39. A New Analytical Formula for Hill's Equation

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The oxygen equilibrium of myoglobin[1] accords completely with the mass action considerations for the reaction, $Mb+O_2=MbO_2$, i.e., if we plot the percentage oxygenation against the partial pressure of oxygen we obtain the theoretical rectangular hyperbola. Whereas in the case of vertebrate hemoglobin, of which that from mammals has been chiefly studied, and other respiratory pigments such as hemerythrin[2], the curve is sigmoid in shape and can be described with a fair degree of accuracy by Hill's empirical equation[3],

$$Y=\frac{Kp^n}{1+Kp^n}. \tag{1}$$

Here Y denotes the partial degree of saturation with oxygen, p the partial pressure of the gas in equilibrium with the solution of the respiratory pigment. K is a constant characteristic to the individual respiratory pigment and depends upon the affinity of the pigment for oxygen. Another constant n expresses to a certain extent the facilitating interaction between the oxygen-combining centers. By this we mean that when an oxygen molecule combines with one center it increases the likelihood that a second oxygen will be attracted to another. When $n=1$ the formula (1) reduced to a formula to be represented by a rectangular hyperbola signifying no appreciable facilitating interaction. Usually n is greater than unity as, for example, in purified horse hemoglobin, for which $n=2.8.$[4]

From the experimental point of view, it is reasonable to plot Y against $\log p$ instead of against the pressure itself, since the percentage error $\delta p/p$ rather than the absolute error δp is nearly uniform over the whole pressure range. In fact many workers[5] prefer $\log p$ to p as the abscissa, though the corresponding analytical formula has not been given as yet. The present writer wishes to propose a new analytical formula which is mathematically equivalent to the equation (1) and meets this experimental requirements. Namely,

$$Y=\frac{1}{2}+\frac{1}{2}\tanh\left(\frac{n}{2}\ln\frac{p}{p_{1/2}}\right), \tag{2}$$

where $p_{1/2}$ is the partial pressure of oxygen in equilibrium with the solution in which the amount of oxygenated hemoglobin is just the same as that of the deoxygenated form. The equation (2) follows a hyperbolic tangent curve, irrespective of the value of n. Hence any