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.

COLUMBIA, MISSOURI RECEIVED MAY 19, 1947

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(10) Unpublished research.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]

BY C. ERNST REDEMANN,[2] SAUL W. CHAIKIN, RALPH B. FEARING[3] AND DORA BENEDICT[4]

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.

TABLE I

CONSTANTS OF THE SUBSTITUTED ARSINES USED

Arsine	Formula	Boiling point °C.	Boiling point Mm.	Refractive Index n_D	Refractive Index °C.	Density g./cc.	Density °C.	Constants for equations A	Constants for equations A'	Constants for equations B
Dichloromethyl[a]	CH_3AsCl_2	131.5[b]	745	1.5588	29	1.8358[c]	20	8.1981[d]	11.6097	2142.6[d]
Dichloroethyl[e]	$C_2H_5AsCl_2$	44	14			1.6808[f]	25	8.4497	11.8997	2331.1
Dibromoethyl[a]	$C_2H_5AsBr_2$	81.5–82.5	15	1.6405	26	2.400	22	8.49558	12.12207	2608.7
Dichloro-5-*n*-propyl[a]	*n*-$C_3H_7AsCl_2$	99	75	1.5297	28	1.5380	20	8.8516	12.3332	2572.0
Dibromo-*n*-amyl[a]	*n*-$C_5H_{11}AsBr_2$	124–125	14	1.5760	31.5	1.939	21	9.06147	12.75225	3132.7
Dichlorophenyl[g]	$C_6H_5AsCl_2$	141.5	30			1.6444	27	8.76036[d]	12.31371	3048.3[d]
Dichloro-(2-chlorovinyl)[g,h]	$ClCH{=}CHAsCl_2$	72–73	10	1.6068	25	1.8799[i]	25	9.1000[i]	12.6281	2786.6[i]
Bis-(2-chlorovinyl)-methyl[a]	$(ClCH{=}CH)_2AsCH_3$	91	12	1.5654	28	1.473	28	9.0918	12.6252	2908.5
Cyanoethyl-*n*-propyl[a]	$CNAs(C_2H_5)(C_3H_7)$	90	13	1.4850	23	1.1587	24	8.9078	12.3511	2850.3

[a] Submitted by Dr. C. S. Hamilton. [b] Seide and Gorski, *Ber.*, 62, 2190 (1929), give the boiling point as 132–133° at atmospheric pressure. Zappi, *Anales soc. quim. Argentina*, **3,** 447 (1915), gives b. p. 132° (760 mm.). [c] Fries and West, ("Chemical Warfare," 1921, McGraw–Hill Book Co., New York), give d^{20} 1.838. [d] Baxter, Bezzenberger and Wilson (ref. 9) give 8.6944 and 2281.7 for dichloromethylarsine and 9.150 and 3164 for dichlorophenylarsine. [e] Submitted by Dr. M. S. Kharasch. [f] Gibson and Johnson (ref. 8) report the density as 1.6595 at 20°. [g] Supplied by Edgewood Arsenal. [h] This is for isomer I. (The method of preparation used gives almost pure isomer I. Careful distillation failed to reveal the presence of any isomer II.) [i] Baxter (see Lewis and Perkins, ref. 10) gave 9.123 and 2789.69, respectively, for these constants. Lewis and Perkins give d^{20} 1.888.

ethyldichloroarsine, 2-chlorovinyldichloroarsine and phenyldichloroarsine. The work reported in the present paper confirms certain of these values but disagrees with others.

Experimental

The apparatus employed in these determinations has been described in earlier reports.[7,12] Dry nitrogen was used as the entrainment gas to avoid any possible oxidation of the arsines. Measurements were made at 20, 40 and 60° for all compounds except dichloromethylarsine, where 0, 20 and 40° were necessary, and for dichlorophenylarsine, where 40 and 60° were used because of the very small volatility at lower temperatures. From three to eight measurements were made at each temperature and the arithmetic mean value was computed for each temperature from these points. Values of known error were discarded, as were high values sometimes obtained in the first measurements after filling the saturator. When there was any definite trend in a series of determinations it was repeated to ascertain whether the trend resulted from a change in composition of the material in the saturator or if it was fortuitous. In some cases the refractive index and the density before and after the run were compared to see if any change in composition had taken place during the run.

The arsines were all prepared in laboratories other than our own (see Table I). In most cases the samples were carefully purified before they were submitted to our laboratory. However, the samples were all fractionally distilled under reduced pressure from all-glass equipment prior to use. Only fractions having essentially a constant boiling point were used.[13] When a new compound was placed in the saturator dry nitrogen was passed through the apparatus to remove traces of more volatile impurities before starting a run. The observed values for the boiling point, refractive index and density of the samples used in the volatility measurements are recorded in Table I.

Discussion

An arithmetic mean of the acceptable points at each given temperature was taken. Curves of the form

$$\log p = A - B/T \qquad (1)$$

and

$$\log WT = A' - B/T \qquad (2)$$

were fitted by the method of least squares to the mean points for the several temperatures studied. The values for A, A' and B thus derived are recorded in Table I. These constants apply when the pressure, p, is in millimeters of mercury, the temperature, T, is in ° K. and the volatility, W, is in milligrams per liter of nitrogen (or air).

The mean and the maximum percentage deviation from the smoothed curve of the experimental points and of the points calculated from the least squares equation are recorded in Table II. The mean deviation for each of these compounds is less than 2%. The small values for the deviations of the mean points from the points calculated from the least squares equations indicate that these equations satisfactorily reproduce the experimentally determined points. An examination of the probable sources of error indicates that if the experimental points are in error the values are apt to be small rather than large.

TABLE II

PRECISION OF DATA

Arsine	Percentage deviation from smoothed curve of Experimental points Maximum	Experimental points Mean	Points calculated from Least squares equation Maximum	Least squares equation Mean
Dichloromethyl	0.15	0.1	Identical	
Dichloroethyl	1.3	0.9	0.7	0.3
Dibromoethyl	2.5	0.8	0.4	0.2
Dichloro-*n*-propyl	1.6	1.1	0.6	0.4
Dibromo-*n*-amyl	7.5	1.9	2.8	1.7
Dichlorophenyl	2.3	1.6	0.9	0.6
Dichloro(2-chlorovinyl)	1.5	0.9	0.2	0.06
Bis(2-chlorovinyl)methyl	0.6	0.3	Identical	
Cyanoethyl-*n*-propyl	6.0	1.9	0.5	0.3

A brief comparison of vapor pressures at different temperatures as calculated from the equations of Baxter and co-workers[9] and from the present equations for two of the arsines is given in Table III. This comparison appears justified since the measurements were made in a similar manner over

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(12) Bent and Francel, THIS JOURNAL, **70**, 634 (1948).

(13) Actually, some variation in boiling point was observed in some cases, probably due to the slight variations in pressure during the course of the distillation. A variation of 1° was tolerated in three cases, see Table I.

part of the same temperature interval by both authors.

TABLE III

COMPARATIVE DATA ON TWO SUBSTITUTED ARSINES

°C.	Pressure in millimeters Dichloromethylarsine Baxter	This Work	Dichlorophenylarsine Baxter	This Work
0	2.20	2.26	0.0037	0.0040
60	70.2	58.6	0.451	0.409
133[a]	1188	832	....	......
250[b]	.....	....	1259	855

[a] This is the value most frequently given in the literature as the boiling point at 760 mm. pressure for dichloromethylarsine. [b] This is an average value for the values quoted for the boiling point at 760 mm. of dichlorophenylarsine.

If we assume the two normal boiling points to be correct,[14] we then see that an error of about 10% is present in values calculated for the vapor pressure at temperatures considerably above the experimental range.

Summary

1. The volatility of nine substituted arsines has been measured between 0 and 60° by a transpiration method.

2. Vapor pressures have been calculated from the volatility measurements, and from these data logarithmic equations have been developed for both the volatility and the vapor pressure as a function of the temperature.

3. The mean molar latent heat of evaporation over the temperature range 0 to 60° has been computed from the vapor pressure equation for each compound.

4. The average precision of these measurements is better than ±2% over the specified temperature range. However, the equations may be used to extrapolate to other temperatures with somewhat less precision.

CHICAGO, ILLINOIS RECEIVED JULY 19, 1947

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[14] This seems unlikely since normal boiling points are quoted for dichlorophenylarsine ranging from 247 to 257°, with the value 250° appearing most frequently.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY AND CHEMICAL ENGINEERING OF THE UNIVERSITY OF PENNSYLVANIA]

The Electrolyte Effects in the Hydration of Isobutene[1,2]

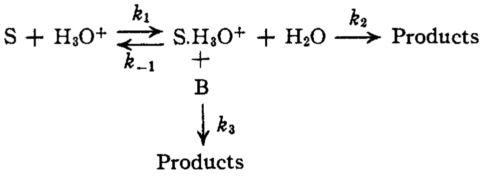
BY FRANK G. CIAPETTA[3] AND MARTIN KILPATRICK[4]

The problem of electrolyte effects of large magnitude in reactions involving an uncharged substrate and the hydrogen ion has been a subject of study in this Laboratory.[5,a,b,c,d] More recently Olson and Tong[6] have attempted to interpret these salt effects, and Sullivan and M. L. Kilpatrick,[7] and M. L. Kilpatrick[8] have advanced a different viewpoint which should be considered.

Whereas Leininger and Kilpatrick[5b] postulated the pre-equilibrium with k_2 the rate determining

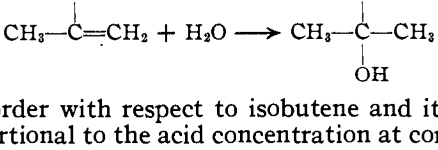
$$S + H_3O^+ \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \{S{\cdot}H_3O\}^+ \xrightarrow{k_2} \text{Products} \quad (1)$$

step, M. L. Kilpatrick[8] for the hydrolysis of cyanamide, where the cation is formed in appreciable concentration, found the rate determining step to be the reaction of the solvated cation with the base water (k_2), and if additional bases are present the rate is higher than that anticipated on the basis of a hydrogen ion catalysis. This is due to the concurrent reaction (k_3) of the base B with the solvated cation.



$$\begin{array}{l} S + H_3O^+ \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} S.H_3O^+ + H_2O \xrightarrow{k_2} \text{Products} \quad (2) \\ \qquad\qquad\qquad\quad + \\ \qquad\qquad\qquad\quad B \\ \qquad\qquad\qquad\quad \downarrow k_3 \\ \qquad\qquad\qquad\quad \text{Products} \end{array}$$

The present investigation deals with the effect of electrolyte concentration on the rate of hydration of isobutene in aqueous solutions of strong acids and the weaker chloroacetic acids. The reaction in nitric acid solution has been shown to be



$$CH_3{-}\underset{}{\overset{\displaystyle CH_3}{\overset{|}{C}}}{=}CH_2 + H_2O \longrightarrow CH_3{-}\underset{\underset{\displaystyle OH}{|}}{\overset{\overset{\displaystyle CH_3}{|}}{C}}{-}CH_3 \quad (3)$$

first order with respect to isobutene and its rate proportional to the acid concentration at constant ionic strength,[9] and this conclusion has been verified by G. R. Lucas and Hammett.[10]

Lucas and Eberz followed the course of the reaction analytically but the dilatometric method

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[1] Abstracted from the dissertation of Frank G. Ciapetta presented to the Faculty of the Graduate School of the University of Pennsylvania in partial fulfilment of the requirement for the degree of Doctor of Philosophy, April, 1947.

[2] Presented before the Division of Physical and Inorganic Chemistry at the 112th meeting of the American Chemical Society at New York, N. Y., September, 1947.

[3] E. I. du Pont de Nemours and Company Fellow, 1946-1947. Present address: The Atlantic Refining Company, Philadelphia, Pa.

[4] Present address: Department of Chemistry, Illinois Institute of Technology, Chicago 16, Illinois.

[5] (a) L. C. Riesch and M. Kilpatrick, *J. Phys. Chem.*, **39**, 561 (1935); (b) P. M. Leininger and M. Kilpatrick, THIS JOURNAL, **60**, 2891 (1938); (c) P. M. Leininger and M. Kilpatrick, *ibid.*, **60**, 2510 (1938); (d) M. Kilpatrick, "Handbuch der Katalyse," Vol. II, Julius Springer, Wien, 1940, p. 258.

[6] A. R. Olson and L. K. J. Tong, THIS JOURNAL, **66**, 1555 (1944).

[7] M. J. Sullivan and M. L. Kilpatrick, *ibid.*, **67**, 1815 (1945).

[8] M. L. Kilpatrick, *ibid.*, **69**, 40 (1947).

[9] H. J. Lucas and W. F. Eberz, *ibid.*, **56**, 460 (1934).

[10] G. R. Lucas and L. P. Hammett, *ibid.*, **64**, 1928 (1942).