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V. F. BAIBUZ

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Abstract

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V. F. BAIBUZ

THE EXPLOSION METHOD AND THE HEATS OF FORMATION OF

CF_4, CF_3Cl, $CFCl_3$, and CCl_4

(Presented by Academician V. N. Kondrat͡ ev on 27 V 1961)

The explosion method is one of the experimental methods for determining the thermodynamic properties of gases at high temperatures. The essence of the method consists in measuring the explosion pressure of a gas mixture and subsequently calculating the heat capacities or thermochemical quantities of the gases. A description of the explosion method and of the method for calculating explosion temperatures is given in ([1], [3–5]). Although the explosion method has been known for more than 50 years, the absence of a reliable way of accounting for, or estimating, the magnitude of energy losses has made it difficult to apply this method in experimental thermochemistry. In the present work a method is proposed and experimentally substantiated for calculating the explosion temperature with allowance for possible energy losses. The entire experimental part of the present work was carried out on an apparatus described in detail earlier ([4], [6]).

The results of studies ([3], [9–19]), as well as the results of explosions of mixtures of H_2, CO, and O_2 carried out by us in spherical bombs with polished and blackened internal surfaces, made it possible to put forward the following assumption concerning the mechanism of energy losses during explosions in a spherical bomb. The main mass of heat losses occurs over a very short period of time immediately before the maximum explosion pressure is reached, by heat conduction of the gas mixture. As a result of the cooling action of the bomb walls, the layer of gas situated directly at the bomb walls does not have time to burn by the moment the maximum explosion pressure is reached, which leads to the nonliberation of a certain amount of heat. It follows from this that the total energy losses during explosions in a spherical bomb must consist of two parts: 1) the heat lost as a result of heat removal into the bomb walls, and 2) the heat not liberated as a result of noncombustion of a certain layer of gas directly adjacent to the bomb walls.

Since, if this assumption is accepted, the explosion process can no longer be regarded as adiabatic, the method for calculating the explosion temperature must consequently also be changed. To derive a new method for calculating the explosion temperature, the theory of the normal velocity of flame propagation was used, from which it follows that, when a flame propagates in a gaseous medium, a preheating zone ([7]), or the thermal zone of the flame ([2], [3]), is formed ahead of the flame front; in this zone the gas mixture is heated by molecular heat conduction to a certain temperature T_p, at which the reaction proceeds sufficiently rapidly. Thus, when a flame propagates in a spherical bomb, the following relation will be fulfilled:

$$\lambda\left(\frac{\partial T}{\partial x}\right)=\frac{up(H_{T_p}-H_{T_0})}{RT_0\left(\frac{p}{p_0}\right)^{\frac{\gamma-1}{\gamma}}}.$$

Here, λ is the coefficient of thermal conductivity of the gas mixture; $(\partial T/\partial x)$ is the maximum value of the temperature gradient in the flame zone; u is the normal ⋯

flame propagation velocity; p —pressure; T_0 and p_0 —the initial temperature and pressure of the mixture; $H_{T_p}-H_{T_0}$ —the change in the heat content of the mixture when it is heated from temperature T_0 to T_p; R —the gas constant; γ —the adiabatic exponent.

As long as the flame is relatively far from the walls of the bomb, the quantity $(\partial T/\partial x)_{\text{st}}$, which determines the heat transfer to the wall, is small and, consequently, the amount of heat given up by the gas to the wall is also small. As the flame approaches the wall, the quantity $(\partial T/\partial x)_{\text{st}}$ increases sharply and, consequently, the amount of heat given up by the gas to the wall must also increase sharply. The increase in heat transfer to the wall leads to the fact that, for a certain interval of time, the flame will be unable to heat a certain layer of the gas mixture near the walls of the bomb to the temperature T_p, and as a result this layer of gas mixture will not have time to burn before the maximum explosion pressure is reached.

Assuming that at the wall

$$\left(\frac{\partial T}{\partial x}\right)_{\text{st}}=c_1\frac{T_p-T_0}{\Delta x},$$

where Δx is the thickness of the layer of unburned gas mixture, and c_1 is a certain constant for the gas layer located near the walls of the bomb, the heat-balance equation may be written in the following form:

$$\frac{u_k p_e\left(H_{T_p}-H_{T_0}\right)}{RT_0\left(p_e/p_0\right)^{\frac{\gamma-1}{\gamma}}}=\frac{u_k p_e\left(H_{T_k}-H_{T_0}\right)}{RT_0\left(p_e/p_0\right)^{\frac{\gamma-1}{\gamma}}}+c_1\lambda\frac{T_p-T_0}{\Delta x}. \tag{1}$$

Here T_k is the temperature of the unburned mixture at the moment when the maximum explosion pressure p_e is reached; u_k is the value of the normal burning velocity at the walls of the bomb.

On the basis of a calculation of the burning velocity in a spherical bomb (^{3}), the value of the normal burning velocity at the walls of the bomb is equal to

$$u_k = \frac{c_2}{p_e - p_0} \left(\frac{p_0}{p_e}\right)^{1/\gamma} \frac{dp}{dt}, \tag{2}$$

where c_2 is a constant, and the value of dp/dt is taken near p_e.

Assuming that $T_k = (T_p + T_0)/2$ and using (1) and (2), we obtain

$$\Delta x = \frac{c_0 \lambda T_0 \left(p_e/p_0 - 1\right)}{\dfrac{H_{T_p} - H_{T_0}}{T_p - T_0} \dfrac{dp}{dt}}. \tag{3}$$

The expression (3) contains the quantity c_0, which depends mainly on the parameters of the experimental apparatus and is determined experimentally.

On the basis of the assumption that the layer of gas near the walls of the bomb does not burn, and the equation of state of an ideal gas, it is easy to obtain an expression for the explosion temperature

$$T_e = T_0 \frac{p_e}{\alpha p_0} \left[1 + \frac{3\Delta x}{r_0}(2\alpha - 1)\right],$$

where r_0 is the radius of the spherical bomb; $\alpha = \sum m_e / \sum m_i$; $\sum m_i$ is the number of moles participating in the reaction, and $\sum m_e$ is the number of moles of the combustion products formed.

The heat-balance equation is set up under the assumption that, in the absence of heat losses, the amount of heat liberated by the layer of gas located at the wall of the bomb is sufficient to heat this layer to the temperature T_p. Hence

$$\sum m_e \Delta E^0_{fT} = \sum m_e \left(E_{T_e} - E_{T_0}\right) + \sum m_i \Delta E^0_{fT_0} + \sum \Delta m \left(E_{T_p} - E_{T_0}\right).$$

Here $\Delta E^0_{fT_0}$ is the heat of formation of the components of the mixture at temperature T_0; $E_{T_e} - E_{T_0}$ is the change in internal energy upon heating from T_0 to T_e, and $\sum \Delta m$ is the number of moles of unburned mixture.

To check the assumptions put forward concerning the mechanism of energy losses and the proposed method for calculating the explosion temperature, several series of explosions of mixtures of H_2, O_2, CO, and H_2O were carried out. The experimental results confirmed the correctness of the proposed method for calculating the explosion temperature and showed that the maximum discrepancy in the heat balance in all experiments did not exceed 170 cal per mole of the initial mixture, averaging 59 cal per mole, or 0.5% of the total heat liberated in the explosion.

The results of the explosions we carried out on mixtures of hydrogen with oxygen and additions of water vapor contradict the conclusions of Wohl and Elbe ([20]) and Wohl and Magat ([21]) that additions of small amounts of water vapor substantially reduce the energy losses in explosions of H_2 and O_2 mixtures. A critical examination of the methodology of the experimental works ([20,21]) and comparison of it with the methodology used in the present work allowed us to establish that the reason for the erroneous conclusion of the cited authors was their neglect of the absorption of water vapor by the walls of the explosion vessel.

The results of the preliminary theoretical and experimental work enabled us to apply the explosion method to determine the heats of formation of CF_4, CF_3Cl, $CFCl_3$, and CCl_4. For these compounds, as a result of explosions of mixtures of H_2, O_2, and CO with the corresponding halogen-substituted methane, the following values of the heats of formation were obtained:

$$\Delta H^0_{f298}(\mathrm{CF_4},\ \mathrm{gas}) = -220.1 \pm 1.4\ \mathrm{kcal/mol},$$

$$\Delta H^0_{f298}(\mathrm{CF_3Cl},\ \mathrm{gas}) = -166.2 \pm 2.2\ \mathrm{kcal/mol},$$

$$\Delta H^0_{f298}(\mathrm{CFCl_3},\ \mathrm{gas}) = -66.4 \pm 2.1\ \mathrm{kcal/mol};$$

$$\Delta H^0_{f298}(\mathrm{CCl_4},\ \mathrm{gas}) = -24.6 \pm 1.9\ \mathrm{kcal/mol}.$$

The obtained values of the heats of formation agree, within the limits of experimental error, with the most reliable values of ΔH^0_{f298} obtained by other authors (see review ([8])).

Institute of Fossil Fuels
Academy of Sciences of the USSR

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