3. Vapor Pressure Data Representation by Polynomials and Equations

3.1 Numerical Methods

Regression of polynomials of various degrees. Linear regression of mathematical models with variable transformations. Nonlinear regression.

3.2 Concepts Utilized

Use of polynomials, a modified Clausius-Clapeyron equation, and the Antoine equation to model vapor pressure versus temperature data

3.3 Course Useage

Mathematical Methods, Thermodynamics.

3.4 Problem Statement

Table (2) presents data of vapor pressure versus temperature for benzene. Some design calculations

Table 2 Vapor Pressure of Benzene (Perry[3])

Temperature, T (^oC)	Pressure, P (mm Hg)
-36.7	1
-19.6	5
-11.5	10
-2.6	20
+7.6	40
15.4	60
26.1	100
42.2	200
60.6	400
80.1	760

require these data to be accurately correlated by various algebraic expressions which provide P in mmHg as a function of T in °C.

A simple polynomial is often used as an empirical modeling equation. This can be written in general form for this problem as

$$P = a_0 + a_1 T + a_2 T^2 + a_3 T^3 + \ldots + a_n T^n \tag{9}$$

where $a_0 \ldots a_n$ are the parameters (coefficients) to be determined by regression and n is the degree of the polynomial. Typically the degree of the polynomial is selected which gives the best data representation when using a least-squares objective function.

The Clausius-Clapeyron equation which is useful for the correlation of vapor pressure data is given by

$$\log(P) = A - \frac{B}{T + 273.15} \tag{10}$$

where P is the vapor pressure in mmHg and T is the temperature in °C. Note that the denominator is just the absolute temperature in K. Both A and B are the parameters of the equation which are typically determined by regression.

The Antoine equation which is widely used for the representation of vapor pressure data is given by

$$\log(P) = A - \frac{B}{T + C} \tag{11}$$

where typically P is the vapor pressure in mmHg and T is the temperature in °C. Note that this equation has parameters A, B, and C which must be determined by nonlinear regression as it is not possible to linearize this equation. The Antoine equation is equivalent to the Clausius-Clapeyron equation when $C = 273.15$.

(a) Regress the data with polynomials having the form of Equation (9). Determine the degree of polynomial which best represents the data.
(b) Regress the data using linear regression on Equation (10), the Clausius-Clapeyron equation.
(c) Regress the data using nonlinear regression on Equation (11), the Antoine equation.