EXPERIMENT 10
EVALUATION OF DATA BY THE STANDARD DEVIATION METHOD

PURPOSE:

1. To find the Mean Value for the "Molarity of a Solution of NaOH standardized by pH titration, based on the experimental data collected in Experiment 9.
2. To become familiar with the concept of Precision.
3. To estimate validity of experimental data.

PRINCIPLES:

Precision is the dispersion of, or closeness of the agreement between successive measurements of the same quantity.
The dispersion in a set of measurements is usually expressed in terms of the **standard deviation,** whose symbol is **"s"**

$$\mathbf{s} = \left[\frac{\Sigma d_i^2}{N - 1}\right]^{1/2}$$

where:

Σ	=	**means the "the sum of"**
d_i	=	$X_i - \bar{X}$ **= deviation**
X_i	=	**a particular value of a measurement**
$\bar{X}$	=	**the Mean Value**
N	=	**the number of measurements**

In order to calculate "**s**" (the standard deviation) the Mean Value ($\bar{X}$) needs to be calculated first.

$\bar{X}$ = **the Mean Value**

$$\bar{X} = \frac{\Sigma X_i}{N}$$

Measurements with high precision are narrowly dispersed, and these measurements have a smaller standard deviation than measurements with lower precision.
Unless the number of measurements of the same quantity is very large, the calculated value of the standard deviation is only an estimate of the true standard deviation. Nevertheless, even a limited set of measurements will allow an estimate of the dispersion in the measurements to be judged.

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How is the formula to calculate "**s**" (standard deviation) used?

The formula states:

Find the sum of the squares of the deviations, divide by one less than the total number of measurements, and take the square root of the result.

The example below illustrates the use of the formula.

We aim to determine the molarity of a solution of NaOH with the highest possible precision. by performing five titrations

The values of the respective molarities calculated from the five titrations **(Xi)** are:

0.09980 M, 0.1011 M, 0.1025 M, 0.1014 M and 0.1009 M

The calculation of the standard deviation of these results is shown in the table below.

Note: Using the same exponent to express the Squared Deviations simplifies the calculations and the interpretation of the values obtained

	Value of Measurement X_i (Molarity of NaOH)	**Deviation d_i $d_i = (X_i - \bar{X})$**	**Squared Deviation d_i^2**
1	**0.09980**	**0.0013**	**1.7×10^{-6}**
2	**0.1011**	**0.0000**	**0.00000000**
3	**0.1025**	**0.0014**	**2.0×10^{-6}**
4	**0.1014**	**0.0003**	**0.09×10^{-6}**
5	**0.1009**	**0.0002**	**0.04×10^{-6}**
Σ (Sum of)	**0.5057**		**3.83×10^{-6}**
$\bar{X}$ (Mean Value)	**0.1011**		

$$\textbf{Mean} = (\bar{X}) = \frac{\Sigma X_i}{N} = \frac{0.5057}{5} = 0.1011 \text{ M}$$

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$$\mathbf{s = \left[\frac{3.83 \times 10^{-6}}{5 - 1}\right]^{1/2} = 0.00098}$$

When a quantity, such as the molarity of a solution, is determined several times, it is customary to report the mean value. The dispersion or precision of the experimental data can be indicated, according to one custom, by writing ± the calculated value of "**s**" after the mean.

Thus we would report: 0.1011 M ± 0.00098

The standard deviation "**s**" must be rounded off to four decimals (**0.0010**) because there are only four figures to the right of the decimal point in the mean.

Hence, when we report **0.1011 M ± 0.0010** as the best value for the molarity, we are stating that the molarity of the solution probably lies between:

0.1011 M + 0.0010 = 0.1021 M

and

0.1011 M - 0.0010 = 0.1001 M

The correct number of significant figures in a mean value will always be the number of certain digits plus one uncertain digit. In the example above we have shown that the molarity of the solution probably lies between:

0.1001 M and 0.1021 M

with a Mean Value of 0.1011 M.

Clearly, the first two decimals in the mean value are certain, and uncertainty occurs in the third decimal:

0.10**0**1 M and 0.10**2**1 M

certain uncertain certain uncertain

However, the measuring devices (Analytical Balance and Buret) used to obtain the experimental data justify four significant figures in the value of the mean value (three certain digits and one uncertain digit).

0.1011 M

certain uncertain

This indicates that the precision of the five titrations is poor and therefore will justify only three significant figures, even though four significant figures were obtained in each measurement.

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Therefore one must admit than one or several of the titrations is (are) in error and it (they) should be discarded. Then, the **Mean** should be recalculated (using the remaining measurements) until an answer could be given in four significant figures.
Logic suggests that the third measurement **(0.1025 M)** be discarded since it is the one with the highest deviation **(0.0014)**

	Value of Measurement X_i (Molarity of NaOH)	**Deviation d_i $d_i = (X_i - \bar{X})$**	**Squared Deviation d_i^2**
1	**0.09980**	**0.0010**	**10×10^{-7}**
2	**0.1011**	**0.0003**	**0.9×10^{-7}**
4	**0.1014**	**0.0006**	**3.6×10^{-7}**
5	**0.1009**	**0.0001**	**0.1×10^{-7}**
Σ (Sum of)	**0.4032**		**15×10^{-7}**
$\bar{X}$ (Mean Value)	**0.1008**		

$$s = \left[\frac{15 \times 10^{-7}}{4 - 1}\right]^{1/2} = 0.00071$$

Thus we would report: 0.1008 M ± 0.00071
The standard deviation "**s**" must be rounded off to four decimals (**0.0007**) because there are only four figures to the right of the decimal point in the mean.
Hence, when we report **0.1008 M ± 0.0007** as the best value for the molarity, we are stating that the molarity of the solution probably lies between:

0.1008 M + 0.0007 = 0.1015 M
and
0.1008 M - 0.0007 = 0.1001 M

One more time, the uncertainty occurs in the third decimal. Therefore an answer cannot be given in the required four significant figures.

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Therefore a second analysis of the deviations and a second discard of an odd titration is in order. Logic suggests that the third measurement to be discarded is the one with the highest deviation (**0.1025 M)**

	Value of Measurement X_i (Molarity of NaOH)	**Deviation d_i $d_i = (X_i - \overline{X})$**	**Squared Deviation d_i^2**
2	**0.1011**	**0.0000**	**0.00000000**
4	**0.1014**	**0.0003**	**9×10^{-8}**
5	**0.1009**	**0.0002**	**4×10^{-8}**
Σ (Sum of)	**0.3034**		**13×10^{-8}**
$\overline{X}$ (Mean Value)	**0.1011**		

$$s = \left[\frac{13 \times 10^{-8}}{3 - 1}\right]^{1/2} = 0.000255$$

Thus we would report: 0.1011 M ± 0.000255

The standard deviation "**s**" must be rounded off to four decimals (**0.0003**) because there are only four figures to the right of the decimal point in the mean.
Hence, when we report **0.1011 M ± 0.0003** as the best value for the molarity, we are stating that the molarity of the solution probably lies between:

0.1011 M + 0.0003 = 0.1014 M
and
0.1011 M - 0.0003 = 0.1008 M

The range of the Mean Value is: 0.1014 M – 0.1008 = 0.0006

Note that the values within this range are ≤ 0.0006, which is the fourth decimal.

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This time the first uncertain digit is in the fourth digit.
The precision of these data is acceptable since it reports an answer in four significant figures, consistent with the four digits obtained in each titration.
The result should be reported as: **0.1011 M ± 0.0003**

Acceptable Range of Values:

Another helpful way to look at what is an acceptable Range of Values is to realize that the range of values should be less than 0.0010 M (no variations in the third decimal).

Acceptable Standard Deviation

For the Range of Values to be less than 0.0010 M, the Standard Deviation should be less than 0.0005, as in the example presented above.
(Note that the Range of Values is double the value of the Standard Deviation)

It must be noted however, that at least more than half of the measurements (in our case this is three titrations out of five) must be included in the calculation of the Mean, or otherwise the value reported is meaningless.
If this is not possible, it must be concluded that the experimental data collected is so poor (lacks precision) that additional titrations must be performed.
Collecting additional experimental data from additional titrations will allow to obtain a lower value for the standard deviation, by allowing us to discard a larger number of titrations that are in error.

PROCEDURE:

Report the Mean Value for the Molarity of the NaOH solution to four significant figures based on the experimental data collected from at least five titrations.
Include the acceptable standard deviation in your answer.
The Report Form includes worksheets for your convenience.
Use as many worksheets as appropriate and show your calculations in the same manner as they have been presented in the example.
Attach all your worksheets to your report in the order you have used them.

Bibliography:

R.A.D. Wentworth “Experiments in General Chemistry”, Sixth Edition

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REPORT FORM

NAME: ________________________________ Date: _____________

Table 1
Include all experimentally determined molarities

	Value of Measurement X_i (Molarity of NaOH)	**Deviation d_i $d_i = (X_i - \bar{X})$**	**Squared Deviation d_i^2**
1			
2			
3			
4			
5			
6			
7			
Σ (**Sum of)**			
$\bar{X}$ **(Mean Value)**			

s = [ ]

Molarity of the NaOH solution: [± **(M)**]

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NAME: ________________________________ Date: _____________

Table 2
Include the remaining molarities after one molarity has been discarded.

	Value of Measurement X_i (Molarity of NaOH)	**Deviation d_i $d_i = (X_i - \overline{X})$**	**Squared Deviation d_i^2**
1			
2			
3			
4			
5			
6			
7			
Σ (**Sum of)**			
$\overline{X}$ **(Mean Value)**			

s = [ ]

Molarity of the NaOH solution: [± **(M)**]

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NAME: ________________________________ Date: _____________

Table 3
Include the remaining molarities after two molarities have been discarded

	Value of Measurement X_i (Molarity of NaOH)	**Deviation d_i $d_i = (X_i - \bar{X})$**	**Squared Deviation d_i^2**
1			
2			
3			
4			
5			
6			
7			
Σ (Sum of)			
$\bar{X}$ (Mean Value)			

s = ________

Molarity of the NaOH solution: ________ ± ________ **(M)**

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NAME: ________________________________ Date: _____________

Table 4
Include the remaining molarities after three molarities have been discarded

	Value of Measurement X_i **(Molarity of NaOH)**	**Deviation** d_i $d_i = (X_i - \bar{X})$	**Squared Deviation** d_i^2
1			
2			
3			
4			
5			
6			
7			
Σ (**Sum of)**			
$\bar{X}$ **(Mean Value)**			

s = [ ]

Molarity of the NaOH solution: [± **(M)**]

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NAME: ________________________________ Date: _____________

Complete this page only after all the calculations have been done and the calculated standard deviation has a value that indicates that the precision of the data on which this Molarity is based is acceptable.

Molarity of the NaOH solution:	± **(M)**

The Molarity probably lies between:		**and**	

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