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Theoretical Insight into Shocked Gases

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I. ABSTRACT

I present the results of statistical mechanical calculations on shocked molecular gases. This work provides insight into the general behavior of shock Hugoniots of gas phase molecular targets with varying initial pressures. The dissociation behavior of the molecules is emphasized. Impedance matching calculations are performed to determine the maximum degree of dissociation accessible for a given flyer velocity as a function of initial gas pressure.

II. INTRODUCTION

There has been recent interest in the behavior of shocked gases at or near ambient conditions, a hitherto understudied regime of matter. Such systems can be studied with gas-gun experiments, or with first-principles atomistic simulation, which are taxing of human, financial, and computer resources; however, these results provide much needed data with which to calibrate interaction potentials for statistical mechanical perturbation methods used to calculate equations of state (EOS) as implemented in the LANL EOS code, MAPGIE. Preliminary results using simple models are needed to direct future experimental and first-principles theoretical efforts.

When the monatomic gas Ar, was shocked from near ambient conditions, large compression ratios and thus temperatures were observed experimentally.[1] Such experimental data is an excellent resource from which to develop interatomic potentials of shocked gases. When a molecular system reaches very large temperatures as above, it will dissociate and ionize (likely in that order). We can model such dissociation events with MAGPIE, but we lack good parameterizations for atomic potentials in this regime. This was part of the motivation for the Dattelbaum and Coe ER (20140261ER) to study shocked molecular gases. Some unexpected difficulties arose while pursuing this research. The first experiments were performed on NH_3 at an initial pressure of 100 PSI. There was a (likely) turnaround observed in the $P-\rho$ Hugoniot (error bars are large), but our MAGPIE calculations indicated that this is due to the first dissociation event: $2NH_3 \rightarrow N_2 + 3H_2$. To obtain atomic data, the next dissociation events of $N_2 \rightarrow 2N$ and $H_2 \rightarrow 2H$ must be observed; however, it appeared as though to obtain those conditions would exceed the maximum projectile velocity of the gas guns available at LANL. There were two contributing factors inhibiting the goal of observing atomic dissociation. First, polyatomic molecules such as NH_3 will tend to dissociate into smaller molecules such as N_2 and H_2 before dissociating into atoms. Second, a molecule's heat capacity must be considered. Greater heat capacities will contribute to lesser temperatures along a shock Hugoniot. These two factors are obviously related. The more bonds a molecule has, the greater its heat capacity, and the more energy required to atomize it. To maximize the probability of observing atomic dissociation with achievable gas-gun projectile velocities, we should thus focus on small molecules such as diatomics.

In the next section we will study polyatomic (CO_2) and diatomic (CO) shocked gas Hugoniots in detail to illustrate these points, and predict the most extreme achievable states upon shock loading. In the Appendix, I provide data for several diatomic molecules and one mixture of diatomic molecules.

III. METHODS

Systems were modeled with the LANL thermochemical code MAGPIE. Molecules were described by translational, rotational, vibrational and electronic ideal-gas partition functions, and mixtures of components were created using the ideal-mixing approximation. Equilibrium compositions were determined by minimizing the total Gibbs free energy of the mixture as a function of composition at constant P and T.

The states achieved upon a shock delivered from a flyer plate of a given velocity were calculated via impedance matching[2] assuming a Cu flyer impacting an Al (6061) sample holder in direct contact with the sample.[3] Maximally extreme achievable states are reported assuming a maximum flyer velocity of 6.5 km/s (near the limit of the Ancho Canyon gun at LANL).[4]

All results shown herein were obtained neglecting non-ideal interactions. This is reasonable given the generally low densities observed; however, where interaction potentials were available, the effect of non-ideality was investigated using standard exponential-6 potentials (calibrated for much higher pressures).[5,6] The effect of non-ideality was found to be important for (P,V,T) states, especially for higher P_0 shots (300-400 PSI), but did not affect the conclusions and trends reported herein. It should be noted that the accuracy of these potentials is unknown in this regime, for they were calibrated for much higher densities and pressures. This highlights the need for further experimental and first-principles studies of this regime.

FIG. 1. CO_2 P-compression Hugoniot for initial pressure of 100 PSI.

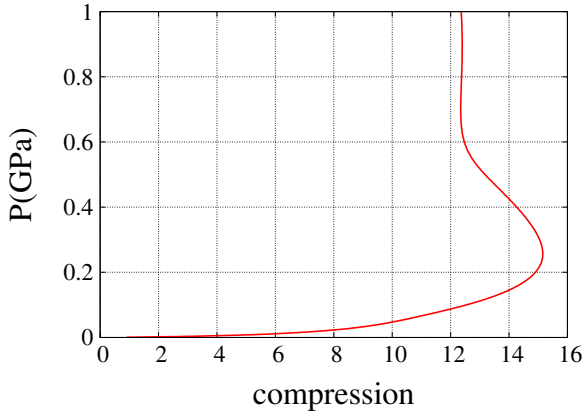


FIG. 2. P vs. mole fraction along CO_2 Hugoniot for P_0=100 PSI

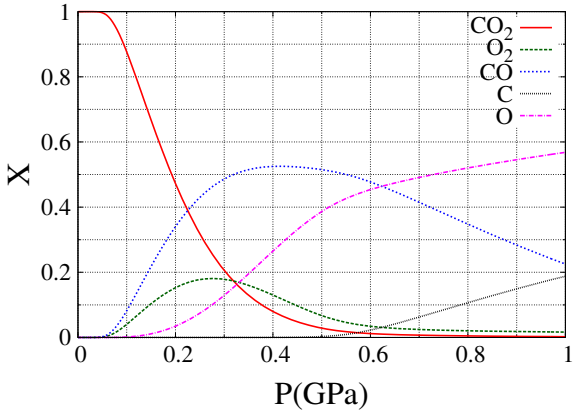
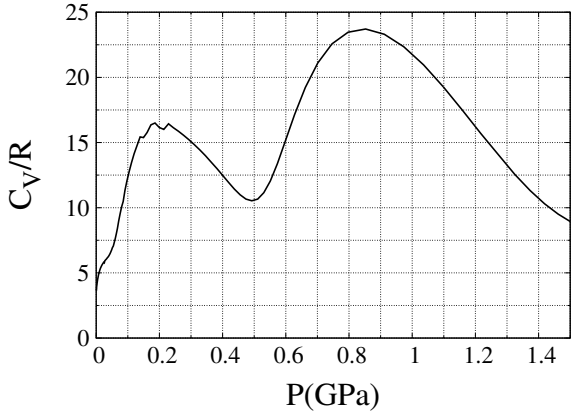


FIG. 3. P-C_V along CO_2 Hugoniot for P_0=100 PSI



IV. RESULTS

I studied the behavior of shocked CO_2 from initial pressures of 100 - 400 PSI at room temperature. The $P-\rho/\rho_0$ Hugoniot is shown in Figure 1, and Figure 2 shows the equilibrium chemical composition along the Hugoniot. It is readily apparent from Figures 1 and 2 that a dissociation event occurs at a compression of 15 and a pressure of 0.2 GPa. This is followed by a very stiff region of the Hugoniot which approaches a temporary maximum compression of about 12. Figure 2 shows that the system is a mixture of mostly CO and O in this region, and the theoretical maximum compression of a CO+O mixture corresponding to the CO_2 $\rightarrow$CO+O reaction is 11. The inclusion of the additional heat capacity due to the presence of other trace species serves to increase the idealized value.

The first major dissociation event of CO_2 is to form CO and O_2. Then O_2 begins to dissociate to form a mixture of primarily CO and O. Finally CO dissociates to form the atomic mixture, but not until pressures of greater than 1 GPa and temperatures greater than 14,000 K. Figure 3 shows the effect of dissociation on C_V (shown in units of R). The rapid C_V increase between the initial state and 0.05 GPa corresponds to classical activation of the vibrational modes of CO_2. The two maxima in C_V near 0.2 GPa and 0.8 GPa correspond to the two most important dissociation events discussed above ($2CO_2$ $\rightarrow$2CO+O_2 and CO$\rightarrow$ C + O).

To ascertain the feasibility of experimentally observing states above 1 GPa with gas guns, we use the P-u_p curves (available from MAGPIE) in impedance matching calculations. Table I shows the most extreme achievable states for various initial pressures of CO_2 assuming a Cu flyer impacting an Al sample holder in contact with CO_2 and a flyer velocity of V=6.5 km/s.

A few trends are worth noting from Table I. As P_0 increases, so does the shock pressure, and thus density along the Hugoniot for a given flyer velocity. The particle and shock velocities decrease as P_0 increases due to the increasing impedance. Finally the amount of atomic dissociation, which is a delicate balance of terms minimizing the Gibbs free energy decreases. One thing is clear from Table I: for initial pressures of 100-400 PSI, we can only just reach the point where appreciable amounts of atomic C begins to form, casting doubt the on the feasibility of studying the atomic C potential in this way. However, valuable information about the atomic O potential could be obtained. Second, the trend shows that lesser initial densities yield greater atomic abundances, but also lesser shocked densities, making the ideal-gas law more likely to prevail. To summarize, lesser initial densities favor higher levels of dissociation, but they also make interaction potentials less important. Thus by varying P_0, one should try to maximize the density obtained along the Hugoniot while maintaining an acceptable amount of atomic dissociation.

The case study of CO_2 reveals clear difficulties; however, upon shocking CO, the first reaction to occur is immediate dissociation into atoms (Figure 4). Observe Table II for the maximum achievable states of CO under the same initial pressure conditions as CO_2. We observe large atomic dissociations over the entire range of 100-400 PSI studied.

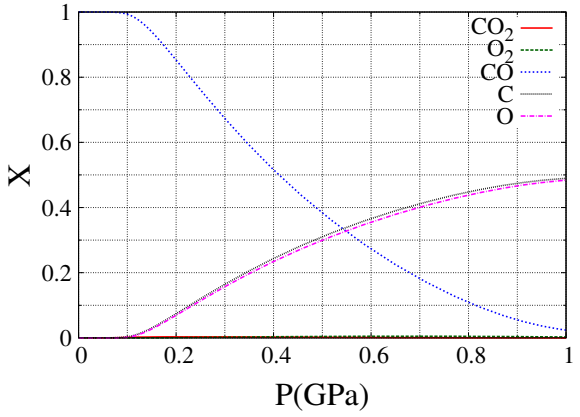
TABLE I. Most extreme achievable states of CO_2 for V=6.5 km/s

$P_0(PSI)$	P(GPa)	T(K)	ρ(g/cc)	U_S (km/s)	u_p (km/s)	X(C)	X(O)
100	1.0413	14439	0.1559	9.48	8.71	0.1942	0.5821
200	2.1338	15154	0.3144	9.43	8.64	0.1761	0.5620
300	3.2867	15545	0.4842	9.36	8.57	0.1625	0.5449
400	4.5167	15792	0.6699	9.29	8.49	0.1507	0.5290

TABLE II. Most extreme achievable states of CO for V=6.5 km/s

$P_0(PSI)$	P(GPa)	T(K)	ρ(g/cc)	U_S (km/s)	u_p (km/s)	X(CO)	X(C)	X(O)
100	0.6449	13926	0.0973	9.50	8.74	0.2210	0.3641	0.3898
200	1.2833	14656	0.1887	9.48	8.70	0.2436	0.3451	0.3770
300	1.9123	15076	0.2786	9.45	8.66	0.2600	0.3316	0.3673
400	2.5330	15362	0.3675	9.42	8.62	0.2735	0.3207	0.3591

FIG. 4. P vs. mole fraction along CO Hugoniot for P_0=100 PSI



In the Appendix, I provide results for a series of other possible candidates for achieving atomic dissociation following the principles above. I omit NH_3, as its theoretical Hugoniots will be published separately with experimental results. The amount of dissociation at the most extreme states for all the diatomic molecules studied as shown in Tables II-III is consistent with the trends in their bond energies: lesser bond energies lead to more dissociation. Table IV provides results for an equimolar mixture N_2 and CO. Those results suggest that mixing diatomic species prior to shock loading to obtain experimental data relevant to fitting cross-potentials for more than two elements may be feasible.

V. SUMMARY

I presented theoretical results and analysis for several shocked molecular gases. The results herein indicate that to achieve atomic dissociation under current gas-gun parameters, one should target small molecules with low bond energies. Pressurizing the target samples is beneficial as it yields greater densities on the Hugoniot, meaning the ideal-gas law is less likely to prevail; however this also yields less dissociation, so these two factors must be balanced. Thermochemical codes are useful in this regard.

VI. ACKNOWLEDGMENTS

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VIII. APPENDIX

TABLE III. Most extreme achievable states

O_2							
$P_0(PSI)$	P(GPa)	T(K)	ρ(g/cc)	U_S (km/s)	u_p (km/s)	X(O_2)	X(O)
100	0.7912	24713	0.0619	10.19	8.73	0.0051	0.9949
200	1.5689	24419	0.1249	10.12	8.68	0.0104	0.9896
300	2.3342	24144	0.1890	10.06	8.63	0.0158	0.9841
400	3.0877	23886	0.2541	10.00	8.58	0.0214	0.9785
N_2							
$P_0(PSI)$	P(GPa)	T(K)	ρ(g/cc)	U_S (km/s)	u_p (km/s)	X(N_2)	X(N)
100	0.6473	14741	0.0923	9.54	8.74	0.2474	0.7526
200	1.2867	15509	0.1792	9.52	8.70	0.2821	0.7179
300	1.9163	15950	0.2644	9.49	8.66	0.3066	0.6934
400	2.5357	16250	0.3487	9.46	8.62	0.3265	0.6735

TABLE IV. Most extreme achievable states for an equimolar mixture of CO and N_2

$P_0(PSI)$	P(GPa)	T(K)	ρ(g/cc)	U_S (km/s)	u_p (km/s)	X(CO)	X(C)	X(O)	X(N_2)	X(N)
100	0.6454	13628	0.0984	9.49	8.74	0.0817	0.2118	0.1985	0.1179	0.3563
200	1.2845	14325	0.1914	9.47	8.70	0.0907	0.2053	0.1889	0.1309	0.3395
300	1.9145	14725	0.2828	9.44	8.66	0.0973	0.2002	0.1820	0.1401	0.3276
400	2.5363	14997	0.3736	9.40	8.62	0.1027	0.1959	0.1763	0.1476	0.3180