[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF MISSOURI]

The Vapor Pressure of "Mustard Gas" (β,β'-Dichloroethylsulfide), Diphenyl Ether and their Mixtures

BY H. E. BENT AND R. J. FRANCEL[1]

In 1940 when this work was begun, vapor pressure data on mustard gas showed poor agreement and data on solutions of mustard were almost lacking. Our object was to develop a physical method of measurement which would be suitable for not only mustard but also other compounds of similar characteristics. We attempted to keep each individual experimental error below 0.1%.[2]

The following corrections have not been applied. The true vapor pressure is less than that under one atmosphere pressure of air by about 0.5%. No correction has been applied for the solubility of air in mustard, which probably introduces an error of 0.1%. No correction has been made for deviations from the gas laws which may introduce an additional error of 0.1% to 0.2%.

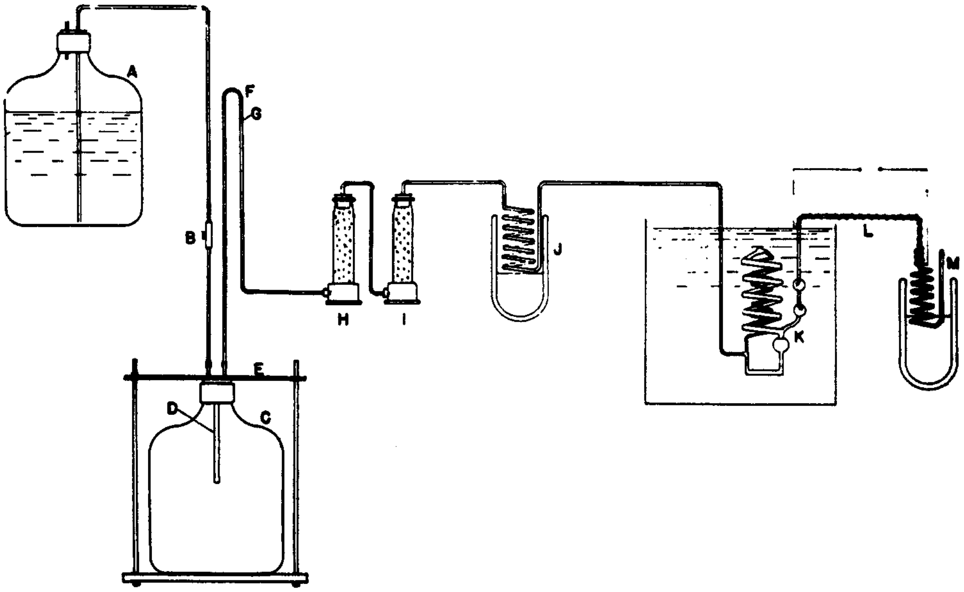

Fig. 1

The dynamic method is well known and perhaps needs little description aside from the information given in Fig. 1. Water in A displaces dry air in C which is in turn again dried by calcium chloride in H, phosphorus pentoxide in I and liquid air in J. The saturator at K is a spiral which exposes a continually fresh surface of liquid since the air stream circulates a small amount of liquid through the apparatus as shown in more detail in Fig. 2. Great care was taken to avoid the formation of spray in this saturator and to avoid fog in the collector at M. Each part of the apparatus was carefully checked and then the apparatus as a whole checked, first by carrying out runs with different rates of flow and second by measuring the vapor pressure of water. The accepted value at 30° is 31.842. We obtained as a result of ten runs 31.79 ± 0.05 mm.

Purity of Compounds.—Mustard was prepared by treating a 15-ml. portion of Union Carbide and Carbon "Kromfax" solvent (β,β'-dihydroxyethylsulfide) with excess of concentrated hydrochloric acid at 60° for thirty minutes. The mustard forms as a water insoluble layer thus

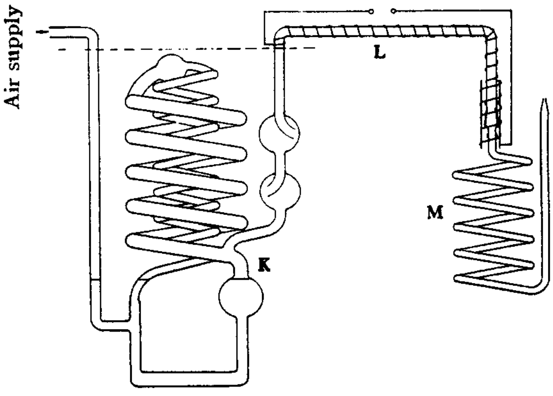

Fig. 2.

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[1] This paper is condensed from a thesis submitted in partial fulfillment of the requirements for the Master's degree.

[2] For a detailed discussion of experimental errors the reader is referred to the original thesis of R. J. Francel, University of Missouri library.

separating it from water soluble impurities possibly present in the original material. No impurities insoluble in water were present in the "Kromfax" solvent. After allowing the reaction mixture to cool, the mustard was separated by decantation and then washed several times with small amounts of distilled water. Since the reaction is slow at 60° with hydrochloric acid, one may infer that at room temperature several rapid washings will not hydrolyze the mustard. The liquid was then distilled under reduced pressure at from 85 to 100° out of contact with rubber. Five fractions were collected, all of which agreed in refractive index to less than 0.0001, but only the middle three fractions were used. Substitution of nitrogen for air in the runs gave no indication of oxidation of mustard.

Diphenyl ether, Eastman Kodak Co. White Label, was distilled under reduced pressure at 95–110°. The two end fractions were discarded.

Solutions of diphenyl ether and mustard were prepared volumetrically and analyzed by determining the refractive index. A refractive index curve (unpublished) prepared by C. A. Krinbill was used. We are also indebted to C. A. Krinbill for assistance during the construction of the apparatus and testing of various designs.

The refractive index for the mustard we found to be 1.5227 at 30° which may be compared with the value calculated from the equation of Mumford, Phillips and Ball[3] of 1.5226. The error in the composition of the solution due to 0.0001 in the refractive index is 0.002 in the mole fraction.

Calculation of Results

Vapor Pressure.—The vapor pressure is obtained with the aid of the expression

$$p = \frac{RT_W}{M} \div \left[V \times \frac{T_2}{T_1} \times \frac{P_1}{P_2 - p} \right]$$

in which V is the volume of bottle C, the next term takes care of the difference in temperature between the bottle and the thermostat and the last takes care of the difference in pressure when the bottle was closed and during a run. "p" is a small correction factor, the vapor pressure of the liquid being studied, obtained by successive approximations.

Values of the vapor pressure are given in Table I and are represented graphically in Figs. 3 and 4. The equations for these curves are for mustard

$$\log_{10} p = 9.4819 - \frac{3117.2}{(t + 273.1)}$$

and for diphenyl ether

$$\log_{10} p = 9.5842 - \frac{3351.9}{(t + 273.1)}$$

which give with the aid of the Clapeyron equation 14,300 ± 50 calories for the heat of vaporization of mustard and 15,300 ± 500 calories for the heat of vaporization of diphenyl ether.

A comparison of our results, Table I, with previous investigators shows poor agreement with Mumford, *et al.*,[3] better agreement with Vedder[4] and still better agreement with the recently published work of Balson and co-workers.[5] The results of Holst and Melander[6] are approximately 100% higher than ours and are not included in the table.

TABLE I

THE VAPOR PRESSURE OF MUSTARD AND DIPHENYL ETHER

The observed values are averages of from three to eight determinations.

				This work	
Temp., °C.	Vedder	Mumford, *et al.*	Balson, *et al.*	Obs.	Calcd. from equation
			Mustard		
15	0.0417	0.075			0.0459
20	.0650	.115	0.072		.0702
30	.1500	.225	.162	0.1575 ± 3	.1576
40		.45	.351	.3363 ± 3	.3358
50		.83	.716	.6822 ± 11	.6826
			Diphenyl Ether		
40				0.0751 ± 1	0.0756
50				.1647 ± 7	.1622
60				.3298 ± 3	.3322

Raoult's law may be expressed as

$$p_1 = p_1^0 N_1$$

Deviations from Raoult's law may be expressed by either of two expressions, one involving the mole fraction and the other involving the volume fraction. Hildebrand[7] has shown the latter is to be preferred when the molecular volumes of the two components differ appreciably. We may write this expression as

$$RT \ln p_1/p_1^0 N_1 = \beta v_1 V_2^2$$

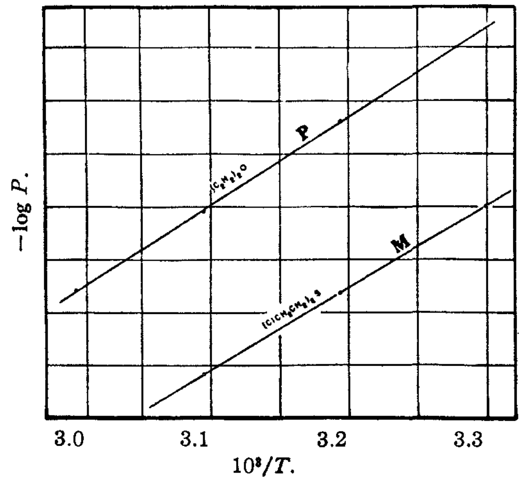

Fig. 3.—P, $(C_6H_5)_2O$; M, $(ClCH_2CH_2)_2S$.

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[3] Mumford, Phillips and Ball, *J. Chem. Soc.*, 589 (1932).

[4] Vedder, "Medical Aspects of Chemical Warfare," Williams and Wilkins Co., Baltimore, Md., 1925, p. 127.

[5] Balson, Denbigh and Adam, *Trans. Farad. Soc.*, **43**, 42 (1947).

[6] Holst and Melander, *Chem. Abs.*, **40**, 2706 (1946).

[7] Hildebrand, "Solubility," Reinhold Publishing Corp., New York, N. Y.

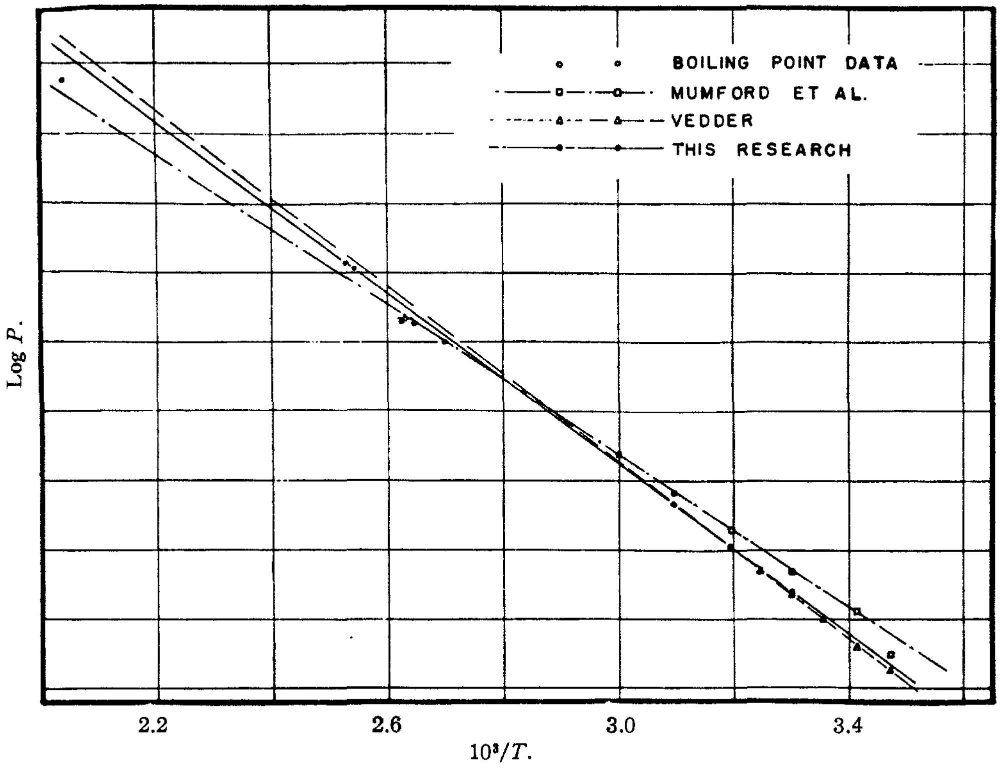

Fig. 4.

and the corresponding equation for the other component with subscripts interchanged. v_1 is the molar volume of the first component and V_2 the volume fraction of the second component. The molar volumes of the pure liquids were obtained using the equation of Wilkinson and Wernlund[8] for the density of mustard and that of Zhuravlev[9] for the density of diphenyl ether. For mustard gas $d = 1.2790 - 1.058 \times 10^{-3} (t - 15)$ and for diphenyl ether $d = 1.0880 - 8.6 \times 10^{-4} t$.

The values obtained for β at a mole fraction of 0.658 are 1.87 at 30°, 1.85 at 40°, 1.83 at 50° and, with a mole fraction of mustard of 0.330, 1.76 at 50°. This lack of constancy of β is not as significant as it might at first appear, as it determines the deviation from Raoult's law and not the part of the volatility to be expected from this law and is not much greater than our experimental error, as can be seen from Table II in which calculated volatilities are compared with the experimental values. In this table an average value of 1.83 is used.

Table II

Comparison of Calculated Values of the Volatility of Solutions of Mustard and Diphenyl Ether with Experimental Values. Volatility is Expressed as Mg./Liter

Temp., °C.	Mole fraction	Calcd. volatility with β = 1.83 Mustard	Ether	Total	Experimental
30	0.658	0.927	0.123	1.050	1.051 ± 2
40	.658	1.910	.268	2.178	2.179 ± 3
50	.658	3.756	.555	4.311	4.316 ± 8
50	.330	2.149	.952	3.101	5.083 ± 3

One objection to using volume fractions instead of mole fractions in calculating deviations from Raoult's law is the added labor in carrying out the calculations. This means having values for the densities of the liquids at various temperatures. In order to eliminate this labor for any one wishing to use our results we have given values for the activity coefficient in Table III.

Table III

Activity Coefficients of Mustard Gas[a]

Values of γ in the equation $p/p^0 = \gamma N$ in which N is the mole fraction.

Mole fraction of mustard gas	30°	40°	50°
0.0	1.466	1.453	1.441
.2	1.306	1.298	1.290
.4	1.179	1.174	1.170
.6	1.084	1.082	1.080
.8	1.022	1.022	1.021

[a] For a more complete table of activity coefficients, order Document 2484 from American Documentation Institute, 1719 N Street, N. W., Washington 6, D. C., remitting $0.50 for microfilms or $0.50 for photoprints.

We may use our average value of β to calculate the heat of vaporization from the relation given by Hildebrand

$$\beta = \left[\left(\frac{E_1}{v_1}\right)^{1/2} - \left(\frac{E_2}{v_2}\right)^{1/2}\right]^2$$

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(8) Wilkinson and Wernlund, This Journal, **42**, 1382–1385 (1920).

(9) Zhuravlev, *J. Phys. Chem.* (*U. S. S. R.*), **9**, 875–882 (1937).

Since our data are better for mustard, we will use this equation to calculate the heat of vaporization of diphenyl ether, giving 13,800 which may be compared with 15,300 ± 500 by the slope of the vapor pressure curve. The discrepancy is somewhat more than might be expected. However, there is an uncertainty of 500 cal. in the heat of vaporization of diphenyl ether, perhaps 100 in the heat for mustard and another hundred in the value for β and of course departures in the behavior of these liquids from the assumptions of Hildebrand in deriving the above equation. Perhaps the most obvious such deviation would be that of association of the mustard. Considering all of these factors perhaps the agreement is as good as can be expected. Finally we may use the value of E/v to place these compounds in Hildebrand's series of internal pressure, the value for mustard being 114.0 and for diphenyl ether 95.9. This places mustard between bromoform and bromine and diphenyl ether with aniline.

As an independent check we have the composition of the vapor as determined by Krinbill[10] using a refractometer. The agreement between the calculated composition using the data from this paper and the observed composition determined with the aid of the refractometer is within the experimental error.

TABLE IV

MOLE FRACTION OF MUSTARD IN LIQUID AND VAPOR AT 50°

Liquid	Vapor	
	Calculated	Observed
0.658	0.877	0.884
.330	.706	.708

We wish to acknowledge indebtedness to our colleagues, particularly to Professor L. B. Thomas, who tested an early form of the apparatus.

Summary

1. The vapor pressure of mustard (β,β-dichloroethylsulfide) is given by the expression

$$\log_{10} p = 9.4819 - 3117.2/(t + 273.1)$$

and for diphenyl ether by the expression

$$\log_{10} p = 9.5842 - 3351.9/(t + 273.1)$$

Results on mustard agree closely with those of Vedder and with Balson, *et al.*, but not with those of Mumford, Phillips and Ball.

2. Mixtures of these two liquids show small positive deviations from Raoult's law which can be expressed by the equation

$$RT \ln \frac{p_1}{p_1^0 N_1} = 1.83 v_1 V_2^2$$

in which v_1 is the molal volume and V_2 is the volume fraction. A table of activity coefficients is given in order to eliminate the labor involved in using the above equation.

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[10] Unpublished research.

[CONTRIBUTION FROM THE UNIVERSITY OF CHICAGO TOXICITY LABORATORY]

The Volatility and Vapor Pressure of Nine Organic Arsines[1]

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As part of a systematic study of the properties of certain toxic compounds the volatility and vapor pressure were determined between 0 and 60° for a series of nine organic arsines. The vapor pressure has been measured for some of these arsines previously; however, these measurements were made at temperatures above 60° in most instances and for lower temperatures values were obtained by extrapolation. To reduce the uncertainty of these values over the desired temperature interval the volatility[5] was measured directly by an air (or nitrogen) saturation method devised by Regnault.[6] The vapor pressure was in turn computed from the volatility by the method outlined in an earlier report.[7]

Gibson and Johnson[8] published data on the vapor pressure of methyldichloroarsine, ethyldichloroarsine and *n*-propyldichloroarsine obtained by measuring the boiling point under various pressures. Baxter and co-workers[9] reported equations for the vapor pressure of phenyldichloroarsine and methyldichloroarsine determined by a procedure very similar to that used by the present authors. Lewis and Perkins[10] cite unpublished data of Baxter on the vapor pressure of 2-chlorovinyldichloroarsine (Lewisite). Boiling point and density measurements as well as vapor pressure are given by Sartori[11] for methyldichloroarsine

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[1] This work was carried out under contract with the National Defense Research Committee of the Office of Scientific Research and Development.

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[5] Volatility is expressed in milligrams per liter of air or nitrogen in this report.

[6] Regnault, *Ann. chim. phys.*, [3] **15**, 129 (1845).

[7] Redemann, Chaikin and Fearing, THIS JOURNAL, **70**, 631 (1948).

[8] Gibson and Johnson, *J. Chem. Soc.*, 2518 (1931).

[9] Baxter, Bezzenberger and Wilson, THIS JOURNAL, **42**, 1386 (1920).

[10] Lewis and Perkins, *Ind. Eng. Chem.*, **15**, 290 (1923).

[11] Sartori, "The War Gases," 1st English Ed., J. and A. Churchill Ltd., London, 1939, Chapt. XV.