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EFFECTIVE LIKE- AND UNLIKE-PAIR INTERACTIONS AT HIGH PRESSURE AND HIGH TEMPERATURE

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We describe how information on effective interactions of chemical species involving C, O, and N atoms at high pressure and high temperature may be inferred from available shock wave data of NO and CO. Our approach uses a modern statistical mechanical theory and a detailed EOS model for the condensed phases of carbon.

1. INTRODUCTION

The detonation of modern explosives produces a mixture of chemical species over a wide range of pressures (1 to 100 GPa) and temperatures (1000 K to 5000 K). To gain a fundamental understanding of high-explosive detonations, we have developed a multiphase, multicomponent chemical equilibrium code (CHEQ).¹ It requires: (1) accurate intermolecular potentials, (2) a mixture theory reliable at high pressure and high temperature, and (3) an equation-of-state (EOS) model to deal with condensed carbon.

A mixture theory suitable for our purpose must satisfy a requirement that it gives the excess Helmholtz free energy within 1 to 3% of the correct value. Such a theory is now available.² We

have recently developed an EOS of carbon³ to deal with requirement (3). Unlike earlier models, it includes all three phases (graphite, diamond, and liquid) of carbon. Furthermore, it includes thermal corrections to the free energy and matches all experimentally relevant information on the condensed phases of carbon. With items (2) and (3) in hand, we can now turn our attention to item (1). In this paper, we describe how information on like- and unlike-pair interactions may be inferred from available shock wave data of NO and CO.

2. EXPONENTIAL-6 POTENTIAL

Intermolecular potentials derived from low-pressure gas-phase data are often not suitable for high-pressure calculations, because the interactions in condensed fluid phases are intrinsically many-body in its character. However, it has been empirically found that an exponential-6 potential can explain a surprisingly large number of experimental data at high pressures and high temperatures. This exponential-six (exp-6) potential between molecules i and j is represented by

$$\phi_{ij}(r) = \frac{\epsilon_{ij}}{(\alpha_{ij} - 6)} \{ 6 \exp[\alpha_{ij}(1 - r / r_{ij}^*)] - \alpha_{ij} (r_{ij}^* / r)^6 \} \quad (1)$$

with three parameters: ϵ_{ij} , the depth of the attraction; r_{ij}^* the size of the repulsive core; and α_{ij} , the slope of the exponential repulsion.

Determining the exp-6 potential parameters for like-molecular pairs ($i=j$) requires experiments on pure systems. Compared to this relatively simple case, the determination of unlike-pair interactions ($i \neq j$) (e.g., N_2 - H_2O) becomes more formidable. We need experimental data of either a prepared mixture or a pure system which is forced to dissociate by sending a strong shock wave. In either case, we can express the exp-6 parameters for unlike-pairs in terms of those of like-pairs by

$$r_{ij}^* = \frac{1}{2} k_{ij} (r_{ij}^* + r_{ij}^*), \quad (2a)$$

$$\epsilon_{ij} = \ell_{ij} \sqrt{\epsilon_{ij} \epsilon_{ij}}, \quad (2b)$$

$$\alpha_{ij} = m_{ij} \sqrt{\alpha_{ii}\alpha_{jj}} \quad , \quad (2c)$$

where k_{ij} , ℓ_{ij} , and m_{ij} , represent small multiplicative factors. The case, $k_{ij} = \ell_{ij} = m_{ij} = 1$, is commonly referred to as the Lorentz-Berthelot combination rule.

We need to describe unlike-pair interactions to understand mixtures systems such as explosives, planetary systems, etc. In particular, unlike-pair interactions are important for a phenomenon generally known as a supercritical fluid phase separation. As an illustration, Fig. 1 shows our earlier calculation⁴ of a theoretical (CHEQ) solubility diagram for a ternary system consisting of N₂, CO₂, and H₂O at a pressure and a temperature near the theoretical Chapman-Jouguet (C-J) point of PBX-9404. (The composition is indicated by the solid circle.) If we use the usual Lorentz-Berthelot rule, we obtain a phase separation within the dark shaded portion. In this case, the C-J point lies within the range for total solubility. We can expand the fluid-phase separation to include the C-J point simply by changing the $r^*(\text{H}_2\text{O}-\text{N}_2)$ -parameter by +3% (indicated by the light-shaded area). Without this seemingly small change, which is well within uncertainties of the Lorentz-Berthelot rule, the detonation properties of PBX-9404 falls outside experimental uncertainties!

Although the most extensive data on mixtures are obtained with high explosives, they produce too numerous detonation products and the composition changes with pressure and temperature in a very complex way. Therefore, their usefulness is primarily limited to testing theoretical models rather than for calibrating the exp-6 potential parameters. For the latter purpose, we need experimental data on simple mixtures in the range of tens of GPa in pressure and several 1000 K in temperature. Such data have started to become available. We show how the shock data^{6,7} of NO and CO can be used to infer intermolecular potential parameters for various dissociation products. A more detailed analysis on the exp-6 parameters for other systems (CO₂, N₂+O₂, etc.) will be given in a separate paper.⁵

3. ANALYSES

For our analysis we chose the Hugoniot data of liquid NO and CO. The simpler of the two, i.e., NO, will be used below to illustrate the procedure employed in analyzing the Hugoniot data.

We assume that NO molecules dissociate to establish a chemical equilibrium with a mixture consisting of N, O, N₂, O₂, NO, O₃, N₂O, and NO₂. These species are chemically reactive; so their concentrations {n_i} will change with temperature T and pressure P. This makes it necessary to determine {n_i} by minimizing the Gibbs free energy G(P,T,{n_i}),

$$G(P,T,\{n_i\}) = \sum_i n_i \mu_i, \quad (3)$$

with respect to {n_i}, using μ_i , the chemical potential of species i. The minimization of G(P,T,{n_i}) is done by the CHEQ code,¹ which evaluates μ_i using Ross's soft sphere theory⁸ and the improved mixture model.² The expression for μ_i is given in Ref. 1. The connection between the intermolecular potential and G(P,T,{n_i}) occurs strictly through μ_i .

Even ignoring minor decomposition products such as O₂, N₂O, and NO₂, the number of the pair interactions needed to be considered are large. We use five like-pair interactions (N₂-N₂, N-N, O₂-O₂, O-O, and NO-NO) and ten unlike-pair interactions (N₂-N, O₂-O, N₂-O₂, N₂-NO, O₂-NO, NO-N, NO-O, N₂-O, O₂-N, and N-O). Thus, a proper interpretation of shock data requires more information on the unlike-pair interactions than the like-pair interactions. Each of these exp-6 interactions is characterized by three exp-6 parameters (ϵ_{ij} , r_{ij}^* , α_{ij}). The exp-6 parameters for N₂-N₂, N₂-N, N-N, O₂-O₂, O₂-O, and O-O were derived from the Hugoniot data of liquid N₂ and O₂.⁹⁻¹⁴ The Hugoniot data⁶ of liquid NO are taken at low pressures where we can ignore a negligible amount of monatomic species (N or O). Thus, we can use the NO data to infer the exp-6 parameters for NO-NO, N₂-O₂, N₂-NO, O₂-NO. We test the self-consistency of the resulting potentials obtained by using the Hugoniot data of doubly shocked NO, liquid N₂+O₂⁶ and liquid air.¹³ If the self-consistency test fails, we further fine-tune the exp-6 parameters until the desired self-consistency is achieved by such an iteration.

Figure 2 shows the theoretical Hugoniot of NO at the end of such an iterative procedure. Agreement with the experimental Hugoniot data⁶ is satisfactory. The self-consistency condition mentioned above implies that the same parameter set should also give a reasonable agreement for N₂, O₂, mixtures of N₂ and O₂. Space limitations prevent from showing the reasonable agreement with Hugoniots of the other systems. These will be discussed in a separate paper with the resultant interaction parameters.⁵

Calculations of the Hugoniot of CO are done basically in the same way. In this case, we employ five gaseous species (CO₂, CO, O₂, O, O₃) and three condensed forms (liquid, graphite, and diamond) of carbon. The condensed phases are included to allow some dissociated carbon atoms to precipitate under high shock pressure. Expressions for their chemical potentials were derived from the three-phase carbon EOS model.³

Figure 3 compares the resulting Hugoniot with the experimental data and our earlier calculation. The old calculation in Fig. 3 utilizes the exp-6 parameter sets obtained from the corresponding states scaling relation¹⁵ and the Murnaghan EOS for graphite and diamond. It does not include liquid carbon. The new calculation includes liquid carbon and its inclusion is responsible for a significantly improved agreement with the experimental data seen in Fig. 2 at high pressures. Further, we had to alter the exp-6 parameters for CO₂-CO₂ interactions in order to fit very recent work of Nellis et al.¹³ and Schott.¹⁶ The new calculation in Fig. 3 uses the exp-6 parameters:¹³ $\epsilon/k = 245.6$ K, $r^* = 4.20$ Å, $\alpha = 13.5$.

A "kink" in the theoretical Hugoniots near 13 GPa signifies the graphite-diamond transition. At pressures below 13 GPa, the experimental data follows close to a nonreactive Hugoniot of CO, while the theoretical calculation predicts liquid CO to dissociate. This difference accounts for the deviations in Fig. 3 at $P < 13$ GPa. From this observation, we conclude that the experimental shock data represent a metastable CO. Otherwise, one would expect the experimental data to agree with the theoretical calculation.

CONCLUDING REMARKS

A theoretical study of strongly shocked molecules involving C, O, and N atoms requires a knowledge of effective interactions of reaction products involving these atoms at high pressure and high temperature. We have described how such an information may be inferred from available shock wave data of liquid CO and NO. This is particularly useful for unlike-pair interactions, because such an information is scarce at present.

As mentioned earlier, unlike-pair interactions are also important in the description of supercritical fluid phase separations. The importance stems from the fact that the free energy difference should vanish at the phase transition point, hence, sensitive to unlike-pair interactions. This suggest an accurate way of determining the unlike-pair interaction in condensed phases; i.e., matching experimental phase-boundary data by adjusting unlike-pair potential parameters in a theoretical model. A heated diamond-anvil cell experiment by Costantino and Rice¹⁷ is in progress at LLNL to determine the phase boundary of supercritical fluid mixtures.

In addition to the unlike-pair interactions, the present investigations provided a new insight into an important role that the liquid carbon plays in interpreting the shock wave data of liquid CO. A precise (P,T) condition where liquid carbon becomes thermodynamically stable is still an experimentally open question. We hope that the present theoretical prediction will provide an impetus to study liquid carbon experimentally. Our analysis of the CO Hugoniot at low P suggests a metastable CO. It will be worthwhile to determine the time scale needed for the chemical equilibrium to set in the metastable liquid CO under shock condition.

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FIGURE CAPTIONS

Figure 1. Phase diagram of a $\text{N}_2\text{-H}_2\text{O-CO}_2$ mixture at $T = 0.35$ eV and $P = 33$ GPa. The shaded region is the demixed phase using the Lorentz-Berthelot rule and the region under dotted line is the demixed phase with a modified parameter set described in the text, circle = the C-J point of PBX-9404.

Figure 2. Hugonoiots of a liquid NO: line = theory; circle = experiment (Ref. 6).

Figure 3. Hugonoiots of liquid CO_2 : solid line= this work, dotted line = calculation based on the corresponding-states scaling relation and the Lorentz-Berthelot rule, circle = *experiment* (Ref. 7).

FIGURE 1

FIGURE 2

FIGURE 3