213. *Explosions of Mixtures of Hydrogen and Air: The Specific Heats of Steam at High Temperatures.*

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IT has generally been held that the "explosion-pressure" method of determining the specific heats of gases at high temperatures is the most satisfactory of those at present available, despite the fact that it is known to involve certain systematic errors. Of these errors, heat-loss due to radiation and pressure-loss due to lack of uniformity of temperature of the products of combustion at the moment of maximum pressure have been held to be the most serious (see Partington and Shilling, "The Specific Heats of Gases," p. 119, London, 1924). Thorp, however (*Phil. Mag.*, 1929, **8**, 829), and, more recently, David, Brown, and El Din (*ibid.*, 1932, **14**, 764), have suggested that, even when a correction can be introduced for heat-losses, a further source of error in the measurement of maximum pressure lies in the fact that chemical equilibrium is not attained (*i.e.*, that there is incomplete combustion) at the moment of maximum pressure.

Thorp's evidence of incomplete combustion rests on the results of series of explosion experiments with hydrogen and "atmospheres" ranging from pure oxygen to a mixture of oxygen and nitrogen in the ratio 1 to 6·8. Calculations of the apparent specific heats of steam at constant volume over various temperature ranges (based on the values for hydrogen, nitrogen, and oxygen given by Partington and Shilling) showed that: (1) They were considerably higher than those accepted by Partington and Shilling for the same temperature ranges; (2) for a given temperature range, the specific heat was higher when it was based on the explosion of a mixture containing an excess of oxygen than if a mixture containing an excess of hydrogen (giving the same explosion temperature) were used; (3) curves relating the apparent specific heat with the upper limit of the temperature range (15° to T°_{m}) ran nearly parallel for mixtures containing an excess of oxygen or an excess of hydrogen; only a slight excess of oxygen was required to give a large increase in specific heat.

Since observations (2) and (3) applied even to mixtures for which the highest explosion temperature was about 1950°, dissociation of steam, or error due to extrapolation of Partington and Shilling's values for the specific heats of oxygen and nitrogen, could not account for the high values observed; whilst observation (3) ruled out the possibility of the specific heat of oxygen at high temperatures being much higher than that of hydrogen. Thorp therefore concluded that the chemical process $H_2 + \frac{1}{2}O_2 \rightleftharpoons H_2O + 57{,}290$ cals. takes an appreciable time and is further from completion at the moment of maximum pressure when there is excess of oxygen than when there is excess of hydrogen. As supporting this conclusion, he cited experiments which suggested that, for a given mixture, the maximum explosion pressure, due correction having been made for loss of heat by conduction and radiation, increased with the size of the explosion vessel. He explained this effect as being due to the greater time afforded, the larger the vessel, for chemical equilibrium to be attained in the bulk of the gases before the maximum pressure was attained.

Thorp's own experiments on the effect of the size of the explosion vessel appear to have been made only with mixtures of carbon monoxide and air (mixtures notoriously uncertain in their behaviour on explosion unless great pains are taken to ensure their saturation with water vapour at a constant temperature), but for explosions of mixtures of hydrogen and air comparison is made between pressures in a sphere 45·4 cm. in diameter and those recorded by other investigators for vessels of smaller size.

David, Brown, and El Din (*loc. cit.*) obtained direct comparison of the pressures of explosions of carbon monoxide and air and hydrogen and air in spheres 15·2 and 45·4 cm. in diameter, and measured, by bolometer, the heat lost during their development. For the same mixtures, higher pressures were obtained in the larger sphere for which differences in the measured amounts of heat lost from the two explosion vessels could not account, and it is concluded that they were due to different degrees of completion of combustion at the moment when flame had traversed the mixtures. The determinations of the losses of heat by radiation, however, were dependent on the use of a galvanometer, of the torsion-string type, having a natural period of vibration of 0·02 sec. (David and Parkinson, *Phil. Mag.*, 1933, **16**, 177). Since the time of explosion of the more rapidly burning hydrogen–air mixtures was less than this, even in the 45·4-cm. sphere, the values recorded are of doubtful significance.

We have made further measurements (see J., 1928, 15) of the explosion pressures of hydrogen–air mixtures in a sphere 19·7 cm. in diameter using a dead-beat electrical pressure-indicator (partly to meet criticism by Thorp of our earlier work, and partly to check the values recorded by David, Brown, and El Din), from which we have made calculations of the mean apparent specific heats of steam over different temperature ranges.

EXPERIMENTAL.

The mixtures of hydrogen and air were initially at atmospheric pressure and 15°, saturated with water vapour at that temperature. The explosion vessel and the method of experiment were substantially as described in J., 1928, 15. The electrical pressure gauge was designed by G. Allsop and H. Lloyd, of the staff of the Safety in Mines Research Board, who are preparing a detailed description of it for publication elsewhere. Briefly, its mode of action is as follows. The pressure produced by the explosion causes the deflexion of a diaphragm of " Invar " steel, clamped at its edges and stretched radially in the manner usually employed in condenser transmitters for acoustic measurements. This diaphragm, the natural frequency of which is of the order of 10,000 cycles per sec., forms one plate of a condenser, and the alteration in capacity of this condenser, resulting from alteration in the distance between its plates due to the deflexion of the steel diaphragm, varies the plate-current of a thermionic valve. The changes in this current are recorded by means of an oscillograph.

The maximum pressures (P_m) and the times of explosion (t) (intervals between ignition and the attainment of maximum pressure) for a series of mixtures of hydrogen and air are recorded in Table I, P_i being the initial pressure. For comparison, Thorp's values for equivalent mixtures $xH_2 + yO_2 + 3{\cdot}9yN_2$, exploded in a sphere 45·4 cm. in diameter, are included. These are obtained from a smooth curve drawn through experimental points.

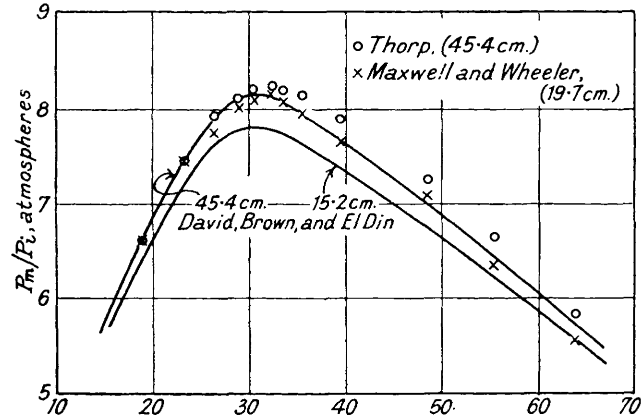
TABLE I.

Explosions of Hydrogen and Air. Maximum Pressures and Times of Explosion.

	Sphere 19·7 cm. diam.		Sphere 45·4 cm. diam. (Thorp).	
H_2, %.	P_m/P_i, atm.	t, millisecs.	P_m/P_i, atm.	t, millisecs.
19·1	6·61	21	6·62	34
23·4	7·42	13	7·42	21
26·45	7·76	11	7·86	16
29·1	8·00	9	8·11	14
30·6	8·07	8	8·19	12·5
32·3	8·14	7·5	8·22	12
33·8	8·07	7·5	8·20	12
35·4	7·94	7·5	8·13	12
39·65	7·66	7·5	7·89	12
48·85	7·09	10	7·26	14·5
55·5	6·37	14	6·66	22
64·0	5·56	39	5·83	39·5

In Fig. 1 the values in Table I are shown graphically with curves representing the results recorded by David, Brown, and El Din for explosions of mixtures $xH_2 + yO_2 + 4yN_2$ in spheres 15·2 and 45·4 cm. in diameter.

FIG. 1.

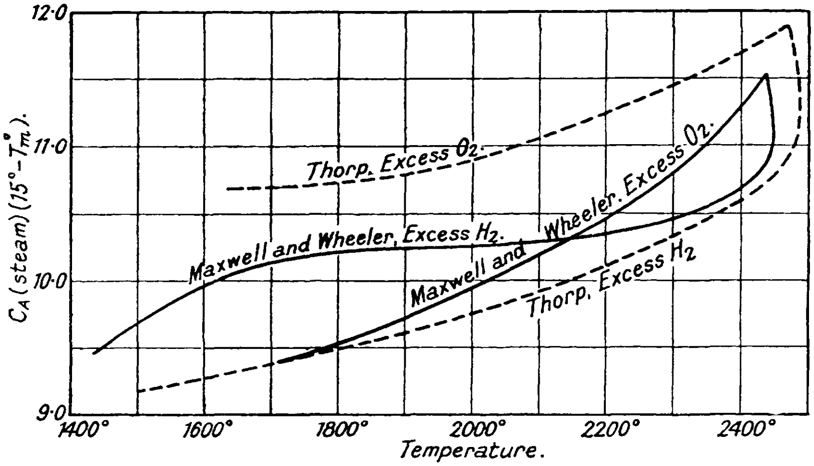


The curves approach each other most closely over the range of mixtures containing excess of oxygen (less than about 25% of hydrogen), a fact at variance with Thorp's suggestion regarding the degree of "incompleteness of combustion" of such mixtures at the moment of maximum pressure. Calculations of the specific heats of steam from the pressure records emphasise this disagreement. The calculations are given in Table II To ensure strict comparison with Thorp's values, we have used the same data and the same method of correcting for loss of heat as he did (*loc. cit.*, pp. 822, 823).

The values given in the fourth column of Table II are considerably higher than those accepted by Partington and Shilling, even when the upper limit of the temperature range does not exceed 2000°. Above that temperature, this method of determining specific heats is admittedly unreliable owing to the unknown effect of dissociation and to errors in the specific heats of the diluent diatomic gases.

In Fig. 2 the specific heats are plotted against the temperature ranges, together with Thorp's values over the same ranges.

FIG. 2.



Our results do not confirm Thorp's. Not only are the values for the specific heats of steam obtained from mixtures containing an excess of oxygen considerably lower than his, but, except when the maximum temperature was higher than about 2,100° (when the effect of dissociation of steam would be more marked with excess of oxygen), they are lower than for mixtures containing an excess of hydrogen.

As regards the more recent experiments by David, Brown, and El Din, it will be apparent from Fig. 1 that their results for mixtures containing an excess of hydrogen differ from Thorp's, obtained in the same explosion vessel (45·4 cm. diameter), by an amount nearly as great as when they used the smaller (15·2 cm.) sphere. Moreover, the results obtained

TABLE II.

Mean Apparent Specific Heats of Steam at Constant Volume, 15°—T_m°.

Hydrogen * in air (xH$_2$+yO$_2$+3·8yN$_2$)	P_m/P_i, atm.	$T°_m$.	C_A steam (15°—$T°_m$).	Hydrogen * in air (xH$_2$+yO$_2$+3·8yN$_2$).	P_m/P_i, atm.	$T°_m$.	C_A steam (15°—T_m°).
17·5	6·29	1708°	9·4	37·5	7·88	2331°	10·5
20	6·80	1900	9·7	40	7·70	2255	10·4
25	7·63	2230	10·55	45	7·33	2104	10·3
27·5	7·88	2350	11·0	50	6·92	1946	10·25
30	8·06	2435	11·55	55	6·48	1783	10·15
31	8·10	2447	11·15	60	6·01	1612	10·0
32·5	8·12	2440	10·9	65	5·50	1433	9·45
35	8·00	2387	10·65				

* Per cent. on dry mixtures.

in our sphere (19·7 cm.) agree more closely with David, Brown, and El Din's with their large sphere.

We therefore cannot accept as conclusive the evidence put forward for a loss of energy during explosions of hydrogen and air due to incomplete combustion of the hydrogen at the moment of maximum pressure. We record our most recent determinations of the mean specific heats of steam at constant volume in support of our previous contention that, at high temperatures, the values accepted by Partington and Shilling are too low.

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