The $\alpha(v)$ curve per se provides a means of estimating the validity of the $\alpha(v)$ approximation. In the limit of low pressures, α should emerge smoothly into the van der Waals b. Hence, as a covolume, α should be about four times greater than the actual volume v_m of the molecules. Hence one should have for the internal energy increase due to the applied pressure p,

$$E_i = -\frac{1}{4} \int_0^p p d\alpha \cong -\frac{nRT}{4} \int_0^v d\alpha/(v-\alpha).$$

The integral has as an upper limit for CHNO explosives a value of about 2·5 giving an upper limit value for E_i of about 200 cal/g. But Q (the heat of explosion) plus the Hugoniot energy $\frac{1}{2}p(v_1-v_2)$ is in this upper limit case about 1800 cal g^{-1} giving $E_i/(Q+\frac{1}{2}p(v_1-v)=0.1$ to 0·15.

One may also estimate E_i directly by the methods used here for thermal expansion and compressibility of solids. Thus

$$E_i = \Delta T = \int_0^p p dv = \int_0^p v_m p \left(\frac{1}{v_m} \frac{dv_m}{dp} \right) dp < v_m \beta p^2/2.$$

The theory for molecules of the type considered here also gives $\beta_0 \le 10^{-6} \cdot \text{atm}^{-1}$. Since \bar{v}_m should have an upper limit of $0.5 \text{ cm}^3 \text{ g}^{-1}$, one thus obtains $E_i \sim 200 \text{ cal g}^{-1}$ in agreement with the above estimate.

According to these estimates therefore, while the $\alpha(v)$ equation of state gives an upper limit for T_2 , the actual value should be no more than 10-15 % (or about 500° K) less. This is, however, in sharp contrast with the approximately 3000° K lower values for T_2 computed for PETN at $\rho_1=1.7$ g cm⁻¹ by Cottrell and Paterson.¹⁹

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