Part II

PHYSICAL PROPERTIES, EVALUATION OF COMPOUNDS AND MATERIALS

Sublimation Pressure of α-*p*-Dichloro-, β-*p*-Dichloro-, *p*-Dibromo-, and *p*-Bromochlorobenzene

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As A PRELIMINARY to the investigation of solid-vapor equilibria in binary systems of *p*-dihalogenated benzenes, the sublimation pressures of *p*-dichloro-, *p*-dibromo-, and *p*-bromochlorobenzene have been redetermined. These materials are common and widely used, but only a few determinations of their sublimation pressures are to be found in the literature, and these are not in good agreement. Speranski (*15*) studied all three compounds, but his results for *p*-dichlorobenzene are markedly lower than those of Darkis, Vermillion, and Gross (*5*), while his *p*-dibromobenzene pressures are higher than those of Küster (*11*) by an equal amount. No other investigation of *p*-bromochlorobenzene has been reported, but since the completion of this study, Stern and Gregory (*16*) have determined the sublimation pressure of *p*-dibromobenzene over a wide range of temperature.

Although the existence of a solid-solid transition in *p*-dichlorobenzene between 30° and 40° C. has been reported by many authors (*1*, *3*, *4*, *6-8*, *10*, *12*), no corresponding discontinuity in the sublimation pressure appears in the data of Speranski (*15*). Darkis and others (*5*) reported pressures at only three temperatures, obviating the question of whether such a break exists in their data. Special attention, therefore, was given to the study of this region in order to detect this transition and measure the corresponding enthalpy change. A transition has also been reported to occur in *p*-dibromobenzene at about 8.5° C. (*1*, *6*), but the equilibrium pressure at this temperature proved to be too low for measurement by the technique employed here.

EXPERIMENTAL

Materials. The compounds (Eastman Kodak White Label) were purified by a procedure similar to that of Campbell and Prodan (*2*). Each of the compounds was distilled at atmospheric pressure through a 4-foot column packed with glass helices, and the middle fraction, having a boiling range of no more than 0.5° C., collected. They were then recrystallized six times from 95% ethyl alcohol which had been refluxed and distilled in contact with KOH. After vacuum drying the compounds were stored, over concentrated H_2SO_4 in separate desiccators.

The freezing points of the purified materials were determined from cooling curves, using a Beckman-type arrangement and a Beckman thermometer calibrated against a Bureau of Standards certified thermometer graduated in tenths. Only an estimated 30 to 40% of the sample could be frozen in this apparatus before stirring failed, but in this interval the temperature varied not more than 0.01° C. and showed no tendency to fall off. The freezing points so obtained were 53.13° ± 0.03°, 64.65° ± 0.03°, and 87.24 ± 0.04° C. for *p*-dichloro-, *p*-bromochlor-, and *p*-dibromobenzene, respectively.

Apparatus. The apparatus used for the sublimation pressure measurements was similar to that of Keavney and Smith (*9*), except that the sample holder, *S*, Figure 1 (*9*), was not jacketed and a stopcock was inserted between *S* and *B*. A few grams of the material being studied were placed in *S*, which was then sealed. The manometer, *M*, was filled with concentrated H_2SO_4 through *A*, and the latter was sealed. First the manometer and next the remainder of the apparatus was evacuated to about 10^{-4} mm. of Hg. The sample was now degassed by alternately boiling and freezing it, with the stopcock nearest the sample closed, and pumping on it with the stopcock open. This procedure was repeated four times to assure a thoroughly degassed solid phase. The apparatus was then completely immersed in a water thermostat. Although experiment showed that a constant pressure was attained in a few minutes, considerably longer intervals were allowed between the attainment of a constant bath temperature and the opening of the stopcock to connect *B* to the manometer. The latter was pumped out after each pressure measurement. Temperatures were maintained and measured with an accuracy of ±0.05° C. The difference in height of the manometer levels was determined with a Gaertner cathetometer of proved reliability (*14*). All pressures were corrected to mm. Hg at 0° C., and should be accurate to ±0.01 mm. Runs were made on each sample with increasing and with decreasing temperature.

Some check runs were made using mercury in the manometer. These agreed exactly with those made using H_2SO_4. Another technique also yielded identical pressures (*18*). For *p*-dichlorobenzene in the vicinity of its transition point, Apiezon Oil A was used in a few experiments to obtain a higher amplification factor and greater precision. Again, agreement was excellent.

RESULTS AND DISCUSSION

The observed sublimation pressures of *p*-dichloro-, *p*-bromochloro-, and *p*-dibromobenzene are listed in Table I. The third columns list the pressures calculated from equations of the type $\log P(\text{mm.}) = A - BT^{-1}$, employing parameters obtained by least-squares treatment of the experimental data. The values of *A* and *B* for each substance are listed in Table II, as are the standard heats and entropies of sublimation. These latter are valid for the mid-range temperatures, which are also listed.

The log *P* *vs.* $1/T$ plot of the *p*-dichlorobenzene data (Figure 1) exhibits a definite break in the vicinity of 40° C. presumably caused by the solid-solid transition discussed above. The heat of transition, equal to the difference in the heats of sublimation of the allotropic forms, is 420 ± 140

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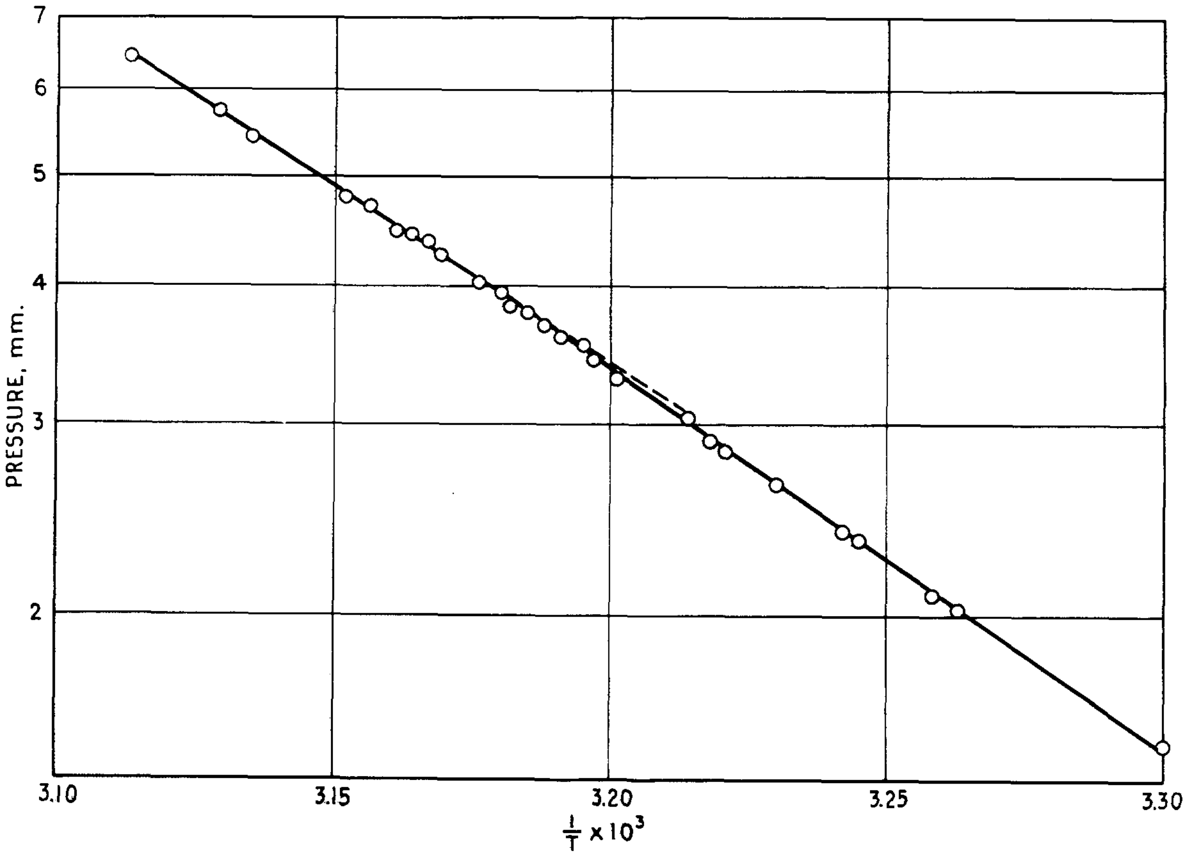

Figure 1. Sublimation pressure of *p*-dichlorobenzene showing the α-β transition

cal. per mole, and the entropy of transition is 1.35 cal. per degree per mole. The closeness of the latter figure to *R* ln 2 may be more than a coincidence, but its significance is not evident. The phases involved are most probably the monoclinic (α) form (*3*) below the transition temperature, and triclinic (β) form (*8*, *10*) above. X-ray powder patterns of a specimen of material stored for a long time at room temperature, and a specimen freshly quenched from the melt agreed with those published by Krishna Murti and Sen (*10*), who showed that their patterns conformed to the reported structures (*3*, *8*) of the two forms. Housty and Clastre (*7*) have shown that the change in crystal symmetry involves only a rotation and short translation of alternate molecules. The relatively small heat of transition, and the small heat effect found at 39° C. by differential analysis (*13*), would seem to be in accord with such a mechanism.

The temperature at which the transition occurs is not clearly defined. Beck and Ebbinghaus (*1*) reported it to be at 39.5° C.; Campbell and Prodan (*2*) attributed a break in a cooling curve at 39.6° C. to this transition. Deffet (*6*) reported 34.5° C. and Danilov and Ovsienko (*4*) 30.8° C. as the transition temperature. Lemanceau and Clément (*12*) claim to have verified the latter figure. Jeffrey and McVeagh (*8*) and Krishna Murti and Sen (*10*) reviewed the subject, and apparently established 40° C. as the upper limit. The differential thermal analysis curves of Ravich and Bogush (*13*) in this region show only a small endothermic effect at 39° C. The calculated intersection of the present log *P* *vs.* 1/*T* lines is at 44.5° C., but this figure is very uncertain because of the small difference in their slopes. Nevertheless, it would seem to favor a value toward the high end of the range found in the investigations cited.

The sublimation pressures of *p*-dichlorobenzene reported here are higher, by roughly 1 mm., than those found by Speranski (*15*). Agreement with the data of Darkis, Vermillion, and Gross (*5*) is good at 30° C., but at higher temperatures their pressures are higher by increasing amounts. The data of Speranski lead to a heat of sublimation of 17.7 kcal. per mole, while those of Darkis and others (*5*) yield 16.3 kcal. per mole, which figures may be compared with those in Table II. The standard entropy of sublimation of α-*p*-dichlorobenzene at 298° K. was found to be 38.7 cal. per degree per mole. The standard entropy in the gaseous state, S°_{298} ($p\text{-}C_6H_4Cl_2$), computed using the vibrational assignment of Tobin (*17*), is 77.5 cal. per degree per mole, making the standard entropy of the α form equal to 38.8 cal. per degree per mole. No other measurement of this quantity has been found in the literature.

The sublimation pressures of *p*-bromochlorobenzene determined in this investigation are approximately 0.1 mm. greater than those of Speranski (*15*), whose data yield a heat of sublimation of 16.5 kcal. per mole. A plot, similar to Figure 1, but for *p*-bromochlorobenzene, reveals the possibility of a change of slope at about 35° to 40° C. but, for lack of any other evidence of a transition for this substance, this has been ignored in Tables I and II. If, however, one attributes the sublimation pressure values at and below 35.6° C. to one form (α), and those above to another (β), and ignores the point for 64.4° C., which appears to have a relatively large error, one obtains an excellent fit for each line with the following *A* and *B* values: α, 12.264, 3831.4; β, 11.427, 3572.2. These parameters give a calculated temperature of intersection of 36.4° C. and imply the following heats of sublimation for the α and β forms: 17.53 ± 0.2 and 16.35 ± 0.1 kcal. per mole, at mid-range temperatures of 302° and 324° K., respectively. The entropy change of the suspected transition would then be 3.8 ± 0.7 cal. per degree per mole.

For *p*-dibromobenzene the calculated heat and entropy of sublimation at 326° K. compare well with the values reported by Stern and Gregory (*16*), who found 17.65 kcal. per mole and 40.3 cal. per degree per mole, respectively.

Speranski's sublimation pressures (*15*) agree well with those reported here above 50° C., but fall off by up to 0.1 mm. below this temperature. His data yield 17.3 kcal. per mole for the heat of sublimation, but elimination of the low temperature points from the calculation improves the agreement with the present results. Küster's pressures (*11*) are lower by several tenths of a millimeter over the temperature range investigated.

Table I. Sublimation Pressure

Temp., ° C.	Pressure, Mm. Hg		Temp., ° C.	Pressure, Mm. Hg	
	Exptl.	Calcd.		Exptl.	Calcd.
α-*p*-Dichlorobenzene			β-*p*-Dichlorobenzene		
20.4	0.70	0.67	37.9	3.02	3.01
23.9	0.91	0.91	39.8	3.52	3.49
26.8	1.17	1.17	40.2	3.58	3.59
29.8	1.52	1.52	40.5	3.68	3.68
33.2	2.02	2.02	40.8	3.76	3.76
33.7	2.08	2.10	41.1	3.81	3.85
35.0	2.34	2.34	41.3	3.92	3.91
35.3	2.38	2.40	41.7	4.01	4.03
36.4	2.63	2.63	42.4	4.26	4.25
37.3	2.81	2.82	42.6	4.38	4.32
37.5	2.87	2.87	42.9	4.45	4.42
39.2	3.30	3.29	43.2	4.48	4.52
39.6	3.41	3.40	43.7	4.72	4.69
			44.1	4.80	4.84
			45.8	5.46	5.49
			46.4	5.75	5.75
			48.0	6.45	6.47
			49.4	7.17	7.16
p-Bromochlorobenzene			51.3	8.20	8.22
21.4	0.17	0.20	51.7	8.51	8.46
24.2	0.25	0.26	52.5	8.94	8.96
26.1	0.28	0.31			
29.0	0.40	0.41	*p*-Dibromobenzene		
30.7	0.44	0.47	25.8	0.07	0.06
35.4	0.72	0.71	26.8	0.07	0.07
35.6	0.70	0.73	27.5	0.08	0.07
40.5	1.08	1.10	31.9	0.11	0.11
40.6	1.08	1.11	38.1	0.20	0.20
44.5	1.50	1.52	42.6	0.29	0.30
45.6	1.66	1.67	42.6	0.30	0.30
48.9	2.13	2.17	44.6	0.36	0.36
49.9	2.35	2.34	50.2	0.55	0.57
53.0	3.01	2.98	51.2	0.63	0.63
54.7	3.43	3.39	56.4	0.97	0.96
57.1	4.09	4.06	57.2	1.02	1.02
59.9	5.05	5.00	57.3	1.06	1.03
60.7	5.33	5.31	64.3	1.79	1.80
64.0	6.77	6.74	71.8	3.15	3.17
64.4	6.84	6.94	80.5	5.94	5.94

Only Stern and Gregory (*16*) made measurements below the reported transition temperature of *p*-dibromobenzene (8° C.). They make no mention of a discontinuity in this region, but it is not clear from their data whether the precision is high enough to exclude such a break.

Table II. Standard Heats and Entropies of Sublimation, and Parameters in the Equations log P(Mm.) = $A - BT^{-1}$

Compound	A	B	ΔH_s°, Kcal. Mole^{-1}	ΔS_s°, Cal. Deg.$^{-1}$Mole^{-1}	Mid-range Temp. ° K.
p-$C_6H_4Cl_2$ (α)	11.347	3382.9	15.48 ± 0.1	38.7 ± 0.1	303
p-$C_6H_4Cl_2$ (β)	11.056	3290.4	15.06 ± 0.1	37.4 ± 0.2	318
p-$C_6H_4BrCl^a$	11.353	3548.4	16.24 ± 0.1	38.8 ± 0.2	316
p-$C_6H_4Br_2$	11.592	3826.2	17.51 ± 0.1	39.9 ± 0.2	326

[a] Assuming no polymorphism.

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