PHYSICAL CHEMISTRY

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Fig. 1

Figure 1: Fig. 1

Fig. 2

Figure 2: Fig. 2

Abstract

Full Text

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DEPENDENCE OF THE LIMITING EXPLOSION PRESSURE OF GASEOUS HYDRAZOIC ACID ON THE POWER OF THE SPARK PULSE

(Presented by Academician N. N. Semenov, May 24, 1961)

According to existing concepts, the limiting explosion pressure (ignition pressure), with increasing energy of the spark pulse, decreases to a certain limit, and a further increase in the power of the spark no longer has any effect. Some authors ([1]) relate the cause of this phenomenon to the presumed existence of two different ignition mechanisms.

Fig. 1

Fig. 2

The study of the explosive properties of gaseous hydrazoic acid does not confirm these conclusions. The experimental results show a continuous decrease in the limiting pressure as the power of the spark pulse is increased.

The experiments were carried out in a spherical glass vessel 11 cm in diameter with fused-in electrodes, which formed a 3-mm spark gap at the center of the sphere. The electrodes were connected to the two ends of the secondary winding of an automobile coil, through whose primary winding capacitors of specified capacitance, charged to a constant voltage, were discharged. The limiting explosion pressures of hydrazoic acid were determined at room temperature; the initial pressure in the explosion vessel was successively reduced from experiment to experiment, until explosion ceased at the given power of the spark pulse. Hydrazoic acid was obtained by the interaction of pure stearic acid and sodium azide.

Fig. 3

Figure 3: Fig. 3

The results of the study of the dependence of the limiting explosion pressure on

capacities of the capacitors discharged through the spark gap are shown in Fig. 1. Plotting the logarithms of the limiting pressures on the ordinate axis and, on the abscissa axis, the quantity reciprocal to the capacitance of the discharged capacitors, we obtain a straight-line dependence (see Fig. 2), which more clearly reflects the monotonic decrease of the limiting pressure as the capacitance of the discharged capacitors increases.

Further experiments showed that the character of the dependence of the limiting explosion pressure on the capacitance of the discharged capacitors remains the same when passing to explosive mixtures of gaseous hydrazoic acid with various gases, although the absolute value of the limiting pressure in this case, as a rule, increases. For illustration, Fig. 3 gives a graph of the dependence of the limiting pressure on the capacitance of the discharged capacitors for a mixture of hydrazoic acid (25%) and air (75%), dried over calcined calcium chloride. Such a dependence becomes still more evident if one takes into account(2) the dependence of the spark efficiency coefficient on the magnitude of the capacitor capacitance and on the pressure of the explosive mixture.

Fig. 3

The experimental results obtained are well described by an empirical formula of the following form: $\lg P = A/C^n + B$, where P is the limiting pressure of hydrazoic acid vapor capable of ignition under the given experimental conditions and for capacitance C of the capacitors discharged across the spark gap; C is the capacitance of the capacitors; A, B, and n are quantities constant for the given mixture, but dependent on its composition.

From comparison with the experimental results of other authors(3) it became clear that this formula describes these processes quite satisfactorily. This must mean that the concept postulated by the authors of the existence of a definite, boundary limiting pressure, below which ignition is impossible at any power of the spark impulse, did not follow directly from their experimental data and, consequently, does not have fully sufficient experimental substantiation.

On the contrary, the conclusion stated above—that the limiting explosion pressure decreases continuously as the power of the spark impulse increases—follows clearly from our experiments and is in complete agreement with previously published experimental results.

Apparently, the well-known formula of N. N. Semenov(4)

$$\lg(P/T^{1+2/n}) = \frac{A}{T_0} + B,$$

derived for the case of thermal self-ignition of combustible mixtures, reflects a more general regularity, encompassing not only oxidation reactions but also decomposition reactions, and not only thermal self-ignition but also spark ignition of the most diverse gaseous explosive systems.

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