

## Uncertainties in Logarithmic and Exponential Measures

The general relationship between uncertainties in logarithmic quantities and their exponential equivalents is best shown as follows.

Suppose  $x$  and  $y$  are related by

$$y = 10^x \text{ (i.e., } x = \log y \text{)}$$

Let  $\Delta y$  represent the uncertainty in  $y$  caused by an uncertainty  $\Delta x$  in the value of  $x$ :

$$y + \Delta y = 10^{x+\Delta x}$$

or

$$\Delta y = 10^{x+\Delta x} - y$$

The fractional error in  $y$  is defined by:

$$\Delta y / y$$

We are interested in how that quantity is related to the fractional error in  $x$ ,  $\Delta x / x$

$$\begin{aligned} \Delta y / y &= (10^{x+\Delta x} - y) / y = (10^{x+\Delta x} - 10^x) / 10^x \\ &= 10^{\Delta x} - 1 = 10^{x(\Delta x/x)} - 1 \end{aligned}$$

To illustrate with a concrete case, consider  $[H^+] = 10^{-\text{pH}}$

What uncertainty in  $[H^+]$  corresponds to a pH reading of **5.00 ± 0.05**?

The percent uncertainty in pH is  $100 \times 0.05 / 5.00 = 1\%$  (0.01)

The corresponding percent uncertainty in  $[H^+]$  is  $100 \times (10^{-5(0.01)} - 1)$

$$= 100 \times (10^{-0.05} - 1) = 100 \times 0.11, \text{ i.e. } 11\%$$

Note that the uncertainty in  $[H^+]$  for a given uncertainty in pH varies with the value of the pH itself.

E.g., consider a pH of **2.00 ± 0.02**. Again, this represents a 1% uncertainty.

However, the corresponding percent uncertainty in  $[H^+]$  is now

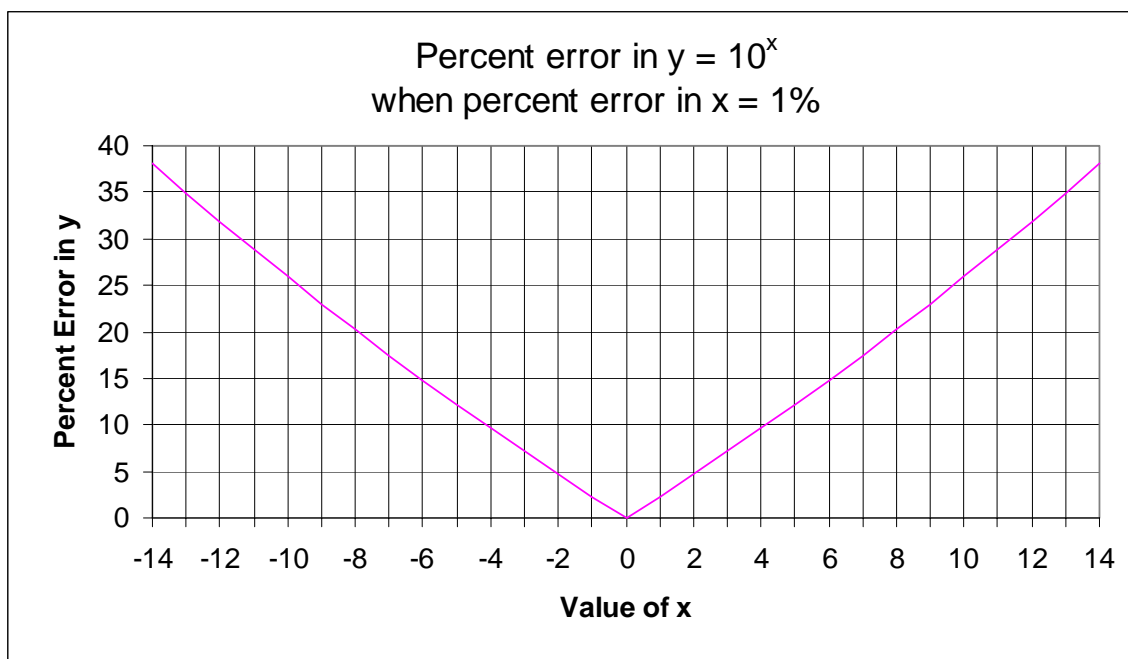
$$\begin{aligned} 100 \times (10^{-2(0.01)} - 1) &= 100 \times (10^{-0.02} - 1) \\ &= 100 \times 0.046, \text{ or only i.e. } 4.6\%. \end{aligned}$$

The effects of non-linearity of pH as a measure of acidity are quite apparent in such an analysis of uncertainties.

Similarly, a pH measurement of  $10.00 \pm 0.10$  again represents a 1% uncertainty in pH. The corresponding percent uncertainty in  $[H^+]$  now is

$$100 \times (10^{-10(0.01)} - 1) = 100 \times (10^{-0.1} - 1) = 0.21, \text{ or } 21\%.$$

The graph below shows the percent error in the value of an exponential when the percent error in the exponent is 1%. Note that it is symmetrical around 0.



A second instance where such consideration would play a role is in the case of **Absorbance** (which, unlike pH, is restricted to positive values) and percent transmittance, which are related by:

$$A = 2.00 - \log(T) = -\log(T/100), \text{ or, } T = 100 \times 10^{-A}$$

Small uncertainties in **Absorbance** could give rise to large uncertainties in **percent transmittance**. Fortunately, most of our use of these quantities is in conjunction with Beer's Law, in which Absorbance is the desired quantity.

On the other hand, when given the opportunity to measure a quantity instead of one that is logarithmically related to it, there may be something to be gained by doing so.

Consider the relationship between the percent error in a measurement of **Percent Transmittance** (a number between 0 and 100) and the percent error in the corresponding **Absorbance**.

Suppose we can measure percent transmittance with a precision of 1% in the range from 0% to 100%. Using an analysis similar to that used earlier, the corresponding percent error in the absorbance will be:

$$100 \Delta A / A = 100 \log (1 + \Delta T / T) / \log (T/100)$$

Our 1% criterion translates into  $\Delta T / T = 0.01$ , and the percent error in absorbance is given by

$$100 \Delta A / A = 100 \log (1.01) / \log (T/100)$$

E.g., if we measure a percent transmittance of  $20.0\% \pm 0.2\%$ , the percent error in the corresponding absorbance will be:

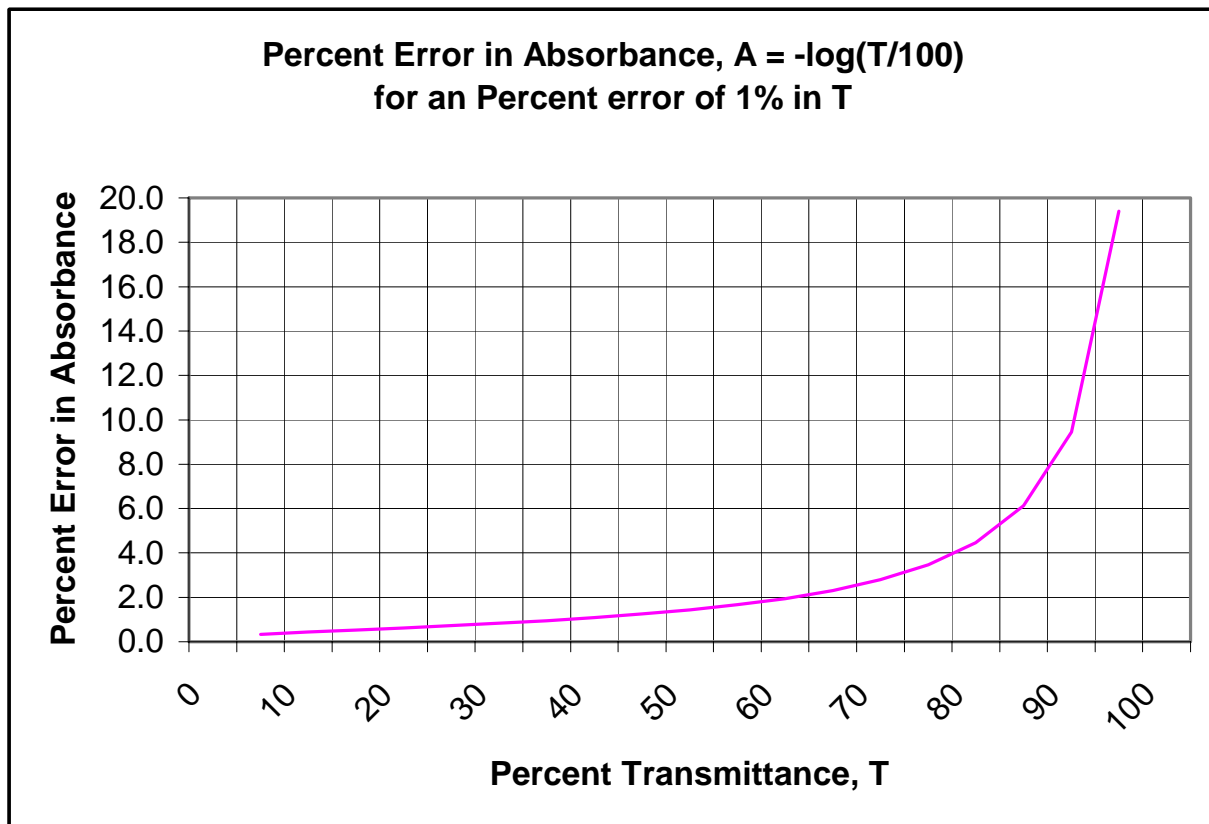
$$= 100 \times 0.00432 / 0.699 = 0.6\%$$

On the other hand, if the percent transmittance is  $70.0\% \pm 0.7\%$  (still a 1% error), the percent error in the corresponding absorbance will be:

$$= 100 \times 0.00432 / 0.155 = 2.8\%$$

**A larger percent error than that which we made in the recorded amount!**

The graph on the following page shows the dependence of the percent error in absorbance on the value of the percent transmittance. The crossover point (The point at which the percent errors in the two quantities are both 1%) is at approximately 37%.



These examples shows that careful consideration must be given in dealing with errors where derived quantities involving logarithms or exponentials of our directly measured quantities are concerned.

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Revised, June 28, 2005