II.—*The Pressures produced on Inflammation of Mixtures of* (a) *Carbon Monoxide and Air, and* (b) *Hydrogen and Air in a Closed Spherical Vessel.*

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RECORDS of the rate of development of pressure in mixtures with air of carbon monoxide and hydrogen, ignited at the centre of a closed spherical vessel, were given in J., 1927, 297. In the present paper, the magnitudes of the pressures are recorded, and deductions are drawn from them as to the dissociation of carbon dioxide and the specific heat of steam. The general character of the apparatus used is described in J., 1918, **113**, 844. The sphere was of bronze, of 4 litres capacity, with its interior highly polished.

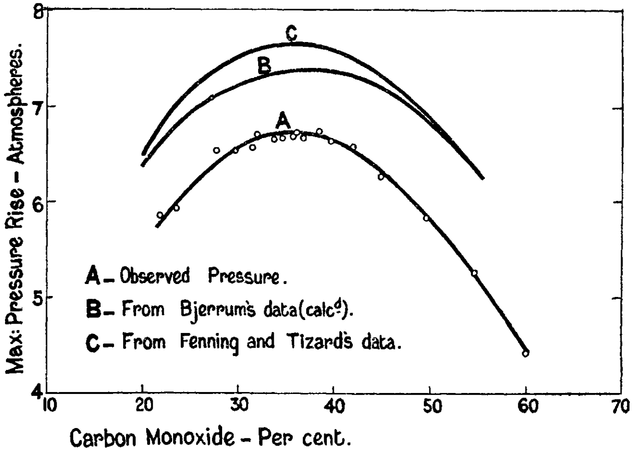
The Dissociation of Carbon Dioxide.

As a result of experiments on the inflammation of mixtures of air with the paraffins (J., 1927, 2069), we called in question Nernst and Bjerrum's values for the dissociation of carbon dioxide. Fenning and Tizard (*Proc. Roy. Soc.*, 1927, *A*, **115**, 318) also have questioned those values, and their experiments indicate that at high temperatures the dissociation has been considerably over-estimated. Fenning and Tizard's method of determining the equilibrium constant of the system $2CO_2 \rightleftharpoons 2CO + O_2$ at different temperatures was to explode carbon monoxide in various proportions with different " atmospheres," ranging from air to pure oxygen, thus finding the " maximum-pressure mixture " for each atmosphere experimentally. This method demands highly accurate relative pressure measurements, since it is not easy to decide which mixture develops the highest pressure on explosion. It was assumed in Fenning and Tizard's calculations that heat losses for mixtures on either side of the " maximum-pressure mixture " would not differ much. This assumption was known to be incorrect (owing to the shape of their explosion vessel) when the times of explosion were widely different, and a correction, in which the heat loss was regarded as proportional to the time of explosion, was then applied.

In our experiments, the results of which are recorded in Table I, differences in heat losses due to conduction appear to have been negligible, for, on explosion of mixtures of the same composition when dried and undried, the pressures developed by the latter were slightly the lower (owing to their moisture contents) despite the fact that their times of explosion were much the shorter. The principal heat loss would be by radiation. This would be minimised by the polished interior of the explosion vessel.

The results for the dried mixtures recorded in Table I were obtained with a Petavel gauge, modified to record comparatively low pressures (up to 20 atm.), which had been calibrated by means of compressed air against a standard Bourdon gauge. The results for the undried mixtures were obtained partly with this gauge and partly with one of the moving-piston type (see J., 1918, **113**, 844), calibrated by means of a dead-weight oil ram.

Fig. 1.



Observed and calculated pressures in CO–Air Mixtures.

TABLE I.

The Explosion of Mixtures of Carbon Monoxide and Air.

(*a*) Mixtures dried by calcium chloride.		(*b*) Mixtures saturated with water-vapour at 15°. (i) Petavel gauge.		(ii) Piston gauge.	
% CO.	Max. press. rise (atm.).	% CO.	Max. press. rise (atm.).	% CO.	Max. press. rise (atm.).
19·40	4·83	21·60	5·83	29·90	6·53
24·90	6·29	23·50	5·93	32·00	6·71
30·55	6·61	27·95	6·53	33·40	6·69
83·10	6·74	31·10	6·56	33·70	6·65
40·00	6·70	36·65	6·67	34·40	6·67
45·80	6·17	39·50	6·62	35·40	6·70
49·65	5·80	44·90	6·29	35·90	6·71
		49·65	5·82	38·10	6·72
		54·75	5·29	42·00	6·58
		60·00	4·42		

The results in Table I (for the undried mixtures only, to ensure strict comparison) are shown graphically in Curve A, Fig. 1. From this curve, when plotted on a larger scale, it can be seen that the

" maximum-pressure mixture " of carbon monoxide and air contains 35·5% of carbon monoxide and develops a pressure of 6·72 atm. Using the same method of calculation as Fenning and Tizard, this result gives for the dissociation of carbon dioxide :

b.	*a*.	$x(=a/b)$.	P_e (atm. abs.).	T_e (° Abs.).	K_p.
3·79	0·283	0·075	7·72	2543	0·0135

The term *b* is the ratio nitrogen : oxygen in the atmosphere (air); *a* appears in the expression for the composition of the original mixture : $2(1 + a)CO + O_2 + bN_2$; P_e is the maximum explosion pressure and T_e the corresponding temperature; K_p is the required dissociation constant $P^2_{CO} \times P_{O2}/P^2_{CO2}$, where P_{CO}, P_{CO2}, and P_{O2} are the partial pressures at equilibrium of carbon monoxide, carbon dioxide, and oxygen.

Fenning and Tizard's value for K_p at 2543° K. is $1·66 \times 10^{-3}$, whilst Bjerrum's (*Z. physikal. Chem.*, 1912, **79**, 513) figure is $6·4 \times 10^{-3}$. Expressed as percentages, the corresponding values at 1 atm. and 2543° K. are : Fenning and Tizard, 14·9; Bjerrum, 23·4; Maxwell and Wheeler, 30·1. Our result thus does not support Fenning and Tizard's, nor our own suggestion that Bjerrum's dissociation values at high temperatures have been over-estimated. It is clear that the absolute values for the dissociation constants obtained by the method of " maximum-pressure mixtures " must be looked on with caution, even when the experimental work has been carried out with great care. In this connexion, it should be noted that in four out of the five series of experiments on which Fenning and Tizard based their calculations, the " maximum-pressure mixture " was deduced from but four trials. Our curve embodies the results of 19 duplicate experiments, in 10 of which the composition of the mixture lay within the range 30—40% carbon monoxide.

Perhaps a more useful test of the relative value of the dissociation constants as determined by the method of " maximum-pressure mixtures " is to use them for calculated pressures, for a range of mixtures, to compare with observed pressures. We have made such calculations (see Appendix) and give the results as curves in Fig. 1, B calculated from Bjerrum's data and C from Fenning and Tizard's. Curve C follows more closely than does Curve B the general form of the experimental curve (A), and from it the calculated and observed maximum-pressure mixtures are identical, whereas from Curve B the maximum-pressure mixture should contain about 38% of carbon monoxide.

The observed maximum pressure-rise (curve A) was 6·72 atm., whereas the calculated values are : Curve B, 7·38 atm.; and

Curve C, 7·65 atm. Inasmuch as our experimental method reduced heat losses during explosion to a minimum, these discrepancies appear excessive, and it must be pointed out that the estimation of dissociation constants from explosion experiments involves the assumption that chemical equilibrium has been attained in the system at the moment of maximum pressure. This assumption does not appear to be warranted in view of the evidence adduced by Ellis and Wheeler (J., 1927, 153) with regard to " afterburning " on explosion of mixtures of carbon monoxide and air.

In general, we suggest that Fenning and Tizard's values for the dissociation of carbon dioxide at different temperatures are, relatively, more consistent with the results of explosion experiments, such as those described in this paper, than are Bjerrum's; but that, if, as seems certain, combustion be incomplete at the moment of maximum pressure, the absolute magnitudes of those values cannot be accepted.

The Specific Heat of Steam.

The pressures (recorded by the Petavel gauge) developed on explosion of mixtures of hydrogen and air in a closed 4-litre sphere are given in Table II.

TABLE II.

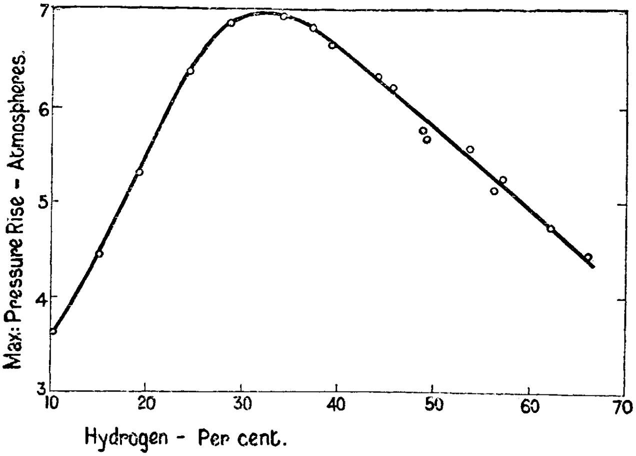
The Explosion of Mixtures of Hydrogen and Air.

% H_2	Max. press. rise (atm.).	% H_2.	Max. press. rise (atm.).	% H_2.	Max press rise (atm.).
10·2	3·63	37·2	6·82	54·0	5·57
15·1	4·45	39·35	6·65	56·2	5·12
19·4	5·30	44·4	6·32	57·2	5·27
24·5	6·38	45·8	6·20	62·3	4·73
28·9	6·89	49·0	5·78	66·1	4·45
34·1	6·92	49·2	5·66		

From Fig. 2, which expresses these results graphically, it appears that the maximum pressure rise (6·98 atm.) would be obtained by a mixture containing 32·5% hydrogen, a displacement of 3% from the theoretical " complete combustion " mixture.

The disagreement amongst recent determinations of the specific heat of steam at high temperatures was commented on in our paper on the explosion of mixtures of air with the paraffins (*loc. cit.*), where it was suggested that the high values obtained by Womersley over the range 1500—2000° (*Proc. Roy. Soc.*, 1921, *A*, **100**, 483) might be nearer the truth than Bjerrum's. In order to estimate the mean values for the specific heat of steam at constant volume from the results of explosion experiments, it is necessary to know the composition of the products at the moment of maximum temperature. By the use of Fenning and Tizard's method of calculating the dissociation of steam in the products of the maximum-pressure hydrogen–air mixture (32·5% hydrogen), it is found that the mean temperature is 2645° K. At that temperature $K_p = 0{\cdot}002$, equivalent to a dissociation of 15·9% at 1 atm. and 2645° K. The value given by Bjerrum (*Z. Elektrochem.*, 1911, **17**, 731; 1912, **18**, 101) is 2·8%. This discrepancy accentuates the untrustworthiness of the "maximum-pressure mixture" method of determining dissociation constants. It also suggests that, under the conditions of explosion experiments, where there is a marked temperature gradient from the centre to the walls of the explosion vessel at the moment when the explosion is completed, an accurate estimation of the composition of the gases at that moment cannot be made from Bjerrum's figures. For this reason, we have chosen, for calculations of the specific heat of steam, mixtures containing sufficient excess of hydrogen to repress the dissociation of steam.

FIG. 2.



Hydrogen–Air Mixtures.

As an example, a calculation based on the pressure produced on explosion of a mixture containing 50% of hydrogen is given in detail. From Fig. 2 the pressure rise with this mixture is found to be 5·80 atm., corresponding with a corrected value (see J., 1927, 2069) of 5·9 atm. The initial mixture, saturated with water vapour at 15° and 1 atm., contained, per unit vol., H_2, 0·4915; O_2, 0·1028; N_2, 0·3887; H_2O, 0·0170. On the assumption that there is complete combustion (and no dissociation) the products at the moment of maximum pressure would contain: H_2, 0·2859; O_2, nil; N_2, 0·3887; H_2O, 0·2226. The "molecular ratio" (see

Appendix) is 0·8972, from which the mean temperature at the moment of maximum pressure, T_e, is 288 × 6·9/0·8972 = 2215° K., or 1942° C.

In order to calculate the mean specific heat of steam at constant volume over the range 15—1950° from these data, the mean specific heats of hydrogen and nitrogen over the same range must be known. We have used the values recorded by Partington and Shilling (" The Specific Heats of Gases," London, 1924), which are based on a number of consistent determinations. We have also taken Nernst's figure, 57,500 cals. per g.-mol. at constant volume, for the lower calorific value of hydrogen. Over the range 0—1950°, C_v for H_2 and $N_2 = 5{\cdot}525$. If C be the mean specific heat of steam over the same range, $0{\cdot}2226C + (5{\cdot}525 \times 0{\cdot}6746) = 0{\cdot}2056 \times 57{,}500/(2215 - 288)$; whence $C = 10{\cdot}8$ cal. per g.-mol.

The results of calculations based on the pressure rise on explosion of four mixtures rich in hydrogen (containing 66·1, 57·2, 50·0, and 45·0%) are given in Table III.

TABLE III.

Mean Specific Heat of Steam at Constant Volume (cals. per g.-mol.).

	Partington and Shilling.	Womersley.	Maxwell and Wheeler.
t°.	0—t°.	100—t°.	15—t°.
1400	7·45	8·35	10·7
1750	8·1	10·2	10·6
1950	8·5	11·4	10·8
2120	8·9	11·7	10·6

Our results thus approximate closely to Womersley's, although they suggest that the specific heat of steam does not increase appreciably over the range 1400—2120°.

NOTE.—There is a possible source of error in Womersley's paper which has been brought to our notice by Professor H. B. Dixon.

Womersley gives as the nett calorific value of hydrogen (hydrogen to steam) 67,840 cals. per g.-mol. The authority is given as Ostwald's "Lehrbuch der Allgemeinen Chemie."

Of course Ostwald gives this figure for the gross value (hydrogen to water). Since Womersley does not give the analyses on which his calculations were based, it is not possible to determine from his paper whether the error affects his results or is only an error of statement.

Appendix.

The calculations from which Curves B and C of Fig. 1 were constructed are given in Table IV. The method of calculation is described in J., 1927, 2069.

TABLE IV.

Mixtures of Carbon Monoxide and Air.

Calculated maximum temperatures and pressures.

(*a*) From Bjerrum's dissociation values.

CO, %.	Products of combustion (% by vol.) at moment of max. temp.				Molecular ratio.*	Max. temp.	Pressure rise (atm.).
	CO_2.	CO.	O_2.	N_2.			
20·0	21·3	0·8	7·9	70·0	0·904	2080°	6·38
25·0	24·4	3·6	5·6	66·4	0·893	2310	7·01
30·0	25·8	8·1	3·6	62·5	0·885	2415	7·26
35·0	26·4	13·2	2·2	58·2	$0{\cdot}883_5$	2455	7·36
38·5	26·4	17·2	1·3	55·1	0·883	2460	7·38
45·0	25·3	25·4	0·3	49·0	0·888	2380	7·17
55·0	20·8	39·9	Trace	39·3	0·906	2045	6·29
(*b*) From Fenning and Tizard's data.							
20·0	21·7	0·5	7·7	70·1	0·902	2115°	6·48
25·0	25·2	3·0	5·1	66·7	0·888	2385	7·19
30·0	27·2	6·9	3·0	62·9	0·880	2515	7·52
35·0	27·9	12·0	1·6	58·5	0·878	2565	7·65
38·5	27·7	16·1	0·8	55·4	$0{\cdot}878_5$	2555	7·62
45·0	25·8	25·0	0·1	49·1	0·886	2415	7·28
55·0	20·8	39·9	Trace	39·3	0·906	2045	6·29

* The ratio of the number of molecules present at the moment of maximum temperature to the initial number.

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