always as small as might be expected from the feebleness of chemical union usually attributed to such compounds. If the rather gross assumption is made that the difference of molar heats of reactants and products remains constant down to absolute zero, then the resulting heats of formation at absolute zero are also the free energies of formation at that temperature. These quantities stand in the relation: 33 : 19 : 16 : 1 for the compounds in the order treated. In agreement with this order, it is found that the compound phenol : urea is by no means completely dissociated in aqueous solution, while salicylic acid : acetamide is. On the other hand the compounds of phenol and *p*-toluidine and of β-naphthylamine and *p*-nitrosodimethylaniline are also completely dissociated in solution. Dissociation in solution, however, is governed by other factors than free energy of formation; neither is it certain that the order of the free energies of formation at absolute zero remains quantitatively or even qualitatively the same at room temperature. The assumption also that the difference $C_{\text{products}} - C_{\text{reactants}}$ remains constant down to the neighborhood of absolute zero is certainly incorrect, so that the values obtained can only be considered crude approximations. Exact calculations can be made by means of the Nernst heat theorem, but this requires an exact knowledge of the behavior of the specific heats between absolute zero and room temperature.

The determination of equilibrium diagrams in the presence of a solvent was only experimentally possible for the systems phenol–urea–water, and salicylic acid–acetamide–water. In the former case the equilibrium solid phase over a large portion of the diagram is the double compound, while in the latter the double compound is still the stable solid phase over a fairly extensive branch of the diagram. Here, again, there is no direct connection between the heat of formation, or free energy of formation, and the portion of the diagram occupied by double compound, other factors, such as solubility, entering in.

Summary

1. The object of this paper is to obtain some measure of the energy change involved in the formation of organic addition compounds.
2. Using the systems phenol–urea, phenol–*p*-toluidine, β-naphthylamine–*p*-nitrosodimethylaniline, and salicylic acid–acetamide, experimental determinations have been made, both for reactants and products, of heat of solution, specific heat, and solubility diagram (in the case of two systems only).
3. The heats of formation at room temperature and at absolute zero, have been calculated, the latter approximately only.
4. The equilibrium diagrams for the systems phenol–urea–water and salicylic acid–acetamide–water at 20°, have been outlined. In both cases the molecular compound is stable at room temperature.

WINNIPEG, MANITOBA RECEIVED JULY 31, 1939

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

Thermal Data XI. The Heat Capacities and Entropies of Guanidine Carbonate, Glutamic Acid Hydrochloride, Ornithine Dihydrochloride, *d*-Lactic Acid and *l*-Lactic Acid

BY HUGH M. HUFFMAN, EMORY L. ELLIS AND HENRY BORSOOK

In this paper we present the low temperature heat capacity data for the salts of three nitrogen containing organic compounds and the two optically active forms of lactic acid. These data have been utilized in conjunction with an empirical extrapolation formula to calculate the entropies of these compounds at 298.1°K.

Experimental

In principle the method of Nernst was employed with an aneroid calorimeter to determine the "true" specific heat. The details of the method have been described elsewhere[1] so that only a brief account need be given. In brief it consists of supplying, electrically, a measured amount of energy to the gold calorimeter containing the substance under investigation. To ensure rapid attainment of 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

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(1) Parks, THIS JOURNAL, **47**, 338 (1925).

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.[2]

The guanidine carbonate was an Eastman Kodak Co. product and was used without further purification. Titrations indicated that it was better than 99.8% pure. The ash content was less than 0.1%.

The *d*-glutamic acid hydrochloride was prepared from the glutamic acid used in the investigation of Huffman and Borsook.[3] Titrations indicated that it was better than 99.8% converted to the hydrochloride.

The ornithine dihydrochloride was a commercial product obtained from Hoffman–LaRoche and used without further purification. The stability of the hydrochloride was tested by placing a weighed sample *in vacuo* over phosphorus pentoxide and calcium oxide. The loss observed in twenty-four hours under the above conditions was about 0.01%. The chlorine content, determined volumetrically, was 99.7% of the theoretical. Micro-kjeldahl nitrogen determinations gave 98.8% of the theoretical.

The lactic acids were prepared from commercial lactic acid sirups according to the method of Borsook, Huffman and Liu.[4] Titrations showed that these preparations were better than 99.7% pure.

Discussion

The results of the heat capacity measurements in terms of the defined conventional calorie appear in Table I. In view of the purity of the compounds and the accuracy of the measurements involved, we estimate the absolute error as less than 1% except in the case of ornithine dihydrochloride.

The data for all of these compounds with the exception of those for ornithine dihydrochloride lie on smooth curves. The curve for this substance shows two humps which correspond to the melting and boiling points of hydrochloric acid and hence may indicate that a small amount of free hydrochloric acid was present. If this is the case we have estimated, from the curve, that 0.04% of hydrochloric acid would account for the humps.

TABLE I

SPECIFIC HEAT PER GRAM OF SUBSTANCE

T, °K.	C_p	T, °K.	C_p	T, °K.	C_p
Guanidine carbonate, crystals					
85.6	0.1381	180.0	0.2290	262.4	0.3073
89.5	.1438	200.2	.2488	266.8	.3113
94.1	.1477	220.2	.2679	274.3	.3187
99.9	.1532	240.2	.2866	275.3	.3208
110.0	.1633	244.3	.2905	276.2	.3213
120.0	.1732	250.0	.2962	279.4	.3256
135.6	.1871	255.9	.3015	284.9	.3306
150.2	.2007	259.8	.3050	291.4	.3378
165.5	.2153	261.1	.3067	298.1	.3434
d-Glutamic acid hydrochloride, crystals					
85.1	0.1165	151.0	0.1720	275.7	0.2572
90.5	.1215	170.5	.1856	282.7	.2620
97.3	.1282	190.4	.1998	289.8	.2671
109.3	.1390	210.9	.2134	296.8	.2714
120.0	.1480	231.0	.2262		
134.8	.1595	252.5	.2408		
Ornithine dihydrochloride, crystals					
85.3	0.1223	130.5	0.1700	187.9	0.2313
86.2	.1234	139.7	.1784	191.8	.2181
89.2	.1273	145.2	.1836	195.2	.2162
90.8	.1296	149.3	.1874	200.2	.2176
96.0	.1345	153.5	.1921	200.3	.2177
101.2	.1410	159.6	.1985	220.0	.2284
101.5	.1412	164.8	.2007	241.4	.2418
107.0	.1467	170.1	.2053	260.3	.2542
107.3	.1463	174.6	.2103	275.1	.2653
112.9	.1525	179.7	.2179	276.2	.2661
117.7	.1572	179.8	.2184	279.6	.2686
119.8	.1595	184.0	.2250	286.0	.2727
				292.8	.2778
d(*l*+)-Lactic acid, crystals					
84.2	0.1334	167.7	0.2168	275.7	0.3145
89.6	.1400	180.2	.2279	283.0	.3219
96.0	.1471	193.9	.2405	290.0	.3294
103.5	.1547	206.7	.2523	290.1	.3292
112.6	.1646	219.6	.2642	297.7	.3379
123.5	.1756	231.4	.2747	298.2	.3387
136.3	.1878	243.4	.2854	304.9	.3490
148.0	.1985	254.8	.2958	311.2	.3607
157.2	.2073	266.2	.3061		
l(*d*-)-Lactic acid, crystals					
84.1	0.1328	149.5	0.1997	277.2	0.3152
89.6	.1390	179.5	.2262	282.9	.3217
96.2	.1460	201.7	.2459	290.2	.3307
110.6	.1621	230.1	.2719	297.9	.3411
129.8	.1808	259.5	.2988		

We have determined the entropies of these compounds between 90 and 298.1°K. by graphical integration of a plot of C_p against ln T. In the case of ornithine dihydrochloride we have drawn a smooth curve between 140 and 200°K. The entropy between the experimental curve and the smooth curve was found to be 0.15 entropy unit per mole. If the humps are not characteristic of the substance, we estimate that the total error should not exceed 0.3 entropy unit per mole. The entropy at 90° was obtained by use of the extrapolation formula of Parks, Kelley and Huffman[5] for aliphatic substances (class I). The

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[2] Giauque, Johnston and Kelley, THIS JOURNAL, **49**, 2367 (1927).

[3] Huffman and Borsook, *ibid.*, **54**, 4297 (1932).

[4] Borsook, Huffman and Liu, *J. Biol. Chem.*, **102**, 449 (1933).

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

entropies thus calculated are given in Table II. Here we estimate that the uncertainty in the experimentally determined part should in all cases be less than 1%. For the extrapolated portion of the entropy it is impossible to make a reliable estimate of the uncertainty, especially in the case of the salts.

In addition to the data given above, we have made one determination of the heat of fusion of *d*(*l*+)-lactic acid. As is well known, this compound is not stable, showing a decided tendency to form a lactone and an anhydride with the elimination of water. For this reason the fusion was not very sharp; furthermore, having once been fused it was impossible, in the calorimeter, to obtain it again in the completely crystalline state. Nevertheless we believe it to be of some interest to present this preliminary value of the heat of fusion, which was found to be 4030 calories per mole.

TABLE II

ENTROPIES OF THE COMPOUNDS PER MOLE IN CAL. DEGREE^{-1} MOLE^{-1}

Substance	S_{90}	$\Delta S_{90-298.1}$	$S_{298.1}$
Guanidine carbonate	22.31	48.28	70.59
Glutamic acid hydrochloride	18.39	40.94	59.33
Ornithine dihydrochloride	21.31	48.94	70.25
d(*l*+)-Lactic acid	10.43	23.87	34.30
l(*d*−)-Lactic acid	10.26	23.75	34.00

Summary

1. The heat capacity data between 90 and 298.1°K. for five organic compounds have been presented.
2. The entropies of these five compounds at 298.1°K. have been calculated.
3. A preliminary value for the heat of fusion of *d*(*l*+)-lactic acid has been given.

PASADENA, CALIFORNIA RECEIVED DECEMBER 4, 1939

[CONTRIBUTION FROM THE DEPARTMENT OF METALLURGY, MASSACHUSETTS INSTITUTE OF TECHNOLOGY]

The Equilibrium FeO + H_2 = Fe + H_2O at Temperatures up to the Melting Point of Iron

BY JOHN CHIPMAN AND SHADBURN MARSHALL

Equilibria of iron and its lowest oxide with a gas phase containing steam and hydrogen or carbon dioxide and monoxide have been of interest in connection with the reduction of iron ore, the scaling of steel at high temperatures, the behavior of iron catalysts, and the establishment of the water gas equilibrium. Several careful researches on these equilibria have established the free energy of the lowest oxide in the form which occurs in equilibrium with solid iron at temperatures up to about 1360°. Reviews of the literature on this field were included in the papers of Emmett and Shultz[1] and of Chipman and Murphy[2] and need not be repeated here. One noteworthy paper has appeared more recently in which Britzke, Kapustinsky and Schaschkina[3] report measurements extending up to 1225°.

On account of the importance of ferrous oxide in many metallurgical reactions, a determination of its free energy at higher temperatures was undertaken. The plan of this investigation was to establish the equilibrium conditions involving steam, hydrogen, solid iron and liquid oxide over a sufficient range to permit extrapolation to the melting point of iron. At the same time a redetermination below the melting point of the oxide served as a useful check on existing data.

Experimental Method

A weight change method was adopted for the important reason that it permitted a minimum contact of the iron specimen with its support and hence a minimum contamination of either the metallic or non-metallic phase. It proved admirably suited to the problem at high temperatures where the reaction rate was rapid. As shown in Fig. 1 the specimen K was suspended from a balance A mounted directly over the tubular furnace. Commercial hydrogen was passed over platinized asbestos E at 400°, thence through a water saturator C maintained at a controlled temperature in a well-stirred oil-bath and the steam–hydrogen mixture was delivered to the bottom of the furnace. With the furnace at constant temperature, the saturator temperature was adjusted to create a gain or loss in the weight of the specimen, which, when both phases were present in the specimen, indicated respectively oxidizing and reducing conditions. When the saturator temperature was changed slowly and uniformly, it was

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[1] Emmett and Shultz, THIS JOURNAL, **52**, 4268 (1930); **54**, 3780 (1932).

[2] Chipman and Murphy, *Ind. Eng. Chem.*, **25**, 319 (1933).

[3] Britzke, Kapustinsky and Schaschkina, *Z. anorg. allgem. Chem.*, **219**, 287 (1934).