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Stewart Paterson

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

STEWART PATERSON
Imperial Chemical Industries Limited, Explosives Division,
Stevenston, Scotland
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THE thermal equation of state for any two-parameter substance is included in the general form:

$$pv = nRT + p\alpha(v, T),$$

where p , v , T , n , R represent pressure, specific volume, temperature, number of moles per g, and gas constant per mole, respectively. In attempting to determine the equation of state for gases at high pressures and temperatures from the observed velocities of detonation (D) of explosive compounds, at various densities (Δ), P. Caldirola¹ has assumed that the "covolume" $\alpha(v, T)$ can be regarded under such conditions as a function of v alone. This assumption, criticized by S. R. Brinkley,² finds support in a recent valuable paper by M. A. Cook³ on the same topic. Cook's arguments in favor of the temperature independence of α are partly of an *a posteriori* nature, deduced from the coincidence of the $\alpha(v)$ curves for explosives yielding widely different calculated detonation temperatures, and as such appear to carry considerable weight. The relative constancy of the theoretical second virial coefficient between, say, 2000 and 6000°K provides independent support for the same view, which is largely shared by the writer.

Cook, however, also claims to have evaluated α directly from the experimental detonation velocities, not only on the assumption that $\alpha = \alpha(v)$, but also by an independent and exact method which allows for possible variation with T . If this were so, it would of course enable one to dispense with extraneous and *a posteriori* arguments regarding the temperature dependence of α . However, it does not seem that Cook has in fact carried out such an "exact" solution, nor indeed that it is possible to do so on the basis of experimental velocities for one explosive alone. For since $\alpha(v)$ can evidently be determined to fit the observed velocities for one explosive, these velocities alone do not allow us to discriminate between such a solution and any alternative solution, e.g., Kistiakowsky and Wilson's⁴ in which α depends also on T .

Cook's position is somewhat obscured by the large number of interdependent equations which he writes down. The

solution depends, in fact, upon Cook's Eqs. (2), (6), (9), and (16), together with *any two* of (10), (11), (12), and (13); for these last four are not independent, any two being immediately deducible from the remaining two. Cook ignores Eq. (9), which amounts to discarding the Chapman-Jouguet condition. Then, since W appears only in (2) and p_2 only in (6), we can get these equations also aside, leaving (16) and *any two* of (10), (11), (12), and (13) to be solved for T_2 , v_2 , α , β .

These are apparently the equations from which it is proposed to deduce T_2 , v_2 , α , β by successive approximation. Cook evaluates α from (13) and then v_2 from (12), thereafter calculating β from (11). Since (11) follows at once from (12) and (13), this process would clearly not be expected to define a unique solution. On the other hand, if Cook commenced these "successive approximations" with the values of β given by "method *b*" which as he says preceded "method *a*" in the development of the theory, it seems natural that method *b* should be confirmed.

As indicated above the clearest proof that Cook has not accomplished an exact solution, and that such is not possible on the basis of the experimental velocities for one explosive alone, is given by the fact that equations of state markedly different from his own are capable of giving good agreement with observed velocities. Since Cook's analysis is based solely on the $D(\Delta)$ relation, it is clear, therefore, that this relation alone cannot lead to a unique equation of state. If it does not provide proof that Kistiakowsky and Wilson's equation, for example, is not correct, it evidently cannot prove that an alternative equation is correct.

Regarding "method *b*" itself, a further point may be made. It is stated by Caldirola, and seems implied by Cook, that one can "unequivocally" determine $\alpha(v)$ from the known $D(\Delta)$ relation. One of the five equations available to define v_2 , p_2 , T_2 , W , and α is however a differential equation in α , and the solution therefore would be expected, in general, to embrace not one only but an entire family of $\alpha(v)$ curves. That this is in fact the case may be confirmed by a step-by-step integration, as distinct from the method of successive approximation used by Cook, which should and does lead to the envelope of the family. Physical considerations certainly appear to favor this singular solution, but the point seems to deserve attention.

¹ P. Caldirola, J. Chem. Phys. **14**, 738 (1946).

² S. R. Brinkley, J. Chem. Phys. **15**, 113 (1947).

³ M. A. Cook, J. Chem. Phys. **15**, 518 (1947).

⁴ G. B. Kistiakowsky and E. B. Wilson, OSRD Report 69.