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# Statistical Analysis of Errors: A Practical Approach for an Undergraduate Chemistry Lab

## Part 2. Some Worked Examples

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### Determination of the Normality of an Unknown Solution

The normality  $N_A$  of an unknown solution A may be determined by titration using a solution of known normality. The following equation is used

$$N_A = \frac{N_B V_B}{V_A}$$

where  $N_B$  is the normality of the known solution B;  $V_B$  is the volume of B, determined by the content of the pipet; and  $V_A$  is the volume of the solution A, determined by measuring the volume added from the buret.

Because it is standard practice to determine at least four values for  $V_A$ , start by computing the average and the standard deviation of  $V_A$  in order to calculate the error on  $N_A$ . Let us concentrate on a particular example that will clarify the general procedure.

#### Problem

Prepare solution B (e.g., hydrated oxalic acid) with normality of approximately 0.1000 eq/L, and determine this normality as accurately as possible. Pipet exactly 25.00 mL of solution B, and titrate with solution A. Determine the normality of A ( $N_A$ ) and the error.

#### Procedure

**Step 1.** One can prepare a solution of 0.1000 eq/L of hydrated oxalic acid by dissolving 3.152 g in water and diluting it to exactly 500.00 mL. The exact normality of the solution we pipet is not really important as long as we know the actual normality with adequate precision. Thus, all we must do is dilute approximately 3.152 g of hydrated oxalic acid in the specified amount of water and compute the resulting normality.

#### Result

$$m = (3.041 \pm 0.5) \text{ mg}$$

where  $m$  is the mass of the hydrated oxalic acid.

Dissolve hydrated oxalic acid in water, and dilute to 500.00 mL using a class A volumetric flask. Determine the normality  $N_B$ .

$$\begin{aligned} N_B &= \frac{\left( \frac{3.041}{\text{MW}/2} \right)}{0.5000} \\ &= \frac{\left( \frac{3.041}{126.066/2} \right)}{0.5000} \\ &= 0.09649 \text{ eq/L} \end{aligned}$$

**Step 2.** Compute the error on the normality  $N_B$  of B.

First, we determine the relative error on  $N_B$ .

$$RE(N_B) = \sqrt{\left( \frac{0.5}{3.041} \right)^2 + \left( \frac{0.25}{500.00} \right)^2} = 0.000526$$

We take the absolute error on the 500.00-mL volumetric flask to be 0.25 mL (class A glassware), and we assume the error on MW to be negligible. Thus, we get

$$AE(N_B) = 0.000526 \times 0.09649 = 0.00005 \text{ eq/L}$$

**Step 3.** Using 25.00 mL ( $V_B$ ) of the hydrated oxalic acid solution, we perform one gross titration to get an idea of the equivalence point. Then we perform three precise additional titrations.

#### Result

The precise measurements for  $V_A$  (in mL) were

$$25.21 \quad 25.25 \quad 25.23$$

We compute the average value of  $V_A$  and the corresponding error.

$$\bar{V}_A = 25.23 \text{ mL}$$

and

$$\sigma(\bar{V}_A) = \sqrt{\frac{8 \times 10^{-4}}{3(3-1)}} = 0.01 \text{ mL}$$

From this we get

$$AE(\bar{V}_A) = 3\sigma(\bar{V}_A) = 0.03 \text{ mL}$$

In terms of the notation introduced in Figure 2 of the companion paper (1), these three numbers constitute (together with their mean) the first row of data. We could in principle produce a second row, a third, and so forth by repeating the measurements under identical conditions, in each case writing down the mean of the row in the fourth column. If we do this many times we can estimate the variability of the mean volume  $\bar{V}$  by calculating the standard deviation  $\sigma_{\bar{V}}$  of that last column.

Because this is clearly a very impractical solution, we estimate  $\sigma_{\bar{V}}$  by computing the standard deviation of the actual observations and by dividing this result by the number of observations (i.e., 3). Again in terms of the aforementioned figure, this means that we estimate the variance of the last (i.e., mean) column by calculating the variance of the first row.

**Step 4.** Compute the normality  $N_A$  and the error on  $N_A$ .

$$N_A = \frac{25.00 \times 0.09649}{25.23} = 0.09561 \text{ eq/L}$$

and because

$$RE(N_A) = \sqrt{RE^2(\bar{V}_A) + RE^2(V_B) + RE^2(N_B)}$$

We take the absolute error on the 25 mL-pipette to be 0.03 mL (class A glassware). From this we get

$$RE(N_A) = \sqrt{\left(\frac{0.03}{25.23}\right)^2 + \left(\frac{0.03}{25.00}\right)^2 + \left(\frac{0.00005}{0.09649}\right)^2} = 1.8 \times 10^{-3}$$

and thus

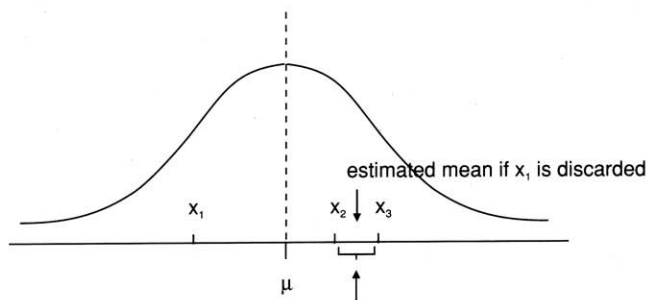
$$AE(N_A) = 1.8 \times 10^{-3} \times 0.09566 = 0.00017 \text{ eq/L}$$

### Conclusion

The normality of A is given by

$$N_A = (95.6 \pm 0.2) \times 10^{-3} \text{ eq/mL}$$

In triplicated experiments the experimenter should not be tempted to select the two "best" results, that is, the two results that are closest together. This would result in a systematic error (2, 3). The easiest way to see this is by looking at the figure below.



## Determination of the Enthalpy of Combustion of an Alcohol

### Problems

**Part 1.** The heat capacity  $C$  is determined by burning a precisely measured quantity of propanol-1. The temperature increment  $\Delta T$  in combination with the known  $\Delta H^\circ$  value, that is,  $(-2,010.4 \pm 0.1) \text{ kJ/mol}$  for propanol-1, yields the desired value for  $C$ .

**Part 2.** Using the heat capacity  $C$  and the temperature increment due to burning a precisely measured quantity of ethanol, we can compute the enthalpy of combustion of ethanol.

### Solution to Part 1

**Step 1.** Weigh a recipient with propanol-1 before and after combustion and determine the decrease in mass. Do this twice.

#### Result

$$\Delta g_1 = (764 \pm 0.7) \text{ mg}$$

and

$$\Delta g_2 = (809 \pm 0.7) \text{ mg}$$

The mass is determined by comparing the weight of the recipient before and after it has been filled with propanol-1. Because the absolute error on each of these two measurements is equal to 0.5 mg, the absolute error on the difference amounts to 0.7 mg (compare to eq 8, part I).

**Step 2.** Determine the increase in temperature in the calorimeter for the two cases.

#### Result

$$\Delta T_1 = (8.3 \pm 0.07) \text{ K}$$

and

$$\Delta T_2 = (8.9 \pm 0.07) \text{ K}$$

Because the absolute error on each of these two measurements is equal to 0.05 K, the absolute error on the difference is 0.07 K.

**Step 3.** Compute the heat capacity of the calorimeter.

To this end we use the following formula.

$$C = \frac{\Delta H^\circ \Delta g}{MW_{\text{propanol-1}} \Delta T}$$

where  $MW_{\text{propanol-1}} = 60.033$ , the molecular weight of propanol-1.

First we concentrate on the result itself.

$$C_1 = \frac{2,010.4 \times 0.764}{60.033 \times 8.3} = 3.0825 \approx 3.1 \text{ kJ/K}$$

$$C_2 = \frac{2,010.4 \times 0.809}{60.033 \times 8.9} = 3.0440 \approx 3.0 \text{ kJ/K}$$

Hence the average value for  $C$  is given by

$$\bar{C} = 3.0633 \text{ kJ/K}$$

**Step 4.** Compute the error on the result.

First we determine the relative errors on the individual values of the heat capacities. Using eq 10 from part I, we get

$$RE(C_1) = \sqrt{\left(\frac{0.7}{764}\right)^2 + \left(\frac{0.07}{8.3}\right)^2 + \left(\frac{0.1}{2,010.4}\right)^2} = 0.0085$$

$$RE(C_2) = \sqrt{\left(\frac{0.7}{809}\right)^2 + \left(\frac{0.07}{8.9}\right)^2 + \left(\frac{0.1}{2,010.4}\right)^2} = 0.0079$$

From this we get

$$AE(C_1) = 0.0085 \times 3.1 = 0.026 \approx 0.03 \text{ kJ/K}$$

$$AE(C_2) = 0.0079 \times 3.0 = 0.024 \approx 0.02 \text{ kJ/K}$$

Therefore

$$AE(\bar{C}) = AE\left(\frac{C_1 + C_2}{2}\right) = \frac{1}{2} \sqrt{(0.03)^2 + (0.02)^2} = 0.018 \approx 0.02 \text{ kJ/K}$$

### Conclusion 1

The heat capacity of the calorimeter is given by

$$C = (3.06 \pm 0.02) \text{ kJ/K}$$

In this case we prefer to use the accuracy as it is determined by the statistical analysis of the errors although the number of significant digits suggests a wider range of inaccuracy. However, closer examination of the data shows that the reason that we can only recover two significant digits can be traced back to the temperature determination (8.3 K and 8.9 K). This is close enough to 10.0 that it is reasonable to accept a result with three significant digits.

### Solution to Part 2

**Step 1.** Weigh a recipient with ethanol before and after combustion, and then determine the decrease in mass. Do this twice.

## Result

$$\Delta g_1 = (942 \pm 0.7) \text{ mg}$$

and

$$\Delta g_2 = (898 \pm 0.7) \text{ mg}$$

**Step 2.** Determine the increase in temperature in the calorimeter for the two cases.

## Result

$$\Delta T_1 = (8.8 \pm 0.07) \text{ K}$$

and

$$\Delta T_2 = (9.1 \pm 0.07) \text{ K}$$

**Step 3.** Determine the corresponding change in enthalpy using the following formula.

$$\Delta H^\circ = -C\Delta T \frac{MW_{\text{ethanol}}}{\Delta g}$$

We find

$$\Delta H_1^\circ = -3.06 \times 8.8 \times \frac{46.021}{0.942} = -1,315.556 \text{ kJ/mol}$$

and

$$\Delta H_2^\circ = -3.06 \times 9.1 \times \frac{46.021}{0.898} = -1,427.061 \text{ kJ/mol}$$

The corresponding errors are given by

$$RE(\Delta H_1^\circ) = \sqrt{\left(\frac{0.02}{3.06}\right)^2 + \left(\frac{0.07}{8.8}\right)^2 + \left(\frac{0.7}{942}\right)^2} = 0.0103$$

and

$$RE(\Delta H_2^\circ) = \sqrt{\left(\frac{0.02}{3.06}\right)^2 + \left(\frac{0.07}{9.1}\right)^2 + \left(\frac{0.7}{898}\right)^2} = 0.0101$$

From this we get

$$AE(\Delta H_1^\circ) = 0.0103 \times 1,315.556 \approx 14 \text{ kJ/mol}$$

$$AE(\Delta H_2^\circ) = 0.0101 \times 1,427.061 \approx 14 \text{ kJ/mol}$$

4. Compute the average value of the enthalpy of combustion and the error.

$$\overline{\Delta H^\circ} = -1,371.309 \text{ kJ/mol}$$

and

$$AE(\overline{\Delta H^\circ}) = \frac{1}{2} \sqrt{14^2 + 14^2} \approx 10 \text{ kJ/mol}$$

## Conclusion 2

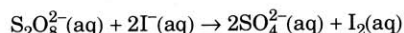
The enthalpy of combustion of ethanol is given by

$$\Delta H^\circ = (-1,370 \pm 10) \text{ kJ/mol}$$

## Determination of the Rate Constant (*k*) of a First-Order Reaction

### Problem

The reaction we have studied



is a pseudo-first-order reaction when the concentration of  $\text{I}^-$  is in excess. Thus,

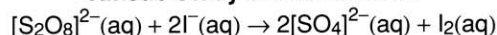
$$v = k'[\text{S}_2\text{O}_8^{2-}]$$

and

$$k' = k[\text{I}^-]$$

Determine the rate constant (*k*) and its error for this reaction.

## Kinetic Study of the Reaction



time (min)	$[\text{I}_2]$ ( $10^{-3}$ mol/L)	$[\text{K}_2\text{S}_2\text{O}_8]$ ( $10^{-3}$ mol/L)	$\ln [\text{K}_2\text{S}_2\text{O}_8]$
2.11	1.473	6.045	-5.1085
5.03	2.723	4.795	-5.3042
7.03	3.404	4.114	-5.4934
12.08	4.724	2.794	-5.8803
20.04	5.989	1.529	-6.4831
30.08	6.812	0.706	-7.2559
40.07	7.213	0.305	-8.0952
55.12	7.427	0.091	-9.3047

Data obtained at 25 °C.

## Procedure

Start with a known concentration of  $\text{K}_2\text{S}_2\text{O}_8$ , and follow the decrease in concentration as a function of time. A measure of this decrease is the formation of  $\text{I}_2$ , which can be determined by titration with  $\text{Na}_2\text{S}_2\text{O}_3$ . The data of the table were obtained at 25 °C.

## Determination of *k*

Because we know that the reaction is first-order, it follows that

$$[\text{S}_2\text{O}_8^{2-}] = \alpha e^{-kt}$$

where  $\alpha = [\text{S}_2\text{O}_8^{2-}]_0$ .

Thus, taking logarithms converts this to a linear equation.

$$\ln [\text{S}_2\text{O}_8^{2-}] = \beta - kt$$

with

$$\beta = \ln \alpha$$

We therefore make a plot of  $\ln [\text{S}_2\text{O}_8^{2-}]$  against time and draw the best straight line by means of the least-squares method (4, 5). This yields the following estimates for the slope and intercept of the straight line.

- intercept =  $\beta = -4.9280$  (*se* = 0.0145)
- slope =  $k = 0.0789$  (*se* = 0.0005)

where *se* stands for standard error.

The determination of the standard error is slightly complicated, but any statistical package will yield it as part of its default output. Although the actual formula to compute this standard error looks different from the one we used to compute the standard deviation of the mean, conceptually they are identical. The standard error measures the variation obtained when these coefficients are calculated for an infinite repetition of the experiment. Hence, in accordance with our definition of the theoretical absolute (statistical) error in part I it follows that 3 times this standard error will yield the absolute error on the coefficient.

Because we are only interested in *k* (i.e., the slope) we conclude that

$$AE(k) = 3se(k) = 3 \times 0.0005 \approx 0.002 \text{ min}^{-1}$$

Thus, we get

$$k = (0.079 \pm 0.002) \text{ min}^{-1}$$

The results of the regression analysis allow us to estimate the error on the initial concentration  $\alpha = [\text{S}_2\text{O}_8^{2-}]_0$ . We know that  $\alpha = e^\beta = 7.241 \times 10^{-3}$ . Thus,

$$RE(\alpha) = AE(\beta)$$

(compare to eq 11 of part I)

$$AE(\beta) = 3 \times 0.0145 = 0.04$$

which is the definition of the theoretical absolute error from part I.

From this we get

$$AE(\alpha) = 0.04 \times 7.241 \times 10^{-3} = 0.3 \times 10^{-3} \text{ mol/L.}$$

Therefore

$$[\text{S}_2\text{O}_8^{2-}]_0 = (7.2 \pm 0.3) \times 10^{-3} \text{ mol/L}$$

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