

Letters

Soviet Scientific Publications

The member organizations of the National Federation of Science Abstracting and Indexing Services are very pleased that through the excellent and informative editorial "In perspective" [*Science* 130, 7 (1959)], the attention of the entire scientific community has been drawn to the improvements in the communication of science information that have been brought about during the past 18 months. However, lest some readers ascribe to Russia more scientific diligence and industry than is justified, I should like to correct one point.

My estimates of the annual abstract and citation coverage by abstracting and indexing services in the United States and Russia referred to the scientific and technical publications of the entire world, not the publications of the Soviet Union alone. The total annual Soviet output of such literature probably represents about 10 percent of the world's total; certainly it is no more than 15 percent.

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Titration Curves

The report "Linear titration curves of acids and bases," by N. R. Joseph [*Science* 129, 1493 (1959)] calls for comment. A transformation is proposed consisting of the substitution of the operator p for the operator " $-\log$ " in the standard Henderson-Hasselbalch equation. The resulting straight-line plot, $pA-pB$ against pH , does not differ except in labeling of the axes from a plot of $\log B/A$ against pH . This plot has undoubtedly been used often to show roughly the goodness of fit of an experimental set of points on a titration curve of a monovalent acid, or of polyvalent acids with widely separated proton donor groups. The transformation per se does not avoid the use of a logarithm table, for how else can one obtain the p values? If semilogarithmic graph paper is used, it is the logarithmic scale which makes a logarithm table unnecessary, not the "transformation." When such a graph is used, division is needed to obtain A/B instead of the subtraction of the two logarithms that is necessary when regular grids are used.

In the particular illustrative example used, four reactions involving H^+ are stated and "four transformed mass action law equations" are given. It is apparent that $A_2=B_1$, $A_3=B_2$, and $A_4=$

B_3 . The author's statement that his Fig. 1 "clearly indicates the distribution of electrical charge over the molecule as a function of pH " is misleading, because of the failure to make these identifications (1). The figure indicates that the four mass action law equations are independently solvable when in fact they are simultaneous equations and only if the pK 's are far apart is it possible to make the necessary approximations to solve them independently. The lines given end arbitrarily at $pA-pB=\pm 2$ and give a discontinuous appearance to what is in fact a smooth continuous titration with only a slight "break" between the third and fourth group as given in the original paper (2).

A very important feature of traditional titration curves is lost in Joseph's transformation." It is difficult or impossible to "add" the segments of titration for the four pK 's in the transformation, whereas this is a simple matter with traditional plots. Thus, it is awkward to obtain a valid comparison between experimental and constructed curves in the form used by Joseph for any polyvalent acid when the groups are not widely separated.

The usefulness of the d'Ocagne nomogram proposed is not apparent. Most people would find it easier and more accurate to do the simple subtraction necessary to determine the difference between pH and pK rather than to use the nomogram. The same is true for the other possible combinations for which the nomogram might be used. D'Ocagne nomograms are useful when relationships are complex, but not when the arithmetical relations are as simple as the one demonstrated.

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References and Notes

1. J. T. Edsall and J. Wyman, Jr., [*Biophysical Chemistry* (Academic Press, New York, 1958), vol. 1, chap. 9] point out that for each charge type there are a number of "microscopically different species" differing in the location of the charge(s) but not in net charge. Thus, in the example used by Joseph there are four microspecies included in $A_2(B_1)$, six in $A_3(B_2)$, and four in $A_4(B_3)$. This important aspect of distribution of charges on a molecule is neglected here, as it was by Joseph.
2. J. P. Greenstein and N. R. Joseph, *J. Biol. Chem.* 110, 619 (1935).

In his letter Levy has criticized some of the procedures and results described in my recent report. The questions raised are of two kinds, mathematical and chemical, and will be discussed in that order.

A glance at the earlier report [*Science* 128, 1207 (1958)] would have shown Levy that the symbols pA and pB were used to explain the construction and op-

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eration of a semilogarithmic pH calculator. This yields the term $(pA - pB)$ in place of the usual $\log B/A$; in all subsequent equations or graphs the terms may be used interchangeably. The usage was retained in the second report in formulating two nomograms for glycyl aminotricarballylic acid. If the pH range of the straight lines of Fig. 1 be extended beyond four pH units, the apparent discontinuities noted by Levy do not appear. When, as in the d'Ocagne nomogram (Fig. 2), the pH scale runs from 2 to 10, no breaks occur.

The physicochemical questions concern the number of ionic species required for a given polyelectrolyte. Since each titratable group involves two forms, a proton-donor A and an acceptor B , the number of mathematically possible species s is 2^n , where n is the number of titratable groups and pK 's. For glycyl aminotricarballylic acid, n is 4 and s is 16. When n is 10, s is 1024; when n is 20, s exceeds 10^6 . Proteins may contain 100 or more titratable groups; when n is 100, s is about 10^{30} . This is more than 10^6 moles; if a molecular weight of 10^5 is assumed, the weight is about 10^8 kilograms. Obviously, only an infinitesimal fraction of the mathematically possible species can or should be considered.

The number of equations necessary to

represent a complex polyelectrolyte is much nearer to n than to s . For glycine, n is 2 and s is 4. One of these is the uncharged neutral molecule present to the extent of about one molecule in 10^8 . The curve requires two equations, relating three ionic species. When n is 4, s is 16. If these are tabulated for glycyl aminotricarballylic acid, 8 or 10 of the 16 forms are found to be of very low probable occurrence, as for example the uncharged neutral molecule. The curve may be described by four pK values relating five ionic species. For higher values of n , s becomes successively 32, 64, 128, and so on. For most purposes the distribution of charge is given by n equations and pK values, relating $(n+1)$ ionic species. A generalized nomogram is derived on this basis.

Levy, apparently well content with algebraic formulations, considers nomograms superfluous. Others, seeking elegance, find nomograms useful and rewarding. In a system containing several polyelectrolytes, algebraic formulations and curvilinear diagrams become inadequate. In biological systems there are large numbers of simultaneous reactions involving not only hydrogen ions but also other cations and anions. There are also numerous oxidation-reduction reactions which depend on pH . Algebraic

formulations consist of numerous simultaneous equations. When the number exceeds five or ten, it is difficult for one not using visual aids to coordinate all the simultaneous processes. Geometrical transformation to curved polydimensional surfaces is difficult and does little to clarify the relations. Formulation of the equations as straight lines and construction of nomograms go far toward simplifying these problems. This is a well-established procedure in many branches of science. At certain levels of complexity two-dimensional linear nomograms become preferable not only to algebraic formulations but also to curved polydimensional surfaces or their projections.

I find no statement in either of my reports asserting nonexistent advantages over standard methods. In the second, the entire emphasis was placed on the construction of a simple linear d'Ocagne nomogram illustrative of general methods for complex problems. By these methods diagrams based on three rectangular coordinates are easily transformed to nomograms with three or more parallel coordinates.

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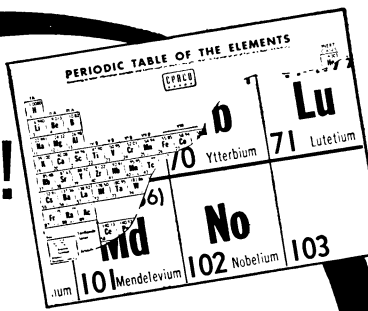


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