

LA-UR-15-27596

Approved for public release; distribution is unlimited.

Title: Product equation of state for polysulfone

Author(s): Ticknor, Christopher

Intended for: Report

Issued: 2015-09-30

Disclaimer:

Los Alamos National Laboratory, an affirmative action/equal opportunity employer, is operated by the Los Alamos National Security, LLC for the National Nuclear Security Administration of the U.S. Department of Energy under contract DE-AC52-06NA25396. By approving this article, the publisher recognizes that the U.S. Government retains nonexclusive, royalty-free license to publish or reproduce the published form of this contribution, or to allow others to do so, for U.S. Government purposes. Los Alamos National Laboratory requests that the publisher identify this article as work performed under the auspices of the U.S. Department of Energy. Los Alamos National Laboratory strongly supports academic freedom and a researcher's right to publish; as an institution, however, the Laboratory does not endorse the viewpoint of a publication or guarantee its technical correctness.

Product equation of state for polysulfone

Christopher Ticknor

Theoretical Division, Los Alamos National Laboratory,

Los Alamos, New Mexico 87545, USA

(Dated: September 28, 2015)

Abstract

Here we review the new polysulfone product equation of state (EOS) made with magpie, a chemical equilibrium code.

PACS numbers:

I. INTRODUCTION

Here we discuss the polysulfone product equation of state (EOS), number 97611, which was produced by Magpie.

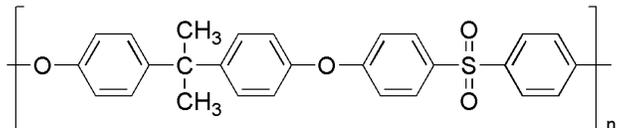


FIG. 1: (color online) The polysulfone repeating unit, image from wikipedia.

We have produced a table spanning a portion of the standard Sesame grid. The table has a density range of 0.124- 3.1 g/cc with 43 density points and a temperature range of 696-8123 K with 25 points. With a nominal density of 1.24 g/cc, this covers 10 times expanded up to 2.5 compressed. Additional work can be done to expand the table as needed.

The table has limited range due to the limited validity of the chemical picture. In particular moving to higher density and/or temperature would require a series of alternate approaches to handle dissociation and ionization. For lower temperatures, there needs to be a means to transition to a condensed matter formulation of the material. Previous work has been done to extend a limited range table [1].

Throughout this work, we use the nominal composition of polysulfone determined from the repeating unit with a ratio of 22:27:4:1 for H:C:O:S. See Fig. 1 to see the repeating unit of polysulfone.

II. METHODS

We used Magpie, a code developed under ASC-PEM-HE, to generate the product EOS. This code was developed following the lead of M.S. Shaw's code HEOS [2].

The products are modeled under the assumption of full chemical and thermodynamic equilibrium. We assume pressure and temperature (PT) equilibrium between components and optimize the populations via Gibb's free energy minimization. We assume that the only solid - bulk carbon - is in the form of diamond. In reality the situation is far more complicated.

To model the molecular degrees of freedom, we use a statistical treatment as outlined

by Refs. [2, 3]. This model thermally populates molecular rotational and vibration states. Molecular parameters were obtained from standard NIST tables [4]. For the thermal electric contribution, we use a united atom semiclassical model (Thomas Fermi Dirac, TFD) that is added to the density-temperature (RT) table after the chemical equilibrium calculation has been done.

To treat the intermolecular interactions we use Ross perturbation theory, which is based on a hard sphere plus a $1/r^{12}$ repulsive reference [5]. The interaction potentials are modeled with an EXP6 potential:

$$\phi(r) = \frac{\epsilon}{\alpha - 6} \left(6e^{-\alpha(r/r_0-1)} - \alpha \left(\frac{r_0}{r} \right)^6 \right). \quad (1)$$

Where α sets the steepness of the repulsive wall, ϵ is related to the energy depth of the potential, and r_0 gives the scale the intermolecular potential. Nominally, EXP6 parameters for each species were calibrated to shock data on the pure fluid for most molecules. See Table I for the parameters used in this work.

We included small polyatomic sulfur molecules with negative heats of formation (HOF). There is very little data on these Sulfur compounds under shock compression. So we used corresponding states [3] to determine the molecular parameters.

The EOS for bulk diamond was developed by J. Coe and uses $\rho_0 = 3.51$ g/cc [6]. It uses a Mie Grueneisen form built from a Murnaghan cold curve with $B_0 = 440$ GPa and $N = 3.65$, and a Debye thermal ionic contribution ($\theta_D=1850$ K). The free energy of the complete mixture (fluids+solid) was minimized as a function of chemical composition subject to conservation and non-negativity of elemental mass fractions. Molecular fluids were combined in the form of an ideal mixture (having an entropic contribution).

We believe that a graphite model is not needed due to the pressure at which polysulfone decomposes ($P>25$ Gpa). This pressure makes it likely that diamond will be the primary form of carbon, but this could be further explored as needed.

The polysulfone heat of formation is unknown. So first it was set to zero, and then it was altered to get better agreement with shock data.

component	r_0/A	α	$(\epsilon/k_B)/K$
<i>C(liq)</i>	3.64	12.0	95.1
<i>H₂</i>	3.43	11.1	36.4
<i>CH₄</i>	4.22	12.5	154.1
<i>H₂O</i>	3.5	10	424
<i>CO</i>	4.2	11.1	88
<i>CO₂</i>	4.096	13.781	335
<i>O₂</i>	4.11	13.117	75
<i>HCOOH</i>	4.096	13.781	184.5
<i>HCCH</i>	4.41	13	250
<i>OCS</i>	4.68	13	305.4
<i>SH₂</i>	4	13	244
<i>SO₂</i>	4.523	13	347

TABLE I: Ross exp-6 parameters used in the calculation of the EOS.

III. COMPARISON TO SHOCK DATA

In Fig. 2 we show the Marsh shock data [7] (shown as red stars) compared to three different Hugoniot with different heats of formation: 0 (blue x), 1 (magenta box), and 2 (black square) kJ/g.

When we change the HOF from 0 to 1kJ/g the density changes on average by 1% at a given pressure. but this ranges from over 2% to less than 0.8% with the largest density changes occurring at low pressure.

Polysulfone has a volume collapse near 25 GPa. Above this region, we expect the product EOS to reproduce the Hugoniot well. We note the Hugoniot seems to be too soft at high pressure. This fact needs to be investigated by testing molecular parameters of the products to see if the agreement can be improved. Additionally, we could look into different models. For example, we could include TFD at the component level -for each molecule- and then do the chemical equilibrium including this contribution.

Fig. 3 shows the Us-Up plot for the polysulfone EOS. The different lines are for different heats of formation: 0 (blue x), 1 (magenta box), and 2 (black square) kJ/g.

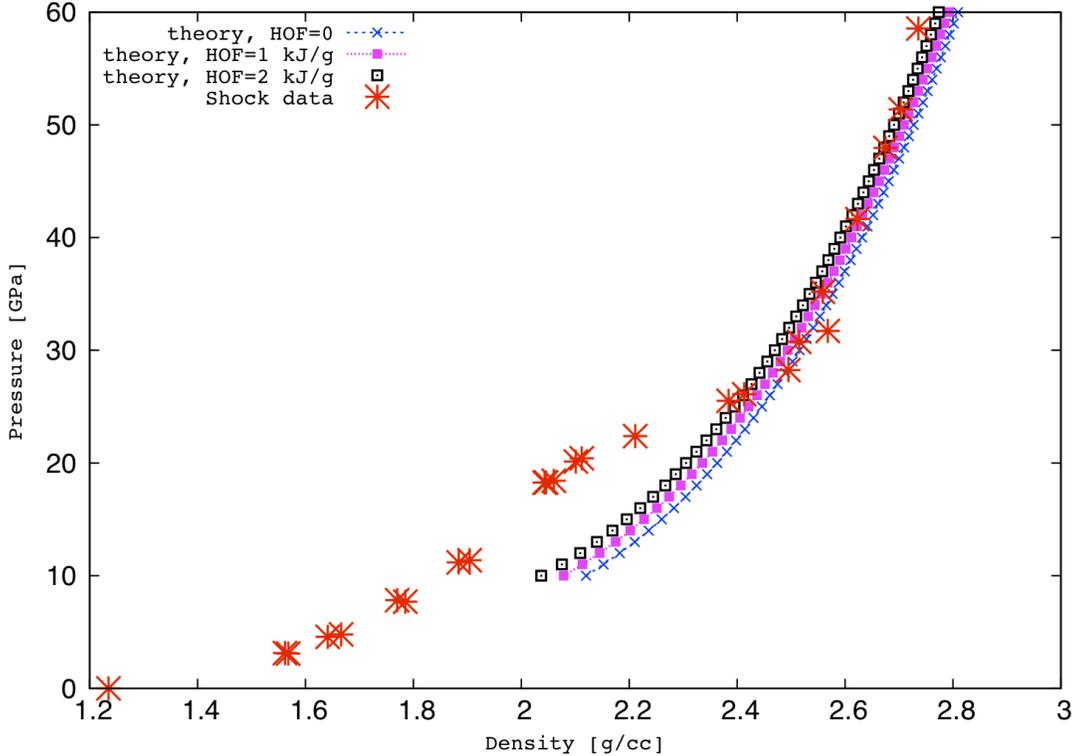


FIG. 2: (color online) The polysulfone Hugoniot for the new product EOS compared to Marsh shock data (red stars) compared. The different Hugoniot are for different heats of formation: 0 (blue x), 1 (magenta box), and 2 (black square) kJ/g.

IV. EVOLUTION OF CHEMICAL COMPOSITION

We will now look at the composition along the principal Hugoniot as a function of pressure. The chemical elements shown in Fig. 4 are: diamond (green star), sulfur dioxide (magenta square), methane (black +), water (orange x), and formic acid (blue star).

The primary chemical reaction along the Hugoniot is



Where x represents other chemical compounds in the mixture. On the Hugoniot we see that water is produced and not carbon dioxide or carbon monoxide in contrast to Fig. 5 below where we look at isochores.

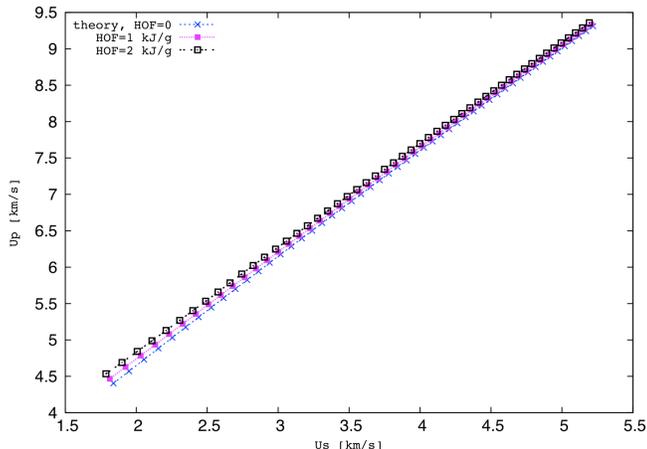


FIG. 3: (color online) The U_s - U_p plot for the product EOS. The different lines are for different heats of formation: 0 (blue x), 1 (magenta box), and 2 (black square) kJ/g.

The sulfur chemistry is rather straight forward. Essentially everything is in the form of sulfur hydride. We previously included SH and SO in our calculations, but these two compounds made negligible contributions. Furthermore, we had little justification to set their molecular parameters because there is no pure shock data. Additionally, these radicals do not have critical properties and thus cannot use corresponding states [3]. So they have been omitted. We have included sulfur hydride, OCS and sulfur dioxide, see Table I.

A. Further composition studies

In Fig. 5 we show the evolution of the composition for three different densities: 0.124 (top), 1.24 (middle), and 2.1 g/cc (bottom). Only the last one is relevant to the Hugoniot. The chemical elements shown in the plot are: diamond (green star), liquid carbon (blue star), acetylene (magenta square), methane (black +), water (orange x), carbon monoxide (gray circle), and carbon dioxide (red triangle).

At low density (top plot) liquid carbon makes an important contribution (and at high temperature). This is where carbon shifts between diamond to a liquid state, and then it takes up more volume.

At the nominal density (middle plot) and the low density (top plot), we see that the

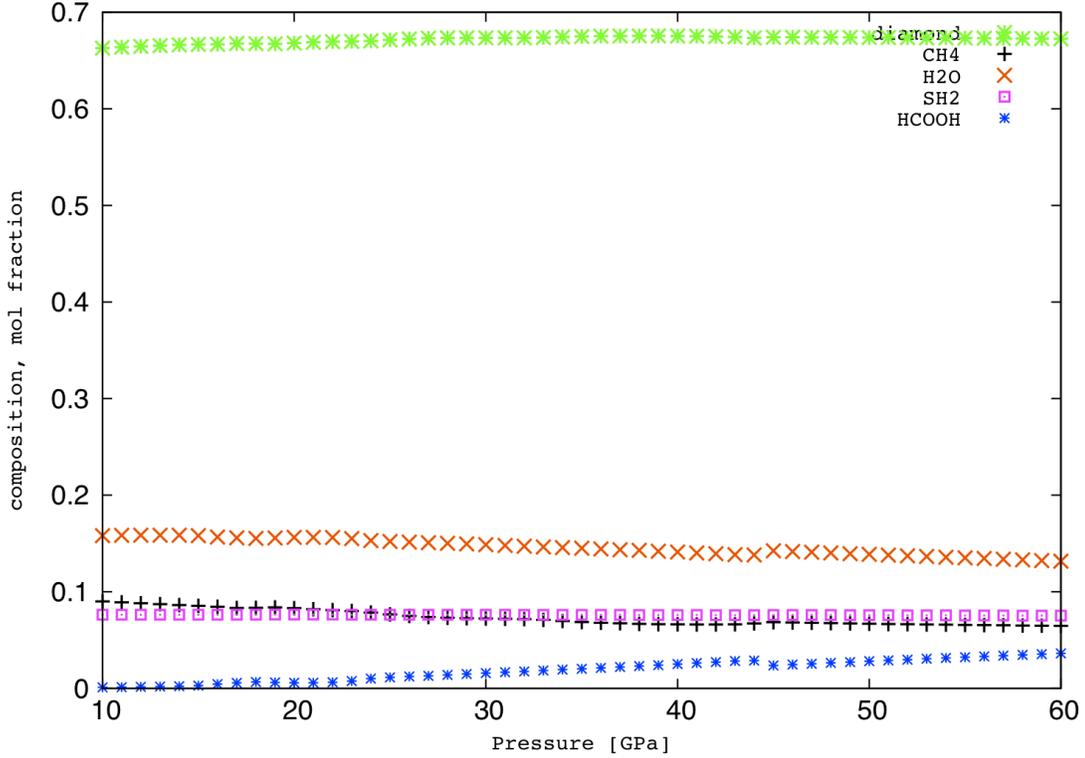
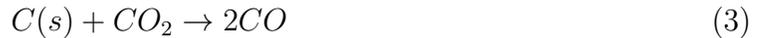


FIG. 4: (color online) The composition along the polysulfone Hugoniot as a function of pressure. The chemical elements are: diamond (red star), sulfur dioxide (magenta square), methane (black +), water (orange x), and formic acid (blue star).

primary reactions as temperature increases are:



These reactions create one more mole of gas. The true reactions are of course more complex (we only show 7/13 components), but these give a reasonable picture of what is happening.

At high density, the concentrations are much more stable. Most of the system is in the form of diamond. There is some increase carbon dioxide and acetylene as temperature is increased, but not as significant as the two lower densities.

For all of these plots, the sulfur chemistry is rather straight forward. The sulfur is in the

form of SH_2 with little exception.

V. CONCLUSION

Future work will include: (1) Testing how effectively we can optimize the molecular parameters of sulfur compounds to improve the EOS. (2) Expanding the table range. The models run into their physical limits and encounter numerical problems at high density [1]. Furthermore, we will need to extend the range to high temperature and include dissociation and eventually ionization. These capabilities will be the precursors to having a full Sesame range table.

Acknowledgments

The authors are acknowledge illuminating discussions with J. Coe. The authors gratefully acknowledge support from ASC, computing resource from CCC, and LANL which is operated by LANS, LLC for the NNSA of the U.S. DOE under Contract No. DE-AC52-06NA25396.

-
- [1] S. Crockett, *Extending high-explosives equations of state*, unpublished; LA-UR-06-5738 (2006).
 - [2] M. S. Shaw, Eleventh Symposium (International) on Detonation pp. 933–941 (1998).
 - [3] M. Ross and F. H. Ree, *The Journal of Chemical Physics* **73**, 6146 (1980), URL <http://scitation.aip.org/content/aip/journal/jcp/73/12/10.1063/1.440106>.
 - [4] *Computational chemistry comparison and benchmark database*, <http://cccbdb.nist.gov/> (2013).
 - [5] M. Ross, *The Journal of Chemical Physics* **71**, 1567 (1979), URL <http://scitation.aip.org/content/aip/journal/jcp/71/4/10.1063/1.438501>.
 - [6] J. D. Coe, *Sesame equations of state for "epoxy"*, unpublished; LA-UR-15-23248 (2015).
 - [7] e. S. P. Marsh, *LASL Hugoniot Data* (University of California Press, 1980).

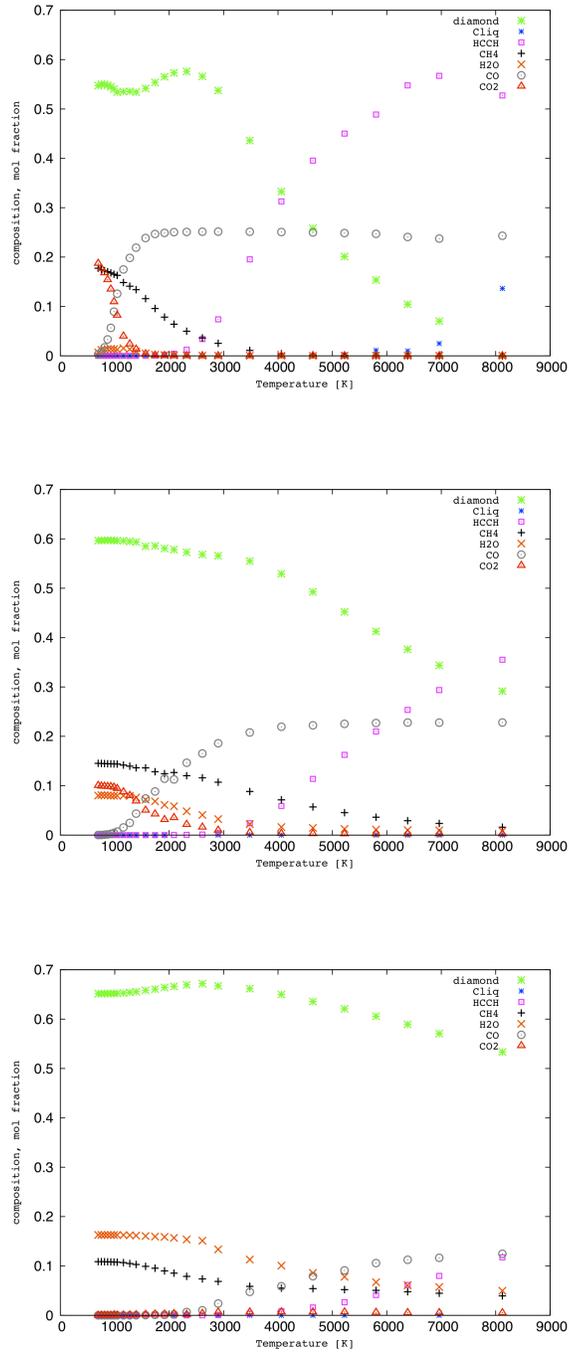


FIG. 5: (color online) The composition evolution as function of temperature for three different densities: 0.124 (top), 1.24 (middle), and 2.1 g/cc (bottom). The chemical elements shown are: diamond (green star), liquid carbon (blue star), acetylene (magenta square), methane (black +), water (orange x), carbon monoxide (gray circle), and carbon dioxide (red triangle).