3. From these results and previous work of others the dissociation of water in strontium chloride solutions has been calculated.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF STANFORD UNIVERSITY]

Thermal Data on Organic Compounds. XI. The Heat Capacities, Entropies and Free Energies of Ten Compounds Containing Oxygen or Nitrogen

BY GEORGE S. PARKS, HUGH M. HUFFMAN AND MARK BARMORE

The previous papers[1] of this series have dealt mainly with thermal data for hydrocarbons and for some aliphatic alcohols and acids. From these studies it has become evident that the entropy and free energy of an organic compound are related to its constitution in a simple additive manner, and we have been able to assign definite numerical values to the changes in these thermodynamic quantities, corresponding to the introduction of a CH_2 group into an aliphatic chain, to the substitution of a methyl or ethyl branch for a hydrogen atom, to the replacement of a hydrogen atom by an alcoholic hydroxyl group, etc. The work now seems to warrant greater diversification of the substances to be studied, and accordingly in the present investigation we have measured the heat capacities of the following ten organic compounds containing oxygen or nitrogen: urea, glycine, ethyl acetate, *n*-amyl alcohol, *tert*-amyl alcohol, isopropyl ether, phenol, aniline, benzoic acid and sucrose.

These data have then been utilized to calculate, by the third law of thermodynamics, the corresponding entropies and free energies.

Materials

Urea and Glycine.—These were C. P. Pfanstiehl products. The urea had a melting point of 132° and a water content guaranteed to be less than 0.05%. The glycine was guaranteed to be free of ammonia and chlorides and to have less than 0.15% water content and less than 0.08% ash.

Ethyl Acetate.—This was one of the very pure standard samples prepared in the laboratory of Professor Timmermans at the University of Brussels. It had a certified melting point of −83.6°, while we found −83.76° by a rough measurement with a thermocouple in the course of our fusion determinations.

***n*-Amyl Alcohol, *Tert*-amyl Alcohol, and Isopropyl Ether.**—These compounds were very carefully prepared for us by Dr. H. E. Buc of the Standard Oil Development Company. The *n*-amyl alcohol boiled at 137.9° at 760 mm. pressure. The *tert*-amyl alcohol boiled between 102.33 and 102.35° at 762 mm., and melted at −9.1°, which is 2.8° above the point given in the "International Critical Tables." The isopropyl ether boiled between 68.9 and 69.15°.

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[1] See, for instance, Parks, Kelley and Huffman, THIS JOURNAL, **51**, 1969 (1929); Huffman, Parks and Thomas, *ibid.*, **52**, 3241 (1930); Parks and Huffman, *ibid.*, **52**, 4381 (1930); and Huffman, Parks and Barmore, *ibid.*, **53**, 3876 (1931).

Phenol.—A C. P. material was fractionally crystallized several times, and the best crystals were then remelted and fractionally distilled three times with a special still. The final product had a boiling range of 0.05° and melted at 40.9° (I. C. T. value, 41.0°).

Aniline.—A high grade C. P. material was subjected to a fractional distillation and was then further purified by six fractional crystallizations. The resulting product had a very sharp melting point at −6.3°.

Benzoic Acid and Sucrose.—These were "standard" samples obtained from the United States Bureau of Standards. Impurities in each material were less than 0.01%.

Experimental Results

In principle, the method of Nernst was employed with an aneroid calorimeter in determining the "true" specific heats and the fusion data. The apparatus and details of experimental procedure have been fully described in other places.[2] In view of the accuracy of the various measurements involved, the error in the experimental values thereby obtained is probably less than 1%, except in so far as impurities in a sample may cause premelting or otherwise influence the results.

The specific heats and the fusion data, expressed in terms of the 15° calorie[3] and with all weights reduced to a vacuum basis, appear in Tables I and II.

TABLE I

SPECIFIC HEATS

Urea: Crystals

Temp., °K.	93.4	99.2	111.6	130.5	160.3	190.2
C_p per g.	0.158	0.163	0.176	0.194	0.224	0.255
Temp., °K.	220.0	249.8	275.0	275.3	286.2	298.0
C_p per g.	0.288	0.319	0.347	0.345	0.359	0.373

Glycine: Crystals

Temp., °K.	93.2	98.9	104.6	112.8	131.7	150.5	173.1	192.1
C_p per g.	0.129	0.136	0.142	0.151	0.169	0.187	0.208	0.224
Temp., °K.	207.3	225.7	243.6	260.3	278.9	282.8	290.9	299.5
C_p per g.	0.237	0.252	0.267	0.280	0.297	0.299	0.310	0.320

Ethyl Acetate: Crystals

Temp., °K.	92.2	96.5	97.1	102.3	104.0	108.5	114.2	125.2
C_p per g.	0.199	0.205	0.206	0.213	0.214	0.219	0.225	0.237
Temp., °K.	131.0	136.1	145.3	151.9	156.0	159.9	167.3	
C_p per g.	0.243	0.248	0.257	0.263	0.269	0.275	0.285	

Liquid

Temp., °K.	195.7	205.1	225.2	244.5	258.3	274.9	288.7	293.6
C_p per g.	0.435	0.434	0.435	0.438	0.443	0.450	0.456	0.459

n-Amyl Alcohol: Crystals

Temp., °K.	93.7	99.1	100.2	108.4	117.2	122.4
C_p per g.	0.192	0.199	0.202	0.212	0.225	0.236
Temp., °K.	127.3	132.5	140.1	149.7	158.9	164.9
C_p per g.	0.265	0.257	0.267	0.277	0.303	0.332

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[2] Parks, THIS JOURNAL, **47**, 338 (1925); also Parks and Kelley, *J. Phys. Chem.*, **30**, 47 (1926).

[3] The factor 0.2390 has been used in converting the joule to the 15° calorie.

TABLE I (*Concluded*)

Liquid

Temp., °K.	204.1	240.1	277.1	283.2	290.4	298.0
C_p per g.	0.447	0.475	0.525	0.536	0.550	0.567

Tert-amyl Alcohol: Crystals I

Temp., °K.	92.4	97.0	103.0	107.5	115.6	122.3	129.0	135.1
C_p per g.	0.178	0.188	0.199	0.208	0.223	0.235	0.250	0.266

Crystals II

Temp., °K.	152.5	158.1	166.8	175.0	187.0	194.7
C_p per g.	0.327	0.330	0.334	0.344	0.359	0.371
Temp., °K.	207.0	212.6	214.3	222.7	229.6	242.2
C_p per g.	0.398	0.420	0.406	0.396	0.417	0.460

Liquid

Temp., °K.	275.0	281.7	288.4	294.4
C_p per g.	0.615	0.627	0.644	0.662

Isopropyl Ether: Crystals

Temp., °K.	91.7	97.6	104.0	111.5	130.3	148.4	156.4
C_p per g.	0.189	0.200	0.211	0.225	0.259	0.291	0.317

Liquid

Temp., °K.	194.5	210.8	225.3	239.9	255.6	275.2	283.3	293.1
C_p per g.	0.435	0.446	0.454	0.465	0.476	0.491	0.498	0.506

Phenol: Crystals

Temp., °K.	92.7	98.7	106.1	122.0	137.2	148.6	171.3	191.8
C_p per g.	0.129	0.134	0.139	0.151	0.162	0.172	0.191	0.209
Temp., °K.	200.4	209.3	235.8	252.7	260.0	277.1	290.3	295.8
C_p per g.	0.217	0.226	0.252	0.270	0.278	0.306	0.328	0.338

Aniline: Crystals

Temp., °K.	93.5	99.8	107.7	118.6	139.5	159.9
C_p per g.	0.128	0.133	0.141	0.152	0.172	0.195
Temp., °K.	180.3	200.2	211.3	220.2	229.1	236.3
C_p per g.	0.219	0.245	0.260	0.270	0.282	0.293

Liquid

Temp., °K.	275.7	285.8	298.2
C_p per g.	0.481	0.482	0.490

Benzoic Acid: Crystals

Temp., °K.	92.6	98.7	105.5	121.2	135.5	148.9	161.5	174.2
C_p per g.	0.120	0.125	0.130	0.141	0.151	0.160	0.169	0.179
Temp., °K.	188.0	202.5	208.7	229.1	234.6	256.1	276.6	295.1
C_p per g.	0.191	0.204	0.208	0.225	0.230	0.248	0.267	0.284

Sucrose: Crystals

Temp., °K.	93.9	101.6	109.4	117.8	126.7	137.1	152.8	170.3
C_p per g.	0.095	0.104	0.112	0.120	0.128	0.138	0.153	0.169
Temp., °K.	190.4	210.3	229.6	251.4	275.7	282.0	289.8	297.0
C_p per g.	0.188	0.207	0.226	0.247	0.272	0.279	0.287	0.295

TABLE II

FUSION DATA[a]

Substance	M. p., °K.	Heat of fusion (cal. per g.) 1st result	2d result	Mean
Ethyl acetate	189.3	28.41	28.45	28.43
n-Amyl alcohol	194.2	26.65	...	26.65
Tert-amyl alcohol	264.0	11.90	12.26	12.08
Isopropyl ether	186.3	25.80	25.79	25.79
Aniline	266.8	27.09	...	27.09

[a] In the calculation of these fusion values, the marked rise in the specific heat of the crystals as the melting point is approached was attributed to premelting; and the heat absorbed in this region in excess of that obtained by extrapolation of the specific heat data at lower temperatures was added to the heat absorbed at the melting point.

For comparison with these values the literature[4] contains only very meager data. Our present specific heat curve for urea falls about 20% below that of Gibson, Latimer and Parks,[5] who used a calorimeter which was poorly adapted to determinations on a solid material; but, on the other hand, Magie's value for urea at 20° is still 11% below our present curve. The specific heat result for liquid ethyl acetate reported by Timofejew at 20° lies 4.0% above the curve for our data; while Saphir's recent value for the heat of fusion (25.9 cal./g.) is 8.8% lower than our mean result. For liquid *n*-amyl alcohol Battelli's two values at −10 and −49° come 4.0 and 1.3%, respectively, below our curve for this substance. The single result of Fife and Reid for isopropyl ether at 22° is 3.6% higher than our present data. For phenol and sucrose Magie's specific heats at 20° are 69 and 3.3% above our present curves; evidently his result for phenol is considerably affected by premelting. The value of Andrews, Lynn and Johnston for benzoic acid at 25° is about 5.7% above our curve. In the case of liquid aniline, the tables give specific heat values obtained by Bartoli at 20°, by Griffiths at 15°, and by Timofejew at 20°. These differ from our curve by +2.6, +6.2 and +1.0%, respectively. Our present fusion value for this compound is 28% higher than that (20.95 cal./g.) reported by de Forcrand.

Tert-amyl alcohol was found to exist in two crystalline forms with a fairly definite transition temperature at 146.0°K. Two separate measurements of the heat of transition, carried out by the same procedure used in the fusion determinations, yielded the identical result of 5.32 cal. per g. In the case of the high temperature form a small maximum or "hump" was also observed in the neighborhood of 213°K. This hump rises about 8% above the regular specific heat values and corresponds to an energy effect of 0.45 cal. per g. or 40 cal. per mol.

Similarly with *n*-amyl alcohol a small hump, corresponding to 0.13 cal.

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(4) (a) Landolt-Börnstein-Roth-Scheel, "Tabellen," Julius Springer, Berlin, 1923, pp. 1265-1274 and 1471-1474; (b) 1st Ergänzungsband, 1927, pp. 692-696 and 801-803; (c) 2d Ergänzungsband, 1931, pp. 1194-1215 and 1480-1482.

(5) Gibson, Latimer and Parks, THIS JOURNAL, **42**, 1533 (1920).

per g., was discovered at about 128°K. Above 130° the specific heats lie on a straight line which is about 4.0% higher than an extension of the specific heat curve at lower temperatures. This fact suggests that possibly a small portion of our supposedly crystalline sample was really in the form of a glass at the lowest temperatures.

Discussion

Entropies of the Compounds.—Using the data contained in Tables I and II in conjunction with the third law of thermodynamics, we have calculated the molal entropies at 298.1°K. for the various compounds. In these calculations we have employed the extrapolation method of Kelley, Parks and Huffman[6] for estimating the entropy increase for the crystals, Col. 2 of Table III, from 0 to 90°K. The various entropy increments from 90 to 298.1°K., which appear in Cols. 3, 4 and 5 of the table, were obtained by the usual methods directly from the experimental data. The results for the total entropy in calories per degree appear under the heading "S_{298} experimental" in the sixth column. In the cases of phenol and benzoic acid, compounds which are normally crystalline at 298°K., it has seemed desirable for purposes of comparison to have values for the entropy of the liquid, even though the liquid state is unstable at this temperature. Accordingly we have calculated roughly their entropies of fusion at 298° by the method previously employed by Huffman, Parks and Daniels.[7] In this connection we have used the value obtained by Stratton and Partington[4a] for the heat of fusion of phenol and that of Andrews, Lynn and Johnston[4b] for benzoic acid.

TABLE III

ENTROPIES OF THE COMPOUNDS PER MOLE

Substance	Crystals 0–90°K.	Crystals Above 90°K.	Fusion	Liquid	S_{298} exptl.	S_{298} predicted
Urea	7.93	17.25	...	...	25.2	24.8
Glycine	7.55	18.57	...	...	26.1	29.6
Ethyl acetate	15.01	15.96	13.23	17.77	62.0	61.3
n-Amyl alcohol	13.78	16.81	12.06	18.28	60.9	62.0
Tert-amyl alcohol	11.18	32.86[a]	4.03	6.73	54.8	53.0
Isopropyl ether	14.65	19.44	14.14	22.21	70.4	67.2
Phenol (solid)	11.72	22.36	...	...	34.1	35.0
Phenol (liquid)	...	...	8.57	...	42.6	44.5
Aniline	10.82	20.57	9.46	4.95	45.8	44.5
Benzoic acid (solid)	14.16	26.63	...	...	40.8	40.8
Benzoic acid (liquid)	...	...	8.77	...	49.6	52.2
Sucrose	22.06	64.05	...	...	86.1	...

[a] This value includes the entropy increase for both crystalline forms as well as the entropy effect (3.22 E. U.) for the transition between them at 146°K.

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(6) Kelley, Parks and Huffman, *J. Phys. Chem.*, **33**, 1802 (1929).

(7) Huffman, Parks and Daniels, THIS JOURNAL, **52**, 1547 (1930).

From a consideration of the data available for one hundred and twenty organic compounds Parks and Huffman[8] have derived empirical values for the changes in molal entropy accompanying various structural modifications at 298.1°K. Thus, for example, for a compound in the liquid state they assign 25.0 E. U. as the fundamental or *basic* molal entropy, 19.5 for the effect of a phenyl group, and 7.7 for the substitution of COOH for H to form a carboxylic acid. Hence, for liquid benzoic acid $S_{298} = 25.0 + 19.5 + 7.7 = 52.2$ E. U., a result which is in fairly good agreement with the "experimental" value of 49.6 E. U. In a similar fashion the various values of "S_{298} predicted" (given in the last column of Table III) have been obtained for all the substances except sucrose.[9] On the average, these predictions differ from the experimental entropies by only 3.7% or 1.6 E. U.; and in no case is the numerical magnitude of the discrepancy greater than 3.5 E. U., an amount corresponding to 1000 calories in the resulting free energy calculations.

The Free Energies of Nine Compounds.—We have also calculated the free energies of nine of these compounds by means of the third law of thermodynamics and the fundamental equation, $\Delta F = \Delta H - T\Delta S$. The absence of a combustion value for isopropyl ether precludes such a calculation in its case at the present time.

The essential data are given in Table IV. For obtaining the ΔH of formation of urea we have used the heat of combustion selected by Kharasch;[10] and for *n*-amyl alcohol we have employed the experimental value of Verkade and Coops.[11] For ethyl acetate primary reliance has been placed upon the recent result of Roth,[12] which is in fairly good agreement with

Table IV

Thermal Data at 298.1°K.

The 15° cal. is used throughout and all weights have been reduced to a vacuum basis

Substance	Heat of combustion at constant pressure	ΔH_{298}, cal.	ΔS_{298}, E.U.	ΔF°_{298}, cal.
Urea (s)	151,500	− 79,360	−108.9	− 46,900
Glycine (s)	233,800	−125,460	−126.5	− 87,800
Ethyl acetate (l)	538,000	−112,200	−117.2	− 77,300
n-Amyl alcohol (l)	795,000	− 86,060	−157.5	− 39,100
Tert-amyl alcohol (l)	784,600	− 96,460	−163.6	− 47,700
Phenol (s)	732,000	− 38,370	− 91.9	− 11,000
Aniline (l)	811,860	+ 7,340	− 94.2	+ 35,400
Benzoic acid (s)	771,400	− 93,210	−111.0	− 60,100
Sucrose (s)	1,348,900	−533,400	−542.7	−371,600

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[8] Parks and Huffman, "The Free Energies of Some Organic Compounds," The Chemical Catalog Co., New York, 1932, p. 209.

[9] The inadequacy of the available entropy data pertaining to five- and six-membered rings containing oxygen and the rather hypothetical character of the proposed constitutional formula of Haworth make any prediction in the case of sucrose quite uncertain at the present time.

[10] Kharasch, *Bur. Standards J. Research*, **2**, 406 (1929).

[11] Verkade and Coops, *Rec. trav. chim.*, **46**, 910 (1927).

[12] Reference 4b, p. 876.

Thomsen's very early value. In the cases of the remaining six compounds we have taken the heats of combustion as given in the "International Critical Tables."[13] For our present purposes we have converted all these combustion data to 298.1°K. The ΔH_{298} values were then calculated by use of 68,310[14] and 94,240[15] cal. for the heats of combustion of hydrogen and graphitic carbon, respectively.

Column 4 contains the entropy of formation of each compound, which is simply the difference between its S_{298} and the corresponding values for the entropies of the elements contained therein. For this purpose we have used the following atomic entropies: C(graph.), 1.3; $^1/_2H_2$, 15.615; $^1/_2O_2$, 24.52; and $^1/_2N_2$, 22.89 E. U.[16]

The molal free energies appear in the last column of the table. For the most part the accuracy of these values is largely limited by the accuracy of the combustion data employed. In the cases of urea, glycine, *n*-amyl alcohol and benzoic acid the error in the free energy is probably less than 1000 cal.; for ethyl acetate, phenol, aniline and sucrose it may be somewhat larger, but even here it is probably within 2000 cal. In the case of *tert*-amyl alcohol, however, the uncertainty in ΔF°_{298} is undoubtedly as great as 3000 cal., since the heat of combustion of this substance was determined by Zubow in 1899 when thermochemical technique and standards had not attained to the precision of the present day.

A Test of the Third Law of Thermodynamics.—The free energy of formation of urea which has just been obtained in Table IV by means of the third law of thermodynamics is in excellent agreement with an entirely independent value obtained from equilibrium measurements.

Lewis and Burrows[17] in a classical investigation of the equilibria in the reversible synthesis of urea found $\Delta F^\circ_{298} = 290$ for the reaction

$$CO_2(g) + 2NH_3(g) = H_2O(g) + CO(NH_2)_2(s)$$

If this free energy value is now combined with the following data for the formation of water, carbon dioxide and ammonia

$$H_2 + {}^1/_2O_2 = H_2O(g);\quad \Delta F^\circ_{298} = -54{,}507^{18}$$
$$C(\text{graph.}) + O_2 = CO_2(g);\quad \Delta F^\circ_{298} = -94{,}100^{19}$$
$$^1/_2N_2 + {}^3/_2H_2 = NH_3(g);\quad \Delta F^\circ_{298} = -3{,}910^{18}$$

we can obtain

$$C(\text{graph.}) + 2H_2 + N_2 + {}^1/_2O_2 = CO(NH_2)_2(s);\quad \Delta F^\circ_{298} = -47{,}120$$

This result is only 220 calories lower than our present third law value.

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[13] "International Critical Tables," Vol. V, p. 163.

[14] Rossini, *Bur. Standards J. Research*, **2**, 373 (1929).

[15] Roth and Naeser, *Z. Elektrochem.*, **31**, 461 (1925). We here have reduced their value to a vacuum basis.

[16] Reference 8, p. 46.

[17] Lewis and Burrows, THIS JOURNAL, **34**, 1515 (1912).

[18] Lewis and Randall, "Thermodynamics," McGraw-Hill Book Co., New York, 1923, pp. 485 and 557.

[19] Ref. 8, p. 49.

Before concluding, the authors wish to thank the Standard Oil Development Company for the samples of *n*-amyl alcohol, *tert*-amyl alcohol and isopropyl ether used in this investigation.

Summary

1. The specific heats of ten organic compounds containing oxygen or nitrogen have been measured over a wide range of temperatures. Heats of fusion and of transition have also been determined in five cases.

2. The entropies of the ten compounds have been calculated from these heat capacity data. In general, the results are in good agreement with the corresponding values predicted by the use of some empirical entropy regularities.

3. The corresponding free energies for nine of these compounds have also been calculated. The result in the case of urea provides an excellent check upon the third law of thermodynamics.

STANFORD UNIVERSITY, CALIFORNIA

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Indium Sulfate

BY RALPH P. SEWARD

The only sulfates of indium, with the exception of the alums and other double salts, discussed by Mellor[1] are the acid salt $In_2SO_4 \cdot H_2SO_4 \cdot 8H_2O$ attributed to R. E. Meyer[2] and $In_2(SO_4)_3 \cdot 9H_2O$ prepared by C. Winkler[3] by evaporation of indium sulfate solution to dryness at 100°. The observations reported here are in substantial agreement with those of R. E. Meyer but not with those of C. Winkler. Some additional data on the properties of indium sulfate have been secured.

The source of indium for the work was "99.99" pure metallic indium obtained from the Grasselli Company. A sulfate solution was first prepared by the addition of sulfuric acid in slight excess to a suspension of indium hydroxide. On concentration a thick sirup formed from which crystals were secured with some difficulty. Analysis of the product showed the presence of 1.8 moles of sulfate per atom of indium. Since it appeared that the material might be a mixture, the effect of changing the amount of free sulfuric acid was investigated.

Indium Acid Sulfate.—When indium sulfate solution containing a large excess of sulfuric acid was concentrated at about 50°, crystallization occurred readily. After washing with acetic acid and drying, the product was analyzed for indium by precipita-

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[1] J. W. Mellor, "Comprehensive Treatise," Vol. V, p. 404.

[2] R. E. Meyer, "Das Indium," Leipzig, 1868.

[3] C. Winkler, *J. prakt. Chem.*, [1] **102**, 373 (1867).