TABLE I

ELECTROMOTIVE FORCES OF THE CELLS $Pb \mid PbSO_4 \mid H_2SO_4(m) \mid PbSO_4 \mid PbO_2 \mid Pt^+$ at 0° AND CONSTANTS OF EQUATION (10)—VALID FROM 0 TO 60°

m	E_0^1	$a \times 10^6$	$b \times 10^9$
0.05	1.76874	−310	134
.1	1.80207	−265	129
.2	1.83495	−181	128
.5	1.87910	− 45	126
1	1.91737	56.1	108
2	1.96637	159	103
3	2.00874	178	97
4	2.04789	177	91
5	2.08502	167	87
6	2.11910	162	85
7	2.15071	153	80

Our experience with the individual cells indicates that the cell reactions were those postulated and that the cell reaction corresponding to cell (9) is

$$PbO_2 + Pb + 2H_2SO_4(m) = 2PbSO_4 + 2H_2O$$

under conditions approaching reversibility which corresponds to the double sulfate theory first proposed by Gladstone and Tribe.[5]

Summary

1. Measurements of electromotive forces of the cells

$Pb(\text{2-phase lead amalgam}) \mid PbSO_4 \mid Na_2SO_4 \mid Hg_2SO_4 \mid Hg^+$

have been made from 0 to 60°.

2. The molal electrode potentials of the electrodes reversible to the sulfate ion and those related to the electrodes of the lead accumulator have been evaluated. The results are expressed as a function of the temperature by quadratic equations.

3. Electromotive forces of the cells

$Pb \mid PbSO_4 \mid H_2SO_4(m) \mid PbSO_4 \mid PbO_2 \mid Pt^+$

through concentration and temperature ranges from 0.05 to 7 M and from 0 to 60°, respectively, have been expressed by quadratic equations. The constants of these equations are given in Table I.

[5] Gladstone and Tribe, "The Chemistry of the Secondary Batteries of Planté and Faure." The Macmillan Co., London, 1933.

NEW HAVEN, CONN. RECEIVED AUGUST 30, 1934

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

Studies on Hydrazine: Heat Capacities of Aqueous Hydrazonium Salts at 20 and 25°[1]

BY ALAN W. COBB AND E. C. GILBERT

Search of the literature reveals that data on the thermodynamic properties of hydrazine and its salts are few and scattered. As the basis of an extensive investigation of these properties the heat capacities of solutions of certain hydrazonium salts have now been determined.

The choice of calorimetric design and procedure was governed by the necessity of using the same apparatus for widely varied types of determination, such as specific heat, heat of solution, heat of reaction, etc. An adiabatic calorimeter of the general type developed by Daniels and his co-workers[2] was finally adopted. The essential characteristics of this design are three: first, the adiabatic condition is maintained by electrolytic heating of the bath liquid; second, the temperatures are measured in the outer bath so as to eliminate thermal leakage along the platinum resistance thermometer to the calorimeter; third, the adiabatic control is made automatic by the use of a photo-electric cell.

Apparatus

The calorimeter resembled in design that of Urban,[2c] who gives an excellent diagram in his paper. The principles laid down by White and by Barry[3] were also applied in the details of construction. The innermost container which held the solutions was of copper, heavily gold plated inside and out, and coated with baked Bakelite lacquer inside. The capacity was 0.9 liter. It was supported on Bakelite pegs within another gold-plated vessel with an air gap of 11 mm. The lid of this larger vessel supported the gold-plated, lacquered stirrer upon two ball bearings, and also, in conical stuffing boxes, a heating element and one arm of a 17-junction thermel. The ground joint between the lid and can was lubricated with stopcock grease and held tightly closed by thumb screws. The chimney for the stirrer was lined with hard rubber, and the stirrer shaft had a 5-cm. insert of Bakelite to prevent excessive heat leakage.

The calorimeter assembly was supported below the water level on three Bakelite pegs in a well-lagged copper

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[1] Taken from a thesis submitted by Alan W. Cobb in partial fulfilment of the requirements for the degree of Master of Science at the Oregon State College, June, 1934.

[2] (a) Daniels, THIS JOURNAL, **38**, 1473 (1916); (b) Williams and Daniels, *ibid.*, **46**, 903 (1924); (c) Urban, *J. Phys. Chem.*, **36**, 1108 (1932).

[3] (a) White, "The Modern Calorimeter." The Chemical Catalog Co., New York, 1928; (b) Barry, THIS JOURNAL, **44**, 899 (1922).

can of 12 liters capacity. This bath could be heated electrolytically and cooled by allowing a supply of the bath electrolyte to flow from an elevated reservoir through a copper coil immersed in ice into the bath, the overflow being saved and returned to the reservoir. Equality of temperature between the outer bath and the inner solution was established when the thermel with one arm in each showed no difference in potential. This 17-junction thermel was constructed according to White[4] in a thin glass jacket containing naphthalene to reduce thermal lag. The junctions in each arm were spaced over a distance of several cm., and the leads ran 20 cm. through the bath to avoid heat leakage. The thermel was connected to a Leeds and Northrup H. S. galvanometer with a standard sensitivity of 10 mm. per microvolt. The scale was placed at a distance of 4 meters so that a deflection of 1 cm. corresponded to a temperature difference of 0.0008°.

The exact temperature of the outer bath was measured with a Leeds and Northrup platinum resistance thermometer and a Mueller type bridge specially constructed by the Gray Instrument Co. The thermometer was calibrated at the ice point, the boiling point of water and the transition point of sodium sulfate decahydrate. With reasonable care differences of 0.0005° could be read.

The stirring rate of the inner solution was maintained exactly constant at 230 r. p. m. by means of a large synchronous motor. At this rate the heat of stirring was approximately 0.0002° per minute, a rather low figure. The exact value was determined for each solution. The heater element for the inner solution was of the type described by Urban. Two heaters having a resistance of approximately 35–40 ohms were constructed, using No. 32 bare constantan wire with appropriate current and potential leads. They were used interchangeably during the work.

The electrical system for accurately measuring the energy input was similar to that of Williams and Daniels[2b] who give a complete diagram in their paper. Heating current at 18 volts was supplied from storage batteries. The volt box, standard cell, and standard one ohm resistance were calibrated with standards certified by the Bureau of Standards.

The automatic control for the heating of the outer bath while similar to that of Ewing and collaborators[5] possessed certain advantages in sensitivity. This was brought about by dividing the a. c. heating current into two parts, one of which ran continuously at a rate nearly sufficient to keep the bath up to temperature, while the other shunt acted as a fine control for the exact regulation of the bath heating. This shunt could be controlled manually or, by means of a Weston Photronic Cell, automatically. The Photronic Cell was activated by light reflected from the thermal galvanometer. Time lag in the system was very small with the greater part occurring in the thermel. Regulation was very close, the adiabatic condition being maintained usually within ±0.0016° with rarely a difference of ±0.0025°. While a temperature was being taken, control was usually shifted to manual operation which was closer. Temperatures were read only when there was no observable temperature difference recorded by the thermel.

Operation

The outer bath was cooled usually to about 17° before the start of a series of experiments. The cooled solution to be tested was weighed into the inner vessel and immediately assembled in the submarine jacket. Following this, thermal equilibrium was established and a temperature reading taken. Current was then passed through the heater for about twenty-two minutes, the exact time being measured with a calibrated stop watch. Seven or eight minutes after the discontinuance of the heating was allowed for the apparatus to come to equilibrium and then the second temperature reading was taken. Following this reading the heating current was turned on again for a repetition of the process. Usually three separate determinations were made over a total interval of about 9° with one assembling of the apparatus.

As an illustration the details of a typical series are given in Table I. The mean value of the heater current was obtained by averaging the potentiometer readings across the one-ohm standard resistance and subtracting a correction for current that flowed through the volt box, which usually amounted to about 0.017 ampere. Blank runs using water gave an average value of 97.0 joules for the calorimeter equivalent. For the specific heat of water the values 0.9988 and 0.9979 at 20 and 25° were taken from the "I. C. T."[6] The factor 4.1833 was used for the conversion of international joules into 15° calories following Rossini.[7] It is obvious that the specific heats obtained in this work are average values over a range of 3 to 3.5°.

TABLE I

TYPICAL SPECIFIC HEAT DETERMINATION, 0.5 *M* N_2H_5Cl

Experiment	1	2	3
Time of heating, sec.	1320.2	1320.4	1320.1
Mean temp. of run, °C.	18.93	22.22	25.02
Corrn. for heat of stir, °C.	0.0053	0.0051	0.0054
Corrected temp. rise, °C.	3.2902	3.2887	3.2821
Heater current, (mean) amp.	0.52008	0.52012	0.51996
Mean potent. across heater, v./26.009	0.71221	0.71224	0.71195
Heat input per degree rise, joules	3865.6	3868.4	3872.5
Calorim. equiv., joules	97.0	97.0	97.0
Corr. wt. soln., (*in vac.*) g.	937.53	937.53	937.53
Calcd. sp. ht., joules/degree	4.0197	4.0226	4.0269
Calcd. sp. ht., 15° cal.	0.9609	0.9616	0.9626

At the end of each run, weighed samples of the solutions were analyzed for hydrazine content as a check on the concentrations.

Accuracy

As a check on the integrity of the apparatus and the accuracy of the method of calculation the specific heat of two potassium chloride solutions was determined. The values obtained at 25° are: 1.000 *M*, 0.9120 cal./deg.; 0.500 *M* 0.9517. These compare favorably with the highly accurate results of Randall and Rossini,[8] who obtained 0.9118 and 0.9518, respectively. The determination on

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(4) White, THIS JOURNAL, **36**, 2292 (1914).

(5) Ewing, Rogers, Miller and McGovern, *ibid.*, **54**, 1335 (1932).

(6) "International Critical Tables," Vol. VII, p. 32.

(7) Rossini, *Proc. Nat. Acad. Sci.*, **16**, 694 (1930).

(8) Randall and Rossini, THIS JOURNAL, **51**, 323 (1929).

TABLE II

SPECIFIC HEATS OF AQUEOUS HYDRAZONIUM SALTS AT 25°

Rounded values of Φ were taken from the curves of Φ against the square root of the molality, such as are shown in Fig. 1, and used for the calculation of the quantities in the last three columns.

Salt	Molality	Sp. ht. in 15° cal. per g.	Φ	$\bar{C}_{p1} - \bar{C}^0_{p1}$	$\bar{C}_{p1}$	$\bar{C}_{p2}$
			Cal. per mole		Cal. per mole	
			Solute	H_2O	H_2O	Solute
$N_2H_6Cl_2$	1.000	0.8969	− 6.8	−0.323	17.6546	11.56
	0.5000	.9396	−17.5	− 1169	17.8607	− 4.52
	.2000	.9723	−27.1	− .0296	17.9480	−18.88
	.1000	.9847	−32.0	− .0105	17.9671	−27.19
	.0000	.9979			17.9776	
$N_2H_6Br_2$	1.000	.8297	− 6.9	− .356	17.6216	13.0
	0.5000	.9012	−18.2	− .1260	17.8516	− 4.22
	.2000	.9541	−28.8	− .0313	17.9463	−19.95
	.1000	.9756	−34.0	− .0113	17.9663	−27.74
	.0000	.9979			17.9776	
N_2H_5Cl	1.0000	.9294	− 2.5	− .1144	17.8632	4.10
	0.5000	.9620	− 6.0	− .0404	17.9372	− 1.51
	.2000	.9826	− 9.0	− .0102	17.9674	− 6.16
	.1000	.9900	−10.8	− .0036	17.9740	− 8.80
	.0000	.9979			17.9776	
N_2H_5Br	1.000	.8939	− 3.0	− .1362	17.8414	4.57
	0.5000	.9412	− 7.2	− .0482	17.9294	− 1.84
	.2000	.9735	−11.3	− .0122	17.9654	− 7.92
	.1000	.9852	−13.6	− .0043	17.9733	−11.20
	.0000	.9979			17.9776	
$N_2H_5ClO_4$	1.000	.9056	28.0	− .226	17.7516	40.57
	0.5000	.9453	20.4	− .0801	17.8975	28.29
	.2000	.9749	14.0	− .0202	17.9574	19.62
	.1000	.9856	10.8	− .0072	17.9704	14.78
	.0000	.9979			17.9776	

the 0.500 *M* solution was made at the beginning of the work and the other more than a year later.

Errors in the measurement of current and potential were very small and may be neglected. Error due to variation in heat of stirring was rendered unlikely by the use of a synchronous motor. The main source of error would therefore lie in the measurement of time, temperature, and in the purity of the salts. Time was measured with a calibrated stop watch. Making allowance for a possible error of 0.4 sec. in opening and closing the heater switch, and assuming a probable accuracy of ±0.001° in determining the temperature rise, the probable error in the specific heats may be shown by the method of Ewing and Rogers[9] to amount to ±2.7 joules in a total of 3870, or 0.7 joule per 1000 in the heat input for 1° rise.

The salts were carefully purified by repeated recrystallization, and the purity checked by analysis of the dry salts. The accuracy of the titrations was of the same order as that of the heat determination. A large number of independent runs were made and the results treated graphically since the temperatures were not identical. Except for one run which was discarded by reason of a gross error, the individual points fell within limits of variation which were for the most part smaller even than the calculated probable error.

Results

Determinations of heat capacity were made for solutions of five hydrazonium salts, the dichloride, dibromide, monochloride, monobromide, and monoperchlorate, over a range of concentration from 1.0 to 0.1 molal. The results for each concentration were plotted on a large scale against temperature and values read from the curves at exactly 20 and 25°.

These are recorded in Tables II and III. Included also are the calculated thermodynamic quantities, Φ the apparent molal heat capacity, $\bar{C}_{p_2}$, the partial molal heat capacity of the solute, $\bar{C}_{p_1}$, that of the solvent, and $\bar{C}_{p_1} - \bar{C}^0_{p_1}$, the relative partial molal heat capacity of the solvent. These were calculated on the following basis. The apparent molal heat capacity Φ was plotted against the square root of the molality.

$$\Phi = [(1000 + mM_2)S_2 - 1000S_1]/m$$

where m = molality of solute, M_2 = mol. wt. of solute, S_2 = sp. ht. of solution, S_1 = sp. ht. of water. Following the nomenclature of Randall and Rossini[8]

$$\Phi = (C_p - 55.508\ \bar{C}^0_{p1})/m$$

whence

$$\bar{C}_{p2} = \Phi + {}^1/_2 \cdot m^{1/2}(\mathrm{d}\Phi/\mathrm{d}m^{1/2}) \text{ and } \bar{C}_{p1} = (C_p - m\bar{C}_{p2})/55.508$$

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(9) Ewing and Rogers, THIS JOURNAL, **55**, 3605 (1933).

and

$$\overline{C}_{p1} - \overline{C}^0_{p1} = -(m/55.508)[{}^1/_2 \cdot m^{1/2}(\mathrm{d}\Phi/\mathrm{d}m^{1/2})]$$

Discussion

It has been observed by a number of investigators[2c,8,10] that a plot of Φ against $m^{1/2}$ gives approximately, though not necessarily, a straight line for a number of salts investigated by them in aqueous solution. The salts used in the present work are quite different in type from the more commonly investigated ones in that hydrazine is a base weaker than ammonia and in addition the dichloride and dibromide function more or less as acid salts due to dissociation. It was thought worth while to test the data by the above-mentioned criterion, with the results shown in Fig. 1.

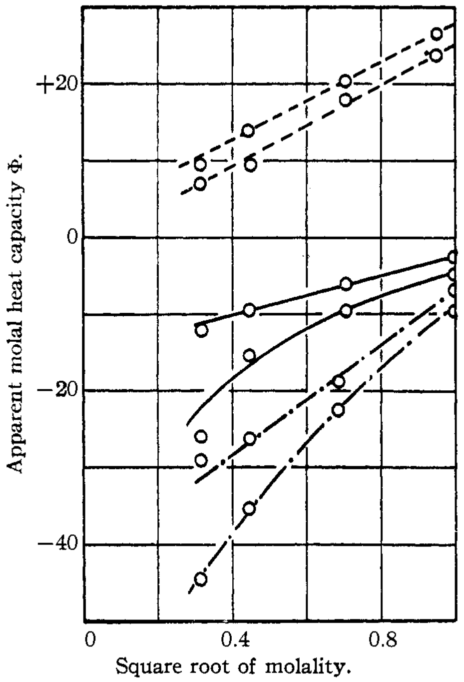

Fig. 1.—Variation of Φ with $m^{1/2}$ of hydrazonium salts at 25 and 20°: – – – – monoperchlorate, ———— monochloride, —·— dichloride, upper curve of each pair, 25°; lower curve, 20°.

To avoid confusion of curves only three are shown. Excellent straight line relationships are observed at 25° for all five salts, and for the perchlorate at both 20 and 25°. The 20° curves for the other four, particularly the monochloride and bromide, show a decided downward inflection. Unfortunately values of Φ are so sensitive to small errors in the specific heat at low concentration (less than our probable error) that no theoretical conclusions may safely be drawn concerning the deviation from linearity.

TABLE III

SPECIFIC HEATS OF AQUEOUS HYDRAZONIUM SALTS AT 20°

Salt	Molality	Sp. ht., 15° cal. per g.	Φ cal. per mole of solute
$N_2H_6Cl_2$	1.000	0.8955	− 9.4
	0.4750	.9411	−22.5
	.2000	.9713	−35 3
	.1845	.9736	−34.2
	.1000	.9840	−44.5
	.0000	.9988	
$N_2H_6Br_2$	.9959	.8301	− 8.3
	.5000	9007	−21 3
	.2000	.9536	−40.9
	.1691	.9618	−32.0
	.0995	.9753	−46.0
	.0000	.9988	
N_2H_5Cl	.9935	.9306	− 4.8
	.4979	.9612	− 9.5
	.2008	.9822	−15.4
	.1000	.9894	−26.0
	.0000	.9988	
N_2H_5Br	.9375	.8989	− 4.8
	.4961	.9412	− 9.5
	.1964	.9733	−19.7
	.0997	.9846	−31.0
	.0000	.9988	
$N_2H_5ClO_4$	.9088	.9107	23.9
	.4994	.9451	18.0
	.2009	.9748	9.3
	.1001	.9862	7.0
	.0000	.9988	

When $\overline{C}_{p_2}$ is plotted against $m^{1/2}$ the values of the slope for the dichloride and dibromide agree very well with that observed by Randall and Rossini[8] for typical bi-univalent salts, though other types of evidence seem to point to practically complete dissociation of these hydrazonium salts into the uni-univalent salt and free halogen acid in solution.

Acknowledgment.—The authors wish to acknowledge their indebtedness to the National Research Council for a generous grant which made this work possible, and to the General Research Council of this College for a research assistantship held by one of us (A. W. C.) during the construction of the apparatus.

Summary

The heat capacities of aqueous solutions of hydrazonium dichloride, dibromide, monochloride, monobromide and monoperchlorate were determined for 20 and 25° from 0.1 to 1 molal.

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[10] Gucker and Schminke, THIS JOURNAL, 54, 1358 (1932).

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.

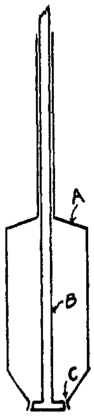

Fig. 1.—Pipet for introduction of salt into calorimeter.

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).