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Energy Referencing in LANL HE-EOS Codes

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I. INTRODUCTION

Here, We briefly describe the choice of energy referencing in LANL's HE-EOS codes, `HEOS` and `MAGPIE`. Understanding this is essential to comparing energies produced by different EOS codes, as well as to the correct calculation of shock Hugoniots of HEs and other materials. In all equations after (3) throughout this report, all energies, enthalpies and volumes are assumed to be molar quantities.

II. THERMOCHEMICAL CODES

LANL's HE-EOS codes occupy a class of programs called "thermochemical codes." These codes are designed with a chemical viewpoint in mind, in which each component of a chemical mixture is described by a partition function ($Q\left(N,V,T\right)_{tot}$), which is a product of translational, rotational, vibrational and electronic partition functions and a configurational integral ($Z\left(N,V,T\right)$), which accounts for non-ideal interactions. See (1)-(3). The $\mathbf{s}_i$s are the length-scaled coordinates ($\mathbf{r}_i/V^{1/3}$) of the atoms in the system, and $E\left(\mathbf{s}_1,\mathbf{s}_2,\ldots,\mathbf{s}_N\right)$ is the many-body interaction energy of a given configuration. LANL HE-EOS codes currently approximate $Z\left(N,V,T\right)$ with Ross perturbation theory and spherical interaction potentials, the details of which we will not discuss here.[1] Currently, the total Gibbs free energy, $G_{\mathrm{mix}}\left(P,T\right)$, is constructed for the mixture using the ideal-mixing approximation, and the equilibrium composition is determined by minimizing $G_{\mathrm{mix}}\left(P,T\right)$ as a function of chemical composition, subject to a mass constraint.

$$Q\left(N,V,T\right)_{tot} = Q\left(N,T\right)_{id} Z\left(N,V,T\right) \tag{1}$$

$$Q\left(N,T\right)_{id} = \frac{q_t\left(T\right)^N q_r\left(T\right)^N q_v\left(T\right)^N q_e\left(T\right)^N}{N!} \tag{2}$$

$$Z\left(N,V,T\right) = V^N \int \ldots \int e^{-E(\mathbf{s}_1,\mathbf{s}_2,\ldots,\mathbf{s}_N)/kT} d\mathbf{s}_1 d\mathbf{s}_2 \ldots d\mathbf{s}_N \tag{3}$$

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III. THE REFERENCE STATE

LANL's legacy `HEOS` code (written by Sam Shaw, T-1, retired)[2, 3] used the elements in their standard state at $0K$ as the reference state as shown in (4). χ_i symbolizes the mole fraction of element i per mole of the compound of interest. (An example will be provided in a later section.) This is convenient as there are no PV contributions to correct for in the heats found in the JANAF tables[4] at $0K$ in order to obtain an energy. LANL's HE-EOS codes require the input of heats of formation ($\Delta_f H$) for every component whose EOS is to be calculated; however, it should be carefully noted by the practitioner that *heats of formation at* $0K$ *should be supplied* in order to maintain consistency with our chosen reference state.

$$E_{ref} = \sum_{i=1}^{n_{\text{elements}}} \chi_i E_i^\circ \left(0K\right) \tag{4}$$

IV. HUGONIOT CALCULATIONS

With this energy reference in mind, we turn our attention to how we calculate shock Hugoniots. For this, we require the energy of the initial state undergoing shock compression (E_0), in order to solve the Hugoniot relation, as shown below.

$$E - E_0 = \frac{1}{2}\left(P + P_0\right)\left(V_0 - V\right) \tag{5}$$

Typically for HEs, the only energies readily available are room temperature standard heats of formation, symbolized as $\Delta_f H^\circ\left(298K\right)$. Room temperature standard heats of formations have a different reference state than our chosen one, and thus must be corrected to obtain E_0. We must first correct the reference heats of the elements as shown in (6). We use the symbol $\Delta_f H^*\left(298K\right)$ to indicate the heat of formation at $298K$ relative to the elements at $0K$. The subscript "c" refers to the compound of interest.

$$\Delta_f H_c^*\left(298K\right) = \Delta_f H_c^\circ\left(298K\right) + \sum_{i=1}^{n_{\text{elements}}} \chi_i \left[H_i^\circ\left(298K\right) - H_i^\circ\left(0K\right)\right] \tag{6}$$

$$E_0 = \Delta_f E_c^*\left(298K\right) = \Delta_f H_c^*\left(298K\right) - P_c V_c \tag{7}$$

Historically, equation (6) has been used to calculate E_0 for a shock Hugoniot calculation in LANL HE-EOS codes. However, this is not strictly correct, for $\Delta_f H^*\left(298K\right)$ has an enthalpic contribution (PV) which should technically be removed as in (7); however, in most situations relevant to solid HEs, it is negligible compared to $\Delta_f H^*\left(298K\right)$. Caution should be exercised at conditions away from ambient, or for other materials, as this may not always be the case. For example, for an ideal gas, the PV contribution can be non-neglible due to the much larger molar volume of an ideal gas as compared to a solid HE at ambient conditions. See the appendix for proof of (7).

V. EXAMPLE

Here we provide a brief example for clarity. Consider the molecule NH_3 at densities low enough that the ideal-gas law is applicable. `MAGPIE`'s models for NH_3 would then be as described in the Thermochemical Codes section, except $Z(N,V,T) = V^N$. The energy zero of NH_3 is entered in `MAGPIE` as -38.907 kJ/mol, which is the NIST-JANAF value of $\Delta_f H^\circ(0K)$. Consider a Hugoniot for which the initial state is ambient. For an HE, we would likely lack models to calculate E_0, so we would apply the correction to $\Delta_f H^\circ(298K)$ as discussed above. The result of applying equations (6) and (7) is shown below, where 8.670 kJ/mol and 8.467 kJ/mol are the JANAF[4] values of $[H_i^\circ(298K) - H_i^\circ(0K)]$ for N_2 and H_2 respectively. Equation (9) employs the PV correction as shown in (7); however, in (9) we have replaced PV with RT as we are treating NH_3 as an ideal gas. Thus, for an ideal-gas, this correction can be important.

$$\Delta_f H_c^*(298K)\,\mathrm{kJ/mol} = -45.898 + \frac{1}{2}\times 8.670 + \frac{3}{2}\times 8.467 = -28.863\ \mathrm{kJ/mol} \tag{8}$$

$$E_0 = \Delta_f H_c^*(298K) - 8.314\times 10^{-3}\mathrm{kJ/(mol\ K)}\times 298K = -31.340\mathrm{kJ/mol} \tag{9}$$

The energy calculated by `MAGPIE` for NH_3 at ambient conditions is -31.335 kJ/mol, thus illustrating the consistency of this choice of energy reference. The discrepancy of 0.005 kJ/mol is easily accounted for by small differences in fundamental and spectroscopic constants.

VI. ACKNOWLEDGMENTS

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VII. APPENDIX

Starting from (6), and expanding, we obtain:

$$\begin{aligned}
\Delta_f H_c^*(298K) &= H_c^\circ(298K) - \sum_{i=1}^{n_{\mathrm{elements}}} \chi_i H_i^\circ(298K) + \sum_{i=1}^{n_{\mathrm{elements}}} \chi_i \left[H_i^\circ(298K) - H_i^\circ(0K)\right] \\
&= H_c^\circ(298K) - \sum_{i=1}^{n_{\mathrm{elements}}} \chi_i H_i^\circ(0K) \\
&= E_c^\circ(298K) + P_c V_c - \sum_{i=1}^{n_{\mathrm{elements}}} \chi_i E_i^\circ(0K) \\
&= \Delta_f E_c^*(298K) + P_c V_c
\end{aligned} \tag{10}$$

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