EXPERIMENTAL ERRORS IN DERIVED THERMODYNAMIC CONSTANTS

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EXPERIMENTAL ERRORS IN DERIVED THERMODYNAMIC CONSTANTS

C. R. Frink and P. E. Waggoner

Experimental determination of thermodynamic equilibrium constants is a popular and powerful technique of soil chemistry. The applicability of a particular theory is generally established by demonstrating that the constant in the mathematical statement of the theory is invariant over a wide range of conditions. Even when the theory applies, however, the estimates of the constant will vary because the observations from which they are derived are inexact. Thus, a statistical test is required to determine whether the variability in the estimates of the derived constant exceeds the error inherent in their measurement.

The usual analysis of variance (12) would be a satisfactory test, provided that the necessary replicate chemical determinations were made. Unfortunately, chemists rarely provide such data, owing either to an aversion towards extra work or towards statistics. However, many procedures have been in use so long that an estimate of their precision can be taken as the precision of the entire population of determinations by these methods (12). Thus, we feel justified in estimating the precision of routine chemical analyses from experience. Now we inquire how we may use these estimates to predict the variability expected in a derived constant from a knowledge of the variability of its several constituent measurements.

Kolthoff and Sandell (9) have summarized earlier work (1) and discuss the errors expected in derived results. If the result, e.g. a constant, is calculated as a sum or difference of its constituent measurements, its variance is the sum of the variances of the individual measurements. If the result is a product or quotient, its squared coefficient of variation is the sum of the squared coefficients of variation of the individual measurements. Similar procedures are used in separating sampling from analytical errors (12). While these methods seem satisfactory for many purposes, they do not indicate clearly how sums containing various coefficients are treated, nor do they describe products with exponential terms. A more serious defect is the neglect of cases where two or more variables are correlated. In this case, a correction term containing the correlation coefficient must be introduced (11).

Recently, Ku (10) has treated the problem of propagation of errors in a more systematic fashion. He utilized a theorem which relates the variance of a function f(x,y) to the first and second partial derivatives with respect to the arguments x and y, as well as to the variance and covariance of x and y. For simple functions where the partial derivatives may be written explicitly, his approach is more elegant; however, this is not always the case in the functions we shall encounter. In some instances, the partial derivatives could be evaluated graphically. In general, however, the approach we propose below seems more suitable for the functions likely to be encountered in chemical equilibria.

Thus, we shall apply these concepts to an evaluation of the errors to be expected in derived thermodynamic constants and then compare our predicted errors with those observed in experimental data. Different ways of reading this bulletin are suggested for different purposes. Logically, THEORY and COMPUTATIONAL AIDS precede APPLICATIONS, and this is the order that follows. Many may wish, however, first to see the usefulness of the methods in testing the constancy of the equilibrium constant in a specific chemical reaction. They should go to APPLICATIONS first and return to THEORY and AIDS as needed.

Theory

Inasmuch as indicated products or quotients in equilibrium constants can easily be expressed as linear functions of logarithmic terms, we need only develop an equation for the variance of a sum of variates. Following Weatherburn (11), we let u_i be a linear function of the variates x_i, y_i, z_i . . . , with known constants a, b, c . . . either positive or negative:

$$u_i = ax_i + by_i + cz_i + \dots \qquad [1]$$

The expectation or limiting mean of u_i is related to the other variates thus:

$$E(u) = aE(x) + bE(y) + cE(z) + \dots \qquad [2]$$

From [1] and [2] we obtain by subtraction:

$$\delta u_i = a\delta x_i + b\delta y_i + c\delta z_i + \dots \qquad [3]$$

where δ indicates the deviations of the variates about their limiting means. If we recall that the variance of any of the variates, say x, is by definition:

$$\sigma_x^2 = E(\delta x)^2 \qquad [4]$$

and that the correlation coefficient between any two variates, say x and y, is:

$$\rho_{xy} = \frac{1}{\sigma_x \sigma_y} E(\delta x)(\delta y) \qquad [5]$$

we may find the desired formula from [3] by squaring both sides and taking expectations. The result is:

$$\sigma_u^2 = a^2\sigma_x^2 + b^2\sigma_y^2 + c^2\sigma_z^2 + 2ab\rho_{xy}\sigma_x\sigma_y + 2ac\rho_{xz}\sigma_x\sigma_z + 2bc\rho_{yz}\sigma_y\sigma_z \qquad [6]$$

Since u_i in [1] corresponds to –log K or pK in the usual logarithmic expression of equilibrium constants, the hypothesis to be tested is that u_i is constant. In other words we shall test whether the observed variance of u_i given by:

$$s_u^2 = \frac{1}{n-1} \sum_i (u_i - \bar{u})^2 \qquad [7]$$

exceeds the predicted variance σ_u^2 given by [6]. Since we are comparing an observed variance with a theoretical one, a chi-square test is appropriate for testing whether the quantity calculated by equation [7] is statistically greater than that given by [6].

At this point, we must recognize several complications in using equation [6]. First, the variates x_i, y_i, z_i . . . are usually not measured directly, but will be calculated from analytical determinations of the experimental variables R_i, S_i, T_i . . . . Further, the calculated variates may be non-linear functions of more than one experimental variable, so we define:

$$x_i = f(R_i, S_i, T_i) \qquad [8]$$

$$y_i = g(R_i, S_i, T_i) \qquad [9]$$

$$z_i = h(R_i, S_i, T_i) \qquad [10]$$

Thus, an experiment consists of measuring R_i, S_i, T_i . . . during some systematic manipulation of the experimental conditions, and then calculating u_i from equations [1] and [8] to [10]. More specifically, u_i would be a pK_i, while x_i might be the concentration of Al^{+3} ions calculated from R_i, a pH measurement, and S_i, a measurement of total aluminum (6, 7).

Since we want to calculate the predicted variance from [6], we must be prepared to cope with the non-linearity of [8] to [10]. The consequence of this non-linearity, of course, is that the mean of x_i, for example, is not equivalent to $f(\bar{R}, \bar{S}, \bar{T})$. Furthermore, even though the experimental errors, which we will define as δR_i, δS_i, δT_i . . ., may be independent with zero expected means, the errors δx_i, δy_i, δz_i . . . are neither independent nor have zero expectations.

To examine the magnitude of the errors introduced by these assumptions, we may express [8] as:

$$x_i = f(\bar{R} + \delta R_i, \bar{S} + \delta S_i, \bar{T} + \delta T_i) \qquad [11]$$

Here we have chosen to use sample estimates, rather than population parameters, i.e. $\bar{R}$ rather than $E(R)$, since we have defined R_i, S_i, T_i . . . as the experimental observations. Expansion of the right-hand member of [11] by means of Taylor's series (cf. (2) for a similar treatment of sampling errors) leads to:

$$\begin{aligned} x_i = f(\bar{R}, \bar{S}, \bar{T}) &+ \delta R_i f'_R(x_i) + \tfrac{1}{2}\delta R_i^2 f''_R(x_i) + \ldots \\ &+ \delta S_i f'_S(x_i) + \tfrac{1}{2}\delta S_i^2 f''_S(x_i) + \ldots \\ &+ \delta T_i f'_T(x_i) + \tfrac{1}{2}\delta T_i^2 f''_T(x_i) + \ldots \qquad [12] \end{aligned}$$

We may obtain the expectation of [12] by summing over all values of i and dividing by N. It is evident that if the function is linear, the expectation of x_i is indeed $f(\bar{R}, \bar{S}, \bar{T})$. Furthermore, if the errors of observation δR_i, δS_i, δT_i . . . are small, or the departure from linearity is not great, we may approximate the expectation of x_i as $f(\bar{R}, \bar{S}, \bar{T})$. Similar considerations hold for [9] and [10]. In practice, we shall usually find that both of these criteria are met; if not, a graphical evaluation of [12] is probably the easiest approach.

The second complication in using equation [6] concerns the nature of the population from which our observations of u_1, u_2 . . . u_n are drawn. Equation [6], as derived, is applicable to repeated observations of R_i, S_i, T_i . . . and the subsequent calculation of u_i from x_i, y_i, z_i . . . for samples drawn from the same population. We wish to enquire, however, whether u_i is constant when the experimental conditions R_i, S_i, T_i . . . are varied in a deliberate fashion as by dilution or acidification. Thus, we have created several populations of samples, and consequently the means $\bar{R}$, $\bar{S}$, $\bar{T}$ . . . have little meaning since the bulk of the variation is nonrandom. In addition, since these samples are drawn from different populations, we cannot assume homogeneity of variance; in fact, we find from numerical calculations that the variance of x_i, y_i, z_i . . . depends on the values of R_i, S_i, T_i . . . .

Obviously, we need to compare values of u_i from different populations in order to provide a discriminating test of the constancy of pK over varying conditions. Thus, we must cope with the heterogeneous variance introduced. One solution is to calculate from [6] the estimated σ_u^2 for each u_1, u_2 . . . u_n determined. Then, these estimates of the variance may be weighted in the computation of chi-square as follows:

$$\chi^2 = \frac{(n-1)s_u^2}{\sigma_u^2} \cong \sum_i \left[\frac{(u_i - \bar{u})^2}{\sigma_u^2}\right] \qquad [13]$$

where it is understood that the variance σ_u^2 is taken at each value of i. We assume that this statistic is distributed approximately as chi-square with n − 1 degrees of freedom.

Finally, we must recognize one further complication in the use of equation [6], which requires that we distinguish carefully between errors of measurement which are correlated and those which are not. Normally, in chemical equilibria, a change in the concentration of one chemical species produces changes in the concentration of all other species; consequently, all the variates are correlated. Clearly, this is the case when replicate samples are prepared: an error in one variate will produce corresponding errors in the other variates. As a simple example, consider the preparation of three replicate solutions of KCl, either by weighing three portions of salt or by dilution of three aliquots of a standardized stock solution. In either case, the analyst is not likely to measure the resulting concentrations, but will calculate them from the known weight or dilution factors. Since errors in weighing or dilution are inevitable, he has thus introduced an error which we will call the sample error. If we now require the concentration of K^+ plus Cl^- ions in the solution, the variance of the sum will be given by equation [6]. Obviously, in this case, since the correlation coefficient between the calculated concentrations of the two ions is positive and equal to unity, and their individual variances are the same, the variance of the sum is four times the variance of the original error made in preparing the sample. At this point, it is well to note that this use of the term sampling error is quite specific and does not coincide with the usual usage: we are not concerned here with the ability of the analyst to obtain replicate sub-samples of a bulk shipment of muriate of potash in order to determine its KCl content.

Continuing with this example, suppose now that we wish to measure the K^+ and Cl^- concentrations in three replicate solutions. Since we cannot measure these variates precisely, we introduce additional uncertainties. However, unless one variate is calculated from measurements of another, as implied in [8] to [10], the uncertainties of observation are not correlated. For example, we might determine K^+ by flame photometry and Cl^- by titration with $AgNO_3$. Then the variance of the sum of the two observations would be merely the sum of the variances of the two independent analytical methods. Notice, however, that if we determined only the Cl^- content, and calculated the K^+ content by equating the two, the errors of observation would be correlated and the variance would increase accordingly.

Thus our definition of the deviations δR_i, δS_i, δT_i . . . and the corresponding δx_i, δy_i, δz_i . . . which specifies that they are measured about the observed means includes both of these error terms. We may redefine

$x_i = E(x) + \delta x_{oi} + \delta x_{si}$ or $R_i = \overline{R} + \delta R_{oi} + \delta R_{si}$ where s indicates the sample error and o the observational error. If we assume that there is no correlation between these two sources of error, the expected variance can be derived in the same fashion as equation [6]. The result for two variates is:

$$\sigma^2_{su} + \sigma^2_{ou} = a^2\sigma^2_{sx} + a^2\sigma^2_{ox} + b^2\sigma^2_{sy} + b^2\sigma^2_{oy} + 2ab\rho_s\sigma_{sx}\sigma_{sy} + 2ab\rho_o\sigma_{ox}\sigma_{oy} \qquad [14]$$

This equation is of course identical to [6] and merely indicates that the two variances are additive. Note that the additivity of the two components of variance is only true for single observations on single samples. Since replicate observations will reduce σ^2_o but not σ^2_s, while replicate samples will reduce the variance from both components (3), the variance of the mean of n observations of k samples is $(\sigma^2_o/n + \sigma^2_s)/k$. It appears simpler to retain our original definitions of δR_i, δS_i, δT_i . . . to include all deviations about the means and simply choose the proper correlation coefficients. Thus, we need to distinguish carefully between the variance expected for replicate observations of a single sample, or single observations of replicate samples. The variance expected for replicate observations may be estimated from our chemical experience (12). We may also estimate the errors in preparation of replicate samples from our knowledge of the errors of common laboratory operations. If other types of replication are involved, as in the determination of solubility products in replicate soil extracts, the greater variability inherent in soil samples could be estimated.

In summary, we have derived the necessary equation for the variance of a sum of variates and have explored the complications in its use: first, the calculated variates must be nearly linear functions of the experimental variables which in turn are measured with small error; second, the non-homogeneous variance from one population to another must be compensated for by the proposed weighted chi-square; and third, sampling and observational errors must be clearly distinguished.

Computational Aids

Before turning to the experimental examples, we must consider several computational aids. Data frequently are collected in both arithmetic and logarithmic units and confusion often arises over their inter-conversion. Furthermore, since many analytical errors are proportional to the amount taken for analysis, statistical practice (3, 12) calls for a transformation to logarithmic units to provide homogeneity of variance. We shall show that for all practical purposes, when the errors of observation are small, the required calculations of means and standard deviations may be made before or after inter-conversion from arithmetic to logarithmic units.

Let w_i be a measurement that has not been converted to logarithms and e_i be its relative error, $1 - w_i/\overline{w}$. Then we require the relationship between $\overline{\log w}$ and $\log \overline{w}$, and between $s^2_{\log w}$ and s^2_e Again, we prefer the notation for sample estimates, rather than population parameters E(log w) and log E(w). Use will be made of the series:

$$\log(k + e) = M \ln(k + e) = M\left\{\ln k + 2\left[\frac{e}{2k + e} + \frac{1}{3}\left(\frac{e}{2k + e}\right)^3 + \ldots\right]\right\} \qquad [15]$$

Since:

$$\overline{\log w} = \frac{\Sigma \log w_i}{n} = \frac{\Sigma \log(w_i/\overline{w})(\overline{w})}{n} = \log \overline{w} + \frac{1}{n}\Sigma \log \frac{w_i}{\overline{w}} \qquad [16]$$

we see that the last term in the right-hand member of [16] is the difference between the mean of the logarithms and the logarithm of the means. The error introduced by this term is evaluated by equation [15]. Since $w_i = \overline{w} + e_i\overline{w}$:

$$\log \frac{w_i}{\overline{w}} = \log \frac{\overline{w} + e_i\overline{w}}{\overline{w}} = \log(1 + e_i) \qquad [17]$$

If we expand [17] with [15] and realize k = 1, we see:

$$\frac{\Sigma \log(1 + e_i)}{n} = \frac{2M}{n}\sum\left[\frac{e_i}{2 + e_i} + \frac{1}{3}\left(\frac{e_i}{2 + e_i}\right)^3 + \ldots\right] \qquad [18]$$

In laboratory analyses of the sort considered here, a relative error e_i of 0.1 would be extremely large. Therefore, the goodness of approximation is conservatively evaluated by assuming half the e_i are—0.1 and half are 0.1. When e_i is 0.1, the cubic term in [18] is negligible and can be omitted, and:

$$\overline{\log w} - \log \overline{w} = \frac{2M}{n}\left[\frac{n}{2}\left(\frac{-0.1}{1.9}\right) + \frac{n}{2}\left(\frac{0.1}{2.1}\right)\right] = -0.002 \qquad [19]$$

Thus, we conclude that the mean of the logarithms is for all practical purposes equal to the logarithm of the means.

Now we consider the relationship between $s^2_{\log w}$ and s^2_e.

Employing [17]:

$$(n-1)s^2_{\log w} = \Sigma(\log w_i - \log \overline{w})^2 = \Sigma[\log(1-e_i)]^2 = M^2\Sigma[\ln(1 + e_i)]^2 \qquad [20]$$

Expanding [20] by means of [15]:

$$(n-1)s^2_{\log w} = 2^2M^2\sum\left[\left(\frac{e_i}{2+e_i}\right)^2 + \frac{2}{3}\left(\frac{e_i}{2+e_i}\right)^4 + \frac{1}{9}\left(\frac{e_i}{2+e_i}\right)^6 + \ldots\right] \quad [21]$$

Again, if the extreme case that half the e_i are -0.1 and half 0.1 is assumed, only the first term within the brackets of [21] need be retained. For this case, we shall demonstrate that $s^2_{\log w}$ is approximately $M^2s^2_e$ by dividing

$$(n-1)M^2s^2_e = M^2\Sigma(e_i-\bar{e})^2 = M^2\Sigma e^2_i \quad [22]$$

into [21]. The quotient is:

$$s^2_{\log w}\Big/M^2s^2_e = 2^2\sum\left(\frac{e_i}{2+e_i}\right)^2\Big/\sum e^2_i$$

$$s^2_{\log w}\Big/M^2s^2_e = 2^2\left[\frac{n}{2}\left(\frac{-0.1}{1.9}\right)^2 + \frac{n}{2}\left(\frac{0.1}{2.1}\right)^2\right]\Big/n(0.1)^2 = 1.008 \quad [23]$$

Thus, for relative errors of 0.1 or less and for all practical purposes, $s^2_{\log w}$ equals $M^2s^2_e$. In addition, it is readily shown that s^2_e is the square of the coefficient of variation, namely $s^2_e = s^2_w/\bar{w}^2$. Thus, we can convert between linear and logarithmic data as necessary.

For computational purposes, it is frequently convenient to have an expression for the variance of a product or ratio without the necessity for conversion to logarithms. Using our previous approximation $s^2_{\log w} \cong M^2s^2_w/\bar{w}^2$, we may derive the variance of $u = xy$. Since the variance of log u is:

$$s^2_{\log u} = s^2_{\log x} + s^2_{\log y} + 2rs_{\log x}\,s_{\log y} \quad [24]$$

we readily obtain:

$$\frac{s^2_u}{\bar{u}^2} \cong \frac{s^2_x}{\bar{x}^2} + \frac{s^2_y}{\bar{y}^2} + \frac{2rs_xs_y}{\overline{xy}} \quad [25]$$

Since, according to [12], $\bar{u}$ is approximately equal to $\overline{xy}$ for small variations in x and y:

$$s^2_u \cong (\bar{y})^2s^2_x + (\bar{x})^2s^2_y + 2r\,\overline{xy}\,s_xs_y \quad [26]$$

By a similar process, we obtain the variance of $u = x/y$:

$$s^2_u \cong \frac{(\bar{x})^2}{(\bar{y})^2}\left[\frac{s^2_x}{\bar{x}^2} + \frac{s^2_y}{\bar{y}^2} - \frac{2rs_xs_y}{\overline{xy}}\right] \quad [27]$$

Thus, within the limits of the indicated approximations, and if no correlation exists, [25] and [27] reduce to the sum of the squared coefficients of variation as previously noted. The same expressions for the variance of a sum or product were obtained by Ku (10) using propagation of error formulas. He also presents a more detailed discussion of the necessary assumptions and approximations. With these computational aids, we now consider some numerical examples.

Applications

Example One

Predicted variance. First, we examine the errors inherent in the determination of the first stage hydrolysis constant of aluminum (7). The chemical reaction involved is:

$$Al^{+3} + H_2O = AlOH^{+2} + H^+ \quad [28]$$

Thus, the negative logarithm of the equilibrium constant, pK_1, is defined according to the theory under test:

$$pK_1 = pAlOH^{+2} + pH^+ - pAl^{+3} \quad [29]$$

where the symbol p denotes the negative logarithm of the individual ion activities (the activity of water is assumed to be unity). Since most chemical methods measure concentrations, not activities, we immediately find ourselves faced with the situation anticipated in equations [8] to [10]. First, we recall that ion activities are defined by:

$$-pH = \log(H) = \log\gamma_H + \log[H] \quad [30]$$

where parenthesis indicate activities, brackets indicate concentrations, and γ is the appropriate activity coefficient. Although activity coefficients are a complex function of the concentration of all ions in solution (i.e. the ionic strength), at any given concentration they are constant, and moreover, we shall assume they are known without error. This latter assumption can never be proved wrong, since single ion activity coefficients can never be measured, but are calculated from one of a number of theories. In any event, different theories are in reasonably good agreement for dilute solutions, so we shall proceed.

With these definitions in mind, we can rewrite [29] as:

$$pK_1 = -\log[AlOH] - \log[H] + \log[Al] - \log\frac{\gamma_{AlOH}\,\gamma_H}{\gamma_{Al}} \quad [31]$$

where the chemical valences have been omitted for simplicity. For the calculation of pK_1, the analytical determination of pH (note that the glass electrode determines activity) is required. The total amount of aluminum present, $[Al_t]$, could be determined analytically, but in this case (7) it was calculated from the serial dilution of a carefully standardized stock solution. Since one $[H^+]$ is produced for each $[AlOH^{+2}]$, we equate their concentrations. The concentration of $[Al^{+3}]$ is then equal to $[Al_t - H^+]$. Thus we may write [31] as:

$$pK_1 = -2\log[H] + \log[Al_t - H] - \log\frac{\gamma_{AlOH}\,\gamma_H}{\gamma_{Al}} \qquad [32]$$

Now we may use equation [6] to calculate the variance expected, σ^2_{pK}, if replicate determinations were made on solution No. 1 shown in Table 1 (7). First, we must evaluate the expected observational variance of the term $\log[Al_t - H]$. While this term could be expanded with Taylor's series as in [12], it is simpler to use [6] for the variance of $[Al_t - H]$, and then convert to logarithms using the approximation $\sigma_{\log w} \cong M\sigma_e$. A graphical evaluation of the data (Table 1) indicates that $[Al_t - H]$ is a nearly linear function of $[Al_t]$ over the whole range of concentrations studied, and is nearly linear in [H] for small deviations about a particular observation. Thus, little error is introduced by our implicit assumption that the expectation or mean of $[Al^{+3}]$ is the expectation of $[Al_t - H]$ either for replicate observations or for replicate samples.

Since the concentration of aluminum was not determined analytically but was calculated from dilution, the errors of observation of $[Al_t]$ are obtained from an estimate of dilution errors. If we assume the errors (σ_e) of dilution to be one per cent, the variance of $[Al_t]$ in solution No. 1 is $(0.01 \times 1.00 \times 10^{-2})^2$ or $(1 \times 10^{-4})^2$. We estimate the standard deviation ($\sigma_{\log w}$) of a pH measurement or of $-\log[H]$ to be 0.02 pH units (7) or $\sigma_e = 4.61$ per cent. Since $-\log[H]$ is 3.63 or $[H] = 2.34 \times 10^{-4}$, the variance of [H] is $(0.0461 \times 2.34 \times 10^{-4})^2$ or $(1.08 \times 10^{-5})^2$. In addition, we require the correlation coefficient between $[Al_t]$ and [H] for replicate observations on a single sample. Although $[Al_t]$ and [H] appear (Table 1) to be positively correlated, the correlation between the errors of observation $\delta[Al_t]$ and $\delta[H]$ is zero as previously discussed. Thus, the variance of $[Al_t - H]$ is merely the sum or $(1.00 \times 10^{-4})^2$. Since $[Al_t - H] = 97.7 \times 10^{-4}$, the standard error ($\sigma_e$) is 1.03 per cent or the expected observational variance, σ^2_o, of $\log[Al_t - H]$ is $(0.0045)^2$.

Having determined the observational variance, we now inquire what the expected variance of $\log[Al_t - H]$ would be for the preparation of replicate samples. Again, we assume the error of dilution in preparing $[Al_t]$ is one per cent. From a graphical evaluation of the data in Table 1, we find that this will produce a 0.60 per cent error in [H]. From the chemistry of equation [28] or from the experimental data it is evident that an increase in $[Al_t]$ is accompanied by an increase in [H]. Thus, the correlation is positive, and, for small deviations about the mean is nearly perfect; accordingly we assume $\rho = 1.0$. Then the sampling variance predicted for $[Al_t - H]$ is:

$$\begin{aligned}\sigma^2_s = {} & (1)^2\,(0.01 \times 1.00 \times 10^{-2})^2 + (1)^2\,(0.006 \times 2.34 \times 10^{-4})^2 + \\ & (2)\,(1)\,(-1)\,(1.0)\,(0.01 \times 1.00 \times 10^{-2})\,(0.006 \times 2.34 \times 10^{-4}) = \\ & (9.86 \times 10^{-5})^2 \end{aligned} \qquad [33]$$

or the variance of $\log[Al_t - H]$ is $(0.0044)^2$. Owing to the correlation between the variates, the effect is to reduce the predicted variance. Indeed, we should anticipate this from [6], which for only two variates would be:

$$\sigma^2_u = a^2\sigma^2_x + b^2\sigma^2_y + 2ab\rho\sigma_x\sigma_y \qquad [34]$$

Clearly, if a^2 equals b^2, and the errors of x and y are equal, the predicted variance is zero if the errors are perfectly correlated and $2ab\rho$ has a negative sign. The negative sign, of course, arises in one of two ways: either the sum of two negatively correlated variates or the difference between two positively correlated variates is calculated. As previously indicated, this situation is usually encountered in the determination of thermodymanic equilibrium constants, and decreases the expected variance from one sample to another.

Since we require the expected variance for analyses of replicate samples, the variance of $\log[Al_t - H]$ is clearly the sum of the observational and sampling errors, or $(0.0063)^2$. However, the present experiment was based on single analyses of three replicate solutions for each pK_i determined, with the mean pK values reported. This condition, or the reverse, namely replicate analyses of single samples with only the means reported, is fairly common in chemical data. Thus we inquire how the sampling and observational errors are to be combined. Since replicate observations will reduce σ^2_o but not σ^2_s, while replicate samples will reduce the variance from both components, the variance of the mean of n observations of k samples is $(\sigma^2_o/n + \sigma^2_s)/k$ as previously stated. Thus, the variance of $\log[Al_t - H]$ for three replicate samples is $[(0.0045)^2 + (0.0044)^2]/3$ or $(0.0036)^2$. Before continuing with the calculation of the variance of pK_1 we will calculate the observational and sampling variance expected for the remainder of the experimental observations (Table 1). Since we will later require the individual estimates of each component of the variance, they have not been summed in the tabulated data. Initially, the variance of $\log[Al_t - H]$ is dominated by the variance of $[Al_t]$, since $[Al_t] >> [H]$. Then, as [H] approaches $[Al_t]$, the variance increases considerably, reflecting the much greater uncertainty in the measurement of [H].

Now we have estimates of the variance of all three terms in [32], having assumed that the variance of the activity coefficient term is zero.

Note that if these uncertainties were known, they could be included at this point. In order to determine the predicted variance of pK_1 for analyses of replicate samples, we need to consider again the difference between observational and sample preparation errors. In the case of errors of observation, it is clear that $\log[H]$ and $\log[Al_t - H]$ are correlated, since $[Al_t - H]$ is calculated from the observed $[H]$. Further, an increase in $[H]$ causes a decrease in $[Al_t - H]$, so the correlation is negative and we estimate $\rho = -1.0$. Using our estimate of the observational variance of $\log[Al_t - H] = (0.004)^2$, we find the observational variance of pK_1 for sample No. 1 is:

$$\sigma_o^2 = (-2)^2 (0.02)^2 + (1)^2 (0.004)^2 + (2)(-2)(1)(-1.0)(0.02)(0.004)$$
$$= (0.044)^2 \qquad [35]$$

We now inquire what the sample preparation variance would be. Again we assume a one per cent error in $[Al_t]$, which will produce an error of 0.60 per cent in $[H]$ and a 1.01 per cent error in $[Al_t - H]$. On conversion to logarithms, and realizing that the correlation between $\log[H]$ and $\log[Al_t - H]$ for replicate samples is still negative, since one is calculated from the other, we may write the sampling variance as:

$$\sigma_s^2 = (-2)^2 (0.003)^2 + (1)^2 (0.004)^2 + (2)(-2)(-1.0)(0.003)(0.004)$$
$$= (0.010)^2 \qquad [36]$$

Thus the total expected variance is merely the sum of the two, or $(0.045)^2$.

We may also obtain this directly, by using the sum of the sampling and observational variance expected for $\log[Al_t - H]$ and $\log[H]$. We have already shown that the expected variance for $\log[Al_t - H]$ is $(0.006)^2$, while for $\log[H]$ it is $(0.02)^2 + (0.003)^2$ or $(0.020)^2$. Now we see the utility of retaining our original definition of the δx_i, δy_i, δz_i . . . to include all deviations about the means. This allows us to determine the correlation coefficient between $[H]$ and $[Al_t - H]$ no matter what the cause: the coefficient is always negative since one is calculated from the other. Thus we may write:

$$\sigma_{pK}^2 = (-2)^2 (0.02)^2 + (1)^2 (0.006)^2 + (2)(-2)(1)(-1.0)(0.02)(0.006)$$
$$= (0.046)^2 \qquad [37]$$

We have gone through this example in considerable detail, since some of the calculations and assumptions are not at all obvious. The remainder of the predicted values for σ_{pK}^2 were calculated according to [35] and [36] and compared with [37]. In all cases the agreement was excellent.

In the present case we require the variance of the mean pK for single observations of three replicate samples; thus, the predicted variance for sample No. 1 should be $[(0.044)^2 + (0.010)^2]/3$ or $(0.026)^2$. Since we have already calculated the sampling and observational terms for the variance of $\log[Al_t - H]$, we may use their sum or $(0.006)^2$ in [37] and divide by 3; the result is $(0.026)^2$. Since the difference between these two methods is quite small for the first few solutions in Table 1, the expected variance for the mean pK was calculated in both ways. Again the agreement was good and the estimates for the variance of the mean pK are shown in Table 1. Clearly, we were correct in anticipating non-homogeneity of variance; the predicted values depend on the magnitude of and the correlations between the variates calculated from the experimental observations, as well as on the errors of sampling and observation.

Now we may use our weighting scheme, equation [13], to compare the predicted with the observed variance. We estimate chi-square as follows:

$$\chi^2 = \frac{(n-1)s_{pK}^2}{\sigma_{pK}^2} \cong \sum_i \left[\frac{(pK_i - \overline{pK})^2}{\sigma_{pK}^2} \right] \qquad [38]$$

The result, 64.2, should be distributed as chi-square with $n - 1$ or 7 degrees of freedom. Since the probability is less than one per cent that this value would be obtained in random sampling, we reject the hypothesis that pK_1 is constant over the range of experimental conditions. Closer examination of the data in Table 1, however, indicates that the value for pK_1 for the most dilute solution (No. 8) is suspiciously low: the mean pK for these 8 observations is 4.970 with a standard deviation calculated in the usual fashion of 0.135. We recall that in this particular case, three replicate samples were prepared for each pK_1, so that a t-test applied to the original data would indicate whether this mean pK should be rejected. An analysis of the original unpublished data indicates that indeed this is the case. However, we wish to proceed with an analysis of the data as presented, which usually will not involve sufficient replications for the usual statistical tests. Bliss (3) describes a simple test for rejecting outliers; the ratio of the range to the standard deviation is calculated and then compared with expected values (3) for sampling from a normal population. In this case, the ratio is 0.44/0.135 or 3.26. The probability of obtaining this large a ratio is only 0.10 and strengthens our suspicion that this sample should not be included; indeed, cogent chemical reasons have been advanced (7) for rejecting this sample. Chi-square computed according to [38] for the remaining 7 samples is 13.9, which is slightly greater than the expected value for $p = 0.05$. Thus, we tentatively accept the hypothesis that the remaining 7 samples with mean $pK = 5.02$ and standard deviation 0.041 are drawn from the same population; i.e. pK_i is a constant.

Since our predicted variances, σ_{pK}^2, seem reasonably homogeneous, we inquire whether a pooled variance would be acceptable in the calculation of chi-square. Bartlett's test or a maximum variance ratio test (3) does not provide an unequivocal answer, since we have assumed σ^2_{pK} to represent the population variance with infinite degrees of freedom. However, the maximum variance ratio is $(0.031)^2/(0.026)^2 = 1.42$, which is not significant (3) unless the degrees of freedom allowed exceed 60 and approach infinity. For practical purposes, it is useful to have a pooled variance, and we shall assume for this reason that the variance is in fact homogeneous. The pooled variance for the 7 observations is then $1/n \sum_{i} \sigma^2_{pK} = (0.0276)^2$, and chi-square computed in the usual manner is 13.3. Thus, our weighting scheme has not altered chi-square materially. However, had the predicted variance been less homogeneous, as for all 8 samples, similar calculations yield a chi-square of 117 compared with 64.2 from equation [38].

We conclude, therefore, that the constant in the mathematical statement of the theory is in fact observed to be constant. Conversely, if the chemical theory, equation [28], is accepted, the near equality of the observed variance of pK_1 with that predicted from equation [37] establishes the validity of our estimation procedure.

Observed variance. Further verification is provided by an analysis of variance of the original data whose means were used for the calculations in Table 1. Three observations were made on each of 3 solutions (No. 6) diluted to 1×10^{-4} *M* in $[Al_t]$. The calculated pK_1 values and the analysis of variance are shown in Table 2. Since the replicate observations 1, 2 and 3 on sample A do not necessarily correspond to the same observations on sample B or C, only a one-way classification is presented. The mean square for error is then an estimate of the observational variance, σ^2_o, for repeated observations on the same sample. From Table 2, this is $(0.048)^2$, which is remarkably close to the predicted σ^2_o of $(0.049)^2$ from [35] for solution No. 6 as shown in Table 1. Similarly, the mean square for samples is an estimate (3) of $\sigma^2_o + 3\sigma^2_s$; solving for the sampling variance, σ^2_s, we obtain $(0.012)^2$ which compares very favorably with the value $(0.011)^2$ from [36] for solution No. 6 (Table 1).

A similar analysis of variance was made of the original observations of three replicate samples for each pK_1 whose means are shown in Table 1. Solution No. 8 was omitted as already discussed and solution No. 3 was omitted because of incomplete replication. The results are shown in Table 3, where treatments indicate different solutions, i.e. different concentrations of $[Al_t]$. Differences among treatments were not significant, substantiating our previous conclusion that pK_1 is a constant. Differences among sample means were not significant either, but the magnitude of the sample mean square suggests rather large sampling errors. In this case, the sample mean square is an estimate of $\sigma^2_i + \sigma^2_o + 6\sigma^2_s$ and the error mean square is an estimate of $\sigma^2_i + \sigma^2_o$, where σ^2_i is an interaction term. Thus, we find $\sigma^2_s = (0.031)^2$ which is considerably larger than predicted or observed in the data of Table 2. The error mean square corresponds to $(0.052)^2$; therefore our best estimate of the population variance is $(0.031)^2 + (0.052)^2$ or $(0.060)^2$. This may be compared with the sum of the predicted sampling and observational errors from Table 1, which when pooled are $(0.010)^2 + (0.047)^2$ or $(0.048)^2$. A chi-square test is appropriate for comparing our prediction with the observed variance; thus chi-square is $12(0.060)^2/(0.048)^2 = 18.8$ which is not significant ($p > 0.05$). Again, however, it is evident that our prediction is somewhat conservative. In fact, if our predicted variance $(0.048)^2$ is used to test the significance of the treatment mean square, chi-square is $5(0.078)^2/(0.048)^2$ or 13.2, which is greater than the value of 11.1 for $p = 0.05$. Thus, we might reject the hypothesis that pK_1 is constant, when in fact the analysis of variance shows it to be constant within our ability to dilute and measure pH on that particular occasion. Of course, it is evident that a chi-square test is considerably more conservative than an F test, since infinite degrees of freedom are assumed for the variance of the denominator in a chi-square test.

If we look for an explanation for our conservative estimate of the sampling variance of pK_1, it is possibly our estimate of the errors of dilution; however, it is doubtful if a careful analyst would make an error as large as one per cent. Another possibility is some systematic error, such as failing to properly calibrate the pH meter or using dirty glassware. Again this implies an unusually sloppy analyst. More likely, the observed sampling variability is due to some failure of the theory. Ion activity coefficients might have been calculated improperly, but this should only affect the treatment mean square. Frink and Peech (7) found that these solutions were supersaturated with respect to gibbsite, and that $Al(OH)_3$ sometimes precipitated. This precipitation would be different from sample to sample, and thus we suspect a chemical rather than statistical failure. However, it is apparent that in an important experiment, it may be worthwhile for the investigator to obtain accurate estimates of his precision, even though he still may not wish to replicate the entire experiment. In any event, we conclude that our estimation procedure produces valid results when the experimental uncertainties are known.

Finally, we should point out that the statistical test previously applied (7) to this data is incorrect. First, an error was made in the coefficient of the variance of $-2 \log[H]$; it is of course $2^2(0.02)^2$ rather than $2(0.02)^2$ as stated. Second, the correlation between the variables was neglected. However, the present examination of the data leads to the same conclusions as Frink and Peech (7).

Other methods. An alternative method for determining whether the experimental data fit the theoretical model is suggested by Draper and Smith (5) in an analysis of the distinction between "lack of fit" and "pure error". Again, such an analysis is only possible when replicate observations are available. Moreover, since it involves regression analysis, we must specify the experimental variable which might be expected to cause changes in the observed constant. However, it is instructive to apply their methods to the present data.

It is common in thermodynamics to assume that apparent changes in equilibrium constants in aqueous solutions are due to changes in ion activity coefficients. Specifically, since the logarithm of the activity coefficient is a function of the square root of the ionic strength, it is customary to plot the observed constant against the square root of the ionic strength and extrapolate to zero, i.e. to an ideal solution at infinite dilution. Thus, we shall test by linear regression analysis whether pK_1 is a function of the square root of the ionic strength of the various solutions. These solutions correspond, of course, to treatments in the previous analysis of variance.

The regression analysis follows its usual form, with the results shown in the bottom half of Table 3. Having demonstrated that the linear regression is not significant, we can use the methods of Draper and Smith (5) to partition the residual mean square into lack of fit and pure error terms. Now, since there was no significant lack of fit to the linear model, we have the remaining pure error mean square which is an estimate of the population variance. Comparing this term with the pooled error term from the analysis of variance in the top half of Table 3, we find they are identical and correspond to a population variance of $(0.061)^2$. Moreover, the treatment mean square from the analysis of variance corresponds to the pooled regression and lack of fit mean squares from the regression analysis. Thus, this analysis also shows that pK_1 is not dependent on treatment as measured by ionic strength and provides us with an estimate of the population variance.

Example Two

Continuing with other examples, we evaluate errors inherent in the determination of solubility products. For gibbsite, the crystalline form of $Al(OH)_3$, we write (6):

$$pK_{sp} = pAl^{+3} + 3pOH^{-} \qquad [39]$$

Separating activity coefficients, we may express the terms in [39] as functions of the measured variates:

$$pK_{sp} = -\log[Al_t] + \log[1 + K_1/H] + 3\log[H] - 3\log K_w + \log f(\gamma) \qquad [40]$$

where K_1 is the first stage hydrolysis constant, K_w is the ionization constant of water, and $f(\gamma)$ contains the activity corrections. Again, we assume that these constants are known without error, and that the variance of $-\log[H]$ is $(0.02)^2$. Since in this case $[Al_t]$ is determined analytically, the errors are of the usual sort: we estimate the variance of $-\log[Al_t]$ from six analytical determinations as $(0.015)^2$. The variance for replicate observations of $[1 + K_1/H]$ was evaluated for each value of [H] by first evaluating the variance of $[K_1/H]$ using either [27] or a log conversion to permit the use of [6]. Then, the variance of $\log[1 + K_1/H]$ was evaluated in a manner similar to that previously described for $\log[Al_t - H]$, with no correlation between variates (Table 4). Since $[1 + K_1/H]$ is non-linear, we should inquire if errors are introduced by these methods. Again, we find (Table 4) that for small deviations about the mean, the departure from linearity is not serious.

Finally, we require the correlation coefficients between the variates in [40] for replicate observations. In this case, only [H] and $[1 + K_1/H]$ are correlated, and the coefficient is obviously close to -1.0 for small deviations about the means. Thus, the variance of pK_{sp} expected for the first sample in Table 4 is:

$$\begin{aligned}\sigma^2_{pK} &= (-1)^2 (0.015)^2 + (1)^2 (0.001)^2 + (3)^2 (0.02)^2 \\ &\quad + (2)(1)(3)(-1.0)(0.001)(0.02) = (0.061)^2 \qquad [41]\end{aligned}$$

If we inquire what the error in analyzing replicate samples would be, we find we have no basis for prediction in this experiment. Most determinations of solubility products are based on the preparation of solutions containing the necessary constituent ions (in this case Al^{+3} and OH^-) at concentrations slightly greater and less than the equilibrium concentrations. The solutions are then seeded with the crystalline solid, and equilibrium approached from the resulting supersaturated and undersaturated solutions. In this sense, preparation of replicate samples is impossible: the original solutions may be the same, but each approaches equilibrium independently and the final observed concentrations reflect not only the errors in preparation of the solution, but also inherent differences in apparent equilibrium concentrations. It appears, then, that this could only be measured by experiment. In any event, our previous analysis shows that errors of sample preparation are much smaller than errors of observation. Since the present experiment is based on observations of single samples, the remainder of the estimates of σ^2_{pK} were calculated from [41] and are shown in Table 4. Note that σ^2_{pK} decreases as $[Al_t]$ approaches [H], reflecting the decreased variance as the correlation term becomes more important.

Chi-square was computed as before. The result is 158; obviously these samples are not drawn from the same population, and we reject the hypothesis that pK_{sp} is a constant. Chemical evidence (6) suggests that equilibrium was probably not established in these experiments. A recent examination by Kittrick (8) of solutions equilibrated for four years was much more likely to fit [39]: from five determinations he obtained a mean pK_{sp} of 34.03 with standard deviation 0.066, compared with the value 33.57 with $s = 0.282$ from Frink and Peech (6). Inasmuch as the calculated variance (Table 4) is reasonably homogeneous, we will use a pooled variance of $(0.059)^2$ to test Kittrick's data. In this case, chi-square calculated in the usual fashion is $(4)\ (0.066)^2/(0.059)^2$ or 5.00 which is not significant (probability > 0.20). Clearly, Kittrick's data indicate that pK_{sp} for gibbsite is constant when adequate equilibration occurs. In addition, we have increased confidence that our test agrees with deductions from chemical evidence regarding the constancy of equilibrium constants.

Example Three

Finally, we test an extreme case where large exponents are encountered as in the solubility product of hydroxyapatite. Following Clark (4), we write:

$$pK_{sp} = 10pCa^{+2} + 6pPO_4^{-3} + 2pOH^- \qquad [42]$$

Again, we wish to express this equation in terms of the experimental variables. The concentration of $[PO_4]$ is given by the following approximation in the pH range 5 to 9 studied by Clark:

$$[PO_4] = \frac{[P_t]\ K_2K_3}{[H^2 + K_2H]} \qquad [43]$$

where K_2 and K_3 are the appropriate ionization constants of phosphoric acid. Thus we may express [42] as:

$$\begin{aligned} pK_{sp} &= -10 \log[Ca] - 6 \log[P_t] + 6 \log[H^{7/3} + K_2H^{4/3}] \\ &\quad - 6 \log[K_2K_3] - 2 \log K_w + \log f(\gamma) \qquad [44] \end{aligned}$$

Here, we have a complex function in [H] to evaluate, which can most easily be done by our now familiar scheme of finding the variance of $[H^{7/3} + K_2H^{4/3}]$ first and then converting to logarithms, realizing of course that $[H]^{7/3}$ and $K_2[H]^{4/3}$ are correlated for replicate observations. The calculations are tedious and will not be presented here; the variance of $\log[H^{7/3} + K_2H^{4/3}]$ for the data in Clark's Table 1 decreased from $(0.047)^2$ for the most acid solution (No. 1) to $(0.027)^2$ for the most alkaline solution (No. 27). We assume the variance of the $\log[Ca]$ and $\log[P_t]$ determinations to be $(0.015)^2$, the same precision with which we measured $[Al_t]$. Again, we require the expected variance for replicate observations on a single sample, and in this case the variates are not correlated. The predicted variance of pK_{sp} is then merely the sum, or:

$$\sigma^2_{pK} = (-10)^2\,(0.015)^2 + (-6)^2\,(0.015)^2 + (6)^2\,(0.047)^2 = (0.332)^2 \qquad [45]$$

The remainder of the values for σ^2_{pK} were calculated according to [45]. Chi-square was then computed and found to be 143 which is highly significant ($p<0.01$). Since Clark obtained a mean pK_{sp} of 115.40 with standard deviation 0.707, we could anticipate this result since the predicted standard deviation, equation [45], is much smaller and decreases from 0.332 for solution No. 1 to 0.238 for solution No. 27. Thus, we must conclude that these observations of pK_{sp} were not drawn from the same population, or in other words pK_{sp} is not constant over the range of experimental conditions. We might inquire whether we have estimated the experimental uncertainties properly, a question of considerable significance where large exponents are involved. This is possible, but our examination of Kittrick's data leads us to believe that our estimates of precision can be attained in practice.

Conclusions

The applicability of a thermodynamic theory is tested by observing whether the constant in the mathematical expression of the theory is in fact constant. Since the observations from which the constant are calculated are necessarily inaccurate, a chi-square test compares the ratio of the variance of the constant to the variance estimated from the constituent observations.

Thermodynamic equilibrium constants are usually expressed as linear functions of logarithmic terms, calculated from experimental data over a wide range of conditions. However, the variance of the derived constant cannot be seen intuitively, particularly when large exponential terms are included. An equation was derived, therefore, to describe the variance of a sum of variates, with explicit treatment of exponential terms, corrections for correlations among the experimental uncertainties, and separation of sample preparation and observational errors. In addition, the problems of translation of linear to logarithmic units were considered. Comparison with several sets of experimental data indicates that the derived equation correctly predicts the observed variance of the constant caused by experimental uncertainties.

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Table 1. Thermodynamic hydrolysis constant of aluminum derived from changes in pH and $[Al_t]$ on dilution

Experimental			Derived				Var. $\log[Al_t-H]$		Var. pK		
No.	$-\log[Al_t]$	pH	$-\log[H]$	$-\log[Al_t-H]$	$\log\frac{\gamma_{AlOH}\,\gamma_H}{\gamma_{Al}}$	pK_1	σ_o^2	σ_s^2	σ_o^2	σ_s^2	Σ^*
1	2.00	3.70	3.63	2.01	0.29	4.96	$(0.004)^2$	$(0.004)^2$	$(0.044)^2$	$(0.010)^2$	$(0.026)^2$
2	2.30	3.84	3.78	2.32	0.23	5.01	$(0.004)^2$	$(0.004)^2$	$(0.044)^2$	$(0.010)^2$	$(0.026)^2$
3	2.60	3.95	3.91	2.62	0.18	5.02	$(0.005)^2$	$(0.004)^2$	$(0.045)^2$	$(0.010)^2$	$(0.027)^2$
4	3.00	4.13	4.10	3.04	0.13	5.03	$(0.005)^2$	$(0.004)^2$	$(0.045)^2$	$(0.010)^2$	$(0.027)^2$
5	3.30	4.29	4.27	3.35	0.10	5.09	$(0.006)^2$	$(0.004)^2$	$(0.046)^2$	$(0.010)^2$	$(0.027)^2$
6	4.00	4.61	4.60	4.13	0.05	5.02	$(0.009)^2$	$(0.005)^2$	$(0.049)^2$	$(0.011)^2$	$(0.029)^2$
7	4.30	4.76	4.75	4.49	0.03	4.98	$(0.013)^2$	$(0.005)^2$	$(0.053)^2$	$(0.011)^2$	$(0.031)^2$
8	5.00	5.13	5.13	5.59	0.02	4.65	$(0.060)^2$	$(0.009)^2$	$(0.099)^2$	$(0.015)^2$	$(0.058)^2$

*The variance expected for the mean pK derived from single observations of three samples, or $(\sigma_o^2/1+\sigma_s^2)/3$.

Table 2. Thermodynamic hydrolysis constant of aluminum for three observations on three samples and an analysis of variance

	Samples		
Observations	A	B	C
1	5.04	4.93	5.04
2	5.04	5.02	4.98
3	4.98	4.93	4.93
Σ	15.06	14.88	14.95

Source	SS	DF	MS	F
Total	0.019355	8	—	—
Samples	0.005488	2	0.002744	1.19^{ns}
Error	0.013867	6	0.002311	—

Table 3. Analysis of variance of the original data for aluminum hydrolysis from Table 1

Source	SS	DF	MS	F
Total	0.07476	17	—	—
Treatments	0.03023	5	0.006046	2.21^{ns}
Samples	0.01714	2	0.008570	3.13^{ns}
Error	0.02739	10	0.002739	—
Pooled error	0.04453	12	0.003711	—

Source	SS	DF	MS	F
Total	0.07476	17	—	—
Regression	0.00639	1	0.006390	1.49^{ns}
Residual	0.06837	16	0.004273	—
Lack of fit	0.02384	4	0.005959	1.61^{ns}
Pure error	0.04453	12	0.003711	—
Reg + LoF	0.03023	5	0.006046	—

Table 4. Thermodynamic solubility product for gibbsite derived from measurements of pH and $[Al_t]$

Experimental		Derived				Variance	
$-\log[Al_t]$	pH	$-\log[H]$	$\log[1+\frac{K_1}{H}]$	$\log f(\gamma)$	pK_{sp}	$\log[1+\frac{K_1}{H}]$	pK_{sp}
2.00	3.70	3.63	0.018	0.41	33.60	$(0.001)^2$	$(0.061)^2$
2.02	3.91	3.84	0.028	0.41	33.00	$(0.001)^2$	$(0.061)^2$
3.00	3.96	3.93	0.034	0.21	33.51	$(0.002)^2$	$(0.060)^2$
3.05	4.01	3.98	0.038	0.18	33.39	$(0.002)^2$	$(0.060)^2$
4.08	4.21	4.20	0.061	0.06	33.66	$(0.003)^2$	$(0.059)^2$
4.20	4.23	4.22	0.063	0.06	33.72	$(0.003)^2$	$(0.059)^2$
5.46	4.58	4.58	0.134	0.05	33.96	$(0.005)^2$	$(0.057)^2$
5.59	4.72	4.72	0.177	0.02	33.69	$(0.007)^2$	$(0.055)^2$

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