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An Equation of State for Gases at High Pressures and Temperatures from the Hydrodynamic Theory of Detonation

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THIS note is in reply to comments by S. Paterson[1] on my recent article.[2] Paterson first challenged the (supposed) claim that method (a) of my article is an "exact" solution. As a matter of fact, no such claim was made. In the summary of the paper I referred to method (a) as ". . . in principle at least, a general solution." However, I hastened to add that, in fact, a general solution was impossible because of the necessity of postulating a particular form of $\alpha(T,v)$ in evaluating the detonation temperature. Paterson merely restated my own arguments in pointing out that ". . . (detonation) velocities alone do not allow us to discriminate between such a solution (i.e., of $\alpha(v)$ from velocity data) and any alternate solution, e.g., Kistiakowsky and Wilson's in which α depends also on T." Thus my article stated that "it is quite evident that the detonation temperature is really the only detonation property which may be used to provide experimental information on the accuracy of the various equations of state . . . all other quantities being relatively insensitive to the particular equation of state employed." Realizing the limitations of the hydrodynamic theory in providing by itself an unambiguous equation of state, I considered it necessary to bring in several external evidences to support the $\alpha(v)$ approximation and discussed the agreement between methods (a) and (b) as supporting evidence. It was required by sufficiently strong implications that the final answer should rest entirely on comparisons between experimental and theoretical detonation temperatures in view of the impossibility of evaluating the heat capacity (Eq. (17)) from detonation velocities and the hydrodynamic theory alone.

Paterson is in error in his statement that ignoring Eq. (9) in method (a) "amounts to discarding the Chapman-Jouguet condition." As a matter of fact, Eq. (11) is nothing more than the Chapman-Jouguet postulate allowing the completely justifiable approximation $p_2 \cong p_2 - p_1$. That is, the Chapman-Jouguet postulate is expressed in the equation

$$-(dp_2/dv_2)_s = (p_2 - p_1)/(v_1 - v_2) = p_2\beta/(v_2 - \alpha) \qquad \text{(a)}$$

which, upon canceling $p_2 - p_1$ with p_2, gives Eq. (11).

Paterson argued that, since Eq. (13) follows from Eqs. (11) and (12), one does not obtain a unique solution by solving Eqs. (11), (12), (13), and (16) for the four independent variables T_2, v_2, α, and β. While it is true that Eq. (11) may be derived from (12) and (13), this is made possible only by virtue of the approximation $p_2 \gg p_1$; the four equations are in reality independent. The five independent equations are (1), (2), (3), (4), and (6). Under the approximation $p_2 \gg p_1$ and employing the auxiliary Eq. (8), Eq. (11) is equivalent to Eq. (4); Eq. (12) follows from (1) and (6); Eq. (13) may be derived from (1), (2), and (6); Eq. (16) follows from (3). Hence, it is only the very small value of p_1 relative to p_2 that makes it appear that Eqs. (11), (12), (13), and (16) are not independent. Paterson was evidently troubled by the consideration that six independent unknown variables W, T_2, α, β, p_2, v_2 were evaluated from five independent equations, evidently overlooking or ignoring the fact that the condition $p_2 \gg p_1$ is, in fact, the sixth condition needed to complete the solution. I fail to see, therefore, why the solution obtained by solving the four Eqs. (11), (12), (13), and (16) for β, α, v_2, T_2 by the method of successive approximations should not be a unique solution.

Paterson suggested that since method (b) preceded (a) in the development of the theory, the results obtained in method (b) would influence those in method (a). Such a suggestion could have been easily evaluated by Paterson himself if he had been willing to carry out a few series of approximations starting with different assumed values of β.

Paterson's argument that a step-by-step integration of the fifth equation of the theory (Eq. (a) above) leads to an entire family of $\alpha(v)$ curves is incorrect because it fails to recognize that in this problem we are dealing with well-defined thermodynamic functions. Equation (9) derived from the laws of thermodynamics and the assumed equation of state gives β as follows:

$$\beta = (C_v + R)/C_v - (\partial\alpha/\partial v_2)_s + (\partial E/\partial v)_T nR/C_v p_2. \qquad \text{(b)}$$

Since no critical points are involved, obviously the two functions α and $(\partial E/\partial v)_T$ are single valued in v, and one should thus expect β to be a single-valued function of v. However, if one needs an additional argument, the integration constant referred to by Paterson may be established as zero from the fact that Eq. (b) must reduce to $\beta = C_p/C_v = \gamma$ for the case where factors for non-ideality become vanishingly small, a condition which applies in the detonation of gaseous explosives. In fact, Paterson's argument should apply equally well to any assumed equation of state but is invalidated for one thing by the experimental verification of the hydrodynamic theory for gaseous explosives.

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[1] S. Paterson, J. Chem. Phys. **16**, 159 (1948).

[2] M. A. Cook, J. Chem. Phys. **15**, 518 (1947).