[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF TEXAS]

Heats of Dilution and Heat Capacities of Aqueous Solutions of Mono-, Di- and Trimethylamine Hydrochlorides[1]

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Introduction

This investigation was undertaken as the logical continuation of the work of Jones, Spuhler and Felsing,[3] who determined the values of the activity coefficients of the methylamine hydrochlorides in aqueous solution by the freezing point depression method for the concentration range 0.001 to 1.0 molal. In order to establish final values for the activity coefficients at 25°, it became necessary to determine the heats of dilution and heat capacities of such solutions. The theoretical basis underlying the calculations is presented by Lewis and Randall.[4] Use was made of their equation

$$\log \gamma = \log \gamma' - \frac{55.506}{\nu} \int_0^m \frac{\mathrm{d}X}{m} \quad (1)$$

where γ is the final value of the activity coefficient for an electrolyte breaking up into ν ions and γ' is the value obtained provisionally by Jones, Spuhler and Felsing[3] by neglecting the relative partial molal heat content $\overline{L}_1$ and the partial molal heat capacity $\overline{C}_{p_1}$ of the solvent. The quantity X is defined by

$$X = -\overline{L}_{1(T')} \left[\frac{T'' - T'}{2.303RT''T'}\right] + (\overline{C}_{p_1} - \overline{C}^0_{p1}) \left[T'' \frac{T'' - T'}{2.303RT''T'}\right] - \frac{1}{R} \log \frac{T''}{T'} \quad (2)$$

An examination of the expression for X reveals that for its evaluation there must be known the relative partial molal heat content and the partial molal heat capacity of the water at the various concentrations at which γ' values were determined.

Since these data were not available in the literature, it became the object of this investigation to make these determinations.

The quantity $\overline{L}_1$ is the difference between the values of the absolute partial molal heat content in the particular solution under consideration and in the standard state (the infinitely dilute solution). It is, therefore, the *differential* heat of solution, the heat change accompanying the addition of one mole of solvent to an infinite quantity of solution of the concentration under consideration.

The relative partial molal heat capacity of the solvent is defined as the difference between the partial molal heat capacity of the solvent in a particular solution and that in the standard state (*i. e.*, of the pure solvent). A determination of the specific heats of the solutions yields data from which the partial molal heat capacity of the solvent at any concentration may be calculated.

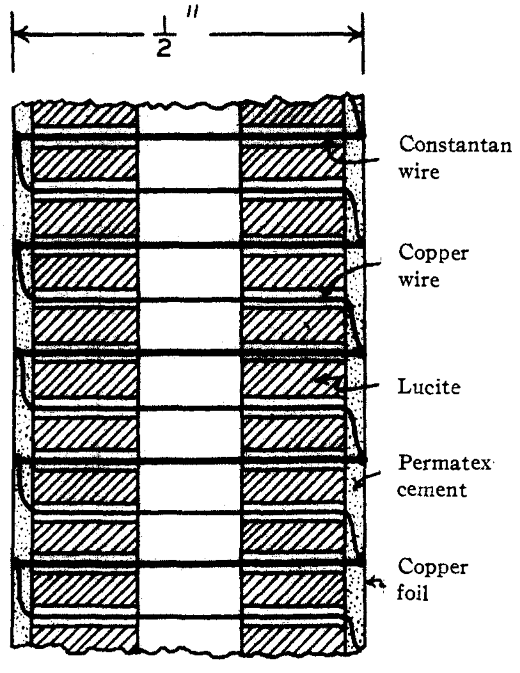

Fig. 1.—Details of thermocouple.

Methods and Apparatus

A. The Heat of Dilution Calorimeter.—For the determination of the heats of dilution, there was constructed a differential calorimeter of the type described by Lange and Robinson.[5] Improvements and changes suggested by Gulbransen and Robinson[6] and by Gucker, Pickard and Planck[7] were found useful during the construction. Thus the calorimeter was essentially that of Lange and Robinson[5] except for the following modifications.

(1) A silvered 3-liter dewar flask was used for the **calorimeter vessel** because of the better insulation of a silvered vessel.

(2) The **thermopile** consisted of 1300 copper–constantan couples mounted in a Lucite frame. Lucite was chosen because of its low electrical and thermal conductivities. The details of construction are shown in Fig. 1. Insulation of the junctions was secured by covering them with Permatex[8] cement no. 1. This cement has a very high electrical resistance when thoroughly dry. After drying, the surface of the cement was sanded down until a smooth, flat surface was attained and until the end of each

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[1] Constructed from a portion of a thesis presented to the Graduate Faculty of the University of Texas by Eugene Payne Whitlow in partial fulfillment of the requirements for the degree of Doctor of Philosophy, June, 1944.

[2] Present address: Servel, Inc., Evansville, Ind.

[3] Jones, Spuhler and Felsing, THIS JOURNAL, **64**, 965 (1942).

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

[5] Lange and Robinson, *Chem. Rev.*, **IX**, 89 (1931).

[6] Gulbransen and Robinson, THIS JOURNAL, **56**, 2637 (1934).

[7] Gucker, Pickard and Planck, *ibid.*, **61**, 459 (1939).

[8] Form-a-Gasket No. 1, Permatex Co., Inc., Sheepshead Bay, N. Y.

thermopile junction was exposed. A thin coating of Glyptal lacquer was applied and after drying the surface was coated with paraffin. Finally, a sheet of gold-plated copper foil (0.006" thick) was pressed onto the surface by means of a hot steel plate; the excess paraffin was forced out and, on cooling, the foil remained attached firmly.

This method of insulation combined a maximum electrical resistance with a minimum of thermal resistance. After several months' use, the electrical resistance was essentially unchanged.

The junctions were formed from no. 24 B. and S. constantan and no. 30 copper wires. These sizes of wire and the number of couples were chosen to yield a high sensitivity and a resistance equal to the critical damping resistance of the galvanometer.

(3) A type HS Leeds and Northrup **galvanometer** was connected directly to the thermopile; a shunting switch was connected across the galvanometer to protect it while thermal equilibrium was being attained. This shunting device was completely out of the circuit when final observations were being made; this was done to avoid any possible contact potentials.

(4) The **pipets,** approximately 25-ml. capacity, were made of brass; they were heavily gold-plated and were supported from the lid by means of Lucite rods (to reduce heat leakage).

(5) The **stirrer shafts** were also made of Lucite, again to lessen heat leakage.

(6) The **calorimeter heaters** were made by coiling manganin wire around a piece of glass tubing sealed at one end. The heater leads were threaded through small holes in the glass tube and brought out through the top of the tube. The electrical insulation of the heater was effected by application of the usual baked-on type of electrical insulating varnish; this insulation showed no deterioration after months of service.

(7) **Energy** for the heaters was supplied by a heavy-duty storage battery. The voltage applied across the heaters was determined by means of a Type K, Leeds and Northrup, potentiometer; the time of heating was measured by use of an electric timer built by the Standard Electric Time Company of Springfield, Massachusetts. The dial of the timer was graduated in hundredths of a second.

(8) The **constant temperature bath** in which the calorimeter was submerged followed conventional design. Kerosene was the bath liquid. A toluene–mercury thermoregulator was constructed from 40 feet of $^5/_{16}$" copper tubing. The adiabatic control was similar to that described by Lange and Robinson.[5]

B. The Specific Heat Calorimeter.—The specific heat determinations were made by using a conventional calorimeter employing a silvered dewar flask. The temperature changes due to additions of known amounts of energy were determined by means of 25-ohm platinum resistance thermometer connected to a Mueller bridge. The usual precautions taken to avoid heat leakages through the stirrer shaft and heater leads were carefully observed.

C. The Materials Used.—The **salts** used were the "White Label" grade of the Eastman Kodak Company; they were further purified. **Monomethylamine Hydrochloride.**—The sample of material was subjected to a chloroform extraction in a Soxhlet extractor; the mono salt is very slightly soluble in chloroform while the di and tri salts are soluble. The salt was then recrystallized twice from anhydrous ethanol and finally dried in a vacuum desiccator. **Dimethylamine Hydrochloride.**—This salt was recrystallized three times from chloroform, after which it was dried in a vacuum desiccator. **Trimethylamine Hydrochloride.**—This salt was recrystallized once from chloroform and twice from anhydrous *n*-propyl alcohol. It also was dried in a vacuum desiccator.

The purity of the salts after recrystallization was checked by gravimetric chloride analysis. The results are presented in Table I.

The uniformly slightly low results are due, most probably, to the fact that these salts are extremely hygroscopic and are, therefore, not easily weighable in a completely dry condition.

TABLE I

CHLORIDE CONTENT OF PURIFIED SALTS

	Chloride, %	
	Calcd.	Foun
$CH_3NH_2 \cdot HCl$	52.52	52.43
$(CH_3)_2NH \cdot HCl$	43.49	43.40
$(CH_3)_3N \cdot HCl$	37.09	37.06

D. Preparation of Solutions.—All solutions were made by weight; all weights were reduced to vacuum conditions.

The procedure for measuring the heat of dilution was essentially that of Lange and Robinson[5] with the exception that, in all cases, the solution to be diluted was placed into the calorimeter and the diluting water into the pipet. Thus differential rather than integral heats of dilution were obtained.

E. Calibrations.—In order to calibrate the dilution calorimeter a weighed amount of water was put into each half of the calorimeter. This amount of water had a volume equal to the volume of the solution used in all subsequent dilutions. The pipets were filled with water and the whole calorimeter and contents were allowed to attain thermal equilibrium with the surrounding thermostated bath.

After equilibrium was attained, a small but known quantity of energy was added to one of the halves of the calorimeter; galvanometer deflections were noted before and after the energy addition. From these data, a cooling curve was constructed; by extrapolating the straight-line portion of the curve to the mid-point of the heating interval, the galvanometer deflection corresponding to the amount of heat added was determined.

From a number of such determinations, a curve relating galvanometer deflections to heat input was constructed for each half of the calorimeter. These calibration curves were checked at intervals and were found to remain valid throughout the entire period of the investigation.

The specific heat calorimeter was calibrated by adding a known amount of energy to a weighed amount of water in the calorimeter and noting the temperature rise. From these data, the energy equivalent of the calorimeter was calculated. The temperature rise in all cases was approximately *two* degrees. The value 0.9979 cal. (15°) per gram per degree was taken from "I. C. T." as the specific heat of water at 25°. The factor 4.1833 was used to convert international joules to calories.

The Data and their Treatment

Aqueous solutions of the three amine hydrochlorides were prepared for the heats of dilution and specific heat determinations; for each salt, fourteen solutions in the concentration range 0.05 to 1.0 molal were used in the heats of dilution measurements. At each concentration studied, two solutions of approximately the same concentration were used as a check. Throughout the calculations, the 15° calorie was employed.

Since the concentration changes during the dilutions were relatively small, the observed heats of dilution were essentially the *differential* heats of dilution, defined as the relative partial molal heat contents, $\bar{L}_1$, of water in the solutions. Thus, the values of $\bar{L}_1$, shown in Table II, are the experimentally determined heats of dilution. In order to check the validity of this procedure, large scale graphs of $S(= \Delta\phi H/\Delta m^{1/2})$ *versus* $m^{1/2}$ were constructed according to the short-chord method of Young and Vogel[9] and $\bar{L}_1$ values were

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[9] Young and Vogel, THIS JOURNAL, **54**, 3030 (1932).

calculated. The differences between the values of $\bar{L}_1$ calculated by this procedure and those listed in Table II were found to be less than the uncertainties involved in the construction of the S-curve through the experimentally determined chords. Consequently, the shorter method of evaluating $\bar{L}_1$ was used. Figure 2 shows the relation between $\bar{L}_1$ values as a function of the concentration of the three salts.

TABLE II

RELATIVE PARTIAL MOLAL HEAT CONTENT OF WATER AT 25° IN SOLUTIONS OF MONO-, DI- AND TRIMETHYLAMINE HYDROCHLORIDES

Soln no.	Concentration, molality Initial	Final	Av.	$\bar{L}_1$ cal./mole water
	A. Monomethylamine Hydrochloride			
1	0.0427	0.0414	0.0420	−0.0317
2	.0358	.0347	.0352	− .0190
3	.0919	.0891	.0905	− .0531
4	.0906	.0879	.0892	− .0590
5	.2090	.2027	.2058	− .1003
6	.1863	.1807	.1835	− .0991
7	.4223	.4095	.4159	− .2309
8	.4383	.4249	.4316	− .2380
9	.6077	.5890	.5984	− .3550
10	.6246	.6054	.6150	− .3576
11	.8024	.7775	.7899	− .4946
12	.8030	.7781	.7906	− .5067
13	1.0159	.9841	1.0000	− .7443
14	0.9959	.9647	0.9803	− .7272
	B. Dimethylamine Hydrochloride			
20	0.0525	0.0509	0.0517	−0.0207
21	.0551	.0534	.0542	− .0258
22	.1138	.1104	.1121	− .0427
23	.1118	.1085	.1102	− .0405
24	.1984	.1925	.1954	− .0549
25	.1948	.1890	.1919	− .0498
26	.4022	.3899	.3960	− .0986
27	.4083	.3958	.4020	− .0913
28	.6093	.5904	.5998	− .1735
29	.6092	.5903	.5998	− .1757
30	.8363	.8099	.8231	− .3381
31	.8134	.7878	.8006	− .3179
32	1.0041	.9721	.9881	− .5273
33	1.0125	.9802	.9964	− .5425
	C. Trimethylamine Hydrochloride			
40	0.0479	0.0464	0.0471	0.0000
41	.0602	.0584	.0593	.0000
42	.0951	.0923	.0937	.0103
43	.1034	.1003	.1018	.0169
44	.2053	.1991	.2022	.1130
45	.1983	.1923	.1953	.0985
46	.3901	.3781	.3841	.3784
47	.4041	.3916	.3978	.3976
48	.5948	.5762	.5855	.7850
49	.5914	.5729	.5821	.8136
50	.8113	.7854	.7984	1.2319
51	.8026	.7771	.7898	1.1859
52	1.0136	.9807	.9972	1.5380
53	1.0293	.9959	1.0126	1.5815

The experimental specific heat values for the three series of solutions are presented in Table III. From these data, the molal heat capacities were calculated; these values are shown in Table IV. In order to determine the partial molal heat content of water in these solutions, the method of intercepts[10] was used. The values are shown graphically in Fig. 3, in which molal heat capacities are presented as a function of the mole-fraction. The actual determination of the partial molal heat capacities was made on a large scale plot of Fig. 3; tangents were drawn, using the mirror–T square method. A sample tangent is shown in Fig. 3.

TABLE III

SPECIFIC HEATS OF SOLUTIONS OF MONO-, DI- AND TRIMETHYLAMINE HYDROCHLORIDES AT 25°

Specific heat of pure water at 25°: 0.9979 cal./deg./g.

Soln. no.	Concn., molality	Sp. ht., cal./deg./g.
	A. Monomethylamine Hydrochloride	
3	0.0891	0.9922
4	.0879	.9925
5	.2027	.9848
6	.1806	.9883
7	.4095	.9735
8	.4249	.9743
9	.5890	.9645
10	.6054	.9635
11	.7775	.9522
12	.7781	.9515
13	.9841	.9422
14	.9647	.9417
	B. Dimethylamine Hydrochloride	
22	0.1104	0.9884
23	.1085	.9925
24	.1925	.9857
25	.1890	.9836
26	.3899	.9734
27	.3958	.9737
28	.5904	.9643
29	.5903	.9628
30	.8099	.9489
31	.7878	.9503
32	.9721	.9428
33	.9802	.9402
	C. Trimethylamine Hydrochloride	
42	0.0923	0.9885
43	.1003	.9898
44	.1991	.9820
45	.1923	.9826
46	.3781	.9718
47	.3916	.9687
48	.5762	.9566
49	.5729	.9590
50	.7854	.9457
51	.7771	.9480
52	.9807	.9351
53	.9959	.9347

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[10] Lewis and Randall, "Thermodynamics," McGraw-Hill Book Company, Inc., New York, N. Y., 1923, p. 38.

TABLE IV

RELATIVE PARTIAL MOLAL HEAT CONTENTS AND PARTIAL MOLAL HEAT CAPACITIES OF WATER IN THE SOLUTIONS AT EVEN CONCENTRATION INTERVALS AT 25°

Concn. molality	$\overline{L}_1$, cal./mole	$\overline{C}_{p_1}$, cal./deg./mole
A. Monomethylamine Hydrochloride		
0.00		17.978
.025		17.973
.05	−0.032	17.972
.10	− .059	17.973
.15	− .081	17.974
.20	− .102	17.975
.30	− .156	17.978
.40	− .219	17.982
.50	− .285	17.984
.60	− .351	17.989
.70	− .422	17.992
.80	− .511	17.995
.90	− .623	18.003
1.00	− .747	18.009
B. Dimethylamine Hydrochloride		
0.00		17.978
.025		17.972
.05	−0.023	17.972
.10	− .040	17.971
.15	− .050	17.972
.20	− .054	17.972
.30	− .071	17.972
.40	− .096	17.973
.50	− .130	17.973
.60	− .174	17.974
.70	− .236	17.975
.80	− .318	17.972
.90	− .424	17.975
1.00	− .546	17.972
C. Trimethylamine Hydrochloride		
0.00		17.978
.025		17.972
.05		17.972
.10	0.015	17.969
.15	.054	17.961
.20	.106	17.951
.30	.237	17.940
.40	.404	17.927
.50	.610	17.913
.60	.834	17.906
.70	1.039	17.897
.80	1.221	17.886
.90	1.390	17.859
1.00	1.553	17.836

From the values of $\overline{L}_1$ (Table II) and $\overline{C}_{p_1}$ (Table IV), values of X in the equation (2)

$$X = -\overline{L}_{1(T'')} \frac{T'' - T'}{2.303RT''T'} + (\overline{C}_{p_1} - \overline{C}^0_{p_1}) \left[T'' \left(\frac{T'' - T'}{2.303RT''T'}\right)\right] - \frac{1}{R} \log \frac{T''}{T'}$$

were calculated. Values of X now being available, the last term of Eq. 1 could be evaluated by graphical integration. From Eq. 1, the activity coefficients, γ, for the three amine hydrochlorides in aqueous solution at 25° could be calculated from the γ' values of Jones, Spuhler and Felsing.[3] Table V lists the values of γ' at 0°, the correction factors, and the γ values at 25°.

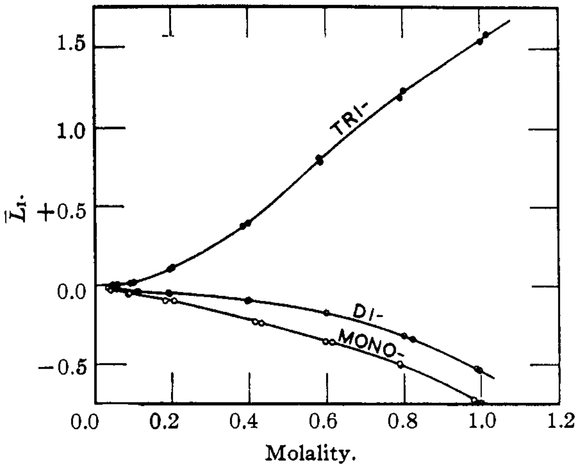

Fig. 2.—Relative partial molal heat content of water at 25° in aqueous solutions of the amine hydrochlorides.

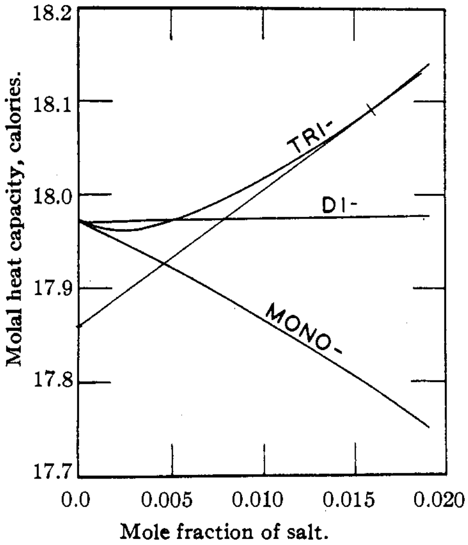

Fig. 3.—Molal heat capacity at 25° of aqueous solutions of the amine hydrochlorides.

Discussion of Results

No values for the heats of dilution or specific heat measurements for these particular salts are available in the literature for comparison; hence any estimates of the accuracy of these data must be made on the basis of the degree of accuracy of the apparatus and methods employed.

From the galvanometer constants and the number of thermocouple junctions used, it has been calculated that the sensitivity of the thermopile–galvanometer system was 3.3 × 10^{-6} per mm. deflection when the galvanometer was one meter from the scale.

TABLE V

ACTIVITY COEFFICIENTS FOR SALTS IN AQUEOUS SOLUTIONS AT 25°

Concn., molality	γ' Act. coef. at F. P.	γ/γ'	γ Act. coef. at 25°
A. Monomethylamine Hydrochloride			
0.001	0.961	....	0.961
.002	.943	....	.943
.005	.909	....	.909
.010	.877	....	.877
.020	.838	....	.838
.050	.778	....	.778
.100	.729	0.9989	.728
.200	.677	.9974	.675
.300	.649	.9962	.647
.400	.627	.9953	.624
.500	.611	.9945	.608
.600	.599	.9938	.595
.700	.590	.9931	.586
.800	.581	.9925	.577
.900	.575	.9919	.570
1.000	.569	.9913	.564
B. Dimethylamine Hydrochloride			
0.001	0.959	....	0.959
.002	.941	....	.941
.005	.904	....	.904
.010	.869	....	.869
.020	.827	....	.827
.050	.762	....	.762
.100	.708	1.0000	.708
.200	.654	0.9997	.654
.300	.622	.9995	.622
.400	.601	.9993	.601
.500	.584	.9991	.583
.600	.571	.9989	.570
.700	.563	.9986	.562
.800	.553	.9984	.552
.900	.546	.9982	.545
1.000	.542	.9980	.541
C. Trimethylamine Hydrochloride			
0.001	0.955	....	0.955
.002	.932	....	.932
.005	.888	....	.888
.010	.842	....	.842
.020	.789	....	.789
.050	.715	....	.715
.100	.661	1.0013	.662
.200	.606	1.0055	.609
.300	.572	1.0090	.577
.400	.550	1.0123	.557
.500	.533	1.0152	.541
.600	.520	1.0177	.529
.700	.509	1.0200	.519
.800	.499	1.0220	.510
.900	.492	1.0238	.504
1.000	.486	1.0256	.498

The calibration data for the dilution calorimeter showed that the average galvanometer deflection for a heat change of 0.1 calorie in either side of the calorimeter was 1.3 centimeters. In the graphical treatment of the ΔT–time curves it was observed that the extrapolation was reproducible to 0.5 millimeter. Hence for a heat change of 0.1 calorie, the maximum error in the measured heat of dilution would be $0.5/13.0 \times 100$ or 3.8%.

In addition to the possible errors involved in the measurement of the heat change during the dilution, there were the possibilities for errors due to heat leakages into the calorimeter, in the composition of solution, and in the volume of solution charged into the calorimeter.

An estimate of five per cent. for the over-all accuracy in determining the *heats of dilution* is reasonable on the basis of the above considerations and is also in line with the accuracy claimed for similar calorimeters described in the literature.

Likewise an estimation of the accuracy of the *specific heat* data must be based on the characteristics of the apparatus and method employed.

Heat leakage into the specific heat calorimeter was much more serious than in the case of the dilution measurements due to the greater temperature differential encountered between the calorimeter liquid and the surrounding bath. Thus, although the instantaneous temperatures could be measured accurately to 0.001°, the extrapolations from the ΔT–time curves introduced an appreciable error. These extrapolations were reproducible only to 0.01°, and the corresponding error for a temperature change of two degrees would be 0.5%.

Considering the uncertainties in the composition of the solutions, the possible errors involved in filling the calorimeter and other minor uncertainties, an over-all accuracy of 1.0% may be taken as a conservative figure for the specific heat measurements. This method does not represent, of course, the greatest possible accuracy obtainable for specific heat measurements. It is, however, well within the limits of accuracy desired for this purpose.

Because of the large number of graphical methods employed throughout the calculations, no satisfactory estimation of the accuracy of the correction factor for the provisional activity coefficient was found. However, all calculations, especially the graphical determinations, were rigorously checked.

In all calculations involving the specific gravity of the solutions the specific gravity data of Spuhler[11] were used.

In addition to the activity coefficients for mono-, di- and trimethylamine hydrochlorides—the determination of these activity coefficients being the primary object of this work—there have been obtained specific heat data and differential heat-of-dilution data for aqueous solutions of these three salts at 25°.

Summary

1. Differential heats of dilution for aqueous

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(11) Spuhler, Ph.D. Thesis, University of Texas, June, 1938.

solutions of mono-, di- and trimethylamine hydrochloride have been determined experimentally at 25° in the concentration range 0.05 to 1.0 molal.

2. Heat capacities of these solutions have also been determined at 25°.

3. From these data and the activity coefficients near the freezing point reported by Jones, Spuhler and Felsing, the activity coefficients of these amine hydrochlorides in aqueous solution at 25° have been calculated.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF TEXAS]

The Heat Capacity of Gaseous 1,3-Butadiene from 0 to 100°

BY D. H. TEMPLETON[1] AND D. D. DAVIES[2] WITH W. A. FELSING

Introduction

Since there was considerable disagreement between calculated values of the heat capacity of gaseous butadiene, and a lack of direct experimental data, this Laboratory was asked to undertake the direct calorimetric determination in the temperature range 0 to 100°.

Stull and Mayfield[3] and Stull[4] have presented calculated values for C_p^0 and C_p', respectively, over a large temperature range, which values were based upon spectroscopic data. Workers at the National Bureau of Standards calculated some values[5] of such heat capacities, based upon thermodynamic properties of the liquid and solid butadiene. In another special report[6] two values based upon the heat capacity ratio, as determined by the velocity of sound method, are given, together with values calculated from spectroscopic data. These data are presented, for comparison, in Fig. 1 with the data of this investigation. After the results of the present paper were reported to the National Bureau of Standards, some direct calorimetric data, obtained in the Cryogenic Laboratory there, were reported[7] to the authors. These data are also included in Fig. 1.

Method and Apparatus

The Method.—The method used in this investigation was the constant flow method of Scheel and Heuse.[8] The apparatus was that used by Felsing and Drake[9]; only minor changes were made.

The Thermocouple.—A 10-junction copper-constantan thermocouple was calibrated by the use of two Beckmann thermometers measuring two temperatures 3 to 5° apart in the neighborhood of 25°. These Beckman thermometers were calibrated immediately before use against a platinum resistance thermometer certified by the National Bureau of Standards. An average value of 2505 degrees per volt was obtained for this 10-junction couple. At other temperatures, it was assumed that the values of $\Delta T/E$ were proportional to those calculated by means of Adams' table.[10]

Electrical Measurement.—A Leeds and Northrup Mueller bridge was used to measure the resistance of the platinum resistance thermometer and of a10-ohm resistance used in the heater current measurements. All other measurements were made with a Leeds and Northrup Type K-2 potentiometer. The Eppley standard cell had been certified recently by the National Bureau of Standards.

The Thermostat.—The temperature of the thermostat was maintained constant (±0.01°) at *one* degree below the temperature of measurement.

Temperature Elevation on Heating.—The temperature of the gas (air, butane, or butadiene) passing through the heating element increased approximately two degrees in all the experiments.

Materials Used

The heat capacities of air and *n*-butane were determined in the apparatus as a check. **Air.**—It was purified by passing over potassium hydroxide, calcium chloride, and anhydrone. **Butane.**—The sample was some of the material used by Dailey and Felsing.[11] It contained approximately 1% impurities, chiefly isobutane. It was purified further by distillation, as described below. **Butadiene.**—The 1,3-butadiene sample was furnished through the National Bureau of Standards by Mr. A. E. Buell of the Phillips Petroleum Company of Bartlesville, Oklahoma. Its quality was stated to be the same as that previously furnished to and tested by the National Bureau of Standards; it was stated to contain 0.0017 ± 0.0006 mole-fraction of impurity. The liquid butadiene in the steel cylinder contained 0.02% of butyl catechol to prevent polymerization. This inhibitor and the other impurities were essentially eliminated by the distillation procedure described below.

The butane (or butadiene) cylinder was connected to the calorimeter system by means of a rubber connection. After thorough evacuation of the system, a sample from the cylinder was distilled into a glass reservoir cooled to Dry Ice temperature. Any permanent gases and a portion of the condensed phase were removed by another evacuation. From the glass reservoir, under proper temperature control, enough of the liquid sample was evaporated into the evacuated calorimeter system to fill it at the desired pressure. Thus, only a middle portion was introduced into the calorimeter.

Methods of Calculation

The rate of flow was determined in terms of volume at 25° and atmospheric pressure. Densities used in the calculations were 0.001185[12] for

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(1) Present address: 5473 Ellis Avenue, Chicago, Illinois.

(2) Present address: Pan-American Refining Corp., Texas City, Texas.

(3) Stull and Mayfield, *Ind. Eng. Chem.*, **35**, 639 (1943).

(4) Stull, *ibid.*, **35**, 1303 (1943).

(5) Scott, Rands, Brickwedde and Bekkedahl, *Special Report, Natl. Bur. Standards*, July 23, 1943, Table IV.

(6) Aston, Szasz and Brickwedde, Private Report, July 23, 1943, Tables 2 and 3.

(7) Private communication from C. S. Cragoe, July 22, 1944.

(8) Scheel and Heuse, *Ann. Physik*, **37**, 79 (1912); **40**, 473 (1913).

(9) Felsing and Drake, THIS JOURNAL, **58**, 1714 (1936).

(10) "Temperature," Amer. Inst. Physics, Reinhold Pub. Corp., New York, 1941, Table 9, p. 1306.

(11) Dailey with Felsing, THIS JOURNAL, **65**, 44 (1943).

(12) "International Critical Tables," Vol. III, pp. 3 and 10.