Found: N, 6.6. Calculated for $C_{26}H_{26}O_6N_2$: N, 6.1. Difficulty was experienced in completely freeing the compound from traces of pyridine, and this is believed to be the cause of the rather high nitrogen percentage.

When dissolved in acetic anhydride, treated with bromine, and the temperature raised, a finely pulverulent, heavy precipitate separated on cooling, melting at 264° (uncorr.), which was probably the corresponding ethyl dibenzoylaminoterephthalate.

ORGANIC LABORATORY, COLUMBIA UNIVERSITY,
January, 1907.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF WESLEYAN UNIVERSITY].

THE RATE OF COMBUSTION AND PRESSURE DEVELOPED IN A CALORIMETRIC BOMB[1]

BY FRANCIS G. BENEDICT AND FRANK. P. FLETCHER.

Received February 9, 1907.

The development of the high explosive industry has resulted in an unusually large number of tests of the force of the various explosives. For the most part, these tests, being designed to measure excessively high pressures, depend upon the expansion or compression of cylinders, capsules or rods of a metal or alloy. In the internal combustion engine the measurement of the force of the explosion is now accurately made with the ordinary indicator. So far as we are aware, no observations have been recorded regarding the pressures developed inside of a calorimetric bomb during the process of combustion. The early observations of Frankland[2] that complete combustion of carbon monoxide could be obtained by burning it in an atmosphere of oxygen, under pressure, has led to the rapid development of numerous forms of calorimetric bombs for the determination of the heat of combustion of various organic materials. The most noted of these bombs is that of Berthelot[3] which has been modified in many ways by Hempel[4], Atwater[5], and Williams[6].

The use of the calorimetric bomb has extended with great rapidity in the last few years, and observations regarding the development of pressure during combustion are of decided value in estimating the size of the bomb, thickness of the walls, and strength of other parts in their manufacture. The present proportions of the bomb are empirical, and undoubtedly with a very large safety factor. The large mass of metal now

[1] The expense of this research was in part borne by the Carnegie Institution of Washington.

[2] Pr. Roy. Soc. **16**, 419 (1868).

[3] Traité pratique de calorimétrie chimique, Paris (1893), p. 128.

[4] Gasanalytische Methoden (1890), p. 355.

[5] Bull. 21, Office of Experiment Stations, U. S. Dept. of Agriculture, (1895), p. 124. See also Atwater and Snell. This Journal, **25**, 623. (1903).

[6] See description in Wiley: Principles and Practice of Agricultural Analysis. Chem. Pub. Co. (1897), p. 570.

employed in the construction of most of these bomb calorimeters is on one hand, desirable to insure absence of explosion, and on the other hand, it is undesirable as furnishing a large mass of metal, the hydro-thermal equivalent of which must be determined with great accuracy. The hydraulic tests with the Berthelot-Atwater calorimeter have shown that it is capable of withstanding pressures of 4,500 pounds per square inch without perceptible expansion. At this pressure it was found impossible to close the cover of the bomb sufficiently tight with a lead gasket to prevent leakage. Snell working in this laboratory has measured by an extremely sensitive manometer, the very slight expansion of the bomb under these high pressures ; but these results are as yet unpublished. From the cubical contents of the bomb, the pressure of gas when filled with oxygen and the total heat liberated in a combustion, it is possible to compute approximately the pressure developed inside the bomb during a combustion. The theoretical pressures possible under such conditions are very much lower than the pressures that the bomb has been shown to readily withstand, and it seems desirable, therefore, with a view of possibly minimizing the mass of metal in the bomb, to study accurately the pressure developed during the combustion of different typical materials. The conditions under which the combustions in the calorimeter are made are such that the combustion, while rapid, rarely partakes of the nature of an explosion, but does occupy some definite time for its completion. In the experiments made and here reported it was possible, furthermore, to determine with a certain degree of accuracy, the rate of combustion of different materials.

Apparatus :—The apparatus used in these tests was a Berthelot-Atwater bomb calorimeter[1] with the valve opening connected with a sensitive pressure gauge. A number of preliminary tests on a crude high pressure gauge have shown that the pressure developed inside the bomb rarely exceeds 1,000 pounds. Hence in these experiments a more sensitive gauge with a maximum registration of 1,100 pounds was used.

A special top to the bomb was made with a large opening to connect with the pressure gauge and thus minimize the resistance between bomb and gauge.

The material to be tested was weighed and placed in a capsule inside the bomb, which was filled to 300 pounds with compressed oxygen and then connected with the pressure gauge. The material was ignited as usual, by means of a fine wire through which a current of electricity was passed by closing a switch. A pendulum swinging at intervals of three seconds was so adjusted that it could be readily seen and the observer thus time his readings on the gauge.

[1] Atwater and Snell, loc. cit.

Typical materials such as sugar, benzoic acid, cellulose blocks, edestin, plasmon, dried feces and olive oil, were tested in a variety of ways. Ordinarily a sufficient amount of the material to be burned in the bomb calorimeter was taken to liberate not far from four to six large calories of heat, the amount usually liberated in an ordinary combustion. Of cellulose, carbohydrates, vegetable food materials, etc. about one gram was used while with fats, oils, coals, etc. (with a considerably higher heat of combustion) from 0.5-0.6 gram was used.

The two problems attracting the most attention were the pressure developed and the rate of combustion, but numerous other problems of varying interest were also studied. Those here reported are, the influence on the pressure developed and the rate of combustion, of fluctuations in the initial pressure, of the various sizes and forms of containers for the pellets into which the material is compressed before combustion, of different amounts of material, the effect of material not compressed in the pellet form, and of the incorporation of inert material with the substance to be burned. Of fundamental interest is a series of observations on the pressures developed by the explosion of varying amounts of gunpowder in the bomb with and without a charge of compressed oxygen.

Experiments with gunpowder. The ignition of gunpowder results in an instantaneous explosion unaccompanied by subsequent combustion and hence a series of experiments was made to note the sensitiveness of the pressure gauge to explosions of varying force; and also to note the rapidity of the return to the initial pressure.

Several experiments were made with the bomb closed at atmospheric pressure, and one gram of ordinary black sporting powder exploded in it. The results of three experiments showed a maximum pressure as indicated by the gauge of 170, 178 and 177 lbs. respectively. Two similar experiments in which two grams were exploded showed maximum pressures of 320 and 315 lbs. respectively.

Recognizing that the further compression of a previously compressed gas would result in still higher maximum pressures, a series of experiments was made in which the gunpowder was exploded in the bomb after it had been charged with oxygen gas at 300 lbs. initial pressure. The results are recorded in Table I.

Five experiments are recorded in which one-half gram portions of gunpowder were exploded and three in which one gram portions were used. In interpreting the results of these experiments it is important to bear in mind that the "base line" or initial pressure is always not far from 300 lbs. and that the pressures are all absolute values and not simply the increase pressure over the initial. When one-half a gram of gunpowder is thus exploded, there is an instant maximum vibration of the pointer on the pressure gauge which registers not far from an average of 650 pounds, or 350 pounds above the base line. Inasmuch as this is a simple

TABLE I

Gunpowder.—Pressure of filling (300 lbs) and size of capsule (large) remaining constant.

Amount	Highest pressure	After 3 sec.	6	9	12	15	18	21	24	27	30	33	36	39	42	45	48	51	54	57	60
½ gr.............	....[1]	400	350	335	325	320	318	317	316	315	314	313	312	311	310	309	309	308	308	308	307
	600	395	350	335	325	320	318	317	316	315	314	313	313	312	311	310	310	309	309	309	309
	650	380	350	335	325	320	318	317	316	316	315	315	314	313	313	312	311	310	310	310	310
	650	425	350	330	320	317	316	315	314	313	312	311	310	309	308	307	307	306	306	306	306
	675	390	345	325	320	315	313	312	310	308	306	305	304	303	303	302	302	301	301	300	300
Average..........	644	398	349	332	323	318	317	316	314	313	312	311	311	310	309	308	308	307	307	307	306
Rise (+) Fall (—)		+98	—49	—17	—9	—5	—1	—1	—2	—1	—1	—1	—0	1	—1	—1	0	—1	—0	—0	—1
1 gr.............	1000	435	380	355	335	330	327	325	324	323	321	320	319	318	318	318	318	317	316	315	315
	800	450	375	350	340	335	327	325	323	320	318	318	317	317	316	316	315	315	315	315	314
	1100	430	375	345	335	330	326	323	320	318	317	316	316	315	315	314	314	313	313	313	312
Average..........	967	438	377	350	337	332	327	324	322	320	319	318	317	317	316	316	316	315	315	314	314
Rise (+) Fall (—)		+138	—61	—27	—13	—5	—5	—3	—2	2	—1	—1	—1	—0	—1	—0	—0	—1	—0	1	0

[1] The explosion was so rapid and the excursion of the pointer so instantaneous that in one instance the highest pressure could not be read and in all others it could only be approximated.

explosion, not followed by combustion, the pressure recorded at the end of three seconds has fallen to 398 pounds or but 98 pounds above the base line. There is a further fall of 49 pounds at the end of six seconds, 17 pounds at the end of nine seconds, nine pounds at the end of 12, five pounds at the end of 15, and the fall from there on is at the rate of about one pound every three seconds. When one gram of powder is burned, the pressure gauge registers about 1000 pounds, although it is difficult to record this with accuracy. At the end of six seconds, the pressure is 77 pounds above the base line and there are respective falls then at the end of each three seconds, of 27, 13, 5 and 5 pounds, while the remainder of the fall is at the rate of about one pound every three seconds.

It is thus clear that when there is an explosion inside the bomb calorimeter, there is a maximum excursion of the pointer followed by an immediate rapid return to the base line.

Of interest is the comparison of the pressures developed by the explosion of the two different quantities of gunpowder. Under atmospheric pressure the explosion of twice the amount of gunpowder increases the pressure not quite in proportion 175 : 318 or 1 : 1.8.

Under the initial pressure of 300 pounds, double the quantity of gunpowder increases the maximum pressure as 644 : 967 or 1 : 1.5.

It is hardly to be conceived that there was any appreciable combustion of the gunpowder as a result of the explosion in an atmosphere of compressed oxygen, but a series of experiments in which gunpowder should be exploded in several inert gases under corresponding pressures should yield results of interest. Such experiments have not been made with this apparatus and pressure of other work compels us to abandon the investigation.

Experiments with Cellulose.—In determining the heat of combustion of solids in the calorimetric bomb, it is customary to compress the material to be burned into a small pellet in order to prevent the loss of particles of material that might be mechanically blown out of the small capsule either by the inrush of oxygen when filling, or by the current of hot gas resulting from the combustion. These pellets are hard and consequently tend to retard the combustion to such a degree that there is no violent combustion, with consequent loss of material. In determining the heat of combustion of urine the cellulose filter blocks of Kellner have been generally used. These cellulose blocks are light, porous and therefore furnish large surface for the combustion. It is reasonable to suppose therefore that so far as rapidity of combustion is concerned, probably no material burns as rapidly as do these cellulose blocks. Accordingly inasmuch as the pressures developed inside the bomb would of necessity be larger the more rapid the combustion, a series of experiments was made in which these cellulose blocks were burned.

To secure evidence on the probable rapidity of combustion inside the calorimeter bomb, an apparatus was adjusted in such a manner that the filter block could be burned in oxygen at atmospheric pressure in a glass vessel. A tubulated bell jar was inverted and oxygen admitted through the neck. A heavy wire gauze shelf was placed in the bell jar and a filter placed upon it in such a manner that it could be ignited by the electric current. After filling the bell jar with oxygen, the block was ignited and the length of time required to complete combustion in a rapid flow of oxygen gas was noted. This in general occupied about 25 seconds for one-half a filter block weighing about 0.35 gram, and about 35 to 40 seconds for an entire block. These experiments show then that the cellulose blocks when burned under atmospheric pressure in a current oj oxygen gas require considerable time for their combustion ; and while it is conceivable that when the interstices between the fibers are filled with compressed oxygen there might be a rapid combustion, 30 to 40 seconds are required to completely burn these blocks in oxygen at atmospheric pressure.

Influence of Different Amounts of Material Upon Combustion Pressure. —The effect of using various quantities of material on the pressures developed inside the bomb was studied first by using the pure cellulose blocks weighing not far from 0.69 gram each. They are strung on the fine iron wire which is commonly used in bomb combustions, and a current of electricity passing through the wire ignites the filter block, which falls burning upon the nickel plate placed at the base of the bomb to protect the platinum with which the bomb is lined. The quantities of filter blocks used were 0.35 gram, 0.69 gram, and 1.05 gram, corresponding to one-half, one, and one-half blocks respectively. In this series of experiments, the pendulum was arranged to vibrate through 2.7 seconds and consequently the records are expressed in corresponding fractions of seconds. The results are given in Table II.

The pressure of filling remained at about 300 lbs. throughout the series. In the experiments in which one-half of a cellulose block was used, the highest pressure reached, was on the average 573 pounds or 272 pounds above the average initial pressure. This occurred at the end of 2.7 seconds. There was then a rapid decrease, and at the end of 5.4 seconds, the pressure was 442 pounds or 141 lbs. above the initial. The fall in pressure during the second period (of 2.7 seconds) was therefore 131 lbs.

As the block burns in the bomb the high temperature of the flame causes a marked expansion of the compressed gas. As the flame decreases in size there should be a rapid diminution of pressure from period to period while with the cessation of combustion the decrease in pressure from period to period should become very much less since the decrease is due to the cooling of the gases.

From the experiments in which blocks were burned in oxygen at atmospheric pressure, it was found that from 25 to 30 seconds were required to complete the combustion of one-half of a block. In this series

TABLE II

Showing Effect of Different Amounts of Material upon Combustion-pressure. Kind of Material (Cellulose) and pressure of filling (300 lbs.) remaining constant. Blocks suspended on a wire.

Amount	Initial pressure	Highest pressure	After 2.7 sec.	5.4 sec.	8.1 sec.	10.8 sec.	13.5 sec.	16.2 sec.	18.9 sec.	21.6 sec.
½ block	304	585	585	440	375	340	328	320	315	312
(0.35 gr.).......	300	575	575	430	360	340	325	320	316	314
	300	560	560	455	375	350	335	325	320	318
Average..........	301	573	573	442	370	343	329	322	317	315
Rise (+) Fall (—)			+272	—131	—72	—27	—14	—7	—5	—2
1 block	303	625	625	500	400	370	350	335	330	325
(0.69 gr.).......	300	660	660	555	475	400	370	350	340	335
	305	660	660	550	380	350	340	334	325	323
	298	640	640	525	450	385	355	340	330	325
Average..........	302	646	646	533	426	376	354	340	331	327
Rise (+) Fall (—)			+344	—113	—107	—50	—22	—14	—9	—4
1½ blocks	302	820	820	575	430	380	350	335	326	320
(1.05 gr.).......	300	955	955	550	415	365	340	330	325	323
	300	885	885	560	450	385	355	340	330	323
	299	825	825	590	445	380	355	330	323	320
Average..........	300	871	871	569	435	378	350	334	326	322
Rise (+) Fall (—)			+571	—302	—134	—57	—28	—16	—8	—4

of experiments with one-half a block the last large decrease in pressure occurs between 13.5 and 16.2 seconds after the ignition and consequently the average length of combustion according to these observations was not far from 16 seconds.

When an entire block weighing 0.69 gram was used the highest pressure was 646 pounds or 344 pounds above the initial. This likewise occurred at the end of 2.7 seconds. The decrease in the pressure as the time progressed, was correspondingly slower, and at the end of 21.6 seconds instead of being 14 pounds above the initial pressure, it was 25 pounds. Similarly, with the combustion of one and one-half blocks (1.05 grams) the highest pressure developed was 871 pounds or 571 above the base line. Singularly enough at the end of 10.8 seconds, the pressure is essentially the same as when only one block is burned.

A comparison of the combustions made with one and one half blocks is hardly justified however, in that the two portions of cellulose (the entire block and the half block) were probably both ignited at the first instant, then fell to the base of the bomb and *both* portions burned at the same time, thus giving a much larger surface for combustion than would have been the case had the whole mass of cellulose been in one block. This would tend to accelerate the combustion during the first few seconds when it is most rapid, and thus possibly account for the fact just noted that by the end of 10.8 seconds the pressure is essentially the same in the case of the two larger amounts.

The result, therefore, of increasing the amount of material to be burned is to increase the maximum pressure, although these two factors are not directly proportional. There is also a marked increase in pressure during the first 8 seconds, after which the pressures for the different amounts are more nearly uniform (although the pressures for one half a gram remain somewhat lower than the others throughout the experiment). Judged from the rate of decrease of pressure the combustion must have ceased at about 19·20 seconds after the ignition.

Influence of Different Initial Pressures upon the Combustion Pressure.— A series of experiments was made in which the initial pressure of the compressed oxygen in the bomb was varied from 300 to 400 pounds. The cellulose blocks used were strung on the ignition wire as in the preceding series of experiments. The results recorded in Table III show the determinations when the bomb is filled with compressed oxygen at a pressure of 300, 350, and 400 pounds.

A similar set of experiments was made in which the filter block, instead of being strung on a wire and allowed to fall and burn freely at the bottom of the cup, was placed in a small nickel capsule, suspended about half way down the cup.

Several sizes of nickel or platinum capsules are used in this form of bomb calorimeter three of which were used in the tests here reported, the small capsule is 15 mm. inside diameter at the bottom, 22 mm. at the top and 9 mm. deep. It holds about 2 cc. of liquid. The medium size capsule is 13 mm. in diameter at the bottom, 23 at the top, and 16 mm. deep. It holds about 4 cc. The large capsule is 17 mm. in diameter at the bottom; 31 at the top; 21 mm. deep, and holds approximately 10 cc.

The results at 300 pounds are repeated in this table for purposes of comparison. They are identical with those given for one filter block in Table II. When the initial pressure of filling was increased to 350 pounds, the average of the highest pressures recorded was 801 pounds, 453 pounds above the initial. This is over 100 pounds greater than when the initial pressure was 300 pounds. It is of interest to note that at the end of 5.4 seconds, however, the pressures above the base line were practically the same in both series of experiments, *i. e.*, 231 and 222 pounds, respectively. When the initial pressure was raised to 400 pounds, the average of the highest pressures recorded was 922 pounds or 522 above the initial, which is an increase of 69 pounds above that when the bomb was filled at 350 pounds. Here, again, at the end of 5.4 seconds, the pressure above the initial is essentially that found when the bomb is filled at 300 and 350 pounds, respectively, namely about 230 pounds.

TABLE III

Showing Effect of Different Pressures of Filling upon Combustion-pressure. Kind (Cellulose block) and amount (0.69 gr.) of material remaining constant.

Pressure of Filling.	Initial pressure	Highest pressure	After 2.7 sec.	5.4 sec.	8.1 sec.	10.8 sec.	13.5 sec.	16.2 ec.	18.9 sec.	21.6 sec.
(a) Suspended on Wire										
300 lbs.	303	625	625	500	400	370	350	335	330	325
	300	660	660	555	475	400	370	350	340	335
	305	660	660	550	380	350	340	334	325	323
	298	640	640	525	450	385	355	340	330	325
Average	302	646	646	533	426	376	354	340	331	327
Rise (+) Fall (—)			+344	—113	—107	—50	—22	—14	—9	—4
350 lbs.	340	775	775	600	450	400	375	368	352	348
	350	827	827	560	440	400	380	370	360	355
	353	800	800	550	450	410	385	373	365	360
Average	348	801	801	570	447	403	380	370	359	354
Rise (+) Fall (—)			+453	—231	—123	—44	—23	—10	—11	—5
400 lbs.	400	840	840	650	520	450	425	415	405	398
	400	950	950	635	505	455	427	415	406	400
	400	975	975	600	500	450	425	415	410	405
Average	400	922	922	628	508	452	426	415	407	401
Rise (+) Fall (—)			+522	—294	—120	—56	—26	—11	—8	—6
(b) In medium capsule										
300 lbs.	298	545	545	510	465	435	390	360	340	335
	300	550	525	540	485	425	375	355	340	332
	295	527	500	527	500	425	375	350	335	330
	302	530	505	527	480	430	390	365	345	335
Average	299	538	519	526	483	429	383	358	340	333
Rise (+) Fall (—)			+220	+7	—43	—54	—46	—25	—18	—17
350 lbs.	354	685	650	650	525	450	420	405	395	390
	354	715	675	715	525	450	415	405	395	390
Average	354	700	663	683	525	450	418	405	395	390
Rise (+) Fall (—)			+309	+20	—158	—75	—32	—13	—10	—5
400 lbs.	400	785	785	700	550	500	460	445	428	424
	400	735	700	700	600	515	470	445	430	420
	400	790	790	660	535	480	455	435	425	420
Average	400	770	758	687	562	498	462	442	428	421
Rise (+) Fall (—)			+358	—71	—125	—64	—36	—20	—14	—7

The increase in the initial pressure of 50 pounds from 300 to 350, results in an increase of the maximum pressure above the initial of 109 pounds (453—344), while an increase in initial pressure of 50 pounds, from

350 to 400, results in an increase of the maximum pressure above the initial of but 69 pounds (522–453).

The effect of increasing the initial pressure on the rate of combustion is strikingly shown by the figures in this table.

Thus at the end of 21.6 seconds, when the combustion is made at 300 pounds initial pressure, the pressure inside the bomb averages about 25 pounds above the initial pressure; while when the initial pressure is 350 pounds the internal pressure had fallen to within about 30 pounds of the initial pressure at the end of 13.5 seconds.

When the initial pressure was 400 pounds, the internal pressure fell to within 26 pounds of the initial in 13.5 seconds.

It thus appears that the combustion is considerably more rapid with higher pressures.

When the experiments were carried out in such a manner that the block was burned in a medium capsule instead of being strung on a wire, the highest pressures observed were in all cases considerably lower than when the capsule was not used. Otherwise, the results at different initial pressures are generally similar to those in the upper part of the table.

An increase of 50 pounds in the initial pressure (300–350) results in an increase of the maximum above the base line of 107 pounds (346–239) as against a corresponding increase of 109 pounds when the capsule was not used. Similarly an increase of 50 pounds in the initial pressure (350–400), results in an increase in the maximum above the base line of 24 pounds (370–346), which is considerably less than the corresponding result obtained without the use of the capsule, *i. e.*, 69 pounds.

The rate of combustion in these experiments may be approximately noted by the pressures at the end of each series. At 300 pounds, the final pressure at the end of 21.6 seconds was 34 pounds above the base line; at 350 pounds pressure, it was 36 pounds above the base line; while at 400 pounds pressure, it was but 21 pounds above the base line, thus indicating again a more rapid combustion, at the highest pressure.

The effect of the use of a capsule upon combustion pressure may best be observed by comparing, at the same pressures of filling, the combustions in the capsule with those where the block was suspended on a wire. Such a comparison shows a lower maximum pressure in each instance when the capsule is used. Thus at 300 pounds initial pressure, this difference amounts to 108 pounds; at 350, to 101 pounds; and at 400, to 152 pounds. The effect of the capsule in retarding the combustion is also shown by a comparison of the readings at the end of 5.4 seconds. Thus while at 300 and 350 pounds in the case where the capsule was not used there was a fall in pressure from 2.7 to 5.4 seconds of 113 and 231 pounds respectively, in the case of the combustions in the capsule there was an actual gain in pressure of 7 and 20 pounds respectively during this interval. Although at 400 pounds initial pressure there was a fall in pressure of 71 pounds when the capsule was used, there was nevertheless a decidedly greater fall (294) pounds when the combustion was free. So great is the retarding influence of the capsule that, although the maximum pressures are decidedly lower than with the block suspended on a wire, nevertheless after 5.4 seconds every pressure recorded is greater in combustions where the capsule was used.

The most noticeable effects of the use of a capsule, then, are to lower considerably the maximum pressures developed, and to retard noticeably the rate of combustion.

It should be stated, however, that the use of a capsule in this experiment is accompanied by a change in the position of the burning material, since without the capsule the combustion proceeds at the bottom of the cup, while with the capsule it takes place a little below the center. Experiments on the effect of varying the position of the pellet are reported beyond in Table V.

Experiments with Miscellaneous Materials.—As a result of the preliminary observations with cellulose, a large number of experiments with various organic bodies were made, in which a number of factors influencing the pressure and rate of combustion were studied. Some of the observations which were made only at ten-second intervals, were of a preliminary nature and are recorded simply to indicate the maximum pressures with little regard to the rate of combustion. They include the determinations on benzoic acid, fat extracted from feces, and a pure vegetable proteid, edestin. The edestin was kindly furnished by Dr. T. B. Osborne, of the Conn. Agr. Experiment Station of New Haven, Conn. It had a heat of combustion of not far from 5.20 calories per gram on the materials which contained about 8 per cent. of water. The fat from feces was extracted by ether in connection with some experiments on the digestibility of cheese. The results are here included simply as indicating the general nature of the combustion of fat. The benzoic acid was pure fused acid, which has frequently been used for testing the accuracy of the bomb calorimeter. The heat of combustion was 6.322 calories per gram.

The results are recorded in Table IV.

Contrary to the method of expressing the results in other tables, each series of observations is given in this table. The highest pressures developed with either of these materials was 610 pounds in the case of the feces fat, although 0.65 gram of benzoic acid gave 570 pounds.

Influence of the Size of Capsule.—In the combustion of various materials in the bomb calorimeter, use is made of varying sizes of capsules to contain the various materials, and, as has been pointed out in the preceding discussion, the use of a capsule retards perceptibly the rate of combustion and also decreases the maximum pressure in the case of cellulose blocks. The results of a large number of experiments in which the

TABLE IV

Pressures Developed during the Combustion of Benzoic Acid, Fat (feces) and Edestin.

Material and Amount	Initial pressure	Highest pressure	After 10 sec.	20	30	40	50	60	70	80
Benzoic acid										
0.65 gr.	315	570	563	435	376	353	342	337	333	330
0.42 gr.	302	490	490	375	340	325	317	315	313	310
Fat (feces)										
0.6 gr.	297	585	575	372	336	323	315	310	307	305
0.6 gr.	280	610	600	350	320	310	304	300	297	295
Average	289	598	588	361	328	317	310	305	302	300
Rise (+) Fall (−)			+299	−227	−33	−11	−7	−5	−3	−2
Edestin										
1 gr.	300	520	513	495	395	350	333	326	320	318
1 gr.	301	523	500	500	385	341	329	320	316	312
1 gr.	299	505	496	435	348	317	303	293	285	282
Average	300	516	503	477	376	336	322	313	307	304
Rise (+) Fall (−)			+203	−26	−101	−40	−14	−9	−6	−3

same material was burned in different sizes of capsules are recorded in Table V. Averages of three or more duplicate combustions only are reported.

In addition to the data for the different sizes of capsules, this table also includes the results of experiments especially designed to study the influence of other factors, such as the amount of pressure developed when the substance burned is in loose or in pellet form; and when it has incorporated with it inert material such as silicon dioxide or sodium chloride.

An examination of the data in this table shows that the influence of the different sized capsules was most marked in the case of the medium size capsule. This is noted in two distinct ways. First, in decreasing somewhat the observed maximum pressure, and second, in delaying the combustion as observed by comparing the pressures at any given period after 12-15 seconds. Thus with cellulose it is seen that the maximum pressure with the small capsules was 593 pounds, with medium capsules but 538, and with large capsules 580 pounds. On the other hand examining the pressure at 12 seconds those for the small and large capsules are essentially the same while the pressure for the medium capsule averages some 50 lbs. higher, thus giving unmistakable evidence of an appreciable delay in the rate of combustion over that in the other capsules. Com-

5

TABLE V

Pressure Developed during the Combustion of Various Materials under Different Conditions.

Material and Amount	Capsule*	Highest pressure	After 3 sec.	6	9	12	15	18	21	24	27	30	33	36	39	42	45	48	51	54	57	60	63	66	69	72	75
Cellulose 0.69 g.	[1]S	593	593	515	430	378	349	337	328	323	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..
	[1]M	538	519	526	483	429	383	358	340	333	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..
	[1]L	580	580	518	433	383	353	338	330	323	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..
Compressed	S	489	425	480	487	472	448	425	405	383	365	351	343	337	332	328	326	324	322	320	319	318	317	317	316	316	315
"	[2]	512	450	498	504	471	439	422	404	329	357	341	333	329	325	322	321	320	319	318	317	317	316	316	315	315	315
Uncomp'd	[2]	680	680	530	437	383	357	343	338	332	328	325	323	322	320	318	318	318	317	317	317	316	316	316	315	315	315
Sugar 0.5 g.	S	487	352	413	453	462	395	363	345	335	327	322	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..
	M	480	355	415	468	458	412	375	355	344	335	329	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..
	L	483	363	422	470	438	392	367	350	341	333	329	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..
1 g.	[2]	616	455	577	612	582	513	430	385	367	352	344	336	332	329	327	325	323	322	321	320	319	319	318	318	318	317
	[1]S	548	387	462	503	542	538	473	435	405	380	362	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..
	[1]M	503	357	412	448	487	498	483	472	432	410	387	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..
	L	512	389	446	482	509	498	474	433	409	380	361	349	341	..	..	..	..	..	..	..	..	..	..	..	..	..
Loose	L	555	338	425	490	550	517	468	430	400	382	368	357	351	344	338	334	330	327	324	322	321	319	317	316	315	314
Plasmon 0.5 g.	S	441	392	435	441	434	423	408	383	360	346	336	332	328	325	323	321	319	318	317	316	315	..	..	..	..	..
	M	435	373	418	430	431	430	427	393	373	354	345	338	333	329	325	323	321	318	317	317	316	..	..	..	..	..
	L	448	373	432	447	447	428	414	387	364	353	348	342	337	332	329	327	325	323	321	320	319	..	..	..	..	..
1 g.	S	492	417	485	492	488	481	464	444	425	405	378	357	342	335	323	318	312	309	307	..	..	..	..	..	..	..
	M	477	400	452	464	468	476	475	468	453	437	415	388	369	353	346	339	333	328	324	322	319	..	..	..	..	..
	L	488	425	472	486	484	477	464	443	422	405	393	373	358	350	343	339	335	331	327	324	323	322	320	318	316	315
Loose	L	498	425	495	497	494	492	483	476	458	442	402	378	367	358	350	344	339	335	332	329	327	325	323	322	320	..
With 1/3 g SiO_2	S	481	445	479	478	465	454	440	429	419	410	399	387	375	365	359	351	343	337	332	327	323	321	318	316	315	314
" 1/3 g NaCl	S	513	455	513	510	498	485	468	448	428	410	396	378	367	353	344	339	334	330	327	325	324	322	320	319	319	318
Olive Oil 0.5 g.	M	567	507	542	558	532	453	407	383	367	353	347	339	333	328	325	323	321	319	317	316	315	..	..	..	..	..
	L	562	502	552	540	473	425	393	377	363	353	346	341	336	..	..	..	..	..	..	..	..	..	..	..	..	..
1 g.	L	593	508	565	578	587	588	568	532	470	433	402	382	365	351	342	335	329	325	321	319	315	313	311	309	307	305
Feces 0.5 g.	S	434	379	422	427	433	432	403	374	348	338	328	322	317	314	314	..	..	..	..	..	..	..	..	..	..	..
	M	445	378	419	433	439	444	427	397	371	354	344	337	332	331	331	..	..	..	..	..	..	..	..	..	..	..
	L	455	395	437	450	453	452	418	388	371	356	350	346	339	..	..	..	..	..	..	..	..	..	..	..	..	..
1 g.	S	478	432	472	475	474	472	464	455	442	430	417	400	387	370	358	347	340	336	331	327	325	323	321	320	319	318
	M	459	396	434	446	452	455	455	455	449	441	434	428	413	395	381	368	357	350	343	338	334	329	327	324	322	321
	L	476	425	465	473	473	469	466	456	437	421	402	385	370	352	342	335	331	-	..	..	..	..	..	..	..	..
Loose	L	535	492	528	529	524	523	500	451	420	395	379	367	355	346	340	336	332	328	325	323	322	321	320	318	316	313

* S means small capsule ; M, medium ; L, large.

1 Readings taken every 2.7 seconds instead of every 3 seconds.

2 Material burned at bottom of bomb on a flat capsule.

paring the results with one half gram and one gram of sugar, plasmon, feces, etc. it is seen that this difference due to the medium sized capsule is appreciable only when one gram of the substance to be burned is used; in all cases where one-half gram of substance is used (except feces) there is however a slight influence due to the medium capsule on the maximum pressure, and also in all cases on the rate of combustion.

The special retarding influence of the medium capsule is probably due to its size and shape. Its internal diameter at the bottom is 13 mm., which is only a trifle larger than the pellet to be burned. Moreover it is almost as deep as the large capsule. Thus a pellet fits more snugly into the medium capsule and less opportunity is afforded for a ready combustion.

Comparison of the loose with compressed materials. The practice of pressing materials into a pellet form has long obtained with investigators using the calorimetric bomb. A study therefore of the relative pressures when the materials are burned uncompressed is of unusual interest. Such a study was made in this instance with cellulose, sugar, plasmon and and feces. The pellets were about 13 mm. in diameter and 8-10 mm. in thickness when a gram sample was taken.

In all instances, save with cellulose, one gram of material was used, and the combustions of the loose material were made in a large capsule. The cellulose blocks used in many of the experiments reported in the earlier part of this paper are by nature loose material, and hence for purposes of comparison, 0.69 gram of the cellulose was placed in the pellet mould and compressed to a firm pellet and burned in a small capsule. The pressures developed in the combustion of this material are given in in Table V immediately beneath the comparison of the three sizes of capsules. The influence of the compression in this case is very marked both in lowering the highest pressure observed and delaying the rate of combustion. Thus while with the uncompressed material burned in the small capsule the maximum pressure was 593 pounds, the compressed material produced only 489 pounds pressure, or over 100 pounds less. On the other hand, comparing the pressures at the end of the combustions, it is seen that in 24 seconds, the uncompressed material registered a pressure of 323 pounds in the bomb while with the compressed cellulose at the end of this period there was a pressure of 383 pounds. Indeed not until the expiration of 48 seconds had the pressure become as low as 323 pounds. While the observations for the uncompressed cellulose unfortunately were not completed for more than 24 seconds, they certainly permit of no other deduction than that the compressed form of cellulose required a much longer time for combustion than did the loose blocks.

Comparing the results on sugar, much less difference is to be observed. The sugar burned loose in the capsule resulted in a somewhat higher maximum pressure than did the pellets and the combustion was somewhat more rapid as judged by the rate at which the pressure inside the bomb tended to return to the initial pressure. Thus the maximum pressure observed was 555 pounds, which was 43 pounds above that observed with the sugar in the pellet form burned in the same sized capsule, but only seven pounds higher than the sugar when burned in the small capsule.

The pressures by periods where the loose sugar is burned are from the 9th. to the 15th. seconds, somewhat higher than with the pellet form. After 18 seconds, no material differences in the pressures are to be observed until the 30th. second, when there seems to be again a variation between the two series of observations.

With the plasmon, substantially the same results were obtained as with sugar, *i. e.*, a slightly increased maximum pressure, with, however, somewhat higher pressure throughout the succeeding periods. With feces, however, there seems to be a marked effect of the compression of the material into pellet form. This is noted especially in the maximum pressure observed, which is some 60 pounds less when the pellet is burned than when the loose samples are burned. Furthermore, the loose sample seems to burn more rapidly since the return to the initial pressure is more rapid.

The influence then, of compressing materials to be burned into pellet form is to diminish the maximum pressure observed and to decrease the rate of combustion.

Another method of comparing the effect of the compressed with the loose material may be found in a series of observations in which the cellulose in pellet form was burned at the bottom of the bomb calorimeter cup and is thus comparable with the experiments in which the filter block was strung on a wire and ignited. The results for these are the last two given under cellulose. Here again, there is a marked decrease in the maximum pressure caused by the compression of the cellulose. The compressed cellulose giving but 512 pounds as compared to 680 pounds, resulting from the combustion of the uncompressed block. The rate of combustion as noted by the return to the initial pressure is likewise retarded. The two sets do not reach approximately the same pressure until after the expiration of some 40 seconds.

The observations on feces fat as reported in the small table were considered insufficient, and a number of observations on olive oil were included. The effect of the variations in the amounts of material used, shows that as with all other substances the larger the amount of material, the larger the maximum pressure, and similarly, the delay in the combustion as noted by the rate of return to the initial pressure. The comparison of the medium and large size capsules was possible only with one-half gram of olive oil, and as with the other half-gram samples no marked difference can be ascribed to the size of the capsule.

Influence of the incorporation of inert material. The long delay in the return to the initial pressure observed in combustion of feces may possibly be accounted for by the fact that the feces contained as a rule about 20 per cent. of ash, and the presence of this inert material may retard perceptibly the rate of combustion. The chemical composition of feces is at present only too unsatisfactorily known, and yet there are material quantities of fat or crude ether extract, nitrogenous material commonly called protein, with commonly but small amounts of carbohydrates. The effect on combustion pressure of incorporating inert material was determined in the following manner: Three grams of plasmon were mixed with one gram of pure pulverized quartz, and one and one-third grams of this mixture corresponding to one gram of plasmon was moulded in pellet form and burned in the calorimeter. The averages given in this table are in each case the results of three or more individual determinations. They may be compared with the results immediately above them of the combustion of one gram of plasmon in a small capsule. The influence of this inert material is scarcely to be observed on the maximum pressure, which was 492 pounds without the quartz and 481 with it. On the other hand, an examination of the figures shows that the return to the initial pressure is very much delayed by the presence of this inert material. Thus for example at the end of the 48th. second, while the pressure with the pure plasmon had decreased to 312 pounds with the plasmon mixed with silica, it was 343 pounds.

It is thus apparent that the incorporation of inert silica with plasmon has but slight influence on the maximum pressure but does delay materially the rate of combustion.

The infusible nature of quartz makes it hardly strictly comparable to the ash of feces, and consequently a series of experiments was made in which the more readily fusible sodium chloride was mixed with the plasmon in the same proportion as was the silica. One and one-third grams of the mixture of sodium chloride and plasmon representing one gram of pure plasmon, was then compressed in the pellet form and burned in the bomb. The influence on the combustion is somewhat more marked. Thus there is an unaccountable increase in the maximum pressures observed, *i. e.* 513 pounds as compared with 481 with silica, and 492 with the pure plasmon. The rate of combustion is however apparently delayed exactly as was the case with silica. But the return to the initial pressure is, if anything, somewhat more rapid.

Combustion of alcohol. The experiments thus far reported indicate that the more readily volatilized the material to be burned, the more rapid is the combustion, and the greater the maximum pressure. A series of experiments was made in which alcohol was burned. Fifteen drops of commercial alcohol were placed on a cellulose block suspended on a wire and ignited inside the bomb at an initial pressure of 300 pounds. While with the block itself the maximum pressure is not far from 650 pounds the addition of alcohol resulted in a maximum pressure of 1075 pounds. The pressures at the ends of the successive 10 second periods were 480, 330, 316, 311, 305, and 302 pounds.

A large number of determinations of the heat of combustion of ethyl alcohol have been made in this laboratory in which the alcohol was enclosed in a gelatin capsule and then ignited. A series of experiments was made therefore in which approximately 0.5 gram of alcohol was enclosed in a gelatin capsule weighing not far from 0.11 gram. The average maximum pressures observed in a series of five experiments was 683 lbs. and the pressures at the end of successive three-second periods were 600, 620, 492, 411, 337, 377, 351, 341, 335, 330, 326, 324.

Combustion of coal. The extensive use of the calorimetric bomb for the determination of the heat of combustion of coal lends an unusual interest to a series of experiments made with bituminous and anthracite coal. It was found impossible to compress the anthracite coal into a pellet and hence the results given in Table VI are those obtained on the loose material in the large size capsule at 300 pounds initial pressure. The bituminous coal was that commonly used in this section of the country and was undoubtedly from Pennsylvania. The anthracite coal was that commonly furnished to houses in Middletown. No special analyses of either samples of coal were made as pressure of other work prevented.

In the table the individual records for each experiment are included and these may be taken as fair samples of the agreement of duplicate combustions reported as averages in Table V. Of especial interest is the slow rate of combustion of the anthracite coal. With this coal there was a continued rise in pressure until the 24th. second, and the decrease in pressure was likewise remarkably slow, indeed no other compound we have thus far burned gave results that are at all comparable to it. The time records on the anthracite coal were carried to 114 seconds. On the other hand, when bituminous coal is burned the maximum pressure is reached at six seconds; and, while the decrease in pressure is uniform, it is much more rapid than when anthracite coal is burned.

Summary

The results of these investigations may be summarized as follows:

First, with an initial pressure of 300 lbs., the pressures in the calorimetric bomb rarely exceeded 700 lbs.

Second, the greater the quantity of material, the greater the pressure, although the pressure is not proportional to the weight of substance.

TABLE VI

Pressures Developed during the Combustion of Bituminous and Anthracite Coal. Initial Pressure 300 lbs.

Kind and amount	Capsule	Highest	After 3 sec.	6	9	12	15	18	21	24	27	30	33	36	39	42	45	48	51	54	57	60	63	66	69	72	75	78
Bituminous	L	520	450	520	520	515	470	440	420	400	380	365	355	348	340	335	330	327	325	323	321	319	318	317	317	316	316	315
0.5 g.	L	530	430	530	520	515	470	445	420	400	380	365	355	346	340	335	332	328	326	324	322	320	319	318	317	317	316	316
Average		525	440	525	520	515	470	443	420	400	380	365	355	347	340	335	331	328	326	324	322	320	319	318	317	317	316	316
Rise (+) Fall (−)			140	85	−5	5	45	27	23	20	20	15	10	8	7	5	4	3	2	2	2	2	1	1	1	0	1	0
Anthracite	L	412	325	350	365	390	400	410	412	412	412	410	405	403	398	393	388	384	378	370	365	362	353	350	345	342	338	334
0.5 g.	L	397	320	340	360	370	385	390	395	397	397	396	395	393	389	387	386	382	380	377	370	367	362	357	352	348	344	340
	L	408	320	335	365	385	395	405	408	408	407	405	403	400	398	395	390	385	380	376	370	365	360	355	350	317	342	338
Average		406	322	342	363	382	393	402	405	406	405	404	401	399	395	392	388	384	379	374	368	365	358	354	349	346	341	337
Rise (+) Fall (−)			22	20	21	19	11	9	3	1	1	1	3	2	4	3	4	4	5	5	6	3	7	4	5	3	5	4
																					..							..
		Secs. =	81	84	87	90	93	96	99	102	105	108	111	114	..	..	..	..	..	..	..	..	..	..	..	...	..	..
Anthracite continued			330	327	325	324	323	322	321	320	319	318	318	318	..	..	..	..	..	..	..	..	.	..	..	..	..	..
			338	334	330	327	325	322	321	320	319	318	318	318	..	..	..	..	..	..	..	..	..	..	..	..	..	..
			335	332	328	326	325	324	323	321	320	319	318	318	..	..	..	..	..	..	..	..	..	..	..	..	..	..
			334	331	328	326	324	323	322	320	319	318	318	318	..	..	..	..	..	..	..	..	..	..	..	..	..	..
			−3	−3	−3	−2	−2	−1	−1	−2	−1	−1	−0	−0	..	..	..	..	..	..	..	..	..	..	..	..	..	..

Third, the greater the initial pressure the greater the maximum pressure, although regularity and proportionality are not observed.

Fourth, the medium size capsule used in these experiments has a distinct tendency to decrease the maximum pressure and to retard combustion. The other capsules have a much less marked but similar effect.

Fifth, the pellet form of material in all cases markedly decreases the maximum pressure and retards the combustion.

Sixth, the incorporation of inert material is without appreciable effect on the maximum pressure, but markedly retards the rate of combustion.

Seventh, anthracite coal results in low maximum pressures, but the rate of combustion is extremely slow, sharply contrasting with results from bituminous coal.

SOIL ACIDITY IN ITS RELATION TO LACK OF AVAILABLE PHOSPHATES

Preliminary Report.

A. R. WHITSON AND C. W. STODDART.

Received February 4, 1907.

Experience has shown that a direct determination of the amount of the essential elements present in a soil does not show its fertility, since it does not consider the degree of availability. It is unquestionably true, however, that the processes by which these elements become available are chemical, and depend upon the conditions existing in the soil. A determination of the conditions which influence the rate at which the elements become available and which affect the accumulation of the available material would enable us to diagnose the needs of the soil more quickly and surely than by direct field and pot experiments.

It is a well recognized fact that a soil should be tested for acidity, whether this condition affects the physical, biological, or chemical reactions of the soil.[1] The general question of upland soil acidity has been discussed in considerable detail and with an excellent bibliography by Wheeler[2] and his associates of the Rhode Island Station.[3] The most interesting fact in this connection, however, is that investigations of the fertilizer requirements of soils during the past two or three years have shown that whenever a soil is acid it needs phosphates. The work of H. J. Wheeler[4] of Rhode Island, and C. E. Thorne[5] of Ohio, on acid soils has shown that these soils need phosphates, although neither author has commented upon the connection between acidity and lack of available phosphates.

[1] Snyder, Pr. Am. Assoc. Off. Agr. Chem., 1898, p. 60.

[2] Wheeler, R. I. Sta. Rept., 1900, pp. 293-327. Hilgard, "Soils," p. 322.

[3] R. I. Sta. Rept., 1895, pp. 232-280.

[4] U. S. Dept. of Agr., Farmers' Bull. No. 77; R. I. Expt. Sta. Bull. No. 68.

[5] O. Expt. Sta. Bull. No. 159.