hydrides with rotating molecules differ little from liquids.

Summary

The dielectric constants and specific conductances of solid hydrogen cyanide and hydrogen selenide have been measured from liquid air temperature to the regions of the melting point and those of arsine have been measured from liquid hydrogen temperature to the region of the boiling point over a frequency range from 0.5 to 50 kilocycles. No molecular rotation is found in solid hydrogen cyanide while the molecule rotates freely in the selenide even at liquid air temperature. The arsine molecule rotates freely down to 32.1°K. where a transition sets in, which is not complete at 20.5°K. and is accompanied by some anomalous dispersion. The molecules of the hydrides tend to rotate more readily the smaller their dipole moments.

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

Thermal Data. VI. The Heats of Combustion and Free Energies of Seven Organic Compounds Containing Nitrogen

BY HUGH M. HUFFMAN, EMORY L. ELLIS AND SIDNEY W. FOX

In the first paper[1] of this series we presented heat capacity data for the following seven compounds, *d*-alanine, *l*-asparagine (anhydrous), *l*-asparagine monohydrate, *l*-aspartic acid, *d*-glutamic acid, creatine and creatinine. These data were used to calculate the entropies of the compounds, which were further utilized in conjunction with the heats of combustion and certain other auxiliary data to calculate the standard free energies of formation of these compounds.

Due to the general unreliability of the older combustion data appearing in the literature, we have redetermined this quantity for each of the seven compounds mentioned above. In so doing we have kept constantly before us the necessity of establishing the purity and the physical state of the compounds as well as the need for calorimetry of high precision and accuracy.

These new combustion data have been used in conjunction with the entropies obtained by Huffman and Borsook[1] and certain other auxiliary data to calculate new and more reliable free energy data for these compounds.

Calorimetric Method

The method and apparatus used have been described in previous communications.[2] No essential changes in method or apparatus have been made. All of the combustions were made in a Parr bomb having a volume of 0.380 liter with an initial oxygen pressure of 30 atm. and with 1 ml. of water in the bomb. The platinum wire technique[2a] was used exclusively. During the course of this investigation our resistance thermometer developed a short circuit. After repair the thermometer characteristics were found to have changed but upon recalibration identical results for the energy equivalent of the calorimeter were found. Numerous calibrations of the calorimeter have been made, at irregular intervals throughout the course of this investigation, with Bureau of Standards benzoic acid, samples 39d and 39e, having for its isothermal heat of combustion at 25.0° the value 26,419 international joules per gram true mass. We have used oxygen from several cylinders supplied by the "Linde Air Products Company" and at cylinder pressures varying from 1950 to 450 pounds. The precision of our calibration data has remained the same as that previously reported, namely, an extreme deviation from the mean of slightly more than 0.01%. The precision error calculated from the formula recommended by Rossini[3] was 0.005%.

In several cases we have found it necessary to use oil as an auxiliary substance. The combustion value of this oil has been controlled by occasional combustions and the value found was 10,830 ± 3 cal. per gram weighed in air. When the mass of the oil is determined by difference after adding it directly to the sample in the crucible an additional uncertainty is introduced when the material is hygroscopic. To avoid this uncertainty as well as to permit the addition of small quantities, the following method was adopted. The oil was kept in a small hypodermic syringe and the amount added was determined from the mass difference in this syringe.

Units and Corrections

The unit of energy used throughout this paper is the defined conventional calorie which is derived from the international joule by multiplying by the factor 1.0004/4.185. The method of calculation, the corrections and the symbols used are the same as those given by Stiehler and Huffman.[2b] The molecular weights are based on the 1935 table of atomic weights. In applying the correction for true mass

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

[2] (a) Huffman and Ellis, *ibid.*, **57**, 41 (1935); (b) Stiehler and Huffman, *ibid.*, **57**, 1734 (1935).

[3] Rossini, *Chem. Rev.*, **18**, 233 (1936).

we have used approximate densities obtained from the mass and volume of the pelleted material when other data were not available in the literature. All of the thermal data are given for the isothermal process at 25°.

In some cases the combustion was incomplete, leaving a small residue of carbon in the crucible. The mass of this carbon was determined from the mass of the crucible before and after ignition and corrected for. In no case did this correction exceed 0.003%. Some of the preparations left a residue of ash in the crucible. When this was appreciable it was corrected for by arbitrarily subtracting the weight of the ash from the weight of the sample. In the extreme case this correction was about 0.03%.

Purity and Dryness of the Materials Used

We have followed the general methods of Stiehler and Huffman[2b] to assure ourselves of the purity and dryness of the combustion samples. As mentioned above we have made routine ash determinations on each sample burned. We have also made suitable analyses such as nitrogen determinations, titrations and measurement of the optical rotation. We have attempted, furthermore, to define accurately the physical state of the compounds by photomicrographs of their crystalline condition (Fig. 1) as well as by a precise description of the method of preparation.

Preparation, Purification and Heats of Combustion of the Compounds

d-Alanine.—Combustions were made on two commercial samples of this material which were purified in the following manner.

(a) A material from an unknown source was twice crystallized from water[4] by dissolving in hot water and allowing the solution to cool and deposit crystals.

(d) A Hoffmann–LaRoche product was twice crystallized from water in the above manner.

Nitrogen determinations[5] on sample (a) gave the theoretical results. The ash content of (a) was less than 0.01% and that of (d) undetectable. The specific rotation of (d) has been reported by Huffman and Borsook.[1]

This compound was very troublesome to burn as it had a decided tendency to jump out of the crucible when partially burned. We have tried all of the tricks at our command to overcome this unfortunate tendency, such as varying the crucible weight, using large amounts of oil, increasing the oxygen pressure, etc., but with little success. In all five preparations of *d*-alanine were used and the three values given in the table are the usable results from fifteen attempted combustions. *d*-Alanine appears to exist in at least two crystal modifications (see Fig. 1). Since our combustions are on a single type we cannot be sure that these are polymorphous forms.

l-Asparagine Hydrate

Material from four different commercial sources was utilized to prepare eleven combustion samples.

(a) Merck *l*-asparagine, which had been recrystallized several times for heat capacity measurements, was subjected to three additional crystallizations by dissolving in boiling water and allowing crystals to form as the solution cooled.

(b) A preparation from Hoffmann–LaRoche was used without further purification.

(c) A portion of (b) was once crystallized from water by cooling the hot solution.

(d) A portion of (b) was twice crystallized from water as in (c).

(e) Material from Pfanstiehl was twice crystallized from water.

(f) Material from Eastman was twice crystallized from water.

(g) A sample from Merck recently purchased (1936) for this research was twice crystallized from water.

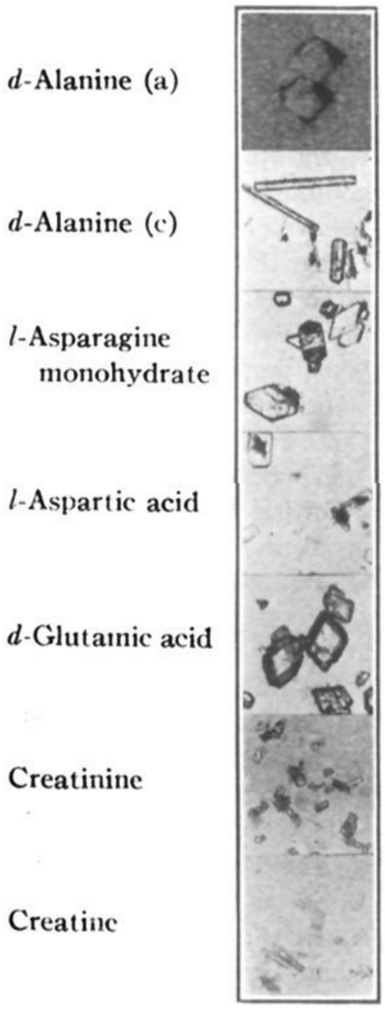

Fig. 1.

(h) A portion of (a) was converted to the copper salt, which was purified by one crystallization from a large volume of water. The copper was precipitated with hydrogen sulfide and the regenerated asparagine was further purified by several crystallizations from water.

(i) A portion of (e) was recrystallized by dissolving in hot water and seeding heavily with *l*-asparagine which had been dehydrated at 100°.

(j) A portion of (e) which had been dehydrated at 100° was rehydrated by allowing to stand several days covered with water at room temperature.

(k) A part of (a) was twice more crystallized from water.

The nitrogen content of (a) was the theoretical. Measurements of the rotation of samples (a) and (b) in HCl solutions with the ratio (HCl/asparagine hydrate) equal to 12.3 gave values for $(\alpha)^{20}{}_{\mathrm{D}}$ of 30.3 and 27.9, respectively. The ash content of all of the samples with the exception of (a), (h) and (k) was undetectable. In sample (h), the worst case, it was less than 0.01%.

Numerous combustions on sample (a) dehydrated at 100° consistently gave results about five calories higher than the accepted value. For this reason preparations (h) and (k) were made. The result of one combustion on (k) agreed with those on (a) while the result of one combustion on (h) was about midway between those on (a) and the accepted value. Further attempts at purification were impossible because of lack of this material. When a new sample (g) was purchased from Merck it was found to yield values which agreed with the accepted result.

The combustions on anhydrous *l*-asparagine are further complicated by the fact that it appears to exist in two modi-

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(4) Redistilled water for all of the purifications.

(5) All of the nitrogen determinations with the exception of that on creatine were by micro Kjeldahl.

fications.[5a] Several combustions on specimens of (a) and (b) which had been dehydrated in the vacuum oven at 65–70° gave results from 23 to 28 calories higher than those dehydrated at 100°. Furthermore, this difference tended to decrease with the heating time, indicating that the material was changing continuously into the stable form. As a test of this hypothesis we have included in the table the result of one combustion on a sample which had been heated for seventy-eight days at 65–70° followed by eighteen hours at 100°. This additional heating caused no change in the mass of the pellet but did cause the combustion value to drop about 28 calories (as determined by comparison with a sample whose history was identical except for treatment at 100°) to agree with that of other samples dehydrated at 100°. The removal of the water of hydration takes place so slowly at room temperature that we have not been able to obtain a completely anhydrous material in this manner. At elevated temperatures the fact that dehydration is accompanied by the transition to the stable form makes it impossible to obtain a reliable combustion value for the high temperature form. We believe, however, that it is probably about 30 calories higher than that of the stable modifications.

To see if this apparent dimorphism persisted in the hydrate two attempts were made to obtain a different crystal type, preparations (i) and (j). The results of the combustions of these two hydrated samples agreed perfectly with those on the hydrate obtained in the usual manner.

Where the hydrated asparagine has been burned the following method was resorted to. The crystalline material protected from contamination by dust particles was allowed to come to equilibrium in the air of the room. Pellets were made and also allowed to equilibrate with the air of the room before burning. At the time of burning, a pellet was also dehydrated at 100° and the amount of hydration determined. In the case of sample (i) the loss in mass corresponded to 99.68% hydrate, hence a suitable correction was applied for the amount of anhydrous material present. In the other cases the material was 100% hydrated within the error ±0.02% of the measurements. Due to the fact that it is impossible to be sure that the substance is free from adsorbed gases or water the mass determinations in this case are probably less reliable than in the other cases.

***l*-Aspartic Acid.**—Material from two commercial sources was treated in the following manner to make three combustion samples.

(a) An Eastman product which had been subjected to seven recrystallizations for use in heat capacity measurements[1] was recrystallized three more times from water by dissolving in hot water and allowing the solution to cool.

(b) A portion of (a) was subjected to two additional crystallizations from water in the same manner.

(c) Material obtained from Hoffmann–LaRoche was once crystallized from water.

The nitrogen content of (a) was found to be theoretical. The rotation of the original material of sample (a) has been given in a previous communication.[1] The ash content of each of the preparations was less than 0.01%.

In addition to the values given in the table combustions on samples of (b) and (c) which had been dried for several days at 100° gave values about 2.5 calories higher than the mean value reported. These pellets showed signs of decomposition and hence the results have been discarded.

***d*-Glutamic Acid.**—A commercial sample from Pfanstiehl and a preparation made from Ajinomoto by the method of Schmidt and Foster[6] were the starting materials for the preparation of five combustion samples.

(a) A large amount of *d*-glutamic acid had been prepared from Ajinomoto and carefully purified for heat capacity measurements.[1] A portion of this material was subjected to two fractional crystallizations from water by solution at 100° and subsequent rapid cooling to zero degrees. This material was discarded when found to contain glass from the sintered glass filters used.

(b) A sample of Pfanstiehl *d*-glutamic acid was subjected to five crystallizations under the same conditions as (a).

(c) The same original material as used in preparation (a) was three times crystallized from water by dissolving at 75° and subsequent cooling rapidly to zero degrees.

(d) A portion of sample (a) was once more crystallized from water by dissolving at 100° and rapidly cooling.

(e) A portion of sample (b) was dissolved in water at 60° and rapidly cooled.

The nitrogen content of samples (a), (b) and (c) was found to be theoretical. The ash content of all of the above samples was negligible. The optical rotation of the original material for (a) has been reported previously.[1]

In addition to the values given in the table, several combustions were made on material dried at 100°. These samples were discolored and the combustion values increased with the time of heating.

Creatine (Anhydrous).—Two commercial products were utilized to prepare three different combustion samples.

(a) Eastman creatine was twice crystallized from water by dissolving in boiling water and cooling the solution.

(b) Creatine from Hoffmann–LaRoche was twice crystallized from water as above.

(d) A portion of sample (a) was dissolved in boiling water and crystallization started by seeding with anhydrous creatine which had been dehydrated at 100°.

The nitrogen content was theoretical and the ash content negligible. It was necessary to use oil to initiate the combustion.

During the course of this investigation of anhydrous creatine we have again found evidence of dimorphism. As in the case of *l*-asparagine different values were obtained for the anhydrous material depending merely on its heat treatment. Thus creatine (samples (a) and (b)) which was crystallized in the usual manner and heated to 100° for dehydrating has a lower combustion value by about five calories than that which has been dehydrated at room temperature. We have included two values obtained on sample (d), dehydrated at room temperature, which agree with combustions on the other samples dehydrated at 100°. We are investigating this phenomenon further and will make a report in a future publication.

These phenomena in the case of *l*-asparagine and creatine serve again to emphasize the necessity for a positive definition of the physical state when reporting physical properties.

[5a] Since submitting this article for publication, the existence of the two polymorphic forms of anhydrous asparagine has been confirmed by x-ray pictures, which were taken for us by Mr. G. Albrecht working in Professor Pauling's laboratory.

[6] Schmidt and Foster, *J. Exptl. Biol. Med.*, **18**, 205 (1920–21).

Creatinine.—Materials from two commercial sources were utilized to prepare four combustion samples.

(a) A sample of Pfanstiehl creatinine purchased in 1931 and extensively purified for heat capacity measurements[1] was dissolved in water at 65° and precipitated with purified acetone according to the method of Edgar and Hinegardner.[7]

(b) A portion of the starting material in (a) was converted to the hydrochloride and neutralized with ammonia according to Edgar and Hinegardner's[7] methods (a) and (b). It was finally washed with ammonia and ethyl alcohol.

(c) A sample from Eastman was dissolved in water and precipitated with acetone as in (a).

(d) A sample of Pfanstiehl creatinine especially purchased for this research (1936) was dissolved in boiling water and immediately placed in an ice-bath to crystallize. The crystals were slightly greenish. This material was again dissolved in hot water and treated with norite. The crystals from the above were again dissolved in hot water and allowed to cool and crystallize.

Nitrogen determinations on (a) gave theoretical values. Sample (c) was found to have a high ash content 0.02–0.03% while that of samples (a) and (d) was negligible. In view of the uncertainty introduced into the combustion values of (c) by the high ash content we have reported the weights only to the nearest 0.1 mg. Sample (b) was discolored and gave low combustion values, hence it was discarded.

Since most of these compounds are more or less hygroscopic the following method was adopted for an accurate determination of the mass. The pelleted samples were kept in open weighing bottles during the desiccation process, after which they were stoppered immediately and kept over phosphorus pentoxide in a desiccator until time for their combustion. The bottle was then transferred to the balance case and allowed to equilibrate for a short time. The bottle plus pellet was weighed and the pellet transferred to the crucible and the empty bottle weighed. As a check on the weight thus obtained the weight was also determined by weighing the crucible plus the pellet.

When these materials were hygroscopic it was observed that the pellet usually gained weight rapidly when first exposed to the air, the rate falling off with time and approaching a steady state. There is of course the possibility that the reaction between the material and water may appreciably change the energy content of the sample. In the case of creatinine we have investigated this possibility by burning a sample in the bomb without having any water present. The sample was transferred as rapidly as possible to the bomb and then evacuated for some time before admitting oxygen which had been passed over drierite. This combustion when corrected in a suitable manner for the initial absence of water agreed exactly with the rest of the combustions in that series. There is some uncertainty in the corrections to be applied as we found that the oxygen still contained a small and unknown amount of water vapor. For this reason we have not included this value in the table but feel that it shows that creatinine values are not appreciably affected by sorbed water.

The use of oil as an auxiliary substance serves also to give at least partial protection against sorption of water. Our feeling is that any energy effect due to this phenomenon is well within the experimental error.

There is, furthermore, the possibility that oil may react with the materials in such a manner as to affect the energy content. In the cases where we have used oil we have either varied the amount of oil or have made combustions in which no oil was used. The results show that this effect if present is negligible.

The experimental results of the combustion on these seven compounds are given in Table I. We have utilized the experimental values to calculate certain other useful data. These appear in Table II along with some auxiliary data which have been used. Finally we have utilized these new values for ΔH_f^0 in conjunction with the entropy data of Huffman and Borsook[1] to calculate new and more reliable values for the free energies of formation. We have used the same values for the entropies of the elements and the heats of formation of water and carbon dioxide as were used by Stiehler and Huffman.[2b]

Discussion of the Results

As in the previous papers in this series we have chosen as our limits of error the extreme deviation from the mean of the experimental results in each case and have also allowed for an additional uncertainty of 10% in the Washburn correction. We have taken numerous precautions to assure ourselves of the purity, dryness and physical state of these compounds so that we feel that absolute errors due to these factors have been largely eliminated. We have not assigned any limits of error to the heats or free energies of formation of these compounds, due to uncertainties in the accuracy of certain of the auxiliary data required. We have included photomicrographs of the crystalline compounds which were burned. In the case where the original material was hydrated, the physical state of the anhydrous material must be defined by the method of dehydration.

All of these compounds have been burned by earlier workers. Wrede[8] has burned *d*-alanine, Fischer and Wrede[9] have burned *l*-aspartic acid and *d*-glutamic acid, Emory and Benedict[10] have burned all of the compounds except anhydrous *l*-asparagine. Stohmann and Langbein[11] have burned anhydrous *l*-asparagine and anhydrous creatine.

With the exception of Wrede[8] none of the above authors include sufficient data for correcting their values in terms of newer thermochemical standards. We have, however, made approximate

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[7] Edgar and Hinegardner, *J. Biol. Chem.*, **56**, 881 (1923).

[8] Wrede, *Z. physik. Chem.*, **75**, 81 (1910).

[9] Fischer and Wrede, *Sitzber. kgl. preuss. Akad. Wiss.*, 687 (1904).

[10] Emory and Benedict, *Am. J. Physiol.*, **28**, 301 (1911).

[11] Stohmann and Langbein, *J. prakt. Chem.*, **44**, 336 (1891).

TABLE I

THE EXPERIMENTAL DATA

Sample	P_2O_5 vac.	Desiccation Vac. 70° hours	Oven 100°	True mass	Total heat evolved, cal.	Cal. from HNO_3	Cal. from oil	Cal. from paper and Elt	$-\Delta U_B$/m, cal. g.$^{-1}$	Deviation
d-Alanine (a)	2232			1.47660	6452.6	18.6		17.1	4345.7	−0.8
d-Alanine (a)	168			1.22765	5845.9	16.7	474.4	17.3	4347.8	1.3
d-Alanine (d)			120	1.35550	6411.9	20.0	484.2	16.5	4346.1	−0.4
Mean									4346.5	±0.8
l-Asparagine (b)			240	1.81750	6385.1	19.4		17.6	3492.8	−0.3
l-Asparagine (b)		1872	18	1.77845	6252.9	21.7		17.8	3493.7	.6
l-Asparagine (c)			120	1.80005	6322.3	19.6		16.5	3492.3	− .8
l-Asparagine (d)			96	1.82520	6414.3	22.0		16.1	3492.9	− .2
l-Asparagine (e)			456	1.80440	6340.7	20.9		16.6	3493.3	.2
l-Asparagine (f)			146	1.80615	6346.6	21.2		16.7	3492.9	− .2
l-Asparagine (g)			116	1.82215	6403.0	20.1		16.9	3493.7	.6
Mean									3493.1	± .4
l-Asparagine hyd. (e)				2.05405	6309.2	16.0		17.8	3055.2	− .5
l-Asparagine hyd. (e)				2.05475	6311.4	16.2		16.8	3055.6	.1
l-Asparagine hyd. (i)				2.08370	6405.0	17.0		16.7	3056.3[a]	.6
l-Asparagine hyd. (j)				2.07860	6385.5	16.0		17.1	3055.6	− .1
Mean									3055.7	± .3
l-Aspartic acid (a)	1008			2.18075	6312.9	12.2		17.0	2881.4	− .5
l-Aspartic acid (a)	1032			2.18255	6318.6	11.9		17.2	2881.7	− .2
l-Aspartic acid (a)		144		2.18315	6322.0	12.1		16.6	2882.7	.8
l-Aspartic acid (a)			96	2.17760	6307.9	12.3		18.5	2882.6	.7
l-Aspartic acid (b)	216	192		2.12940	6164.2	11.9		16.7	2881.4	− .5
l-Aspartic acid (c)	216			2.18060	6310.9	11.6		17.3	2880.8	−1.1
l-Aspartic acid (c)		336		2.16625	6272.9	11.5		17.2	2882.5	0.6
Mean									2881.9	± .7
d-Glutamic acid (b)	216			1.73255	6365.8	13.3		16.4	3657.1	.2
d-Glutamic acid (b)		52		1.65785	6310.9	12.5	218.8	16.5	3657.2	.3
d-Glutamic acid (b)		52		1.65460	6300.9	11.6	223.6	16.6	3655.9	−1.0
d-Glutamic acid (b)		72		1.72440	6556.4	13.4	218.5	17.1	3657.7	0.8
d-Glutamic acid (b)		168		1.67065	6361.6	12.6	222.3	16.4	3657.5	.6
d-Glutamic acid (c)	360			1.71895	6535.9	12.9	220.1	17.4	3656.6	− .3
d-Glutamic acid (c)	192	4		1.65770	6310.3	12.3	221.1	17.4	3655.3	−1.6
d-Glutamic acid (d)	96			1.66820	6354.6	13.1	222.4	17.5	3657.6	0.7
d-Glutamic acid (d)	192	4		1.66365	6338.5	12.6	224.0	17.4	3657.3	.4
d-Glutamic acid (e)		10		1.66830	6343.4	13.2	212.5	17.4	3656.3	− .6
Mean									3656.9	± .6
Creatine (a)			192	1.44350	6324.1	25.2	164.7	17.2	4237.6	− .5
Creatine (a)			192	1.40560	6293.4	24.8	293.0	17.4	4238.9	.8
Creatine (a)	648	96[b]		1.27975	6322.9	24.7	859.4	17.2	4237.5	− .8
Creatine (a + b)	120		168	1.43285	6347.8	25.1	232.0	16.5	4239.2	1.1
Creatine (b)			216	1.44615	6352.5	25.2	181.1	16.6	4237.6	−0.5
Creatine (d)	570			1.36670	6455.3	26.0	620.1	17.1	4238.0	− .1
Creatine (d)	1416			1.31245	6345.4	24.4	740.8	17.6	4238.4	.3
Mean									4238.1	± .6
Creatinine (a)	380			1.27175	6330.2	30.1		17.0	4940.7	.6
Creatinine (a)	48	400		1.27245	6332.8	29.5		16.6	4940.6	.5
Creatinine (a)	48		42	1.27450	6343.1	30.0		17.7	4939.8	− .3
Creatinine (a)	48		72	1.27385	6340.2	30.4		16.9	4940.3	.2
Creatinine (a)	48		72	1.27485	6344.6	29.5		16.2	4940.9	.8
Creatinine (c)	720			1.2747	6345.0	29.9		17.4	4940.4	.3
Creatinine (c)	720			1.2746	6343.6	30.6		17.8	4939.0	−1.1
Creatinine (c)	720			1.2761	6350.1	29.8		16.9	4939.6	−0.5
Creatinine (d)			90	1.27400	6342.1	29.7		19.1	4939.8	− .3
Mean									4940.1	± .5

[a] This value is corrected for the fact that the sample was only 99.68% hydrated.

[b] Temperature of vacuum oven 45–50°.

TABLE II

SUMMARY OF DERIVED DATA

Substance	Formula	Mol. wt.	Density	$-\Delta U_B$, kcal. mole^{-1}	$-\Delta U_R$, kcal. mole^{-1}	$-\Delta H_R$, kcal. mole^{-1}	$-\Delta H^0_f$ kcal. mole^{-1}	$\Delta U_R/dT$ mole^{-1} cal.	$-\Delta F^0_f$ kcal. mole^{-1}
d-Alanine	$C_3H_7O_2N$	89.063	1.38	387.11 ± 0.11	386.86 ± 0.13	387.10 ± 0.13	134.81	38	88.99
l-Asparagine (anhyd.)	$C_4H_8O_3N_2$	132.078	1.44	461.36 ± 0.13	460.93 ± .17	460.63 ± .17	189.58	43	127.58
l-Asparagine (hyd.)	$C_4H_{10}O_4N_2$	150.094	1.54	458.64 ± .15	458.25 ± .19	457.95 ± .19	260.57	50	184.74
l-Aspartic acid	$C_4H_7O_4N$	133.063	1.66	383.47 ± .15	383.01 ± .19	382.57 ± .19	233.49	36	175.59
d-Glutamic acid	$C_5H_9O_4N$	147.078	1.54	537.85 ± .23	537.36 ± .28	537.31 ± .28	241.30	49	174.94
Creatine (anhyd.)	$C_4H_9O_2N_3$	131.094	1.33	555.59 ± .16	555.21 ± .20	555.06 ± .20	129.31	48	64.20
Creatinine	$C_4H_7ON_3$	113.079	1.31	558.62 ± .12	558.26 ± .16	558.11 ± .16	57.94	38	7.89

corrections and these corrected values are compared with our values in Table III. In the case of creatinine Emory and Benedict[10] calculated their result on the basis of the carbon dioxide found. We have corrected their reported value back to the mass basis which brings it into much better agreement with our value.

TABLE III

COMPARISON OF THE PRESENT DATA WITH VALUES FROM THE LITERATURE

Substance	Older data: Reference	Older data: $-\Delta H_R$, kcal. mole^{-1}		New value: $-\Delta H_R$, kcal. mole^{-1}		Difference %
d-Alanine	8	386.87	±0.19	387.10	±0.13	−0.06
d-Alanine	10	390.6	±1.2	387.10	± .13	.90
l-Asparagine (anh.)	11	462.3	±1.2	460.63	± .17	.37
l-Asparagine (hyd.)	10	458.4	±1.2	458.50	± .19	− .01
l-Aspartic acid	10	381.9	±1.1	382.57	± .19	− .18
l-Aspartic acid	9	384.7	±1.3	382.57	± .19	+ .48
d-Glutamic acid	9	541.7	±0.7	537.31	± .28	+ .82
d-Glutamic acid	10	536.6	±1.3	537.31	± .28	− .13
Creatine	11	558.4	±1.5	555.06	± .20	+ .54
Creatine	10	553.8	±1.3	555.06	± .20	− .23
Creatinine	10	556.4	±1.3	558.11	± .16	− .31

In a recent paper Zittle and Schmidt[12] report the heat of hydration of anhydrous *l*-asparagine as 2250 ± 200 calories. This compares favorably with the value of 2680 ± 330 calories as calculated from our combustion data on these two compounds. They do not state how the anhydrous material was obtained but it was very probably by treatment at 100° or above.

Summary

1. The experimental values of the heats of combustion at constant volume and at 25° of seven organic compounds are given.

2. From the experimental values the heat of combustion at constant pressure and the heat of formation have been calculated.

3. These new values for heats of formation have been used with existing entropy data to calculate more reliable free energy data.

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(12) Zittle and Schmidt, *J. Biol. Chem.*, **108**, 161 (1935).

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[CONTRIBUTION FROM THE GEORGE HERBERT JONES LABORATORY OF THE UNIVERSITY OF CHICAGO]

Coördination Compounds of Platinous Halides with Unsaturated (Ethylene) Substances

BY M. S. KHARASCH AND T. A. ASHFORD[1]

Introduction

Platinum is an unusually versatile element. It has primary valences of two and four, and it forms two series of coördination compounds with both organic and inorganic substances. In these the metal exhibits the coördination numbers of four and six, respectively. Stereoisomers have been obtained in both series. Where the coördination number is six, the accepted view is that the valence bonds of the platinum atom are directed toward the corners of an octahedron; giving rise to the following two stereoisomeric configurations for compounds of the type PtX_4A_2.[2] Some compounds of the type PtX_2A_2 also exist in two stereoisomeric forms: *cis* and *trans*[2] (p. 338).

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(1) This communication is an abstract of a dissertation submitted by T. A. Ashford in partial fulfilment of the requirements for the degree of Doctor of Philosophy in Chemistry at the University of Chicago.

(2) Werner, "Lehrbuch der Stereochemie," Gustave Fischer, Jena, 1904, p. 350.