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Letters

Plotting Titration Data

The method of plotting titration data suggested by B. H. J. Hofstee [*Science* **131**, 39 (1960)] is open to question because the value of one of the variables appears in both the ordinate and abscissa. The suggested form of his Eq. 1,

$$P = (XY) + K(XY)/(Y) \quad (1)$$

does not separate the two variables. A preferable way to plot the data would be

$$1/(XY) = 1/P + (K/P)/(Y) \quad (2)$$

Thus a plot of $1/(XY)$ versus $1/(Y)$ gives a slope of (K/P) and intercept of $1/P$.

This method of plotting is used in the treatment of closed-chamber data on gun propellants. In that case the maximum pressure P_m is related to the density of loading Δ , the force λ , and the covolume η , by the relation

$$P_m = \Delta\lambda / (1 - \eta\Delta) \quad (3)$$

Observed values of P_m obtained through varying Δ are easily treated by rearranging Eq. 3 to give

$$1/\Delta = \lambda/P + \eta \quad (4)$$

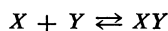
so that a plot of $1/\Delta$ versus $1/P$ gives a slope λ and intercept η .

One effect of graphs that contain one of the variables in both ordinate and abscissa is to give a smoothing effect that conceals real variability which may exist. The case of nonlinear relations plotted on logarithmic paper is even more important, since the combining of variables may suggest exponents of the terms that are different from those found when the variables are properly separated.

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Wiegand's Eq. 2 is one of the three possible linear nonlogarithmic equations for the graphical determination of the kinetic constants of a reaction of the type



whereby X is titrated with Y . The three forms were first proposed (but not published) by Woolf (see 1) for the estimation of the maximal rate and the Michaelis constant of an enzymic reaction. The plot of $1/(XY)$ versus $1/(Y)$ was first applied to actual cases by Lineweaver and Burk (2).

The latter procedure, like the one in which (Y) is plotted versus $(Y)/(XY)$, has the disadvantage that it overemphasizes experimental points on one side of the curve at the cost of those on the other side and thus tends to produce a lopsided stretching that obscures experimental errors and deviations from theory (3-5). Furthermore, it does not allow the summation of the curves of simultaneous reactions involving Y (4, 6).

The (XY) versus $(XY)/(Y)$ plot, not inverted with respect to (XY) , does not have these disadvantages. Like the semilogarithmic plot of (XY) versus pY , it is symmetrical with respect to the "halfway point" corresponding to K . It allows all the data between $(Y) \rightarrow 0$ and $(Y) \rightarrow \infty$ to be plotted on a finite scale between the two limiting values $P = (X) + (XY)$ and P/K that are given by the intercepts with the co-ordinates. The noninverted plot also demonstrates more clearly whether the data justify such extrapolation.

The fact that the two variables are not separated on the co-ordinates does not detract from the value of the plot, at least not when (Y) is known accurately, as, for instance, in the case of hydrogen ion concentration in acid base titrations and the substrate concentration in isolated enzyme systems, for which the plot has been recommended. In such cases the experimental points may be placed on pre-established lines through the origin corresponding to the various values of (Y) . Errors in the measurement of (XY) simply displace the experimental points along such lines, which, in fact, represent a separate scale for (Y) . The points can be expected to lie in a zone that, in contrast to the case of the $1/(X)$ versus $1/(XY)$ plot, runs parallel to the theoretical curve (5).

In cases where the error in the measurement of both (Y) and (XY) must be considered, it would indeed be more convenient to have the two variables separated on the co-ordinates. However, on account of the drawbacks of the $1/(Y)$ versus $1/(XY)$ plot discussed above, it would seem preferable in these cases also to apply the non-inverted plot and to use the lines through the origin to separate the variables for the purpose of weighting of data.

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References and Notes

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