CCLXXIV.—*The Inflammation of Mixtures of the Paraffins and Air in a Closed Spherical Vessel.*

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IN a previous paper on the inflammation of mixtures of methane and air in a closed spherical vessel (J., 1918, **113**, 840), ignition being at the centre, it was recorded that the maximum pressures developed were about 10% less than the calculated values. For the calculations, the degree of dissociation of the products when inflammation had spread through the vessel was determined by analyses of samples rapidly withdrawn at the moment of attainment of maximum pressure; and Langen's values for specific heats were used. Close agreement between results obtained for mixtures of the same composition, inflamed within spheres of 4 and 16 litres capacity, showed that losses due to conduction of heat could not entirely account for the low experimental values, which were ascribed mainly to radiation losses. Experiments by Tizard and Pye (Empire Motor Fuels Committee, Report, 1923—24) with internal-combustion engines, gave surprisingly high results for the pressures produced on explosion of mixtures of heptane and air, the observed pressures being but little less than those calculated. Either the heat loss during the inflammation of heptane is considerably less than with methane, or the method of calculating explosion-temperatures used by Tizard and Pye gave low values.

The work herein described was undertaken to elucidate this matter and to study the factors which influence the rate of inflammation of hydrocarbons. The hydrocarbons used were the first five members of the paraffin series. Save that the pressure-gauge was fitted with a stronger spring than in the earlier determinations, the explosion-vessel (a 4-litre sphere) and the method of experiment were as described previously (*loc. cit.*). To ensure strictly comparable results throughout the series, the experiments with methane and ethane (see J., 1919, **115**, 81) were repeated. The pressures measured were slightly higher than in the earlier records, but the results, given in the tables that follow, did not otherwise differ materially. Each table of observed results is followed by calculations of the maximum temperatures attainable and the theoretical maximum pressures for a number of mixtures. The method of calculation, which is explained in the experimental portion of the paper, was based on that used by Tizard and Pye (*loc. cit.*), whose data we have employed. The theoretical composition of the products of combustion of each mixture, and the ratios of the number of molecules present at the moment of maximum temperature to the initial number ("molecular ratios") are also recorded. All the mixtures were at an initial temperature and pressure of 15° and 1 atmosphere, and were ignited at the centre of the sphere.

TABLE I.

Mixtures of Methane and Air.

Theoretical mixture for complete combustion : 9·47% CH_4.
Approximate limits of inflammability : 5·6—13·6% CH_4.

Methane, %.	Time from ignition to first indication of press. (sec.).	Time from ignition to maximum press. (sec.).	Maximum press. above atmospheric (atm.).
6·05	0·167	0·545	2·67
6·40	0·122	0·340	3·80
7·15	0·076	0·151	5·08
7·35	0·058	0·119	5·69
8·30	0·025	0·081	6·63
8·60	0·025	0·078	6·91
9·15	0·031	0·070	7·21
9·65	0·021	0·069	7·35
9·70	0·031	0·068	7·37
10·20	0·020	0·067	7·43
10·40	0·038	0·068	7·28
10·80	0·021	0·071	7·21
11·40	0·040	0·087	6·88
11·90	0·045	0·102	6·54
12·10	0·041	0·137	6·41
12·70	0·071	0·257	5·35
13·40	0·166	0·368	4·23

Calculated Maximum Temperatures and Pressures.

CH_4, %.	Products of combustion * at moment of maximum temperature, %.						"Molecular ratio."	Maximum temp.	Press. rise, atm.
	CO_2.	CO.	H_2O.	H_2.	O_2.	N_2.			
7·00	6·70	0·17	15·40	0·05	5·46	72·22	1·0005	2005°	6·90
8·00	7·27	0·56	17·21	0·14	3·54	71·28	1·0010	2155	7·48
9·00	7·37	1·41	18·87	0·39	1·85	70·11	1·0072	2265	7·88
9·47	7·21	1·98	19·47	0·58	1·28	69·48	1·0130	2300	8·04
9·70	7·00	2·42	19·80	0·65	0·92	69·21	1·0135	2310	8·10
10·00	6·79	2·87	20·20	0·77	0·69	68·68	1·0185	2320	8·17
11·00	5·52	4·93	20·70	1·72	0·13	67·00	1·0275	2275	8·10
12·00	4·03	7·15	20·68	3·30	0·01	64·83	1·0550	2185	8·00
13·00	2·30	9·30	20·02	6·20	Trace	62·18	1·0934	2050	7·82

* CH_4 = nil.

TABLE II.

Mixtures of Ethane and Air.

Theoretical mixture for complete combustion : 5·64% C_2H_6.
Approximate limits of inflammability : 3·1—10·7% C_2H_6.

Ethane, %.	Time from ignition to first indication of press. (sec.).	Time from ignition to maximum press. (sec.).	Maximum press. above atmospheric (atm.).
4·10	0·056	0·113	6·34
4·45	—	0·097	6·70
4·90	0·039	0·076	7·36
5·15	0·035	0·066	7·39
5·55	0·030	0·055	7·62
6·15	0·024	0·050	7·87
6·30	0·024	0·052	7·94
6·75	0·029	0·056	7·81
6·95	0·034	0·060	7·89
7·50	0·037	0·083	7·42
7·60	0·051	0·088	7·35
8·20	0·078	0·172	6·94

Calculated Maximum Temperatures and Pressures.

C_2H_6, %.	Products of combustion * at moment of maximum temperature, %.						"Molecular ratio."	Maximum temp.	Press. rise, atm.
	CO_2.	CO.	H_2O.	H_2.	O_2.	N_2.			
4·00	7·52	0·18	13·18	0·04	5·96	73·12	1·0269	1990°	7·04
4·80	8·34	0·84	15·24	0·17	3·48	71·93	1·0288	2210	7·88
5·20	8·37	1·51	16·20	0·26	2·43	71·23	1·0347	2280	8·18
5·80	8·05	2·83	17·38	0·57	1·17	70·00	1·0463	2350	8·51
6·00	7·79	3·42	17·68	0·76	0·86	69·49	1·0515	2355	8·59
6·20	7·54	4·01	18·06	0·85	0·52	69·02	1·0561	2350	8·61
7·00	5·69	7·00	18·37	2·23	0·05	66·66	1·0824	2280	8·57
8·00	3·27	10·58	17·94	4·41	Trace	63·80	1·1481	2110	8·50

* C_2H_6 = nil.

TABLE III.

Mixtures of Propane and Air.

Theoretical mixture for complete combustion : 4·02% C_3H_8.
Approximate limits of inflammability : 2·2—7·3% C_3H_8.

Propane, %.	Time from ignition to first appearance of press. (sec.).	Time from ignition to maximum press. (sec.).	Maximum press. above atmospheric (atm.).
2·45	0·143	0·303	4·37
3·50	0·039	0·073	7·51
3·70	0·038	0·063	7·83
4·25	0·033	0·055	8·00
4·60	0·035	0·055	8·09
5·15	0·034	0·062	7·90
5·25	0·043	0·062	7·89
5·65	0·049	0·087	7·59
6·45	0·102	0·198	6·13

Calculated Maximum Temperatures and Pressures.

C_3H_8, %.	Products of combustion * at moment of maximum temperature, %.						“ Mole-cular ratio.”	Maxi-mum temp.	Press. rise, atm.
	CO_2.	CO.	H_2O.	H_2.	O_2.	N_2.			
2·5	7·16	0·04	11·25	0·01	7·59	73·95	1·0248	1850°	6·56
3·0	8·21	0·36	13·01	0·07	5·24	73·11	1·0317	2075	7·43
4·0	8·65	2·54	16·06	0·45	1·61	70·71	1·0551	2340	8·56
4·4	8·03	4·10	16·95	0·79	0·63	69·50	1·0693	2370	8·80
4·6	7·47	5·11	17·27	1·08	0·36	68·71	1·0790	2365	8·88
5·5	4·58	9·76	17·00	3·63	0·09	64·94	1·1345	2190	8·71
6·0	2·80	12·40	16·80	5·18	0·02	62·80	1·1813	2065	8·59

* C_3H_8 = nil.

TABLE IV.

Mixtures of Butane and Air.

Theoretical mixture for complete combustion : 3·12% C_4H_{10}.
Approximate limits of inflammability : 1·65—5·7% C_4H_{10}.

Butane, %.	Time from ignition to first appearance of press. (sec.).	Time from ignition to maximum press. (sec.).	Maximum press. above atmospheric (atm.).
2·05	0·078	0·149	5·20
2·55	0·043	0·078	7·42
3·00	0·027	0·059	8·15
3·60	0·027	0·055	8·48
3·70	0·029	0·054	8·33
3·75	0·027	0·057	8·59
4·40	0·041	0·080	7·78
4·75	0·081	0·117	7·18
4·85	0·061	0·127	7·03
5·15	0·136	0·221	5·83

Calculated Maximum Temperatures and Pressures.

C_4H_{10}, %.	Products of combustion * at moment of maximum temperature, %.						“ Mole-cular ratio.”	Maxi-mum temp.	Press. rise, atm.
	CO_2.	CO.	H_2O.	H_2.	O_2.	N_2.			
2·0	7·55	0·10	11·19	0·02	7·19	73·95	1·0301	1905°	6·80
3·0	8·89	2·26	15·16	0·36	2·03	71·30	1·0581	2330	8·56
3·5	7·94	4·77	16·59	0·87	0·51	69·32	1·0821	2380	8·95
3·7	7·20	6·09	16·79	1·38	0·20	68·34	1·0955	2355	9·00
4·5	2·76	12·24	16·28	5·11	0·01	63·60	1·2091	2020	8·62

* C_4H_{10} = nil.

The Pressures developed.—Comparison between the observed and the calculated pressures is made in Fig. 1. Both experiment and calculation show the maximum pressure to be given in each instance by a mixture containing an excess of hydrocarbon over that required for complete combustion. The amounts of these “ displacements ” are recorded in Table VI, together with the observed and calculated maximum pressures and the amounts of “ lost pressure ” expressed as % of the calculated values.

FIG. 1.

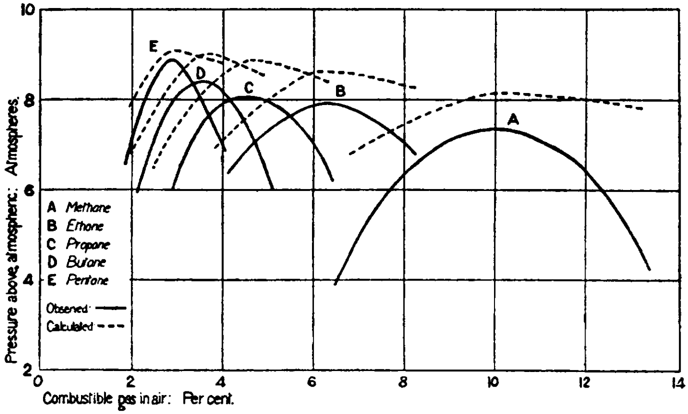


TABLE V.

Mixtures of Pentane and Air.

Theoretical mixture for complete combustion : 2·55% C_5H_{12}.
Approximate limits of inflammability : 1·35—4·5% C_5H_{12}.

Pentane, %.	Time for ignition to first appearance of press. (sec.).	Time for ignition to maximum press. (sec.).	Maximum press. above atmospheric (atm.).
1·95	0·057	0·110	6·65
2·05	0·056	0·089	7·54
2·30	0·045	0·071	7·80
2·40	0·044	0·069	8·10
2·70	0·038	0·059	8·74
2·80	0·024	0·056	8·93
3·00	0·030	0·059	8·87
3·15	0·033	0·064	8·77
3·45	0·037	0·065	8·09
3·60	0·063	0·099	7·91
3·85	0·076	0·021	7·58
4·10	0·113	0·191	6·97

Calculated Maximum Temperatures and Pressures.

C_5H_{12},	Products of combustion * at moment of maximum temperature, %.						"Molecular	Maximum	Press. rise,
%.	CO_2.	CO.	H_2O.	H_2.	O_2.	N_2.	ratio."	temp.	atm.
2·0	8·82	0·62	12·88	0·09	4·56	73·03	1·0340	2155°	7·80
2·5	9·06	2·49	15·08	0·39	1·78	71·20	1·0645	2350	8·70
2·75	8·52	3·98	15·77	0·81	0·92	70·00	1·0799	2380	8·94
3·0	7·45	5·98	16·45	1·21	0·27	68·64	1·0985	2370	9·07
4·0	2·04	14·04	16·64	4·87	Trace	62·41	1·1959	2075	8·75

* C_5H_{12} = nil.

The close agreement in composition between the observed and calculated maximum-pressure mixtures leads to the conclusion that

TABLE VI.

Compositions of Mixtures giving Maximum Pressures. Lost Pressures, %.

	Theoretical mixture for complete combustion, %.	Mixture giving maximum press., %.		Maximum press.		Lost press., %.
		Calc.	Obs.	Calc.	Obs.	
Methane	9·47	10·00	10·00	8·18	7·38	9·80
Ethane	5·64	6·20	6·30	8·63	7·91	8·35
Propane	4·02	4·60	4·60	8·87	8·09	8·80
Butane	3·12	3·70	3·65	9·00	8·50	5·55
Pentane	2·55	3·00	2·95	9·07	8·85	2·45

the " displacements " are the effects of dissociation on the explosion-temperatures and " molecular ratios," for which allowance was made in the calculations.

The " lost pressure " may be due to loss of heat by conduction and radiation or to incomplete combustion. It was shown in a previous paper (*loc. cit.*) that, in mixtures of methane and air containing between 7·5 and 12·5% of methane, a loss of heat by conduction of 2—3% can be presumed during the attainment of uniformity of temperature after inflammation. Such a loss may be assumed also with the other hydrocarbons. It is not easy to obtain a comparison of radiation losses during combustion of each hydrocarbon from the calculated compositions of the products. The intensities of radiation from steam and from carbon dioxide have been determined by Julius (" Die Licht- und Warmestrahlung verbrannter Gase," Berlin, 1890) and R. von Helmholtz (" Die Licht- und Warmestrahlung verbrennender Gase," Berlin, 1890), but the most trustworthy figures seem to be those recorded by Haslam, Lovell, and Hunneman (*Ind. Eng. Chem.*, 1925, **17**, 272), who estimated (by measuring the radiation from flames of methane and carbon monoxide, the theoretical amount of primary air being used with each) that the intensity of radiation from steam was about 1·7 times that from carbon dioxide. If these results be accepted, a comparison can be made of the relative " radiating powers " of the mixtures of carbon dioxide and steam in the products of combustion of the different hydrocarbons. Such a comparison is made in Table VII. The figures in columns 2 and 3 give the relative numbers of molecules of carbon dioxide and steam calculated to be present in the products of combustion of each maximum-pressure mixture at the moment of maximum pressure. These values were obtained from Tables I—V by multiplying the respective volume percentages by the corresponding molecular ratio.

The radiating power thus decreases from the methane to the pentane mixture, which is in accord with the decrease in " lost

TABLE VII.

Relative Radiating Powers of Products of Combustion of Maximum-Pressure Mixtures.

Mixture.	CO_2, g.-mols.	H_2O, g.-mols.	Ratio, H_2O/CO_2.	Relative radiating power. (CO_2% + 1·7 H_2O %.)
CH_4, 10·0%	0·0691	0·2058	2·98	41·8
C_2H_6, 6·2%	0·0796	0·1907	2·40	40·3
C_3H_8, 4·6%	0·0806	0·1863	2·31	39·7
C_4H_{10}, 3·7%	0·0789	0·1838	2·33	39·1
C_5H_{12}, 3·0%	0·0818	0·1808	2·21	38·9

pressure" (Table VI). It must be borne in mind, however, that the calculated maximum explosion-temperature rises from the methane to the pentane mixture, which would offset the decreasing H_2O/CO_2 ratio because of the difference in the mean wave-lengths of the radiations. It is, on the whole, improbable that differences in radiation loss account entirely for the differences in "lost pressure."

A more probable explanation lies in errors in the values for specific heats (Bjerrum, *Z. Elektrochem.*, 1911, **17**, 731; 1912, **18**, 101) on which our calculations, as also Tizard and Pye's, were based. Recent work by Womersley (*Proc. Roy. Soc.*, 1921, *A*, **100**, 483) suggests that Bjerrum's values for steam at high temperatures were much too low. Womersley's results extend only to 2000°, and for calculations of explosion-temperatures higher than this figure extrapolated values must be used. A few calculations are recorded in Table VIII, and if they are compared with those given in Table I, it will be seen that the composition of the mixture for which the calculated pressure is greatest (10% methane) is unchanged, but that the value for the pressure, 7·59 as compared with 8·17 atm., is considerably lower when Womersley's figures are used. The calculated pressure is, in fact, very near that found experimentally (7·38 atm.). No doubt the true value for the mean specific heat of steam over the range 100—2000° lies between

TABLE VIII.

Calculated Maximum Temperatures and Pressures on Explosion of Methane–Air Mixtures.

(Based on Womersley's values for the specific heat of steam.)

CH_4 in original mixture, %.	Products of combustion * at moment of maximum temperature, %.						"Molecular ratio."	Maximum temp.	Press. rise, atm.
	CO_2.	CO.	H_2O.	H_2.	O_2.	N_2.			
9·8	7·80	1·71	20·12	0·58	0·42	69·37	1·0112	2160°	7·54
10·0	7·52	2·16	20·35	0·70	0·30	68·98	1·0145	2165	7·59
10·2	7·25	2·62	20·56	0·81	0·13	68·63	1·0174	2150	7·57

* CH_4 = nil.

Bjerrum's (8·42 cals. per g.-mol.) and Womersley's (11·69). If so, calculations of maximum explosion-temperatures based on Bjerrum's figures would be too high, and the amount of the error would increase with the amount of steam in the products of combustion. Values for the amounts of steam in the products of combustion of unit volume of the maximum-pressure mixture for each hydrocarbon at the moment of maximum pressure are given in Table VII, from which it appears that over-estimation of loss of pressure would be greatest with methane and least with pentane (see Table VI).

There may also be error in the values (from Nernst, *Z. anorg. Chem.*, 1905, **45**, 130; and Bjerrum, *Z. physikal. Chem.*, 1912, **79**, 513) used in estimating the amount of dissociation of carbon dioxide and steam. In this connexion, it is of value to compare the analyses of samples of the gases rapidly withdrawn from the explosion-vessel at the moment of maximum pressure with methane–air mixtures (J., 1918, **113**, 840) with the calculated compositions of the products of combustion of similar mixtures (Table IX).

TABLE IX.

Observed and Calculated Compositions of Products of Combustion, %.

CH$_4$ in original mixture, %.	CO$_2$,		CO,		H$_2$,		O$_2$,		CH$_4$,
	obs.	calc.	obs.	calc.	obs.	calc.	obs.	calc.	obs.*
7·90	9·25	7·21	0·15	0·49	Nil	0·11	3·82	3·72	Nil
9·40	11·14	7·20	0·26	1·96	,,	0·50	0·74	1·31	,,
9·90	10·66	6·84	1·12	2·74	0·40	0·77	0·13	0·77	0·24
10·00	10·86	6·79	1·08	2·87	0·68	0·77	0·04	0·69	0·04
10·70	9·04	5·95	3·63	4·30	2·21	1·40	Nil	0·24	0·10
11·05	9·00	5·45	3·44	5·00	1·95	1·77	,,	0·13	0·23
12·10	8·09	3·84	5·85	7·30	4·00	3·46	0·07	0·01	0·07
12·90	6·08	2·51	7·78	9·02	6·73	5·80	0·05	Nil	0·36
13·90	5·45	0·84	8·95	11·50	9·45	9·50	Nil	,,	1·00

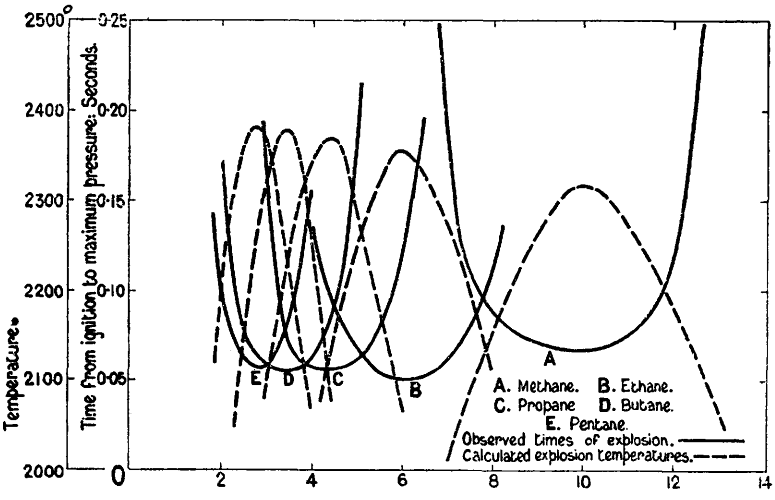
* "Calc. = nil."

There is an indication from these results that the extent of the dissociation of carbon dioxide has been over-estimated in the calculations, for the experimental values for the amounts of this gas in the products of combustion at the moment of maximum pressure are consistently high. In part, the discrepancy might be due to recombination during cooling of the samples (which was, however, very rapid), but this is not likely in view of the close agreement of the observed and calculated figures for hydrogen. Further, Fig. 1 shows that the discrepancy between observed and calculated pressures is greatest for mixtures containing an excess of combustible gas, a result which can be attributed to over-estimation of the "molecular ratios" in the calculations. It would thus seem that the decrease in "lost pressure" in passing from methane to pentane

(Table VI) may be more apparent than real. It is probable that the unexpectedly close agreement between calculated and observed engine efficiencies with heptane as fuel, recorded by Tizard and Pye, was also due to errors in the data on which the calculations were based.*

The Rate of Development of Pressure.—With a given hydrocarbon, it is apparent that the main factor controlling the mean rate of pressure development on explosion of its mixtures with air is the mean temperature of explosion. This is clear from Fig. 2, in which the effect of variation in composition of the mixtures on the rate of development of pressure is shown graphically for each hydrocarbon, together with the calculated explosion-temperatures. Table X has been compiled from Fig. 2, and makes comparison between the observed "maximum-speed" mixtures and the calculated "maximum-temperature" mixtures. The "maximum-speed" mixture for each gas is that in which the time from ignition to the attainment of maximum pressure is least.

FIG. 2.



Combustible gas in air, %.

As a corollary to the observation that, under the conditions of these experiments, the mean rate of pressure development with a given paraffin is determined by the mean explosion-temperature, it follows that the "displacement" of the maximum-speed mixture

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* Fenning and Tizard have recently published a paper on the dissociation of carbon dioxide at high temperatures (*Proc. Roy. Soc.*, 1927, *A*, **115**, 318) which confirms our conclusion. (Added July 10th, 1927.)

TABLE X.

Composition of Maximum-speed and Maximum-temperature Mixtures.

	Hydrocarbon in maximum-speed mixture (obs.), %.	Hydrocarbon in maximum-temperature mixture (calc.), %.	Mean temp. (calc.).	Time (obs.) from ignition to maximum-pressure (sec.).
Methane	10·0	10·0	2320°	0·067
Ethane	6·05	6·0	2355	0·051
Propane	4·45	4·4	2370	0·055
Butane	3·50	3·45	2380	0·055
Pentane	2·90	2·8	2380	0·057

is due to the same cause, dissociation, as displaces the calculated maximum-temperature mixture.

In this connexion, it is of interest to compare the results recorded in Table X with Mason's determinations (J., 1923, **123**, 210) regarding the mixture of each of the paraffins with air which gave the maximum speed of uniform movement of flame. Mason's results are summarised in Table XI. There is general agreement between the compositions of the maximum-speed mixtures under the two different conditions of experiment, and the order of speed of flame in the series of mixtures is the same. This is in accord with our recent observation (this vol., p. 297) that the generalisation known as " the law of speeds," first formulated with respect to the uniform movement of flame, applies also to the rate of spread of flame within a closed sphere.

TABLE XI.

Uniform Movement in Paraffin–Air Mixtures.

Maximum-speed Mixtures. (Mason.)

Paraffin.	Maximum-speed mixture, %.	Speed of uniform movement (5-cm. diam. tube) (cm. per sec.).
Methane	9·65	91
Ethane	6·05	127
Propane	4·45	114
Butane	3·65	113
Pentane	2·90	115

EXPERIMENTAL.

The explosion-vessel and its fittings have been described in J., 1918, **113**, 854. Ignition of the mixtures was at the centre of the vessel by a secondary discharge from a " 10-inch " induction-coil at a 1 cm. gap between pointed copper electrodes, the current through the primary circuit being 10 amps. and the trembler of the coil being locked.

The pressure-gauge was calibrated by compressed air at intervals during the series of experiments against a standard Bourdon gauge. The mean of the calibrations, which checked well amongst themselves, showed a deflexion of the manometer stylus of 1 cm. for a pressure increase of 7·85 atm.

The hydrocarbons were obtained as follows: Methane, from a blower of fire-damp in S. Wales; ethane, (*a*) by the action of water on zinc ethyl, or (*b*) from a cylinder of the compressed gas obtained (from America) by the fractionation of natural gas; propane and butane, by the action of the zinc–copper couple on the corresponding alkyl iodide in alcoholic solution; pentane, from a petroleum distillate, b. p. 35—40°. Each gas, after purification by washing with suitable solvents, was twice liquefied, the middle-boiling fraction only being retained. The ratios C/A (C = contraction on explosion analysis; A = subsequent absorption by potassium hydroxide solution) were: Methane, 1·995; ethane, (*a*) 1·253, and (*b*) 1·245; propane, 1·003; butane, 0·878; pentane, 0·804.

Each gas mixture was prepared in a 20-litre glass gas-holder over a dilute solution of potassium hydroxide and was analysed before use. Before an experiment, the explosion-vessel was exhausted of air to within a few mm. of mercury, filled with the mixture required, re-exhausted and filled again.

Calculation of Explosion Temperatures and Pressures.—The explosive mixtures were assumed to be saturated with water vapour at 15° and the analyses (which take no account of water vapour) were adjusted accordingly. The analytical figures were then proportional to the numbers of molecules of each constituent present in unit volume, and to their partial pressures.

In unit volume of the products of explosion, the numbers of molecules of the constituents can be expressed by $a\ CO_2 + b\ CO + c\ H_2O + d\ H_2 + e\ O_2 + f\ N_2$.

The ratio of the total number of molecules per unit volume at the moment of maximum temperature to the total number in unit volume of the original mixture (the "molecular ratio," M) is $(a + b + c + d + e + f)/1$. The partial pressure of, say, carbon dioxide at the moment of maximum temperature is aP_e/M, whilst $P_e = MT_e/T_i$, where P_e is the explosion-pressure in atmospheres, and T_e and T_i are the explosion-temperature and the initial temperature in °K. For example, in a mixture of pentane and air containing in unit volume: C_5H_{12}, 0·0246; O_2, 0·2005; H_2O, 0·0170; N_2, 0·7579, there are only five unknowns, for the number of molecules of nitrogen, f, can be regarded as remaining constant. Five independent relationships are therefore required to determine them. By equating the carbon, oxygen, and hydrogen before and after explosion, the following relationships are obtained :

$$a + b = 5 \times 0{\cdot}0246 = 0{\cdot}1230 \quad . \quad . \quad . \quad . \quad . \quad . \quad \text{(i)}$$

$$2a + b + c + 2e = 2 \times 0{\cdot}2005 + 0{\cdot}0170 = 0{\cdot}418 \quad . \quad \text{(ii)}$$

$$c + d \qquad = 6 \times 0{\cdot}0246 + 0{\cdot}0170 = 0{\cdot}1646 \;. \quad \text{(iii)}$$

The equilibrium constants, K_1 and K_2, can be obtained from Nernst's data, thus :

$$K_1 = \frac{P^2_{\mathrm{CO}} \times P_{\mathrm{O_2}}}{P^2_{\mathrm{CO_2}}} = \frac{b^2e}{a^2} \cdot \frac{T_e}{T_i}; \text{ whence } \frac{b^2}{a^2}\,e = K_1\frac{T_i}{T_e} \quad . \quad . \quad \text{(iv)}$$

$$\text{and } \; K_2 = \frac{P_{\mathrm{CO}} \times P_{\mathrm{H_2O}}}{P_{\mathrm{CO_2}} \times P_{\mathrm{H_2}}} = \frac{bc}{ad} \,. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad \text{(v)}$$

Expressions (iv) and (v) involve the explosion-temperature, T_e. A value for this is assumed and the equations are then solved. The simplest method of solution is to attribute different values to one of the unknowns, say e, until the relationship $bc/ad = K_2$ is satisfied.

From the solutions of the equations the rise in temperature can be calculated, since it represents the ratio between the thermal energy released on explosion of unit volume of the mixture and the thermal capacity of the products of explosion of unit volume. In the pentane–air mixture chosen as an example, the thermal energy released is that from 0·0246 g.-mol. of pentane less the calorific value of b g.-mol. of carbon monoxide and d g.-mol. of hydrogen. The thermal capacity of the products = amount of each constituent multiplied by its mean specific heat between 15° and the assumed explosion-temperature.

If the explosion-temperature so calculated does not agree within 5° of the predicted value, a fresh calculation is made with a new value for T_e. In the example given, the value for T_e finally chosen was 2618° K. and the calculated value then was 2623° K. The latter was accordingly taken as representing the maximum explosion-temperature. The molecular ratio was found to be 1·0645, so that the explosion-pressure, P_e, was $(2623/288) \times 1{\cdot}0645 = 9{\cdot}7$ atm. The pressure rise above atmospheric was therefore 8·70 atm.

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