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SUPERCRITICAL FLUID PHASE SEPARATIONS INDUCED BY CHEMICAL REACTIONS

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ABSTRACT

Our statistical mechanical studies predict that a chemically reactive system containing species composed of C, H, N, O atoms can exhibit a phase separation into a N₂-rich and a N₂-poor phase. The present work is concerned with the effect of the fluid phase separation upon addition of F atoms in the system. Our study shows that F atoms mainly appear as a constituent of HF in a N₂-poor fluid phase up to a certain pressure beyond which they occur as CF₄ in a N₂-rich phase and that the phase separation may be abrupt in thermodynamic sense. The pressure at the phase boundary can occur at about 30 GPa at 3000 K and about 10 GPa to 20 GPa at 1000 K. Some of these ranges may be accessible by present-day experimental high-pressure techniques. We discuss implications of this study to detonation physics.

INTRODUCTION

Currently available studies on supercritical fluid phase separations are limited to chemically nonreactive systems. The present study is concerned with possible influence of chemical reactions on such a phase change at high pressure (P) and high temperature (T). Such a study is important to a reliable prediction of the performance of high explosives. High explosives molecules are mainly composed of C, H, N, O atoms. Their detonation produces a mixture of many species such as N₂, CO₂, CO, H₂O, and condensed carbon plus minor amounts of H₂, NH₃, O₂, NO, etc. Hence, we use high explosives at P = 1 to 100 GPa and T = 100 to 5000 K as the chemically reactive systems to examine a possible supercritical fluid phase separation and its effect on post-detonation product mixtures.

In this regard we have earlier used the statistical mechanical chemical equilibrium (CHEQ) code¹ to investigate the occurrence of supercritical fluid phase separations in binary and ternary mixtures of N₂, CO₂, and H₂O molecules and in detonation products of a condensed explosive, PBX-9404.² The most significant result of our analysis was that the N₂-H₂O system may exhibit a supercritical fluid phase separation in the same (T, P) range as we encounter in explosives experiments. This prediction has been validated by diamond-anvil-cell experiments up to P less than 3 GPa and T less than 1000 K.² The most significant practical result of such a prediction for explosives is that, by incorporating the N₂-fluid phase separation in modeling the detonation of high explosives, we obtain better agreement with the experimental detonation data.

Most modern high explosives are "composites" with two main components; explosive molecules and organic binders to hold, mold, and pack the explosive powders. Recently, binders containing fluorine atoms are drawing interest for the safety reason. Typical ones are Kel-F with polymeric composition (C₈H₂Cl₃F₁₁)_n and viton A with composition (C₅H_{3.5}F_{6.5})_n. LX-17 uses the KelF binder to mold high explosive, TATB (= C₆H₆N₆O₆), while LX-04 uses the viton A binder to mold HMX (= C₄H₈N₈O₈). The former is insensitive and the latter more sensitive. Results presented below show that the fluorine chemistry can critically influence the supercritical

fluid phase separation between the N₂-rich and the N₂-poor phases in detonation product mixtures and that it in turn affects the detonation properties of LX-17 and LX-04.

FORMULATION

Theory

LX-17 is a composite explosive with C_{2.29}H_{2.18}N_{2.15}O_{2.15}F_{0.2}Cl_{0.054} per 100 g, while 100 g of LX-04 is represented by C_{1.55}H_{2.58}N_{2.30}O_{2.30}F_{0.52}. The amount of Cl in LX-17 is small and will be neglected in the present work. We assume that these explosives produce gaseous species (N₂, CO₂, CO, H₂O, H₂, NH₃, O₂, NO, etc.) and condensed carbon in a graphite, diamond, or liquid phase. The Gibbs free energy of this heterogeneous system can be obtained as a sum of the Gibbs free energies for the gaseous mixture phase and the condensed carbon phases. The Gibbs free energy for carbon has been discussed in detail and will not be repeated here.³ We sketch below only the pertinent portions of the fluid-phase Gibbs free energy.

We use exp-6 potentials to represent interactions between a (i, j) pair of detonation product species in a fluid mixture;

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

For polar molecules such as H₂O and HF, the well depth ϵ is made temperature dependent by introducing an additional parameter λ ,

$$\epsilon = \epsilon_0(1 + \lambda/T), \quad (2)$$

which describes the increasingly attractive hydrogen-bonding character of the interaction as the temperature decreases.

Mixture systems will be described by using the improved van der Waals one-fluid model.⁴ It assumes that all molecules in mixtures are identical and interact with an effective exp-6 potential whose parameters depend on the mole fractions $\{x_i\}$ and (α, ϵ, r^*) parameters of individual pair interactions as follows:

$$\begin{aligned} (r^*)^3 &= \sum x_i x_j (r_{ij}^*)^3, \\ \epsilon &= \sum x_i x_j \epsilon_{ij} (r_{ij}^*/r^*)^3, \\ \alpha &= \sum x_i x_j \alpha_{ij} \frac{\epsilon_{ij} (r_{ij}^*)^3}{\epsilon (r^*)^3}. \end{aligned} \quad (3)$$

The improved van der Waals one-fluid model has been verified with Monte Carlo simulations.⁴

Parameters α , ϵ , and r^* in Eq. (1) for like-pair species ($i = j$) are mostly obtained by matching shock wave data or from various theoretical methods. Parameters α , ϵ , and r^* for unlike-pair interactions ($i \neq j$) are derived from the generalized Lorentz-Berthelot equations,¹

$$\epsilon_{ij} = k_{ij} \sqrt{\epsilon_{ii} \epsilon_{jj}}; \quad r_{ij}^* = \frac{1}{2} (r_{ii}^* + r_{jj}^*); \quad \alpha_{ij} = m_{ij} \sqrt{\alpha_{ii} \alpha_{jj}}, \quad (4)$$

by using (α , ϵ , r^*) parameters for the homo-molecular interactions ($i = j$) and by modifying (k_{ij} , l_{ij} , m_{ij}) parameters, originally set equal to 1, if there is suitable data to do so.

We compute the Helmholtz free energy (hence, the Gibbs free energy) of the fluid-phase mixture system by using the effective one-component potential [Eqs. (1) - (4)] in the Ross variational theory which is an improved version of Mansoori's original hard-sphere variational theory. The Ross theory shows excellent agreement with computer simulation data for a wide variety of potentials that include the exp-6 form.

The above mathematical formulations are programmed into the CHEQ code. The CHEQ code solves for $\{x_i\}$ by minimizing the Gibbs free energy of the entire heterogeneous mixture system (containing fluid mixtures and condensed phase carbon) and computes thermodynamic quantities by taking appropriate numerical derivatives of the free energy.

HF-HF intermolecular potential

Detonation of LX-17 and LX-04 produces hydrogen fluoride (HF). Hence, explosive performance prediction requires information on intermolecular pair potentials with HF. However, experimental data (e.g., shock wave) on HF needed for the present work do not exist because of its corrosive nature. Furthermore, HF is a strongly hydrogen bonding system, which, in spite of its simplicity, makes predicting its intermolecular potential difficult. We describe below our attempt to obtain the HF pair potentials based on available information.

We use the structure of condensed HF at low temperatures as a guide. HF molecules have a hydrogen bond strength of about 0.3 eV and form chain- and ring- clusters in the gas and liquid phases. The crystals structure of HF is orthorhombic with space group C_{2v}^{12} . It consists of zigzag hydrogen bonded F-F chains that are parallel to the [100] plane. The F-F bond distance in the chain is 2.49 Å at 148 K and the nearest neighbor inter-chain distances are 3.12 to 3.20 Å.

We have examined several quantum mechanical and semiempirical HF-HF potentials which are consistent with the inter- and intra-chain distances of the crystal structure by representing them by an exponential-6 potential. One of them (hereafter, referred to as HFb) has a minimum value at r^* ($= 2.95$ Å) $< r_c = 3.12$ Å ($=$ the smallest inter-chain F-F distance) was obtained by fitting the parameters to the detonation velocity of a high explosive 1,2DP($C_3H_6N_2F_2$). But it gave inconsistent detonation velocities of some other explosives, i.e., FEFO($C_5H_6N_4O_{10}F_2$), FM1($C_{1.906}H_{2.872}N_{1.265}O_{3.164}F_{0.308}$), PF($C_6H_2N_3O_6F_1$), and LX-17. The best available potential (referred to as HFa) was obtained by spherically averaging the ab initio data of Barton and Howard weighted by a Boltzman factor.⁶ Numerical values of the potential HFa and HFb are:

HFa: $\epsilon/k = 188.6$ K, $r^* = 3.19$ Å, $\alpha = 13.01$, $\lambda = 368.6$ K,

HFb: $\epsilon/k = 188.6$ K, $r^* = 2.95$ Å, $\alpha = 13.01$, $\lambda = 368.6$ K,

Note that the potential minimum ($r^* = 3.19$ Å) of HFa is close to r_c . The differences in the calculated detonation velocities (D_{CJ}) between the HFa and HFb potentials are about 2.5 % for FEFO and LX-04. These are still significant differences, since uncertainties in many experimental D_{CJ} are usually within 1%. Table 1 shows two sets of unlike pair potential parameters that fine

tune the interactions HFa-X ($X \equiv \text{CO}, \text{CO}_2, \text{H}_2\text{O}$) for two sets of experimental data. The present work shows that accurate knowledge of the HF interaction potential as well as good experiments is critical to the HE performance prediction.

Table 1. Lorentz-Berthelot correction factors, Eq. (4), for unlike-pair interaction constants..

Correction factors	Set A			Set B		
	k	l	m	k	l	m
H ₂ O - HF	1.0	1.101	1.0	1.0	0.976	1.0
CO ₂ - HF	1.0	0.841	1.0	1.0	1.095	1.0
CO - HF	1.0	1.0	1.0	1.0	1.080	1.0

Influence of fluorine chemistry

As mentioned earlier, our statistical mechanical calculations revealed that post-detonation mixtures containing C, N, H, O atoms separate into an N₂-rich and an N₂-poor fluid phases near or above the CJ point. In addition, F atoms in Kel-F or viton A binder react with H or C atoms

Figure 1. Hugoniot of LX-17 using the HFa parameters for the HF-HF potential and Set A for unlike-pair potentials, and assuming that it burns 96.5% of the original sample. Also shown are: experimental data of Green et al. in Ref. 7.

to produce HF and CF₄. Here we need to be concerned with a possible influence of chemical reactions involving these additional species on the N₂-rich and an N₂-poor phases. Such calculations are carried out here for LX-17 and LX-04.

Figure 1 shows the Hugoniot of LX-17 based on CHEQ, assuming that the HE burns 96.5% which reflects the fact that LX-17 is very insensitive and has significant detonation kinetics effects. The calculation uses the HFa for the HF-HF potential and Set A (in Table 1) for the HF-X set. The Hugoniot shows a 'kink' near 50 GPa. This is attributed to the fluorine chemistry which drastically complicates the previously known phase separation between the N₂-rich and

N_2 -poor phases. Namely, up to about 50 GPa, F atoms prefer to form HF molecules and occur in the N_2 -poor phase, which contains mostly H_2O molecules. As HF and H_2O are the two strongest hydrogen-bonding molecules, they prefer to associate with each other. However, above 50 GPa, F atoms form CF_4 molecules in the N_2 -rich phase. Namely, high pressure forces F atoms to be in a more compact configuration to lower the free energy of the mixture (Le Chaterlier's principle). The 'softening' of the Hugoniot by the shift, $HF(\alpha) \rightarrow CF_4(\beta)$, is seen to bring the calculation closer to experiment.⁷

In Fig. 2 we examine this shift in fluorine chemistry in detail by comparing the mole fractions (= moles/total number of moles in a given phase) of N_2 , H_2O , HF, and CF_4 along the 0.5-eV isotherm of LX-04. We note that the addition of F atoms produces three different characteristics to the N_2 -rich and an N_2 -poor phases at different levels of pressures, $P_1 < P_2 < P_3$.

Figure 2. Mole fractions of detonation products along the 0.5 eV isotherm of LX-04, based on the HFa parameters for the HF-HF potential and Set A for unlike-pair potentials: solid line = Phase α and dashed line = Phase β .

First, within a small pressure interval (P_1, P_2) indicated by an open arrow at $P = 30$ GPa in Fig. 2, fluid mixtures separate into Phases α and β , in which Phase α is rich in HF and Phase β is rich in both N_2 and H_2O . At the next pressure interval, $P_2 < P < P_3$, H_2O molecules in Phase β gradually change their phase preference to Phase α so that they can be close to similar hydrogen-bonding molecules, HF. At the third pressure interval, $P > P_3$, HF molecules in Phase α become thermodynamically less stable with respect to formation of CF_4 molecules, which prefer to be in Phase β , associated with the N_2 -rich phase. This last phase separation occurs at pressure P_3 which is well above P_1 and is abrupt in thermodynamic sense.

Examination of Fig. 2 shows that this phase separation involves the formation of diamond through a chemical reaction,

The pressure P_3 at the third phase boundary can be as low as about 10 GPa to 20 GPa at 1000 K. These ranges should be accessible to present-day experimental high-pressure techniques; hence, it will be worthwhile to experimentally confirm the prediction made here.

However, it should be noted that this shift in fluorine chemistry is extremely delicate and sensitive to unlike pair potentials between HF and other species. For example, if Set B is used instead of Set A, the shift in fluorine chemistry, $\text{HF}(\alpha) \rightarrow \text{CF}_4(\beta)$, coincides with the pressure (P_1) where the N_2 -rich fluid phase separation occurs at first and no additional change in the character of the fluid phase separation is predicted at higher pressures.

SUMMARY

The present nonempirical calculations show that addition of a small amount of fluorine can drastically alter the supercritical fluid phase separation in a system with C, H, N, O atoms. A small change in unlike-pair interaction parameters between HF and other chemical species can lead to the first order fluid phase separation involving the shift in fluorine chemistry, $\text{HF}(\alpha) \rightarrow \text{CF}_4(\beta)$. Detonation properties of high explosives such as LX-17 and LX-04 are sensitive to such a fluid phase separation. Moreover, these changes are predicted to occur in the pressure and temperature regime accessible by the diamond-anvil-cell technology. Such an experiment will provide an accurate way of determining the unlike-pair potential parameters involving HF molecules.

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