represent the set of "N" experimental data points

$$Y_n, X_{1n}, X_{2n}, \ldots, X_{qn}, \ldots, X_{Qn} \tag{16}$$

where Y_n is the dependent variable for the nth data point and X_{qn} is the qth independent variable for the nth data point. The weighting factor is most usually described as the reciprocal of the variance

$$W = \frac{1}{\sigma_Y^2}, \tag{17}$$

which takes into account the variance of the dependent variable.

Since both the independent and dependent variables affect the final fit of the function to the data, the weight function for the nth data point is expressed as

$$W_n = \frac{1}{\sigma_{Y_n}^2 + \sum_{q=1}^{Q} \left(\frac{\partial f}{\partial x_{qn}} \sigma_{qn} \right)^2}. \tag{18}$$

Since P was chosen as the dependent variable in eq (14), Y becomes

$$Y = \ln P - EP. \tag{19}$$

To obtain σ_{Y_n} for eq (18) for the nth data point,

$$\sigma_{Y_n} = \frac{\partial Y}{\partial P_n} \sigma_{P_n} = \left(\frac{1}{P} - E \right) \sigma_{P_n}. \tag{20}$$

Also from eq (18) and the vapor pressure equation (14),

$$\sum_{q=1}^{Q} \left(\frac{\partial f}{\partial X_{qn}} \sigma_{qn} \right)^2 = \left(\frac{\partial f}{\partial T_n} \sigma_{T_n} \right)^2 \tag{21}$$

and

$$\frac{\partial f}{\partial T_n} = \frac{B}{T_n} + C - \frac{A}{T_n^2}. \tag{22}$$

If the experimental uncertainty of the nth data point for the qth variable, "ΔX_{qn}", corresponds to a 95 percent confidence interval on the observed X_{qn}, then the standard deviation "σ_{qn}" is related to ΔX_{qn} as

$$\sigma_{qn} = \tfrac{1}{2} \Delta X_{qn}. \tag{23}$$

The vapor pressure equation (14) is a function of pressure and temperature. Applying eq (23), gives

$$2\sigma_{T_n} = \Delta T_n \tag{24}$$

and

$$2\sigma_{P_n} = \Delta P_n. \tag{25}$$

Substituting the necessary expressions into (18), a weighting function for the nth data point is obtained:

$$W_n = \frac{4}{\left(\frac{B}{T_n} + C - \frac{A}{T_n^2} \right)^2 \Delta T_n^2 + \left(\frac{1}{P_n} - E \right)^2 \Delta P_n^2}. \tag{26}$$

Equation (26) was then used as the weighting function for all of the vapor pressure data except the data of Clark et al. [14]. The vapor pressure data of Clark consisted of several hundred observations. The method which Clark used was a comparison of the vapor pressure of argon with that of oxygen as determined by Hoge [21], and using the latter as a measure of the temperature. In this manner, the temperatures were measured with a mercury-in-glass manometer over most of the temperature range. At higher pressures, the temperature was measured with a copper-constantan thermocouple. Clark stated that the measurements were taken with a reproducibility of about 0.05 percent at low pressures. At higher pressures he found that the temperature control on his apparatus would not maintain the temperature constant with the same precision as at the lower temperatures, resulting in an uncertainty of about 0.2 percent in pressure for a given temperature.

Clark et al. [14] published a plot of deviation (from a fitted equation) in $\Delta \log P$ versus $\log P$. From this plot it appeared that there were about three to four times as many data points at low pressures than at pressures near the critical point. From the description of the experimental techniques used, the uncertainty limits, and the variable density distribution of Clark's data, an arbitrary modifying function was developed to modify the weighting function eq (26) for Clark's data. This function, as described by Gosman [22], is

$$M = \frac{1}{5 - \frac{375}{T}} - 0.28. \tag{27}$$

Since Clark's lower temperature range included more data points than the high temperature range, and since the temperature control on Clark's apparatus was less precise at the higher temperatures, the modifying function (27) was made to reflect the lower reliability at the higher temperatures.

Equation (27) was used to modify the variance of the fit, so that the weighting factor for Clark's data resulted in

$$W_c = \frac{1}{(\sigma/M)^2}. \tag{28}$$

Using eq (28), the final weighting expression for Clark's data is

$$W_c = WM^2, \tag{29}$$

where W is the general weighting function eq (26).

The nine vapor pressure data points of van Itterbeek, Verbeke, and Staes [9] were not used in the final determination of the vapor pressure equation. These nine points were omitted from the final evaluation because, within a year of the vapor pressure observations of van Itterbeek et al. [9], a new set of vapor pressure data was reported by van Itterbeek, de Boelpaep, Verbeke, Theeuwes, and Staes [16] which deviated considerably from the earlier data [9], but appeared to be more consistent with the vapor pressure observations from other sources.

The uncertainties in the vapor pressure data were estimated from the statements of the investigators, the description of the experimental procedures, the deviations between the different sets of data, and the apparent random deviations of each set of data.

The resulting uncertainties for all of the vapor pressure data were estimated to be

$$\frac{\Delta T}{T} = 0.00025$$

$$\frac{\Delta P}{P} = 0.00025. \tag{30}$$

Substituting eqs (30) into (26) and (29),

$$W = \frac{4 \times 10^8}{6.25 \left[\left(B + CT - \frac{A}{T} \right)^2 + (EP)^2 + 1 \right]} \tag{31}$$

and for Clark's data,

$$W_c = WM^2. \tag{32}$$

For each data point, the weighting functions (31) or (32) were substituted into the normal least-square equations as shown by Hust and McCarty [20].

In addition, it was considered desirable to make the vapor pressure equation (14) pass through the critical pressure and temperature so as to be consistent with the equation of state at the critical point. This required adding a constraining equation to the normal least-square equations so that the coefficients of the vapor pressure equation would satisfy the least-square criteria, as well as simultaneously constrain the vapor pressure equation to pass through the critical point. The generalized normal least-square equations with constraints are shown by Hust and McCarty [20] and Gosman [22].

A preliminary weighted-least-square fit with one constraint indicated that the low temperature data of van Itterbeek et al. [16] exhibited a scatter of about three to four times as great as the higher temperature data. Since low temperature vapor pressure data from other investigators were available, these low temperature data of van Itterbeek et al. [16] were omitted from the final fit.

The resulting fit of the vapor pressure equation (14) to the data is illustrated in figure 4, where the deviation between the temperature predicted by eq (14) and the experimental temperature is plotted as a function of pressure.

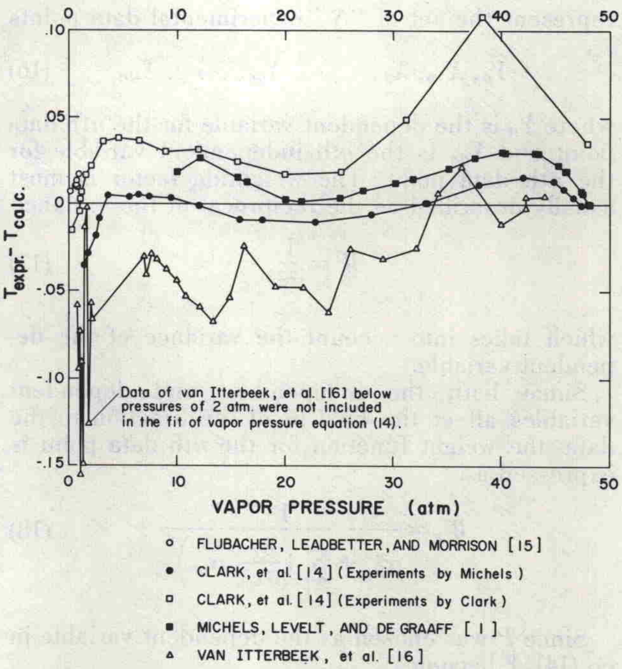

FIGURE 4. *Deviations of vapor pressure data from eq (14).*

In figure 4, it is seen that the characteristic shape of all five of the deviation curves is the same, except for the low temperature data of van Itterbeek et al. [16] (which was not included in the fitted data). From figure 4 it is also noted that the data of van Itterbeek et al. [16] exhibits a pattern of generally wider scatter at the higher temperatures when compared with the other data sources.

The similarity in the basic shape of the deviation curves of figure 4 may be interpreted to indicate a fundamental consistency between the selected vapor pressure data. The deviation curves also indicate the possibility of a disagreement in the temperature scales between the different data sources. This disagreement of temperature scales is inferred from the essentially constant shift or displacement between any one of the deviation curves and any of the others. This displacement of the deviation curves exists despite the fact that an effort was made to convert all of the temperature scales to a common thermodynamic temperature scale. An additional correction of less than 0.01 deg (see sec. 9) was made to the data of Clark et al. [14], since he stated that his data were based on an ice-point temperature of 273.16 K, whereas the other vapor pressure data sources were based on the ice-point temperature of 273.15 K.

From figure 4 it is seen that the maximum temperature deviation is 0.108 deg. This particular point is in the Clark et al. [14] set of data and may be questionable since it contributes a sharp spike in the deviation curve. For Clark's data, the mean of the absolute values of the temperature deviations is 0.0290 deg. If the single questionable data point is omitted, the mean deviation of Clark's data is 0.0240 deg. For the data of Flubacher et al. [15],