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DENSITY OF LIQUID ARSINE

THE DENSITY OF LIQUID ARSINE

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The determination of the liquid density of carefully purified arsine over the temperature range -85° to $+48^{\circ}$ C is reported. The liquid density is found to be expressed by the equation :

 $\rho_t = 1.413 - 3.602 \times 10^{-8}t - 4.321 \times 10^{-6}t^2$.

The published data on the density of liquid arsine comprise measurements at five temperatures between -112° C and -60° C by Johnson and Pechukas¹ and at seven temperatures between -60° C and 0° C by Durrant, Pearson and Robinson.² The agreement between these two sets of data is not good and a complete redetermination of the density over a wider temperature range is desirable. Furthermore, Durrant, Pearson and Robinson made no allowance for the mass of arsine in the vapour phase in their pyknometers, with the result that their density values diverge progressively from the true values with increase in temperature. This statement is confirmed by the results of work recorded here. Considerable care has been taken in obtaining arsine of high purity and in handling the gas and liquid under high-vacuum conditions.

Experimental

Preparation and Purification of Arsine.—The arsine used in this work was obtained by the reaction of 10 % hydrochloric acid on powdered zinc arsenide, Zn_3As_2 . This method has been shown to be the most convenient in the laboratory; the yield is good (~86 % theoretical) and the subsequent purification of the product relatively straightforward. The gas evolved contained 91-93 % arsine, the remainder being mainly hydrogen and water vapour, although small amounts of stibine and hydrogen sulphide are likely to be present.

Powdered zinc arsenide, prepared by direct combination of the elements in stoichiometric proportions in a Rose crucible of Battersea ware in a stream of hydrogen, was reacted with 10 % hydrochloric acid in a stream of hydrogen. The evolved gases were passed through lead acetate solution to remove sulphur compounds, through glacial phosphoric acid to remove water vapour and unprecipitated spray, and collected in two internally sealed traps, cooled to - 180°C in liquid air. Uncondensed hydrogen left the system through a concentrated sulphuric acid safety bubbler. After sweeping the system with hydrogen at the completion of the reaction, the system was pumped free of non-condensable gases and the condensables distilled *in vacuo* into a U-trap.

¹ J. Amer. Chem. Soc., 1937, 59, 2065.

² J. Chem. Soc., 1934, 730.

This product was then fractionated with pumping according to the scheme :

	(Alcohol-ether	(Pentane coo	led
Ватн	$\langle \text{ cooled with }$	\rightarrow with liquid	\longrightarrow Liquid nitrogen
	liquid nitrogen	nitrogen	-
TEMPERATURE (°C)	- 125°	— 148°	— 196°
ARSINE VAPOUR	~10	~1	<10-4
Pressure			
(mm. Hg)			
	Ļ	Ļ	Ļ
FRACTIONS	Less volatile	Arsine	More volatile
	impurities		impurities
	(water, stibine)		(hydrogen sulphide)

Part of the arsine was lost in the tail and head fractions, which were rejected. The process may be repeated with the middle fraction, without the system being under continuous evacuation. The purity of the sample was checked by taking a series of vapour pressure measurements with head and tail fractions obtained from it by simple distillation. Two separate preparations of zinc arsenide were used in this work and both lots of purified arsenic gave identical vapour pressure-temperature data.

The Density Determinations.—Three pyknometers of the same design were used : each consisted of a thick-walled capillary of ~ 1 mm. bore with a bulb of 1-2 cm.³ capacity blown on one end. The wall thickness of the bulb was comparable with that of the capillary so that the glass would have sufficient strength to withstand 30-40 atm. pressure. A thick scratch toward the bottom of the capillary served as a reference mark. The whole pyknometer was annealed thoroughly and uniformly to relieve any strain in the glass. Each pyknometer was calibrated for volume up to the reference mark and for uniformity of bore over the whole range of the capillary using redistilled Merck's thiophen-free benzene over freshly-cut sodium. The density and coefficient of expansion were derived from published data ³ and the calibration performed with the benzene always within the temperature range of these data, so that extrapolation of the density-temperature relation was unnecessary.

Volume measurements were made with the pyknometer immersed in a large silvered Dewar vessel having an unsilvered vertical slot, through which the pyknometer could be observed by means of a cathetometer capable of measurement of differences in length of 0.001 cm. Between -90° and -70° the bath was of acetone cooled with liquid nitrogen; between -70° and $+10^{\circ}$, acetone cooled with solid carbon dioxide and between $+10^{\circ}$ and $+50^{\circ}$, water. The bath was stirred mechanically. Temperatures were measured by (i) a carbon dioxide vapour-pressure thermometer in the range -90° to -70° , (ii) an ammonia vapour-pressure thermometer in the range -70° to -20° and (iii) standard mercury thermometers, graduated in 0.1°, in the range -20° to $+50^{\circ}$.

Following calibration, the pyknometers were filled with the requisite amount of arsine by high-vacuum distillation, care being taken to exclude mercury vapour completely from the system. The pyknometers were sealed off under vacuum and the seals carefully annealed. Volume measurements were made over a range of temperature. The capillaries were then carefully marked with a glass knife near to the tips to facilitate opening of the tubes. The pyknometers were allowed to come to room temperature, when they were carefully weighed. The arsine was then frozen solid in liquid nitrogen and the tip of each capillary broken off sharply at the file mark. The arsine was allowed to evaporate, the tube evacuated, dried in an air oven and the two pieces of the pykonmeter weighed. The weight of arsine was obtained by difference.

Results

Three pyknometers, two from the same length of capillary, were calibrated as indicated previously. All capillaries proved to be uniform in bore to within 1 part in 2000, and the volume unit length therefore to 1 part in 1000, over the entire length. The relevant data for the pyknometers used are given for 20° C.

In calculating densities from the measured volume of liquid arsine, three corrections must be considered (i) the elastic deformation of the glass under vapour pressures of the order encountered in the temperature range, (ii) the

³ Landolt-Börnstein Tabellen (Berlin, 1936).

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TABLE I

Pyknometer	Volume to Reference Line (cm. ³)	Volume/unit length of capillary (cm. ³ /cm.)	
1	1·2962	0·1940	
2	0·8008	0·02848	
3	1·9479	0·02848	

TABLE II.-DENSITY OF LIQUID ARSINE

\$ (°C)	Pyknometer	ρ_t (obs.)	ρ_t (calc.)	Deviation
- 84.9	I	1.680	1.688	- 0:00I
- 80.6	I	1.676	1.675	- 0.001
- 74.4	I	1.650	1.657	- 0.002
- 70.3	ī	1.648	1.645	- 0.003
- 67.5	I	1.630	1.637	0.003
- 64.5	I	1.620	1.628	- 0.001
- 63.6	T	1.624	1.625	- 0.001
- 62.8	2	1.622	1.622	0
- 61.6	2	1.610	τιστο	Ő
- 60.8	2	1.019	1.616	0
- 50.6	2	1.010	1.010	
58.3	2	1.600	1.013	0001
- 57.3	2	1.605	1:605	0
- 55.5	2	I GOJ	1.003	
- 54.7	2	1,506	1.507	
J4 / - 52.5	2	1 590	1 39/	+ 0.001
- 50.7		1 591	1 394	+ 0.003
- 50 7 - 50 6	1	1.202	1.202	0
- 30 0	2	1.203	1.504	+ 0.001
- 45 0	2	1.203	1.207	+ 0.004
- 39 1	2.	1.242	1.547	+ 0.002
- 35'3	2	1.532	1.535	- 0.003
- 35.0	1	1.535	1.534	- 0.001
- 30.9	2	1.517	1.520	+ 0.003
- 24.0	2	1.498	1.500	+0.002
- 191	2	1.479	1.400	+ 0.001
- 14.1	2	1.400	1.403	+ 0.003
- 10.0	2	1.440	1.449	+ 0.003
- 4.1	2	1.427	1.428	+ 0.001
- 2.8	1	1.425	1.423	-0.005
+ 0.0	2	1.411	1.411	0
+ 5.3	2	1.392	1.394	+ 0.005
+ 0.4	3	1.395	1.300	- 0.002
+ 7.3	2	1.385	1.387	+ 0.005
+10.0	3	1.381	1.322	0.004
+11.0	2	1.372	1.323	+ 0.001
+15.0	3	1.303	1.328	- 0.002
+19.8	3	I·344	1.340	- 0.004
+ 20.0	I	1.339	1.339	0
+21.5	3	1.332	I·334	- 0.003
+22.3	3	1.333	1.331	-0.005
+ 23.4	3	1.330	1.327	- 0.003
+ 24.0	3	1.358	I·324	- 0.004
+ 25.0	3	1.324	1.320	- 0.004
+ 38.0	3	1.207	1.270	+ 0.003
+ 41.4	3	1.250	1.257	+ 0.001
+ 43.0	3	1.249	1.250	+ 0.001
+ 45 9	3	1.230	1.239	+ 0.003
+ 48.0	3	1.223	1.230	+ 0.002

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change in volume of the pyknometers with temperature, (iii) the mass of arsine in the gaseous phase. Durrant, Pearson and Robinson² neglected any correction for change in volume under pressure, since, after subjection to the vapour pressures of the order of 10-20 atm., no change in volume of the pyknometer could be detected. However, one must consider the elastic deformation of the pyknometer, giving rise to a change in volume $\Delta V = \frac{V p}{k}$ cm.³, where k is the bulk modulus of elasticity of the glass, p the pressure difference in dyne cm.⁻² and V the original volume. For a pyknometer of 2 cm.³ capacity, constructed of glass of bulk modulus 5×10^{11} dyne cm.⁻², the change in volume $\Delta V \sim 10^{-4}$ cm.³ at the highest pressures encountered (~ 26 atm.) is negligible and no correction need be applied. On the other hand, the change in volume of the pyknometer due to thermal changes amounts to 0.005 cm.⁸ for a 2 cm.³ pyknometer at the lowest temperatures and corrections must be made throughout. The coefficient of cubical expansion ⁴ of the soft glass used was taken as 2.55×10^{-5} . Since the total mass of arsine in the pyknometer is not wholly in the liquid phase, a correction (negative) must be applied to the weight of arsine. This correction amounts to

$$\Delta m = \frac{v p M \ 273 \cdot 2}{224 14}$$

where

and

v is volume of vapour phase,

p the vapour pressure of arsine in atmospheres,

 \hat{M} the molecular weight of arsine,

T the absolute temperature,

amounts to some 2 % of the total mass under some of the experimental conditions and cannot be neglected. Corrections were applied in the calculation of the densities.

The density was measured at 48 temperatures in the range; the results are tabulated in Table II and plotted in Fig. 1.



FIG. 1.—Density-temperature relation for liquid arsine. Experimental points: ● Johnson and Pechukas; ● Durrant, Pearson, and Robinson; O this work. Continuous curve calculated from least squares expression.

The empirical relationship---

 $\rho_t = 1.413 - 3.602 \times 10^{-3}t - 4.321 \times 10^{-6}t^2,$

⁴ Kaye and Laby, Tables of Physical and Chemical Constants, 9th ed. (1944).

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obtained by applying the method of least squares to the experimental data, has been used to calculate the density at each temperature ; these are tabulated in Table II and the continuous curve in Fig. 1 has been drawn from this relation. The standard error is

$$\sqrt{\frac{\sum d_i^2}{n}} = 0.0027.$$

Experimental points obtained by other observers shown in Fig. 1, diverge progressively from our data as the temperature increases, due evidently to the failure to correct for the mass of arsine in the vapour phase.

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