In actual fact, and with resonance present, the value of Δ log k for the dimethylamino ester is -1.53. The maximum increase in the free energy of activation (2.303 RT Δ log k) which can be ascribed to the resonance of the dimethylamino group, then, is 2700 cal. The actual decrease in the free energy of activation caused by damping the resonance is about 1800 cal. It is clear that the major portion of the stabilization has been eliminated by damping the resonance.

A more significant calculation, which would permit an estimate of the effect of damping on the interaction of the dimethylamino group with the carbethoxy group alone, and free from electrostatic effects, must await the determination of the direction of the moment of the hindered dimethylamino group.

The authors wish to acknowledge the valuable help and advice of Dr. G. W. Wheland.

Summary

1. Ethyl 3,5-dimethyl-4-dimethylaminobenzoate has been synthesized.

2. The rates of saponification of ethyl p-dimethylaminobenzoate, ethyl 3,5-dimethylbenzoate, ethyl 3,5-dimethyl-4-nitrobenzoate, ethyl 3,5-dimethyl-4-aminobenzoate and ethyl 3,5-dimethyl-4-dimethylaminobenzoate have been measured.

3. As predicted from the theory of damped resonance, the rate of saponification of ethyl 3,5-dimethyl-4-dimethylaminobenzoate greatly exceeds that of ethyl 3,5-dimethyl-4-aminobenzoate.

4. It is concluded that the low rate of saponification of ethyl p-aminobenzoate relative to that of ethyl benzoate is primarily caused by resonance interaction of the amino and carbethoxy groups.

CHICAGO, ILLINOIS RECEIVED JANUARY 15, 1941

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, PURDUE UNIVERSITY]

The Heat Capacity of Organic Vapors. I. Methyl Alcohol

BY THOMAS DE VRIES AND BEN T. COLLINS

In order to calculate the potential of the barrier hindering the rotation of the methyl group in methyl alcohol, the heat capacity and fundamental vibration frequencies of the vapor must be known. In this paper are presented the experimental data for the heat capacity of the vapor from 75 to 170°. The continuous flow electric method of Callender and Barnes[1] was used with the improvements of Scheel and Heuse.[2]

The data in the literature are meager and questionable. Regnault[3] obtained an average value for the temperature interval 100–223° and Thibaut[4] obtained a value at 340°, both by calorimetric methods. The results obtained by Stevens[5] and by Dixon and Greenwood[6] with the velocity of sound method are too low because it is known that the conversion of translational or rotational energy into vibrational energy is too slow a process for the frequencies used in sound velocity measurements.

Apparatus and Method

Methyl Alcohol.—One of the best grades of commercially available methyl alcohol was dried with magnesium methylate and redistilled within 0.1° of its correct boiling point. The alcohol was vaporized in a Pyrex glass tube by means of controlled electrical heat. A uniform rate of flow of the vapor was obtained by surrounding the boiler with a Dewar flask and by insulating the exit tube to prevent refluxing. Before entering the calorimeter, the vapors were led through a long glass spiral to bring the vapors to the temperature of the thermostat. This equality of temperature was checked with a thermocouple. Both the rate of flow and the rate of heating were varied in order to obtain by extrapolation of the data a value corrected for heat losses. After leaving the calorimeter, the vapor was condensed and collected in a closed receiver.

Calorimeter.—The calorimeter was similar in general design and dimensions to that used by Scheel and Heuse[2] for their determination of the specific heat of gases. It was fabricated from Pyrex glass and was 25 cm. long and 4.6 cm. in diameter (Fig. 1). It was silvered and thoroughly evacuated. A tube with activated charcoal was sealed on which made it possible to compare the results of two series of determinations in one of which liquid air was used around the charcoal tube. There was not enough difference in the results to warrant the use of liquid air for the other determinations. The calorimeter was placed vertically in an oil filled thermostat, regulated to 0.01° with a mercury-in-glass regulator. The thermostat was 23 cm. in diameter and 54 cm. deep and a hydrogenated

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[1] Callender and Barnes, *Trans. Roy. Soc.* (London), **199A**, 55–263 (1902).

[2] Scheel and Heuse, *Ann. Physik*, (4) **37**, 79 (1912).

[3] Regnault, *Ann. chim. phys.*, **24**, 342 (1871).

[4] Thibaut, *Ann. Physik*, (4) **35**, 347 (1911).

[5] Stevens, *ibid.*, **7**, 285 (1902).

[6] Dixon and Greenwood, *Proc. Roy. Soc.* (London), **105A**, 199 (1924).

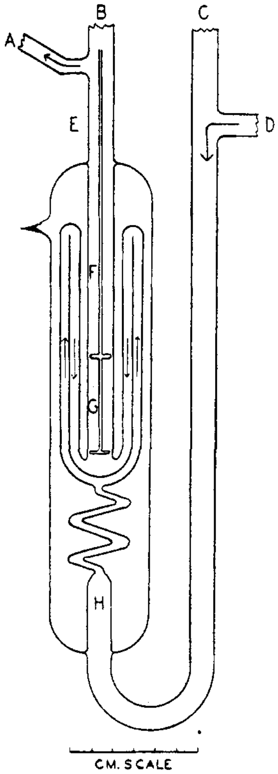

Fig. 1.—Sketch of calorimeter; details of accessories and thermostat not shown.

cooking fat was used for the bath liquid. Electric heating coils were wound around the well-insulated tank used for the thermostat and auxiliary heaters were placed in the bath.

The increase in temperature of the vapor was measured with a ten junction copper–constantan thermel with one end at H, the other at F. The wires were brought in at B and C, some distance above the oil level, and were sealed in with a dental plastic of high electrical resistivity. The wires for the heater, G, were brought in at B inside the small glass tube which supported the thermel and had at its lower end the support for the spirally wound electric heater.

The lead-out wires of the thermel junctions at F were a much shorter distance in the bath than those from the junctions at H, with the result that there was an approximate temperature difference of about 0.04° because of heat leakage along the wires. A barrier for this heat leak was made by raising the temperature of the lead-out wires at position E to equal the temperature at the junctions. This was accomplished by passing a regulated current through a few turns of resistance wire wrapped around the bundle at E. A copper–constantan thermocouple with one junction at F, the other inside the bundle of wires at E, was used to determine that there was no difference of temperature at all times during a determination.

Electrical.—The ten-junction thermel was made from copper and constantan wire, no. 30 B. and S. gage, using the precautions recommended by White.[7] It was used to measure the rise in temperature of the vapors flowing past the heater. Auxiliary thermocouples were used to measure temperatures of the thermostat and the vapor at position D before it entered the calorimeter. The thermel and thermocouples were calibrated at the boiling points of water and naphthalene. The Adams reference table was used for the calculations of temperature.

The heater in the calorimeter was made by coiling 60 cm. of chromel-A wire, no. 28 B. and S. gage, to a diameter of 5 mm. and supporting on a glass tube, 3 mm. in diameter. Its resistance was approximately 8 ohms. Two lead-out wires of copper, no. 26, were used at each end of the coil, one for the current, the other for measuring the potential across the heater. The current through the heater was computed from the potential drop across a standard resistance, made of manganin wire, no. 20 gage, with a resistance of 1.1287 ± 0.0004 ohm, which was in series with the heater. The maximum current through the standard resistance and heater was about 0.15 ampere.

Constancy of current from a two-volt storage battery was obtained by charging it with current from a six-volt battery through a variable resistance of about 10 ohms. The six-volt battery in turn was charged at a uniform rate of one ampere from the direct current supply in the building. In this way it was possible to obtain a current which was constant to one part in 17,000 for fifteen minutes, and to one part in 3000 for as long as one hour. The charging rate of the two-volt battery had to be varied according to the current required for the heater.

Procedure.—Preliminary to a determination, the rate of flow of the methyl alcohol vapor and the current through the heater were adjusted to the desired values and observed for fifteen to twenty-five minutes. During this time the temperature of the bundle of wires at E was also checked and made to equal the temperature at F. After all the adjustments had been made, alcohol was collected for about an hour, during which time readings were taken of the temperatures and potentials across the resistances. The alcohol was weighed at the conclusion of a determination. The values for the rate of flow (F) used in the calculations recorded in Table I are given in units of grams per second. The temperature rise recorded in Table I is the average of as many as twelve readings during a run, the average deviation being usually less than 1%. The current was constant to at least 0.05%. Slight fluctuations in temperature were due more to a variation in the rate of flow of the vapor than to a variation in the heating current. All determinations were made at a pressure of approximately 750 mm. of mercury.

The data were corrected for heat lost to the surroundings according to the following equation. If E represents the rate of heat input, e the rate of heat loss and m the rate of flow, the specific heat (or heat capacity, depending on the units which are used) is given by $C_p = (E - e)/m\Delta T$. The heated vapor will lose heat to the incoming vapor at a rate proportional to the increase in temperature, *i. e.*, $e' = k_1\Delta T = k_2E/m$. This will heat the incoming vapor by an amount $\Delta T' = e'/m$. The loss to the surroundings will be $e = k_3\Delta T' = k_3e'/m = k_4E/m^2$. Using this last relation in the first equation above, we have[8]

$$C_p = \frac{E}{m\Delta T}\left(1 - \frac{k_4}{m^2}\right) = C_p(1 - k/m^2)$$

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[7] White, This Journal, 36, 2922 (1914).

[8] J. R. Partington and W. G. Schilling, "The Specific Heats of Gases," E. Benn, Ltd., London, 1924, page 46.

The evidence for the validity of this equation is that straight lines were obtained, all with practically the same slope, when the calculated values were plotted against the reciprocal of the square of the rate of flow. A representative line is shown in Fig. 2. The extrapolated values at infinite rate of flow were the desired specific heats and were calculated by applying the method of least squares to obtain equations for the straight lines. The data of the experiments are presented in Table I with a summary in Table II.

TABLE I

DATA OF EXPERIMENTS AND CALCULATIONS FOR SPECIFIC HEAT AT INFINITE RATE OF FLOW (F)

Temp., °C.	Cal./sec.	ΔT, °C.	Alcohol, g.	Min.	$1/F^2$	Specific heat
76.5	0.04631	5.169	59.63	60	3648	0.541
	.04674	4.660	67.20	60	2873	.537
	.04631	4.319	71.28	60	2551	.542
	.03150	2.604	85.37	65	2089	.553
	.04662	3.752	82.13	60	1919	.545
	.04674	2.464	94.45	45	818	.542
					0	.542
85.0	.04614	5.371	66.15	60	2962	.468
					0	.446
85.7	.04664	3.305	91.85	50	1106	.461
					0	.452
86.7	.04674	2.455	100.59	40	569	.454
					0	.450
95.0	.04641	5.405	70.39	60	2616	.439
	.04689	2.488	105.61	40	517	.428
109.0	.04609	6.453	58.80	60	3748	.437
	.04623	5.936	65.04	60	3064	.431
	.04638	5.332	73.24	60	2415	.428
	.04641	4.553	86.85	60	1718	.423
	.04651	4.191	95.25	60	1429	.420
	.04635	3.740	106.75	60	1137	.418
	.04686	2.532	107.55	40	498	.413
	.04681	2.073	97.99	30	338	.415
					0	.409
128.0	.04560	5.227	60.63	50	2448	.432
	.02750	2.810	75.70	55	1901	.427
	.04417	4.341	87.76	60	1683	.417
	.04436	3.801	66.45	40	1305	.422
	.04652	3.191	84.24	40	812	.415
	.04513	2.765	82.93	35	641	.413
	.04641	2.364	86.44	30	434	.409
					0	.406
147.0	.04478	4.206	81.56	55	1637	.431
	.04400	2.928	96.77	45	778	.419
	.04429	1.814	88.97	25	284	.412
					0	.408
169.5	.04435	4.515	59.90	45	2032	.443
	.04373	3.166	85.85	45	989	.434
	.04403	2.527	85.04	35	610	.430
					0	.425

TABLE II

HEAT CAPACITY OF METHYL ALCOHOL

t, °C.	Cal./mole	t, °C.	Cal./mole
76.5	17.37	109.0	13.10
85.0	14.29	128.0	13.01
85.7	14.48	147.0	13.07
86.7	14.42	169.5	13.62
95.0	13.62		

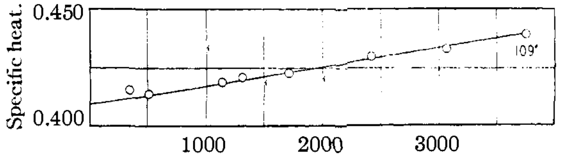

Fig. 2.—Extrapolation of specific heat data to infinite rate of flow.

At the boiling point the heat capacity at constant pressure of the vapor appears to be in the neighborhood of the values for the liquid as determined by Fiock, Ginnings and Holton.[9] There is no logical reason why this should be the case. However, Newton[10] has shown that for many liquids and vapors the values for the heat capacity at constant volume are nearly identical. This equality appears to be true also for methyl alcohol. The value of $C_p - C_v$ for the liquid was calculated to be 4.88 and 4.85 cal. for 40 and 60°, respectively, from the data by Bridgeman and others.[11] For the vapor the value of 2 cal. can be used. Thus the minimum in the curve at 120° is still more than 5 cal. below the value of C_v at the boiling point (Fig. 3).

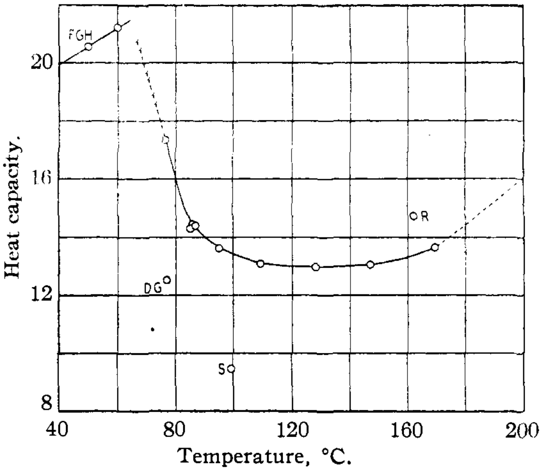

Fig. 3.—Variation of heat capacity with temperature, data of other investigators: FGH, Fiock, Ginnings and Holton; DG, Dixon and Greenwood; S, Stevens; R, Regnault. Dotted line at right increases to Thibaut's value at 340°.

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[9] Fiock, Ginnings and Holton, *Bur. Stand. J. Research*, **6**, 881 (1931).

[10] Newton and Eyring, *Trans. Faraday Soc.*, **33**, 75 (1937).

[11] "International Critical Tables," Vol. III, pp. 27, 41.

The anomalous behavior of the heat capacity of methyl alcohol vapor, showing first a decrease with a minimum at about 120° and then a normal increase of heat capacity with temperature, can be explained by assuming that part of the energy is required for the dissociation of associated methyl alcohol molecules. Vapor densities of methyl alcohol determined by Young[12] are probably of sufficient reliability to calculate the order of magnitude of the association. Assuming dimer formation, the fraction, x, of the molecules which were associated was calculated (Table III). A mixture of dimers and trimers is probably formed at higher pressures. Upon the assumption that trimers were formed, the fraction, x', was also calculated. By glancing at the tabulated results it is evident that association of the vapor occurs at the boiling point under atmospheric pressure. An extrapolation of the calculated values for 120 and 160° to one atmosphere of pressure shows that 0.8 and 0.3% of the molecules are associated at these temperatures as contrasted with about 9% at the boiling point. In view of the above discussion a new apparatus has been built to determine the heat capacity of the vapor at temperatures above 200° and at pressures less than one atmosphere.

TABLE III

DEGREE OF ASSOCIATION OF METHYL ALCOHOL VAPOR

t, °C.	Pressure in mm.	Mol. wt.	x	x'
20	96.0	32.3	0.016	
40	260.5	32.9	.054	
60	625.0	33.4	.083	0.062
70	927	33.8	.105	.079
80	1341	34.2	.128	.096
100	2621	35.3	.187	.140
120	1520	32.54	.031	.023
120	3040	34.16	.125	.094
120	4560	36.52	.245	.188
160	1520	32.11	(.004)	(.003)
160	3040	32.86	.050	.038
160	4560	33.63	.095	.071

Summary

The heat capacity of methyl alcohol vapor was determined at selected temperatures in the interval from 75 to 170°, using a Scheel and Heuse flow calorimeter. The vapor was heated electrically and the increase in temperature was measured with a ten-junction copper–constantan thermel. There is a flat minimum in the heat capacity curve from approximately 110 to 150°. This minimum can be explained by assuming the presence of associated molecules in the vapor state.

WEST LAFAYETTE, INDIANA RECEIVED FEBRUARY 7, 1941

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[12] Landolt–Börnstein, "Tabellen," 5th ed., Vol. I, p. 278, Vol. II, p. 1361; "International Critical Tables," Vol. III, p. 436.

[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT OF DUKE UNIVERSITY]

Solubility Studies. VI. The Solubility of Nitrobenzene in Deuterium Water and in Ordinary Water

BY HERBERT E. VERMILLION,[1] BURTON WERBEL, JOHN H. SAYLOR AND PAUL M. GROSS

In connection with our investigations of the solubilities of organic compounds in aqueous solutions, it was thought to be of interest to compare the solubilities of nitrobenzene in deuterium water and in ordinary water.

Experimental

The solubilities of nitrobenzene in deuterium water were determined both by the use of a Zeiss liquid–gas interferometer and by an analytical method.

The interferometer method previously described[2] was modified so that small samples could be used. An 8-cm. gold-plated interferometer cell was employed in the measurements. While the total capacity of the cell is about 25 ml., a cross section of only approximately 4 sq. mm. in each compartment is needed to permit passage of the light beam through the cell. Therefore a brass insert channelled to pass the light beam was fitted into each compartment of the cell to reduce the volume until a 5-ml. sample completely filled the cell.

Standard solutions for the calibration of the interferometer were prepared by weighing on a microbalance a droplet of nitrobenzene placed in the center of a weighed capillary tube. The tube and its contents were then dropped into a weighed Pyrex vial with a constricted neck and the desired amount of water (about 6 g.) added. The vial was then sealed off and weighed. The vials were then shaken until the nitrobenzene was in solution. Any transfer of deuterium water was always made in a special cabinet capable of maintaining a dry atmosphere.

The saturated solutions were prepared by shaking an excess of nitrobenzene with about 5 ml. of the solvent in

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[1] This paper was taken in part from the thesis submitted by Herbert E. Vermillion to the Graduate School of Duke University in partial fulfillment of the requirements for the degree of Doctor of Philosophy, June, 1939.

[2] Gross and Saylor, THIS JOURNAL, **53**, 1744 (1931).