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.

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[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).

TABLE I

SPECIFIC HEATS PER GRAM OF SUBSTANCE

T, °K.	C_p	T, °K.	C_p	T, °K.	C_p
		β-Thiolactic Acid, crystals			
85.3	0.131	149.4	0.198	203.7	0.256
88.9	.136	164.7	.214	212.3	.266
93.9	.141	167.3	.217	215.1	.269
100.3	.148	179.7	.230	220.4	.275
107.9	.156	187.0	.238	228.5	.285[a]
119.3	.168	194.9	.246	236.2	.295[a]
134.4	.182	200.0	.254	245.2	.312[a]
		Liquid			
299.8	0.456	304.5	0.460	309.9	0.462
		β,β'-Dithiodilactic acid, crystals			
84.9	0.110	144.6	0.159	277.1	0.257
89.2	.114	159.0	.169	282.0	.261
94.1	.118	180.6	.186	290.1	.268
99.6	.123	188.5	.191	290.2	.267
105.3	.128	200.0	.200	296.6	.272
111.7	.133	220.0	.215	296.8	.272
120.0	.140	240.1	.230	305.1	.278
129.7	.148	260.1	.245		
		l-Cysteine, crystals			
85.1	0.114	149.6	0.177	260.7	0.280
90.4	.121	165.2	.191	275.6	.296
97.2	.128	179.8	.203	282.8	.304
105.9	.137	199.9	.222	290.0	.312
119.3	.149	220.4	.240	297.6	.320
134.5	.163	240.2	.259		
		l-Cystine, crystals			
85.6	0.0968	150.0	0.156	260.3	0.238
91.3	.103	164.7	.167	276.0	.250
97.1	.109	179.7	.179	282.8	.255
105.8	.118	199.9	.195	290.0	.261
119.3	.130	220.0	.209	297.3	.267
135.0	.143	240.3	.224		

[a] These values include an appreciable amount of premelting.

of that obtained by extrapolating the specific heat data at lower temperatures was added to the heat absorbed at the melting point. The mean value of two fusions was 38,22 $\text{cal.}_{15°}$ per g. The entropy of fusion was calculated from this fusion value as though the energy had all been absorbed at the melting point. The entropies of the compounds appear in Table II.

TABLE II

ENTROPIES OF THE COMPOUNDS PER MOLE

Compound	$C_3H_6O_2S_{(liq.)}$	$C_6H_{10}O_4S_{2(c)}$	$C_3H_7O_2NS_{(c)}$	$C_6H_{12}O_4N_2S_{2(c)}$
Crystals (0–90°K.)	11.88	20.18	11.71	18.99
Crystals (above 90°K.)	27.86	45.28	28.85	49.51
Fusion	13.90	...	...	...
Liquid	1.04	...	...	...
$S_{298.1}$	54.7	65.5	40.6	68.5

In the first paper of this series[1] we stated that there was no entropy effect on substituting an $-NH_2$ group for a hydrogen atom. We have here a further test of this rule. In the case of β-thiolactic acid and l-cysteine, when β-thiolactic acid is corrected to the hypothetical solid state at 298°K., the entropy is about 40.6 and the change for substituting an amino group is zero. In the case of β,β'-dithiodilactic acid and l-cystine there is an increase of 1.5 E. U. per amino group. It thus appears that though the entropy involved in such a substitution may not be zero it is at any rate quite small. We may also test the effect of substitution of an $-SH$ group for a hydrogen in the case of l-alanine and l-cystine; here we find alanine to be 31.6[1] and cystine to be 40.6, an increase of 9 E. U. We may go further and predict from the method of Parks and Huffman[5] that propionic acid would have an entropy of 46.0 E. U. per mole, which is 8.7 E. U. less than that found for β-thiolactic acid. It thus appears that the effect of an $-SH$ substitution on the end of a hydrocarbon chain involves an increase in entropy of about 9 E. U.

The Free Energies.—We have also calculated the free energies of these four compounds from the fundamental thermodynamic equation $\Delta F = \Delta H - T\Delta S$. The essential data are given in Table III. The heats of combustion of these four compounds are those determined by us in the preceding paper.[2] The heats of formation have been calculated with the values 68,310 and 94,240, respectively,[5] for the combustion values of hydrogen and graphitic carbon. The energy due to the formation of sulfuric acid was corrected for by using the data of Roth and Meichener, and Brönsted as tabulated in our preceding paper.[2] The values of ΔS_{298}, the entropy of formation, were obtained by subtracting from the S_{298} of the compounds the values of the elements contained therein. For the entropies of the

TABLE III

THERMAL DATA AT 298.1°K.

The 15° Cal. is used throughout and all weights are reduced to vacuum

	$C_3H_6O_2S$	$C_6H_{10}O_4S_2$	$C_3H_7O_2NS$	$C_6H_{12}O_4N_2S_2$
Heat of comb. at const. π.	511,500	946,800	532,420	998,170
$\Delta H^\circ_{298.1}$	−111,940	−231,770	−127,660	−251,520
$\Delta S_{298.1}$ (E. U.)	− 99.7	−212.0	−152.3	−286.1
$\Delta F^\circ_{298.1}$	− 82,220	−168,570	− 82,260	−166,230

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(5) Parks and Huffman, "The Free Energies of Some Organic Compounds," The Chemical Catalog Co., New York, 1932, p. 209.

elements we have used 1.36,[6] 31.23, 45.78, 49.03, and 7.6 E. U.[7] per mole, respectively, for carbon, hydrogen, nitrogen, oxygen and sulfur. With the exception for carbon and sulfur, the values are the same as in our first paper.[1]

Except in the case of β-thiolactic acid, we believe the error involved in the $T\Delta S$ term does not exceed ±300 calories. In this particular case this uncertainty is increased to ±450 calories. The absolute accuracy of the free energies of these compounds is still restricted by uncertainties in the combustion values and the heats of formation of the auxiliary substances used. Rossini[8] has recently pointed out that the accepted value for the heat of formation of carbon dioxide is uncertain to the extent of 100 calories. This alone would introduce an uncertainty of 1200 calories in the free energy of the largest molecules we have considered. Fortunately, for intercomparison, uncertainties of this type will tend to cancel.

Summary

1. The heat capacities of four sulfur containing organic compounds have been measured over the temperature range 90 to 298°K.

2. The entropies of these four compounds have been calculated from the heat capacity data.

3. The standard free energies of formation of these compounds have been calculated.

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(6) Jacobs and Parks, THIS JOURNAL, **56**, 1513 (1934).

(7) Kelley, *Bur. Mines, Bull.*, No. 350, p. 59, 1932.

(8) Rossini, *Bur. Standards J. Research*, **13**, 21 (1934).

[CONTRIBUTION FROM THE DEPARTMENT OF ENGINEERING RESEARCH, UNIVERSITY OF MICHIGAN]

A New Approximate Equation for Heat Capacities at High Temperatures

BY JOHN CHIPMAN AND M. G. FONTANA

The classical form of expression for the heat capacity of a substance at elevated temperature is

$$C_p = a + bT + cT^2 + dT^3 + \dots \qquad (1)$$

The failure of equations of this type to represent actual heat content data has been pointed out by Maier and Kelley,[1] who proposed the expression

$$C_p = a + bT - cT^{-2} \qquad (2)$$

This same equation has been arrived at from theoretical considerations by Bronson, Chisholm and Dockerty,[2] who have shown that it is applicable to certain metals in the range 0 to 500°.

For purposes of practical thermodynamic calculations it is desirable to limit the number of terms to three and from this viewpoint each of the above expressions may be regarded as a special case of a more general formula

$$C_p = a + bT + cT^n \qquad (3)$$

The success of this expression in reproducing experimental data depends upon the value of n employed. It is desirable that a single value of n be selected which will be applicable, at least approximately, to a wide variety of substances and it is essential that the equation be readily integrated for expressing heat content and free energy.

If we consider the best available data on the heat capacities of solid substances at temperatures ranging from 0° upward, we find a marked curvature in the lower ranges and a nearly linear relationship at the higher temperatures. Values of n greater than unity are incompatible with this experimental fact. On the other hand, Equation 2 is in many instances far too strongly curved at the lower temperatures to afford an accurate representation of the data.

A comparison of equations employing values of n of $^1/_2$, $-^1/_2$, -1, and -2 has indicated that for the majority of substances for which accurate data are available an expression in which $n = -^1/_2$ conforms most closely to the experimental points. Accordingly we propose the equation

$$C_p = a + bT + cT^{-1/2} \qquad (4)$$

and the corresponding expressions for heat content and free energy

$$H = H_0 + aT + {}^1/_2bT^2 + 2cT^{1/2} \qquad (5)$$

$$F = H_0 - aT\ln T - {}^1/_2bT^2 + 4cT^{1/2} + IT \qquad (6)$$

Some of the data which were used in arriving at the selected value of n are discussed below with special reference to the choice between Equations 2 and 4. Among the most accurate of all high temperature data are those of W. P. White[3]

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(1) Maier and Kelley, THIS JOURNAL, **54**, 3243 (1932).

(2) Bronson, Chisholm and Dockerty, *Can. J. Research*, **8**, 282 (1933).

(3) White, *Am. J. Sci.*, [4] **28**, 334 (1909); **47**, 1 (1919).