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**Abstract**

**Full Text**

## **Physical Chemistry**

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# **A Method for Testing the Equation of State of Gases at High Temperature**

*(Presented by Academician V. N. Kondrat'ev on 11 XII 1956)*

For the investigation of the properties of gases at high temperatures, the shock tube has recently been used\*. In the present work a method is considered for testing the equation of state and determining the dissociation and ionization energies of gases\*\* in a shock tube. In work (2), the results of measurements of the velocity of steady detonation in a 50% mixture of oxygen and dicyanogen were compared with calculations according to Zel'dovich's theory (3) for conditions of thermodynamic equilibrium immediately behind the detonation front. It was established that the most probable values are  $D_{N_2} = 9.76$  eV and  $D_{CO} = 11.1$  eV. However, work (2) has substantial shortcomings, and the method cannot be regarded as universal (4).

Other methods of investigation are based on measuring the velocity of the shock wave, which completely determines the equilibrium state of the gas behind its front, and on measuring another parameter, which together make it possible to check the constant in the equation of state that is in doubt (for example, the dissociation or ionization energy). Thus, in work (4), in addition to the shock-wave velocity, the velocity of the piston producing this wave was measured, and in work (5) the velocity of the shock wave reflected from the closed end of the tube was measured. In work (6), the second measured parameter was the number  $M^{***}$ .

In note (7) it was proposed to determine the change in the shock-wave velocity when the concentration of the gas under investigation is changed in a mixture with some monatomic gas (in order to weaken the effect of nonidentity of diaphragm rupture, the pressure of the driver gas and of the mixtures under study is taken to be constant). All these methods have a number of shortcomings.

It is known that immediately behind the front of incident and reflected shock waves there exist large relaxation zones in which thermodynamic equilibrium is absent. This is explained by the fact that at relatively low temperatures behind the shock wave there occurs slow excitation of vibrational degrees of freedom, while at high temperatures large deviations of the internal energy from equilibrium values arise, as a result of which the dissociation energy is, as it were, overestimated. In addition, when a shock wave is reflected, there is

Fig. 2

Figure 1: Fig. 2

a considerable (5-10-fold) reduction of the region of homogeneous parameters, which makes the investigation difficult.

Furthermore, the presence of a boundary layer that has developed on the walls of the shock tube affects the velocity of the gas behind the incident wave and determines—

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\* See the bibliography to work (1).

\*\* Spectral data for a number of fundamental diatomic molecules (for example,  $N_2$ , CO, etc.) cannot be unambiguously interpreted (13) for determining their dissociation energies. A check can be carried out, though not always exhaustively, by the explosion method (11) or mass-spectroscopically (12).

\*\*\* We note that in the pressure range investigated in work (6), the dependence of the number  $M$  on the shock-wave velocity is not single-valued, as its authors suppose.

...affects the interaction of the reflected wave with the boundary layer; this introduces errors into the measurements. It is also known that the shock-wave front may not coincide with the onset of luminosity <sup>(8)</sup>.

Thus, the inaccuracy in measuring the velocity of the shock wave and of the particles behind it can give large errors in the value of the relative density. In a shock tube another method of checking the equation of state can be successfully applied, in which, along with the shock-wave velocity, the angle of the attached oblique shock is measured on wedge-shaped models of different wedge angle. The density ratio in the oblique compression shock is equal to

$$\frac{\bar{\rho}}{\rho_0} = \frac{\operatorname{tg} \vartheta}{\operatorname{tg}(\vartheta - \varphi)},$$

where  $\rho_0$ ,  $\bar{\rho}$  are, respectively, the gas density ahead of the shock and behind it;  $\vartheta$  is the angle of the attached oblique compression shock when the flow is turned through an angle  $\varphi$ .

Comparison of the experimental data with the theoretical calculation makes it possible to determine the true equation of state.

**Fig. 2.** Check of the equation of state.  $a$ , —experiment in a shock tube ( $a$ —nitrogen, —air), ———theoretical calculation. Air: —according to the thermodynamic functions of work <sup>(10)</sup>,  $D_{N_2} = 7.38$  eV, —according to the functions of the Energy Institute of the Academy of Sciences of the USSR,  $D_{N_2} = 9.76$  eV. Nitrogen: —according to the data of work <sup>(9)</sup>,  $D_{N_2} = 7.38$  eV, —according to

the data of work <sup>(9)</sup> and the Energy Institute of the Academy of Sciences of the USSR,  $D_{N_2} = 9.76$  eV.

The advantages that ensure the high accuracy of the present method are as follows:

1. The density ratio in an oblique compression shock is very sensitive to the energy of dissociation and ionization.
2. In the presence in the shock tube of a flow of sufficient duration (a longer time for establishing equilibrium in the gas behind the shock wave and for forming the oblique compression shock), nonequilibrium will not have a noticeable effect on the value of the angle of the attached oblique shock, since the incoming gas flow has a high temperature, and the disturbances of the parameters in oblique shocks are relatively small.
3. The principal experimental data are angular quantities, which can be measured rather simply and with the necessary degree of accuracy. The correction associated with the presence of a boundary layer on the model is small and is easy to take into account.
4. The influence of the boundary layer that has arisen on the walls of the tube is substantially weakened.
5. The values of the angles of the attached shock depend relatively weakly on the velocity of the incoming shock wave, and also on the pressure in the gas at rest ahead of it.
6. The method is universal and can be used to check the equation of state of any gas over a wide range of temperatures and pressures.

Typical experimental results are shown in Fig. 1, which presents shadow photographs of the flow behind a shock wave in air. Weak disturbances are visible (from which the Mach number can be determined), as well as the shock wave and the attached compression shock. In Fig. 2 the theoretical data are compared with experiment. For the calculation of the oblique compression shock in nitrogen, data from the Energy Institute of the Academy of Sciences of the USSR and work...

*To the article by S. V. Nerpin and N. F. Bondarenko, p. 834*

**Fig. 1.** Structure of a highly concentrated emulsion (not limiting).

*To the article by S. S. Semenov, p. 842*

*A*

*B*

**Fig. 1.** *A*—attached compression shock on a wedge behind a shock wave in air: **1**—shock wave, **2**—compression shock, **3**—rarefaction; *B*—attached compression shock and Mach wave on a half-wedge behind a shock wave in air: **1**—shock wave, **2**—compression shock, **3**—rarefaction, **4**—Mach wave.

...and for air—the thermodynamic functions of Bethe ( $D_{N_2} = 7.38$  eV)<sup>10</sup> and of the Power Engineering Institute of the Academy of Sciences of the USSR ( $D_{N_2} = 9.76$  eV).

On the basis of the results obtained, one may conclude that the dissociation energy of nitrogen is  $D_{N_2} = 9.76$  eV and that the thermodynamic functions of air based on this value of the dissociation energy of nitrogen are very close to the true ones.

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*Note: Figure translations are in progress. See original paper for figures.*

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