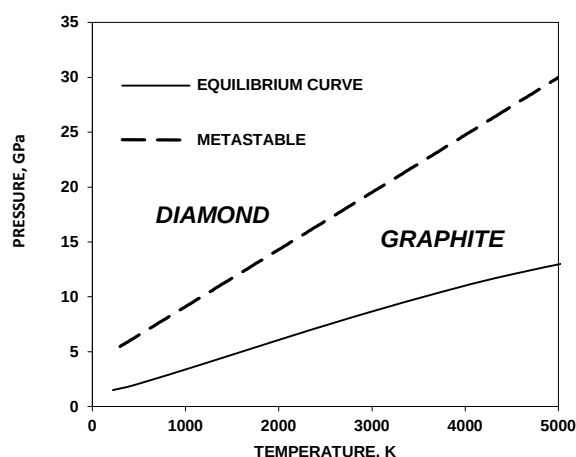


Figure 6. Nonequilibrium carbon transitions.

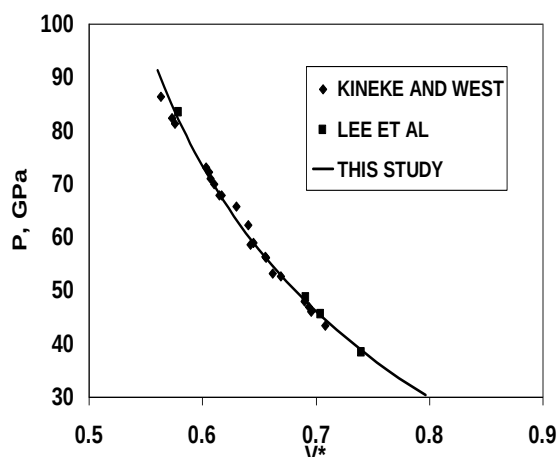


Figure 7. PBX-9404 Hugoniot values.

6. Detonation properties of explosives

Preliminary comparisons have been performed on the accuracy of the relationships and the procedures presented in this study for the calculation of the detonation properties of oxygen-deficient explosives. In figure 7 close agreement is exhibited between experimental overdriven Hugoniot values for PBX-9404 [20,21] and values calculated with the relationships of this study. This explosive forms moderate amounts of carbon at these conditions. Similarly good agreement with Hugoniot data [20] is shown in figure 8 for COMP-B which forms substantial amounts of carbon in the chemical equilibrium calculations.

Results of comparisons of detonation velocities for the highly oxygen-deficient explosive TNT for a wide range of densities [22] are presented in figure 9. The relationships of this study for carbon properties and the application of equation (6) for the proper phase selection result in a two-phase graphite diamond mixture at the highest density, and the formation of the graphite form at lower densities. For most of the range somewhat closer agreement results with the graphite form, while diamond would be the correct form for the entire range if the phase equilibrium of figure 3 were applicable. Similar conclusions about the correct carbon forms exhibited by this data were reached by van Thiel and Ree [16], who suggested the use of a modified heat of formation of diamond for thermochemical calculations.

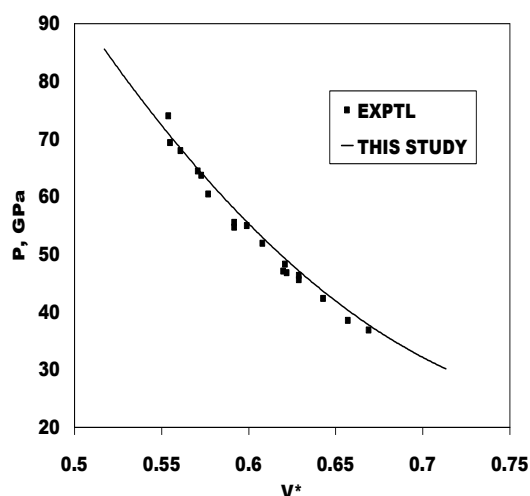


Figure 8. COMP-B Hugoniot values.

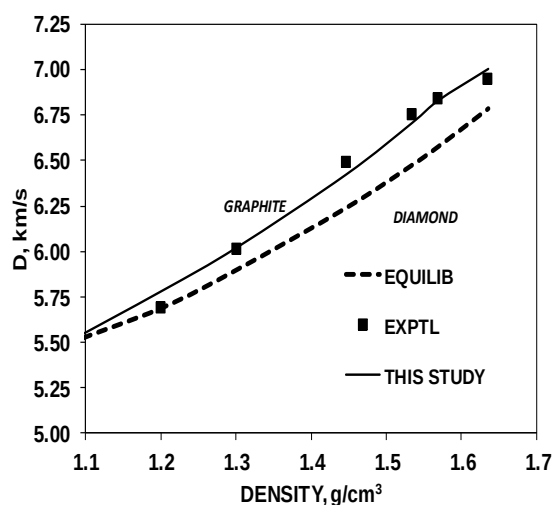


Figure 9. TNT detonation velocities.

7. Conclusions

The relationships of this study represent the information currently available for the properties of carbon graphite and diamond phases at elevated temperatures and pressures. The resulting calculations of diamond-graphite phase transitions are in general agreement with the available experimental values. Hugoniot data for hydrocarbons and explosives were utilized to establish an approximate boundary curve for metastable graphite-diamond phase behavior under shock conditions. The procedures of this study are indicated to enable the accurate calculation of detonation properties of explosives. This approach will be extended to include additional carbon phases at elevated temperatures.

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