

Calculation of thermo-chemical equilibrium using phase diagram methods

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1 Introduction

The present work describes a method to perform thermo-chemical equilibrium calculations for reactive systems with a high fraction of condensed-phase products, such as thermites and metal-sulphur mixtures. Equilibrium codes designed for gaseous products such as CEA or CHEETAH use equations of states that are not well-suited for condensed phases and typically become increasingly inaccurate as the fraction of solid or liquid products increases. In contrast, CALPHAD (Calculation of Phase Diagrams) [1]- type software is designed specifically to handle condensed phases and uses polynomial thermodynamic functions to represent the phase diagrams of a wide range of metals, oxides, and salts. This formulation is well-suited for solution-finding in condensed phase space, especially with mixtures of different substances. The method can be used to analyze systems with little to no gaseous products, and can be used for calculations of various combustion modes such as constant pressure flames known as Self-propagating High-temperature Synthesis (SHS) reactions.

A particular case of interest was the possible existence of gasless detonation, or heat detonation, and CALPHAD methods were previously used to analyze this mode of combustion in Al-Fe₂O₃ mixtures [2]. The presence of several condensed phases in the products leads to complex shock states, and the Chapman Jouguet (C-J) detonation solution is not straightforward for systems with complex phase diagrams which give rise to shock Hugoniot curves that do not have a smooth hyperbolic shape. As a result, a single tangency solution may or may not be possible. The existence of gasless detonation thus depends on additional criteria compared to traditional gaseous detonations. The dependence of the shock states on the condensed phase behavior, and its subsequent effect on the C-J detonation solution are discussed, and three test cases are presented with the Ti-Si, Al-Fe₂O₃-Al₂O₃, and Zn-S systems. These cases are chosen for their relatively simple high-pressure phases to demonstrate the CALPHAD method of detonation analysis, and constitute a starting point for analyzing systems with more complex phases.

2 Condensed-phase Equilibrium Calculations

The condensed-phase equilibrium calculations are performed using CALPHAD-type software called FactSage [3]. FactSage consists of a collection of thermodynamic databases for pure, condensed-phase substances combined with algorithms to perform thermodynamic manipulations and calculations within the databases. Users have access thermodynamic data for thousands of substances such as metals, oxides, slags, mattes, molten and solid salts, aqueous solutions, light metals, steels, solder alloys. The calculated databases have been developed by modeling and optimizing of all available phase equilibrium and thermodynamic parameters to match existing experimental data using advanced modeling techniques. Some of these databases furthermore contain information on densities and lattice parameters as a function of temperature and composition, as well as the viscosity for a limited number of the liquid phase components. Some of the main purposes of the FactSage software are to calculate phase diagrams and conditions of phase equilibria in multi-component systems, to predict the freezing range, volume change, segregation of alloying elements and phase formation with their accompanying volume and enthalpy changes, and to calculate the amounts of various precipitates during subsequent annealing. Moreover, reactive processes such as the adiabatic and non-adiabatic flame temperature can also be predicted for multi-component systems, including gasless ones.

For the liquid phase, the well-documented Modified Quasichemical Model (MQM) in the pair approximation [4] can be used in FactSage. The MQM has been successfully applied to alloy liquid solutions [5] and [6], molten oxides [7] and [8], molten salts and [9], and molten metal-sulphides systems [30]. The MQM for liquid alloys permits us to obtain mixing entropies that are more reliable than those based on the Bragg–Williams random mixing model which does not take short-range ordering into account. The Compound Energy Formalism (CEF) introduced by Hillert [10] is used to describe the Gibbs energy of solid phases in distinct sub-lattices. When there is only one lattice for the mixing, the model reduces to a simple random mixing model as is the case for the solid solutions.

3 Choice of Candidate Systems

Several mixtures that have garnered interest for their speculated potential for sustaining shock-driven reactions include: Zn-S, Mn-S, Al-S, Ti-Si, Ni-Al, Zr-Al, Ti-B, Ti-C, Al-MoO₃, Ti-B-Zn, Ti-B-Al, and Al-Fe-Fe₂O₃-Al₂O₃. Condensed-phase reactive systems must be analyzed on a case by case basis due to the complexity of the phase diagrams of the reactants and products at high pressure. Because the phase diagrams are typically validated using independent high-pressure thermodynamic data, the availability, or lack thereof, can impose a limitation on the use of CALPHAD for particular systems. For example, the CALPHAD method cannot be used to predict the appearance of new phases. Only the relatively stable phases for which the thermodynamic properties are already determined can be treated. Thus the extrapolation of phase equilibria to very high pressure is valid only if no new phases appear, or if thermodynamic properties of metastable phases at atmospheric pressure are well-known and become stable at higher pressure. For example, the phase equilibria of metal-semiconductor systems are difficult to predict at high pressure, since it is very likely that a compound appears at moderate pressure. One such case is Au-Si, for in which a compounds appears at only 4.2 GPa, which is much smaller than the typical CJ pressure for gasless system [2]. A first selection criterion for gasless detonation candidates is therefore to consider the high-pressure stability of the phases of the products.

A second step to selecting potential candidates involves assessing the temperature-composition dependencies of molar volume at ambient pressure. The molar volumes of reaction components can be

calculated using existing alloy thermochemical databases and determining the volume change after adiabatic reaction. If the volume change is negative, the system is unlikely to detonate according to C-J theory and can be eliminated. Among the systems that exhibit positive volume change, the candidates more likely to sustain shock-driven reactions can be selected for further study by favouring those with the largest volume change, highest adiabatic reaction temperature, and lowest amount of gaseous products.

Following the above down-selection process, three systems with reasonably well-characterized products were chosen for further analysis in this work: Ti-Si, Al-Fe₂O₃-Al₂O₃, and Zn-S.

4 Analysis and Results

The basic detonation analysis method developed by Gheribi et al. [2] consists of first calculating the equilibrium states for the gasless reaction at ambient pressure (i.e. $P=10^5 \text{ Pa}$) using the FactSage code. The composition, temperature, pressure of the equilibrium phases (which can be stoichiometric compounds and/or solutions) are calculated by minimizing the Gibbs free energy of the system. The thermochemical models of these candidate systems can then be extended to high pressures using the method developed by Gheribi et al. [11]. The CJ detonation parameters, pressure and velocity, are calculated from the Hugoniot EOS of both reactant and product mixtures using the formulation found in [2]. Mixtures rules within FactSage are employed for the prediction of the properties of both reactant and product mixtures.

Analyses of Ti-Si, Al-Fe₂O₃-Al₂O₃ (thermite), and Zn-S systems were performed using this method, and the thermodynamic properties are summarized as:

- 1) $3 \text{ Si}_{(s)} + 5 \text{ Ti}_{(s)} = \text{Si}_3\text{Ti}_5_{(liq)}$; Heat of detonation = -248 kJ (49.6.93 kJ/mol), $\Delta V=7\%$ $T=T_{ad}$, $T=2390 \text{ K}$
- 2) $2\text{Al}_{(s)} + \text{Fe}_2\text{O}_{3(s)} = 2\text{Fe}_{(liq)} + \text{Al}_2\text{O}_{3(liq)}$; Heat of detonation = -56.76kJ (18.3kJ/mol), $\Delta V=11.60\%$ $T_{ad}=3129.3 \text{ K}$ (~boiling point Fe)
- 3) Zn-S: $T=T_{ad}=1906 \text{ K}$, $\text{Zn}_{(s)} + \text{S}_{(s)} = \text{ZnS}$; Heat of detonation = -106.23 kJ (53.11 kJ/mol), $\Delta V=2.72\%$

The detonation properties are shown in Figure 2. All three systems exhibit modest detonation pressures compared to conventional high explosives, and marginal volume expansion when considering the porosity typically observed in loose-packed powder mixtures (typically 20-50% void fraction).

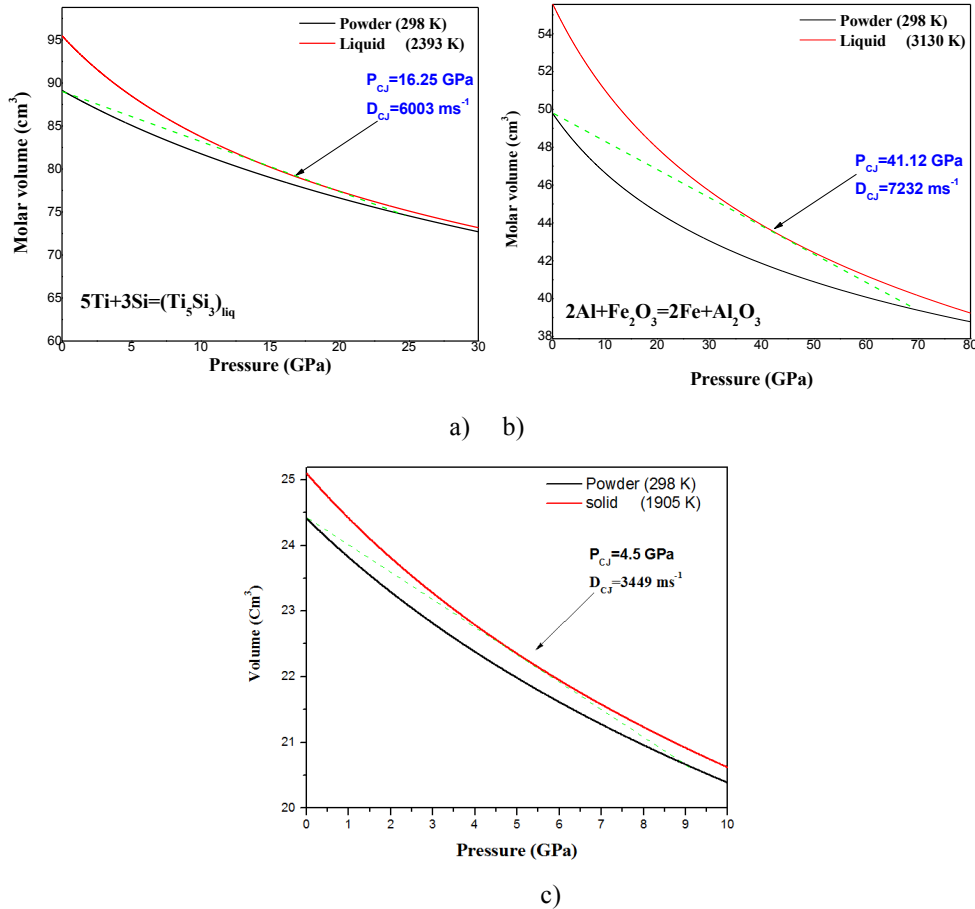


Figure 2: The tangency C-J solution for a) Ti-Si, b) Al-Fe₂O₃, and c) Zn-S, calculated using the methodology of Gheribi et al. [2]. Note that the pressure is shown in the abscissa rather than the ordinate axis

5 Discussion and conclusions

The results show that while detonation may be possible in the chosen systems, the CJ parameters indicate that the detonation conditions are somewhat marginal and would be challenging to achieve in practice. The low volume expansion suggests that a very low void fraction must be achieved in the mixture so that expansion can overcome the porosity. In addition, the very weak pressure dependence of certain condensed-phase reactions [12] suggests that it may be difficult to achieve a reaction rate capable of sustaining detonation in a charge of practical size.

The main interest of this work, however, is to demonstrate a robust thermo-chemical analysis approach for condensed phases which shows that certain reactive systems could exhibit a new mode of condensed-phase detonative reaction. The power of the CALPHAD method lies in the detailed analysis of condensed phases, which opens the possibility of other types of energy release. For example, while pressure-induced phase transitions were not considered in this work, the CALPHAD method can identify systems where

phase transitions could release energy rapidly enough to drive a detonation. This would be more likely to occur in a system with a low-pressure phase transition, or one where the CJ pressure is very high. While the present analysis method is currently limited to stable substances where no new phases appear, it can be extended to unstable phases if high-pressure experimental data is available, or through more involved modeling of high-pressure phase equilibria using atomistic methods. This effort constitutes a near-term objective in the continuation of this work.

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