AN ESTIMATE OF ABSOLUTE ZERO — A PHYSICAL CHEMISTRY EXPERIMENT WITH AN INTRODUCTION TO A STATISTICAL TREATMENT OF DATA

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ABSTRACT.—An Experiment is described in which error estimates associated with extrapolated quantities may be made.

The *Chem Study Teachers Guide* [McLellan, 1963, p. 43] suggests that the development of predictive power is one of the rewards of scientic activity. These predictive powers are: repetition, interpolation, and extrapolation. The first of the Chem Study demonstrations is the development of a pressure-temperature relation and an extrapolation of the relation to $P=0$ for an estimate of absolute zero [McClellan, 1963, p. 125]. A further treatment of the data by statistical methods which would give an estimate of the errors associated with the pressure-temperature relation would provide a suitable introduction to a method of estimating errors. Error estimates of quantities obtained from other physical chemistry experiments such as rate constants from slopes or activities from extrapolated EMF measurements may then be made.

The most frequently encountered statistical treatment of data is that of regression analysis [Hald, 1952, p. 522], that is, an analysis which is used to determine the association between two variables in an experiment where one of the variables has little or no error associated with it and whose values are pre-determined when the experiments are planned. Such an estimate of a line on which the data may lie may be obtained by the method of least squares. This is a method of estimating the equation for a line that minimizes the sum of the squares of the deviations from the estimate. Such an estimate is called a regression line. If few observations are taken it may be desirable to associate a certain degree of confidence with an estimate of any error calculated by a least squares method. This degree of confidence may be called a Confidence Limit. Confidence Limits are somewhat arbitrary, but approximately indicate how sure we are that a true value of an observation lies within an indicated range of error. The true value here refers to a statistical value not to an absolute value. Generally, Confidence Limits are tabulated in terms of a probability P and as a function of a distribution called t which is associated with a certain number of degrees of freedom, f, for the observations. The values of t are related to a known error distribution and are used to aid in error estimates.

The equation for the pressure-temperature relation in the demonstration may be approximated by the equation for a straight line since the pressure-temperature changes are obtained at constant volume. Recall that the equation for a straight line through two given points (x_1, y_1) and (x_2, y_2) is:

$$(y-y_1)/(x-x_1) = (y_2-y_1)/(x_2-x_1) \quad (1)$$

rearrangement yields

$$y = y_1 + [(y_2-y_1)/(x_2-x_1)]\,(x-x_1) \quad (2)$$

The quantity $(y_2-y_1)/(x_2-x_1)$ corresponds to the slope called b. The symbol P will represent the pressure (the dependent variable) and the symbol T the temperature (the independent variable).

A suitable experiment may proceed as follows:

A. The pressure is recorded at two accurately known temperatures. The equation for the straight line through the data points is written and the intercept calculated for the case $P=0$.

B. The error associated with the pressure-temperature relation is derived by a regression analysis. An error range for the intercept is estimated.

C. The pressure is recorded at a few more accurately known temperatures. A regression analysis is performed, the intercept calculated and an estimate of the range of the intercept for a given set of Confidence Limits is made.

D. Several pressure readings at each accurately known temperature are made and a regression analysis performed as in C.

The temperatures suggested are: near the boiling point of water, room-temperature, an ice-water slush, and a Dry-Ice isopropanol slush. A suitable apparatus is available from Welch Scientific Company, Skokie, Illinois. Typical data and the results of the regression analysis are tabulated in Table 1. An expanded form of Table 1 which includes all pertinent equations and calculations for the data tabulated is available from the author upon request.

It should be pointed out that a statistical treatment of data only gives error information within the range of the observations. Although the apparent error for the intercept decreases with an increase in the total number of observations, reasonably accurate values of quantities desired from extrapolation are often not obtained. The experiment illustrates this point since outside the range of observations the proposed model (the straight line in our case) fails.

This experiment illustrates the advantage of accumulating as many observations as possible and also the hazard associated with extrapolation.

Literature Cited

McClellan, A. L., Ed. 1963. Teachers Guide for Chemistry An Experimental Science. W. H. Freeman and Company, San Francisco. 785 pp.

Hald, A. 1952. Statistical Theory with Engineering Applications. John Wiley and Sons, Inc., New York. 783 pp.

Hald, A. 1952. Statistical Tables and Formulas. John Wiley and Sons, Inc. 97 pp.

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TABLE 1.—Estimate of absolute zero and associated error estimates

A. Two observations. The equation for a straight line, $y = y_1 + [(y_2 - y_1)/(x_2 - x_1)](x - x_1)$, is used to calculate the intercept when the pressure is zero.

Typical Data:

Temperature, °C	Pressure
$T_1 = 95.0$	$P_1 = 18.5$
$T_2 = -78.5$	$P_2 = 9.5$

$$P = 18.5 + [(9.0)/(173.5)](T - 95.0)$$

$$P = 18.5 + 5.187 \times 10^{-2} (T - 95.0)$$

When P is zero, $T_0 = -262°C$

B. The pressure is assumed to have an error and a regression analysis is performed for the two data points. Since two points determine a linear function, there is no statistically calculable error in the equation or intercept.

An estimate of absolute zero based on the data in A together with an estimate of the derived error is $-262°C \pm 0$

C. Four sets of observations, one observation within each set.

D. Four sets of observations, sixteen total observations.

Symbol				
Temperature T	95.0	25.0	00.0	−78.5
Pressure P	18.5	15.0	13.5	9.5

(C)

$$P = 14.125 + 5.2046 \times 10^{-2} (T - 10.375)$$

The intercept at $P = 0$ together an estimate of the error (at 95% confidence limits) is:

$$T_0 = -261°C \pm 14$$

Regression analysis yields the equations for the pressure.

(D)

95.0	25.0	00.0	−78.5
18.4	14.9	13.4	9.4
18.5	15.0	13.5	9.4
18.6	15.1	13.5	9.5
		13.5	9.6
		13.6	9.6

$$P = 13.469 + 5.2039 \times 10^{-2} (T + 2.0312)$$

The intercept at $P = 0$ together with an estimate of the error (at 95% confidence limits) is:

$$T_0 = -261°C \pm 4$$