44. *Heat of Combustion of Calcium Cyanamide.*

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How much of heat is developed when nitrogen is fixed by carbide of calcium in the form of cyanamide of calcium is a question which remains still to be solved. One of the present authors¹⁾ tried to determine it calorimetrically, soon after he had succeeded to prepare calcium cyanamide of high purity by the repeated calcination of calcium oxide with dicyanodiamide in current of nitrogen. The cyanamide burns in oxygen quantitatively according to the following equation:

This reaction was utilized for the determination of heat of combustion of the cyanamide and the result was 1935.5 calories per gram of CaCN_2 , which gave the following value for the heat of formation of the cyanamide from the carbide:

In the Fixed Nitrogen Research Laboratory of the United States, the heat of the last named reaction was determined directly by the nitrogenation of calcium carbide in the calorimetric bomb, and the result was 97,800 cal.²⁾ As this value was widely different from the above mentioned, it was much desired to redetermine the heat of combustion, though it was not possible at the time to do it, because the author had been staying in Europe. Recently the work was resumed with improvements in many points and has lead to the result here to be presented. During the while, another work done by Frank and Hochwald³⁾ was published, and the heat of combustion was found to be 2036 cal. per gram of CaCN_2 , and, the heat of formation of the cyanamide $70,500 \pm 2,600$ cal. from the heat of combustion and $72,000 \pm 2,000$ cal. from the result of the direct nitrogenation of the carbide.

1) N. KAMEYAMA, Journ. Coll. Engin., Tokyo Imp. Univ., Vol. X, No. 8, 9 & 10.

2) Krase and Yee, J. Amer. Chem. Soc. 1364, 1924.

3) Frank and Hochwald, Zeit. f. Elektroch., 31, 581, 1925.

In the present measurements a bomb calorimeter of Berthelot-Mahler type was used. The water put in it was always 2200 grams and oxygen was filled up to 25 atmospheres. The corrections applied were: for the change of specific heat of water with temperature, heats due to combustion of iron wire and to the formation of nitric acid, exchange of heat with the surrounding and for the setting of Beckmann thermometer. All the heat values refer to room temperature, which varied from 17° to 24°C, and all the weighings refer to those in air. The water value of the calorimeter excluding of the water was 445.0 as given by the average of 444.5, 447.0, 445.0, 444.7, 445.1, and 443.5. Heat of combustion of naphthalene was taken as 9614 cal. per gram and that of benzoic acid 6324 cal.

As the ignition was not possible when the cyanamide was heated alone in the calorimetric bomb, incorporation of a substance that is easy to ignite was necessary, and benzoic acid was used as such an agent. The amount of benzoic acid to be incorporated required some consideration. If it was too much, the heat due to the cyanamide was much less than that due to benzoic acid and the result was not accurate enough, and if too little, the mixture did not ignite well. Therefore it was examined specially how much could the proportion of benzoic acid be reduced without detriment to the complete combustion of the cyanamide. In the series of measurements given in the table, amount of benzoic acid in the mixture was well within the limit of the complete combustibility of the cyanamide. The cyanamide used contained CaCN_2 98.25%, CaCO_3 0.81% and CaO 0.94%.

TABLE I.

	Sample contains		Heat due to		Ratio of heats $\frac{\text{Benzoic acid}}{\text{CaCN}_2}$	Heat of Combustion per gram of CaCN_2
	CaCN_2	Benzoic acid.	Benzoic acid (calculated)	CaCN_2 (found)		
A.	0.9543 ^{gram}	0.3885 ^{gram}	2434.3 ^{cal.}	1947.0 ^{cal.}	1.25	2040.2 ^{cal.}
B.	0.9574	0.3899	2465.7	1924.6	1.28	2010.3
C.	0.9578	0.3900	2466.3	1932.3	1.28	2017.4
D.	0.9578	0.2917	1844.9	1910.1	0.97	1994.3
E.	0.9524	0.2905	1837.1	1921.7	0.96	2017.8
F.	0.9516	0.2905	1837.1	1912.6	0.96	2009.8
G.	0.9587	0.2919	1346.0	1941.9	0.95	2025.6
H.	0.9550	0.2906	1838.0	1921.7	0.96	2012.3
						2016.0

The residue of combustion consisted chiefly of calcium oxide, but lost a few centigram of its weight when ignited, this showing the presence of carbonate or hydroxide of calcium in it. If the correction had been applied for the heat produced by the formation of these compounds, it would amounted to the deduction of about 1% from the heat of combustion given above. Estimation with some degree of accuracy of carbonate and of hydroxide in the residue was not found possible owing to the small quantity. Moreover it was quite uncertain whether these compounds had been formed during the combustion period and had contributed any to the measured heat, or they had been the products of the subsequent period of manipulations and contributed nothing to the heat measured. Therefore the authors abstained from applying these corrections.

Taking the mean of the last series, we have:

Heat of combustion 2016 ± 3 cal. per gram CaCN_2

$\text{CaCN}_2 + 3/2 \text{ O}_2 = \text{CaO} + \text{CO}_2 + \text{N}_2 + 161,170$ cal.

This differs a little less than 4% from the former value.

With the following known values:

(Ca, O) $152,700$ cal. (Guntz and Benoit, 1925)

($\text{C}_{\text{diamond}}$, O_2) $94,480$ (Roth, 1925)

Diamond $\rightarrow$ Graphite 160 (ditto)

(Ca, $2 \text{ C}_{\text{diamond}}$) $13,500$

we arrive at:

$\text{Ca} + \text{C}_{\text{diamond}} + \text{N}_2 = \text{CaCN}_2 + 86,010$ cal.

$\text{CaC}_2 + \text{N}_2 = \text{CaCN}_2 + \text{C}_{\text{graphite}} + 72,700$ cal.

The heat of reaction:

$\text{CaCN}_2 + 3\text{H}_2\text{O}_{\text{liquid}} = \text{CaCO}_{3\text{calcite}} + 2\text{H}_2\text{O}_{\text{gas}}$

is given as 500 kg. cal. per kilogram of ammonia liberated, for which Landis¹⁾ estimated as 200–300 kg. cal. from his experiences in the works.

The details of the measurements are given in the report of the Nitrogen Research Laboratory, Japan, that will be issued about in May.

1) Landis, Met. Chem. Eng. 1916, 14, 88.