

[CONTRIBUTION FROM THE LABORATORY OF FOODS AND SANITATION, UNIVERSITY OF WISCONSIN]

## THE VAPOR PRESSURE OF SULFUR MONOCHLORIDE<sup>1</sup>

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Sulfur monochloride seems to have been definitely known since 1803 when Thomson<sup>2</sup> first described it, but in contradiction to this statement is that of Payen<sup>3</sup> who reports that it was first obtained by Hagemann in 1782, although its constitution was not fully ascertained until it was studied by Davy and Bucholz in 1810.

In view of the diversity of directions in which sulfur monochloride finds technical application, it is pertinent to note that a very careful search of the literature failed to disclose any record of vapor-pressure measurements which had been made on highly purified material. It is the purpose of this communication to present such measurements, the heat of vaporization and the molecular elevation which have been calculated from these data.

### Experimental Procedure

**Materials.**—A commercial grade of sulfur monochloride served as the source material from which a highly purified preparation was obtained for use in these measurements. Redistillation is not satisfactory since Thorpe<sup>4</sup> found that under such conditions there is a partial decomposition into the dichloride and sulfur. This observation led Pope<sup>5</sup> to propose a method which yields a pure sulfur monochloride. It is the method of purification used in this investigation.

Sulfur monochloride of "pure" grade was mixed with 1% by weight of highly absorbent charcoal and sulfur. This mixture was distilled under atmospheric pressure in an all-glass apparatus, the fraction distilling above 137° being redistilled in a vacuum after the addition of sulfur and charcoal. Under a pressure of 28 mm., pure sulfur monochloride distilled at 41°. Its golden-yellow color, free from any tinge of red, was indicative of the absence of the higher chlorides of sulfur. It possessed the following physical constants:  $d_4^{25}$  1.67328; surface tension (capillary rise method), 40.78<sup>22</sup>; relative viscosity, 1.908<sup>18</sup>.

<sup>1</sup> Taken from a thesis submitted by E. H. Harvey to the Faculty of the Graduate School of the University of Wisconsin in partial fulfillment of the requirements for the degree of Doctor of Philosophy, January, 1926.

<sup>2</sup> Thomson, *J. Nat. Philosophy, Chem. Arts* (W. Nicholson), **6**, 92 (1803).

<sup>3</sup> Payen, "Manual of Industrial Chemistry," trans. by Paul, Wiley, 1878, p. 176.

<sup>4</sup> Thorpe, *J. Chem. Soc.*, **37**, 356 (1880).

<sup>5</sup> Pope, *ibid.*, **119**, 634 (1921).

Due precautions were taken to keep the material dry and out of contact with the air.<sup>6</sup>

**Apparatus.**—Ordinary methods of vapor-pressure measurement cannot be used on sulfur monochloride since it reacts with the mercury of the manometer. Its corrosive nature and susceptibility to decomposition by moisture make imperative the use of an all-glass apparatus. Satisfactory methods for determining the vapor pressures of corrosive liquids have been described within recent years, the method and form of apparatus used by Daniels and Bright<sup>7,8</sup> serving our purposes.

The essential feature of the method consists in the use of a glass diaphragm, sensitive to about 1 mm. pressure, whose movement makes or breaks an electric circuit and permits the balancing of an air pressure against the unknown pressure. The latter is read directly on a mercury manometer.

### Experimental Results

Using standard methods of thermostatic control, pressure readings were made at temperatures indicated in Table I. Owing to temperature lag,

TABLE I  
VAPOR PRESSURE OF SULFUR MONOCHLORIDE

Temp., °C.	—Pressure, mm. of Hg—		$P_{\text{obs.}} - P_{\text{calcd.}}$
	Obs.	Calcd.	
0	3.7	3.7	0.0
10	6.4	6.4	.0
20	10.7	10.8	+ .1
31	18.6	18.6	.0
40	28.0	28.8	+ .8
50	43.0	43.9	+ .9
59	60.0	59.9	- .1
70	93.0	94.1	+1.1
80	135.0	134.6	-0.4
90	186.4	188.7	+2.3
100	257.0	259.8	+2.8
110	351.5	351.8	+0.3
120	469.7	469.0	- .7
130	615.2	615.2	.0
138	760.0	760.0	.0

Mean deviation,  $\pm 0.6$  mm.

<sup>6</sup> A drying agent which offers possibilities here might be found in clean, dry, metallic sodium for it was observed that it does not react with pure, dry sulfur monochloride. We have not verified this observation with experimental proof. Nicolardot [*Compt. rend.*, **147**, 676 (1908)] claims that sulfur monochloride is without action on the alkali metals.

<sup>7</sup> Daniels and Bright, *THIS JOURNAL*, **42**, 1131 (1920).

<sup>8</sup> Dr. Daniels has improved his original pressure cell in that he has materially simplified the diaphragm without changing the principles involved in its operation. A description of the cell will be published in the near future.

a sufficient interval of time was allowed to elapse after the thermostat had come to the desired point before a reading was made. The latter was then corrected for the "zero" point of the apparatus.

Upon the completion of the first series of measurements, the pressure cell was opened at a point where a constriction had been drawn on the side arm while the latter was covered with rubber tubing to prevent ingress of air. It was then re-evacuated and the vapor pressures were again determined. Criteria for the workability of the method and for complete evacuation of the cell preliminary to making observations of pressures lay in the satisfactory duplication of data. Results are given in Table I.

Col. 3 of the table gives the vapor pressures for the temperatures at which the observations were made, calculated by the equation  $\log_{10} P_{(\text{mm.})} = 7.4550 - (1880.1/T)$ . This *empirical* equation gives the vapor pressure of this compound as a function of the temperature up to 760 mm. Just how far above this pressure the equation is applicable is uncertain in view of the inevitable dissociation of sulfur monochloride into the dichloride and sulfur at sufficiently high temperatures. It is quite probable that this point lies just beyond the temperature at which the monochloride boils. When these data are plotted, a curve is obtained whose regularity is indicative of no dissociation. The measured vapor pressures appear to be normal in every respect. This evidence points to the fact that sulfur monochloride is a well-defined, stable compound up to its boiling point.

The heat of vaporization, calculated with the aid of the Clausius-Clapeyron equation,  $L(\text{cal./g.}) = [2.303 R/M][T_1 T_2 / (T_2 - T_1)][\log_{10} P_2 / P_1]$ , is 63.9 calories per gram. In this equation  $R$  is the gas constant (1.99),  $M$  the molecular weight calculated for the formula  $\text{S}_2\text{Cl}_2$  and  $P_2$  and  $P_1$  are the vapor pressures corresponding to the absolute temperatures  $T_2$  and  $T_1$ , respectively. This calculation may be made most conveniently by multiplying the constant of the equation (1880.1) by the gas constant (1.99) and the conversion factor of logarithms (2.303). Ogier<sup>9</sup> reported a value of 49.4 calories per gram from data determined calorimetrically. It is believed that the results obtained above are more nearly correct for reasons which are emphasized in the calculation of the molecular elevation.

A knowledge of the heat of vaporization makes possible the calculation of another constant. When Orndorff and Terrasse<sup>10</sup> determined the molecular weight of sulfur in sulfur monochloride they had at hand no reliable data for the heat of vaporization of the latter. They calculated its molecular elevation from the boiling point ( $138.12^\circ_{760 \text{ mm.}}$ ) as given by Thorpe.<sup>4</sup> They found it to be 52.8, a value which was thought to be very nearly correct, inasmuch as they successfully applied it to the determination of

<sup>9</sup> Ogier, *Compt. rend.*, **92**, 922 (1881).

<sup>10</sup> Orndorff and Terrasse, *Am. Chem. J.*, **18**, 173 (1896).

the molecular weight of triphenylmethane in sulfur monochloride. Application of the formula  $K = 0.02 T^2/L$ , in which  $K$  is the molecular elevation,  $T$  the boiling point on the absolute scale and  $L$  the heat of vaporization (63.9) gives the value 52.9 which substantiates that of the above investigators.

### Summary

1. The vapor pressure of sulfur monochloride has been determined through the temperature range  $0^\circ$  to its boiling point. The equation for the corresponding curve is  $\log P = (7.4550) - (1880.1/T)$ .

2. Sulfur monochloride is a stable, well-defined compound at these and intermediate temperatures.

3. The heat of vaporization has been determined and found to be at variance with previously reported values.

4. The molecular elevation agrees with that calculated from boiling-point data by other investigators.

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## THE IONIZATION OF WEAK ELECTROLYTES

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Arrhenius' theory that the degree of ionization can be obtained from the conductance ratio,  $\Lambda/\Lambda_0$ , is now quite generally conceded to be untrue for strong electrolytes, since it involves the assumption that the mobilities of the ions do not change from infinite dilution to the concentration in question. The properties of a large group of strong electrolytes can, in fact, be most readily explained by the theory that they are completely ionized. The decrease in the value of the equivalent conductance with concentration is, almost certainly, due to decrease in the ionic mobilities, caused by an inter-ionic attraction which steadily gains strength as the concentration increases. If, therefore, Arrhenius' method for computing the degree of dissociation is not valid for strong electrolytes, it seems improbable that it can be used without modification for weak electrolytes since, as will be shown below, the ion concentrations can attain values large enough to cause appreciable changes in the mobilities of the ions.

It has appeared to me, however, that a more nearly correct degree of dissociation can be obtained by comparing the measured equivalent conductance with that of an equivalent of the ions *at the same ion concentration*, a quantity which will be represented by  $\Lambda_e$ . Thus the degree of dissociation of acetic acid at 0.01  $N$  may be computed by dividing the  $\Lambda$  value for that concentration by the equivalent conductance of completely dis-