Table II gives the values calculated by means of Eq. 3 and Eq. 4 for the four salts.

From the difference in the heat of solution of the monoperchlorate in the hydrated and anhydrous forms the heat of hydration may be obtained. Using graphical means, since the molalities were slightly different in the two cases, the heat of hydration was found to be

$$N_2H_5ClO_4(s) + {}^1/_2H_2O\ (liq.) = N_2H_5ClO_4{\cdot}{}^1/_2H_2O(s) \qquad \Delta H_{298} = -1913 \pm 20\ cal.$$

From the dissociation pressure of the hydrate Christensen and Gilbert obtained[1,8]

$$N_2H_5ClO_4(s) + {}^1/_2H_2O(g) = N_2H_5ClO_4{\cdot}{}^1/_2H_2O(s) \qquad \Delta H_{298} = -6977\ cal.$$

Utilizing the heat of vaporization of water at 25° $\Delta H = +10{,}504$ cal./mole.[9]

$${}^1/_2H_2O(liq.) = {}^1/_2H_2O(g);\ \Delta H_{298} = +5252\ cal.$$

and adding the two expressions

$$N_2H_5ClO_4(s) + {}^1/_2H_2O(liq.) = N_2H_5ClO_4{\cdot}{}^1/_2H_2O(s) \qquad \Delta H_{298} = -1725\ cal.$$

This is considered reasonable agreement in view of the probable experimental error and the simplifying assumptions made in applying the Clausius–Clapeyron equation to the dissociation of the salt hydrate.

The authors wish to express their indebtedness to the National Research Council and to the General Research Council of this College for grants which made this work possible.

Summary

New data are reported on the heats of solution in water at 25° of hydrazonium dichloride, monochloride and monobromide from 0.1 to 1.0 molal, of the perchlorate hemihydrate from 0.1 to 0.6 molal, and of the anhydrous perchlorate at 0.1 molal.

From these are computed values of the partial molal heat of solution of the solvent and the solute.

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[8] Attention should be called to the fact that the heats of dehydration calculated by Christensen and Gilbert are reported as calories *per mole of water vapor* formed. For a salt containing one-half molecule of water like the perchlorate the reported value should be divided by two, while for the dibromide with two molecules of water the reported value should be multiplied by two to obtain values *per mole of salt.*

[9] Osborne, Stimson, Fiock and Ginnings, *Bur. Standards J. Research*, **10**, 155 (1933).

[CONTRIBUTION FROM THE WILLIAM G. KERCKHOFF LABORATORIES OF THE BIOLOGICAL SCIENCES, CALIFORNIA INSTITUTE OF TECHNOLOGY]

Thermal Data. II. The Heats of Combustion of *l*-Cysteine, of *l*-Cystine, β-Thiolactic Acid and β,β'-Dithiodilactic Acid

BY HUGH M. HUFFMAN AND EMORY L. ELLIS

In determinations of the free energies of organic compounds by means of the third law of thermodynamics and the fundamental thermodynamic equation $\Delta F = \Delta H - T\Delta S$, accurate values for the heats of combustion are required. At present these values are often unavailable or unreliable. We have therefore undertaken the task of determining the required data with relatively high accuracy.

In this paper we present a description of the method and apparatus used, data on its calibration, data on the auxiliary substances required, and the values of the heats of combustion of four compounds.

Method and Apparatus

Since all of the compounds we expect to burn are either solid or liquid, we have chosen the "bomb calorimeter" method. Two methods are in common use with a calorimeter of this type, the "ordinary" and the "adiabatic." We have adopted the first in which the rise in temperature of the calorimeter is observed while that of the jacket is kept constant. The two methods have been shown to have the same accuracy.[1]

The calorimeter system was essentially that of Dickinson.[1a] It was so arranged that the calorimeter was completely surrounded by a well-stirred water-bath kept constant to within ±0.002°. The water in the calorimeter was stirred by a propeller driven by a constant speed motor at 380 r. p. m. This rate was found to be adequate and introduced a not too large amount of mechanical energy. To prevent evaporation from the calorimeter, the stirrer, thermometer, and electrical leads were brought in through water-tight seals. To minimize transfer of energy between the calorimeter and the room all external leads to the calorimeter were first brought into good thermal contact with the jacket.

A "Parr bomb" having a capacity of 380 ml. was used. This was so modified that it could be made gas tight by means of a gold washer. The standard illium electrodes and crucible supports were replaced with platinum elec-

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[1] (a) Dickinson, *Bull. Bureau of Standards*, **11**, 243 (1915); (b) Schläpfer and Fioroni, *Helv. Chim. Acta*, **6**, 725 (1923); (c) White, "The Modern Calorimeter," The Chemical Catalog Co., N. Y., 1928.

trodes equipped with threaded binding posts for making the electrical connections to the fuse wire.[2] The material to be burned was placed in a platinum crucible.

The temperature measuring system consisted of a platinum resistance thermometer, calibrated by the Bureau of Standards, a "Mueller Thermometer Bridge" and a high sensitivity galvanometer all supplied by the Leeds and Northrup Co. The sensitivity of the system was such that 0.00001 ohm (0.0001°) was equivalent to about 0.5 mm. on the galvanometer scale. The galvanometer was used as a null point instrument. The times at which a predetermined series of resistances were reached were recorded on a drum type chronograph with a precision of 0.2 second.

To fire the charge we have used one of two methods. The first consisted of supplying electrical energy to a piece of No. 38 iron wire of known weight and resistance until it was ignited. The second consisted of supplying electrical energy to a piece of No. 34 platinum wire of fixed length, for a fixed time, the heated wire igniting a piece of filter paper which in turn ignited the charge. The magnitude and constancy of the electrical energy required for firing were determined in a series of measurements in which the current, voltage and time were measured by means of an oscillograph. The conditions of voltage, resistance and time have been so standardized that the iron wire requires 0.6 ± 0.2 calorie and the platinum wire 1.4 ± 0.2 calories for ignition.

The mass of the calorimeter and water was determined to 0.1 g. or better by means of a large capacity balance having a sensitivity of 0.01 g. The mass of the charge was determined to 0.0001 g. by means of an analytical balance.

The bomb was usually evacuated to a pressure of a few mm. and then filled with commercial oxygen to a pressure of 30 atm. at a temperature of 21 ± 1°.

Calibration of the Calorimeter.—The energy equivalent of the calorimeter was determined by burning benzoic acid, sucrose and naphthalene supplied by the Bureau of Standards. Benzoic acid has been chosen as the primary standard for combustion calorimetry and the value selected for its isothermal heat of combustion at 20° is 6319.0 $\text{cal.}_{15°}$ per gram *in vacuo*.[3] From this value and the equations of Washburn[4] for the temperature coefficient of the bomb reaction we have calculated the heat of combustion of benzoic acid at 25° to be 6317,8 $\text{cal.}_{15°}$.

Since the commercial oxygen used always contained a small amount of nitrogen, small quantities of nitrogen oxides were formed. Colorimetric tests[5] were made on several combustions selected at random and the amount of nitrous acid formed was found to be negligible. The nitric acid formed was determined by titration with $N/14{,}55$ sodium hydroxide using brom cresol green as the indicator. The amount usually present necessitated a correction of about 1 $\text{cal.}_{15°}$ on the basis of an evolution of 14,550 $\text{cal.}_{15°}$[3] (p. 5) per mole of aqueous nitric acid formed.

The corrected temperature rise was calculated by the method of Dickinson[1a] (p. 229). From the temperature rise, the sum of the energies supplied, the heat capacities of the initial and final contents of the bomb, the energy equivalent of the calorimeter at 25° was calculated. This value is for the system less the contents of the bomb.

In Table I are presented some values of the energy equivalent of the calorimeter as determined from the combustion of benzoic acid. These determinations represent only a fraction of the total number of combustions which were made with benzoic acid under varying conditions. They will serve to illustrate the precision of our measurements, since this series is in excellent agreement with the other groups.[6]

The results of our combustions on sucrose and naphthalene are given in Table II. The naphthalene is not guaranteed as to purity by the Bureau of Standards; however, its heat of combustion is given as 9614 $\text{cal.}_{20°}$. The sucrose is of high purity and the heat of combustion given by the Bureau is 3949 $\text{cal.}_{20°}$. These values when converted into $\text{cal.}_{15°}$ per g. true mass by multiplying the factors 0.9991/1.0009 and 0.9991/1.0006 become 9596.8 and 3,943.0 $\text{cal.}_{15°}$, respectively.

As a better means of comparing our results with the values given by the Bureau of Standards we include in Table II the ratios between these three substances as obtained by the authors and the Bureau of Standards. It should be noted that the temperatures for the combustion of sucrose and naphthalene are not given. We have assumed them to be at 20° and have recalculated them to 25° to obtain the given ratios.[7]

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[2] In our experience we found that the usual wrapped connection was subject to variable contact resistance, thereby greatly affecting the amount of electrical energy required for combustion.

[3] First Report of the Permanent Thermochemical Commission, 1933, page 2.

[4] Washburn, *Bur. Standards J. Res.*, **10**, 551 (1933).

[5] Treadwell-Hall, "Analytical Chemistry," John Wiley & Sons, New York, p. 306.

[6] We were not always able to obtain complete combustion of benzoic acid in our bomb. However, in those cases where carbon appeared it was always in such small amounts as to be unweighable on our balance. In consequence we feel justified in stating that the effect of incomplete combustion was within the experimental error of our measurements.

[7] We should like to state that sucrose and naphthalene are not highly desirable substances for calibrations. Naphthalene has a rather high vapor pressure, necessitating a correction for loss of material by vaporization. Sucrose is hygroscopic and furthermore is not readily ignited without the use of an auxiliary substance.

TABLE I

CALIBRATION WITH BENZOIC ACID

Comb.	Obs. rise, ohms	Net corr., ohms	ΔR corr. rise, ohms	Δt, corr. rise, °C.	t_m, mean temp.	True mass benzoic acid	Cal. from b. a.	Cal. from Fe + HNO_3 + EIt	Energy equiv. g. cal.$_{15°}$ per °C.
24A(c)[a]	0.20200	0.00004	0.20204	2.0048	25.0	1.00380	6341.8	10.6	3164.5
25A	.23550	.00025	.23575	2.3393	25.0	1.17145	7401.0	11.2	3164.4
26A(c)[a]	.21770	− .00003	.21767	2.1599	24.9	1.08160	6833.3	11.7	3165.1
27A(c)[a]	.23320	.00034	.23354	2.3174	25.0	1.16055	7332.1	11.3	3164.6
28A(c)[a]	.20330	.00000	.20330	2.0174	25.0	1.00755	6365.5	27.1[b]	3164.6
29A	.20230	.00000	.20230	2.0074	25.0	1.00470	6347.5	12.6	3164.5
30A	.20640	.00033	.20673	2.0515	25.1	1.02430	6471.3	30.3[b]	3165.3
								Mean value	3164.7

Extreme variation from the mean 0.6 cal. or 0.02%. Mean variation from the mean 0.3 cal. or 0.01%.

[a] (c) small amounts of carbon produced. [b] Ignition with platinum wire and filter paper.

TABLE II

THE COMBUSTION OF SUCROSE AND NAPHTHALENE AT 25°

Substance burned	Sucrose	Naphth.
Heat of comb. cal.$_{15°}$/g. true mass	3939.6	9595.0
Number of comb.	4	6
Mean variation from the mean	0.7	1.1
Extreme variation from the mean	1.1	2.0
Difference between extremes	1.8	3.4
Ratio to b. a. (H. and E.)	1.6037	1.5187
Ratio to b. a. (B. S.)	1.6031	1.5188
Temp. coeff. (cal./g. degree)	−0.31	−0.33

From the above results we believe that we are justified in assigning to our calorimeter with 2785.4 g. of water the value of 3164.7 ± 0.3 cal.$_{15°}$ for the energy equivalent per degree C. at 25°.

Auxiliary Substances.—It is often necessary to use an auxiliary substance with difficultly combustible materials. For this purpose we have selected a high grade vacuum pump oil supplied by the Central Scientific Co. From analysis this oil was found to have the empirical composition $CH_{1.8}$ and to contain about 0.2% sulfur. As a result of five combustions we have found this oil to have a combustion value of 10,843 ± 2 cal.$_{15°}$ per gram in air. In addition to the oil we have used filter paper as a fuse in our platinum wire ignition. The paper was found to be hygroscopic in consequence of which the moisture content would vary from day to day depending on the humidity. The supply of paper was kept at constant humidity. Its heat of combustion under these conditions was found to be 3961 ± 1 cal.$_{15°}$ per gram in air. Where iron wire was taken as the fuse the value 1590 cal.$_{15°}$ per gram was used in applying the correction.

The Heats of Combustion of Four Sulfur Containing Compounds

The combustion of sulfur containing compounds involves a procedure differing in several details from that of CHO compounds. Complete combustion of sulfur to SO_3 takes place only in the presence of a relatively large amount of nitrogen. Hence the bomb was not evacuated before filling with oxygen. The bomb was always filled to a pressure of 30 atmospheres which corresponded to an oxygen content of 0.47 mole. Furthermore, due to the large heat of dilution of sulfuric acid, an accurate knowledge of its concentration was required. It was found that when water was introduced into the bomb before a combustion there was a large difference in the concentration of the solution in the bottom of the bomb and the condensate on the walls. For this reason no water was introduced into the bomb.

In all of these combustions we have used the platinum wire method of firing and except in the case of β-thiolactic acid it was necessary to use oil as an auxiliary substance. The materials were dried for several days over phosphorus pentoxide and when solid were compressed into pellets for burning.

In addition to the usual products of combustion small amounts of nitric acid and nitrous acid were formed. In order that a correction might be applied for these substances it was necessary to determine their amounts. The gas from the bomb was passed through a scrubbing column containing a known amount of standard sodium hydroxide solution which absorbed the acids. The amount of acid absorbed was determined by titrating the excess base with standard hydrochloric acid and the amount of nitrous acid by the colorimetric method given before.[5] Since the amounts of sulfur acids coming over in the gas phase were found to be negligible, the amount of nitric acid could be obtained by difference. After the bomb pressure had been reduced to atmospheric, the contents were washed carefully into a volumetric flask and analyses performed on aliquots for total acidity, sulfuric acid and nitrous acid. The amount of nitric acid was obtained by difference.

Corrections.—A value was calculated for the isothermal bomb process at 25° from the corrected temperature rise, the heat capacities of the calorimeter and bomb contents before and after combustion. These values were then corrected in the usual manner for the heat effects due to oil, cellulose, nitric acid, nitrous acid and electrical energy. The quantities thus obtained were not comparable since in each case the final concentration of sulfuric acid was different. To bring the values to a comparable basis a correction was applied for the calculated amount of sulfuric acid formed at the concentration maintaining at the end of the combustion. By correcting in this manner we were able to calculate the value of the hypothetical combustion in which elemental sulfur was formed. This is the value given in the last row of Tables IV, V, VI and VII.

Correction for Sulfuric Acid.—Using the value given by Roth, Grau and Meichsner[8] of 125,790 $\text{cal.}_{15°}$, at constant pressure and at 20° for the reaction

$$S_{(c,rh)} + 3/2O_{2(g)} + H_2O_{(liq)} = H_2SO_4{\cdot}0H_2O_{(liq)}$$

and the data of Brönsted[9] for the heat of dilution of concentrated solutions we have calculated the values for the heat of formation of aqueous H_2SO_4 from S, O_2 and H_2O at several concentrations. These values are given in Table III which contains in addition values for the constant volume process. A plot was made from these data and the values for a particular concentration were read from this curve.

TABLE III

THE TOTAL HEAT OF FORMATION OF $H_2SO_{4(aq)}$ AT ABOUT 20°

$$S_{(rh)} + 3/2O_2 + n\ H_2O_{(liq)} = H_2SO_4{\cdot}(n-1)(H_2O)$$

$(n-1)$ moles H_2O/ moles H_2SO_4	Heat of dilution	$-\Delta H$ Heat of formation constant pressure	$-\Delta U$ calcd. Heat of formation constant volume
0.0000	0	125,790	124,900
1.0000	6,730	132,520	131,630
1.2222	7,680	133,740	132,850
1.5000	8,630	134,420	133,530
1.8571	9,650	135,440	134,550
2.3333	10,710	136,500	135,610
3.0000	11,880	137,670	136,780
4.0000	12,940	138,730	137,840

Vacuum Correction.—Since we were unable to find density values for any of these compounds, we made rough estimates of these values from the mass and dimensions of the pellets used. The uncertainty introduced by these crude determinations is at the most only 0.01 or 0.02%.

Correction to Constant Pressure.—Because no method for correcting the combustion values for sulfur-containing compounds to the standard state proposed by Washburn[4] (p. 525) has been given by the thermochemical commission, our final values are given for the bomb process at 25° both at constant volume and at constant pressure.

β-Thiolactic Acid.—This material was prepared according to the method of Biilmann[10] from β-iodopropionic acid and potassium ethyl xanthate. The resulting β-thiolactic acid was purified by repeated vacuum distillation in a modified Hickman[11] molecular still. The product thus obtained was water white and had an apparent melting point of 16.5° (Biilmann 16.8°). This material was used in specific heat measurements (see following paper) and was found to show a marked amount of premelting and no sharp melting point. The material which had been used for heat capacity measurements was dried in contact with calcium chloride and again fractionated in the molecular still with the final retention of the middle two-thirds. Combustions 3, 4 and 5 were made on this material. The end-portions from the purification of the above materials were also collected, dried and subjected to

TABLE IV

THE COMBUSTION OF β-THIOLACTIC ACID ($C_3H_6O_2S$, MOL. WT. = 106.11)

Substance *in vacuo*, g.	1.6604	1.5099	1.5185
Oil *in vacuo*, g.	.....	.....	.....
Total calories to calorimeter	8010.1	7276.0	7326.7
Total correction in calories	17.2	18.5	19.9
Moles H_2SO_4 formed	0.01565	0.01423	0.01431
$(n-1)$ = (moles H_2O/ moles H_2SO_4)	2.009	2.010	2.011
Calories/gram (reaction to form $S_{(c,rh)}$)	3542.3	3535.1	3540.4

Mean value, 3537.8.

Mean deviation from the mean, 3.6.

Extreme deviation from the mean, 4.5.

For the reaction

$$C_3H_6O_2S_{(liq)} + 5O_{2(g)} = 3CO_{2(g)} + H_2SO_4{\cdot}2H_2O_{(liq.)}$$

Molal heat of combn. at constant vol., 510,300 ± 800 cal.

Molal heat of combn. at constant press., 511,500 ± 800 cal.

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[8] Roth, Grau and Meichsner, *Z. anorg. allgem. Chem.*, **193**, 161 (1930).

[9] Brönsted, *Z. physik. Chem.*, **68**, 693 (1910).

[10] Biilmann, *Ann.*, **339**, 351 (1905); **348**, 120 (1906).

[11] Hickman, *J. Franklin Inst.*, **213**, 119 (1932).

several fractionations. Combustion 2 was made on the resulting middle portion of this material. An additional combustion (not published) was made on the end-portions of this material and gave a value about 1% higher. Evidently the impurity is such as to lead to high values for the heat of combustion. We feel that this β-thiolactic acid was undoubtedly the least pure of any of the four compounds. Ash content was found to be negligible. The results of three of the combustions on this substance are given in Table IV.

β,β′-Dithiodilactic Acid.—This material was prepared from β-thiolactic acid by oxidizing with the theoretical quantity of iodine. The product was purified by repeated crystallization from water. The melting point by the capillary method was 155–156° with decomposition. Titration with sodium hydroxide using phenolphthalein for the indicator in the hot solution required 0.3% more (average of two determinations) than the theoretical amount. The ash content was inappreciable. The results of three combustions of this material are given in Table V.

TABLE V

THE COMBUSTION OF β,β′-DITHIODILACTIC ACID ($C_6H_{10}O_4S_2$, MOL. WT. 210.20)

Substance *in vacuo*, g.	1.2503	1.2183	1.2317
Oil *in vacuo*, g.	0.0809	0.0742	0.1040
Total calories to calorimeter	6514.7	6306.0	6691.4
Total correction in calories	896.8	829.7	1148.6
Moles H_2SO_4 formed	0.01190	0.01160	0.01173
$(n-1)$ = (moles H_2O/moles H_2SO_4)	1.996	1.975	2.144
Calories/gram (reaction to form $S_{(c,rh)}$)	3209.3	3211.3	3212.3

Mean value = 3210.9 $cal_{15°}$ per gram.

Mean deviation from mean, 1.1.

Extreme deviation from the mean, 1.6.

For the reaction

$$C_6H_{10}O_4S_{2(c)} + 19/2O_{2(g)} = 6CO_{2(g)} + 2(H_2SO_4{\cdot}2H_2O)_{(liq.)} - H_2O_{(liq.)}$$

Molal heat of combn. at constant vol., 944,730 ± 900 cal.

Molal heat of combn. at constant press., 946,800 ± 900 cal.

***l*-Cysteine.**—This material was prepared from *l*-cysteine hydrochloride (Hoffman–La Roche) according to the procedure of Du Vigneaud, Audrieth and Loring[12] by dissolving the hydrochloride in absolute alcohol and precipitating *l*-cysteine by exact neutralization of the hydrogen chloride with alcoholic ammonia solution. The product was perfectly white. The average result of two micro-Kjeldahl analyses was *nitrogen found* 11.63%, *nitrogen calculated* 11.58%. The results of three combustions on this material are given in Table VI.

TABLE VI

COMBUSTION OF *l*-CYSTEINE ($C_3H_7O_2NS$, MOL. WT. 121.12)

Substance *in vacuo*, g.	1.3388	1.1988	1.4175
Oil *in vacuo*, g.	0.1446	0.1661	0.1376
Total calories to calorimeter	7459.9	7085.6	7731.8
Total correction in calories	1586.3	1822.7	1513.7
Moles H_2SO_4 formed	0.01106	0.00991	0.01171
$(n-1)$ = (moles H_2O/moles H_2SO_4)	3.441	3.703	3.346
Calories/gram (reaction to form $S_{(c,rh)}$)	3252.7	3252.8	3253.2

Mean value, 3252.9.

Mean deviation from the mean, 0.2.

Extreme deviation from the mean, 0.3.

For the reaction

$$C_3H_7O_2NS_{(c)} + 21/4O_{2(g)} = 3CO_{2(g)} + 1/2N_{2(g)} + (H_2SO_4{\cdot}3.5H_2O)_{(liq.)} - H_2O_{(liq.)}$$

Molal heat of combn. at constant vol., 531,380 ± 500 cal.

Molal heat of combn. at constant press., 532,420 ± 500 cal.

***l*-Cystine.**—A high grade (Hoffman–LaRoche) *l*-cystine was subjected to several recrystallizations from water. The results of two micro-Kjeldahl analyses were *nitrogen found* 11.67%, *nitrogen calculated* 11.66%. In a formol titration 0.2% less than the theoretical amount of sodium hydroxide was required. The results of three of the combustions on this material are given in Table VII.

TABLE VII

THE COMBUSTION OF *l*-CYSTINE ($C_6H_{12}O_4N_2S_2$, MOL. WT. 240.23)

Substance *in vacuo*, g.	1.2757	1.2216	1.8558
Oil *in vacuo*, g.	0.0645	0.1057	0.1086
Total calories to calorimeter	6004.7	6235.6	8891.9
Total correction in calories	718.8	1169.3	1196.3
Moles H_2SO_4 formed	0.01062	0.01017	0.01545
$(n-1)$ = (moles H_2O/moles H_2SO_4)	2.448	2.759	2.511
Calories/gram (reaction to form $S_{(c,rh)}$)	3012.6	3011.8	3014.8

Mean value, 3012.9 cal.

Mean deviation from the mean, 0.6 cal.

Extreme deviation from the mean, 1.1 cal.

For the reaction

$$C_6H_{12}O_4N_2S_{2(c)} + 10O_{2(g)} = 6CO_{2(g)} + N_{2(g)} + 2(H_2SO_4.2.7H_2O)_{(liq.)} - 1.4H_2O_{(liq.)}$$

Molal heat of combn. at constant vol., 996,390 ± 900 cal.

Molal heat of combn. at constant press., 998,170 ± 900 cal.

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(12) Du Vigneaud, Audrieth and Loring, THIS JOURNAL, **52**, 4500 (1930).

Discussion of the Results

Except in the case of β-thiolactic acid the precision of our measurements is very high. There is always an uncertainty due to impurities in the compounds, which we were unable to check by further purification on account of the small amounts of the material available. For this reason in estimating the limits of accuracy of our results as given in the tables we have not used any particular formula but have selected limits which we believe are great enough to include error which might be due to impurities.

There are no values in the literature for these compounds which may be compared with ours. Emory and Benedict[13] have burned *l*-cystine. These authors do not state what the end-products of their combustion were. Kharasch[14] in his compilation of combustion data states that the end-product was gaseous sulfur dioxide. However, Benedict[15] feels that sulfur dioxide was not formed. At any rate the value given by Kharasch is of no use for thermodynamic calculations.

Acknowledgment.—We wish to express our thanks to the National Research Council for a grant in aid which in part made possible the construction of our calorimetric system.

Summary

1. A brief description of a precise calorimetric system for measuring heats of combustion, and data on its calibration have been presented.

2. Values for the heats of combustion of β-thiolactic acid, β,β'-dithiodilactic acid, *l*-cysteine, and *l*-cystine are given, for the constant pressure process at 25°.

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[13] Emory and Benedict, *Am. J. Physiology*, **28**, 311 (1911).

[14] Kharasch, *Bur. Standards J. Res.*, **2**, 421 (1929).

[15] Private communication.

PASADENA, CALIFORNIA RECEIVED SEPTEMBER 17, 1934

[CONTRIBUTION FROM THE WILLIAM G. KERCKHOFF LABORATORIES OF THE BIOLOGICAL SCIENCES, CALIFORNIA INSTITUTE OF TECHNOLOGY]

Thermal Data. III. The Heat Capacities, Entropies and Free Energies of Four Organic Compounds Containing Sulfur

BY HUGH M. HUFFMAN AND EMORY L. ELLIS

In continuation of our general plan of collecting thermal data on physiologically important organic compounds,[1] we present in this paper the low temperature specific heat data, obtained in the usual manner,[1] for the four compounds: β-thiolactic acid, β,β'-dithiodilactic acid, *l*-cysteine and *l*-cystine. These data have been used to calculate the entropies, from which values and the heats of formation the free energies of formation have been computed.

Materials

β-Thiolactic Acid.—This material was prepared in the manner described in the preceding paper.[2] It was not particularly pure, as premelting could be detected at about 70° below its melting point.

β,β'-Dithiodilactic Acid.—This material was prepared from β-thiolactic acid by oxidation with iodine and the resulting compound purified by crystallizing several times from water.

***l*-Cysteine.**—This compound was prepared from cysteine hydrochloride (Hoffman-La Roche) according to the procedure of Du Vigneaud, Audrieth, and Loring.[3]

***l*-Cystine.**—A commercial product (Hoffman-La Roche) was found to be sufficiently pure.

The specific heat data in terms of the 15° cal. and with all weights reduced to a vacuum basis appear in Table I.

Discussion

Entropies of the Compounds.—From the data in Table I we have calculated the entropies at 298.1°K. in the usual manner using the extrapolation formula of Kelley, Parks and Huffman[4] for the increment between 0 and 90°K. and graphical integration between 90 and 298.1°K. In the case of β-thiolactic acid the marked rise in the specific heat of the crystals as the melting point was approached was attributed to premelting, and the heat absorbed in this region in excess

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[1] Huffman and Borsook, THIS JOURNAL, **54**, 4297 (1932).

[2] Huffman and Ellis, *ibid.*, **57**, 41 (1935).

[3] Du Vigneaud, Audrieth and Loring, *ibid.*, **52**, 4500 (1930).

[4] Kelley, Parks and Huffman, *J. Phys. Chem.*, **33**, 1802 (1929).