From these data were calculated the apparent and partial molal heat capacities of the solute and the partial molal heat capacity of the water.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, OREGON STATE COLLEGE]

Studies on Hydrazine: Heats of Solution of Hydrazonium Salts at 25°

BY E. C. GILBERT AND ALAN W. COBB

Continuing the investigation of the thermodynamic properties of hydrazine and its salts this paper presents the determination of the total and partial molal heat of solution of hydrazonium dichloride, monochloride, monoperchlorate hemihydrate, anhydrous monoperchlorate, and the monobromide, together with the relative partial molal heat content of the solvent, water. The determinations on the two forms of the perchlorate permit a check to be made on the heat of hydration, for comparison with the result recently obtained in this Laboratory by vapor pressure measurements.[1]

The heats of solution of the monochloride and dichloride have been measured by Bach,[2] at two concentrations. Unfortunately these measurements were made at fortuitous temperatures and only small amounts of material were available. In the interests of completeness new determinations were made, with the advantage of improved technique and, it is believed, with purer materials.

Experimental

Apparatus.—The calorimeter has been described recently.[3] It was modified for this work by the introduction of a thin glass pipet shown in Fig. 1. The pipet had a capacity of 50 cc. The mushroom head of the glass rod B fitted closely into a ground joint at C, and was sealed there with a film of beeswax. The pipet was held closely in a rubber lined chimney in the lid of the submarine vessel in such a position that all the salt was below the level of solution in the inner can. By careful regulation of the opening at C the mixing of the salt and solution could be made to take place with almost any desired slowness, thus aiding in the maintenance of adiabatic conditions. The addition of the pipet changed the heat capacity of the calorimeter. Calculation from the weight of material showed it should be 113.6 joules/degree instead of the former value, 97.0. Two experimental determinations gave 112.0 and 118.5. The apparatus was otherwise unchanged.

Heat Leakage.—From the nature of the operation it was impossible to regulate the temperature differential between inner and outer bath as closely as in the previous work on specific heats, so the heat leakage was tested. For a considerable time period the outer bath was maintained at a temperature 0.02° higher than the inner temperature. A uniform temperature rise of 0.0001° per minute (corrected for heat of stirring) was observed in the inner can. This corresponds to 0.005° minute^{-1} degree^{-1} of thermal head. In actual runs the thermal head never amounted to more than a fraction of the 0.02° used in the test.

Procedure.—A portion of salt was placed in the dry pipet, weighed, and the apparatus assembled with water or a known solution in the inner can. All weights were reduced to vacuum. The temperature was now adjusted to 25 ± 0.01° under adiabatic conditions and time allowed for all parts to come to this temperature. The ground joint C was then opened by twisting or a slight shock and the salt allowed to mix slowly with the solution or water. The pipet was then opened fully at the last. The opening was so related to the stirrer that thorough mixing and equalization of salt concentration was effected within the time allotted to the experiment. In every case a cooling effect was found, in some instances so pronounced that finely mushed ice was added to assist in cooling the outer bath. Temperature readings were taken with all the precautions observed in the previous work.

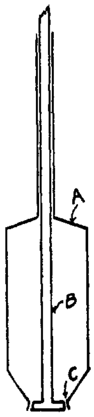

Fig. 1.—Pipet for introduction of salt into calorimeter.

The solution obtained in the first experiment was used as the starting point for the next, instead of water. The concentration gradually increased up to approximately 1 molal at which point the solution was analyzed as a check on the weighing procedure, evaporated for the recovery of the salt and the process repeated. In this way no attempt was made to prepare exact duplicates, though several independent runs were made at the lower concentrations.

Materials.—Special precautions were taken to obtain the salts in pure, dry condition. The dichloride was the Eastman product recrystallized from water and dried over potassium hydroxide. The other salts were prepared by reaction of the pure components, followed by repeated recrystallization from 80% methanol. The anhydrous monoperchlorate was dried over phosphorus pentoxide. The monochloride and bromide were dried over sulfuric acid. All were analyzed for hydrazine content and found to be pure within the limits of the analysis. The monochloride melted at 91.4° and the monobromide at 84.5°

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[1] Christensen and Gilbert, THIS JOURNAL, **56**, 1897 (1934).

[2] R. Bach, *Z. physik. Chem.*, **9**, 241 (1892).

[3] Cobb and Gilbert, THIS JOURNAL, **56**, 35 (1934).

instead of 89° and 80° as previously recorded in the literature, and represent, it is believed, purer products than those used by other investigators.[4]

Results and Calculations

The trustworthiness of the apparatus was tested by a single measurement of the heat of solution of sodium chloride at 20°. Comparison with the work of Lipsett, Johnson and Maass[5] showed agreement closer than 0.2%.

Experimental results are shown in Table I. In making calculations the necessary specific heats were taken from a previous paper.[3] All results are given in 15° calories using the factor 4.1833 for the conversion of international joules to calories, as in the work on specific heats.

TABLE I

HEATS OF SOLUTION AT 25° (IN 15° CAL.)

Molality Initial m_1	Molality Final m_2	Heat per mole of salt dissolved	Total molal heat of solution at m_2
	Hydrazonium Dichloride		
0.00	0.1134	6035	6035
.00	.1706	6022	6022
.00	.2820	5999	5999
.1706	.4355	5822	5901
.2820	.5579	5685	5843
.4355	.7272	5510	5744
.5579	.8251	5408	5702
.7272	.9856	5245	5613
	Hydrazonium Monochloride		
0.00	0.1527	5213	5213
.00	.2911	5217	5217
.00	.2341	5217	5217
.3411	.5169	5197	5207
.2341	.5462	5189	5201
.5169	.7609	5138	5185
.5462	.7733	5142	5183
.7609	.9775	5108	5168
	Hydrazonium Monobromide		
0.00	0.1089	6371	6371
.00	.2044	6368	6368
.2044	.4773	6271	6313
.4773	.7290	6149	6256
.7290	1.0240	6020	6188
	Hydrazonium Perchlorate Hemihydrate		
0.00	0.0834	11160	11160
.00	.0836	11180	11180
.0836	.3068	10858	10946
.0834	.3099	10840	10926
.3068	.5545	10393	10700
.3099	.5563	10375	10682
	Hydrazonium Perchlorate (Anhydrous)		
0.00	0.0935	9261	9261
.00	.0971	9238	9238

The molalities of the perchlorate are expressed in every case as moles of anhydrous salt in 1000 g. of water in the resulting solution.

Column 1 represents the molality of the solution to which the salt was added, Col. 2 the molality of the resulting solution. In Col. 3 is given the experimental quantity of heat absorbed, calculated on the basis of one mole of salt, *i. e.*, when one mole of salt is added to a sufficient quantity of solution whose molality is m_1 to give a molality m_2. When $m_1 = 0$ the heat absorbed by the addition of one mole of salt to sufficient water to make the molality m_2 is ΔH the total molal heat of solution given in Col. 4. This observed molal heat of solution is related to the partial molal quantities, using the nomenclature of Lewis and Randall[6] by the expression

$$\Delta H = [\overline{H}_2 - H_2\,(\text{solid})] + n_1/n_2\,(\overline{H}_1 - \overline{H}_1^0) \quad \text{(Eq. 1)}$$

Likewise

$$\Delta H = \Phi_h - H_2\,(\text{solid}) \quad \text{(Eq. 2)}$$

where Φ_h represents the apparent molal heat content of the solute. The present apparatus is unsuited for the exact evaluation of $\overline{H}_2$ but the total quantity $[\overline{H}_2 - H_2(\text{s})]$ which represents the partial molal heat of solution of the solute, and also $(\overline{H}_1 - \overline{H}_1^0)$ the relative partial molal heat content of the solvent, may readily be obtained. The relationships involved may be derived by the use of Eq. 2 together with Eq. 38 and 39 of a paper by Rossini[7] with the results

$$\overline{H}_2 - H_2\,(\text{s}) = \Delta H + {}^1/_2 m^{1/2}\,[\text{d}(\Delta H)/\text{d}m^{1/2}] \quad \text{(Eq. 3)}$$

$$\overline{H}_1 - \overline{H}_1^0 = -(m/55.508)\,[{}^1/_2 m^{1/2}\,\text{d}(\Delta H)/\text{d}m^{1/2}] \quad \text{(Eq. 4)}$$

TABLE II

PARTIAL MOLAL HEATS OF SOLUTION OF SOLUTE AND SOLVENT AT 25° IN 15° CAL.

	$N_2H_6Cl_2$		N_2H_5Cl	
Molality	$\overline{H}_2 - H_2(\text{s})$	$\overline{H}_1 - \overline{H}_1^0$	$\overline{H}_2 - H_2(\text{s})$	$\overline{H}_1 - \overline{H}_1^0$
0.1	6017	+0.0361	(5222)	−0.0272
.2	5956	.2095	5224	− .0317
.3	5839	.7401	5211	+ .0333
.5	5603	2.406	5168	.3338
.75	5359	5.101	5124	.8335
1.0	5104	9.075	5088	1.395

	N_2H_5Br		$N_2H_5ClO_4\cdot{}^1/_2H_2O$	
Molality	$\overline{H}_2 - H_2(\text{s})$	$\overline{H}_1 - \overline{H}_1^0$	$\overline{H}_2 - H_2\,(\text{s})$	$\overline{H}_1 - \overline{H}_1^0$
0.1	6372	0.0	11051	+1.880
.2	6344	+ .0846	10845	7.380
.3	6296	.2997	10619	17.60
.5	6191	1.051	10229	46.18
.75	6080	2.254	...	.....
1.0	5967	4.058	...	.....

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[4] J. W. Mellor, "Comprehensive Treatise on Inorganic and Theoretical Chemistry," Longmans, Green and Co., New York, Vol. VIII, pp. 323–324.

[5] Lipsett, Johnson and Maass, THIS JOURNAL, **49**, 1940 (1927).

[6] Lewis and Randall, "Thermodynamics," McGraw-Hill Book Co., Inc., New York, 1923.

[7] Rossini, *Bur. Standards J. Research*, **6**, 791 (1931).

Table II gives the values calculated by means of Eq. 3 and Eq. 4 for the four salts.

From the difference in the heat of solution of the monoperchlorate in the hydrated and anhydrous forms the heat of hydration may be obtained. Using graphical means, since the molalities were slightly different in the two cases, the heat of hydration was found to be

$$N_2H_5ClO_4(s) + {}^1/_2H_2O\ (liq.) = N_2H_5ClO_4 \cdot {}^1/_2H_2O(s) \quad \Delta H_{298} = -1913 \pm 20 \text{ cal.}$$

From the dissociation pressure of the hydrate Christensen and Gilbert obtained[1,8]

$$N_2H_5ClO_4(s) + {}^1/_2H_2O(g) = N_2H_5ClO_4 \cdot {}^1/_2H_2O(s) \quad \Delta H_{298} = -6977 \text{ cal.}$$

Utilizing the heat of vaporization of water at 25° $\Delta H = +10{,}504$ cal./mole.[9]

$${}^1/_2H_2O(liq.) = {}^1/_2H_2O(g);\ \Delta H_{298} = +5252 \text{ cal.}$$

and adding the two expressions

$$N_2H_5ClO_4(s) + {}^1/_2H_2O(liq.) = N_2H_5ClO_4 \cdot {}^1/_2H_2O(s) \quad \Delta H_{298} = -1725 \text{ cal.}$$

This is considered reasonable agreement in view of the probable experimental error and the simplifying assumptions made in applying the Clausius–Clapeyron equation to the dissociation of the salt hydrate.

The authors wish to express their indebtedness to the National Research Council and to the General Research Council of this College for grants which made this work possible.

Summary

New data are reported on the heats of solution in water at 25° of hydrazonium dichloride, monochloride and monobromide from 0.1 to 1.0 molal, of the perchlorate hemihydrate from 0.1 to 0.6 molal, and of the anhydrous perchlorate at 0.1 molal.

From these are computed values of the partial molal heat of solution of the solvent and the solute.

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[8] Attention should be called to the fact that the heats of dehydration calculated by Christensen and Gilbert are reported as calories *per mole of water vapor* formed. For a salt containing one-half molecule of water like the perchlorate the reported value should be divided by two, while for the dibromide with two molecules of water the reported value should be multiplied by two to obtain values *per mole of salt*.

[9] Osborne, Stimson, Fiock and Ginnings, *Bur. Standards J. Research*, **10**, 155 (1933).

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

Thermal Data. II. The Heats of Combustion of *l*-Cysteine, of *l*-Cystine, β-Thiolactic Acid and β,β'-Dithiodilactic Acid

BY HUGH M. HUFFMAN AND EMORY L. ELLIS

In determinations of the free energies of organic compounds by means of the third law of thermodynamics and the fundamental thermodynamic equation $\Delta F = \Delta H - T\Delta S$, accurate values for the heats of combustion are required. At present these values are often unavailable or unreliable. We have therefore undertaken the task of determining the required data with relatively high accuracy.

In this paper we present a description of the method and apparatus used, data on its calibration, data on the auxiliary substances required, and the values of the heats of combustion of four compounds.

Method and Apparatus

Since all of the compounds we expect to burn are either solid or liquid, we have chosen the "bomb calorimeter" method. Two methods are in common use with a calorimeter of this type, the "ordinary" and the "adiabatic." We have adopted the first in which the rise in temperature of the calorimeter is observed while that of the jacket is kept constant. The two methods have been shown to have the same accuracy.[1]

The calorimeter system was essentially that of Dickinson.[1a] It was so arranged that the calorimeter was completely surrounded by a well-stirred water-bath kept constant to within ±0.002°. The water in the calorimeter was stirred by a propeller driven by a constant speed motor at 380 r. p. m. This rate was found to be adequate and introduced a not too large amount of mechanical energy. To prevent evaporation from the calorimeter, the stirrer, thermometer, and electrical leads were brought in through water-tight seals. To minimize transfer of energy between the calorimeter and the room all external leads to the calorimeter were first brought into good thermal contact with the jacket.

A "Parr bomb" having a capacity of 380 ml. was used. This was so modified that it could be made gas tight by means of a gold washer. The standard illium electrodes and crucible supports were replaced with platinum elec-

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[1] (a) Dickinson, *Bull. Bureau of Standards*, **11**, 243 (1915); (b) Schläpfer and Fioroni, *Helv. Chim. Acta*, **6**, 725 (1923); (c) White, "The Modern Calorimeter," The Chemical Catalog Co., N. Y., 1928.