

(3) and those reported by Eubank (4). The reference values in Figure 2 are those calculated by Goodwin (5) and have been chosen only as a convenient reference point without regard to their overall accuracy.

Table III lists selected saturated liquid densities which were obtained by calculating the intersection of the smoothed isochores and the vapor pressure curve. Data were not obtained above 304 K due to the difficulties encountered with the smoothing equation in the critical region. Figure 3 graphically compares these densities to those of ref 3 and 4.

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## Vapor Pressures and Enthalpies of Vaporization of Benzyl Halides

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Vapor pressures over a range of temperatures have been measured for the benzyl halides using an isoteniscope. The calculated enthalpies of vaporization at 25 °C are 44.5 ± 0.4, 50.1 ± 0.5, 50.5 ± 0.5, and 50.6 ± 1.4 kJ mol<sup>-1</sup>, respectively, for the fluoride, chloride, bromide, and iodide. The enthalpies of fusion of benzyl bromide and iodide, measured by differential scanning calorimetry, are 13.7 ± 0.2 kJ mol<sup>-1</sup> at -1.4 °C and 13.2 ± 0.4 kJ mol<sup>-1</sup> at 26.3 °C, respectively.

During thermochemical measurements on benzyl halides (2) a literature search revealed that values of the enthalpies of vaporization were available only for the chloride and bromide members of the series, and that these were based on old work (7). Accordingly, a study of the temperature dependence of vapor pressures of all four benzyl halides was undertaken.

#### Experimental Section

**Materials.** Benzyl chloride, benzyl bromide, and *n*-heptane (all from British Drug Houses) and benzyl fluoride (P.C.R. Chemicals, Gainesville, Fla.) were dried and fractionally distilled before use. Benzyl iodide was prepared by the method of Coleman and Hauser (5) and purified by fractional crystallization. The purities of these materials, as determined by GLC, are reported in Table I which also includes melting temperatures and enthalpies of fusion. Analyses were by a Philips PV4000 gas-liquid chromatograph, equipped with a 3 m × 2 mm column (10 mass % squalane on diatomite 'C') and a flame ionization detector. Nitrogen was used as a carrier gas. It is considered that this equipment could detect impurities with the exception of water, down to 0.01 mass % or better. Enthalpies of fusion were found by differential scanning calorimetry (Perkin-Elmer DSC-1) only for the bromide and iodide.

**Vapor Pressures.** Vapor pressures were measured directly by means of an isoteniscope and a vacuum system using standard techniques (11). A closed-ended mercury manometer was

used to record the pressure, the mercury height being read with a cathetometer. Pressures were corrected to 0 °C and standard gravity. The isoteniscope was immersed in a stirred, thermostated oil bath of which the temperature close to the bulb was read by a series of short-range mercury thermometers (British Standards 593) calibrated on the IPTS 68 scale.

#### Results

Between three and six readings of vapor pressure were taken at each temperature, the mean values of each group being reported in Table II. The scatter of the values about these means was about 0.1 °C and 0.1 mmHg, respectively, although the thermometers could be read to the nearest 0.02 °C and the cathetometer to the nearest 0.01 mm.

The original, unaveraged results were fitted to the Antoine equations

$$\log p \text{ (mmHg)} = A - B/(t + C)$$

by a least-squares procedure with *t* as the independent variable, the value of the constant *C* being first calculated from the correlation given by Kreglewski and Zwolinski (8)

$$C = 273.2 - 0.04T_b - 3 \times 10^{-4}T_b^2$$

where *T<sub>b</sub>* (K) is the boiling temperature (Table III). The calculated Antoine constants are presented in Table III together with their

Table I. Purities (GLC), Melting Temperatures, and Enthalpies of Fusion of Benzyl Halides

Compound	Purity, mass %	Melting temp, °C	Δ <sub>f</sub> H at melting temp, kJ mol <sup>-1</sup>
Benzyl fluoride	99.50		
Benzyl chloride	99.85		
Benzyl bromide	99.80	-1.4	13.7 ± 0.2
Benzyl iodide	99.87	26.3	13.2 ± 0.4

Table II. Vapor Pressures of Benzyl Halides (Mean Values)

Benzyl fluoride		Benzyl chloride		Benzyl bromide		Benzyl iodide	
Temp, °C	<i>p</i> , mmHg	Temp, °C	<i>p</i> , mmHg	Temp, °C	<i>p</i> , mmHg	Temp, °C	<i>p</i> , mmHg
24.73	6.79	47.84	4.81	67.10	7.14	87.33	8.43
35.08	11.37	53.37	6.79	79.27	13.25	96.37	12.07
41.73	16.50	70.60	16.33	90.23	22.09	108.80	18.91
48.03	23.44	85.63	31.85	99.63	31.68	115.53	25.43
55.67	34.39	95.35	47.48	106.23	40.57	121.70	33.25
63.87	50.10	100.20	59.29	112.00	49.67	126.90	38.22
70.70	68.04	106.97	79.25	118.07	62.47	133	dec
76.10	85.70	112.67	96.63	123.38	76.76		
79.17	97.37	117.08	113.94	128.98	92.67		
83.30	116.62			135.65	117.69		

Table III. Antoine Constants for *n*-Heptane and Benzyl Halides

Compound	No. of data points	Temp range, °C	Boiling temp, °C	Antoine constants <sup>a</sup>			Stand. dev. (mmHg)
				A	B	C	
<i>n</i> -Heptane	18	17–44	98.42 (6)	6.904	1269	216.9	0.73
Benzyl fluoride	33	25–83	140.2 <sup>b</sup>	6.966	1417	205.4	0.94
Benzyl chloride	43	48–117	179.3 (6)	6.801	1477	193.7	1.26
Benzyl bromide	37	67–136	201 (6)	6.519	1437	186.8	1.07
Benzyl iodide	22	87–127	220 <sup>c</sup>	6.088	1385	180.5	0.80

<sup>a</sup>  $\log p$  (mmHg) =  $A - B/(t(^{\circ}\text{C}) + C)$ . <sup>b</sup> Estimated from 139.8 °C at 753 mmHg (6). <sup>c</sup> Estimated.

Table IV. Standard Enthalpies of Vaporization of Benzyl Halides at 25 °C

Compound	$\Delta_{\text{lg}}H^{\circ}$ , kJ mol <sup>-1</sup>
Benzyl fluoride	44.5 ± 0.4
Benzyl chloride	50.1 ± 0.5
Benzyl bromide	50.5 ± 0.5
Benzyl iodide	50.6 ± 1.4

temperature range of validity and the standard deviations in pressure.

As a check for systematic errors the vapor pressure of *n*-heptane was studied at 18 temperatures. Within its restricted range of validity the Antoine equation for *n*-heptane gives good agreement with the data of Ambrose (7) and Zwolinski (14). For example, at a series of 20 temperatures the calculated pressures deviate from those given in reference 1 by 0.3 mmHg on average.

It seemed preferable to calculate enthalpies of vaporization by comparison of the vapor pressures with those of a standard compound (9). The procedure adopted here was to determine by a least-squares method, the gradient, and hence the ratio  $\Delta_{\text{lg}}H/\Delta_{\text{lg}}H(\text{standard})$ , of  $\log p/\log p(\text{standard})$  expressed as a function of temperature, the standard compound being chosen to be chemically similar to the materials under investigation. Chlorobenzene was used as a standard since its vapor pressure (4) and Antoine constants (3) are accurately known, and its enthalpy of vaporization at 25 °C has been measured calorimetrically (13) to be 40.97 ± 0.06 kJ mol<sup>-1</sup>.

Enthalpies of vaporization are given in Table IV. Uncertainty intervals throughout this paper are twice standard deviations, including component uncertainties for derived quantities. The

enthalpies increase as expected from the fluoride to the iodide although the last three values differ only slightly. The large uncertainty associated with the iodide value probably reflects some thermal decomposition at the higher temperatures. The vapor pressures reported by Kahlbaum (7) for the chloride and bromide agree quite well with those given here. The enthalpy of vaporization of *n*-heptane at 25 °C calculated by the comparison method (36.5 kJ mol<sup>-1</sup>) is in satisfactory agreement with 36.6 kJ mol<sup>-1</sup> given by Zwolinski et al. (14).

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