

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

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(d)  $r(\text{C}-\text{H}) = 1.10 \pm .05\text{\AA}$ : Linnett quotes 1.094\text{\AA}. The spread in the values of  $\alpha = \text{HC}-\text{Br}$  corresponding to these data is from  $107^\circ$  to  $118^\circ$ . Unless  $r(\text{C}-\text{Br})$  is greater than 1.93\text{\AA}, there is no "flattening" of the  $\text{CH}_3$  group.

(4) *Methyl Iodide*

(a)  $I_B = 111.4 \times 10^{-40} \text{ g cm}^2$ , as quoted by Gordy, Smith, and Simmons.<sup>4b</sup>

(b)  $I_C = 5.54 \times 10^{-40} \text{ g cm}^2$ , from the doublet spacings.

(c)  $r(\text{C}-\text{I}) = 2.11 \pm .03\text{\AA}$ . This is an estimated value, based on the electron diffraction values for  $r(\text{C}-\text{I})$  in  $\text{CH}_2\text{I}_2$  and  $\text{CHI}_3$  reported by Hassel<sup>11</sup> (2.12\text{\AA} in both these compounds).

(d)  $r(\text{C}-\text{H}) = 1.10 \pm .05\text{\AA}$ : Linnett quotes 1.092\text{\AA}.

The values of  $\alpha = \text{HC}-\text{I}$  complying with the range in the values  $r(\text{C}-\text{H})$  and  $r(\text{C}-\text{I})$  extend from  $104^\circ$  to  $121^\circ$ , but unless  $r(\text{C}-\text{I})$  is greater than 2.12\text{\AA}, there can be no "flattening" in the  $\text{CH}_3$  group.

While the experimental data do not exclude the possibility that the  $\text{CH}_3$  groups in the methyl halides are slightly "flat," it seems unlikely that the extent of their flattening amounts to more than two or three degrees, and is certainly less than suggested by Bak to be the case in  $\text{CH}_3\text{Cl}$  and  $\text{CH}_3\text{Br}$ . Moreover, it would seem that those factors which might be expected to flatten the  $\text{CH}_3$  group (mentioned by Coulson) are either small in themselves or are offset in their effect by steric repulsion between the H and X atoms.

<sup>1</sup> B. Bak, J. Chem. Phys. 14, 698 (1946).

<sup>2</sup> C. A. Coulson, V. Henri Memorial Volume (Liège, in press).

<sup>3</sup> D. M. Dennison, Rev. Mod. Phys. 12, 175 (1940).

<sup>4</sup> (a) Gordy, Simmons, and Smith, Phys. Rev. 72, 344 (1947); (b) Gordy, Smith, and Simmons, Phys. Rev. 72, 249 (1947).

<sup>5</sup> K. P. Yates and H. H. Nielsen, Phys. Rev. 71, 349 (1947).

<sup>6</sup> D. M. Dennison and M. Johnston, Phys. Rev. 47, 93 (1935).

<sup>7</sup> Stevenson and Schomaker, J. Am. Chem. Soc. 63, 37 (1941).

<sup>8</sup> Linnett, Trans. Faraday Soc. 41, 223 (1945).

<sup>9</sup> Sutton and Brockway, J. Am. Chem. Soc. 57, 473 (1935).

<sup>10</sup> Levy and Brockway, J. Am. Chem. Soc. 59, 1662 (1937).

<sup>11</sup> Hassel and Viervoll, Acta chim. Scand. 1, 149 (1947).

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

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March 5, 1948

THIS note is in reply to comments by S. Paterson<sup>1</sup> on my recent article.<sup>2</sup> 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  $\alpha$  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  $p_2 \approx p_2 - p_1$ . That is, the Chapman-Jouguet postulate is expressed in the equation

$$-(dp_2/dv_2)_s = (p_2 - p_1)/(v_1 - v_2) = p_2\beta/(v_2 - \alpha) \quad (a)$$

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  $T_2$ ,  $v_2$ ,  $\alpha$ , and  $\beta$ . 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  $W$ ,  $T_2$ ,  $\alpha$ ,  $\beta$ ,  $p_2$ ,  $v_2$  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  $\beta$ ,  $\alpha$ ,  $v_2$ ,  $T_2$  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  $\beta$ .

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  $\beta$  as follows:

$$\beta = (C_v + R)/C_v - (\partial\alpha/\partial v)_T + (\partial E/\partial v)_T nR/C_v p_2. \quad (b)$$

Since no critical points are involved, obviously the two functions  $\alpha$  and  $(\partial E/\partial v)_T$  are single valued in  $v$ , and one should thus expect  $\beta$  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.

<sup>1</sup> S. Paterson, *J. Chem. Phys.* **16**, 159 (1948).

<sup>2</sup> M. A. Cook, *J. Chem. Phys.* **15**, 518 (1947).

### Ignition of Explosive Gas Mixtures by Electric Sparks. Minimum Ignition Energies

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March 10, 1947

IN a recent paper<sup>1</sup> Lewis, von Elbe, and co-workers conclude that there exist minimum values for the energies of electric sparks which initiate flames in explosive gas mixtures, and that these values may be considered as absolute minimum values. In a second paper<sup>2</sup> Lewis and von Elbe develop a theory showing the existence of an absolute minimum energy in the case of flames propagated from an instantaneous point source of ignition, and they consider that the theory can be applied to capacitance sparks.

Attention must be paid to the fact that other experiments<sup>3</sup> have given results contradictory to the conclusions of the authors. These experiments have shown that for given mixtures effective minimum energy values exist, but that these are not absolute values and depend (1) on the voltage applied to the spark gap and (2) on the shape of the electrodes. For the best inflammable mixtures the relationship between the voltage applied to the gap and the capacity of the system is of the form  $CV^x = \text{constant}$ , with  $x \approx 3$  when the two electrodes have sharp points,  $x \approx 6$  if one of them has a sharp point, the other being a large sphere or a plane surface,  $x \approx 9$  if the two are large spheres or plane surfaces.

No theory has been developed to explain these results. But it appears that they may agree with Lewis and von Elbe's theory provided that the following assumptions are made: (1) the maximum amount of energy distributed in the ignition zone depends directly on the energy of the fastest electrons initiating an avalanche process in the first steps of the spark discharge and (2) chain carriers in this

zone are, or are generated by, charged particles, which travel through the gap with a mean velocity approximately proportional to that of particles starting from the electrodes. Since the energy of such particles is proportional to  $V$ , and because the minimum energy values are inversely proportional to  $V$  in the case of sharp electrodes, this suggests that the energy in the ignition zone depends directly on the energy per initiating particle, and that the geometry of the gap need not to be taken into account. If one of the electrodes is a plane surface, the field distribution is different, the lines of force being approximately parallel near the surface. In this case it is necessary to take into account the effect of this non-radial distribution on the density of chain carriers in active zones, such as are formed along current bursts or streamers in the spark gap during the first steps of the discharge. The factor  $V^3 = (V^1)^3$  is apparently due to this non-radial field distribution. This factor may be introduced on the assumptions (1) that the number of carriers given rise to by an electron of energy  $eV$  is proportional to  $V$  and (2) that the rate of formation of carriers depends directly on the velocity of such an electron, proportional to  $V^1$ . In the case of two spheres or plane surfaces, the proportionality to  $1/V \cdot 1/V^3 \cdot 1/V^3$  appears also to be due to the geometry of the gap. The double factor  $(1/V^3 \cdot 1/V^3)$  suggests that both electrodes are effective in the generation of carriers.

<sup>1</sup> M. V. Blanc, P. G. Guest, Guenther von Elbe, and Bernard Lewis, *J. Chem. Phys.* **15**, 798 (1947).

<sup>2</sup> Bernard Lewis and Guenther von Elbe, *J. Chem. Phys.* **15**, 803 (1947).

<sup>3</sup> Rodolphe Vialard, *Comptes Rendus* **207**, 1405 (1938); *J. de chim. Phys.* **40**, 101 (1943).

### Low Frequency Raman Spectrum of Calcite

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IT has been demonstrated by Raman and Nedungadi<sup>1</sup> that because of their particular polarization characters two low frequency Raman lines in a  $\text{NaNO}_3$  crystal are attributable to angular oscillations of  $\text{NO}_3$  ions. Later Kastler, Rousset, and other authors<sup>2</sup> established that also in organic crystals (benzene, naphthalene, paradichlorobenzene, paradibromobenzene) low frequency lines, which disappear at the liquid state giving place to a continuum at the sides of the exciting line, are to be assigned to oscillations of the same type.

However, for  $\text{NaNO}_3$  the question has not yet been cleared entirely; in fact, we are not aware that the presence of two low frequency Raman lines, both attributable to angular oscillations, has been explained. Also the calcite, which has a structure analogous to the  $\text{NaNO}_3$ , presents two low frequency Raman lines. We have examined the polarization state of these lines illuminating a calcite crystal parallel to the optic axis, and collecting the diffuse light perpendicular to it.

In Fig. 1 (a) and (b) the microphotometer curves of two spectra relative to the electric vector, and respectively parallel and perpendicular to the optic axis, are repro-