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THE VAPOR PRESSURE AND ENTHALPY OF VAPORIZATION OF M-XYLENE

Abstract — We measured the vapor pressure of *m*-xylene over the temperature range 273 to 293°K with a single-sided capacitance manometer. The enthalpy of vaporization was 42.2 ± 0.1 (SE) kJ/g•mol. Combining our own data with previously published data, we recommend using the values 42.0, 40.6, and 39.1 (± 0.1) (SE) kJ/g•mol for the enthalpy of vaporization of *m*-xylene at 300, 340, and 380°K, respectively, and a value for the change in heat capacity on vaporization (ΔC_p°) of 35 ± 3 (SE) J/g•mol•K over the temperature range studied.

PRINCIPAL INVESTIGATORS

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Xylenes are used in the manufacture of resins and plastics, as diluents or solvents in surface coating, printing, and rubber manufacture,¹ and as an aviation fuel component.² Xylene is generally transported in bulk, which leads to the possibility of accidental exposure due to the rupture of solvent tanks in transit. Vapor pressures of organic compounds such as xylene are of interest to toxicologists for estimating inhalation exposure to vapor after accidental solvent spills. When heats of vaporization and of combustion are also known, the fire hazard from a solvent spill may be modeled.

Forziati *et al.*³ measured saturation vapor pressures (P°) of sixty purified hydrocarbons over the pressure range 48 to 780 torr and the temperature range 60°C to 140°C. We measured P° values from 0°C to 20°C using a more sensitive pressure gauge than that employed by Forziati *et al.*³ We noted the expected decrease in the heat of vaporization (ΔH°) with increase in temperature. This encouraged us to use the treatment suggested by Clarke and Glew⁴ for evaluating thermodynamic functions. We combined our own data with that of Forziati *et al.*³ to derive values for both ΔH° and ΔC_p° .

EXPERIMENTAL

We used a single-sided capacitance diaphragm manometer (type 315 HS, range 10^{-3} to 100 Torr, MKS Instruments, Inc.) to measure pressure. Purity of *m*-xylene (Eastman Kodak, Rochester, NY) was assessed using high performance liquid chromatography (HPLC), gas chromatography (GC), and mass spectroscopy (MS), and was determined to be greater than 99%. Identity was established by GC/MS (Hewlett Packard Model 5970). Only one GC peak was observed, which produced predominant mass spectral peaks 108 and 93.

The *m*-xylene sample was placed in a flask which was connected (Fig. 1) to a vacuum microbalance, pumping assembly and pressure gauge. The sample tube (Fig. 1) was cooled by a constant head reservoir, which was kept at constant temperature ($\pm 0.02^\circ\text{C}$) using a Lardner-Brinkman recirculating bath or an ice and water bath (0°C). Immediately prior to each measurement, the vacuum line was evacuated to 2×10^{-5} Torr.

After flushing the apparatus with *m*-xylene for 1 min, the butterfly valve to the pumping stack (Fig. 1) was closed. When liquid was seen condensing at the bottom of the cooled sample tube, the tap to the flask was closed. Three readings of the vapor pressure were taken at 5 min intervals

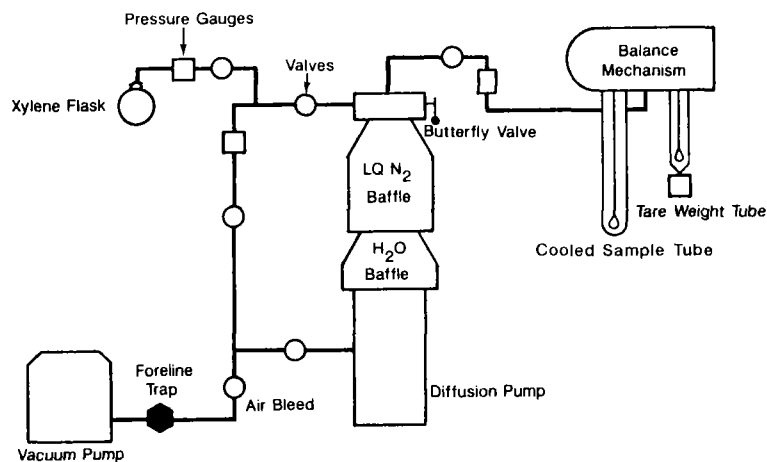


Figure 1. The apparatus (schematic) consisted of a vapor admission line from the m-xylene flask to a pumping stack and then to a cooled sample tube connected to a precision pressure gauge.

after the pressure stabilized. The water bath was then reset to a higher temperature and the next set of data obtained.

Data were evaluated using curve-fitting sub-routines available within RS/1 software.⁵ These sub-routines used standard statistical formulae to provide tables and graphs of residuals, and tables of analysis of variance, Student's t test and F values.

RESULTS

A good fit to the data ($r^2 > 0.999$) was obtained with the integrated Clausius-Clapeyron⁶ equation, which has the form:

$$\ln(P^\circ) = A + B/T, \quad (1)$$

where P° is the saturation vapor pressure, T is the temperature in K, and A and B are constants. The enthalpy of vaporization is RB where R is the gas constant, $8.3143 \text{ J/g}\cdot\text{mol}\cdot\text{K}$. Our data are compared to the data of Forziati *et al.*³ in Figure 2A; Figure 2B shows the residuals ($Y_{\text{observed}} - Y_{\text{predicted}}$) obtained from the curve fit. Residuals for the data of Forziati *et al.* show a marked trend, confirming their observation³ that the Clausius-Clapeyron equation did not provide the "best" description of their data. Enthalpies of vaporization derived from the values of B for different temperature ranges were $42.2 \pm 0.1 \text{ kJ/g}\cdot\text{mol}$ (0 to 20°C), $40.6 \pm 0.5 \text{ kJ/g}\cdot\text{mol}$ (60 to 90°C), and $38.5 \pm 0.1 \text{ kJ/g}\cdot\text{mol}$ (100 to 140°C).

A better fit was obtained when we employed the mathematical approach of Clarke and Glew,⁴ which was previously used by Jacobs *et al.*,⁷ for treatment of vapor pressure data. We employed the equation:⁶

$$R \ln(P^\circ) = A + B \left[\frac{x}{1+x} \right] - C \left(0.5 x^2 - \frac{2}{3} x^3 + \frac{3}{4} x^4 - \frac{4}{5} x^5 \dots \right), \quad (2)$$

where $x = (T - \Theta)/\Theta$; Θ is a temperature within the range of experimental data; T is the temperature of measurement (K); and A , B , C are constants. This gave a good fit to the data ($r^2 > 0.9999$), provided we chose Θ such that $x < 0.4$, and employed terms of up to x^4 in Equation 2.

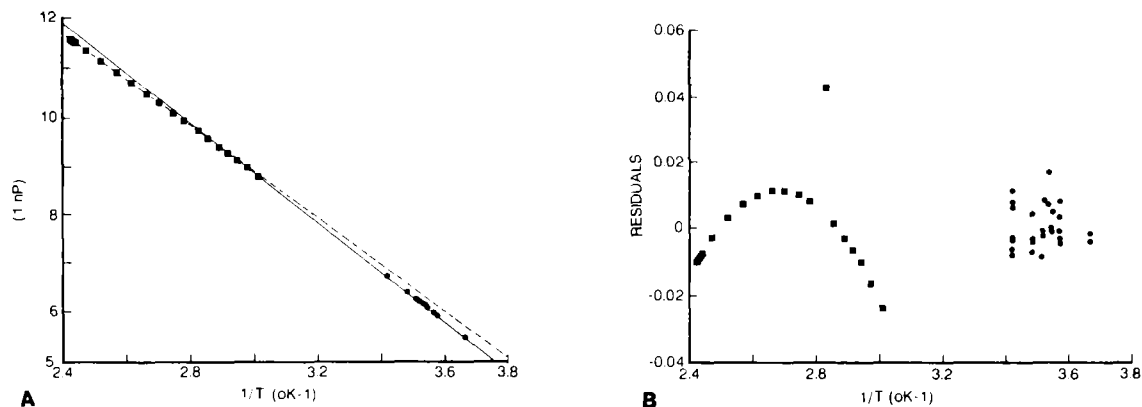


Figure 2 A. Variation of the vapor pressure of m-xylene with temperature and curves showing the best fit to the Clausius-Clapeyron equation ($\ln P^\circ = A - B/T$); — = $24.051 - 5.075 X$; - - - = $22.986 - 4.721 X$; ● = vapor pressure, this work; ■ = vapor pressure, Forziati *et al.* B. ● = residuals ($Y_{\text{observed}} - Y_{\text{predicted}}$), this work; ■ = residuals, Forziati *et al.*, which demonstrate a marked trend.

A plot of $\ln(P^\circ)$ against X for Θ of 340°K is shown in Figure 3A. Residuals obtained using only the first two terms in Equation 2 (i.e., $C = 0$) and residuals obtained using three adjustable constants ($A, B, C \neq 0$) are shown in Figure 3B. Similar plots were obtained with Θ values of 300 and 380°K . The residuals obtained (Fig. 3B) (●) when Equation 2 has only 2 adjustable constants show a marked systematic variation, but no such trend was observed for the best fit to the 3 parameter equation, suggesting that the fit was improved by using a third adjustable constant. This was confirmed by the method of Gallant,⁸ where the improvement was found significant at the 0.01 level of significance. Enthalpies of vaporization calculated from the values of B ($R\Theta$) and ΔC_p° values, which in turn are calculated from the values of C (RC), are tabulated in Table 1.

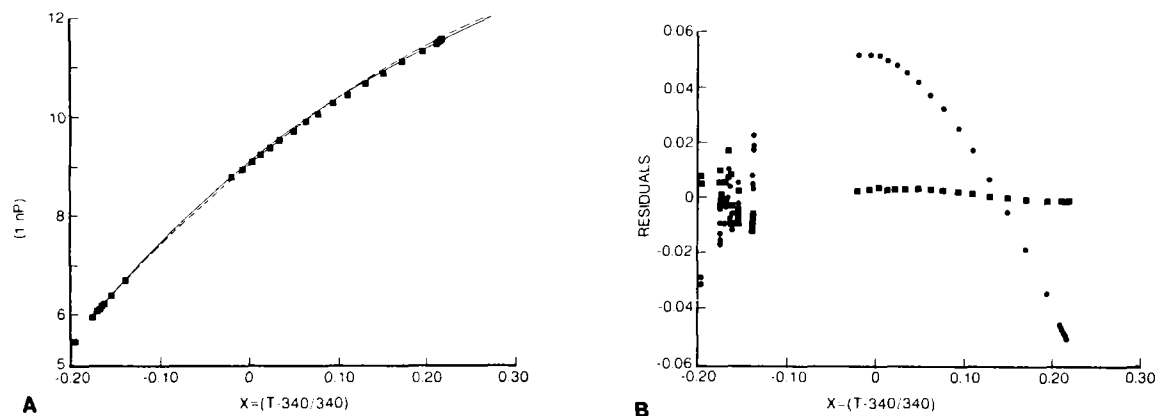


Figure 3 A. Curves showing the fit of the variation of the vapor pressure of m-xylene to the Clark and Glew equations with Θ of 340°K ; — = $9.09 + 14.36 [X/(1 + X)] - 4.32 (0.5 X^2 - 2/3 X^3 + 3/4 X^4)$; - - - = $9.04 + 14.47 (X/(1 + X))$; ■ = vapor pressure. B. ● = residuals, 2-constant equation, which demonstrates a marked trend; ■ = residuals, 3-constant equation.

DISCUSSION

The values of ΔH° obtained by simple Clausius-Clapeyron plots, which decrease from 42.2 to 38.5 $\text{kJ/g}\cdot\text{mol}$ over the temperature range studied, differ by less than 2% from the values obtained using the more sophisticated approach of Clarke and Glew.⁴ Nonetheless, the increase in F values,

Table 1
Thermodynamic Functions Calculated by Fitting the Vapor Pressure
Data to the Equation of Clarke and Glew (Equation 2)^a

Temperature (K)	ΔC_p° (J/g·mol·K)	Standard Error	Enthalpy of Vaporization (kJ/g·mol)	Standard Error
300	32.1	0.9	41.98	0.03
340	35.9	1.0	40.59	0.02
380	37.5	1.0	39.11	0.05

^a $\ln(P^\circ) = A + B [x/(1+x)] - C (0.5x^2 - 2/3x^3 + 3/4x^4)$,
Equation 2; where P° is saturation vapor pressure, and A, B
and C are constants.

Student's t values, r^2 values, and the change in appearance of the residual plots (Fig. 3B) give us confidence in the validity of using our data to derive the ΔC_p° values tabulated in Table 1.

Although we did observe a trend in ΔC_p° , it is in the opposite direction from that which we would have predicted on a thermodynamic basis, because the value must tend to zero at the critical point. We recommend a value of 35 ± 3 (SE) J/g·mol·K for ΔC_p° for m-xylene over the temperature range studied.

Vapor pressure values we obtained for temperatures of 0 to 20°C are a factor of two lower than values obtained by linear extrapolation of the data of Forziati *et al.*, confirming their warnings against such extrapolations.³ The slight curvature of Clausius-Clapeyron plots is a general property of most solvents, displayed for all sixty compounds studied by Forziati *et al.* Our findings for m-xylene are probably applicable to most organic solvents. Thus, estimates of exposure after solvent spills at room temperature derived from vapor pressure data obtained at higher temperatures are often excessive.

REFERENCES

1. Sandmeyer, E. E. Aromatic Hydrocarbons, in Patty's Industrial Hygiene and Toxicology (G. D. Clayton and F. E. Clayton, eds.), Vol. 2B, Interscience, New York, 1983.
2. Encyclopedia of Occupational Health and Safety. Third Edition, Vol. 2, International Labor Office, Geneva, 1983.
3. Forziati, A. F., W. R. Norris, and F. D. Rossini. Vapor Pressures and Boiling Points of Sixty API-NBS Hydrocarbons. J. Res. NBS 43: 555-563, 1949.
4. Clarke, E. C. W. and D. N. Glew. Evaluation of Thermodynamic Functions from Equilibrium Constants, Trans. Faraday Soc. 62: 539-547, 1966.
5. RS/1, Version 3.0. BBN Software Products Corporation, Cambridge, MA, 1988.
6. Clapeyron, E. Memoire sur la Puissance Motrice de la Chaleur, J. Ecole Polytech. 14(23): 153-190, 1834.
7. Jacobs, M. H. G., P. J. van Ekeren, and C. G. deKruif. The Vapor Pressure and Enthalpy of Sublimation of Ferrocene, J. Chem. Thermodynamics 15: 619-623, 1983.
8. Gallant, A. R. Non-Linear Regression, Am. Statistician 29(2): 73-81, 1975.