

THE HEATS OF COMBUSTION OF METHANE AND CARBON MONOXIDE

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ABSTRACT

With the use of the calorimetric apparatus and procedure employed for determining the heat of formation of water (v. supra p. 1), the heats of combustion of methane and carbon monoxide have been measured.

The heat of combustion of CH_4 to form liquid H_2O and gaseous CO_2 is found to be $889,700 \pm 300$ international joules per mole at 30°C . and a constant pressure of 1 atmosphere, which is equivalent to $890,160 \pm 300$ international joules per mole at 25°C . and 1 atm.

The heat of combustion of CO to form CO_2 is found to be $282,925 \pm 120$ international joules per mole at 30°C . and a constant pressure of 1 atm., which is equivalent to $282,890 \pm 120$ international joules per mole at 25°C . and 1 atm.

For comparison with the older work, see Figures 1 and 2.

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I. INTRODUCTION

The heats of formation of methane and carbon monoxide are computed from their heats of combustion because of the difficulties inherent in the problem of measuring the heat effect of their synthesis from or decomposition into the elements. Accurate values of the heats of formation of methane and carbon monoxide are particularly desirable at this time because industrial syntheses of many useful compounds involve one or both of these gases, and a knowledge of the heat effect of a given reaction permits calculation of the change of the equilibrium with temperature.

The usually accepted values for the heats of combustion of methane and carbon monoxide are based primarily upon the measurements made over 50 years ago by Thomsen. Because of the comparatively large uncertainty (one-fourth to one-third per cent) attached to Thomsen's average values, and because calorimetric measuring apparatus, methods, and devices have improved greatly in accuracy and precision since his time, it was desirable that new determinations be made.

II. APPARATUS AND CALORIMETRIC PROCEDURE

It was found that the calorimetric apparatus which was used in this laboratory to determine the heat of formation of water¹ could be used, without alteration, for burning methane and carbon monoxide in oxygen. The reaction vessel and other apparatus have been described in detail.¹

The calorimetric procedure in the experiments involving combustion of methane and carbon monoxide was exactly similar to that employed in the combustion of hydrogen and the experiments here reported were carried out immediately after the completion of the latter combustions.

The data from the calibration experiments at 30° C., listed as Set II in the experiments on hydrogen, were used in conjunction with the combustion experiments on methane and carbon monoxide.

While the curves showing the variation of the calorimeter temperature with time in the combustion experiments on hydrogen were practically identical with those in the calibration experiments, those for the combustion experiments involving methane and carbon monoxide were somewhat different. In the calibration experiments, the temperature rise of about 2.8° C. occurred in 12 minutes, whereas for the combustion experiments on methane and carbon monoxide it was 2.8° C. in 10 minutes and 1.3° C. in 12 minutes, respectively. Since, however, detailed observations in the "fore" and "after" periods were made in each experiment, and since the resistance coils in the thermometer bridge were accurately calibrated, the determination of the true temperature rise in each experiment can be in error by only a negligible amount.

III. MOLECULAR WEIGHTS, CONSTANTS, UNITS, AND FACTORS

The atomic weights of O, H, and C are taken as 16.000, 1.0078, and 12.000, respectively.²

For the reaction between CH₄ and O₂ to form liquid H₂O and gaseous CO₂, ΔC_p is taken as 93 joules per mole per degree,³ that is, the heat evolved in the reaction at constant pressure decreases 93 joules per mole per degree.

For the reaction between CO and O₂ to form CO₂, ΔC_p is taken as -7 joules per mole per degree.³ The heat evolved in this reaction at constant pressure increases 7 joules per mole per degree.

The correction to 1 atmosphere pressure is made by the use of the thermodynamic equation.

$$w = nRT \log_e \frac{P}{760} \quad (1)$$

where n is the number of moles decrease in gaseous volume, R is the gas constant in joules per degree, T is the absolute temperature, P is the pressure in mm of Hg. For the combustion of methane, w is taken as -6.7 joules per mole per mm increase in pressure, while for the combustion of carbon monoxide w is -1.7 joules per mole

¹ Rossini, B. S. Jour. Research, 6, p. 1; 1931.

² Baxter, 1930 Report of the Committee on Atomic Weights, J. Am. Soc., 52, p. 861; 1930.

³ International Critical Tables, 6, p. 80.

per mm increase in pressure. These corrections are strictly valid only for small changes in pressure. The pressures in the reaction chamber for the combustion experiments are given in Tables 4 and 8.

The unit of energy and all other constants, units, and factors are the same as those given in the previous paper.⁴

IV. METHANE

1. CHEMICAL PROCEDURE

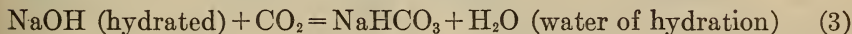
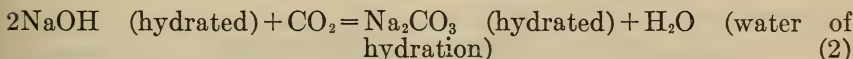
The methane used in this investigation, obtained through the courtesy of the Fixed Nitrogen Research Laboratory, had been prepared synthetically from carbon monoxide and hydrogen and was specially purified by the Du Pont Ammonia Co. The purifying procedure included a fractional distillation to remove other hydrocarbons, hydrogen, and carbon monoxide.

Before entering the reaction vessel, the methane passed successively through tubes containing (1) "ascarite" (sodium hydroxide-asbestos mixture) for removing CO_2 and other acidic oxides, (2) "dehydrite" ($\text{Mg}(\text{ClO}_4)_2 \cdot 3\text{H}_2\text{O}$) for removing water vapor, and (3) P_2O_5 for removing the last traces of H_2O .

The ratio of carbon to hydrogen in the methane was determined by burning the gas in the reaction vessel in an excess of oxygen and absorbing the H_2O in "dehydrite" and the CO_2 in "ascarite." For this absorption, two glass-stoppered U-tubes, similar to that used in the hydrogen combustions, were used in series. The first tube contained "dehydrite" and P_2O_5 , and the second "ascarite" and P_2O_5 . The first tube absorbed only the H_2O while the second absorbed all the CO_2 . Because of the large amount of heat evolved when "ascarite" absorbs CO_2 , the second tube was placed in a beaker of water.

The procedure employed in determining the mass of H_2O formed has been described in detail.⁵

The mass of CO_2 absorbed was determined in the same manner. When "ascarite" absorbs CO_2 , two reactions occur:



The molecular volumes⁶ were taken as follows: NaHCO_3 , 38.2 cm^3 ; NaOH (hydrated) , $18.8 \text{ cm}^3 + 15.6 \text{ cm}^3$ for each mole of water of hydration; Na_2CO_3 , $41.8 \text{ cm}^3 + 15.6 \text{ cm}^3$ for each mole of water of hydration. The increase in volume of the "ascarite" is $0.45 \pm 0.02 \text{ cm}^3$ per gram of CO_2 absorbed. Following a calculation similar to one already described,⁷ the mass of CO_2 absorbed becomes, when the absorber is filled with oxygen at 25°C . and 1 atmosphere.

$$m_{(\text{CO}_2)} = (1.00000 + 0.00059 - 0.00014) \times \Delta m = 1.00045 \Delta m \quad (4)$$

where m is the mass of the brass weights. The uncertainty in this factor is not more than 2 in 100,000. When the absorber is filled

⁴ See footnote 1, p. 38.

⁵ See footnote 1, p. 38.

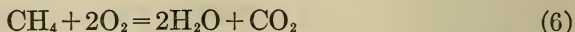
⁶ Calculated from densities and molecular weights given in International Critical Tables, 1, pp. 150, 151.

⁷ See footnote 1, p. 38.

with hydrogen, as it was in some experiments, the mass of CO_2 is obtained from the following equation:

$$m_{(\text{CO}_2)} = (1.00000 + 0.00004 - 0.00014) \times \Delta m = 0.99990 \Delta m \quad (5)$$

The results of four determinations of the ratio of H_2O to CO_2 are given in Table 1. When the methane was burned in oxygen according to the equation



it was found that the ratio of half the moles of H_2O to the number of moles of CO_2 formed was 0.99885 ± 0.00019 .

TABLE 1.—Ratio of H_2O to CO_2 in the combustion products of methane

Experiment	Mole of H_2O	Mole of CO_2	Ratio: $\frac{1/2 \text{ moles } \text{H}_2\text{O}}{\text{moles } \text{CO}_2}$	Deviation from mean
1-----	0.125614	0.062886	0.99875	-0.00010
2-----	.111594	.055855	.99896	.00011
3-----	.081449	.040761	.99911	.00026
4-----	.115400	.057783	.99857	-.00028
Mean-----			.99885	$\pm .00019$

The excess of CO_2 could be explained by the presence in the methane of a small amount of CO . Accordingly, the methane was analyzed directly for CO by the gas chemistry section of this bureau with the aid of the I_2O_5 apparatus developed by them.⁸ The results of their analyses are given in Table 2. While the ratio of H_2O to CO_2 indicated the presence of CO to the extent of (0.115 ± 0.019) per cent, the direct analyses gave (0.1219 ± 0.0013) per cent. For the purpose of correcting the calorimetric data for the amount of CO present, this was taken as 0.122 per cent.

TABLE 2.—Determination of CO in the methane

Experiment	Observed volume of CH_4	Observed volume of $\text{Na}_2\text{S}_2\text{O}_3$ solution	Calculated volume of CO	CO	Deviation from mean
	<i>ml</i>	<i>ml</i>	<i>ml</i>	<i>Per cent</i>	
1-----	486.4	10.80	0.5915	0.1215	-0.0004
2-----	488.0	11.05	.6050	.1239	.0020
3-----	484.0	10.64	.5830	.1204	-.0015
Mean-----				.1219	$\pm .0013$

In the combustion experiments on methane, the amount of reaction was determined from the mass of H_2O formed.

Since the determination of the ratio of H_2O to CO_2 in the products of combustion of the methane gas showed that, exclusive of the 0.122 per cent of CO , the ratio of the number of C atoms to one-fourth the number of H atoms was 1.0000 ± 0.0002 , the amount of H_2 or

⁸ (a) This apparatus and method are described by J. H. Elseman in the Gas Chemists' Hand Book, p. 289; 1929. American Gas Association, New York. (b) Lamb, Bray, and Frazer, Ind. Eng. Chem., 12, p. 213; 1920.

C_2H_6 which could be present in the methane without being detected was about 0.04 or 0.06 mole per cent, respectively. The amount of any hydrocarbon other than C_2H_6 which could have been present is less than 0.06 mole per cent. The following table shows the per cent error in the heat of combustion of methane caused by undetected amounts of these substances:

Impurity	Possible undetected amount	Error in heat effect caused by undetected amount
	<i>Mole per cent</i>	<i>Per cent</i>
H_2	0.04	0.013
C_2H_4	.06	.014
C_2H_2	.02	.011
C_2H_2	.007	.014
C_3H_8	.03	.014

The proper ratio of C to H could have been maintained by suitable amounts of hydrogen and other hydrocarbons than methane. The following table shows the amount of such impurities required to produce an error of 0.01 per cent in the heat of combustion of methane.

Impurity	Amount of impurity required to produce an error of 0.01 per cent in the heat effect
	<i>Mole per cent</i>
$C_2H_4 + H_2$	0.39
$C_2H_4 + 2H_2$.14
$C_2H_2 + 3H_2$.094
$C_3H_8 + 2H_2$.27

2. CORRECTION EXPERIMENTS

As in the combustion experiments with hydrogen, the calorimetric experiments where methane was burned in oxygen had associated with them in addition to the heat of the given reaction, three sources or sinks of energy which were not present in the calibration experiments: (1) the energy given to the calorimeter by the sparking operation (2) the energy required to bring the inflowing gases to the temperature of the calorimeter, and (3) the energy of vaporization of the H_2O not condensed to liquid.

The "spark" energy, determined as in the hydrogen experiments, was found to be 1.60 joules per second. The "gas" energy and the "vaporization" energy were calculated as before.

An experiment involving three separate ignitions and extinctions of the methane flame was made to test the validity of the energy corrections. The data obtained in this experiment are given in Table 3. The measured amount of energy was 3,124.3 international joules, while the calculated sum of the "spark," "gas," and "vaporization" energies, and the energy liberated by the combustion of the CH_4 , is 3,124.8 international joules. The difference of 0.5 joule is well within

the experimental error. The heat effect of the solution of CO₂ in the water formed is calculated to be negligible (1 or 2 parts per 100,000).

TABLE 3.—Correction experiment for combustion of methane

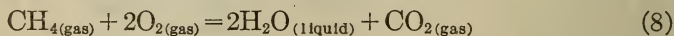
Electrical equivalent of calorimeter-----	int. joules/° C--	15632. 6
Corrected temperature rise-----	° C--	0. 19986
<i>E</i> , the total energy-----	int. joules--	3124. 3
Moles of CH ₄ burned-----		0. 035278
<i>E</i> ₁ , "spark" energy-----	joules--	28. 8
<i>E</i> ₂ , "gas" energy-----	do-----	—5. 2
<i>E</i> ₃ , "vaporization" energy-----	do-----	—38. 3
<i>E</i> ₄ , Heat of combustion of CH ₄ (+0.122 per cent CO)---	int. joules--	3139. 5
<i>E</i> ₁ + <i>E</i> ₂ + <i>E</i> ₃ + <i>E</i> ₄ -----	do-----	3124. 8

3. COMBUSTION EXPERIMENTS

The experiments on the combustion of methane were performed in the same manner as were the hydrogen combustions. The results are given in Table 4. The result of experiment A is not included in obtaining the average. The "error" of the mean⁹ is calculated from the equation

$$\text{"Error" of the mean} = \pm 2\sqrt{\frac{\Sigma(\bar{x}-x)^2}{n(n-1)}} \qquad (7)$$

when $\Sigma(\bar{x}-x)^2$ is the sum of the squares of the deviations of *n* experiments. The value obtained for the heat of the reaction



is 889,700 ± 270 international joules per mole at 30° C. and a constant pressure of 1 atmosphere.

4. DATA OF PREVIOUS INVESTIGATORS

The heat of combustion of methane was measured by Andrews¹⁰ in 1848, Favre and Silbermann¹¹ in 1852, Thomsen¹² in 1880, and Berthelot¹³ in 1881.

TABLE 4.—Experiments on combustion of methane

Experiment	Δ <i>R</i>	<i>k</i>	<i>u</i>	<i>K</i>	<i>U</i>	Δ <i>R</i> _{corr.}	$\frac{dR}{dt}$	Δ <i>t</i> _{corr.}
	<i>Ohm</i>	<i>Ohm/min/ ohm</i>	<i>Ohm/min</i>	<i>Ohm</i>	<i>Ohm</i>	<i>Ohm</i>	<i>Ohm</i> /° C.	° C.
A-----	0. 291604	0. 001873	—0. 0000063	0. 002721	—0. 000101	0. 288984	0. 100730	2. 86890
B-----	. 291832	1899	63	2552	101	. 289179	30	2. 87083
C-----	. 288904	1867	37	3468	59	. 285377	31	2. 83306
D-----	. 287126	1892	106	2722	170	. 284235	30	2. 82175
E-----	. 293829	1903	268	2725	429	. 290375	30	2. 88568
F-----	. 290884	1888	58	2619	93	. 288172	30	2. 86084

⁹ See footnote 1, p. 38.
¹⁰ Andrews, Phil. Mag., **32**, p. 326; 1848.
¹¹ Favre and Silbermann, Annales chim. phys., **34**, p. 426; 1852.
¹² Thomsen, (a) Berichte, **13**, p. 1323; 1880. (b) "Thermochemische Untersuchungen," **4**, p. 48. J. A. Barth, Leipzig; 1886.
¹³ Berthelot, Annales chim. phys., **28**, p. 178; 1881.

TABLE 4.—*Experiments on combustion of methane*—Continued

Experiment	Average temperature	Mass of calorimeter water	One-half mass of liquid H ₂ O formed	Electrical equivalent of calorimeter system	Pressure in reaction chamber	Total energy	"Gas" energy	"Vaporization" energy
	° C.	g	g	Int. joules/ ° C.	mm Hg	Int. joules	Joules	Joules
A-----	30.02	3,687.80	0.86	15,673.6	762	44,966.0	33.8	249.6
B-----	30.03	3,692.00	.90	15,691.3	761	45,047.1	9.1	168.5
C-----	30.01	3,686.63	.88	15,668.8	759	44,390.7	15.5	202.5
D-----	30.03	3,684.10	.88	15,658.2	753	44,183.5	6.9	158.8
E-----	30.02	3,674.80	.89	15,619.5	750	45,072.9	11.5	155.1
F-----	30.02	3,689.43	.88	15,680.7	761	44,860.0	23.8	160.7

Experiment	"Spark" energy	Reaction energy	Moles of CH ₄	Q _p , t	Correc- tion to 30° C.	Correc- tion to 1 atmos- phere	Correc- tion for 0.122% CO	Q _{30° C.} 1 atm.	Devi- ation from mean
	Joules	Int. joules		Int. joules/ mole	Joules/ mole	Joules/ mole	Joules/ mole	Int. joules/ mole	
A-----	16	45,233.4	0.0507360	891,544	-2	+13	-345	(891,210)	-----
B-----	9.6	45,215.1	.0507829	890,361	-3	7	-345	890,020	323
C-----	30.4	44,578.3	.0501019	889,753	-1	-7	-345	889,400	-297
D-----	9.6	44,339.6	.0498038	890,285	-3	-47	-345	889,890	193
E-----	9.6	45,229.9	.0508121	890,141	-2	-67	-345	889,727	30
F-----	9.6	45,034.9	.0506131	889,788	-2	7	-345	889,448	-249
Mean-----	-----	-----	-----	-----	-----	-----	-----	889,700	±218

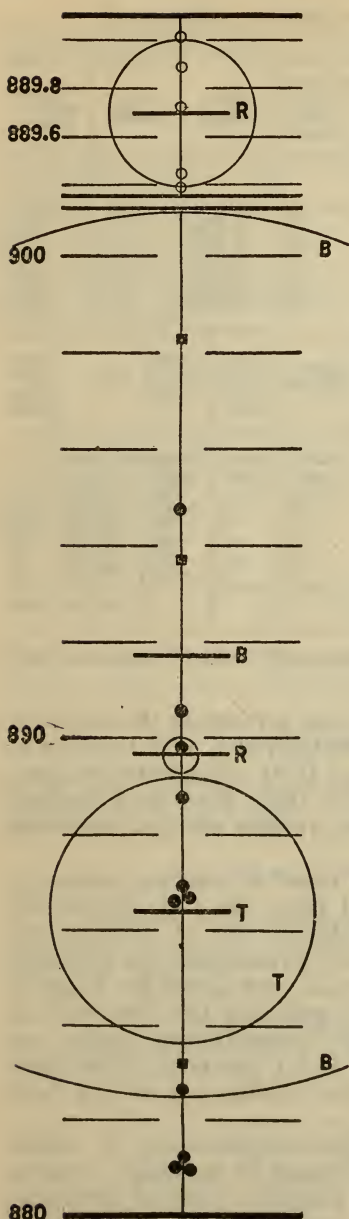
Electrical equivalent of calorimeter system with 3,700.00 g water at 30° C.=15,720.9 international joules per ° C.

Because of the large amounts of impurities present in the methane burned by Andrews and by Favre and Silbermann, and because of the fact that lack of suitable calibration of their calorimeter systems makes sufficiently accurate translation of their data into modern energy units practically impossible, their results are not reviewed here.

Thomsen burned methane in a reaction vessel at constant pressure. The amount of reaction was determined from the CO₂ formed by absorption in KOH solution. The results of the 11 experiments reported by Thomsen, corrected to 30° C. (presumably at 1 atmosphere), and to international joules per mole, are given in Table 5. Computing the "error" of the average by equation (5), the result of Thomsen's data becomes 886,380 ± 2,840 international joules per mole. This includes an estimated error of 0.1 per cent in the calibration of his calorimeter; that is, in his calculation of the heat capacity of his calorimeter.

Berthelot reported the results of three experiments in which methane was exploded with oxygen in a bomb at constant volume. The amount of reaction was determined from the mass of methane, computed from its volume, pressure, and temperature. The data of Berthelot, corrected to international joules per mole at 30° C. and 1 atmosphere, are given in Table 6. The average of these data is 891,700 ± 9,000 international joules per mole. The "error" includes an estimated error of 0.1 per cent in calibration.

The individual values of the experiments by Thomsen and by Berthelot, together with the present data, are shown in Figure 1. The circles or arcs are drawn with radii equal to the assigned



"errors." The upper section of Figure 1 shows a magnified view of that portion of the lower scale in which fall the values obtained in this investigation.

TABLE 5.—Results obtained by Thomsen on the combustion of methane

Experiment	Q 30° C., 1 atm.	Deviation from mean
	<i>Int. joules per mole</i>	
1-----	886, 770	390
2-----	883, 770	2, 390
3-----	881, 020	-5, 360
4-----	889, 820	3, 440
5-----	886, 890	510
6-----	882, 660	3, 720
7-----	881, 240	-5, 140
8-----	886, 630	300
9-----	881, 080	-5, 300
10-----	894, 750	8, 370
11-----	890, 540	4, 170
Mean--	886, 380	$\pm 3, 550$

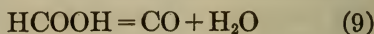
TABLE 6.—Results obtained by Berthelot on the combustion of methane

Experiment	Q 30° C., 1 atm.	Deviation from mean
	<i>Int. joules/mole</i>	
1-----	893, 700	2, 000
2-----	898, 300	6, 600
3-----	883, 200	-8, 500
Mean --	891, 700	$\pm 5, 700$

V. CARBON MONOXIDE

1. CHEMICAL PROCEDURE

The carbon monoxide used in this investigation had been prepared by the Fixed Nitrogen Research Laboratory.¹⁴ The gas was made by decomposing formic acid with phosphoric acid at 170°C., according to the reaction.



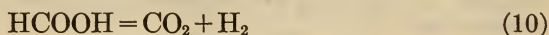
The product was purified from traces of undecomposed acid with sodium hydroxide solution. Scrubbings with potassium hydroxide solution, and passage through a cold trap at -80°C. , preceded

FIGURE 1.—Plot of the data on the heat of combustion of methane

The ordinate scale gives the heat of combustion of methane in international kilojoules per mole at 30° C., and 1 atmosphere. The points designate the data of the various investigators: ■, Berthelot; ●, Thomsen; ○, Rossini.

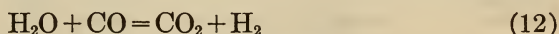
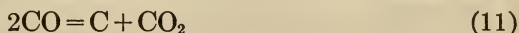
¹⁴ Thompson, Ind. Eng. Chem., **21**, p. 389; 1929.

the compression of the gas into steel cylinders. A possible small impurity of hydrogen might arise from the reaction



Because of its contact with the iron of the steel cylinder in which it was kept, the carbon monoxide contained, besides moisture, a small amount of iron carbonyl whose presence is easily detected by the yellow color it imparts to the flame. This iron carbonyl was decomposed into Fe and CO by passage through a tube filled with preignited asbestos at a temperature of about 500° C.

This process of eliminating the iron carbonyl resulted in the occurrence of two other reactions, as follows:



The C was deposited in the asbestos while the CO₂ formed, along with that which was originally in the carbon monoxide, was removed by passage through a tube containing "ascarite." The H₂ formed in the second reaction between H₂O and CO, remained in the carbon monoxide. The amount of H₂ was determined by absorbing, in separate U-tubes, the CO₂ and H₂O formed, as described in the preceding section under the determination of the ratio of C to H in CH₄. Two determinations of the amount of H₂ in the carbon monoxide entering the reaction vessel gave, respectively, 0.105 and 0.101 mole per cent. This consisted of the H₂ formed in the hot tube, together with a small amount (about 0.04 per cent) which was originally in the carbon monoxide.

In determining the amount of CO burned in the combustion experiments, the mass of CO₂ (plus the small amount of H₂O formed) was obtained, the correction to vacuum being made with the aid of equations (4) and (5). From this mass was subtracted the amount of H₂O absorbed (0.042 weight per cent), and the result divided by 44.000, the molecular weight of CO₂, to give the number of moles of CO burned. The measured reaction energy was decreased by an amount corresponding to the combustion of the 0.103 mole per cent of H₂ to form gaseous H₂O.

2. CORRECTION EXPERIMENTS

Pure dry carbon monoxide is difficult to ignite, but the presence of H₂ or H₂O greatly decreases this difficulty. The presence of the 0.1 per cent H₂ in the carbon monoxide was advantageous in this regard, but even so, it was found that a much longer time of sparking (5 to 30 seconds) was required to ignite the carbon monoxide than was necessary for either the hydrogen or the methane. This accounts for the failure to obtain the expected greater precision in the combustion experiments on carbon monoxide.

The "spark" energy, determined as before, was now found to be 1.28 joules per second. The "gas" energy was calculated as in the previous experiments. In order to check the validity of the "spark" and "gas" energy corrections, three separate experiments were

performed. The results are given in Table 7. The difference between the measured energy, E , and the computed sum of the energies, $E_1 + E_2 + E_4$, are with one exception, well within the experimental error.

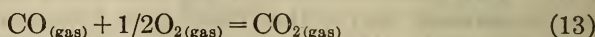
TABLE 7.—Correction experiments for combustion of carbon monoxide

	Experiment		
	1	2	3
Electrical equivalent of calorimeter.....int. joules °C..	15621.3	15621.3	15621.3
Corrected temperature rise.....°C..	0.05167	0.05041	0.03078
E , total energy.....int. joules..	807.1	787.5	480.8
Mole of CO burned.....	0.0027020	0.0025221	0.0014771
E_1 , "spark" energy.....joules..	42.2	80.6	64.0
E_2 , "gas" energy.....do....	-1.5	-1.5	-1.5
E_4 , heat of combustion of CO (+0.103 per cent H_2).....int. joules..	765.2	714.3	418.3
$E_1 + E_2 + E_4$do....	805.9	793.4	480.8
Difference.....joules..	-1.2	+5.9	0.0

3. COMBUSTION EXPERIMENTS

The data of the combustion experiments involving carbon monoxide are given in Table 8. The electrical equivalent of the calorimeter is 0.9 joule per degree less than in the previous experiments because of the removal of 0.24 g of copper.

The average of the eight experiments gives for the heat of combustion of CO, according to the equation



282,925 ± 100 international joules per mole at 30° C. and a constant pressure of 1 atm. The "error" is calculated according to equation (7).

TABLE 8.—Experiments on combustion of carbon monoxide

Experiment	ΔR	k	u	K	U	$\Delta R_{corr.}$	$\frac{dR}{dt}$	$\Delta t_{corr.}$
	Ohm	Ohm/min/ ohm	Ohm/min	Ohm	Ohm	Ohm	Ohms/° C.	° C.
A.....	0.134528	0.001858	0.0000115	0.001538	0.000230	0.132760	0.100730	1.31798
B.....	.111010	1853	65	1857	130	.109023	23	1.08240
C.....	.127761	1855	197	2755	493	.124513	31	1.23609
D.....	.134972	1915	139	1643	278	.133051	30	1.32087
E.....	.130186	1933	241	1786	482	.127918	30	1.26991
F.....	.134312	1881	117	1550	234	.132528	30	1.31568
G.....	.135181	1809	251	1656	502	.133049	30	1.32085
H.....	.118339	1875	28	2036	56	.116247	32	1.15402

Experiment	Average temperature	Mass of calorimeter water	Electrical equivalent of calorimeter system	Pressure in reaction chamber	Total energy	"Gas" energy	"Spark" energy	Reaction energy
	° C.	g	Int. joules/ ° C.	Mm Hg	Int. joules	Joules	Joules	Int. joules
A.....	30.04	3,688.32	15,671.3	760	20,654.5	11.8	10.2	20,656.1
B.....	30.28	3,683.95	15,652.7	754	16,942.5	8.5	15.4	16,935.6
C.....	29.99	3,682.15	15,655.5	750	19,351.6	14.1	32.0	19,333.7
D.....	30.02	3,675.85	15,619.2	750	20,630.9	9.7	32.0	20,608.6
E.....	30.04	3,686.59	15,664.0	749	19,891.9	12.9	48.6	19,856.2
F.....	30.02	3,685.95	15,661.4	750	20,605.4	8.3	28.1	20,585.6
G.....	30.02	3,681.75	15,643.8	753	20,663.1	17.0	35.9	20,644.2
H.....	29.96	3,681.85	15,644.3	753	18,053.8	9.7	23.1	18,040.4

TABLE 8.—Experiments on combustion of carbon monoxide—Continued

Experiment	Moles of CO	$Q_{p,t}$	Correction to 30° C.	Correction to 1 atmosphere	Correction for 0.103 per cent H_2	$Q_{30^\circ C., 1 atm.}$	Deviation from mean
		<i>Int. joules/mole</i>	<i>Joules/mole</i>	<i>Joules/mole</i>	<i>Joules/mole</i>	<i>Int. joules/mole</i>	
A.....	0.0729688	283, 077	0	0	-249	282, 828	-97
B.....	.0597962	283, 223	-2	-10	-249	282, 962	37
C.....	.0682694	198	0	-17	-249	282, 932	7
D.....	.0728097	048	0	-17	-249	282, 782	-143
E.....	.0700779	345	0	-18	-249	283, 078	153
F.....	.0727235	068	0	-17	-249	282, 803	-122
G.....	.0729188	113	0	-12	-249	282, 852	-73
H.....	.0636511	426	0	-12	-249	283, 165	240
Mean.....						282, 925	± 109

Electrical equivalent of calorimeter system with 3,700.00 g water at 30° C.=15,720.0 international joules per ° C.

4. DATA OF OTHER INVESTIGATORS

The heat of combustion of carbon monoxide was measured by Dulong¹⁵ in 1838, Andrews¹⁶ in 1848, Favre and Silbermann¹⁷ in 1852, Berthelot¹⁸ in 1878 and 1880, and Thomsen¹⁹ in 1880. As before, only the results of Thomsen and of Berthelot are compared with those of the present investigation.

Thomsen reported the results of 10 experiments in which carbon monoxide was burned in oxygen at constant pressure. The results of Thomsen, corrected to international joules per mole at 30° C. (presumably at 1 atm.), are given in Table 9. The average value is $284,140 \pm 710$ international joules per mole. The assigned "error" includes an estimated error in calibration of 0.1 per cent and is calculated by equation (7).

TABLE 9.—Results obtained by Thomsen on the combustion of carbon monoxide

Experiment	$Q_{30^\circ C., 1 atm.}$	Deviation from mean
	<i>Int. joules/mole</i>	
1.....	284, 680	580
2.....	284, 120	20
3.....	284, 160	60
4.....	282, 580	-1, 520
5.....	285, 110	1, 010
6.....	283, 980	-120
7.....	282, 250	-1, 850
8.....	283, 930	-170
9.....	285, 630	1, 530
10.....	284, 590	490
Mean.....	284, 140	±735

Berthelot reported two values for constant pressure and two for constant volume. These data, corrected to international joules per mole at 30° C., and 1 atm., are given in Table 10. The average value with its assigned "error" is $284,800 \pm 2,000$ international joules per mole.

¹⁵ Dulong, *Comptes rendus*, **7**, p. 871; 1838.¹⁶ Andrews, *Phil. Mag.*, **32**, p. 325; 1848.¹⁷ Favre and Silbermann, *Annales chim. phys.*, **34**, p. 405; 1852.¹⁸ (a) Berthelot, *Annales chim. phys.*, **13**, p. 1; 1878; (b) **20**, p. 255; 1880.¹⁹ Thomsen, "Thermochemische Untersuchungen," II, p. 288, J. A. Barth, Leipzig, 1886.

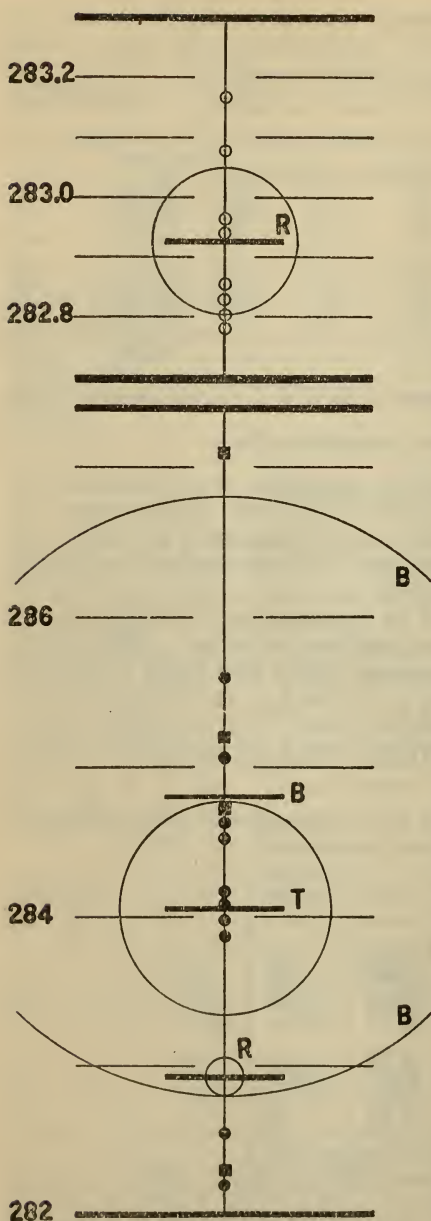


FIGURE 2.—Plot of the data on the heat of combustion of carbon monoxide

The ordinate scale gives the heat of combustion of carbon monoxide in international kilojoules per mole at 30° C. and 1 atmosphere. The points designate the data of the various investigators: Berthelot; ●, Thomsen; ○, Rossini.

TABLE 10.—Results obtained by Berthelot on the combustion of carbon monoxide

Experiment	$Q_{30^{\circ} \text{ C.}, 1 \text{ atm.}}$	Deviation from mean
	<i>Int. joules/mole</i>	
1.....	285, 200	400
2.....	284, 700	-100
3.....	282, 300	-2, 500
4.....	287, 100	2, 300
Mean....	284, 800	$\pm 1, 300$

In Figure 2 are shown the individual values of Thomsen and of Berthelot, together with the data of the present investigation. The circles or arcs are drawn with radii equal to the assigned "errors." The upper part of Figure 2 shows a magnified view of that part of the lower scale in which fall the values of the present work.

VI. CONCLUSION

On comparing the data of Thomsen and of Berthelot on the heats of combustion of methane and carbon monoxide with the data obtained in the present investigation, one finds that (1) the average values of Berthelot, plus or minus the assigned "errors," are in agreement with the values obtained in the present work and (2) that the average values of Thomsen, both for methane and carbon monoxide, have assigned to them "errors" which are too small (made so by the comparatively large number of observations) for agreement with the present data. This latter fact implies the existence of some systematic error in the measurements of Thomsen—of opposite sign in the two sets of data.

Conservative estimates of the uncertainty, from all causes, in the average values of the heats

of combustion of methane and carbon monoxide as determined from the present data are, respectively, ± 300 and ± 120 joules per mole.

From the data of the present investigation the heat of combustion of CH_4 in O_2 to form liquid H_2O and gaseous CO_2 according to equation (8) is $889,700 \pm 300$ international joules per mole at 30°C . and a constant pressure of 1 atm. For small changes in temperature and pressure this value changes, respectively, -93 joules per mole per degree increase in temperature and -6.7 joules per mole per mm increase in pressure.

From the present data the heat of combustion of CO in O_2 to form CO_2 according to equation (13) is $282,925 \pm 120$ international joules per mole at 30°C . and a constant pressure of 1 atm. For small changes, this value changes, respectively, $+7$ joules per mole per degree increase in temperature and -3.7 joules per mole per mm increase in pressure.

At 25°C ., and a constant pressure of 1 atm., these values in various units²⁰ are, per mole:

	International joules	Absolute joules	g-cal ₁₅
CH_4 -----	$890,160 \pm 300$	$890,520 \pm 300$	$212,790 \pm 70$
CO -----	$282,890 \pm 120$	$283,000 \pm 120$	$67,623 \pm 30$

These values are obtained by using the relations: 1 international joule ~ 1.0004 absolute joules, and 1 g-cal₁₅ ~ 4.185 absolute joules.

VII. ACKNOWLEDGMENT

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²⁰ See footnote 1, p. 38.