COMPARISON OF IDEAL AND ACTUAL COMBUSTION TEMPERATURES AND PRESSURES: ANOMALOUS EFFECTS; GAS VIBRATIONS[1]

GUENTHER VON ELBE

Coal Research Laboratory, Carnegie Institute of Technology, Pittsburgh, Pennsylvania

AND

BERNARD LEWIS

Explosives Division, Pittsburgh Experiment Station, U. S. Bureau of Mines,
Pittsburgh, Pennsylvania

Received July 17, 1937

The calculation of flame temperatures, expansion ratios of flames, and explosion pressures for the case of ideal, i.e., complete and adiabatic, combustion, involves the solution of a number of equations, which may be divided into three groups. One equation represents the energy balance of the system; that is, the energy released in the chemical reaction equals the thermal energy gained by the system. The second group comprises several equations describing the material balance of the system, one equation for each atomic species participating in the reaction. The third group comprises the dissociation constants of the chemical equilibria involved. The solution of the equations is a somewhat involved procedure, but it presents no fundamental difficulties. The calculations can be made accurately by the use of energy contents and equilibrium data determined from band spectroscopy (7).

In explosions in closed vessels with local ignition one must also take into consideration the effect of the temperature gradient in the vessel at the end of the explosion on the pressure developed. This has been discussed elsewhere, and it has been shown that the temperature gradient lowers the pressure a few tenths of a per cent, depending on the mixture composition (8).

To approach as closely as possible to adiabatic combustion the flame gases should not be in contact with cooling surfaces. In closed-vessel explosions this condition is most nearly realized in spherical vessels with central ignition. The flame is insulated from the wall by a layer of un-

---

[1] Published by permission of the Director, U. S. Bureau of Mines, and the Director, Coal Research Laboratory, Carnegie Institute of Technology. (Not subject to copyright.)

burnt gas up to the point of maximum pressure. It is, however, unavoidably in contact with the ignition rod. One may minimize heat loss by making the latter as small in diameter as possible and choosing a reasonably large vessel, avoiding, as far as possible, deviations from the spherical contour of the vessel. Radiation loss could be reduced by polishing the wall, but it appears that possibly only in slow carbon monoxide explosions is the thermal radiation of carbon dioxide not negligible.

Table 1 contains a summary of comparisons between ideal and experimental explosion pressures for hydrogen–oxygen explosions (9). The explosion pressures were observed by a number of investigators,—Pier, Bjerrum, Wohl and Magat, and Lewis and von Elbe.

In explosions (a) excellent agreement is obtained between experimental and calculated pressures, indicating that within the limits of accuracy of measurement these explosions are ideal. The slightly low results in explosions (b) have been shown to be due to heat loss to the ignition rod, the gas containing a large excess of hydrogen and therefore being highly conductive.

TABLE 1

Average percentage deviation of observed from calculated explosion pressures for hydrogen–oxygen mixtures containing different inert gases

TYPE OF MIXTURE	NUMBER OF EXPLOSIONS	AVERAGE PERCENTAGE DEVIATION OF OBSERVED FROM CALCULATED PRESSURES
(a) (H_2, O_2) + small excess of H_2 + A + H_2O	15	+0.07
(b) (H_2, O_2) + large excess of H_2 + H_2O	11	−0.61
(c) (H_2, O_2) + large excess of H_2; dried with P_2O_5	10	−2.00
(d) (H_2, O_2) + excess O_2 + H_2O	6	+1.22
(H_2, O_2) + N_2 + H_2O	8	+0.79

Explosions (c) illustrate the results with dry hydrogen–oxygen mixtures. The observed pressures are, on the average, 2 per cent below the calculated, a discrepancy that lies outside the experimental error. When small amounts of water vapor are added to the initial mixture the discrepancy disappears except for the heat loss through the ignition rod, 1.3 mm. of water vapor being sufficient to do this. Furthermore, as shown by other experiments not included in the table, the deviations from the ideal explosion pressures decrease as the initial pressure is increased to several atmospheres. The following explanation has been proposed for the phenomenon. The discrepancy is due to loss of energy by luminescent radiation from the flame front. Highly vibrating molecules of OH or

H_2O are formed in the reaction, which radiate unless quenching takes place by a collision of the second kind with appropriate molecules such as diluent unexcited H_2O. The luminescence radiation may also be quenched by increased pressure. To date, experimental confirmation of this explanation is still lacking.

In explosions (d) the observed pressures are higher than the calculated, the anomalous effect being greater in excess oxygen than in nitrogen mixtures. The effect disappears when the oxygen or nitrogen is replaced by helium or argon. The anomaly can be reasonably explained only by assuming that there is a momentary excess of translational energy at the end of the explosion. This could be the case if a time lag exists in the excitation of the vibrational energy levels in oxygen and nitrogen molecules. The energy released in the chemical reaction then flows first into those degrees of freedom that offer least hindrance. These are particularly translation and also rotation. The explanation is supported by experiments on the velocity of sound in these as well as other gases, notably carbon dioxide, carbon monoxide, nitrous oxide, and chlorine, where the existence of such an excitation lag was established.

It is noteworthy that excitation lag is not observed in explosions of ozone diluted with oxygen (9). This would indicate that the highly energized molecules of oxygen emerging from elementary reactions of decomposing ozone are capable of distributing their excess energy among all degrees of freedom of diluent oxygen molecules,—namely, molecules of their own kind,—in an extremely short period of time compared with the progress of the flame front. The process by which this energy distribution takes place may be discussed briefly. It may be assumed that vibrational quanta are readily transferred in collisions between two oxygen molecules. If the transfer takes place between two neighboring quantum states, there is perfect resonance and no interchange of translational or rotational energy with vibrational energy will occur. If, however, the transfer occurs between more remote quantum states, then, owing to the smaller energy quantum of the upper level, other forms of energy, translational and rotational, must participate in the transfer. Thus in sound velocity experiments (5) which have been carried out near room temperature and where only the first vibrational level is excited, the vibrational quantum has a long lifetime and no interchange with other forms of energy occurs. In ozone explosions the oxygen molecules are excited to various high vibrational levels, and the exchange of vibrational energy leads to interchange with other forms of energy and thus to rapid establishment of thermodynamic equilibrium.

It is of interest that ozone explosions yield a value of the electronic $^1\Delta$ level of the oxygen molecule of 0.85 ± 0.1 volt (10), compared with the spectroscopic value of 0.97 volt (4). The closeness of the agreement is emphasized by the fact that at the highest explosion temperature, 2500°K., the difference between the observed and spectroscopic values amounts to less than 10° difference between the observed and theoretical explosion temperatures and is in the direction to be accounted for by slight heat loss during the explosion.

For carbon monoxide–oxygen explosions experiments of Pier (12) and David and Leah (2) are available. They have been compared with ideal pressures by the present authors.[2] Pier exploded dry and moist mixtures; David and Leah exploded mixtures containing a small percentage of hydrogen. In Pier's experiments the pressures fall generally several per cent below the calculated except for a mixture containing a large excess of carbon monoxide, where the reverse is true. Here the heat loss is presumably overshadowed by excitation lag. David and Leah's experiments show generally much smaller pressure loss. In mixtures containing a large excess of carbon monoxide the observed pressure is again larger than the calculated. That heat losses in carbon monoxide–oxygen explosions considerably exceed those in hydrogen–oxygen explosions is not surprising in view of the much longer duration of the former explosions (of the order of tenfold), which accentuates radiation loss and conduction to the ignition rod and causes early contact of the burnt gas with the wall, owing to convective rise. Concerning the differences in heat losses in Pier's and in David and Leah's experiments, it is probable that the presence of a small amount of hydrogen in carbon monoxide–oxygen mixtures shortens the combustion time more than the presence of water vapor.

Pier's (12) explosions of mixtures of acetylene and oxygen show that excitation lag is more pronounced with oxygen as diluent than with nitrogen. This agrees with the experience in the hydrogen–oxygen explosion series. Diluent carbon dioxide also shows a strong excitation lag.[2]

Expansion ratios have been measured by soap-bubble explosions of mixtures of carbon monoxide and oxygen diluted or not with helium or argon (3). The results show a trend similar to that found for the explosion pressures in spherical vessels. On the lean side the expansion ratios fall below the calculated considerably more than in the case of explosion pressures. Apart from radiation loss one must again consider the cooling effect of the ignition rod. The latter consisted of metal wires. Since the mass of gas used in these soap-bubble explosions was much smaller than in Pier's and in David and Leah's spherical-vessel explosions (of the order of $\frac{1}{100}$), a considerably greater percentage heat loss through the ignition rod is to be expected. On the rich side the expansion ratios

---

[2] For details consult Lewis and von Elbe: Combustion, Flames and Explosions of Gases, Cambridge University Press, in press.

are grouped more closely around the calculated values. It is suggested that here there is a partial cancellation of heat loss by excitation lag.[2]

There does not seem to be any way to reconcile the very low flame temperatures measured by David (1) with a platinum-wire thermometer in the early stages of flame in a spherical vessel, with the above results. One may suspect errors in the temperature measurements. David and Leah's results discussed above are also in disagreement with these wire temperature measurements.

The sodium line-reversal method, the reliability of which has been proved by the work of Kohn (6) and others, is particularly suited for measurement of the temperature of stationary flames. Consideration of the structure of stationary flames such as Bunsen or Méker flames, points to an uncontrollable admixture of the surrounding atmosphere, particularly at the base of the cone. Therefore measurements of the temperature of such flames should be interpreted with caution. If the temperature is measured solely in some interior portion of the flame, then the protection afforded by the outer flame should suffice to bring such measurements into substantial agreement with the experience on explosion pressures and expansion ratios. This is the case. It is, however, to be borne in mind that heat losses occur to the grid of the Méker burner. These losses can be reduced by increasing the gas velocity.

Figure 1 shows some results obtained by Minkowski, Müller, and Weber-Schäfer (11) with rich coal gas-air mixtures containing an unspecified amount of water, using the line-reversal method and a protected flame. The curves are flame temperatures calculated by the present authors for dry and for water-saturated mixtures. It is noted that the experimental points fall below as well as above the theoretical curve, and that they arrange themselves according to the gas velocity. The closer the mixture is to the stoichiometric, the larger the gas velocity required to raise the temperature of a given mixture to or above the theoretical curve. This can be explained by the higher flame speed of such mixtures, which brings the burning gas closer to the grid, thus increasing the grid loss. Some values fall considerably above the theoretical curve, again pointing to excitation lag.

The results with Pittsburgh natural gas described by Kaveler and Lewis in the next paper are in harmony with the above results. Since the flame speed of natural gas is much smaller than that of coal gas, both grid losses and excitation lag are less pronounced, the latter because there is much more time for the establishment of thermodynamic equilibrium.

The excitation lag seems to be responsible for the occurrence of the peculiar gas vibrations that appear in closed-vessel explosions and that have been observed by many investigators (9) with various explosive mixtures between certain limits of composition in vessels of various shapes and sizes. Figure 2 shows the effect in hydrogen–oxygen mixtures diluted with nitrogen. It is observed that the vibrations commence long before maximum pressure, beginning when the pressure starts to rise steeply, and that they occur only in the slower of the two explosions. With an

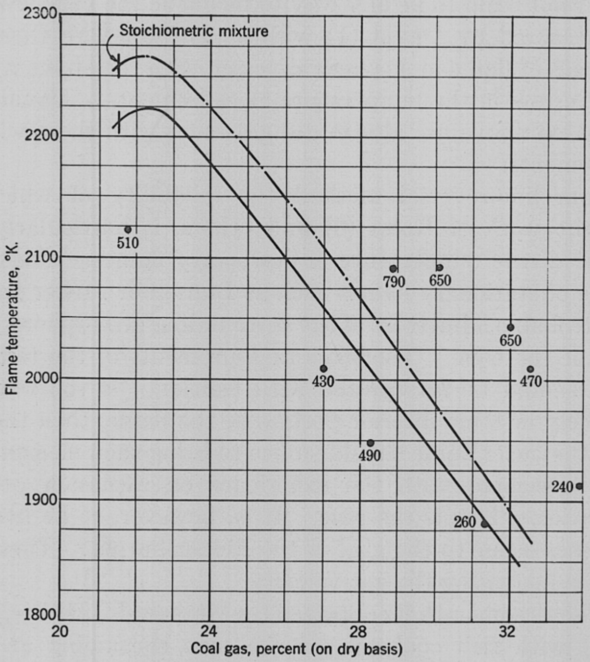

FIG. 1. Comparison of theoretical flame temperatures of coal gas–air mixtures with experimental flame temperatures determined by the line-reversal method. — · —, theoretical curve, dry mixtures; ————, theoretical curve, moist mixtures; ●, sodium line-reversal flame temperatures with gas velocity in centimeters per second.

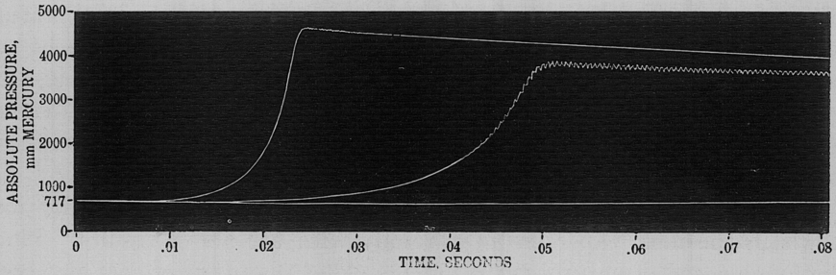

FIG. 2. Vibration effect in hydrogen–air explosions. Slower explosion, 15 per cent of hydrogen; faster explosion, 20 per cent of hydrogen.

equal amount of oxygen as diluent, the vibrations are so intense that it is impossible to obtain a pressure record. The vibrations do not appear in mixtures containing excess hydrogen, helium, or argon. There seems to be little doubt, therefore, that they are in some way connected with the ability of the gas mixture to exhibit the excitation lag. The origin of the vibrations may be proposed as follows: Normally one expects the excitation lag to be localized in the freshly burnt gas forming a shell around the burnt core, since considerable time has elapsed since the core burned. The persistence of the excitation lag is an inverse function of the temperature, probably of an exponential character. Therefore in low-temperature explosions the chances are better that the lag persists in the deeper layers of the core. When the rate of pressure rise becomes steep, there is a steep rise in the temperature of the core, causing a rapid increase in the rate of attainment of energy equilibrium and consequently a rapid shrinkage in volume of the inner layers of gas. This results in a sudden inward mass movement of the gas which may be likened to an implosion. In this way pressure waves are set up which, because of little damping, continue for some time. The disappearance of the phenomenon on enriching the mixture may be ascribed to the higher combustion temperature which shortens the duration of the excitation lag in the inner gas layers.

SUMMARY

In moist hydrogen–oxygen mixtures diluted with argon, helium, or excess hydrogen, explosion pressures are found that agree with the theoretical pressures calculated from band spectroscopic data. In dry mixtures the observed pressures are lower, possibly owing to heat loss by luminescence radiation. In moist mixtures diluted with nitrogen or excess oxygen the pressures are higher. This has been ascribed to the time-dependence of specific heats, called excitation lag. This excitation lag has been linked to gas vibrations which appear early in the explosion. The results with carbon monoxide–oxygen and with acetylene–oxygen mixtures can also be interpreted by heat loss and excitation lag. If a small amount of hydrogen is added to carbon monoxide–oxygen mixtures the heat loss appears to be reduced considerably, probably owing to the shorter duration of the explosion. Excellent agreement is found between experimental and theoretical explosion pressures in ozone–oxygen mixtures. An explanation of the absence of excitation lag in the latter is proposed. Measurements of expansion ratios in soap-bubble explosions of carbon monoxide–oxygen mixtures and flame temperatures by the line-reversal method of coal gas–air mixtures show a trend similar to explosion pressures in hydrogen–oxygen and carbon monoxide–oxygen mixtures.

REFERENCES

(1) David: Phil. Mag. **23**, 251, 345 (1937), and references mentioned in these papers.
(2) David and Leah: Phil. Mag. **18**, 307 (1934).
(3) Fiock and Roeder: Natl. Advisory Comm. Aeronaut. Repts. No. 532, 1935, and 553 (1936).
(4) Herzberg: Nature **133**, 759 (1934).
(5) Kneser: Physik. Z. **35**, 983 (1934).
(6) Kohn: Ann. Physik. **44**, 749 (1914).
(7) Lewis and von Elbe: J. Am. Chem. Soc. **57**, 612, 2737 (1935); for more complete tables consult Lewis and von Elbe: Combustion, Flames and Explosions of Gases, Cambridge University Press, in press.
(8) Lewis and von Elbe: J. Chem. Phys. **2**, 665 (1934).
(9) Lewis and von Elbe: J. Chem. Phys. **3**, 63 (1935).
(10) Lewis and von Elbe: J. Am. Chem. Soc. **57**, 1399 (1935).
(11) Minkowski, Müller, and Weber-Schäfer: Z. Physik. **94**, 145 (1935).
(12) Pier: Z. Elektrochem. **16**, 897 (1910).