

The Vapor Pressure of Dimethylamine from 0 to 40° C.

ELIJAH SWIFT, JR. and HELEN PHILLIPS HOCHANADEL, Indiana University

As part of a series of investigations of the properties of the simple aliphatic amines near room temperature (5, 6, 7), we have measured the vapor pressure of dimethylamine at several temperatures between 0 and 40° C.

Previous determinations of the vapor pressure of dimethylamine have been carried out by Berthoud (3), Simon and Huter (4), and by Aston, Eidinoff and Forster (1). Berthoud measured the vapor pressure of dimethylamine from 5° up to the critical temperature, 164.55°; however, he reports only two values below 40°. The other workers were mainly interested in values up to the normal boiling point, 6.88° C.

Experimental

Two series of measurements were made using a different sample of carefully purified dimethylamine for each series. The purification has been described previously (5). The amine was sealed in an all-glass apparatus, dried over solid potassium hydroxide, and desiccated by dissolving sodium fluorenone in it (2). The dry amine was then evaporated through a spray trap into another bulb and frozen with liquid air. The system was evacuated to 10^{-4} mm. or lower and the amine then allowed to melt. The freezing and melting process was repeated at low pressure until the amine had been reduced to about $\frac{1}{3}$ of the original volume, to make sure that all dissolved gases had been removed.

The vapor pressure at the ice point was then taken. To check the absence of dissolved gases, the vapor was allowed to expand into a much larger volume, and the vapor pressure again measured. Finding the same value of the vapor pressure in the two cases was taken as sufficient proof of the purity of the sample.

The samples were transferred by vacuum distillation to an isotensiscope equipped with a magnetic stirrer which served to break the surface of the liquid about twice a second. The vapor pressure at the ice point was again measured and found to check the previous readings within a millimeter.

At each temperature care was taken to allow sufficient time for equilibrium to be established, as evidenced by a steady reading for at least half an hour while the liquid was being agitated. The mercury levels in the isotensiscope were adjusted to within 0.5 mm. of each other, and the levels in the manometer then read with a Societe Genevoise cathetometer. Since some of the preliminary measurements were made with a Gaertner cathetometer, the two instruments were checked against one another and found to agree within better than 0.5 mm. over the

whole scale. For the pressures greater than 1000 mm., a meter stick was used, and later checked against the cathetometer scale.

The barometric pressure was taken from an open manometer which was read with the same cathetometer as above. The diameters of the reservoir and tube of this manometer were the same as those of the main manometer, to cancel out any bore correction. Brass scale corrections were applied to all readings.

Temperatures were maintained constant to $\pm 0.02^\circ$ C., the absolute value being obtained to 0.01° by comparing the thermometers used with a platinum resistance thermometer calibrated at the ice point.

Results

The corrected observed pressures are shown in the second Column of Table I, as averaged values for all readings. The average deviation from the mean of all these results is 0.3%, and the overall accuracy is estimated to be 0.5%.

Table I. The Vapor Pressures of Dimethylamine

T° C.	P _{mm.obs.}	P _{obs.—P_{calc.}}		
		(a)	(b)	(c)
			(d)	
0	561.3	..	-2	-2
15	1057	..	11	-3
20	1282	21	23	-5
25	1542	..	40	-10
30	1840	32	66	-19
35	2177	—	100	-37
40	2559	36	144	-60

(a) P_{calc.} Values from Berthoud's (3) smoothed data in the International Critical Tables.

(b) P_{calc.} Values calculated by the extrapolated equation of Simon and Huter (4).

(c) P_{calc.} Values calculated by the extrapolated equation of Aston, Eidinoff and Forster (1).

(d) P_{calc.} Values calculated by Equation (1), this paper.

Our values are compared with those of Berthoud (3) in Column 3 of the table. It is seen that his values lie somewhat below ours; but considering that he claimed an accuracy of only 0.1 atmosphere, the agreement is remarkably good.

In Columns 4 and 5 are found comparisons of our data with values calculated from two empirical equations, extrapolated from temperature ranges lower than ours. Both equations were derived from the results of very careful measurements, and give the same value at 0° C., 563.5 mm., which is within the limit of error of our results. At the high temperatures where the equations are extrapolated considerably, Simon and Huter's equation (Column 4) gives low values, while Aston, Eidinoff and Forster's equation (Column 5) gives high values.

Since neither equation yields satisfactory results in our range of temperature, an empirical equation was derived for temperatures between 0 and 40° C. This equation is:

$$(1) \quad \text{Log } P_{\text{mm}} = \frac{-2354.3}{T} - 7.433 \text{Log}_{10} T + 29.47675,$$

where T is the absolute temperature. The agreement between the observed values and those calculated by means of this equation is shown in Column 6 of the table. The differences are well within our limit of error.

Bibliography

1. Aston, J. G.; Eidinoff, M. L., and Forster, W. S., 1939. Journal of the American Chemical Society, **61**:1539.
2. Bent, H. E., and Irwin, H. M., 1936. Journal of the American Chemical Society, **58**:2072.
3. Berthoud, A., 1917. Journal de Chimie Physique, **15**:14.
4. Simon, A., and Huter, J., 1935. Zeitschrift fur Elektrochemie, **41**:28.
5. Swift, E., Jr., 1942. Journal of the American Chemical Society, **64**:115.
6. Swift, E., Jr., and Calkins, C. R., 1943. Journal of the American Chemical Society, **65**:2415.
7. Swift, E., Jr., and Wolfe, D. L., 1944. Journal of the American Chemical Society, **66**:498.