Note on a Proposed Interpretation of the ZetaPotential

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Note on a Proposed Interpretation of the Zeta-Potential

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THE graph of zeta-potential *vs.* concentration in a recent article by this writer[1] should have had the ordinate marked *minus zeta-potential* rather than *zeta-potential* as was shown. It is hoped that this error did not lead to confusion. Examination of the original data would have shown that the zeta-potentials of potassium chloride and barium chloride are negative.

Attention also should be called to another aspect of the new definition of the zeta-potential. Calculations already made by Jones and Wood[2] and Wood and Robinson[3] have shown that Langmuir's theory of the *Jones-Ray Effect* was strikingly substantiated. These calculations were based on the conventional Helmholtz-Perrin values of the ζ-potential. When these corrected surface tensions are recalculated on the basis of the newly defined zeta-potential, no difference in the previous results is obtained (for potassium chloride and barium chloride). The curves given by Jones and Frizzell[4] and Wood and Robinson[3] show that the wetting film thicknesses approach some definite value as the potential increases. The experimental values of the zeta-potential determined in the conventional manner are sufficiently large to be on the part of the curve where further increases in the potential have little or no effect on the thickness of the wetting film. Consequently, the newly defined zeta-potential leaves the corrected values of the surface tension just as they were found from the Helmholtz-Perrin zeta-potentials.

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On the Equation of State for Gases at Extremely High Pressure*

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IN an article bearing the above title, Caldirola[1] has employed the hydrodynamic theory of stationary detonation waves, with experimental values of the detonation velocity, to determine an equation of state valid for the high pressures and temperatures characteristic of the detonation process. The treatment is based upon the Rankine,[2] Hugoniot[3] equations for the continuity of mass, momentum, and energy across the detonation front and the Chapman[4]-Jouget[5] condition for the stable detonation state. The specific-energy increment accompanying the detonation reaction is computed by the thermodynamic relation,

$$E = \bar{C}(T - T_0) - q, \qquad (1)$$

where $\bar{C}$ is the mean specific heat of the detonation products and q the specific heat of reaction at constant volume and at temperature T_0. The equation of state is assumed to be of the form,

$$pv = r(v)T. \qquad (2)$$

We note that Caldirola's calculated values of the detonation temperature increase with increasing density of the explosive.

The writer does not feel that this equation of state is of sufficiently general form for application to the products of detonation of solid explosives, since it implies that the gaseous products are thermodynamically ideal,

$$(\partial E/\partial v)_T = 0.$$

Hirschfelder and his associates[6-7] have pointed out that the internal energy of a gas is a linear function of its density to moderate pressures,

$$E = E_0(T) - \frac{RT^2}{V} \frac{dB(T)}{dT}, \qquad (3)$$

where $B(T)$ is the second virial coefficient, and tables have been provided[7] that permit evaluation of the energy of gas imperfection for substances to which the Lennard-Jones intermolecular potential-energy function applies. The contribution of the second virial coefficient to the energy of gas imperfection is negative at low temperatures and positive for temperatures greater than that for which Em/kT is equal to about 0.04 (Em is the maximum energy of attraction between a pair of molecules). An estimate, based on Eq. (3) and the molecular constants listed by Hirschfelder,[6] leads to a positive value of about 2 kcal./mole for the energy of gas imperfection of CO at 4500°K and density of 1.5. This figure is not negligible in comparison with the temperature-dependent part of the internal energy at zero density and the same temperature, 29 kcal./mole.[8] At the same temperature and density, the second virial coefficient contributes to the internal energies of H_2 and CO_2 of about $+1.2$ kcal./mole and -0.3 kcal./mole, respectively. At high density, terms in higher powers of the density would become significant through the contributions of the third and higher virial coefficients, and one would expect the internal energy to increase exponentially with the density.[6]

From these considerations, it would appear that Eqs. (1) and (2) should be replaced by

$$E = \bar{C}(T - T_0) - q + \int_{\infty}^{v} \left[T \left(\frac{\partial p}{\partial T} \right)_V - p \right] dv, \qquad (1')$$

$$pv = r(v, T)T, \qquad (2')$$

respectively. Rough calculations indicate that the detonation temperature decreases with increasing density of the explosive when the energy of gas imperfection is taken into account. It is unfortunate that, when Eqs. (1') and (2') are employed with the hydrodynamic equations, the ingenious method of Caldirola for determining the equation of state is inapplicable, since evaluation of the integral of Eq. (1') will involve some assumption as to the form of the function $r(v, T)$ for all values of the density from zero to its detonation value.

These considerations are based in part upon work in progress in this laboratory on the equation of state for detonation products of solid explosives. This work is supported from funds derived from the Office of Naval Research for studies of the physics and chemistry of explosive phenomena, and it will be reported upon at a later date.

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