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The Heat of Combustion, Entropy and Free Energy of Cyanogen Gas

BY JOHN MCMORRIS AND RICHARD M. BADGER

Introduction

As was pointed out some time ago by Lewis and Randall in their text "Thermodynamics," the value for the free energy of cyanogen gas which was obtained from the equilibrium measurements of Lewis and Keyes,[1] 92,000 cal., is evidently incompatible with the heats of formation determined by calorimetric measurements. The heat of combustion of cyanogen gas has been determined by Berthelot[2] and by Thomsen,[3] who obtained 261,800 and 259,600 cal. per mole, respectively. If their results are combined with the heat of combustion of graphite one obtains from the heat of formation of cyanogen, 73,300 or 71,000 calories. Now if these data are approximately correct it should be possible to calculate from them the entropy of cyanogen gas, making use of course of the known entropies of graphite and of nitrogen. Actually, however, one obtains for this quantity -14.0 or -21.8 entropy units, using the results of Berthelot or of Thomsen, respectively, which is in definite conflict with the third law of thermodynamics.

Since it is of importance not only to find the cause of this discrepancy but also to have a reliable value for the free energy of cyanogen, the authors have undertaken the investigation described in this article. They have chosen what seemed to be the most direct method of attack, namely, a redetermination of the heat of combustion with the object of finding whether there might have been a large systematic error in the work of previous investigators, and a calculation of the entropy of the gas from spectroscopic and other data. Though the lack of certain data makes this computation somewhat inexact, it is sufficiently accurate so that its combination with the heat of formation yields a new and independent value for the free energy of cyanogen which is probably in error by not more than 1500 calories.

Experimental Details

Although the greatest precision in work of this kind is probably offered by bomb calorimetry, it was decided to use a Sargent automatic gas calorimeter for certain reasons of convenience. In particular, the combustion products may be conveniently withdrawn for analysis, which seemed of considerable importance in this case.

Some preliminary experiments were made to determine whether the gas calorimeter was suitable for the purpose and it was found that under the conditions to be used in the

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(1) Lewis and Keyes, THIS JOURNAL, **40**, 472 (1918).

(2) Berthelot, *Ann. chim. phys.*, **23**, 178 (1881).

(3) Thomsen, "Thermochemistry," Longmans, Green and Co., New York, 1920.

later work the cyanogen apparently burned completely to carbon dioxide and nitrogen. The combustion products had no trace of odor of cyanogen and when they were drawn through a solution of sodium carbonate it was found that the alkalinity was reduced by an amount corresponding to the formation of not more than 1.5×10^{-4} mole of NO_2, which would contribute a negligible error to the heat of combustion as determined.

Measurement of the Gas.—Owing to the considerable solubility of cyanogen in water or in oil it was found inconvenient to use the usual wet meter which is customarily employed in conjunction with a gas calorimeter, and in its place the device represented in Fig. 1 was used to deliver the gas at a constant and measured rate. The cyanogen was contained in the rubber balloon *a*, of 16 liters capacity when distended to full size without stretching. Owing to the thinness of the wall of the balloon the pressure in *a* is practically the same as in the enclosing flask *b*. The arrangement at the left maintains a constant pressure of air in *b* and measures the amount of air fed in to replace the volume of the cyanogen withdrawn. The flask *e* rests on a Troemner balance and communicates with *b* through a flexible rubber connection, *c*. When the pressure in *e* falls by a small amount, water flows in to replace the air withdrawn, and the amount of water in the flask can be determined at any time by use of the balance. The balance arm is provided with electrical contacts so that when the balance "trips" the automatic diverting device on the calorimeter outflow is operated, and water either begins to flow into the weighing bucket, or the flow is interrupted as the case may be.

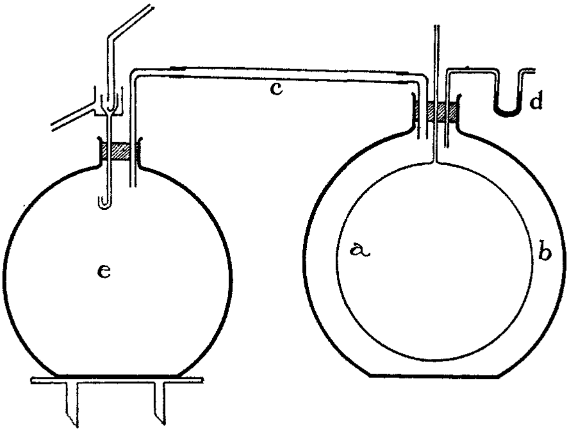

Fig. 1.—Diagram of the device for supplying gas to the calorimeter.

In the beginning of a run the balance is adjusted to trip when sufficient gas has been delivered to bring the calorimeter to a steady state, and the outflow water then begins to be collected. Weights are then added to the balance and when the corresponding amount of water has flowed into the flask *e* the balance trips a second time and the run is concluded.

Temperature Control of Inlet Water.—Water was delivered to the inlet weir of the calorimeter by a gear pump from a 15-gallon metal tub. This was filled before an experiment with water at room temperature to avoid fluctuation during a run, and was fitted with an efficient electrically driven stirrer. It was observed that the temperature of the water entering the calorimeter did not vary by more than 0.01° during any run.

Thermometers.—The thermometers used were of good quality, graduated from 0 to 50° in tenths of a degree, and were calibrated by comparison with a similar thermometer having a Bureau of Standards certificate. Since buret meniscus readers were used the error in reading was not greater than about ±0.01°.

Preparation of the Cyanogen.—Two preparations of cyanogen were made, each of which served for two runs. The gas was generated by dropping sodium cyanide solution onto finely powdered cupric sulfate. The gas evolved was dried with calcium chloride and frozen out in a trap kept at $-55°$ by an ethyl alcohol–solid carbon dioxide bath. The trap was then connected to the balloon and the cyanogen was allowed to evaporate into it. In each of two successive runs about 15% of the cyanogen was used in flushing the balloon five times, and about 30% for the filling. The remaining 10% was discarded.

That the cyanogen so prepared was free from sulfur dioxide or sulfur trioxide was shown by the experiments mentioned above in which the combustion products were analyzed. Air or carbon dioxide should have been removed when the gas was condensed, and any hydrogen cyanide should have remained behind in the discarded fraction owing to its relatively high boiling point. Good evidence for the purity of the gas is the fact that the heats of combustion of the first and second fractions used agreed within the experimental error.

The Combustions.—In all cases the gas was burned for a sufficient length of time to bring the temperature of the calorimeter outlet water to a constant value before the run was begun. When the balance tripped beginning a run, the Nujol manometer, *d* of Fig. 1, was read to determine the pressure on the gas in excess of atmospheric. The inlet and outlet thermometers were each read at fifteen-second intervals during the experiment. At the conclusion of the run the flue gas temperature was read, the room temperature noted, and the atmospheric pressure determined from a barometer. The bucket containing the heated water was then carefully weighed on a balance accurate to better than one gram, with calibrated weights. These same weights were used to calibrate those used on the Troemner balance for measuring the displacing water in the gas delivery apparatus.

Efficiency of the Calorimeter.—It has been shown by Waidner and Mueller[4] in their comprehensive report on gas calorimeters that a Sargent calorimeter of the type used in this investigation yields accurate values for heats of combustion when certain corrections are applied. The corrections for heat carried out in the flue gases and in radiation from the flame with properly adjusted radiation shields are negligible, and in this particular case, where no water is produced in combustion, no account need be taken of humidity. It was thus considered sufficient to apply the correction given by these authors for the heat loss by radiation from the calorimeter body.

It was, however, considered advisable to determine whether the calorimeter was in satisfactory condition by an electrical calibration in which a heater dissipating a measured amount of energy replaced the usual gas burner. Although there was a slight loss by radiation downward from the heating coil, the "electrical efficiency" was very little less than that found by Waidner and Mueller in similar experiments.

Results of the Combustions.—In Table I are given the data for the four experiments. No runs were discarded except a preliminary one of which no accurate record was kept.

The heat of combustion, in 15° calories, per mole of cyanogen has been calculated in two ways. In row (a) of Table I the following equation was used

$$Q = \frac{[(t_0 - t_i)WS + R] \times 82.05\,T}{PV}$$

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(4) Waidner and Mueller, Technologic Papers, Bur. of Standards, No. 36 (1914).

TABLE I

Number of run	I	II	III	IV
Av. outlet water temp. (corr.), °C.	34.26	36.19	37.50	34.15
Av. inlet water temp. (corr.), °C.	23.86	23.79	22.97	23.69
Av. temp. rise, °C.	10.40	12.40	14.53	10.46
Weight of heated water and container (red to vacuum), g.	2698.6	3094.9	2139.9	3577.7
Weight of container, g.	731.0	670.5	731.0	670.5
Weight of water, g.	1967.6	2424.4	1408.9	2907.2
Room temperature, °C.	24.0	26.0	23.1	23.9
Flue gas temp., °C.	24.2	24.2	23.4	24.1
Nujol manometer reading (converted to mm. Hg)	11.1	11.1	11.7	12.0
Barometer reading, mm. Hg	743.9	744.0	745.0	745.0
Total pressure on gas, mm. Hg at 0°C.	752.1	752.2	753.8	754.1
Weight of displacing water (corr. to vac.)	1969.4	2918.9	1982.8	2919.5
Volume of gas burned, cc.	1974.4	2926.7	1987.7	2927.2
Duration of run, minutes	3.0	3.8	2.2	4.6
Calcd. surface loss, cal./min.	16	19	23	16
Total heat loss, cal.	48	72	51	74
Calcd. heat of combustion, 15° cal. per mole				
(a) perfect gas	255,400	254,700	252,400	255,200
(b) corrected by van der Waals eq.	252,300	251,600	249,400	252,100
Mean heat of combustion, cal. per mole		251,400 ± 1200		

where $t_0 - t_i$ is the average rise in temperature of the calorimeter water, W is the weight of heated water, S the specific heat of water at its mean temperature, R the radiation loss correction, P the pressure of the gas in atmospheres, V the volume of the gas in cc. and T its absolute temperature.

Unfortunately accurate density measurements on cyanogen gas do not appear to have been made so it is not possible accurately to correct for deviation from the perfect gas. However, with the use of critical data and the van der Waals equation we estimate that at one atmosphere the deviation of the PV product from NRT is about -1.2%. This correction has been applied in the results in row (b).

For the heat of combustion of graphite we shall accept the value taken from the work of Roth and Naeser[5] quoted in the latest supplement to Landolt–Börnstein, namely, 94,270 cal. Combining this with our value for the heat of combustion of cyanogen we obtain for the heat of formation $H_{298.2} = 62{,}900$ cal.

The Entropy of Cyanogen Gas.—If we may assume that the cyanogen molecule is linear and symmetrical, which seems to be indicated by the infra-red spectrum as far as it is known, the calculation of the entropy of the gas from spectroscopic data is similar to that for acetylene[6] and need not be described in detail. Unfortunately, the spectroscopic data are as yet rather incomplete and it is necessary to make some assumptions.

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(5) Roth and Naeser, *Z. Electrochem.*, **31**, 461 (1925).

(6) Badger and Woo, THIS JOURNAL, **54**, 3523 (1932).

Since the infra-red bands have not been studied under high dispersion we must estimate the moment of inertia of the molecule. We shall assume for the C–C separation a distance of 1.44 Å., and for the C–N separation 1.16 Å.,[7] which yields the value $I = 184 \times 10^{-40}$, with an error of probably not more than 20%.

The cyanogen molecule has three low frequencies of vibration of importance in the entropy calculation, and unfortunately at least one of these is in some doubt. We shall, however, accept the assignment of Woo and Badger,[8] and using their nomenclature[6] assume $\nu_1^{\delta a} = 240$, $\nu_2^{\delta i} = 512$, and $\nu_3 = 860$. Of these only the second is likely to be in considerable error.

The results of the entropy calculation and some of the steps are given in Table II.

TABLE II

ENTROPY OF CYANOGEN GAS AT 298.2°

$I = 184 \times 10^{-40}$		$3/2\ R \ln M = 11.77$
$Q_{\text{rot.}} = 693$	$R \ln Q_{\text{rot.}} = 13.0$	$5/2\ R \ln 298.2 – 28.29$
$Q_{\text{vib.}} = 2.56$	$R \ln Q_{\text{vib.}} = 1.89$	$S_{\text{rot.}} = 15.0$
$RT \dfrac{d \ln Q_{\text{vib.}}}{dT} = 3.14$		$S_{\text{vib.}} = 5.0$
		$S^*_{298.2} = 57.8$

Owing to the uncertainty in one of the vibrational frequencies this entropy may be in considerable error, but probably by not more than two entropy units.

It is now possible, with the above value, the heat of formation of cyanogen, and the entropies of carbon and nitrogen, 1.4 and 45.8 entropy units, respectively, to calculate the free energy of cyanogen gas. We find that $F_{298.2} = 60{,}120$ cal.

This value differs from that obtained by Lewis and Keyes by 31,900 cal. but since this discrepancy is of an entirely different order of magnitude from the inaccuracy which may be present in our estimation (we believe our error not greater than about 1500 cal.), it appears that the equilibrium measurements from which the previous free energy value was obtained must be seriously at fault.[9]

Summary

The heat of combustion of cyanogen gas has been redetermined by the use of a gas calorimeter and has been found to be 251,400 ± 1200 calories.

The combination of this result with the heat of combustion of graphite yields for the heat of formation of cyanogen, $H_{298.2} = 62{,}900$ calories.

The entropy of cyanogen gas at 298.2° and 1 atm. has been calculated by the use of spectral data and an estimated moment of inertia. It is found that the virtual entropy is 57.8 ± 2.0 entropy units.

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(7) These values were suggested by L. Pauling in a private discussion with one of the authors.

(8) Woo and Badger, *Phys. Rev.*, **39**, 932 (1932).

(9) This has been shown to be the case by Yost and Stone. THIS JOURNAL, **55**, 1889 (1933).

The combination of the above results gives for the free energy of cyanogen gas, $F_{298.2} = 60{,}000$ calories.

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A Revision of the Atomic Weight of Arsenic. The Comparison of Arsenic Trichloride with Iodine Pentoxide

BY GREGORY PAUL BAXTER AND WILLIAM ERNEST SHAEFER

The atomic weight of arsenic has been under investigation in this Laboratory during a large part of the time during the past twenty years. Much of the earlier work was concerned with attempts to compare arsenic trioxide with the two oxidizing agents, iodine and iodine pentoxide. As the work progressed, however, it became evident that arsenic trioxide lacked the definiteness in composition indispensable for precise work, for its composition was found to vary with the oxygen concentration prevailing during the sublimation which constituted the final step in preparing the substance for weighing. The maximum reducing power was possessed by material which had been sublimed in an atmosphere containing a mere trace of oxygen. Even vacuum sublimed material possessed slightly less reducing power owing apparently to the fact observed that such material is slightly reduced to the metallic state, while sublimation in oxygen lowered the reducing power materially. The minimum atomic weight of arsenic found in this way was 74.95 (I = 126.917) while the maximum considerably exceeded 75. The minimum is appreciably higher than the one recently adopted by the International Committee on Atomic Weights, 74.93, which depends on Krepelka's analysis of arsenic trichloride, and still higher than the result of our own more recent analyses of arsenic halides,[1] 74.91. The chief outcome of the work with arsenic trioxide seems therefore to be that this compound is not suitable for use as an analytical standard of high precision.[2]

It seemed probable that arsenic trichloride, after solution, would furnish a far more reliable quantitative source of arsenious acid than arsenic trioxide. We therefore undertook a quantitative iodimetric analysis of arsenic trichloride. Because of convenience in handling, iodine pentoxide was first chosen as the oxidizing agent.

In outline, the procedure consisted in dissolving a weighed quantity of arsenic trichloride in sodium hydroxide, in a vacuum in order to avoid oxidation of the alkaline arsenite by the air. The solution was then neutralized,

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[1] Baxter, Shaefer, Dorcas and Scripture, THIS JOURNAL, **55**, 1054 (1933).

[2] The investigations upon arsenic trioxide were carried out under the senior author's supervision by Professors G. W. Harris, P. C. Voter, L. A. Youtz and Drs. G. L. Wendt and E. W. Scripture.