

Williams College Chemistry Department

Evacuation Procedures

In case of power failure:

1. Follow the procedures outlined by the instructor or research advisor.
2. The emergency lighting system will activate automatically but some areas may be dark.
3. Check the building to see if anyone needs help in getting out of restricted areas.
4. Turn off all computer equipment to avoid possible equipment damage from line surges when power is restored.

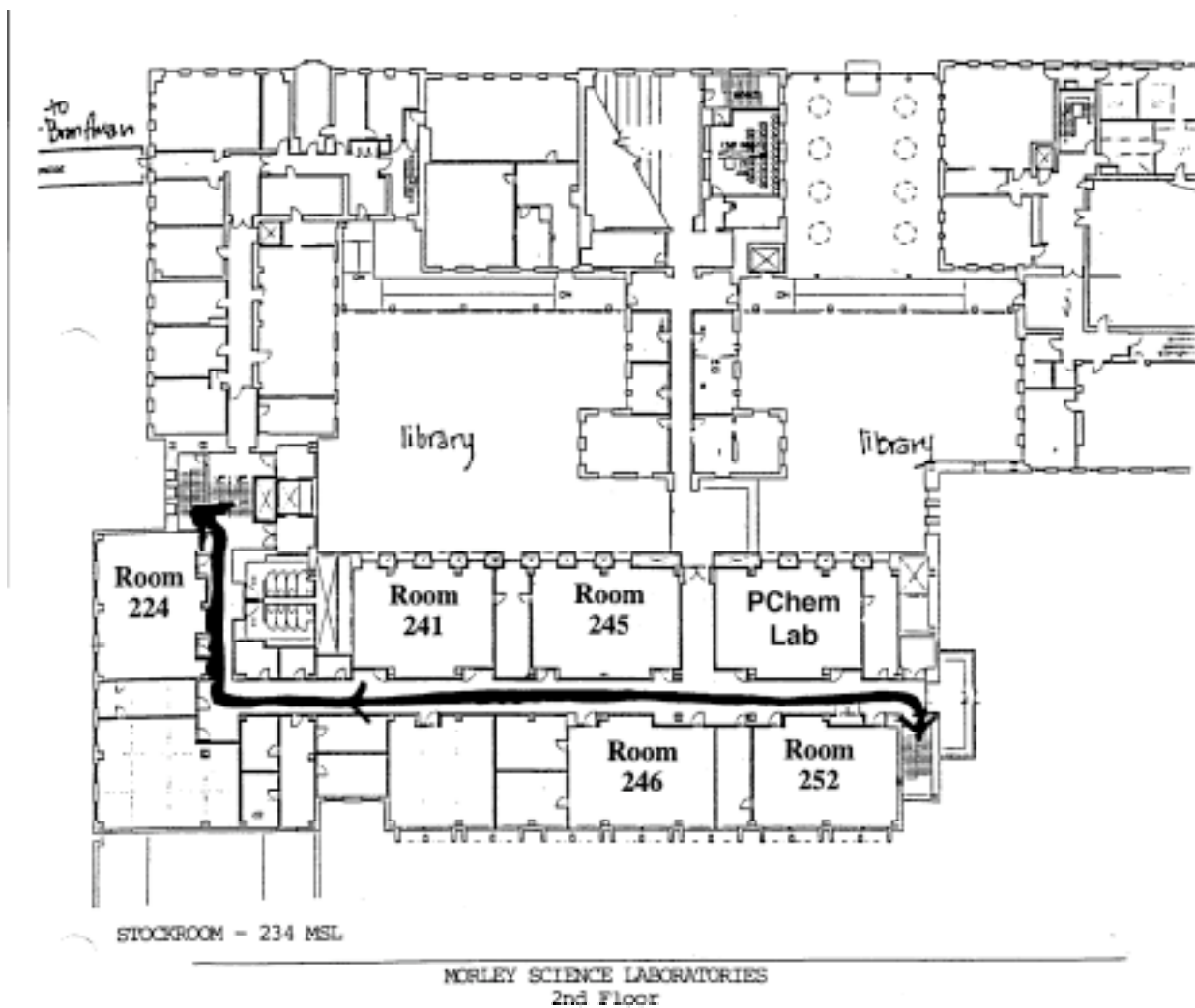
In case of fire or other emergency requiring evacuation:

1. Pull the alarm.
2. Evacuate the building.

Evacuation Procedures:

1. Stay as calm as possible.
2. In an orderly fashion leave by the closest safe exit. The emergency lighting system and emergency exit signs will guide you to these exits, and the diagrams on the accompanying sheets will show general evacuation routes from the labs and the classrooms.
3. Nothing should interfere with the timely and safe evacuation of the building, however, depending upon the circumstances, it may be advisable to turn off equipment that could create an additional hazard.
4. While leaving, do not stop to search the building or argue with others who do not want to leave. Security Officers will take the responsibility for making sure the building is being evacuated.
5. In case of fire, feel any door for heat before opening. If it is hot, use an alternate route. If it is cool, open slowly. If there is smoke, close the door and use an alternate route.
6. Go to the middle of the Morley turnaround circle (by the "fountain" sculpture), well away from the building so that all students and staff may be accounted for.
7. Do not re-enter the building until you are authorized to do so by a Security Officer.

Evacuation Map



EMERGENCY PROCEDURES

NOTIFY INSTRUCTOR OF ANY ACCIDENT. WHEN IN DOUBT ABOUT THE SERIOUSNESS OF PERSONAL INJURY, SEEK THE HELP OF A PHYSICIAN IMMEDIATELY.

FIRE - Telephone: 9-911
SECURITY - Telephone: 4444
PHYSICIAN - Telephone: 2206
AMBULANCE - Telephone: 9-911
POISON INFORMATION - Telephone: 9-1-800-682-9211

BLEEDING - if serious, stop the flow of blood by applying direct pressure to the wound with a sterile pad or cloth. Have the patient lie down and elevate the bleeding extremity. **AVOID** a tourniquet unless the patient's life is at stake. **CALL A PHYSICIAN AT ONCE.**
- if minor, wash the wound, remove any pieces of glass, disinfect the wound and apply a sterile bandage.

BURNS - if serious, **CALL PHYSICIAN AT ONCE.** Treat as for **SHOCK.** Wound may be covered with several layers of sterile gauze. Avoid ointments and other medications.
- if minor, involving merely reddening of a small area, place affected part in cold water or ice for several minutes. Apply burn ointment, if desired. If blisters develop, consult a physician.

CHEMICALS

- A. **IN EYES** - flush with large amounts of cool water from the nearest source while holding the eyelid away from the eye. When the bulk of the chemical is gone, continue the washing at an eyewash fountain for at least 15 minutes. Do not attempt chemical neutralization.
- B. **INHALED (FUMES)** - remove patient to fresh air. Keep patient warm and quiet. Begin artificial respiration at once if breathing has stopped. **CALL PHYSICIAN IMMEDIATELY.**
- C. **SWALLOWED** - if patient is conscious, quickly administer several (2-4) glasses of water and induce vomiting by tickling back of throat. **DO NOT INDUCE VOMITING** in case of acids, bases, organic solvents or petroleum products. Vomiting may be induced with lukewarm salt water (one tablespoon of salt per glass). **CALL PHYSICIAN AT ONCE.**
- D. **ON SKIN** - flush away chemicals immediately with large quantities of cold water. Use the safety shower, if required. Remove all contaminated clothing. Prolonged washing is essential. For organic chemicals after an initial wash with water, scrub the skin thoroughly with soap and water. Then treat as a thermal burn. **DO NOT** apply any oils or ointments.

FAINTING - lower the patient's head and raise feet. Move patient to fresh air. Do not administer liquids while patient is unconscious.

FIRE

- A. CLOTHING - do not run. Avoid inhalation of fumes. Roll on floor to smother flames. Wrap the person in a woolen blanket or apply coats or wet towels. A CO₂ type fire extinguisher may be used with caution (away from patient's head). The safety shower may be used only if very close by.
- B. CHEMICALS - leave the vicinity at once, turning out all flames if possible. Extinguish fire with CO₂ type extinguisher.

SHOCK - keep the patient quiet, lying down and comfortable. Keep the patient warm, and make sure that the patient has an adequate supply of fresh air. Reassure the patient until medical help is obtained.

LABORATORY REGULATIONS

1. Carry out all experiments and manipulations in accordance with instructions, laboratory regulations and accepted procedures to insure the health and safety of all persons working in the laboratory.
2. To protect the eyes, all students and staff working in the laboratory must wear safety goggles which may be obtained from the stockroom. In physical chemistry laboratory you must wear your goggles when preparing solutions, using a vacuum system or manipulating high pressure gas cylinders. Due to certain hazards, CONTACT LENSES are not recommended in the laboratory. Wearers of such lenses should use alternate glasses in the laboratory and consult the campus safety officer, Dr. Skinner.
3. Do not conduct any unauthorized experiments.
4. Do not remove chemicals or apparatus from the laboratory for any reason at any time.
5. Work in the laboratory only during regularly scheduled laboratory periods except when special permission is granted by the instructor.
6. Never work alone in the laboratory.
7. Shoes must be worn in the laboratory at all times. Sandals and open-toe shoes do not provide adequate protection.
8. Hair must be restrained to keep it from accidental contact with flames and chemicals.
9. Smoking is not permitted in the Chemistry Building.
10. Neither eating nor drinking are permitted in a laboratory. Use the fountain at the building entrance.
11. Secure the approval of the Dean for all absence excuses and requests for changes in laboratory periods. First, please consult your instructor with any questions.

LABORATORY PROCEDURES

1. Every student in the laboratory must be familiar with the location and use of the nearest shower, eye-wash fountain, fire blanket, first-aid kit, fire extinguisher, and fire exit.
2. Observe all of the following in your laboratory work:
 - a. Pay attention to the proper disposal for all chemicals, solid or liquid.
 - b. Do not put solids or paper in the sinks.
 - c. When nonpoisonous acids or strong bases are poured into the sinks, wash them down with plenty of water. Deposit all organic solvents and all potentially harmful inorganic solutions and residues in the WASTE receptacles provided in the laboratory. Deposit all other liquid waste into the proper (general solvents, halogenated solvents or heavy metals) waste receptacle in the hood. Use minimal amounts of wash acetone.
 - d. Dilute or neutralize, then sponge up promptly any acids or corrosive liquids spilled on the desks or floor. Use plenty of water to wash them off.
 - e. Never heat a closed system, e.g., a stoppered flask.
 - f. Never heat organic solvents over an open flame. Use a steam bath or an electric hot plate with care. Do not pour or work with organic solvents when flames are in the vicinity. Avoid the storage of large quantities of flammable solvents in your laboratory. Use the stainless-steel safety containers.
 - g. Do not pour reagents above eye level.
 - h. Do not let chemicals contact your skin. Handle solids with a spatula or other appropriate device. Handle volatile organic liquids only when there is adequate ventilation, preferably in the fume hood.
 - i. Do not hold apparatus near face while mixing or heating reagents or observing reactions.
 - j. No open flames are permitted in the organic laboratory except by specific permission of the instructor. When permitted in any course, connect burner tubing to the gas outlet most distant from the apparatus to permit turning off gas with a minimum of danger in case of accident.
 - k. Never taste chemicals of any kind. Do not pipet by mouth.
 - l. When handling glassware, observe the following:
 - (i) Fire-polish the ends of all glass tubing.
 - (ii) When inserting glass tubing or thermometers into stoppers, be sure that the hole is large enough to accommodate the glass. Lubricate the tubing with water or glycerol. Hold the tubing in a towel and hold the stopper between thumb and forefinger, not in the palm of the hand. Grasp the tubing close to the stopper and rotate slightly while pressing.

- (iii) Do not attempt to push or pull glass tubing from stoppers or tubing which has become hardened. Cut the cork or rubber away from the glass.
- (iv) Do not force an oversized stopper into the mouth of a flask, bottle, or test tube.
- (v) Do not use glassware that is nicked or cracked.
- m. Do not waste distilled water. Use a wash bottle when one is provided.
- n. Never use an ordinary wash bottle for organic solvents, e.g., acetone, alcohol. We have specially labeled bottles for various solvents. Use minimal volumes of wash acetone.
- o. Do not return unused reagents to the reagent bottle. Return reagents to proper place on the shelf. Do not use droppers to withdraw reagents from stock bottles except when stock bottles are so equipped.
- p. At the end of each laboratory period wash your work area with water, using a sponge, and remove excess with a rubber squeegee. Wash your hands thoroughly before leaving the laboratory.
- q. Put all your apparatus away. Be sure gas, water and lights are shut off where you have been working.
- r. The last person out of the laboratory should shut off the lights and the appropriate hoods.

LABORATORY NOTEBOOK

All experimental data and observations must be entered, at the time they are taken, in ink (pencil and felt-tip pen smudge and become illegible and are unacceptable), directly into a bound notebook. Loose pieces of paper used to record data are not permitted. Do not erase data or tear pages out of the notebook. If an analysis is discarded, cross or line it out. Begin a new page for each experiment, with date and title on it. A laboratory notebook is an official document in any research work. Emphasis should be on keeping it up to date, legible and well organized.

LABORATORY REPORTS

One of the most important and highly valued skills that you develop during your college education is the ability to communicate information, both in speech and in writing, clearly and concisely to another person. Whatever you are doing ten years from now, your success will depend on your ability to communicate.

As a result of the special nature of much of the equipment in this laboratory, only one set-up for most experiments is available. This means that the order in which the experiments are done will not necessarily follow the lecture material. In order that a student perform the experiments intelligently, quickly and with maximum benefit, preliminary reading will have to be done *before coming to the laboratory*.

Each experiment will be graded not only on the basis of the precision and accuracy of the results but also on the quality, content and neatness of the report. These reports are to be written in a good literary style and should follow the outline given below. Poor spelling and sloppy writing will not be tolerated. Typing is preferred but not required. Reports written in pencil will not be accepted.

You should be aware of several books that are useful references for report writing.

The ACS Style Guide, A Manual for Authors and Editors, Janet S. Dodd (American Chemical Society, Washington, D. C., 1986).

Style Manual, 3rd Edition, D. Hathwell and A. W. K. Metzner, Eds. (American Institute of Physics, New York, 1978).

The Elements of Style, William Strunk, Jr. and E. B. White, 3rd Edition (Macmillan, New York, 1979).

The Chemist's English, Robert Schoenfeld (VCH Verlagsgesellschaft, Weinheim, 1985).

Handbook for Authors (American Chemical Society, Washington, D. C., 1978).

You may find it helpful to look in journals (such as *Journal of Physical Chemistry*, *Journal of Chemical Physics*, *Chemical Physics Letters*, or *Physical Chemistry Chemical Physics*) to see how published articles are formatted.

Your Chemistry 366 laboratory report should be written in such a way that any chemist, not only your own instructor, can completely understand what you have done.

A Chemistry 366 laboratory report should include:

- i) Title page
Title of experiment

Performed by:

Partner:

Date performed:

Date submitted:

Chemistry 366

Williams College

Williamstown, MA

- ii) **Introduction**
This section should contain a clear description, in **your own words**, of the purpose of the experiment with background material sufficient to place the purpose in context. Based on your results you may want to raise certain questions that are answered by the experiment.
- iii) **Experimental**
A very brief (~5 sentences) summary of how the experiment was performed should be included. Note any significant deviations from the lab manual's procedure
- iv) **Results**
This section should include all the relevant data in a clear and organized fashion (e.g. in tabular form). You should introduce all of your tables with text, perhaps pointing out what the reader should note in each table. Each table, figure, and equation should be numbered. Tables and Figures should be given titles.
- v) **Calculations and Error Analysis (may wish to include with results)**
In this section, show how you calculate your results, giving literature references for both important equations and accepted values against which you wish to compare your values. Tables and graphs are often the best methods for presenting your results. Each table should be labeled and a descriptive title should be included (e.g. Table 1. Titration curve of a mixture of hydrochloric acid and phosphoric acid). Any figures should be treated similarly.

Together with a calculation of your final experimental values, you also want to put those numbers into perspective.

You are no longer in high school, where you may have gotten credit for listing as many sources of error as possible (major or absurdly minor). Now we want to discuss *and evaluate* the important sources only.

"The reported value of a physical quantity has little meaning unless it is accompanied by a statement of its uncertainty."¹

*Report your final results together with the uncertainty based on the precision and repeatability (see below) of the data obtained. (e.g., $\Delta H_{\text{vap}} = 40. \pm 3. \text{ kJ/mole}$). From the uncertainty in the measurements, you should be able to calculate an uncertainty in your final numbers. This uncertainty is not the same as the deviation from the literature value (that you should also report if a literature value is available).

v) **Discussion**

This section should explain any agreement and/or disagreement between theory, your experimental results, and the literature values. Also comment on the appropriateness of the method and make suggestions for improvements in the method and/or calculations.

vi) **Summary**

Give a one or two paragraph overview of your work, specifically highlighting the main conclusions or findings that the reader should remember from your report.

vii) **References**

All literature information specifically referred to in the written text or in numerical tables or used as general background in your Report must be accurately listed. A reader must not be left in doubt as to the origin of your information. For example

The sample of ethyl benzoate was dried in the manner suggested. The proton NMR spectrum of ethyl benzoate was recorded in the prescribed manner.² As there was insufficient deuterated compound to record a spectrum, the data of Jones and Smith³ were used in calculating the results for that compound. The observed value of 12.5Hz for the methyl proton-methylene proton coupling constant, J, is in satisfactory agreement with the literature value⁴ of 12.9Hz.

Sample References

1. Modern Chemical Instrumentation (Chemistry 304), Williams College Laboratory Instructions, prepared by James F. Skinner, p. 18, 1988.
2. Reference 1, p. 21.
3. Laboratory results of Mary R. Jones '88 and David F. Smith '89.
4. I. H. Williams, G. M. Maggiora, and R. L. Schowen, *J. Amer. Chem. Soc.* **102**, 7831 (1980).

Common writing errors in scientific reports

1. You should write in complete sentences, using present or past tense with a subject and a verb. Break up your writing with paragraphs. Use past tense for things you did. Use present tense for things that are still true now. (e.g., "The data show...")
2. You should use a dictionary regularly.
3. Unfortunately, the preferred writing style in scientific reports varies significantly. Generalizing, organic chemists tend to prefer totally avoiding the first person (I or we) and often using passive voice.
"The temperature was measured to be 32°C." (Does not specify who took the temperature.)

The editors in physical chemistry journals are trying to get people away from using passive voice and instead using more active voice where the subject of the verb is explicitly included in the sentence. However, physical chemists still disagree on how best to do this.

One way is to rearrange your sentences, still avoiding I or we, but including the subject. This will satisfy almost everybody as long as the sentence does not become awkward.

"The measured temperature was 32°C." or "The temperature was 32°C."

Some people think it is acceptable to use "we" but not "I" (even if you alone did the action). Others feel that it is perfectly acceptable to use "I," as long as you don't use it in every single sentence.

In all cases, do try to vary your writing by using different sentence constructions, particularly in the experimental section where it is easy to drone on monotonously.

4. You should minimize splitting infinitives:
"to effectively measure" should be "to measure effectively".
5. You should eliminate unnecessary words: "The procedure was used in order to determine..." could be "The procedure was used to determine..." or even "The procedure served to determine..."
6. You should avoid colloquial expressions: "The Cary 219" should be "The Cary 219 spectrophotometer."
7. "Absorption" is a general word. "Absorbance" = ϵbC (Beers Law). "Adsorption" refers to something adhering to a surface.
8. "Data", like strata, phenomena and media, is a plural word. "The data are given in the table".
9. "Affects" is the action (the verb) and "effects" is the result (the noun). "The breeze in the room affected the experiment." "The effect of the breeze was to mess things up totally." ("Effects can also be a verb meaning "to bring about." "He effected a change in the law.")
10. Set equations apart from written text and assign numbers, written to the far right of equation.
11. Number all pages of your report.

Spreadsheets

Familiarize yourself with the commercially available software packages that permit rapid tabulation and manipulation of numerical results. There is an introduction to Excel and KaleidaGraph later in this manual.

While carefully prepared, hand-drawn graphs are perfectly acceptable, you should familiarize yourself with some of the excellent commercially available computer software for drawing graphs. The example given below was prepared with Cricket Graph, a now outdated program.

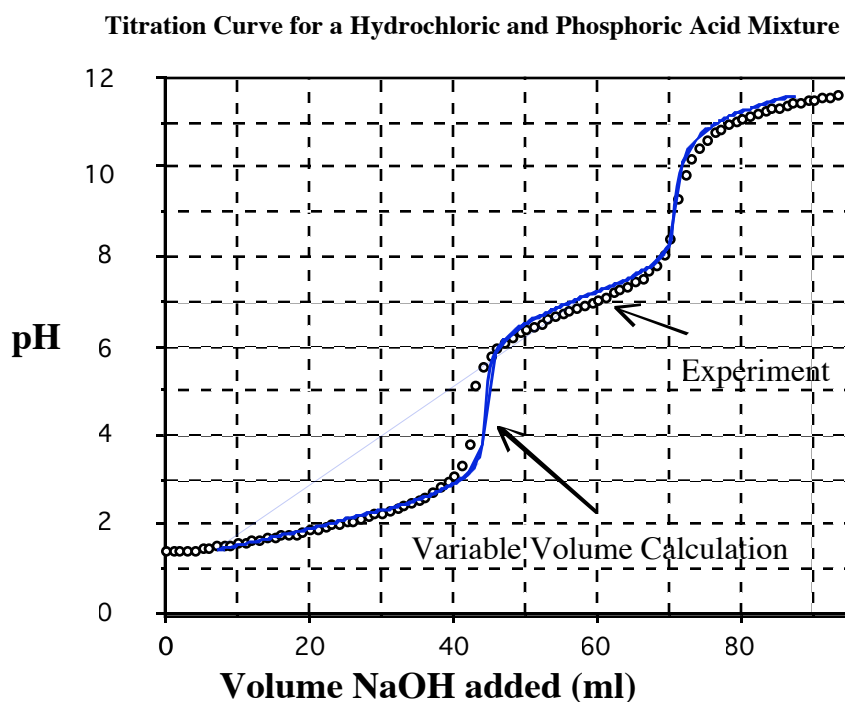


Figure 1. Titration curve of a mixture of hydrochloric acid (HCl) and phosphoric acid (H_3PO_4). Data taken by K. Queeney '92.

TREATMENT OF EXPERIMENTAL DATA

Scientific Notation, Significant Figures

It is customary in scientific work to write a number with the decimal point immediately to the right of the first nonzero digit and to indicate the magnitude of the number by an exponent. It is then understood that there is some uncertainty in the most right-hand digit, usually plus or minus 2. For example, 0.00000190 and 186,175.3 should be written as 1.90×10^{-6} and 1.861753×10^5 with three and seven significant figures, respectively. A calculated result can have no more significant figures than the least number of significant figures found in a piece of data used to calculate the result. Remember that electronic calculators give extraneous digits.

Errors

"By errors we do not mean disasters or blunders - instructors will have their own treatment for students who perpetrate these. Instead, we use the term error to describe the unfortunate tendency of any actual experimental result to be different from the true value of the parameter being measured."²

There are two distinct but equally important goals in presenting a numerical result. The first involves an indication of the *uncertainty* inherent in your value and the second involves a comparison of your value with an accepted value for this quantity. The term "error" is loosely applied to both of these factors.

The first goal encompasses what is referred to as precision or the closeness of approach of a number of replicate results to the average value of these results in a series of measurements. Poor precision is associated with a wide scatter of the individual determinations about the average value. Some scientists make a further distinction between precision and repeatability. In this way, the precision denotes the quality of the measuring instrument whereas the repeatability reflects the different values (judgements) that one or more persons would obtain in attempting to use this instrument for successive readings. Inadequate control of experimental conditions, e.g., temperature, might also affect repeatability.

The second goal aims to indicate the *accuracy*, the closeness of approach of the average measured result to the true or accepted value of the quantity that is being measured.

For example, a student could have made five determinations of the dissociation constant, K_a , of acetic acid:

$$\begin{aligned} &1.637 \times 10^{-5} \\ &1.647 \times 10^{-5} \\ &1.589 \times 10^{-5} \\ &1.619 \times 10^{-5} \\ &1.641 \times 10^{-5} \end{aligned}$$

The study might have been summarized by stating the observed value of K_a in one of the following ways:

- i) $(1.627 \pm 0.002) \times 10^{-5}$
- ii) $(1.627 \pm 0.010) \times 10^{-5}$
- iii) $(1.627 \pm 0.018) \times 10^{-5}$
- iv) $(1.627 \pm 0.023) \times 10^{-5}$
- v) $(1.627 \pm 0.029) \times 10^{-5}$
- vi) $(1.627 \pm 0.045) \times 10^{-5}$

It is certainly not clear what is indicated by the precision. In (i), the student may have just followed the rule that there is ± 2 uncertainty in last significant digit of a number. In (ii), the student may have made some estimate of the experimental uncertainties in making the measurements from which K_a was calculated and came up with the figure ± 0.010 . In (iii), the *average deviation*, i.e., the sum of the absolute values of the individual deviations of each of the five values divided by 5, is noted. In (iv), a range of \pm one *standard deviation*, σ (see below), is given. In (v), one-half of the total range from the lowest to the highest value is given. And finally, in (vi), the "95% confidence level" or $\pm 1.96\sigma$ is indicated. Clearly one must specify how one determined the *precision*.

Finally, if the literature value of K_a is 1.778×10^{-5} ,³ the *accuracy* would be noted as

$$100\% \times \frac{|1.778 \times 10^{-5} - 1.627 \times 10^{-5}|}{(1.778 \times 10^{-5})}$$

or 8.5%. The observed mean differs from the accepted value by 8.5%.

It is important to distinguish between the *random* errors and the systematic errors that contribute to the precision. (A *systematic* error may also affect the accuracy.) If you used an electronic balance correctly and determined the mass of a single object several times, you would get a series of values, some slightly above the mean, some slightly below the mean, the result of judgement in reading the scale and lack of perfect response by the balance. These different values are the result of random errors.

But if you had neglected to zero the balance or the calibration of the standard masses in the balance was in error, all your measured masses would be either too large or too low. These would constitute systematic errors.

Standard Deviation

Random errors in repeated measurements x_i , of the quantity x , for a large number of determinations N , result in a normal or Gaussian frequency distribution of the individual values of x about the average or mean value \bar{x} . Such a distribution is given by the following analytical function:

$$P(x_i - \bar{x}) = \frac{e^{\left[\frac{-(x_i - \bar{x})^2}{2\sigma^2} \right]}}{\sigma\sqrt{2\pi}}, \quad (1)$$

where $P(x_i - \bar{x})$ is the frequency of occurrence of an error, e is the Napierian base, 2.71828..., for natural logarithms. σ (sigma) is the standard deviation which can be calculated from experimental results from the equation:

$$\sigma = \sqrt{\frac{\sum_{i=1}^N (x_i - \bar{x})^2}{N}}. \quad (2)$$

For a large number of measurements ($N > 30$) this formula may be used (the σ_n key on Texas Instruments calculators) to give the population standard deviation while for small N (< 30), $N-1$ is used in the denominator to give the sample standard deviation (σ_{n-1} key).

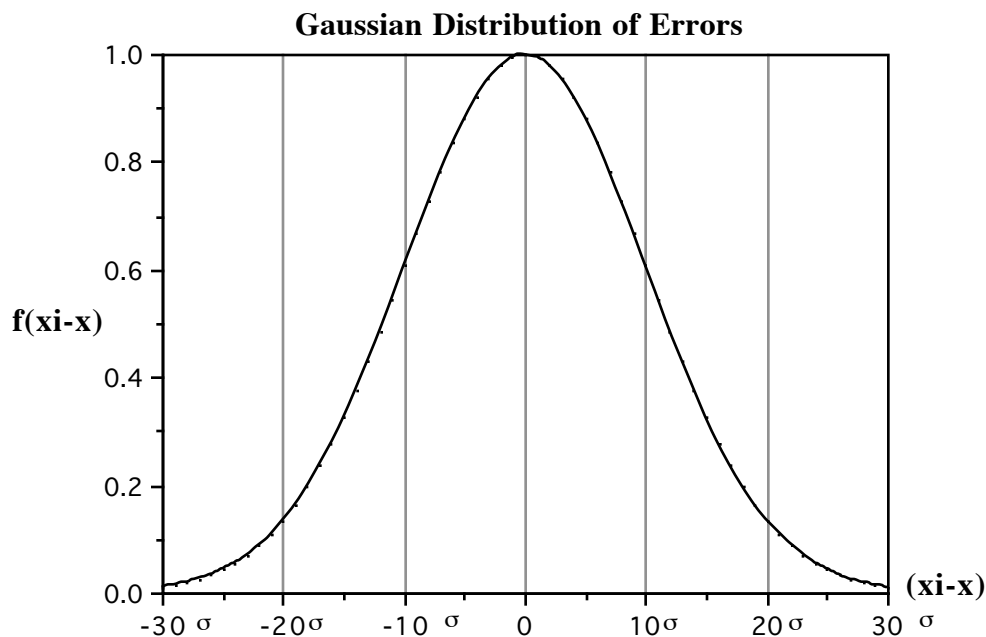


Figure 2. A Gaussian distribution of errors, with $\sigma = 1.0$ and $f(x_i - \bar{x}) = \frac{1}{\sqrt{2\pi}} e^{-\frac{1}{2}(x_i - \bar{x})^2}$.

A large σ means poor precision in the data and a broad distribution, while a small σ means good precision in the data and a narrow, sharp distribution. (See Figure 3.)

The following list of *confidence levels* is often useful. The levels are determined by calculating the area under the Gaussian curve for various boundary limits.

To be certain that this percentage of the results will be included in the sample.	50	68	90	95	96	99	99.7
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You need to include values within these limits.	$\pm 0.67\sigma$	$\pm 1.00\sigma$	$\pm 1.64\sigma$	$\pm 1.96\sigma$	$\pm 2.00\sigma$	$\pm 2.58\sigma$	$\pm 3.00\sigma$
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While not used in this course, there are various statistical tests (χ^2 , F, t) which can be used to determine if the difference between an observed value and an accepted value is the result of random error or could be interpreted as having real significance.⁴

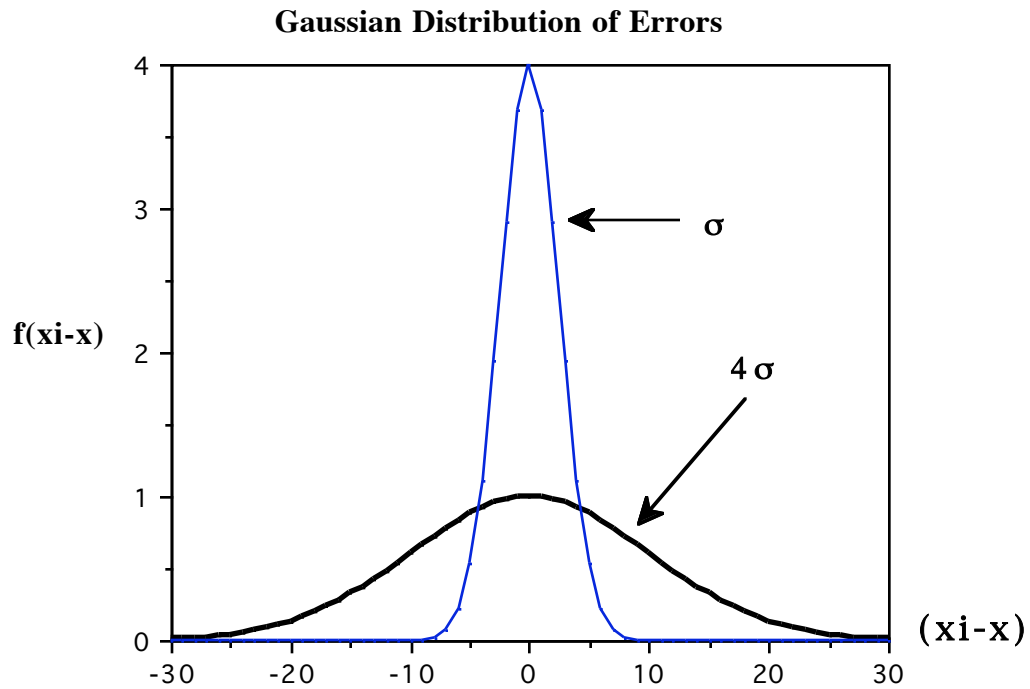


Figure 3. In this case two Gaussian distribution with average \bar{x} are compared. The wider distribution has a standard deviation four times greater than the narrower.

Linear least-squares or linear regression

The equation of a straight line is

$$y = b + mx \quad . \quad (3)$$

The method of least squares selects the best straight line through a set of N data points by minimizing the following summation

$$S = \sum_{i=1}^N (y_{\text{calc}} - y_{\text{obs}})^2 \quad (4)$$

$$= \sum_{i=1}^N [(b + m x_{\text{obs}}) - y_{\text{obs}}]^2 \quad (5)$$

On expanding Eq. (5) and setting the partial derivatives with respect to b and m equal to zero, the following two equations result:

$$m = \frac{N \sum_i x_i y_i - \sum_i x_i \sum_i y_i}{N \sum_i x_i^2 - \left[\sum_i x_i \right]^2} \quad (6)$$

and

$$b = \frac{\sum_i x_i^2 \sum_i y_i - \sum_i x_i \sum_i x_i y_i}{N \sum_i x_i^2 - \left[\sum_i x_i \right]^2} \quad (7)$$

While a linear regression can be done very easily on a calculator, it is important to understand what is actually being achieved in terms of the graphical presentation of the data.

Note: If your computer graphing program provides an equation for your data, use this equation to determine an interpolated or extrapolated value rather than visual estimation.

A further quantity, r^2 , the coefficient of determination or the *correlation coefficient*, measures the "goodness of fit" of the regression line.

$$r^2 = \frac{\left[N \sum_i x_i y_i - \sum_i x_i \sum_i y_i \right]^2}{\left[N \sum_i x_i^2 - \left[\sum_i x_i \right]^2 \right] \left[N \sum_i y_i^2 - \left[\sum_i y_i \right]^2 \right]} \quad (8)$$

A value of $r^2 = 1.0$ suggests a perfect fit of the regression line to the data, but r^2 is a relatively insensitive indication of the quality of typical physical chemical data. Badly scattered data can be fit with an r^2 value of 0.95.

Propagation of errors

The final numerical result in a physical chemistry experiment is usually obtained as the result of calculations involving measured quantities, *e.g.*, temperature, pressure, mass, volume, electrical voltage or resistance, *each with inherent systematic and/or random errors*. The uncertainty specified in the final numerical result must reflect in some systematic way the errors in the measured quantities.

The theory of the propagation of the errors from measured quantities through to the final result has been very thoroughly and rigorously developed. While in practice we can rarely use the theory in

its complete form, needing to make estimates for unavailable factors, an outline of the theory will be presented here.

If the final result, R, is a function of experimentally determined observables, A,B,C..., that is, $R = f(A,B,C\dots)$, the complete differential of R is

$$dR = \left(\frac{\partial R}{\partial A} \right)_{B,C,\dots} dA + \left(\frac{\partial R}{\partial B} \right)_{A,C,\dots} dB + \dots \quad (9)$$

where the partial derivative $(\partial R/\partial A)_{B,C,\dots}$ represents the sensitivity of R to a change (or error) in A, the other variables being held constant. If the changes are finite rather than infinitesimal, we can write the expression as

$$\Delta R = \left| \left(\frac{\partial R}{\partial A} \right)_{B,C,\dots} \right| \Delta A + \left| \left(\frac{\partial R}{\partial B} \right)_{A,C,\dots} \right| \Delta B + \dots \quad (10)$$

For *systematic* errors, we would use the above equation for ΔR but for *random* errors, which can be either positive or negative, we would use an equation of the form

$$(\Delta R)^2 = \left(\frac{\partial R}{\partial A} \right)_{B,C,\dots}^2 (\Delta A)^2 + \left(\frac{\partial R}{\partial B} \right)_{A,C,\dots}^2 (\Delta B)^2 + \dots \quad (11)$$

a) For sums and differences,⁵ for *systematic* errors

$$R = A + B \quad \Delta R = \Delta A + \Delta B \quad (12)$$

$$R = A - B \quad \Delta R = \Delta A - \Delta B \quad , \quad (13)$$

$$\text{and for } \textit{random} \text{ errors} \quad (\Delta R)^2 = (\Delta A)^2 + (\Delta B)^2 \quad (14)$$

ΔR is called the absolute error of R, similar statements hold for the other variables.

In other notation: $(A \pm a) + (B \pm b) = C \pm c$ where $c = \sqrt{a^2 + b^2}$

b) For products and quotients,⁵ for *systematic* errors

$$R = A \cdot B \quad \Delta R/R = \Delta A/A + \Delta B/B \quad (15)$$

$$R = A/B \quad \Delta R/R = \Delta A/A + \Delta B/B \quad , \quad (16)$$

and for *random* errors

$$(\Delta R/R)^2 = (\Delta A/A)^2 + (\Delta B/B)^2 \quad . \quad (17)$$

$\Delta R/R$ is called the relative error of R, similar statements hold for the other variables.

In other notation: $(A \pm a\%) + (B \pm b\%) = C \pm c\%$ where $c = \sqrt{a^2 + b^2}$

c) For powers,⁵ for *systematic* errors

$$R = A^j \quad (\Delta R/R) = j \cdot (\Delta A/A) \quad , \quad (18)$$

and for *random* errors

$$(\Delta R/R)^2 = j^2 \cdot (\Delta A/A)^2 \quad . \quad (19)$$

As an example of how a thorough analysis of the propagation of errors could be attempted. Let us consider the measurement of the density of a 1.000M NaCl solution at 25.00°C and 1.00 atmosphere pressure. The observed density of the solution will depend on the temperature of the thermostatically controlled bath, the barometric pressure and the concentration, and there can be systematic and random errors in all of these variables.

The systematic error in the density of the solution is

$$\Delta d = (\partial d/\partial T)_{P,C} \Delta T + (\partial d/\partial C)_{P,T} \Delta C + (\partial d/\partial P)_{C,T} \Delta P \quad . \quad (20)$$

The partial derivatives could be experimentally determined and the systematic errors, ΔT , ΔC , and ΔP could be estimated. For example, the density of such a solution varies about 0.0001 g/cc °C. If the bath was known to be 0.15°C above 25.00°C, the error from the first term would be 0.0001 x 0.15 or 1.5 x 10⁻⁵ g/cc in the density.

If there was a random error or fluctuation in the temperature of the bath of ±0.05°, then

$$(\Delta d)^2 = (.0001)^2(0.05)^2 \quad , \quad (21)$$

or $\Delta d = 5 \times 10^{-6}$ g/cc error in the density of the solution.

In fact, $d = W/V$, where the weight and volume are the experimentally determined quantities. An equation of the form of (16) should be written for W and V , giving

$$\Delta d/d = \Delta W/W + \Delta V/V \quad . \quad (22)$$

References

1. G. P. Matthews, *Experimental Physical Chemistry*, Clarendon Press, Oxford, 1985, p. xvii.
2. Reference 1, p. xviii.
3. P. W. Atkins, *Physical Chemistry*, 5th Edition, W. H. Freeman, New York, 1994, p. C18.
4. D. P. Shoemaker, C. W. Garland, J. I. Steinfeld, and J. W. Nibler, *Experiments in Physical Chemistry*, 4th Edition, McGraw-Hill, New York, 1981, Chapter II; or D. P. Shoemaker, C. W. Garland, and J. W. Nibler, *Experiments in Physical Chemistry*, 5th Edition, McGraw-Hill, New York, 1989, Chapter II.
5. Reference 1, pp. xx - xxii.

INFORMATION ON LABELLING OF CHEMICALS

All containers of hazardous chemicals must be labelled in such a way that the hazards are easy to identify. There are a number of methods in use. Bottles obtained from the manufacturer will generally have at least some sort of verbal information, and increasingly will have pictographs as well. The levels of verbal warning are: "Caution" -- relatively low-level hazard; "Warning" -- use with care; and "Danger" -- use only after careful consideration of the hazards.

Containers prepared on campus will have labels indicating general hazards. The ones in common use at Williams are "Flammable", "Corrosive", "Poison" and "Cancer Hazard". Others that may be found include "Oxidizer", "Radioactive" and "Water Sensitive". If a label is missing or damaged, please bring it to the attention of your instructor.

Some containers may have the diamond label shown below. This describes hazards as determined by the National Fire Protection Association. Be aware that the vast majority of chemicals have **not** been studied or rated by the NFPA. Therefore, the absence of such a label does not imply that the material is safe! Detailed descriptions of the meaning of the ratings can be found in the main stockroom. For present purposes, you should be aware that a "3" or "4" in any segment of the label, or a notation in the white section, is cause for concern -- investigate further before you use the material.

