The Equilibrium Absorption of Oxygen by *p*-Xylene

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The volume of oxygen absorbed by *p*-xylene was measured at 750 mm. of Hg and at temperatures between 30° and 80° C. at 10° intervals. The reported results are the original data, values of Ostwald's constant between 0.193 and 0.220 cc. of oxygen per cc. of *p*-xylene, and values of Henry's law constant between 840 and 900 atm. of oxygen per unit mole fraction O_2. An average Henry's law constant of 870 adequately represents the data.

THE AIR oxidation of *p*-xylene to *p*-toluic acid and subsequently to terephthalic acid has been performed in batch equipment (*1, 2*) and continuously. The oxidation takes place in the liquid phase in the presence of a cobalt or manganese catalyst, such as cobalt naphthenate. McMinn (*2*) found the reaction to be of zero order and concluded that the rate governing mechanism was the absorption of oxygen by the *p*-xylene. As an initial step toward determining the oxygen absorption rate, the equilibrium absorption was measured and is reported here.

EXPERIMENTAL

The equipment used was constructed of simple pieces of laboratory glassware. A still and condenser were used to reflux for two hours or more a commercial grade of *p*-xylene (Enjay), a 99% pure material with impurities consisting of *o*- and *m*-isomers. A 250-ml. cork-fitted Erlenmeyer flask with a Teflon-coated magnetic stirrer was filled with U.S.P. oxygen saturated with *p*-xylene. Hot *p*-xylene was drained from the refluxing mixture into the flask, which was surrounded with a water jacket. The Erlenmeyer flask was connected to a 100 cc. gas buret which had been part of a standard Orsat apparatus. After the system reached equilibrium, as determined by no further volume changes, the volume of gas displaced by the *p*-xylene was measured at room temperature by the buret. The *p*-xylene was drained into a 100-ml. graduated cylinder to measure the *p*-xylene volume. As a rubber tubing connection was necessary to connect the still to the Erlenmeyer flask, the *p*-xylene was discolored by it before any equilibrium measurements were made.

RESULTS

The original data for one measurement at each temperature and the results which are the averages for at least three measurements at each temperature are reported in Table I. At 30° C., the calculated results for any one measurements were within 1.7% of the average value for all the 30° C. measurements. The measured barometric pressure was 750 ± 2 mm. of Hg for all measurements. Henry's law constants, but not Ostwald's coefficients, are corrected for the decreased pressure of oxygen caused by the vapor pressure of *p*-xylene.

The values of Henry's law constant do not significantly change with temperature; if there is any trend, it would be a decrease with temperature. The measurement errors probably mask any significant trend. Within the accuracy of the measurements, an average value of 870 represents Henry's law constant over the temperature interval considered.

LITERATURE CITED

(1) Brill, W.F., Ind. Eng. Chem. 52, 837 (1960).
(2) McMinn, C.J., M.S. thesis, Vanderbilt University, 1955.

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Table I. Data and Results for Oxygen–*p*-Xylene Equilibrium

Bath Temp., ° C.	Volume of Displaced Gas, Cc.	Volume of *p*-Xylene, Ml. at Bath Temp.	Volume of *p*-Xylene, Ml. at 25° C.	Room Temp., ° C.	Henry's Law Constant Atm. O_2/Mole Fraction $O_2 \times 10^{-2}$	Ostwald's Constant (25° C. Volumes) Ml. O_2/Ml. *p*-Xylene
30.0	74.3	97.8	97.7	8.89	25.2	0.220
40.0	67.6	93.0	92.0	9.00	26.9	0.214
50.0	64.8	94.4	92.5	8.81	24.5	0.215
60.0	52.1	82.0	79.6	8.46	24.8	0.220
70.0	52.0	88.9	84.8	8.40	24.5	0.215
80.0	53.0	98.5	93.1	8.70	25.8	0.193