Experimental Error

Chapter 3

Section 3-4
Propagation of Uncertainty from Random Error

Propagation of Uncertainty from Random Error (1 of 2)

- Most experiments require arithmetic operations on several numbers, each of which has a random error.
- The uncertainty of the final result is *not* simply the sum of individual errors.
  - Random error means some error is positive and some negative.
  - This results in some cancelation of error.
- There are several propagation of error equations to calculate the error associated with the combined values.

Propagation of Uncertainty from Random Error (2 of 2)

Addition and subtraction: use absolute uncertainty of the individual terms (include units)

$$e_{\text{final}} = \sqrt{\sum_i e_i^2} = \sqrt{e_1^2 + e_2^2 + e_3^2 + \cdots}$$

Multiplication and division: use percent relative uncertainty

$$\%e_{\text{final}} = \sqrt{\sum_i \%e_i^2} = \sqrt{\%e_1^2 + \%e_2^2 + \%e_3^2 + \cdots}$$

Mixed operations: follow proper algebraic rules for mathematical manipulation

Propagation of Uncertainty $e_{\text{final}} = \sqrt{\sum_i e_i^2} = \sqrt{e_1^2 + e_2^2 + e_3^2 + \cdots}$

Addition and subtraction: use absolute uncertainty of the individual terms (include units)

$$\begin{array}{r} 1.76\text{ m }(\pm 0.03) \\ +\ 1.89\text{ m }(\pm 0.02) \\ \underline{-\ 0.59\text{ m }(\pm 0.02)} \\ 3.06\text{ m }(\pm 0.04_1) \end{array}$$

$$e_{\text{final}} = \sqrt{(0.03)^2 + (0.02)^2 + (0.02)^2} = 0.041\text{ m}$$

$$\boxed{3.06\text{ m} \pm 0.04_1\text{ m} \qquad \text{(absolute uncertainty)}}$$

Example: Significant Figures in Laboratory Work (1 of 6)

You prepared a 0.250 M NH_3 solution by diluting 8.46 (±0.04) mL of 28.0 (±0.5) wt% NH_3 up to 500.0 (±0.2) mL. [density = 0.899 (±0.003) g/mL]

Find the uncertainty in 0.250 M. The molecular mass of NH_3, 17.031 g/mol, has negligible uncertainty relative to other uncertainties in this problem.

Example: Significant Figures in Laboratory Work (2 of 6)

Solution: To find the uncertainty in molarity, we need the uncertainty in moles delivered to the 500-mL flask. The concentrated reagent contains 0.899 (±0.003) g of solution per mL. Weight percent tells us that the reagent contains 0.280 (±0.005) g of NH_3 per gram of solution. In our calculations, we retain extra insignificant digits and round off only at the end.

$$\begin{aligned}\text{Grams of } NH_3 \text{ per mL in concentrated reagent} &= 0.899\ (\pm 0.003)\,\frac{\text{g solution}}{\text{mL}} \times 0.280\ (\pm 0.005)\,\frac{\text{g } NH_3}{\text{g solution}} \\ &= 0.899\ (\pm 0.3_{34}\%)\,\frac{\text{g solution}}{\text{mL}} \times 0.280\ (\pm 1._{79}\%)\,\frac{\text{g } NH_3}{\text{g solution}} \\ &= 0.251_7\ (\pm 1._{82}\%)\,\frac{\text{g } NH_3}{\text{mL}}\end{aligned}$$

because $\sqrt{(0.3_{34}\%)^2 + (1._{79}\%)^2} = 1._{82}\%$

Example: Significant Figures in Laboratory Work (3 of 6)

Solution: Next, we find the moles of ammonia contained in 8.46 (±0.04) mL of concentrated reagent. The relative uncertainty in volume is 0.04/8.46 = 0.4_{73}%.

$$\text{mol NH}_3 = \frac{0.251_7\,(\pm 1._{82}\%)\,\dfrac{\text{g NH}_3}{\text{mL}} \times 8.46\,(\pm 0.4_{73}\%)\,\text{mL}}{17.031\,(\pm 0\%)\,\dfrac{\text{g NH}_3}{\text{mol}}}$$

$$= 0.125_{04}\,(\pm 1._{88}\%)\,\text{mol}$$

because $\sqrt{(1._{82}\%)^2 + (0.4_{73}\%)^2 + (0\%)^2} = 1._{88}\%$

Example: Significant Figures in Laboratory Work (4 of 6)

Solution: This much ammonia was diluted to 0.500 0 (±0.000 2) L. The relative uncertainty in the final volume is 0 0.000 2/0.500 0 = 0.04%. The molarity is

$$\frac{\text{mol NH}_3}{\text{L}} = \frac{0.125_{04}\,(\pm 1._{88}\%)\ \text{mol}}{0.500\,0\,(\pm 0.04\%)\ \text{L}}$$

$$= 0.250_{08}\ (\pm 1._{88}\%)\ \text{M}$$

because $\sqrt{(1.88\%)^2 + (0.04\%)^2} = 1._{88}\%$. The absolute uncertainty is $1._{88}$ % of 0.250_{08} M = 0.004_7 % M. The uncertainty in molarity is in the third decimal place, so our final, rounded answer is

$$[\text{NH}_3] = 0.250\,(\pm 0.005)\ \text{M}$$

Example: Significant Figures in Laboratory Work (5 of 6)

Calculation Check: The uncertainty in 28.0 wt% NH_3 is $\pm 1._{79}\%$, which is four times the next largest relative uncertainty. Assuming $\pm 1._{79}\%$ dominates, the overall uncertainty yields 0.250 M $(\pm 1._{79}\%)$ = 0.250 $(\pm 0.004_5)$ M, which is in good agreement with our answer.

Example: Significant Figures in Laboratory Work (6 of 6)

Test Yourself: Suppose that you used smaller volumetric apparatus to prepare 0.250 M NH_3 solution by diluting 84.6 (±0.8) μL of 28.0 (±0.5) wt% NH_3 up to 5.00 (±0.02) mL. Find the uncertainty in 0.250 M.

Example: Volumetric Versus Gravimetric Dilution (1 of 5)

Let’s compare the uncertainty resulting from a 10-fold volumetric dilution with a 10-fold gravimetric dilution.

(a) For volumetric dilution, suppose that you have a standard reagent with a concentration of 0.046 80 M with negligible uncertainty. To dilute by a factor of 10, you use a micropipet to deliver 1 000 μL (= 1.000 mL) into a 10-mL volumetric flask and dilute to volume.

(b) For gravimetric dilution, suppose that you have a standard reagent with a concentration of 0.046 80 mol reagent/kg solution. To dilute it by a factor of close to 10, you weigh out 983.2 mg (= 0.983 2 g) of solution (≈1 mL) and add 9.026 6 g of water (≈9 mL). For each procedure, find the resulting concentration and its relative uncertainty.

Example: Volumetric Versus Gravimetric Dilution (2 of 5)

Solution: (a) Tolerance for the volumetric flask (Table 2-3) is 10.00 ± 0.02 mL = 10.00 mL ± 0.2%, and for the micropipet (Table 2-5) is 1 000 μL ± 0.3%. The *dilution factor* is

$$\text{Dilution factor} = \frac{V_{\text{final}}}{V_{\text{initial}}} = \frac{10.00\ (\pm 0.2\%)\ \text{mL}}{1.000\ (\pm 0.3\%)\ \text{mL}} = 10.00 \pm 0.3_6\%$$

because $\sqrt{(0.2\%)^2 + (0.3\%)^2} = 0.3_6\%$. The concentration of the dilute solution is

$$\frac{0.046\ 80\ \text{M}}{10.00 \pm 0.3_6\%} = 0.004\ 680\ \text{M} \pm 0.3_6\% = 0.004\ 680 \pm 0.000\ 017\ \text{M}$$

Example: Volumetric Versus Gravimetric Dilution (3 of 5)

Solution: (b) In the gravimetric procedure, we dilute 0.983 2 g of concentrated solution up to (0.983 2 g + 9.026 6 g) = 10.009 8 g. The dilution factor is (10.009 8 g)/(0.983 2 g) = 10.180 8. Suppose that the uncertainty in each mass is ±0.3 mg. The uncertainty in the mass of concentrated solution is $0.983\ 2\ \text{g} \pm 0.000\ 3\ \text{g} = 0.983\ 2\ (\pm\ 0.03_{05}\%)\ \text{g}$.

The absolute uncertainty in the sum (0.983 2 g + 9.026 6 g) is $\sqrt{(0.000\ 3\ \text{g})^2 + (0.000\ 3\ \text{g})^2} = 0.000\ 4_2\ \text{g}$, which is $0.004_2\%$. The uncertainty in the dilution factor is

$$\text{Dilution factor} = \frac{10.009\ 8\left(\pm 0.004_2\%\right)\text{g}}{0.983\ 2\left(\pm 0.03_{05}\%\right)\text{g}} = 10.180\ 8 \pm 0.03_{08}\%$$

because $\sqrt{(0.004_2\%)^2 + (0.03_{05}\%)^2} = 0.03_{08}\%$. The concentration of the dilute solution is

$$\frac{0.046\ 80\ \text{mol reagent /kg solution}}{10.180\ 8 \pm 0.03_{08}\%} = 0.004\ 596_9 \pm 0.03_{08}\%\ \text{mol reagent/kg solution}$$

$$= 0.004\ 596_9 \pm 0.000\ 001_4\ \text{mol reagent/kg solution}$$

Example: Volumetric Versus Gravimetric Dilution (4 of 5)

Solution: In this example, the gravimetric dilution is 10 times more precise than the volumetric dilution (0.03% versus 0.4%). Increased precision is the reason gravimetric titrations are recommended over volumetric titrations, though the latter are less tedious.

Example: Volumetric Versus Gravimetric Dilution (5 of 5)

Test Yourself: Describe a volumetric dilution procedure that would be more precise than using a 1 000-μL micropipet and a 10-mL volumetric flask. What would be the relative uncertainty in the dilution?

Propagation of Uncertainty

$$y = x^{\alpha} \xrightarrow{\text{Uncertainty}} \%e_y = a\left(\%e_x\right)$$

Exponents and logarithms: For the function $y = x^a$, the relative uncertainty in y ($\%e_y$) is ***a*** times the relative uncertainty in x ($\%e_x$).

If $\boldsymbol{y = \sqrt{x} = (x)^{1/2}}$

a relative uncertainty of $\pm 2\%$ in x will result in $\%e_y = \left(\frac{1}{2}\right)(2\%) = \mathbf{1\%}$

If $\boldsymbol{y = (x)^2}$

a relative uncertainty of $\pm 3\%$ in x will result in $\%e_y = (2)(3\%) = \mathbf{6\%}$

Example: Propagation of Uncertainty in the Product $\boldsymbol{x} \cdot \boldsymbol{x}$ (1 of 4)

If an object falls for t seconds, the distance it travels is $\frac{1}{2}gt^2$, where g is the acceleration of gravity (9.81 m/s^2) at the surface of the Earth. (This equation ignores the effect of drag produced by air, which slows the falling object.) If the object falls for 2.34 s, the distance traveled is $\frac{1}{2}(9.81\ \text{m/s}^2)(2.34\ \text{s})^2 = 26.8_6\ \text{m}$. If the relative uncertainty in time is ±1.0%, what is the relative uncertainty in distance?

Example: Propagation of Uncertainty in the Product $\boldsymbol{x \cdot x}$ (2 of 4)

Solution: Equation 3-7 tells us that for $y = x^a$, the relative uncertainty in y is a times the relative uncertainty in x:

$$y = x^a \quad \Rightarrow \quad \%e_y = a(\%e_x) \qquad \textbf{(3-7)}$$

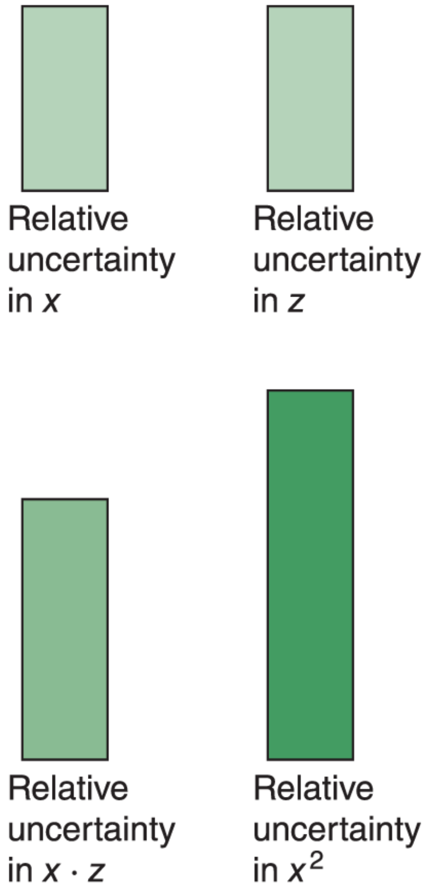
$$\text{Distance} = \frac{1}{2}gt^2 \quad \Rightarrow \quad \%e_{\text{distance}} = 2(\%e_t) = 2(1.0\%) = 2.0\%$$

Example: Propagation of Uncertainty in the Product $\boldsymbol{x \cdot x}$ (3 of 4)

Solution: If you write $\text{distance} = \frac{1}{2} g \cdot t \cdot t,$ you might be tempted to say that the relative uncertainty in distance is $\sqrt{1.0^2 + 1.0^2} = 1.4\%.$ This answer is wrong because the error in a single, measured value of *t* is always positive or always negative. If *t* is 1.0% high, then t^2 is 2% high because we are multiplying a high value by a high value: $(1.01)^2 = 1.02$.

Equation 3-6 presumes that the uncertainty in each factor of the product $x \cdot z$ is random and independent of the other. In the product $x \cdot z$, the measured value of *x* could be high sometimes and the measured value of *z* could be low sometimes. In the majority of cases, the uncertainty in the product $x \cdot z$ is not as great as the uncertainty in x^2.

$$\%e_4 = \sqrt{\%e_1^2 + \%e_2^2 + \%e_3^2} \qquad \textbf{(3-6)}$$



Example: Propagation of Uncertainty in the Product $\boldsymbol{x} \cdot \boldsymbol{x}$ (4 of 4)

Test Yourself: You can calculate the time it will take for an object to fall from the top of a building to the ground if you know the height of the building. If the height has an uncertainty of 1.0%, what is the uncertainty in time?

Example: Uncertainty in H^+ Concentration (1 of 4)

Consider the function pH = − log[H^+], where [H^+] is the molarity of H^+. For pH = 5.21 ± 0.03, find [H^+] and its uncertainty.

Example: Uncertainty in H^+ Concentration (2 of 4)

Solution: First solve the equation pH = –log[H^+] for [H^+]: If $a = b$, then $10^a = 10^b$. If pH = –log[H^+], then log[H^+] = –pH and $10^{\log[H^+]} = 10^{-pH}$. But $10^{\log[H^+]} = [H^+]$. We therefore need to find the uncertainty in the equation

$$[H^+] = 10^{-pH} = 10^{-(5.21 \pm 0.03)}$$

In Table 3-1, the relevant function is $y = 10^x$, in which $y = [H^+]$ and $x = -(5.21 \pm 0.03)$. For $y = 10^x$, the table tells us that

$$\frac{e_y}{y} = 2.302\,6\, e_x$$

$$\frac{e_{[H^+]}}{[H^+]} = 2.302\,6\, e_{pH} = (2.302\,6)(0.03) = 0.069\,1 \qquad \textbf{(3-12)}$$

Example: Uncertainty in H^+ Concentration (3 of 4)

Solution: The relative uncertainty in $[H^+]$ is 0.069 1. For $[H^+] = 10^{-pH} = 10^{-5.21} = 6.17 \times 10^{-6}$ M, we find

$$\frac{e_{[H^+]}}{[H^+]} = \frac{e_{[H^+]}}{6.1_7 \times 10^{-6}\ \text{M}} = 0.069\ 1 \quad \Rightarrow \quad e_{[H^+]} = 4._3 \times 10^{-7}\,\text{M}$$

The concentration of H^+ is $6.1_7\ (\pm 0.4_3) \times 10^{-6}$ M = $6.2\ (\pm 0.4) \times 10^{-6}$ M. An uncertainty of 0.03 in pH gives an uncertainty of 7% in $[H^+]$. *Note that extra digits were retained in the intermediate results and were not rounded off until the final answer.*

Example: Uncertainty in H^+ Concentration (4 of 4)

Test Yourself: If uncertainty in pH is doubled to ±0.06, what is the relative uncertainty in $[H^+]$?

Table 3-1 Summary of rules for propagation of uncertainty

Function	Uncertainty	Function[a]	Uncertainty[b]
$y = x_1 + x_2$	$e_y = \sqrt{e_{x_1}^2 + e_{x_2}^2}$	$y = x^a$	$\%e_y = a(\%e_x)$
$y = x_1 - x_2$	$e_y = \sqrt{e_{x_1}^2 + e_{x_2}^2}$	$y = \log x$	$e_y = \frac{1}{\ln 10}\frac{e_x}{x} \approx 0.434\,29\frac{e_x}{x}$
$y = x_1 \cdot x_2$	$\%e_y = \sqrt{\%e_{x_1}^2 + \%e_{x_2}^2}$	$y = \ln x$	$e_y = \frac{e_x}{x}$
$y = \frac{x_1}{x_2}$	$\%e_y = \sqrt{\%e_{x_1}^2 + \%e_{x_2}^2}$	$y = 10^x$	$\frac{e_y}{y} = (\ln 10)e_x \approx 2.302\,6\, e_x$
		$y = e^x$	$\frac{e_y}{y} = e_x$

a. *x represents a variable and a represents a constant that has no uncertainty.*

b. *e_x/x is the relative error in x and $\%e_x$ is 100 × e_x/x.*

Section 3-5
Propagation of Uncertainty from Systematic Error

The Virtue of Calibration

- A 25-mL Class A volumetric pipet is certified to deliver 25.00 ± 0.03 mL
  - Volume delivered by a given pipet is reproducible and within the range 24.97 to 25.03 mL.
  - This is *systematic error*.
- A pipet can be calibrated by weighing the water it delivers (Chapter 2).
  - A specific pipet delivers 24.991 ± 0.006 mL.
  - Calibration *eliminates* systematic error, leaving only *random error*.
- If pipet delivers 25-mL four times:

Calibrated pipet volume = 99.964 ± 0.012 mL (0.012% RSD)

Uncalibrated pipet volume = 100.00 ± 0.12 mL (0.12% RSD)

Box 3-3 Atomic Mass of the Elements

- Average atomic mass of an element depends on the mole fraction of each isotope in the material.
- Different materials have different isotope fractions.
- Average atomic mass of an element varies from one source to another.