The Experimental Determination of the Heat Capacity of Explosive Gases by a New Method

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A method is described for determining the heat capacity of explosive gases at temperatures up to several hundred degrees above room temperature, by exploding the gas whose heat capacity is to be determined in a spherical bomb. The same data are required as are needed to determine the heat capacity of the burned gas by the explosion method, namely, the maximum pressure developed in the explosion, the initial temperature and initial pressure, the composition of the gas mixture, and the heat of reaction. Equations have been developed, and the method is described in detail. The method is particularly useful for the determination of heat capacities of easily decomposed gases, such as O_3 and Cl_2O, for which the flow method is unsuitable. An interesting consequence of the method is that it permits simultaneous determination of the heat capacity of carbon dioxide at high and low temperatures by exploding mixtures of gaseous ozone and carbon dioxide.

HITHERTO, experiments on explosions of gases at constant volume in a spherical bomb have been utilized to determine the mean heat capacity of the *products* of the explosion between the initial temperature of the gases and the final mean temperature calculated from the maximum pressure by means of the gas law. The present paper deals with a method for employing the same explosion experiments to determine the mean heat capacity of the *reactants* between the initial temperature and the highest temperature reached by the unburned gases due to their adiabatic compression by the expanding burned gases during the explosion process.

The heat capacities of gases between room temperature and several hundred degrees above usually are determined by the flow method; however, there are gases, such as O_3 and Cl_2O, for which this method is not suitable due to the ease with which they decompose. Therefore, the method we shall describe is especially useful in such cases. One particularly interesting consequence of the method is that explosions of mixtures of ozone and carbon dioxide allow simultaneous determination of the heat capacity of carbon dioxide at high and at low temperatures.

The method is based on the principle that the work of compression done on the unburned phase and its temperature rise due to compression may be determined independently, yielding directly the heat capacity of this phase. If the original gas is composed of a single component, the heat capacity so obtained is that of this gas. If it is composed of a mixture of two gases the heat capacity of one should be known to determine the heat capacity of the other. In practice it is usually necessary to dilute the explosive mixture.

All equations needed are contained in the preceding paper.[4] The equation relating the fraction of the total gas burned with the pressure, P, in the bomb, is:

$$1 - \frac{v_i}{V} = \frac{RT_i(P_e/P_i - P/P_i)}{RT_u(\gamma_b - \gamma_u)/(\gamma_u - 1) + (\gamma_b - 1)K}, \quad (1)$$

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where v_i is the volume of the initial gas mixture burned and V the total volume of the bomb.

v_i/V is the fraction of the total gas which has burned when the pressure, P, is established.

P_e is the maximum pressure developed in the explosion.

P_i and T_i are the initial pressure and temperature of the gas mixture.

T_u is the temperature in the unburned phase when the fraction v_i/V has burned. Thus $T_u > T_i$.

γ_u is the ratio of mean heat capacities of the unburned phase at constant pressure and constant volume between the temperatures T_i and T_{ue}, where T_{ue} is the highest temperature reached by the unburned phase just prior to complete combustion or near the wall of the bomb.

γ_b is the same ratio for the burned phase between the temperatures T_{bi} and T_{be}, where T_{bi} is the temperature reached when the gas burns at constant pressure from the initial temperature T_i, and T_{be} is the temperature reached when the gas burns at constant pressure from the initial temperature T_{ue}.

It may be remembered from the previous paper that the temperature T_{bi} or T_{be} is reached when the first or last infinitesimally small amount of gas is burned. Since the combustion of this amount of gas increases the total pressure only infinitesimally, the process takes place at constant pressure.

K is defined by Eq. (2) and is a constant.

$$K = (n_b/n_u)C_bT_b - C_uT_u, \qquad (2)$$

where n_b and n_u are the number of mols per unit mass of burned and unburned gases, respectively.

C_b and C_u are the mean molar heat capacities per mol at constant pressure of the burned and unburned gases between T_{bi} and T_{be}, and T_i and T_{ue}, respectively.

Since the energy $C_u(T_{ue}-T_i)$ must equal the energy $(n_b/n_u)C_b(T_{be}-T_{bi})$, it follows that,

$$K = (n_b/n_u)C_bT_{be} - C_uT_{ue}$$
$$= (n_b/n_u)C_bT_{bi} - C_uT_i. \qquad (2a)$$

The temperature T_{bi} is given by the thermodynamic relation:

$$T_{bi} = q_p/n_bC_{pT_i}{}^{T_{bi}} + T_i, \qquad (3)$$

where q_p is the chemical energy liberated at constant pressure per unit mass of gas, and $C_{pT_i}{}^{T_{bi}}$ is the mean molar heat capacity of burned gas at constant pressure between T_i and T_{bi}.

Likewise, the temperature T_{be} is given by

$$T_{be} = q_p/n_bC_{pT_{ue}}{}^{T_{be}} + T_{ue}. \qquad (4)$$

The temperature T_{ue} is given by the adiabatic law,

$$T_{ue} = T_i(P_e/P_i)^{\gamma_u - 1/\gamma_u}. \qquad (5)$$

On imposing the condition $P = P_i$ and therefore $v_i/V = 0$ in Eq. (1), dividing by RT_i, and substituting the right side of Eq. (2a) for K, one obtains,

$$1 = \left(\frac{P_e}{P_i} - 1\right) \Big/ \left[\frac{\gamma_b - \gamma_u}{\gamma_u - 1} - (\gamma_b - 1)\frac{C_u}{R} + (\gamma_b - 1)\frac{C_b}{R}\frac{n_b}{n_u}\frac{T_{bi}}{T_i}\right]. \qquad (6)$$

Since

$$\frac{\gamma_b}{\gamma_b - 1} = \frac{C_b}{R} \quad \text{and} \quad \frac{\gamma_u}{\gamma_u - 1} = \frac{C_u}{R}, \qquad (7)$$

then

$$\frac{\gamma_b - \gamma_u}{\gamma_u - 1} - (\gamma_b - 1)\frac{C_u}{R} = -\gamma_b, \qquad (7a)$$

and

$$(\gamma_b - 1)C_b/R = \gamma_b. \qquad (7b)$$

Eq. (6) then becomes

$$\gamma_b = \frac{P_e/P_i - 1}{(n_b/n_u)(T_{bi}/T_i) - 1}. \qquad (8)$$

Eq. (8) provides a method for determining the mean heat capacity of the burned gases between T_{bi} and T_{be} which, over this narrow range of temperature, is practically identical with the true specific heat at the mean between these temperatures.

Now repeat the operations performed in obtaining Eq. (6) but substitute for K the left side of Eq. (2a), transpose, and divide by $\gamma_b - 1$. Then

$$\frac{\gamma_u - \gamma_b}{(\gamma_u - 1)(\gamma_b - 1)} RT_i + C_u T_{ue}$$
$$= \frac{n_b}{n_u} C_b T_{be} - RT_i \left(\frac{P_e}{P_i} - 1\right) \frac{1}{\gamma_b - 1}. \quad (9)$$

With the relations (7),

$$(\gamma_u - \gamma_b)/(\gamma_u - 1)(\gamma_b - 1) = (C_u - C_b)/R, \quad (10)$$

so that Eq. (9) becomes,

$$C_u(T_{ue} - T_i) + C_b T_i$$
$$= (n_b/n_u) C_b T_{be} - RT_i(P_e/P_i - 1)/(\gamma_b - 1). \quad (11)$$

Eq. (8) may be written

$$\frac{\gamma_b}{\gamma_b - 1} = \frac{C_b}{R} = \left(\frac{P_e}{P_i} - 1\right) \bigg/ \left(\frac{P_e}{P_i} - \frac{n_b}{n_u} \frac{T_{bi}}{T_i}\right), \quad (12)$$

and also

$$\frac{1}{\gamma_b - 1} = \left(\frac{n_b}{n_u} \frac{T_{bi}}{T_i} - 1\right) \bigg/ \left(\frac{P_e}{P_i} - \frac{n_b}{n_u} \frac{T_{bi}}{T_i}\right). \quad (13)$$

Substituting (12) and (13) in (11) and transposing,

$$C_u = \frac{R(P_e - P_i)}{(n_u/n_b)P_e - (T_{bi}/T_i)P_i} \cdot \frac{T_{be} - T_{bi}}{T_{ue} - T_i}. \quad (14)$$

C_u is the mean molar heat capacity of the unburned gas at constant pressure between T_i and T_{ue}.

If, for example, the original explosive mixture is composed of two components, l and m, having mol fractions x and $1 - x$, respectively,

$$C_u = xC_l + (1 - x)C_m, \quad (15)$$

where C_l and C_m are the mean molar heat capacities at constant pressure between T_i and T_{ue} of the components l and m, respectively. Practically, over this narrow range of temperature, these mean heat capacities are very nearly the true heat capacities at the mean temperature $(T_i + T_{ue})/2$.

The temperatures T_{bi}, T_{be}, and T_{ue} are determined from Eqs. (3), (4) and (5) in combination with Eq. (14) by the method of trial and error. It is necessary to know, therefore, the temperature dependency of the heat capacity of the burned gas, which is obtained by the explosion method in the usual way and for which the same experiments may be utilized. In practice, therefore, this information is available. In working out specific examples it will be found convenient to employ a plot of the mean heat capacity of the burned gas between some low standard temperature such as absolute zero, and T_b. $Cp_{T_{ue}}^{T_{be}}$, for example, may be found from the plot by employing the relation

$$Cp_{T_{ue}}^{T_{be}}$$
$$= (T_{be} Cp_{T_0}^{T_{be}} - T_{ue} Cp_{T_0}^{T_{ue}})/(T_{be} - T_{ue}). \quad (16)$$