Equilibrium Vapor Compositions of *p*-Dichlorobenzene–*p*-Dibromobenzene and *p*-Dichlorobenzene–*p*-Bromochlorobenzene Solid Solutions at 50° C.

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A PREVIOUS article from this laboratory (*2*) on systems of *p*-dihalogenated benzenes reported total pressures of the solid solutions as a function of composition, but direct analysis of the equilibrium vapors, after isolating the latter, was unsuccessful. Analytical treatment of the total pressures by the method of Barker (*1*) had been used to calculate the vapor compositions. Recent, more successful attempts to measure these directly and thus confirm the calculated values are presented below.

EXPERIMENTAL

Materials. The *p*-$C_6H_4Cl_2$, *p*-C_6H_4BrCl, and *p*-$C_6H_4Br_2$ were Eastman chemicals. After recrystallization they had the following melting points: $C_6H_4Cl_2$, 53.0 to 53.5°; C_6H_4BrCl, 64.7 to 65.0°; $C_6H_4Br_2$, 86.7 to 87.3° C.

Apparatus and Procedure. About 5 grams of each solid solution, prepared and analyzed as before (*2*), and ground, was placed in a 50-ml. round-bottomed flask with some lead shot. The flask was fitted with a neck 15 cm. long and 16 mm. O.D. which led through a standard taper joint to another tube, 7 cm. long and the same diameter, which, in turn, terminated in a stopcock leading to a vacuum pump and pressure gage. The lower half of the joint was lubricated with dextrin-glycerol-mannitol, and the upper half with silicone grease. The entire joint was covered by a rubber sleeve for futher protection against leakage. The apparatus was held at 0°, evacuated to a pressure of 1 mm. or less, and then clamped in an upright position with the stopcock closed in a thermostat at 50.00 ± 0.02° C. so as to be entirely immersed (including the stopcock). During the equilibration period the flask was frequently shaken vigorously, the lead shot effecting a grinding action on the solid solution. After 1 to 3 days the apparatus was raised so that the joint was no longer immersed. The tubing above the latter was surrounded by an ice-water mixture and, later, by an acetone–dry-ice bath, causing a layer of sublimate to coat the inside of the upper tube. The agitation of the flask was continued at very frequent intervals during this process. Finally, after several hours, a sufficiently large quantity of sublimate, usually 10 to 20 mg., had formed; it was washed out with dry toluene and analyzed by the usual procedure (*2*). For a given solid solution this technique was found to give reproducible results.

RESULTS AND DISCUSSION

The systems *p*-$C_6H_4Cl_2$–*p*-$C_6H_4Br_2$ and *p*-$C_6H_4Cl_2$–*p*-C_6H_4BrCl gave the results shown in Table I, which includes the vapor compositions calculated by the Barker treatment (*2*), the ideal vapor compositions, and the interpolated measured total pressures (*2*). (The system *p*-$C_6H_4Br_2$–*p*-C_6H_4BrCl, however, in which all the total pressures are less than 2.4 mm., did not give satisfactory results.)

Table I. Coexisting Solid and Vapor Compositions at 50° C.

(Mole per cent of *p*-$C_6H_4Cl_2$)

The System *p*-$C_6H_4Cl_2$–*p*-$C_6H_4Br_2$

Solid Phase		Vapor Phase		Total Pressure, (Mm.)
	Exptl.	Calcd.	Ideal	
9.9	66.7	68.3	59.5	1.58
29.9	87.1	88.2	85.1	3.43
50.0	91.2	93.6	93.0	4.81
70.1	95.8	96.3	96.9	5.88
10.0	21.9	23.6	26.0	2.79
29.9	59.1	57.4	57.5	3.79
49.9	79.8	77.7	75.9	4.96
69.9	80.3[a]	89.1	88.0	6.09

[a] Average of closely agreeing results of completely separate runs.

The table shows, as reported earlier, that neither system deviates widely from ideality. The predictions of the Barker theory are confirmed surprisingly well, considering the difficulties inherent in obtaining an equilibrium sample. The discrepancy in the last row of data for the second system, where the total pressure is high, may be the result of too rapid collection of the sublimate. This would have the effect of impoverishing the surface of the solid phase in the more volatile component (*p*-$C_6H_4Cl_2$) in spite of the agitation.

LITERATURE CITED

(1) Barker, J.A., *Australian J. Chem.* **6**, 207 (1953).
(2) Walsh, P.N., Smith, N.O., *J. Phys. Chem.* **65**, 718 (1961).

RECEIVED for review October 27, 1961. Accepted March 23, 1962.