Suppose you dispense 20 mL of a reagent using the Class A 10-mL pipet whose calibration information is given in Table 4.9. If the volume and uncertainty for one use of the pipet is $9.992 \pm 0.006$ mL, what is the volume and uncertainty when we use the pipet twice?

As a first guess, we might simply add together the volume and the maximum uncertainty for each delivery; thus

$$\text{(9.992 mL + 9.992 mL) ± (0.006 mL + 0.006 mL) = 19.984 ± 0.012 mL}$$

It is easy to appreciate that combining uncertainties in this way overestimates the total uncertainty. Adding the uncertainty for the first delivery to that of the second delivery assumes that with each use the indeterminate error is in the same direction and is as large as possible. At the other extreme, we might assume that the uncertainty for one delivery is positive and the other is negative. If we subtract the maximum uncertainties for each delivery,

$$\text{(9.992 mL + 9.992 mL) ± (0.006 mL - 0.006 mL) = 19.984 ± 0.000 mL}$$

we clearly underestimate the total uncertainty.

So what is the total uncertainty? From the previous discussion we know that the total uncertainty is greater than ±0.000 mL and less than ±0.012 mL. To estimate the cumulative effect of multiple uncertainties we use a mathematical technique known as the propagation of uncertainty. Our treatment of the propagation of uncertainty is based on a few simple rules.

Note

Although we will not derive or further justify these rules here, you may consult the additional resources at the end of this chapter for references that discuss the propagation of uncertainty in more detail.

### 4.3.1 A Few Symbols

A **propagation of uncertainty** allows us to estimate the uncertainty in a result from the uncertainties in the measurements used to calculate the result. For the equations in this section we represent the result with the symbol $R$, and the measurements with the symbols $A$, $B$, and $C$. The corresponding uncertainties are $u_R$, $u_A$, $u_B$, and $u_C$. We can define the uncertainties for $A$, $B$, and $C$ using standard deviations, ranges, or tolerances (or any other measure of uncertainty), as long as we use the same form for all measurements.

Note

The requirement that we express each uncertainty in the same way is a critically important point. Suppose you have a range for one measurement, such as a pipet’s tolerance, and standard deviations for the other measurements. All is not lost. There are ways to convert a range to an estimate of the standard deviation. See Appendix 2 for more details.

### 4.3.2 Uncertainty When Adding or Subtracting

When adding or subtracting measurements we use their absolute uncertainties for a propagation of uncertainty. For example, if the result is given by the equation

$$\text{(9.992 mL + 9.992 mL) ± (0.006 mL + 0.006 mL) = 19.984 ± 0.012 mL}$$
then the absolute uncertainty in $R$ is

$$u_R = \sqrt{u_A^2 + u_B^2 + u_C^2} \tag{4.6}$$

Example 4.5

When dispensing 20 mL using a 10-mL Class A pipet, what is the total volume dispensed and what is the uncertainty in this volume? First, complete the calculation using the manufacturer's tolerance of 10.00 mL $\pm$ 0.02 mL, and then using the calibration data from Table 4.9.

Solution

To calculate the total volume, we simply add the volumes for each use of the pipet. When using the manufacturer's values, the total volume is

$$V = \text{10.00 mL} + \text{10.00 mL} = \text{20.00 mL}$$

and when using the calibration data, the total volume is

$$V = \text{9.992 mL} + \text{9.992 mL} = \text{19.984 mL}$$

Using the pipet's tolerance value as an estimate of its uncertainty gives the uncertainty in the total volume as

$$u_R = \sqrt{(0.02)^2 + (0.02)^2} = \text{0.028 mL}$$

and using the standard deviation for the data in Table 4.9 gives an uncertainty of

$$u_R = \sqrt{(0.006)^2 + (0.006)^2} = \text{0.0085 mL}$$

Rounding the volumes to four significant figures gives 20.00 mL $\pm$ 0.03 mL when using the tolerance values, and 19.98 $\pm$ 0.01 mL when using the calibration data.

4.3.3 Uncertainty When Multiplying or Dividing

When multiplying or dividing measurements, we use their relative uncertainties for a propagation of uncertainty. For example, if the result is given by the equation

$$R = \frac{A \times B}{C}$$

then the relative uncertainty in $R$ is

$$\frac{u_R}{R} = \sqrt{\left(\frac{u_A}{A}\right)^2 + \left(\frac{u_B}{B}\right)^2 + \left(\frac{u_C}{C}\right)^2} \tag{4.7}$$

Example 4.6
The quantity of charge, \( Q \), in coulombs passing through an electrical circuit is

\[ Q = I \times t \]

where \( I \) is the current in amperes and \( t \) is the time in seconds. When a current of \( 0.15 \, \text{A} \pm 0.01 \, \text{A} \) passes through the circuit for \( 120 \, \text{s} \pm 1 \, \text{s} \), what is the total charge passing through the circuit and its uncertainty?

**Solution**

The total charge is

\[ Q = \text{mathrm{(0.15\: A) \times (120\: s) = 18\: C}}] \]

Since charge is the product of current and time, the relative uncertainty in the charge is

\[ \left(\frac{u_R}{R}\right) = \sqrt{\left(\frac{0.01}{0.15}\right)^2 + \left(\frac{1}{120}\right)^2} = 0.0672 \]

The absolute uncertainty in the charge is

\[ u_R = R \times 0.0672 = \text{mathrm{(18\: C) \times (0.0672) = 1.2\: C}}] \]

Thus, we report the total charge as \( 18 \, \text{C} \pm 1 \, \text{C} \).

---

4.3.4 Uncertainty for Mixed Operations

Many chemical calculations involve a combination of adding and subtracting, and multiply and dividing. As shown in the following example, we can calculate uncertainty by treating each operation separately using equation 4.6 and equation 4.7 as needed.

**Example 4.7**

For a concentration technique the relationship between the signal and the an analyte’s concentration is

\[ S_{\text{total}} = k_A C_A + S_{\text{mb}} \]

What is the analyte’s concentration, \( C_A \), and its uncertainty if \( S_{\text{total}} \) is \( 24.37 \pm 0.02 \), \( S_{\text{mb}} \) is \( 0.96 \pm 0.02 \), and \( k_A \) is \( 0.186 \pm 0.003 \, \text{ppm}^{-1} \).

**Solution**

Rearranging the equation and solving for \( C_A \)

\[ C_A = \frac{S_{\text{total}} - S_{\text{mb}}}{k_A} = \text{mathrm{(24.37-0.96)} \over {0.186\: \text{ppm}^{-1}} = 125.9\: \text{ppm}}] \]

gives the analyte’s concentration as \( 126 \, \text{ppm} \). To estimate the uncertainty in \( C_A \), we first determine the uncertainty for the numerator using equation 4.6.

\[ u_R = \sqrt{(0.02)^2 + (0.02)^2} = 0.028 \]
The numerator, therefore, is 23.41 ± 0.028. To complete the calculation we estimate the relative uncertainty in \( C_A \) using equation 4.7.

\[
\left| \frac{u_R}{R} \right| = \sqrt{\left( \frac{0.028}{23.41} \right)^2 + \left( \frac{0.003}{0.186} \right)^2} = 0.0162
\]

The absolute uncertainty in the analyte’s concentration is

\[
u_R = \mathit{ kWhrm{(}(125.9\::\: \text{ppm}) \times (0.0162) = 2.0\::\: \text{ppm}))\]

Thus, we report the analyte’s concentration as 126 ppm ± 2 ppm.

Practice Exercise 4.2

To prepare a standard solution of Cu\(^{2+}\), you obtain a piece of copper from a spool of wire. The spool’s initial weight is 74.2991 g and its final weight is 73.3216 g. You place the sample of wire in a 500 mL volumetric flask, dissolve it in 10 mL of HNO\(_3\), and dilute to volume. Next, you pipet a 1 mL portion to a 250-mL volumetric flask and dilute to volume. What is the final concentration of Cu\(^{2+}\) in mg/L, and its uncertainty? Assume that the uncertainty in the balance is ±0.1 mg and that you are using Class A glassware.

Click here to review your answer to this exercise.

| Table 4.10 Propagation of Uncertainty for Selected Mathematical Functions† |

<table>
<thead>
<tr>
<th>Function</th>
<th>( u_R )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( R = kA )</td>
<td>( u_R = ku_A )</td>
</tr>
<tr>
<td>( R = A + B )</td>
<td>( u_R = \sqrt{u_A^2 + u_B^2} )</td>
</tr>
<tr>
<td>( R = A - B )</td>
<td>( u_R = \sqrt{u_A^2 + u_B^2} )</td>
</tr>
<tr>
<td>( R = A \times B )</td>
<td>( u_R = \sqrt{\left( \frac{u_A}{A} \right)^2 + \left( \frac{u_B}{B} \right)^2} )</td>
</tr>
<tr>
<td>( R = \frac{A}{B} )</td>
<td>( u_R = \sqrt{\left( \frac{u_A}{A} \right)^2 + \left( \frac{u_B}{B} \right)^2} )</td>
</tr>
<tr>
<td>( R = \ln(A) )</td>
<td>( u_R = \frac{u_A}{A} )</td>
</tr>
<tr>
<td>( R = \log(A) )</td>
<td>( u_R = 0.4343 \times \frac{u_A}{A} )</td>
</tr>
<tr>
<td>( R = e^{A} )</td>
<td>( u_R = u_A )</td>
</tr>
<tr>
<td>( R = 10^A )</td>
<td>( u_R = 2.303 \times u_A )</td>
</tr>
<tr>
<td>( R = A^k )</td>
<td>( u_R = k \times u_A )</td>
</tr>
</tbody>
</table>

† Assumes that the measurements \( A \) and \( B \) are independent; \( k \) is a constant whose value has no uncertainty.
4.3.5 Uncertainty for Other Mathematical Functions

Many other mathematical operations are common in analytical chemistry, including powers, roots, and logarithms. Table 4.10 provides equations for propagating uncertainty for some of these functions.

Example 4.8

If the pH of a solution is 3.72 with an absolute uncertainty of ±0.03, what is the \([H^+]\) and its uncertainty?

**Solution**

The concentration of \(H^+\) is

\[ \text{[H}^+\text{] = 10^{−\text{pH}} = 10^{−3.72} = 1.91 \times 10^{−4} \text{ M}] \]

or \(1.9 \times 10^{-4}\) M to two significant figures. From Table 4.10 the relative uncertainty in \([H^+]\) is

\[ \dfrac{u_R}{R} = 2.303 \times u_A = 2.303 \times 0.03 = 0.069 \]

The uncertainty in the concentration, therefore, is

\[ \text{[(1.91} \times 10^{−4} \text{ M}) \times (0.069) = 1.3 \times 10^{−5} \text{ M}] \]

We report the \([H^+]\) as 1.9 (±0.1) \(\times\) 10\(^{-4}\) M.

(Writing this result as 1.9 (±0.1) \(\times\) 10\(^{-4}\) M is equivalent to 1.9 \(\times\) 10\(^{-4}\) M ± 0.1 \(\times\) 10\(^{-4}\) M)

Practice Exercise 4.3

A solution of copper ions is blue because it absorbs yellow and orange light. Absorbance, \(A\), is defined as

\[ [A = -\log \dfrac{P}{P_\text{o}}] \]

where \(P_0\) is the power of radiation from the light source and \(P\) is the power after it passes through the solution. What is the absorbance if \(P_0\) is 3.80 \(\times\) 10\(^2\) and \(P\) is 1.50 \(\times\) 10\(^2\)? If the uncertainty in measuring \(P_0\) and \(P\) is 15, what is the uncertainty in the absorbance?

Click [here](#) to review your answer to this exercise.

4.3.6 Is Calculating Uncertainty Actually Useful?

Given the effort it takes to calculate uncertainty, it is worth asking whether such calculations are useful. The short answer is, yes. Let’s consider three examples of how we can use a propagation of uncertainty to help guide the development of an analytical method.
One reason for completing a propagation of uncertainty is that we can compare our estimate of the uncertainty to that obtained experimentally. For example, to determine the mass of a penny we measure mass twice—once to tare the balance at 0.000 g, and once to measure the penny’s mass. If the uncertainty for measuring mass is ±0.001 g, then we estimate the uncertainty in measuring mass as

$$u_{mass} = \sqrt{(0.001)^2 + (0.001)^2} = \text{0.0014 g}$$

If we measure a penny’s mass several times and obtain a standard deviation of ±0.050 g, then we have evidence that our measurement process is out of control. Knowing this, we can identify and correct the problem.

We also can use propagation of uncertainty to help us decide how to improve an analytical method’s uncertainty. In Example 4.7, for instance, we calculated an analyte’s concentration as 126 ppm ± 2 ppm, which is a percent uncertainty of 1.6%. (\(\text{\frac{2\: ppm}{126\: ppm} \times 100 = 1.6\%}\)). Suppose we want to decrease the percent uncertainty to no more than 0.8%. How might we accomplish this? Looking back at the calculation, we see that the concentration’s relative uncertainty is determined by the relative uncertainty in the measured signal (corrected for the reagent blank)

$$\text{dfrac{0.028}{23.41} = 0.0012 \text{ or 0.12\%}}$$

and the relative uncertainty in the method’s sensitivity, \(k_A\),

$$\text{dfrac{0.003\: ppm^{-1}}{0.186\: ppm^{-1}} = 0.016\: or\: 1.6\%}$$

Of these terms, the uncertainty in the method’s sensitivity dominates the overall uncertainty. Improving the signal’s uncertainty will not improve the overall uncertainty of the analysis. To achieve an overall uncertainty of 0.8% we must improve the uncertainty in \(k_A\) to ±0.0015 ppm⁻¹.

Practice Exercise 4.4

Verify that an uncertainty of ±0.0015 ppm⁻¹ for \(k_A\) is the correct result.

Click here to review your answer to this exercise.

Finally, we can use a propagation of uncertainty to determine which of several procedures provides the smallest uncertainty. When diluting a stock solution there are usually several different combinations of volumetric glassware that will give the same final concentration. For instance, we can dilute a stock solution by a factor of 10 using a 10-mL pipet and a 100-mL volumetric flask, or by using a 25-mL pipet and a 250-mL volumetric flask. We also can accomplish the same dilution in two steps using a 50-mL pipet and 100-mL volumetric flask for the first dilution, and a 10-mL pipet and a 50-mL volumetric flask for the second dilution. The overall uncertainty in the final concentration—and, therefore, the best option for the dilution—depends on the uncertainty of the transfer pipets and volumetric flasks. As shown below, we can use the tolerance values for volumetric glassware to determine the optimum dilution strategy.\(^5\)

Example 4.9

Which of the following methods for preparing a 0.0010 M solution from a 1.0 M stock solution provides the smallest overall uncertainty?
a. A one-step dilution using a 1-mL pipet and a 1000-mL volumetric flask.

b. A two-step dilution using a 20-mL pipet and a 1000-mL volumetric flask for the first dilution, and a 25-mL pipet and a 500-mL volumetric flask for the second dilution.

Solution

The dilution calculations for case (a) and case (b) are

\[
\text{case (a): } 1.0 \text{ M } \times \frac{1.000 \text{ mL}}{1000.0 \text{ mL}} = 0.0010 \text{ M}
\]

\[
\text{case (b): } 1.0 \text{ M } \times \left( \frac{20.00 \text{ mL}}{1000.0 \text{ mL}} \right) \times \left( \frac{25.00 \text{ mL}}{500.0 \text{ mL}} \right) = 0.0010 \text{ M}
\]

Using tolerance values from Table 4.2, the relative uncertainty for case (a) is

\[
\frac{u_R}{R} = \sqrt{\left( \frac{0.006}{1.000} \right)^2 + \left( \frac{0.3}{1000.0} \right)^2} = 0.006
\]

and for case (b) the relative uncertainty is

\[
\frac{u_R}{R} = \sqrt{\left( \frac{0.03}{20.00} \right)^2 + \left( \frac{0.3}{1000.0} \right)^2 + \left( \frac{0.03}{25.00} \right)^2 + \left( \frac{0.2}{500.0} \right)^2} = 0.002
\]

Since the relative uncertainty for case (b) is less than that for case (a), the two-step dilution provides the smallest overall uncertainty. (See Appendix 2 for a more detailed treatment of the propagation of uncertainty.)

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