Vapor Pressure of Liquid Nitrobenzene at Low Temperatures

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IN THE STUDY of the gas phase resistance to mass transfer in packed beds, it is advantageous to use an organic material of low vapor pressure as the transferable medium. Unfortunately, the vapor pressures of such substances are generally not known with certainty, because of the difficulty of the direct measurement of pressures below 1 mm. of mercury. Many such vapor pressure measurements are reported for nitrobenzene, in a review article by Stull (4). In general there is considerable disagreeement among the various authors, and in some cases there is even a lack of thermodynamic consistency. Because it is not possible to use such data with confidence, the vapor pressure of nitrobenzene was studied to provide a basis for calculations in subsequent mass transfer experiments.

In the usual packed bed experiment, the desired information is the rate of mass transfer; consequently, the length of the bed is set so that the concentration of vapor in the exist gas stream is 50 to 80% of saturation. By increasing the length of the bed sufficiently, essentially complete saturation can be obtained. The partial pressure of the transferred component in the effluent gas can then be considered equal to the equilibrium pressure of the solid or liquid material of which the bed is composed. (For the poorest operating conditions used, mass transfer calculations indicate that the exit gas stream was within 0.2% of saturation—an error of ≈ 0.004 mm. in the vapor pressure). In practice only the weight loss of the bed, the flow rate of the carrier gas, the total pressure, and the temperature of the exit gas stream must be measured. The application of Dalton's law then provides the desired vapor pressure.

EXPERIMENTAL

Materials. Nitrobenzene (Eastman Kodak White Label Grade) was distilled under vacuum in an Oldershaw column, the center cut being retained. The boiling point, measured as 210.8° C. agreed with the accepted 210.9° C. (2).

Apparatus and Experimental Procedure. Nitrogen gas from cylinder A was introduced into the system (Figure 1) at a rate controlled by a regulator and needle value, B. The gas was passed through drying tube, C, to remove water that may have been present. A 25-foot length of coiled copper tubing, D, located in the thermostat, E, brought the incoming gas stream to the temperature of the packed bed, F, a glass U-tube with side arms packed with porous Alundum spheres soaked with nitrobenzene. The exit gas stream temperature was determined with a copper-constantan thermocouple, G, and a Leeds & Northrup portable precision

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Figure 1. Schematic drawing of setup

potentiometer, H, to the nearest 0.04° C. The thermocouple was calibrated at the freezing point of water and the triple point of sodium sulfate. The gas passing through the bed was measured with the wet-test meter, J. The bed was weighed to the nearest 0.0001 gram on a Chainomatic balance before and after the run to determine the weight loss.



Figure 2. Vapor pressure of nitrobenzene represented by a modified Clausius-Clapeyron equation

RESULTS

The vapor pressures of nitrobenzenes are given in Table I and Figure 2 for the temperature range from 6.09° to 23.14° C. Figure 2 is plotted according to an empirical method suggested by Calingaert and Davis (1) based on the Clausius-Clapeyron equation. The equation of the line representing the data is:

$$\log_{10}p_{\rm mm.} = 7.545 - \frac{2064}{t+230}$$

where $p_{\rm mm.}$ is in millimeters of mercury, and t is in degrees centigrade. Also shown on Figure 2 are the datum point of Puck and Wise (3) at 25° C. and the extrapolation of the Stull data (4)—pressure-range, 1 to 760 mm. of mercury.

LITERATURE CITED

- (1) Calingaert, George, Davis, D.S., Ind. Eng. Chem. 17, 1287 (1925).
- (2) "International Critical Tables," Vol. II, p. 212, McGraw-Hill, New York, 1928.
- (3) Puck, Th. T., Wise, Henry, J. Phys. Chem. 50, 329-39 (1946).
- (4) Stull, D.R., Ind. Eng. Chem. 39, 517 (1947).

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