[CONTRIBUTION FROM THE CHEMICAL LABORATORY, NORTHWESTERN UNIVERSITY]

A SIMPLIFIED METHOD OF CALCULATING TANGENTS BY THE THEORY OF LEAST SQUARES[1]

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It is frequently necessary to evaluate the tangent to a curve based on experimental measurements. When the data can be represented with sufficient accuracy by a second degree equation $y = c + ax + bx^2$, and the y-axis is made to pass through the point at which the tangent is required

$$(dy/dx)_{x=0} = a \qquad (1)$$

Provided the error in the independent variable is negligible in comparison with that in the dependent, a can be determined by the method of *least squares*. The sum of the squares of the deviations of n equally reliable observations becomes a minimum if the partial derivatives of $\Sigma_n^n = {}_1^n$ $(c + ax + bx^2 - y)^2$ with respect to a, b and c are set equal to 0.[2]

Solving the resulting *normal equations* in the convenient determinant form[3] gives

$$a = \begin{vmatrix} n & \Sigma y & \Sigma x^2 \\ \Sigma x & \Sigma xy & \Sigma x^3 \\ \Sigma x^2 & \Sigma x^2 y & \Sigma x^4 \end{vmatrix} \div \begin{vmatrix} n & \Sigma x & \Sigma x^2 \\ \Sigma x & \Sigma x^2 & \Sigma x^3 \\ \Sigma x^2 & \Sigma x^3 & \Sigma x^4 \end{vmatrix} \qquad (2)$$

If now the values of x are taken at *equal intervals on either side*[4] of the y-axis, Σx and Σx^3 vanish and

$$\left(\frac{dy}{dx}\right)_{x=0} = a = \frac{n\Sigma xy \Sigma x^4 - \Sigma x^2 \Sigma x^2 \Sigma xy}{n\Sigma x^2 \Sigma x^4 - \Sigma x^2 \Sigma x^2 \Sigma x^2} = \frac{\Sigma xy}{\Sigma x^2} \qquad (3)$$

The restriction to equal intervals does not seriously limit the applicability of the method. Data are usually tabulated at equal intervals and experimental results can easily be obtained thus if subsequent reduction is required.

The simplicity of the method is illustrated in Table I, which gives all the work required to calculate ten values of the coefficient of thermal expansion of sodium chloride solutions from the density at five different temperatures.[5] For convenience, the independent variable is made $x = (t - 25)/5$ and the dependent variable $y = 10^4(D_{10} - Dt)$. Then $y = 0$ when $x = -3$, which further simplifies the summation. By definition

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[1] Paper presented before the Buffalo meeting of the American Chemical Society, August 31–September 3, 1931.

[2] *Cf.* Mellor, "Higher Mathematics for Students of Chemistry and Physics," Longmans, Green and Co., 1929, p. 326, for the method applied to the linear equation.

[3] *Ibid.*, p. 584.

[4] Harry M. Roeser, in Scientific Paper No. 388 of the Bureau of Standards, has shown the great advantage of taking observations at equal intervals of the independent variable and gives useful tables for rapid calculation of *all* the coefficients.

[5] "International Critical Tables," Vol. III, p. 79.

$$\alpha = (1/V)\,(\partial V/\partial T)_P = -(1/D)\,(\partial D/\partial T)_P \tag{4}$$

Since $-(\mathrm{d}D/\mathrm{d}t) = 2 \times 10^{-5}\,(\mathrm{d}y/\mathrm{d}x)$ and $\Sigma x^2 = 20$, combination with (3) and (4) gives

$$10^4\alpha = \Sigma xy/100D \tag{5}$$

The whole process of calculating α then consists simply in multiplying each of the three tabulated values of y by the corresponding value of x, adding them together and dividing by 100 times the density.
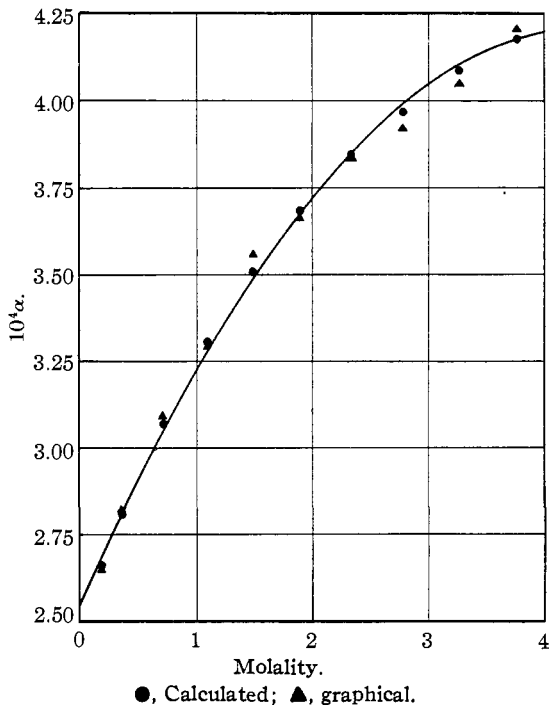

●, Calculated; ▲, graphical.

Fig. 1.—Coefficients of expansion of sodium chloride solutions at 25°.

Graphical values of α, read off the D–t curve by laying a ruler tangent at 25°, are included for comparison. The analytical method is actually more rapid than the graphical. It is also free from the personal bias of judging tangents and gives more concordant results. The average deviations of the graphical values of α from the curve are nearly three times those of the calculated values. This is shown by Fig. 1, where the values of α for sodium chloride solutions at 25° are plotted against concentration. The difference might be greater still if the density data in the tables had not already been smoothed so that the graphical curves can be fitted exactly to the points.

TABLE I

DATA AND CALCULATED VALUES

Wt. % of NaCl	$t..$ 10 $x..$ −3	20 −1	30 1	40 3	Σxy	d_{25}	$-\alpha \times 10^4-$ Calcd.	Graph.
		y						
1	0.0	17.3	44.6	79.9	267.0	1.0041	2.659	2.64
2	.0	19.6	48.5	84.9	283.6	1.0111	2.805	2.82
4	.0	24.0	55.9	94.3	314.8	1.0253	3.070	3.09
6	.0	28.1	62.7	103.0	343.6	1.0396	3.305	3.34
8	.0	31.8	68.8	110.9	369.7	1.0541	3.507	3.56
10	.0	35.1	74.3	118.1	393.5	1.0688	3.682	3.66
12	.0	38.0	79.3	124.7	415.4	1.0837	3.833	3.83
14	.0	40.6	84.0	130.9	436.1	1.0987	3.969	3.92
16	.0	43.5	88.5	136.8	455.4	1.1140	4.088	4.05
18	.0	45.3	92.8	142.5	475.0	1.1295	4.205	4.18

Average deviation from curve ±0.018 ±0.05

Summary

In conclusion, a simplified method of calculating tangents from the theory of least squares has been presented. By choosing equally spaced positive and negative values of the independent variable and making the y-axis pass through the point at which the tangent is desired, $dy/dx = \Sigma xy/\Sigma x^2$. Tangents may thus be calculated more rapidly and precisely than by graphical means. The method may be applied in many other cases beside that used as an illustration.

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THE COLLISION AREAS AND SHAPES OF CARBON CHAIN MOLECULES IN THE GASEOUS STATE: NORMAL-HEPTANE, NORMAL-OCTANE, NORMAL-NONANE

BY RALPH M. MELAVEN AND EDWARD MACK, JR.

In a chapter on "The Effects of Molecular Dissymmetry on Properties of Matter," Langmuir presents[1] plausible reasons, based on surface energy considerations, for believing that a molecule such as palmitic acid, when isolated in the gas phase or in solution, has its carbon chain coiled up into an approximately spherical form rather than fully extended as a straight chain. Du Noüy concludes that the chain of the giant protein molecules is, in certain situations, folded up[2] into a parallelepiped or prism-like form, and Hauser[3] recently interprets the x-ray diffraction patterns, obtained when rubber is stretched and unstretched, as meaning that the

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[1] Alexander, "Colloid Chemistry," The Chemical Catalog Co., New York, 1926, Vol. I, pp. 525–546.

[2] Du Noüy, *J. Biol. Chem.*, **64**, 595 (1925).

[3] Hauser, *Ind. Eng. Chem.*, **21**, 249 (1929).