

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF MONTANA STATE COLLEGE]

Vapor Pressure of Methyl Sulfoxide from 20 to 50°. Calculation of the Heat of Vaporization

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For the calculation of bond energies from the previously reported² heats of two reactions involving liquid methyl sulfoxide, the heat of vaporization of this substance near room temperature must be known. It seemed that this quantity could be most conveniently determined with the required accuracy by measuring the vapor pressure at several temperatures. There was adopted a modification of the gas-saturation method used by Baxter and co-workers³ to determine the vapor pressure of iodine. The amount of methyl sulfoxide evaporated was determined by chemical analysis.

Experimental Procedure

Methyl sulfoxide, prepared as previously described,² was finally purified in a closed system (J in Fig. 1) by four recrystallizations, the last of which did not appreciably change the freezing point (18.42°). The amount of impurity remaining was estimated to be 0.1 mole %, and the vapor pressure values were corrected accordingly.

Air, entering at A, was purified in train B by successive passage over the solids ferrous sulfate, potassium hydroxide, chromium trioxide, potassium hydroxide, and phosphorus pentoxide. Passing through a thermostat over two layers of liquid methyl sulfoxide C (each layer being 5 mm. wide and 25 cm. long) at a rate of two liters per hour (measured by a flowmeter K) and at a pressure 0.1 mm. below atmospheric, the air then bubbled through mercury (D), which completely prevented contamination of the liquid sulfoxide by backward diffusion of water vapor. The saturated sulfoxide vapor was absorbed in two tubes each containing 15 ml. of water (E). The air then emerging from the thermostat, after being thoroughly redried in the train F, was admitted through a system of capillaries (G) to one or two thirteen-liter highly evacuated glass bulbs (H) whose volumes had been (1) determined by filling with water and (2) checked by admittance of dry air and use of its data of state. The final pressure of the collected air was compared with the barometric pressure by means of a butyl phthalate manometer (L).

The temperatures of the thermostat and the collected air were periodically measured to $\pm 0.01^\circ$ by single-junction copper-constantan thermocouples,⁴ using a calibrated Type K potentiometer and correcting for extraneous potentials. (The five thermocouple wells are designated in Fig. 1 by P.) The thermostat temperature remained constant to $\pm 0.005^\circ$, and the total gradient averaged 0.03° at the highest temperatures. The combined absorption solutions produced in each run were withdrawn through tube M (sealed by mercury (N) during runs) and were accurately analyzed for their total content of methyl sulfoxide by the method previously developed,² with use of blanks and the other usual precautions.

Experimental Errors.—Tests were made to determine whether certain suspected sources of systematic error appreciably affected the results.

The contamination of the methyl sulfoxide during the

series of runs was found to be inappreciable. After the completion of half the runs, involving the passage of 170 liters of air, the freezing point of the remaining sulfoxide was redetermined and found to have changed not more than 0.03° . This result indicated also the lack of appreciable reaction between the sulfoxide and oxygen of the air at the temperatures used. Nor did a removal of appreciable sulfoxide vapor by adsorption seem to occur before it reached the absorber tubes. For the various temperatures were run in random order and no chronological trend of vapor pressure values was detectable after three preliminary runs, each of whose values was about 0.5% low on the basis of the remaining fifteen runs.

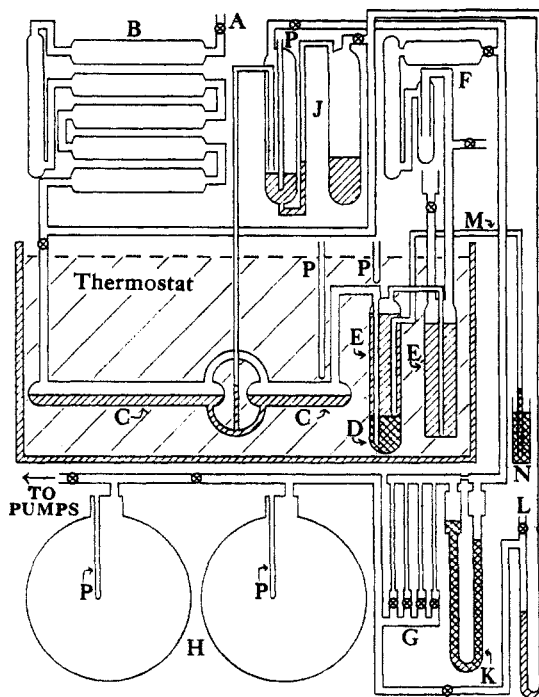


Fig. 1.—Apparatus used for determining the vapor pressure of methyl sulfoxide. No disassembling between runs was necessary. The arrangement permitted the liquid being frozen in J to be stirred by a stream of dry air.

Tests were made to establish whether the normal rate of air flow of two liters per hour was slow enough to permit complete saturation of the air with sulfoxide vapor, and a subsequent complete absorption of the vapor. One extra run at 30° and one at 50° were made at twice⁵ the normal rate of air flow, yielding vapor pressure values which were, respectively, 0.1 and 0.3% lower than at the normal rate, which latter thus appears to be sufficiently slow.

Within the experimental error, all the sulfoxide vapor was found to be retained by the first of the two absorber tubes. One extra run at 30° and one at 50° in which water was present in only the first absorber tube gave vapor

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(2) Douglas, *THIS JOURNAL*, **68**, 1072 ff (1946).

(3) Baxter, Hickey and Holmes, *ibid.*, **29**, 127 ff (1907); Baxter and Grose, *ibid.*, **37**, 1061 ff. (1915).

(4) Calibrated at the ice-point, the steam-point, and the transition temperatures of $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$, $\text{NaBr} \cdot 2\text{H}_2\text{O}$, and $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$ [Richards and Wrede, *Z. physik. Chem.*, **61**, 313 (1907)].

(5) Doubling the rate of flow should provide a more rigorous test than halving it, since the change in observed vapor pressure due to lack of saturation should be much greater in the former case.

pressure values which were respectively 0.1% lower and 0.2% higher than the values obtained using two absorbers. As a check the total water collected from the emerging air from all the runs was found to contain only a mere trace of sulfoxide.

It was feared that some mercury may have been carried into the water absorbing the sulfoxide vapor, causing the subsequent titration of the solution with permanganate to run high. One solution from a 30° run and one from a 50° run were each tested for mercury, which, if present at all, was shown to be insufficient in amount to raise the experimental value of the vapor pressure by more than 0.1%.

The departure of the saturated methyl sulfoxide vapor, mixed with air, from gas ideality is probably small, but seems too uncertain to justify its estimation. During one purification of the sulfoxide a sample was observed to boil at 79° at 16.5 ± 1 mm., whereas extrapolation of the calculated vapor pressure values to this temperature gives 15.5 mm. This comparison indicates that the vapor density does not differ widely from that calculated using the formula (CH₃)₂SO. Nor is departure from this formula, through dissociation or association, to be expected on theoretical grounds.

An estimation of individual errors indicated that the experimental vapor pressure values, as represented by the empirical equation below, are probably accurate in the temperature range of the measurements to within ±1%.

Results

Each value of the vapor pressure was calculated from the experimental data by use of the equation

$$p = \frac{0.9977 P_1}{N \left(\frac{P_2 V_2}{nRT_2} \right) + 1}$$

where p is the vapor pressure of pure methyl sulfoxide, P_1 the average total pressure in the saturator (about 635 mm.), N the estimated mole fraction of methyl sulfoxide in the liquid used, P_2 the pressure of collected air at absolute temperature T_2 , V_2 the volume of collected air, n the moles of methyl sulfoxide evaporated (assuming the formula (CH₃)₂SO), and R the gas constant. 0.9977, the ratio of the fugacity of liquid methyl sulfoxide at pressure p to its fugacity at pressure P_1 ,⁶ corrects the vapor pressure to the value which should be obtained in the absence of the air. Two independent measurements of vapor pressure were made at each temperature at 5° intervals from 20 to 50°. These duplicates at the same temperature agreed on the average to within 0.15% and the maximum difference was 0.5%.

Using the method of least squares and giving

(6) Using $(\partial \ln f / \partial P)_T = v/RT$, where v is the molal volume of the liquid, 71 ml. The ratio of fugacities is practically independent of temperature in the range investigated.

each value of $\log p$ equal weight, the following equation was found for the vapor pressure of methyl sulfoxide from 20 to 50°.⁷ This equation

$$\log_{10} p = 26.49558 - (3539.32/T) - 6.00000 \log_{10} T \quad (1)^8$$

represented the experimental values of vapor pressure with an average deviation of ±0.15%, the maximum discrepancy being 0.4%. Values calculated from equation (1) in this temperature range are given in Table I.

TABLE I

VAPOR PRESSURES OF METHYL SULFOXIDE AT ROUNDED TEMPERATURES

(Calculated from equation (1))			
Temp., °C.	Vapor pressure, mm.	Temp., °C.	Vapor pressure, mm.
20	0.417	40	1.656
25	.600	45	2.27
30	.853	50	3.07
35	1.195		

Equation (1) yields a value of 12.64 kcal. for the molal heat of vaporization of methyl sulfoxide at 25°. This figure was estimated to have an uncertainty of ±0.1 kcal. It is of interest that equation (1) leads to a normal boiling point of 192° and a Trouton constant of 22.9 cal./mole/deg., but these two figures are naturally not highly reliable, because of the wide extrapolations involved.

Summary

The vapor pressure of methyl sulfoxide has been determined by a gas-saturation method at 5° intervals from 20 to 50°.

The values found are expressed, with an average deviation of ±0.15%, by the equation

$$\log_{10} p = 26.49558 - (3539.32/T) - 6.00000 \log_{10} T$$

which gives 12.64 ± 0.1 kcal. for the molal heat of vaporization at 25°.

Various sources of error are discussed. It is estimated that correct vapor pressures are given by this equation, in the temperature range of the measurements, to within ±1%.

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(7) Although the constants given are accurately interconsistent, it was first necessary to find by trial a value for the coefficient of $\log T$ which would approximately minimize the sum of the squares of the deviations. No value of this coefficient between -8 and -4 produces any particular trend of deviations with temperature.

(8) p in mm., T in deg. absolute, and 0°C. = 273.16°K.