

[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT, OKLAHOMA AGRICULTURAL AND MECHANICAL COLLEGE]

## The Specific Heats of Morpholine and its Aqueous Solutions<sup>1</sup>

BY H. M. TRIMBLE, CHARLES J. ENGLE, RALPH A. BROWN AND ROBERT F. SCHMUCK

This paper presents the results of a study of the specific heats of morpholine and its aqueous solutions. This system was chosen for investigation, in part, because of its interesting technical possibilities. Further, its components are soluble in all proportions, there is reason to believe that they react strongly when brought together and the range of temperature within which they are liquid under ordinary conditions is nearly the same and relatively large. It was believed that the results of a study of its specific heats covering the whole concentration range and the temperature range 0 to 130° should have considerable theoretical interest, since few comparable studies have been made.

Morpholine is highly hygroscopic and it reacts readily with carbon dioxide of the air. Moreover, it was necessary to prevent loss of the experimental material by evaporation. For these reasons the method of mixtures was used, specimens for the determinations being prepared by sealing up the liquids in Pyrex glass capsules.

In using this method it is necessary to know the quantity of heat absorbed or released by the container over the different temperature intervals. Three equations setting forth the specific heat of Pyrex glass as a function of temperature have been given in the literature.<sup>2,3,4</sup> Calculations from these equations indicate that the heat capacity of this material varies from sample to sample. The equations for the samples of glass used in these studies have, therefore, also been determined.

**Apparatus.**—The heaters in which the specimens were brought to temperatures above that of the room were similar to that described by Frederick and Hildebrand.<sup>5</sup> They were made of steel, and the specimen chambers were closed below by closely fitting steel stoppers 4 cm. long. They were electrically heated, their temperatures being controlled by means of mercury thermoregulators. They were readily maintained at any desired temperature between that of the room and 150° with a fluctuation not greater than  $\pm 0.05^\circ$ . The temperatures of specimens were measured by means of copper-constantan thermo-

couples in conjunction with a Leeds and Northrup type K-2 potentiometer, the hot junctions being placed directly in the heating chambers in contact with the specimens. Couples were repeatedly calibrated by comparison with the temperatures read from mercury filled thermometers, with Bureau of Standards calibration, at the ice point and at the temperatures of boiling chloroform, water and chlorobenzene, respectively. The specimens, suspended in glass protecting jackets, were brought to 0° in a well stirred ice-water-bath contained in a gallon vacuum beaker. The calorimeter was of the usual metallic air-jacketed form, with convection shield and rotary stirrer. It was immersed in the water of a constant temperature bath held at 30° when the initial temperatures of the specimens were above that of the room and at 35° when the initial temperature was 0°. The water in the calorimeter can was brought to approximately these temperatures at the beginning of the respective experiments. Calibration with a copper specimen, using the same technique as that employed with the other specimens, established the total water equivalent of the calorimeter at  $440 \pm 2$  cal. per deg. The specific heat of copper as given by the expression

$$c_p = 0.09076 + 0.0000415t \text{ cal.}^5$$

was employed in the calculations. A Beckmann thermometer calibrated by the Bureau of Standards was used in measuring the temperature changes in the calorimeter. Its zero point was frequently determined so that the final temperatures as measured by it could be converted to the standard temperature scale.

**Preparation of Specimens.**—Capsules were made for the specimens by constructing short test-tubes from one-inch glass tubing and drawing their open ends down ready for sealing. They were converted to mixing vessels for making up the samples by sealing to them the female portions of 19/38 ground glass joints. Stoppers were made from the other portions of the joints. These vessels were interchangeable with a removable receiver in the purification apparatus.

Morpholine was prepared in the usual manner.<sup>6</sup> It was protected from contamination during purification and distillation by means of a tower filled with fresh soda lime. A portion of the morpholine was first distilled over and rejected, then the weighed mixing vessel was put in place and a suitable quantity was distilled into it. After weighing, the quantity of freshly redistilled water required to make up a solution of approximately the desired concentration was pipetted in. The components were thoroughly mixed by shaking the liquid repeatedly from one portion of the vessel to the other, with cooling to dissipate the heat of mixing. Finally the vessel and its contents were weighed again. From the weights of morpholine and water taken the composition of the sample could be calculated. A portion of the solution was rejected such that

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(2) De Vries, *Ind. Eng. Chem.*, **22**, 617 (1930).

(3) Frederick and Hildebrand, *THIS JOURNAL*, **60**, 1436 (1938).

(4) Frederick and Hildebrand, *ibid.*, **61**, 1556 (1939).

(5) Bronson, Chisholm and Dockerty, *Can. J. Res.*, **3**, 282 (1933).

(6) Dermer and Dermer, *THIS JOURNAL*, **59**, 1148 (1937).

the remainder could not fill the tube and burst it by hydrostatic pressure at the highest temperature to be reached. The tube and its contents were then cooled in a dry-ice-acetone mixture, the capsule was sealed off and a ring for attachment of the supporting thread was formed on it. The specimens contained about 20 ml. of liquid each, and the vapor space was not greater than 3 ml. in any case. The heat capacity of the glass was not greater than one-fifth of the total heat capacity of any specimen.

After the experiments with a given specimen had been completed it was opened and the capsule was washed out with water, dried and weighed. This gave the weight of the glass, and the weight of the solution was found by subtraction from the total weight of the specimen.

The glass specimens were capsules filled with coarsely ground portions of the respective tubes from which they had been made, and sealed as already described.

**Measurements.**—Specimens were allowed to remain in the heaters for about one hour, and in the ice-water-bath for about twice as long, to come to temperature. The maximum temperature change in the calorimeter occurred within about five minutes. The initial temperatures were 0° in the ice-water-bath, and approximately 60, 90, 100 and 130° in the heaters. The final temperatures in the calorimeter fell between 31 and 35°. At least three determinations which gave consistent results were made with each specimen over each interval. Approved calorimetric procedure was followed throughout, and all necessary corrections to the thermometric measurements were made.

**Calculations and Results.**—Determinations of specific heat were made upon five specimens of glass from four different batches. As was anticipated, the specific heats were different for different batches. The specific heat of the glass used in most of our determinations, as shown by two sets of runs, is represented by the equation

$$c_p = 0.1667 + 0.000700t - 0.000003240t^2$$

The changes in heat content for the solutions were found for each interval by subtracting the changes in heat content of the glass in each specimen. Empirical equations of the form:

$$\Delta H/gm = A(t_2 - t_1) + B(t_2^2 - t_1^2) + C(t_2^3 - t_1^3)$$

were formulated for each of the fifteen or more determinations with each specimen, using  $t_2$  as the higher and  $t_1$  as the lower temperature in each case. The several equations were then combined to find the best values of the constants  $A$ ,  $B$  and  $C$ . Substitution in the final equations showed that they fitted the data with a maximum error not greater than  $\pm 0.5\%$  in every case. By taking  $t_1$  as zero these equations assume the simple form

$$\Delta H/gm = At + Bt^2 + Ct^3$$

which gives in each case the quantity of heat required to raise one gram of the material involved

from 0° to  $t^\circ$ . The first derivatives of these equations with respect to temperature are the empirical equations for their specific heats.

The following equations have been found to represent the specific heats of morpholine and of the solutions which were used in the experiments between 0 and 130°.

$$\begin{aligned} \text{Morpholine } c_p &= 0.473 + 0.000096t + 0.00000312t^2 \\ 6.27\% \text{ H}_2\text{O } c_p &= 0.496 + 0.000722t + 0.00000099t^2 \\ 15.37\% \text{ H}_2\text{O } c_p &= 0.552 + 0.001054t + 0.00000180t^2 \\ 27.50\% \text{ H}_2\text{O } c_p &= 0.610 + 0.001127t + 0.00000526t^2 \\ 39.71\% \text{ H}_2\text{O } c_p &= 0.681 + 0.000470t + 0.00001215t^2 \\ 48.85\% \text{ H}_2\text{O } c_p &= 0.728 + 0.000240t + 0.00001290t^2 \\ 61.09\% \text{ H}_2\text{O } c_p &= 0.800 + 0.000500t + 0.00000810t^2 \\ 66.95\% \text{ H}_2\text{O } c_p &= 0.817 + 0.000600t + 0.00000660t^2 \\ 75.04\% \text{ H}_2\text{O } c_p &= 0.860 + 0.000576t + 0.00000450t^2 \\ 81.09\% \text{ H}_2\text{O } c_p &= 0.900 + 0.000358t + 0.00000414t^2 \\ 91.60\% \text{ H}_2\text{O } c_p &= 0.956 + 0.000572t - 0.00000090t^2 \end{aligned}$$

These equations were used in calculating the specific heats of the various mixtures at 0, 25, 50, 75, 100 and 130°. These values were plotted on a large scale and the specific heats at rounded concentrations were read off. They are given in Table I.

TABLE I  
SPECIFIC HEATS OF MORPHOLINE AND ITS AQUEOUS SOLUTIONS

% H <sub>2</sub> O	$c_p$ at					
	0°	25°	50°	75°	100°	130°
0	0.475	0.477	0.486	0.498	0.514	0.538
10	.522	.539	.570	.600	.619	.649
20	.576	.597	.633	.670	.711	.760
30	.629	.651	.690	.729	.791	.871
40	.681	.703	.740	.780	.850	.948
50	.733	.757	.787	.826	.892	.982
60	.787	.807	.831	.871	.929	1.002
70	.840	.858	.877	.910	.954	1.011
80	.892	.905	.919	.942	.972	1.013
90	.946	.952	.960	.971	.991	1.016
100 <sup>a</sup>	1.008	.999	.999	1.002	1.007	1.018

<sup>a</sup> The specific heats of water were taken from the tables given by Dorsey, "Properties of Ordinary Water Substance," Reinhold Publishing Corp., New York, N. Y., 1941, pp. 258 and 261.

The graphs just mentioned were also used in finding the partial molal heat capacities of the components in the various solutions. The graphical application of the method of intercepts was found to be inaccurate, so an analytical method was employed instead. Empirical equations were fitted to the curves; from these equations the slopes of the curves were found at the concentrations of Table I and the intercepts were calculated from these slopes and the corresponding specific

heat values. Multiplication of these intercepts by the respective molecular weights gave the partial molal heat capacities. These values for each component were plotted against their respective mole fractions in the solutions and the partial molal heat capacities were read off at round mole fractions. Specific heat is a rectilinear function of concentration at 0° for this system within the limits of error of the determinations.  $\bar{C}_{\text{H}_2\text{O}}$  is 18.0 and  $\bar{C}_{\text{C}_4\text{H}_8\text{ON}}$  is 41.3 for all mole frac-

tions at this temperature. The values for the other temperatures are given in Table II.

The values of partial molal heat capacity as calculated were checked by means of the equation

$$C = N_1\bar{C}_1 + N_2\bar{C}_2$$

where  $C$  is the heat capacity per total mole for each of the solutions,  $N_1$  and  $N_2$  are the mole fractions of water and morpholine, respectively, and  $\bar{C}_1$  and  $\bar{C}_2$  are their partial molal heat capacities. The values of  $C$ ,  $N_1$  and  $N_2$  were calculated from the original experimental data, and the values of  $\bar{C}_1$  and  $\bar{C}_2$  were read from large scale plots of the data of Table II. The sums of the contributions of the components as calculated were equal to the heat capacities per total mole as found with a mean deviation of  $\approx 1\%$  for all the results, and with a maximum deviation not greater than 2% in any case. It is believed that these figures fairly represent the accuracy of this work as a whole.

The nature of the results will be apparent from the tables. In spite of much study, no simple relationships have been found between the specific heats or the partial molal heat capacities and the concentrations in the system.

### Summary

The specific heats of morpholine and its aqueous solutions have been determined between 0 and 130° and between 0 and 100% water; and the partial molal heat capacities of the components of the system have been calculated at several temperatures.

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TABLE II  
PARTIAL MOLAL HEAT CAPACITIES FOR MORPHOLINE-  
WATER SOLUTIONS

$N_{\text{H}_2\text{O}}$	For $\text{H}_2\text{O}$ at				
	25°	50°	75°	100°	130°
0	19.8	24.2	26.9	28.1	29.1
0.1	19.7	23.5	26.2	28.1	29.1
.2	19.6	22.8	25.4	28.1	29.1
.3	19.5	22.2	24.5	27.9	29.1
.4	19.3	21.5	23.5	27.7	29.1
.5	19.2	20.8	22.4	26.7	29.1
.6	19.0	20.1	21.2	23.2	28.9
.7	18.7	19.3	20.1	21.2	26.9
.8	18.4	18.5	18.9	19.7	21.2
.9	18.1	18.2	18.4	18.6	18.7
1.0	18.0	18.0	18.1	18.2	18.3

  

$N_{\text{C}_4\text{H}_8\text{ON}}$	For morpholine at				
	25°	50°	75°	100°	130°
0	48.4	53.3	63.6	69.4	86.4
0.1	45.0	51.0	58.1	65.8	82.8
.2	43.1	47.4	51.9	59.0	69.9
.3	42.4	45.4	48.5	51.3	55.0
.4	42.1	44.4	46.6	46.8	48.5
.5	41.9	43.7	45.5	45.6	46.9
.6	41.8	43.2	44.8	45.1	46.9
.7	41.7	42.9	44.4	44.9	46.9
.8	41.7	42.7	44.1	44.8	46.9
.9	41.6	42.5	43.9	44.7	46.9
1.0	41.6	42.3	43.7	44.7	46.9