

[CONTRIBUTION FROM THE T. JEFFERSON COOLIDGE, JR., CHEMICAL LABORATORY OF HARVARD COLLEGE.]

THE VAPOR PRESSURES OF CERTAIN SUBSTANCES: CHLOROPICRIN, CYANOGEN BROMIDE, METHYL-DICHLORO-ARSINE, PHENYL-DICHLORO-ARSINE, DIPHENYL-CHLORO-ARSINE AND ARSENIC TRICHLORIDE.<sup>1</sup>

BY G. P. BAXTER, F. K. BEZZENBERGER AND C. H. WILSON.<sup>2</sup>

Received May 3, 1920.

In collaboration with the Bureau of Mines and the Research Division of the Chemical Warfare Service the vapor pressures of various compounds were determined at the Harvard Branch Laboratory. While the necessities of the situation demanded speed rather than a high degree of accuracy, the observations are probably correct with a very few per cent. in most cases, and seem on the whole worth while making a matter of permanent record. This paper contains the results obtained with the following substances: chloropicrin, cyanogen bromide, methyl-dichloro-arsine- phenyl-dichloro-arsine, diphenyl-chloro-arsine and arsenic trichloride.

All the observations were made by the "air current" or "transference" method, except in the case of arsenic trichloride at higher temperatures where a static method was employed. A known volume of air, as determined by the measured volume of water run out of an aspirator, was saturated with the vapor of the substance in question by passing through a weighed receptacle maintained at constant temperature in a water thermostat. The loss in weight of the saturating tube furnished the weight of evaporated substance. From the latter quantity the volume of vapor was calculated on the assumption that the volume of a gram molecule under standard conditions is 22.41 liters. Even with the most volatile substances this assumption is probably true within the accuracy of the experiments. The per cent. of vapor by volume multiplied by the interior pressure, as determined by the barometric reading and an open-arm water manometer attached to the aspirator, gives the vapor pressure.

The control of temperature in the thermostats was within 0.1° except when a freezing mixture was employed where the uncertainty may have been as large as one degree at -18°.

Since nearly all the substances investigated hydrolyze readily, the air was dried, usually by passing over sodium hydroxide, before entering the saturating tube. The saturating tube was constructed as shown in Fig. 1 with 3 U-tubes joined together. The inlet, which could be closed with a glass stopcock, was located above the water of the constant tem-

<sup>1</sup> Published by permission of the Director of the Chemical Warfare Service.

<sup>2</sup> Sergeant, C. W. S., U. S. A. Died, January 10, 1919.

perature bath; the outlet in most cases was immersed in the bath so as to avoid condensation of the vapor when used at temperatures above that of the room, and was connected to a U-tube immersed in the bath and then to the aspirator system by stout rubber tubes. Between the U-tube and the aspirator, when the more volatile substances were under examination, a U-tube immersed in a freezing mixture was introduced, both as a matter of safety and in order to avoid pressure complications in the aspirator bottle.

The coils of the saturating tube were nearly filled with glass beads. If the substance under examination was a liquid, barely enough was introduced to seal the bends of the coils. If the substance was a solid it was either introduced in the molten state or was melted in the tube and caused to solidify over as much of the interior surface of the coils as possible.

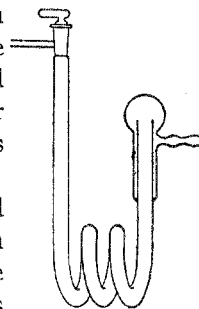


Fig. 1.

No variations in the results with the rate of flow of air were found up to 4 liters of air per hour, but the rate was ordinarily between 2 and 3 liters per hour, and with the more volatile substances such as cyanogen bromide was much less. While all the materials furnished were apparently fairly pure, they all gave evidence of containing a small proportion of more volatile impurities, since the initial results were higher than later ones. In order to provide for this difficulty the first step after filling the saturating tube was to pass a comparatively large volume of air through the tube at an elevated temperature before making any attempt to weigh the tube. After such treatment, constant values for the vapor pressure were always obtained. There is, however, the uncertainty as to less volatile impurities which may have lowered the vapor pressure.

The tubes were weighed by substitution for similar counterpoises, after the usual precautions of wiping with damp cotton cloth and prolonged standing near the balance. Many hours' immersion in the water of the thermostat even at as high a temperature as 75° was found to have no perceptible solvent effect upon the glass.

With all the substances investigated a plot of the logarithm of the vapor pressure against the reciprocal of the absolute temperature gives a very nearly straight line, which therefore, can be represented by an empirical equation of the form

$$\log v. p. = A + \frac{B}{273 + t}$$

Satisfactory values of  $A$  and  $B$  have been computed for each substance.

Vapor pressures calculated by means of these equations agree with the observed values within the experimental error. For a higher degree of

accuracy the equations are not adequate, however, and cannot be trusted for extrapolation over any considerable range.

Details follow for the individual substances.

**Chloropicrin.**—The original material was distilled in a partial vacuum in 2 portions. The first was used at 35°, 25°, 15° and 0°, the second at the other temperatures. The first 2 experiments, at 25°, which gave discrepant results, are not included in the table.

TABLE I.  
Chloropicrin.

$$\log v. p. = 8.2424 - \frac{2045.1}{273 + t}$$

Temperature. ° C.	Volume of air at 0° and 760 mm. Cc.	Loss in weight of tube. G.	Interior pressure. Mm.	Vapor pressure observed. Mm.	Vapor pressure calculated. Mm.	Difference. Calc. — obs. Mm.
35	2151	0.9200	731.0	40.27		
	2575	1.0690	749.5	40.13		
	2317	0.9445	748.0	(39.36)		
	1828	0.7776	730.3	40.01		
			Av.,	40.14	40.04	—0.10
30	2784	0.8638	763.3	30.97		
	2085	0.6505	765.8	31.23		
			Av.,	31.10	31.10	0.0
25	2805	0.6808	742.6	23.78		
	2535	0.6048	756.5	23.83		
			Av.,	23.81	23.97	+0.16
20	2008	0.3626	759.4	18.24		
	2361	0.4300	758.9	18.38		
			Av.,	18.31	18.30	—0.01
15	3287	0.4454	761.3	13.81		
	2657	0.3653	752.0	13.83		
			Av.,	13.82	13.85	+0.03
10	2588	0.2651	758.5	10.45		
	2903	0.2930	758.0	10.29		
			Av.,	10.37	10.37	0.0
0	2407	0.1386	733.2	5.71		
	2712	0.1551	737.5	5.71		
			Av.,	5.71	5.64	—0.07
—18	3299	0.0611	754.1	1.90	1.67	—0.23
—19	3400	0.0566	751.5	1.70	1.55	—0.15
—20	3125	0.0459	751.8	1.50	1.44	—0.06

The approximate volume of air and loss in weight of the saturating tube are given briefly in the following table for the individual experiments with the remaining substances:

	Volume of air. Liters.	Loss in weight of tube. G.
Cyanogen bromide.....	1-2	1.8 -0.07
Methyl-dichloro-arsine.....	1-3	0.17 -0.01
Phenyl-dichloro-arsine.....	6-25	0.025-0.001
Diphenyl-chloro-arsine.....	14-32	0.007-0.0001
Arsenic trichloride.....	2-6	0.85 -0.14

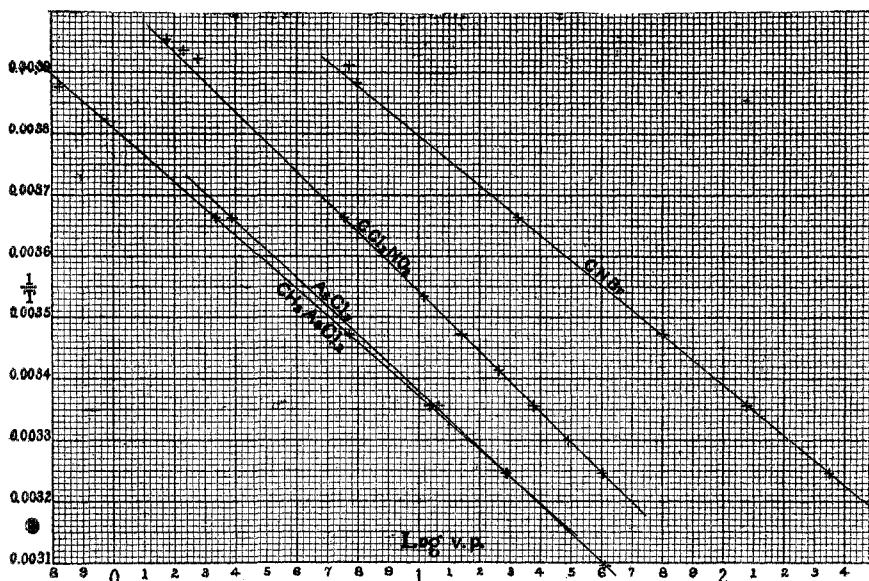


Fig. 2.

TABLE II.  
Cyanogen Bromide.

$$\log v. p. = 10.3282 - \frac{2457.5}{273 + t}$$

Temper- ature. ° C.	Number of observations.	Average vapor pressure observed. Mm.	Average deviation from mean. Mm.	Vapor pressure calculated. Mm.	Difference. Calc.—obs. Mm.
35	4	223.5	2.9	223.5	0.0
25	3	119.5	0.9	120.6	+1.1
15	2	63.3	0.1	62.4	-0.9
0	2	21.2	0.1	21.2	0.0
-15.5	1	6.3	...	6.1	-0.2
-17.3	1	5.9	...	5.2	-0.7

**Phenyl-dichloro-arsine.**—This material contained a relatively large proportion of volatile impurity, which eventually was removed by sweeping out the saturating tube with a current of air for many hours at about 70°.

TABLE III.

## Methyl-dichloro-arsine.

$$\log v. p. = 8.6944 - \frac{2281.7}{273 + t}$$

Temperature. ° C.	Number of observations.	Average vapor observed. Mm.	Average deviation from mean. Mm.	Vapor pressure calculated. Mm.	Difference. Calc. — obs. Mm.
35	2	19.33	0.06	19.33	0.00
25	2	10.83	0.01	10.90	+0.07
15	2	5.94	0.01	5.91	-0.03
0	3	2.17	0.00	2.17	0.00
-15	1	0.67	..	0.71	+0.04
-16.8	1	0.56	..	0.61	+0.05
-17	1	0.53	..	0.60	+0.07

TABLE IV.

## Phenyl-dichloro-arsine.

$$\log v. p. = 9.150 - \frac{3164}{273 + t}$$

Temperature. ° C.	Number of observations.	Average vapor pressure. observed. Mm.	Average deviation from mean. Mm.	Vapor pressure calculated. Mm.	Difference. Calc. — obs. Mm.
45	2	0.159	0.000	0.159	0.000
35	5	0.076	0.001	0.076	0.000
30	2	0.049	0.000	0.051	+0.002
25	2	0.035	0.000	0.034	-0.001
15	5	0.014	0.001	0.014	0.000
0	3	0.004	0.000	0.004	0.000

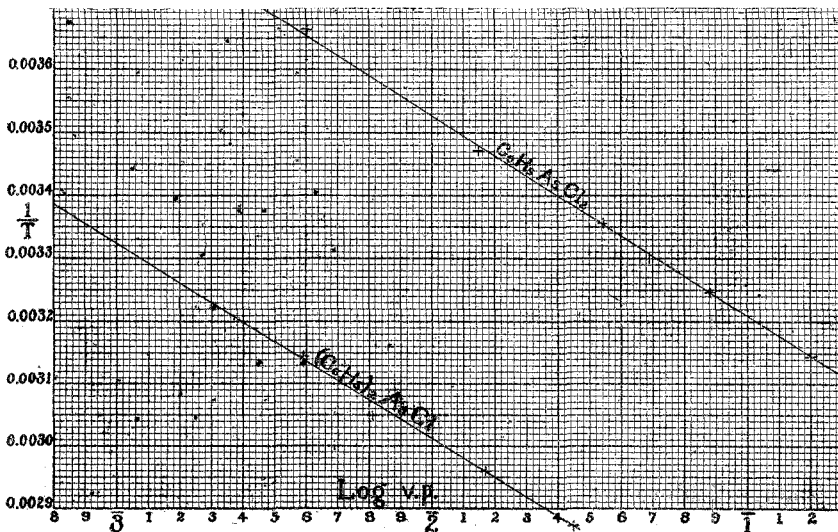


Fig. 2.

**Diphenyl-chloro-arsine.**—Two samples of material were furnished, one of which had been purified by distillation, one by crystallization. No difference could be detected between the 2 samples. The solid substance gave irregular results at temperatures below its melting point, 44°. Therefore, values were found at temperatures above the melting point, with the expectation of extrapolating to lower temperatures. As it turned out, the melted substance remained supercooled long enough to make possible 4 experiments at 25°, although these results at 25° are lower than the results at higher temperatures would lead one to expect. Further determinations at 25° after the substance eventually solidified gave excessively high results, probably owing to separation of volatile impurities during solidification, although the material had been swept out very thoroughly at a high temperature both before and in the course of the earlier experiments.

TABLE V.  
Diphenyl-chloro-arsine.

$$\log v. p. = 7.8930 - \frac{3288}{273 + t}$$

Temperature. ° C.	Number of observations.	Average vapor pressure observed. Mm.	Average deviation from mean. Mm.	Vapor pressure calculated. Mm.	Difference. Calc.—obs. Mm.
75	4	0.0282	0.0013	0.0278	—0.0004
65	5	0.0148	0.0008	0.0146	—0.0002
55	2	0.0065	0.0003	0.0074	+0.0009
45	4	0.0039	0.0001	0.0036	—0.0003
25	4	0.0003	0.0001	0.0008	+0.0005

**Arsenic Trichloride.**—After experiments at temperatures up to 50° had been completed by the air-current method, the observations were extended to nearly 100° by the "submerged bulblet" method of Smith and Menzies.<sup>1</sup> Conc. sulfuric acid was used as the immersion liquid and the capillary ascension in the tube constituting the outlet of the bulb was determined. Four series of measurements were made and the results plotted against the temperature. From the curve, vapor pressures at

TABLE VI.  
Arsenic Trichloride.

$$\log v. p. = 7.5183 - \frac{1720}{241.2 + t}$$

Temperature. ° C.	Number of observations.	Average vapor pressure observed. Mm.	Average deviation from mean. Mm.	Vapor pressure calculated. Mm.	Difference. Calc.—obs. Mm.
50	3	40.90	0.20	40.90	0.00
35	3	19.53	0.03	19.54	+0.01
25	2	11.65	0.04	11.40	—0.25
0	2	2.44	0.02	2.44	0.00

<sup>1</sup> Smith and Menzies, THIS JOURNAL, 32, 907 (1910).

Temperature. °C.	OBSERVED.				Inter- polated. Mm.	Calcu- lated. Mm.	Difference. Calc.—obs Mm.
	I. Mm.	II. Mm.	III. Mm.	IV. Mm.			
100.0					301	300	—1
98.9			290				
98.0		274					
97.9			287				
96.0			264				
94.2		244					
90.7			221				
90.0					211	211	0
89.8		208					
85.7		177					
85.4			181				
81.1		152					
80.3			148				
80.0					145	146	+1
79.4				143			
76.3			124				
76.1		122					
74.5				117			
73.2		109					
71.4	108						
71.0				100			
70.9		99					
70.0					97	98	+1
67.8	89						
67.6		82					
65.6				76			
64.3	79						
61.3				63			
60.2	64						
60.0					64	64	0
58.2				57			
54.7	48						
51.2	43						

10° intervals between 50° and 100° were read off and are given in the column of "interpolated" values. Since the results between 0° and 100° cannot be adequately expressed by the logarithmic equation of the simpler type, the modification of Antoine,<sup>1</sup>  $\log v. p. = A + \frac{B}{C + t}$ , has been used.

The boiling points of arsenic trichloride calculated from the equation are 129.3° and 129.6° at 752 mm. and 760 mm., respectively, while Walden<sup>2</sup> found the boiling point to be 129° at the former and Thorpe<sup>3</sup> 130.2° at the latter pressure.

<sup>1</sup> Antoine, *Compt. rend.*, 110, 632 (1890).

<sup>2</sup> *Z. physik. Chem.*, 43, 420 (1903).

<sup>3</sup> *Proc. Roy. Soc.*, 24, 283 (1876).

The foregoing data obviously furnish evidence from which the heats of vaporization may be computed. Using the Clausius-Clapeyron equation ( $L = T \frac{dp}{dt} (V_{\text{gas}} - V_{\text{liquid-solid}})$ ) and values for the vapor pressures calculated from the logarithmic vapor pressure equations, this has been done for the 3 most volatile substances at various temperatures. The results are expressed in kilogram calories per gram molecule.

TABLE VII.

Temperature. ° C.	Heats of Vaporization.		
	Chloropicrin.	Cyanogen bromide.	Arsenic trichloride.
100	..	..	6.86
50	..	..	7.29
35	6.77	8.08	..
0	7.10	8.60	7.42

CAMBRIDGE, MASS.

[CONTRIBUTION FROM THE LABORATORY OF PHYSICAL CHEMISTRY, PRINCETON UNIVERSITY.]

## STUDIES IN THE ADSORPTION BY CHARCOAL.

### I. THE RELATION OF SERVICE TIME TO ADSORPTION AND ABSORPTION.

BY H. H. LOWRY AND G. A. HULETT.

Received March 29, 1920.

#### Introduction.

Because of the prominence of gas warfare in the recent world war, means of protection against gas had to be developed. Naturally charcoal played a prominent part because of its remarkable properties as an absorbent. Also naturally one sample of charcoal prepared in one way might be better than another for a given use and the test developed to show superiority of one charcoal over another became known as the "service time" test. This method of testing has been described by Lamb, Wilson, and Chaney<sup>1</sup> and was purely an empirical test developed to approximate field conditions. Briefly, it consisted in passing air containing a known concentration of a toxic gas, as chloropicrin, at a definite rate through a sample of charcoal of standard dimensions until the gas could be detected in the effluent air. The test gave the desired data but had no theoretical basis, though many speculations had been made on this point. No known property of a charcoal could, however, lead one to say that it would give a better test than another without actually submitting it to these empirical conditions.

The lack of relation between service time and some physical properties of various charcoals is shown in Table I.

<sup>1</sup> *J. Ind. Eng. Chem.*, 11, 430 (1919).