weight of the components in these original mixtures could not be obtained, the wet solid phases were analyzed.

The results are given in Table I and are shown graphically in Fig. 1. The solid phases were hydrated cadmium sulfate, $3CdSO_4\cdot 8H_2O$, and hydrated lithium sulfate, $Li_2SO_4\cdot H_2O$, and no evidence of a double salt was obtained.

Table I

Compositions of Saturated Solutions and Original Mixtures

Solution		Original mixture	
$CdSO_4$, wt. %	Li_2SO_4, wt. %	$CdSO_4$, wt. %	Li_2SO_4, wt. %
42.5	0.9	63.2	0.5
40.0	2.9	62.6	1.7
36.7	6.6	61.0	3.2
29.5	12.7	59.2	6.2
29.6	12.6	57.7	8.1
29.6	12.5	43.3	22.6
29.5	12.4	41.3[a]	27.2[a]
29.6	12.5	40.6[a]	28.0[a]
29.6	12.5	31.5[a]	34.3[a]
29.7	12.4	28.4[a]	37.6[a]
26.0	13.9	15.0	45.3
15.7	17.8	7.6	52.8
9.7	20.3	4.5	54.0
2.9	23.2	1.3	56.0

[a] These are compositions of wet solid phases as found by analysis.

Summary

The solubility of hydrated cadmium sulfate in solutions containing lithium sulfate and of hydrated lithium sulfate in solutions containing cadmium sulfate have been determined. A solution containing 29.6 wt.-% $CdSO_4$ and 12.5 wt.-% of Li_2SO_4 is saturated with both salts. No evidence of a double salt was obtained.

Durham, N. C. Received August 21, 1937

[Contribution from the Department of Chemistry, Oregon State College]

Studies on Hydrazine: Heats of Solution of Hydrazine and Hydrazine Hydrate at 25°

By V. C. Bushnell,[1] Albert M. Hughes and E. C. Gilbert

Calorimetric determinations of the heat of solution of a number of hydrazonium salts and heat capacities of the solutions previously have been reported from this Laboratory.[2] In this paper are presented data on the heat of solution or dilution of the hydrate (hydrazonium hydroxide), the heat capacity of its solutions, and the heat of solution of anhydrous hydrazine, in water at 25°.

Experimental

Apparatus.—The calorimeter was essentially the same as previously used[2b] but was modified by improvement of the pipet in which the solute was held. In place of the glass pipet used in work with the salts, a new gold-plated brass one of smaller capacity was constructed. This pipet consisted of a cylinder of 12-ml. capacity the upper and lower ends of which, fixed on a metal rod passing through their centers, served as valves. They opened and closed simultaneously and their movement could be regulated closely by means of a knurled nut at the upper end of the bakelite tube which served as the support for the pipet in the chimney of the submarine lid. The calorimeter constant, by reason of these changes, became 108 joules per degree, in good agreement with that calculated from the weight of the new parts.

Materials.—Most of the hydrate used was a fresh Kahlbaum product, *pro analysi*, which proved by analysis to have a slight excess of hydrazine over that required for the monohydrate. It was diluted exactly to 100.0% by the addition of water and preserved in a weight buret from which the calorimeter pipet was filled. Some hydrate was prepared by the method of Hurd and Bennett.[3]

Anhydrous hydrazine was prepared by repeated refluxing and distillation of the hydrate either from potassium hydroxide or barium monoxide in an all glass apparatus, in a vacuum or with the air replaced by hydrogen; b. p. (corr.) 112.9° at 756 mm. Barium monoxide, recommended by Hale and Shetterly,[4] seemed to serve more efficiently as a dehydrating agent but there was a greater loss of material. The purity of the material was also checked by titration with standard acid, using methyl orange.

Conductivity water was used for the dilutions. It had been redistilled from a Pyrex still to ensure absence of copper ions. It was de-oxygenated by repeated saturation with hydrogen followed by boiling at reduced pressure. It was maintained under an atmosphere of hydrogen. In this way decomposition or oxidation was reduced to a minimum.

Manipulation.—Hydrazine or the hydrate was introduced into the reaction pipet from the weight buret into

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[1] This paper is taken in part from a thesis submitted by V. C. Bushnell in partial fulfilment of the requirements for the M.S. degree, Oregon State College, 1936.

[2] (a) Cobb and Gilbert, This Journal, **57**, 35 (1935); (b) Gilbert and Cobb, *ibid.*, **57**, 37 (1935); (c) Gilbert and Bushnell, *ibid.*, **57**, 2611 (1935).

[3] Hurd and Bennett, *ibid.*, **51**, 265 (1929).

[4] Hale and Shetterly, *ibid.*, **33**, 1071 (1911).

which it had been distilled, and the exact amount determined by difference. The desired amount of water was weighed out quickly and the calorimeter assembled. Hydrogen was now introduced through a chimney, replacing the air above the water inside the calorimeter, and the temperature adjusted to 25°. The rest of the operation was conducted in the usual manner, including a determination each time of the heat of stirring. Each solution was analyzed as a check to avoid errors in weighing. Solutions were made up independently for the determination of specific heats. The procedure and calculation followed methods used in the earlier work.[2a]

Results

Specific heats of aqueous solutions of hydrazine hydrate are shown in Table I, together with the apparent molal heat capacity ϕ_c, and the partial molal heat capacities for the solute and the solvent. These quantities may be calculated as shown by Rossini,[2a,5] from the relations

$$\phi_c = \phi_c{}^0 + Am^{1/2}$$
$$\overline{C}_{p2} = \overline{C}^0_{p2} + 3/2Am^{1/2}$$
$$\overline{C}_{p^1} - \overline{C}^0_{p^1} = -\frac{A}{2(55.508)}m^{1/2}$$

TABLE I

SPECIFIC HEATS OF AQUEOUS HYDRAZINE HYDRATE AT 25°

Molality	Sp. ht., cal. per g.	ϕ_c Solute, cal. per mole	$\overline{C}_{p1}$ Cal. per mole H₂O	$\overline{C}_{p2}$ Cal. per mole Solute
0.0000	0.9979	(17.5)[a]	17.978	(17.49)
.1310	.9944	22.5	17.973	24.93
.1537	.9939	22.9	17.970	25.53
.1559	.9938	23.0	17.970	25.65
.2269	.9922	24.1	17.965	27.30
.3731	.9892	25.8	17.949	29.90
.3762	.9891	25.9	17.949	30.02
.6949	.9834	29.0	17.908	34.60

[a] Extrapolated from $\phi_c - m^{1/2}$ curve.

All measurements were made at 25° but the results are given in 15° calories (one cal._{15} = 4.1833 international joules). Concentrations are expressed, except in Table IV, as molality of the hydrate, *i. e.*, the molality of a given solution is the number of moles of $N_2H_4 \cdot H_2O$ per 55.508 moles of the remaining water in the solution, thus treating the hydrate as a stable compound.

In Table II are shown the results obtained for the heats of solution of the hydrate at various concentrations (for methods of calculation see ref. 2b). The concentration has surprisingly little effect on the total molal heat of solution. For dilute solutions Bach[6] obtained a value of −1920 calories per mole as compared to −2095 cal. in the present work.[7]

TABLE II

HEATS OF SOLUTION OF HYDRAZINE HYDRATE AT 25°

Initial m_1	Final m_2	Heat absorbed per mole of hydrazine hydrate added, cal.	Total molal heat, cal. per mole $\phi_h - H_2$(liq.)
0.0000	0.1295	−2095	−2095
.0000	.1722	−2093	−2093
.1295	.3101	−2087	−2091
.1722	.3478	−2086	−2090
.3292	.4820	−2076	−2086
.3101	.5184	−2068	−2079
.3478	.5476	−2065	−2081
.4820	.6616	−2067	−2080
.5476	.7480	−2031	−2068
.6480	.8740	−2067	(−2073)

TABLE III

PARTIAL MOLAL HEATS OF DILUTION OF SOLUTE AND SOLVENT AT 25°

H_2 (liq.) refers to one mole of $N_2H_4 \cdot H_2O$ (liq.)

Molality	$\overline{H}_2 - H_2$ (liq.)	$\overline{H}_1 - \overline{H}_1$
0.0	(−2098)	0.0000
.1	−2094	− .0003
.2	−2087	− .0149
.3	−2082	− .0447
.5	−2066	− .1634
.7	−2049	− .3497

TABLE IV

HEAT OF SOLUTION OF ANHYDROUS HYDRAZINE AT 25°

Molality represents moles of anhydrous hydrazine per 55.508 moles of water

Initial m_1	Final m_2	Heat absorbed per mole of hydrazine, cal.
0.0000	0.1987	−3890
.0000	.2572	−3895

The partial molal quantities for the solute and solvent are shown for rounded concentrations in Table III.

Determination of the heat of solution of anhydrous hydrazine permits a calculation of its heat of hydration or formation of the hydrate. The data are shown in Table IV. If the concentrations are expressed as is customary for thermochemical equations, the calculation may be made as follows from Tables II and IV.

Extrapolation of the data in Table II gives the following

(1) $N_2H_4 \cdot H_2O$ (liq.) + ∞H_2O (liq.) = $(N_2H_4 \cdot \infty H_2O)$ (liq.) $\Delta H_{298} = -2098$ cal.

From Table II also

(2) $(N_2H_4 \cdot H_2O)$ (liq.) + $278H_2O$ (liq.) = $(N_2H_4 \cdot H_2O) \cdot 278H_2O$ $\Delta H_{298} = -2093$

Whence

(3) $(N_2H_4 \cdot H_2O) \cdot 278H_2O + \infty H_2O$ (liq.) = $(N_2H_4 \cdot \infty H_2O)$ (liq.) $\Delta H_{298} = -5$ cal.

Combining this with the results of Table IV

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(5) Rossini, *Bur. Standards J. Research*, **7**, 47 (1931).

(6) Bach, *Z. physik. Chem.*, **9**, 241 (1892).

(7) See also Bichowsky and Rossini, "Thermochemistry of the Chemical Substances," Reinhold Publishing Co., New York, 1936, p. 34.

$$(4)\quad N_2H_4\text{ (liq.)} + 279H_2O = (N_2H_4{\cdot}H_2O){\cdot}278H_2O \qquad \Delta H_{298} = -3890$$

one obtains

$$(5)\quad N_2H_4\text{ (liq.)} + \infty H_2O = (N_2H_4{\cdot}\infty H_2O)\text{ (liq.)} \qquad \Delta H_{298} = -3895$$

From Eqs. (1) and (5) then may be obtained the desired result

$$(6)\quad N_2H_4\text{ (liq.)} + H_2O\text{ (liq.)} = N_2H_4{\cdot}H_2O\text{ (liq.)} \qquad \Delta H_{298} = -1797\text{ cal.}$$

This work has been made possible by grants from the National Research Council, and the General Research Council of this College.

Summary

1. Specific heats for aqueous solutions of hydrazine hydrate are reported.

2. Heats of solution for the hydrate and anhydrous hydrazine have been determined.

3. The heat of hydration of anhydrous hydrazine has been calculated.

CORVALLIS, OREGON RECEIVED JUNE 23, 1937

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

Thermal Data. VII. The Heats of Combustion of Seven Amino Acids

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

In continuation of our program of determining thermal data on organic compounds of physiological importance, we present in this paper the heats of combustion of seven amino acids. In two cases these data enable us to compare the heat content of the optically active with that of the inactive form.

Calorimetric Method

The calorimetric method, apparatus, units and corrections used have been described in previous publications.[1] 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, and with an initial oxygen pressure of 30 atmospheres and with 1 ml. of water in the bomb. The platinum wire technique[1a] was used exclusively. The heat capacity of our calorimeter has been controlled carefully throughout the course of this investigation by numerous calibrations with Bureau of Standards benzoic acid standard samples 39d and 39e, having for its isothermal heat of combustion at 25.0° the value of 26,419 international joules[2] per gram true mass. As previously reported we have used oxygen from a number of cylinders supplied by the Linde Air Products Company and at varying cylinder pressures. We have continued to obtain the same high precision in our calibrations, namely, an extreme deviation from the mean of slightly more than 0.01%. Up to the present time we have been unable to detect any effect, as has been reported by Keffler,[3] due to change in the oxygen pressure in the cylinder or in changing from cylinder to cylinder.

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 those given by Stiehler and Huffman.[1b] The molecular weights are based on the 1937 table of atomic weights. This involves one important change, namely, the change in the atomic weight of carbon to 12.01. This should be borne in mind when utilizing these data in conjunction with earlier values. In applying the correction for true mass we have used approximate values of the 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 25.0°.

In some cases the combustion was incomplete leaving a small residue of carbon. In other cases there was a residue of ash in the crucible. We have corrected for these in the manner previously reported.[1c] The magnitude of these corrections will be discussed further under the section on preparations, etc.

Purity and Dryness of the Materials Used

We have followed the general method of Stiehler and Huffman[1b] to assure ourselves of the pur-

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[1] (a) Huffman and Ellis, THIS JOURNAL, **57**, 41 (1935); (b) Stiehler and Huffman, *ibid.*, **57**, 1734 (1935); (c) Huffman, Ellis and Fox, *ibid.*, **58**, 1728 (1936).

[2] Jessup and Green, *Bur. Standards J. Research*, **10**, 552 (1933).

[3] (a) Keffler, THIS JOURNAL, **56**, 1259 (1934); (b) Keffler, *J. Phys. Chem.*, **39**, 277 (1935); (c) Keffler, *J. chim. phys.*, **32**, 91 (1935).