Studies on Hydrazine: The Heat of Formation of Hydrazine and of Hydrazine Hydrate*

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In order to extend previous results from this Laboratory on the thermochemistry of hydrazine and its compounds in aqueous solution,[1] attention has been turned to heats of combustion. For this a new calorimeter has been constructed, in which, however, the adiabatic principle of the earlier work has been retained.[1a]

Apparatus and Method

In the construction of the calorimeter the general principles and restrictions laid down by White[2] were followed closely. Certain details, however, are pertinent. Automatic temperature control by means of a 17-junction thermel, high sensitivity galvanometer and Weston Photronic cell, and electrolytic heating is the same as in the earlier apparatus.[1a] For the combustion a Parr double valve Illium bomb of 360 cc. capacity was used. The 3-mm. pegs with which it was originally provided were replaced by pegs 12 mm. high which allowed more effective circulation of water around it. The bomb was held in an oval calorimeter of approximately 2000 cc. capacity. This in turn was contained in a submarine jacket with a 12-mm. air gap between the two. The water was stirred by means of a chain driven stirrer and synchronous motor. The heat of stirring was of the order of 0.0001° per minute. The stirrer shaft contained a bakelite insert to minimize heat transfer. The ignition leads were led through copper tubing immersed in the outer bath for the same reason.

A temperature difference of 0.0002° between the calorimeter and the outer bath could be detected by the thermel galvanometer. During the runs the divergence never amounted to more than 0.0006°, and that only for brief intervals during the combustion. The automatic heating was augmented during the rapid temperature rise by the manual addition of hot water. There was a lag of approximately four seconds in the temperature equalization between the calorimeter and the outer bath.

The temperature was measured by means of a Leeds and Northrup platinum resistance thermometer, a "Mueller-type" thermometer bridge, and a Leeds and Northrup galvanometer (2285-b). Resistance could be read under the optimum conditions accurately to 0.00001 ohm. The bridge was newly calibrated in terms of the international ohm.[3] The bomb was provided with special crucible supports constructed by the Parr Instrument Co., having screw binding posts. Heavy platinum wires led from these

to a point near the charge to be burned. The charge was ignited by heating an exactly measured (2–3 cm.) piece of iron wire (no. 36) electrically using a 14-volt transformer. The energy introduced by the heating and combustion of this wire was determined by a series of blank runs, the mean result being 0.00019 ohm (0.0019°) for 3 cm.

The same mass of water was used in the calorimeter each time within 0.1 g. The mass of the charge was determined to 0.00001 g. The crucible for holding the charge was of very thin platinum, a factor which seemed to minimize carbon formation.

The bomb was washed out several times with oxygen at 4–5 atm. to remove residual air. Nitric acid formed in the combustions was determined by titration of the bomb washings with standard base, using brom cresol green as indicator. For the heat of formation of nitric acid at 25° and constant volume the value of 13,960 cal. mole^{-1} was used.[4] This correction was of considerable importance in the compounds burned for this investigation.

The same pressure of commercial oxygen, 30 atm. absolute, was used in every run, and 1 g. of water was added to the bomb.

The results are referred to the standard temperature of 25°, by using in each instance an initial temperature of $25 \pm 0.1°$, and calculations involving the heat capacity of the products of the reaction. This procedure was adopted because of uncertainty regarding the heat capacity of the reactants.

Calibration of the Calorimeter

The energy equivalent of the calorimeter was determined by the combustion of benzoic acid (Standard Sample 39e) supplied by the Bureau of Standards. The isothermal heat of combustion of this sample at 25° is given as 26,419 int. joules per gram true mass when burned under standard conditions.[5] The ratio of mass of acid and water to volume of the bomb being not quite "standard" a small correction ensues[5] (p. 491), which gives a value of 26,418 int. joules developed by the combustion of one gram of benzoic acid under the bomb conditions of this calorimeter. For convenience in making heat capacity calculations and in interpreting results, the results of this paper are largely expressed in conventional calories derived from the international joule by dividing by the factor 4.1833.[6]

Independent determinations were made by two operators (A. M. H. and R. J. C.) and the results are shown in Table I.

Heat of Combustion of Hydrazine Hydrate

Purification.—Purification of this compound is difficult on account of its instability and ease of oxidation, factors which also complicate the problem of securing uncon-

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(1) (a) Cobb and Gilbert, THIS JOURNAL, **57**, 35 (1935); (b) ibid., **57**, 39 (1935); (c) Bushnell and Gilbert, ibid., **57**, 2611 (1935); (d) Bushnell, Gilbert and Hughes, ibid., **59**, 2142 (1937).

(2) White, "The Modern Calorimeter," The Chemical Catalog Co., New York, 1928.

(3) Mueller, National Bureau of Standards, Sci. Paper 288.

(4) (a) Becker and Roth, Z. Elektrochem., **40**, 835 (1934); (b) Huffman, THIS JOURNAL, **60**, 1171 (1938).

(5) Jessup and Green, Bur. Standards J. Research, **13**, 496 (1934).

(6) Rossini, Chem. Rev., **18**, 233 (1936).

TABLE I

CALIBRATION OF CALORIMETER WITH BENZOIC ACID AT 25°

Sample	True mass benz. acid, g.	Corr.[b] temp. rise Ohms	Degrees	Energy from b. a. int. joules	Energy from HNO₃ joules	Heat capacity calor. and products, int. joules deg.⁻¹	Heat capacity products, deg.⁻¹	Energy equiv. of calor., joules deg.⁻¹	Dev. from mean
1[a]	1.00134	0.24853	2.4764	26454.7	2.5	10683.6	16.9	10666.7	−0.6
2	1.00543	.24929	2.4840	26538.7	3.7	10685.3	16.9	10668.4	+1.1
3	0.99810	.24772	2.4683	26368.8	2.2	10683.7	16.9	10666.8	−0.5
4	1.02603	.25461	2.5370	27106.7	2.5	10685.5	17.0	10668.5	+1.2
5	0.98751	.24510	2.4422	26089.0	2.5	10683.5	16.9	10666.6	−0.7
10	.98488	.24450	2.4362	26019.5	6.3	10682.8	16.9	10665.9	−1.4
13[c]	.62341	.15475	1.5420	16468.7	6.3	10684.5	16.1	10668.4	+1.1
14[c]	.62438	.15499	1.5443	16494.3	3.8	10683.0	16.1	10666.9	−0.4
15[c]	1.08859	.27017	2.6920	28759.4	5.5	10685.0	17.2	10667.8	+ .5

Mean energy equivalent, int. joules deg.⁻¹ 10667.3 ± .8

calories deg.⁻¹ 2550.0 ± .2

[a] Expts. 1–5 were performed by A. H., the remainder by R. C.   [b] Corrected for heat of stirring, evaporation, etc., and for "ignition" energy.   [c] (Fused.)

taminated samples in the glass ampoules, a necessary step in the process. The freezing point curve for the system hydrazine–water has been established recently by Semishin.[7] From this it appears that upon freezing, any solution of hydrazine and water containing between 30 and 60% hydrazine should yield crystals of the hydrate (m. p. −46.8°). This was attempted with the apparatus used for anhydrous hydrazine and described below, but the product obtained after two recrystallizations contained hydrazine in nearly 5% excess over the amount needed to make the hydrate. Combustions were run on this material and are reported with the other results. Since the heat of solution of anhydrous hydrazine in the hydrate is not known, no worthwhile conclusions may be drawn from these values except as they indicate the reproducibility of the combustion process, with a given sample. A number of samples of Kahlbaum hydrazine hydrate "pro analysi" (99.8–100.5%) were available and the procedure finally adapted was the same as that used in the earlier work,[1d] which was to take the distilled Kahlbaum preparation, determine the hydrazine content by the iodic acid method[8] (which in our experience is the most accurate available) and add the proper amount of water to give the exact composition of the hydrate (64.03% N₂H₄) (all weights reduced to vacuum). This material was then used for filling the ampoules for combustion. The air in the ampoules was replaced by hydrogen, and hydrate introduced by evacuation in a hydrogen-filled desiccator. They were filled completely, sealed off and used for combustion runs within a few hours. The results are shown in Table II.

The precision of the analysis rather than of the combustion is presumably the limiting factor. Combustions conducted on samples of hydrate from widely different batches over a year apart and by different individuals gave quantitative agreement, however.[9] The only impurity to be obvious would be ammonia, but tests for this substance were negative. Since the heat of combustion of ammonia is higher than that of hydrazine, its presence would give high results.

(7) Semishin, J. Gen. Chem. (U. S. S. R.), 8, 654 (1938).

(8) Bray and Cuy, THIS JOURNAL, 46, 858 (1924).

(9) Albert L. Hughes, Master's Thesis, Oregon State College, 1938.

TABLE II

THE ISOTHERMAL HEAT OF COMBUSTION OF HYDRAZINE HYDRATE AT 25°

Sample	True mass, g.	Total heat[b] evolved at 25°, cal.	Heat from HNO₃, cal.	−ΔU_B/m, cal. g.⁻¹	Deviation from mean
1[a]	1.70351	5,186.1	18.6	3,033.4	
2[a]	1.88990	5,756.6	21.0	3,034.8	
3[a]	1.73356	5,275.0	20.1	3,031.3	
4	1.89781	5,588.8	19.5	2,934.7	−0.5
5	1.49717	4,408.9	13.6	2,935.9	+ .7
6	1.57381	4,635.6	15.4	2,935.6	+ .4
7	1.95292	5,751.9	19.8	2,935.7	+ .5
8	1.75321	5,161.8	17.3	2,934.3	− .9

Mean −ΔU_B/m = 2,935.2   ±0.6 cal. g.⁻¹

−ΔU_B = 146,936 ± 30 cal. mole⁻¹

[a] The samples checked by analysis to contain 0.0539% by wt. N₂H₄ and 0.9461% N₂H₄·H₂O, hence were not used in further calculations.   [b] Corrected for heat of stirring, evaporation, etc., and for the ignition energy.

Purity of the Reaction.—A question also of considerable importance is that of the purity of the reaction and the absence of side reactions. The following products that might conceivably occur were tested for in the bomb washings: nitrites,[10] ammonia[10] (p. 468), hydrazoic acid, and excess hydrazine hydrate. None was found, except in a few bad runs there was some unburned hydrate, apparently from splashing. Flattening the sides of the ampoules and filling them fuller seemed to obviate this difficulty.

Calculation of Results.—Due to the fact that hydrazine hydrate contains only nitrogen, hydrogen and oxygen, it was necessary to depart from the classical equations of Washburn[11] for the heat capacity of the products. The pure reaction for the combustion is

$$N_2H_4 \cdot H_2O(liq) + O_2(g) \longrightarrow N_2(g) + 3H_2O(liq)$$
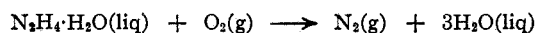
from which it may be seen that the only pressure change will be due to oxygen used in the forma-

(10) Mahin, "Quantitative Analysis," 4th ed., McGraw-Hill Book Co., Inc., N. Y., 1932, p. 473.

(11) Washburn, Bur. Standards J. Research, 10, 525 (1933).

tion of the small amount of nitric acid and ferric oxide. Also the appearance of nitrogen, mole for mole, for the oxygen consumed otherwise further simplifies the problem, since their thermodynamic properties may be considered equal. Due however to the large amount of water formed, a significant correction is introduced. From the figures of Washburn[11] (p. 556) and making due allowance for the water present as vapor at 25°, the mass of liquid water after the combustion will be

$$(m_w + 54.06 m_h/50.06 - 0.0068)$$

where m_w = mass of water initially placed in the bomb and m_h = mass of hydrate burned.

Any correction for the heat of dilution of nitric acid is disregarded since Becker and Roth[4a] have shown that this may be done safely. Allowance was made, however, for the fact that the specific heat of the resultant nitric acid solution is significantly less than that of pure water. The final expression developed for the heat capacity of the products for an average charge of hydrate is

$$S_F = 5.01(n_{O_2} - \phi_{HNO_3} - \phi_{F_6}) + 0.965\ (m_w + 54.06\ m_h/50.06 - 0.0068) + 0.7\ V + 0.158\ m_{F_6} + 0.0024\ cal._{15}\ deg.^{-1}$$

using the notation of Washburn. All other calculations followed the usual procedure and need not be described.

Heat of Combustion of Anhydrous Hydrazine

Purification.—Kahlbaum hydrazine hydrate was dehydrated with sodium hydroxide in an all-glass apparatus with a fractionating column by the method of Raschig[12] and the product which analyzed variously 99–100% pure was subjected to fractional crystallization in the apparatus shown in Fig. 1, in an atmosphere of dry hydrogen. In this apparatus the hydrazine could be crystallized repeatedly and melted with no exposure to moisture, oxygen or ground-glass surfaces. Since the f. p. is in the neighborhood of 2.0°, the manipulation and temperature control is much simpler than for the hydrate, which perhaps accounts for the lack of success with the latter. The material froze in the arm A to give beautiful, long, loose crystals of the anhydrous hydrazine. When about two-thirds was frozen the apparatus was turned so the residual liquid could be forced out through the platinum filter plate F and side tube B by hydrogen pressure. The solid was then melted and the process repeated. The material thus obtained analyzed to be 99.90% anhydrous hydrazine. Two samples were prepared by freezing and one was prepared by dehydration of the hydrate by barium oxide followed by fractional distillation. The procedure for filling the ampoules was the same as for the hydrate. The results of the combustion are shown in Table III. In calculating the heat capacity of the products the same

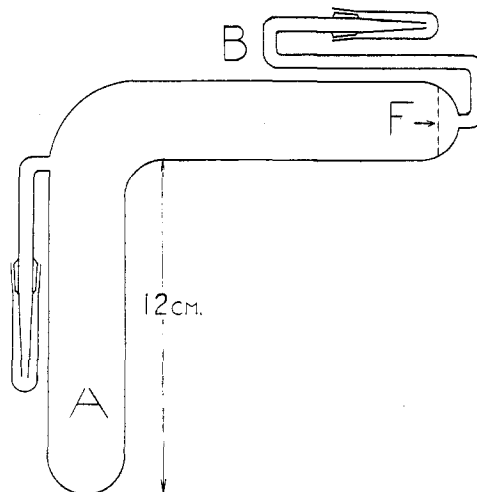(12) Raschig, *Ber.*, **43**, 1927 (1910).

Fig. 1.—Device for fractional crystallization of hydrazine in an inert atmosphere.

equation was used as for the hydrate, due allowance being made for the different amount of water produced.

TABLE III

THE ISOTHERMAL HEAT OF COMBUSTION OF HYDRAZINE AT 25°

Sample	True mass, g.	Total heat[a] evolved at 25°, cal.	Heat from HNO₃ cal.	$-\Delta U_B/m,$ cal. g.$^{-1}$	Deviation from mean
2(b)	1.28528	5,979.8	25.4	4,633.2	+0.3
2(c)	1.13373	5,274.6	24.9	4,630.7	−2.2
3(b)	1.49549	6,955.7	26.5	4,633.4	+0.5
3(d)	1.09253	5,087.4	24.1	4,634.2	+1.3
(X)				4,630.7	

Mean $-\Delta U_B/m$ for 99.90% N₂H₄ = 4,632.9   ±1.1 cal. g.$^{-1}$
Calcd. mean $-\Delta U_B/m$ for 100% N₂H₄ = 4,637.6 cal. g.$^{-1}$
Calcd. $-\Delta U_B$ = 148,635 ± 30 cal. mol^{-1}

[a] Corrected for heat of stirring, evaporation, etc., and for ignition energy.

(X) This value was obtained by A. L. H. (Thesis, ref. 9) with a different calorimeter, on hydrazine prepared by fractional distillation of the hydrate from barium oxide, but not analyzed.

Discussion of Results

The heat quantity obtained, $-\Delta U_B$, is the heat of the reaction under bomb conditions and to be useful should be converted to $-\Delta U_R$, the heat evolved by the reaction in the reference state of 1 atm. and 25°. Following the system of Washburn as closely as the difference in types of reaction permitted, this correction proved to amount to 0.003% and was disregarded, $-\Delta U_B$ and $-\Delta U_R$ being taken as equal. From the stoichiometric reaction also it may be seen that $-\Delta U_R = -\Delta H_R$ the heat of the isothermal reaction at constant pressure.

On this basis the results permit some interesting calculations.

(1) $-\Delta H^{\circ}_{298.1}$, the heat of formation of the compounds may be obtained from $-\Delta H_R$ with the use of $-68,318.1$ cal.[15] as the heat of formation of liquid water at 25°. For the hydrate is thus obtained

(a) $N_2(g) + 2H_2(g) + H_2O(liq) \longrightarrow$
$$N_2H_4 \cdot H_2O(liq) \quad \Delta H^{\circ}_{298.1} = 10,300 \text{ cal.}$$
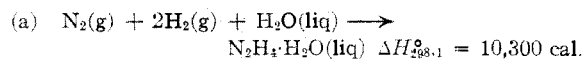
and for anhydrous hydrazine, from the combustion data

(b) $N_2(g) + 2H_2(g) \longrightarrow N_2H_4(liq) \quad \Delta H^{\circ}_{298.1} = 12,000 \text{ cal.}$

Incorporating with (a) the following quantity previously found in this Laboratory by direct measurement[1d]

$$N_2H_4(liq) + H_2O(liq) \longrightarrow N_2H_4 \cdot H_2O(liq)$$
$$\Delta H^{\circ}_{298.1} = -1800 \text{ cal.}$$
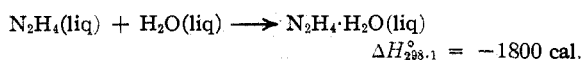
a slightly different figure is obtained for (b), i. e.

$$\Delta H^{\circ}_{298.1} = 12,100 \text{ cal.}$$

(2) In converse manner, the difference between the molal heat of combustion of the hydrate and anhydrous hydrazine should give the heat of hydration. Thus is found

$$N_2H_4(liq) + H_2O(liq) \longrightarrow N_2H_4 \cdot H_2O(liq)$$
$$\Delta H_{298.1} = -1700 \text{ cal. } (\pm 45)$$
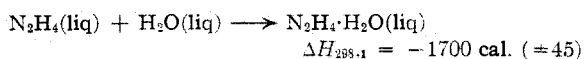
in comparison with the value -1800 cal. found by dilution measurements.[1d] Both of these quantities are obtained by differences and errors are magnified.

(3) From (1) and (2) may be obtained, by using a mean value $\Delta H^{\circ}_{298.1} = 12,050$ cal. for hydrazine, and the following quantity[1d]

$N_2H_4(liq) + Aq. \longrightarrow N_2H_4 \cdot Aq \quad \Delta H_{298.1} = -3890 \text{ cal.}$
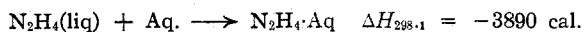
a value for the heat of formation in dilute solution;

$N_2(g) + 2H_2(g) + Aq \longrightarrow N_2H_4 \cdot Aq \quad \Delta H_{298.1} = 8160 \text{ cal.}$

(13) Rossini, Bur. Standards J. Research, 22, 407 (1939).

From earlier thermochemical work, by indirect calculation, Bichowsky and Rossini[14] give three estimates for this quantity, viz., $+3500$, $+4500$, and $+5800$ with apparent preference for the middle value. From the lack of agreement among themselves it would seem that little dependence may be placed on these earlier values.

(4) From $\Delta H^{\circ}_{298.1}$ for anhydrous hydrazine and its heat of vaporization ($\Delta H_v = +10,200$ cal. at 25°) reported recently by Hieber and Woerner,[15] $-\Delta H^{\circ}_{298.1}$ for the formation of hydrazine gas may be found. Our figures yield a value for this quantity $\Delta H^{\circ}_{298.1}$ (gas) $= 22,250$ cal., which compares interestingly with a value calculated from theoretical reasoning by Pauling,[16] of 22,100 cal. (0.96 e. v. mole^{-1}).

Summary

1. An adiabatic calorimeter for precise determinations of heats of combustion has been described briefly, along with its calibration.

2. Heats of combustion for hydrazine and hydrazine hydrate have been determined.

3. The standard heat of formation of hydrazine, liquid and gas; hydrazine hydrate, liquid and aqueous; and the heat of hydration of anhydrous hydrazine have been calculated.

(14) Bichowsky and Rossini, "The Thermochemistry of Chemical Substances," Reinhold Publishing Corp., N. Y., 1936, p. 217.
(15) Hieber and Woerner, Z. Elektrochem., 40, 252 (1934).
(16) Pauling, THIS JOURNAL, 54, 3570 (1932).