bustion of the active and inactive forms of alanine and leucine and in both cases we find that the active form has the higher value and in these two cases values which are the same within the experimental error, namely, 0.68 and 0.77 kcal., respectively. This result may also have been expected, as it is well known that the properties of the inactive form are often markedly different from those of the active form.

Summary

1. The experimental values of the isothermal heats of combustion at constant volume and at 25° of seven amino acids are given.

2. The methods of preparation and purification and photomicrographs of the crystalline condition of these amino acids are given.

3. These new values for the heats of combustion have been compared with older values when available.

4. In two cases the optically active form has been found to have a higher heat of combustion than the inactive form.

PASADENA, CALIF. RECEIVED AUGUST 13, 1937

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

Thermal Data. VIII. The Heat Capacities, Entropies and Free Energies of Some Amino Acids

BY HUGH M. HUFFMAN AND EMORY L. ELLIS

In the preceding paper[1] of this series we have presented accurate combustion data on seven amino acids. In this paper we present the low temperature heat capacity data of four amino acids from the above-mentioned group. These data have been used to calculate the entropies of the compounds, and the entropy data in conjunction with the corresponding heats of formation to calculate the free energies of the amino acids. In one case we have determined experimentally that the entropies of the active and inactive forms are the same. We have made further use of this observation in calculating the free energies of two substances whose heat capacities were not measured.

Experimental

In principal the method of Nernst was employed with an aneroid calorimeter to determine the "true" specific heats. The details of the method have been described elsewhere[2] so that only a brief account will be given.

In brief it consists in supplying a measured amount of heat to a gold calorimeter containing the substance under investigation. To ensure rapid thermal equilibrium the substance is pressed into dense pellets, about 2 mm. thick, and spaced along the centrally located thermocouple well by means of thin gold disks which are in good thermal contact with the walls of the calorimeter. The electrical measurements of current and voltage are made on a "White" double potentiometer by the proper use of accurately calibrated resistances. Time measurements are made by means of a calibrated stop watch. The temperature measurements are made by means of the White potentiometer in conjunction with a single-junction copper–constantan thermocouple. This couple is periodically standardized against one of the couples calibrated in the investigation of Giauque, Johnston and Kelley.[3]

Materials.—The *dl*-alanine was a commercial product obtained from Pfanstiehl, and was subjected to several fractional crystallizations from water. The nitrogen determined by the Kjeldahl method was the theoretical. The ash content was of the order of 0.03 to 0.04%. This material crystallized in the form of long narrow rods.

The *dl*-leucine used in this investigation was prepared in the Carlsberg laboratories and was carefully purified in this Laboratory by K. Linderstrøm-Lang. The nitrogen content was the theoretical and the ash content negligible.

The *d*-arginine was loaned to us for this investigation by Hoffmann–LaRoche. It was fractionally crystallized several times from water taking care to exclude carbon dioxide. The nitrogen as determined by microkjeldahls was low, only about 97% of the theoretical value being found. The ash content was negligible.

l-Tyrosine was prepared from silk by the method of Abderhalden and Teruuchi.[4] It was purified carefully by crystallizing several times from water. The nitrogen content was the theoretical and the ash content negligible.

In view of the accuracy of the measurements and the purity of the compounds involved the error in the experimental results is probably less than 1%.

The specific heat data in terms of the defined conventional calorie and for true mass appear in Table I.

Discussion

Entropies of the Compounds.—From the data in Table I we have calculated the entropies of the compounds in the usual manner using the extra-

(1) Huffman, Ellis and Fox, THIS JOURNAL, **59**, 2144 (1937).
(2) Parks, *ibid.*, **47**, 338 (1925).
(3) Giauque, Johnston and Kelley, *ibid.*, **49**, 2367 (1927).
(4) Abderhalden and Teruuchi, *Z. physiol. Chem.*, **48**, 528 (1906).

TABLE I

SPECIFIC HEATS PER GRAM OF SUBSTANCE

T, °K.	C_p	T, °K.	C_p	T, °K.	C_p
		dl-Alanine, crystals			
85.3	0.1206	170.3	0.2133	259.5	0.2928
91.1	.1285	189.9	.2318	274.9	.3064
97.7	.1368	196.2	.2372	282.4	.3136
109.2	.1506	204.4	.2448	286.1	.3164
129.4	.1730	220.6	.2591	290.0	.3199
149.4	.1935	240.4	.2761	297.5	.3265
		dl-Leucine, crystals			
86.0	.1298	149.2	.2028	260.1	.3146
91.9	.1376	164.2	.2188	277.6	.3323
99.2	.1469	179.8	.2326	282.6	.3379
107.5	.1565	202.8	.2564	290.1	.3465
119.1	.1709	219.9	.2737	296.6	.3540
134.3	.1876	239.8	.2934		
		d-Arginine, crystals			
85.7	.1195	133.7	.1670	235.2	.2591
90.8	.1249	149.5	.1816	255.3	.2785
97.8	.1330	164.7	.1950	276.2	.2988
106.0	.1410	179.7	.2085	283.1	.3051
115.0	.1497	196.2	.2231	290.0	.3124
125.2	.1596	215.8	.2415	296.8	.3188
		l-Tyrosine, crystals			
86.8	.0954	150.0	.1527	239.6	.2303
91.8	.1001	165.1	.1653	260.2	.2486
97.1	.1053	171.8	.1710	275.9	.2641
103.6	.1111	180.1	.1779	280.2	.2683
111.2	.1182	200.3	.1959	287.5	.2756
120.1	.1266	219.8	.2134	294.6	.2827
135.1	.1399				

polation method of Kelley, Parks and Huffman[5] for the increment between 0 and 90°K. For this extrapolation alanine, arginine and leucine were placed in class I and tyrosine in class II. The extrapolated portion of the entropy may involve relatively large absolute errors due to structural differences between these compounds and those for which the empirical extrapolation formulas were derived. However, for intercomparison this extrapolation should not cause any large errors.

In the case of *dl*-alanine we are able to compare the entropy of the inactive form with that of *d*-alanine[6] and find that they are identical. From this we predict that the entropies of optical isomers are the same within the errors of our measurements and of the extrapolation. The entropy data are given in Table II.

TABLE II

ENTROPIES OF THE COMPOUNDS PER MOLE

	S_{90}	$\Delta S_{90-298.1}$	$S_{298.1}$
dl-Alanine	8.84	22.80	31.6
dl-Leucine	13.91	35.61	49.5
d-Arginine	17.52	42.52	59.9
l-Tyrosine	15.43	37.60	53.0

(5) Kelley, Parks and Huffman, *J. Phys. Chem.*, **33**, 1802 (1929).
(6) Huffman and Borsook, THIS JOURNAL, **54**, 4297 (1932).

The Free Energies.—We have also calculated the free energies of these compounds by means of the fundamental thermodynamic equation $\Delta F = \Delta H - T\Delta S$. The essential data are given in Table III. We have used the heats of combustion and heats of formation of Huffman, Ellis and Fox.[1] The values of $\Delta S_{298.1}$, the entropy of formation, were obtained by subtracting from the entropy of the compound the entropies of the elements contained therein. For the entropies of the elements we have used 1.36,[7] 31.23,[8] 45.78[9] and 49.03,[10] respectively, for graphitic carbon, hydrogen, nitrogen and oxygen.

TABLE III

THERMAL DATA AT 298.1

Substance	Heat of comb. at const. π, cal.	$\Delta H^\circ_{298.1}$, cal.	$\Delta S_{298.1}$, e. u.	$\Delta F^\circ_{298.1}$, cal.
dl-Alanine	386,550	−135,260	−153.7	−89,440
d-Arginine	893,480	−150,160	−307.5	−58,490
Glycine	232,570	−126,690	−126.6	−88,950
d-Leucine	856,010	−153,470	−233.6	−83,830
l-Leucine	855,980	−153,490	−233.6	−83,860
dl-Leucine	855,230	−154,250	−233.6	−84,610
l-Tyrosine	1,058,340	−165,540	−227.4	−97,750

In the case of glycine we have used the entropy data of Parks, Huffman and Barmore,[11] and for *d*-leucine and *l*-leucine we have used the same value for their entropies as was found for *dl*-leucine.

The error in the $T\Delta S$ term is probably of the order of 300 calories due largely to the uncertainty of the extrapolated portion of the entropy of the compound. We have not assigned any absolute error to the free energies because of uncertainties in some of the auxiliary data used. However, for intercomparison purposes we believe the uncertainty should be of the order of 300 to 600 calories.

Summary

1. The heat capacities of *dl*-alanine, *d*-arginine, *dl*-leucine and *l*-tyrosine have been determined over the temperature range 90 to 298.1°K.

2. From the heat capacities and an empirical extrapolation formula the entropies at 298.1°K. have been calculated.

3. Using these entropies, entropy data from

(7) Jacobs and Parks, *ibid.*, **56**, 1513 (1934).
(8) Giauque, *ibid.*, **52**, 4816 (1930).
(9) Giauque and Clayton, *ibid.*, **55**, 4875 (1933).
(10) Giauque and Johnston, *ibid.*, **51**, 2300 (1929).
(11) Parks, Huffman and Barmore, *ibid.*, **55**, 2733 (1933).

the literature, and predicting the entropy of two compounds we have calculated the free energies of seven amino acids.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF NORTHWESTERN UNIVERSITY]

The Specific Heats of Aqueous Solutions of Urea from 2 to 40° and the Apparent Molal Heat Capacity of Urea[1]

BY FRANK T. GUCKER, JR., AND FRED D. AYRES

Introduction

A study of the properties of non-electrolytic solutions may help the interpretation of electrolytic solutions, by indicating a *normal* solute behavior, deviations from which may be ascribed to the charges of the ions. We have undertaken a study of the heat capacities of solutions of non-electrolytes and already have determined[2] the specific heats of aqueous sucrose solutions. In the same place we discussed the apparent molal heat capacity of sucrose and of other non-electrolytes for which suitable results were found in the literature. The present work deals with solutions of urea, studied over a wide range of temperature and concentration, to find the effect of each upon the apparent molal heat capacity.

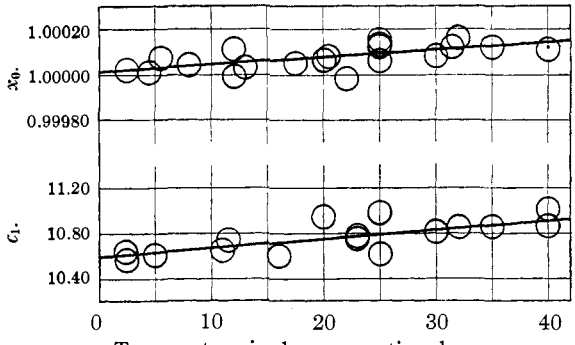

Fig. 1.—Temperature variation of the balancing ratio (x_0) and the heat capacity of the working calorimeter (c_1).

Preparation of the Urea Solutions.—The urea used in these experiments was prepared from the commercial C. P. product by two crystallizations from water with centrifugal drainage. The temperature of the solutions during the crystallizations was not allowed to exceed 65°, to prevent the conversion of urea to ammonium cyanate. After a preliminary drying in air, the product was ground to a fine powder in an agate mortar and then dried *in vacuo* (about 0.01 mm.) at 50–60° for five hours. The melting point of the product was 132.6–132.8° as determined with a standard thermometer totally immersed in a well-stirred bath. The rate of temperature rise near the melting point was about 0.2° per minute. This agrees very well with the values of 132.6 and 132.7° given by Shnidman and Sunier[3] for specially purified urea from different sources. All solutions were made up determinate from urea and freshly deaerated distilled water, except for three which were prepared by quantitative dilution of more concentrated solutions. All weighings were made with standardized weights, and reduced to the vacuum basis.

Experimental Methods and Results.—The differential twin-calorimeter apparatus which has been described previously[4] was used for determining the specific heats of the urea solutions. Since these measurements were to be made over a range of temperature extending from 2 to 40°, the apparatus was standardized over this same temperature range. The procedure was identical with that described in the previous paper, to which the reader is referred for details. The same symbols are used in this paper. The balancing ratio for equal weights of water in both calorimeters (x_0) was found to increase by about 0.01% as the temperature rose from 2 to 40°. Figure 1 shows a plot of the results of all these determinations, which were made at more or less evenly spaced intervals throughout the course of the measurements. The radius of each circle represents 0.005% in the ordinate. Of the twenty points only one falls more than 0.006% from the straight line. The heat capacity of the hollow copper displacer, used in determining that of the working calorimeter, was also measured at intervals over the entire temperature range. The effective heat capacity of the working calorimeter (c_1) was then calculated at frequent intervals. It increases linearly from 10.60 $cal._{2°}$ at 2° to 10.91 $cal._{40°}$ at 40°, as Fig. 1 shows. The method of calculation makes the percentage uncertainty in c_1 much larger than in x_0, but the effect of this upon the final specific heat is reduced in the same ratio to a negligible quantity. These calibrations made possible the direct calculation of all heat capacities, including those of the urea solutions, in calorie units at the various experimental temperatures and all the results are so expressed.

The usual experimental procedure was to make up by weight 269 ml. of the solution in a special volumetric flask, weigh this fixed volume into the working calorimeter and the same volume of distilled water, freshly deareated by means of a water aspirator, into the tare and assemble the

(1) Part of this paper was presented before the Division of Physical Chemistry at the Chapel Hill meeting of the American Chemical Society, April 14, 1937.

(2) Gucker and Ayres, THIS JOURNAL, **59**, 477 (1937).

(3) Shnidman and Sunier, *J. Phys. Chem.*, **36**, 1232 (1932).

(4) Gucker, Ayres and Rubin, THIS JOURNAL, **58**, 2118 (1936).