PROPAGATION OF UNCERTAINTY

CHEM 251 SDSU

UNCERTAINTY IN VALUES

- Every measurement has some uncertainty associated with it.
- The uncertain can be reported in a number of ways, such as the standard deviation, range, or tolerances of the measurement.
- For the calibration of the pipette to the right the delivered volume could be expressed as:
  - 10.006 ±0.002 mL (based on stdev.)
  - 10.006 ±0.006 mL (based on range)
  - 10.00 ±0.02 mL (based on tolerance)

10 mL Pipette Calibration

Trial	Vol.
1	10.003
2	10.008
3	10.006
4	10.009
5	10.004
Avg.	10.006
Stdev.	0.0025
Range	0.006
Tolerance	±0.02

WHAT IS THE ERROR IN REPLICATE DELIVERIES?

If the calibrated pipette from the previous slide was used to deliver 30 mL of solution, what would be the volume delivered and the uncertainty in that volume?

We cannot assume that the uncertainties are directly additive, some of the uncertainty could be positive, some could be negative, and the volumes will vary.

Delivery 1 uncertainty	Delivery 2 uncertainty	Delivery 3 uncertainty	Total Uncertainty
+0.0011	-0.0004	-0.0019	-0.0023

PREDICTING TOTAL UNCERTAINTY

- To account for the random nature of uncertainties, specific calculations are used to determine how the uncertainty propagates.

- Crucially, the uncertainty has to be determined in the same way (e.g. stdev, range…) for each measurement and be in the same units.

Table 4.10 Propagation of Uncertainty for Selected Mathematical Functions†

Function	u_R
$R = kA$	$u_R = ku_A$
$R = A + B$	$u_R = \sqrt{u_A^2 + u_B^2}$
$R = A - B$	$u_R = \sqrt{u_A^2 + u_B^2}$
$R = A \times B$	$\frac{u_R}{R} = \sqrt{\left(\frac{u_A}{A}\right)^2 + \left(\frac{u_B}{B}\right)^2}$
$R = \frac{A}{B}$	$\frac{u_R}{R} = \sqrt{\left(\frac{u_A}{A}\right)^2 + \left(\frac{u_B}{B}\right)^2}$
$R = \ln(A)$	$u_R = \frac{u_A}{A}$
$R = \log(A)$	$u_R = 0.4343 \times \frac{u_A}{A}$
$R = e^A$	$\frac{u_R}{R} = u_A$
$R = 10^A$	$\frac{u_R}{R} = 2.303 \times u_A$
$R = A^k$	$\frac{u_R}{R} = k \times \frac{u_A}{A}$

† Assumes that the measurements A and B are independent; k is a constant whose value has no uncertainty.

CALIBRATED VS. UNCALIBRATED UNCERTAINTIES

- The propagation of uncertainty is significantly different when the source of the uncertainty is a **random** or **determinate** error.
- For the 10 mL pipette, before it is calibrated the 10 mL pipette has an uncertainty of ±0.02 mL. This could be a positive error, or negative, but it will not fluctuate between the two.
- As such, determinate errors (uncalibrated glassware) have their uncertainties propagated in a linear fashion: $\mu_T = \mu_A + \mu_B + \ldots$

UTILITY OF PROPAGATED UNCERTAINTIES

- Calculating the propagation of uncertainty can be rather time consuming, but it provides important information about the system.
    - Compare actual uncertainty with expected uncertainty - can reveal unanticipated sources of uncertainty/problems.
    - Diagnose weaknesses in analysis methods - find the points of improvement to increase the precision of the analysis.
    - Determine the most precise method that can be used for a given procedure.