

CHM 3400L

FUNDAMENTALS OF

PHYSICAL CHEMISTRY

LABORATORY MANUAL

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2020

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Safety in the Laboratory

Laboratory work has a number of hazards associated with it. There is no need for laboratory work to be dangerous, as long as everyone working in the lab is aware of potential problems that can occur, works in a safe manner at all times, and knows how to respond in case of an accident.

The following safety rules will be enforced in the laboratory:

1) **Eye protection will be worn in the laboratory at all times.**

2) Students are expected to be familiar with the methods and procedures of the experiments they are working on, including any special hazards as listed below. You are expected to read the experimental write up before coming to class and doing an experiment. When in doubt about how to proceed in an experiment ask the laboratory instructor for assistance.

3) Students are expected to know the location of the nearest safety shower, eye wash, fire extinguisher, and telephone, and to know the exits to the building.

4) **In the event of an accident, the first priority is to ensure the safety of everyone in the building.** The laboratory instructor should be notified as quickly as possible following an accident so that appropriate action may be taken.

5) There is a telephone in the laboratory, to be used for emergencies only. Important phone numbers are as follows:

Police (on campus, emergency): 7-5911

Fire rescue (off campus, emergencies only): 9 (for an outside line) 911

Chemistry office: x-2606

Jeff Joens: x-3121 (office - CP 331)

Error and Error Analysis

Whenever an experimental measurement is made there will be some error associated with the measurement. In reporting the results from an experiment it is important to report not only the best value for the experimental quantity but also an estimate of the error for that quantity. The error estimate tells us the degree of confidence we have in the experimental result, and places constraints on how we use the result to compare with theoretical predictions or other experimental measurements.

Before discussing error and error analysis, we need to first define some terms.

Precision and accuracy. Precision refers to the reproducibility of an experimental measurement. Accuracy refers to the correctness of the measurement, that is, how close the experimental result is to the actual value of the quantity being measured. Note that a measurement may be precise without being accurate, which indicates a systematic error (bias) in the experimental measurement.

Random and systematic error. An experimental measurement involves a large number of individual actions on the part of the experimenter. For example, when a strong acid is titrated with a strong base, the volume of acid to be titrated must be measured with a pipet or other volumetric glassware, the initial volume of titrant in the buret must be read, the end point of the titration must be observed by a color change in an indicator, and the final volume of titrant must be read. None of these steps can be carried out perfectly, and so there will always be some error due to random variations in the way in which the measurements are made. This variation is referred to as random error.

Random error can often be made smaller by selection of the appropriate equipment used to carry out an experiment and care in execution of the measurements. For example, in a titration, a volumetric pipet is used to measure the amount of solution to be titrated rather than a graduated cylinder because a pipet is a more precise means of measuring volume. However, no matter how carefully an experiment is carried out, there will always be some random error associated with a measurement.

Systematic error, or bias, in an experimental measurement refers to a non-random deviation in the measurement. A few examples will make this more clear.

1) An analytical balance is used to weigh several samples of a compound. The balance has been zeroed incorrectly, however, so that it reads 0.0020 g when the balance pan is empty. This will cause each of the experimental sample weights to be too large by 0.0020 g.

2) The volume of a glass bulb is determined by weighing the bulb when it is filled with a known gas at a particular temperature and pressure, then removing the gas and weighing the bulb when at vacuum. The ideal gas law is used to determine the volume of the bulb. Since the ideal gas law is an approximation for the behavior of a real gas, there will be some systematic error associated with its use. In this case, a better gas law, such as van der Waals equation, could be used if a more accurate approximation of the behavior of the real gas was required.

In principle systematic error can always be corrected. In practice this is often not possible. To correct for systematic error requires that the error be detected, that a specific cause for the error be assigned, and that a procedure to correct the error be developed. Problems can arise in any of these steps. In fact, for many experiments, systematic errors are a greater source of error in experimental results than random errors.

Several techniques have been developed for estimating errors in experimental measurements. We will discuss some of these methods below. A few cautionary points should first be made, however. First, the statistical analysis of data assumes that all experimental errors are due to random errors in the measurements. This means that any systematic errors in a measurement will not be accounted for in the error analysis. Second, the procedures

developed for analysis of experimental data do not work well with small data sets. When only a few measurements of an experimental quantity are made, error estimates based on statistical considerations should be used cautiously.

Reproducibility of a measurement. When an experimental quantity is determined by several independent measurements, an estimate of the precision of the result can be made based on the reproducibility of the measurement. The error in the measurement is often estimated by calculating the estimated standard deviation, s , defined by the expression

$$s = [\sum_{i=1}^N (x_i - \mu)^2 / (N-1)]^{1/2} \quad (1)$$

where N is the total number of independent measurements that have been made, x_i is the value obtained for the i^{th} measurement, and μ is the average (mean) of all the measurements

$$\mu = [\sum_{i=1}^N x_i] / N \quad (2)$$

For example, consider the following set of measurements of the mass of a metal block

<u>Trial</u>	<u>Value</u>
1	10.2986 g
2	10.2980 g
3	10.2991 g
4	10.2990 g
5	10.2985 g
$\mu = 10.29864 \text{ g}$	$s = 0.000439 \text{ g}$

The average value for the mass of the block is $\mu = 10.29864 \text{ g}$. The estimated standard deviation in the value of the mass, calculated from eq 1, is $s = 0.000439 \text{ g}$. This number represents an estimate of the precision of the measurement, and should be consistent with the error expected in using an analytical balance to determine mass. In this case, the estimated standard deviation is about what we would expect based on the fact that mass on an analytical balance can be read to the nearest 0.0001 g , and that the random error in determining mass is probably a bit larger than the reading error.

A quantity closely related to the estimated standard deviation is the estimated standard deviation of the mean, s_m . This represents the estimated value for the uncertainty in the average value for the quantity being measured. The estimated standard deviation of the mean is defined by the relationship

$$s_m = s / N^{1/2} \quad (3)$$

For the above data set, $s_m = 0.000196 \text{ g}$. Note that in the limit of a large number of measurements ($N \rightarrow \infty$) the value of s_m goes to zero. What this means is that as we increase the number of measurements the uncertainty in the average value decreases, as we would expect.

Once we have found the average and estimated standard deviation of the mean for a data set we can determine confidence limits (Δ) for the mean. The confidence limits represent an interval about the mean for which the probability that the actual value for the quantity being measured is within these limits is P . The confidence limits can be found using the equation

$$\Delta = t_{v,P} s_m \quad (4)$$

where $t_{v,P}$ is the critical value for t and s_m , as before, is the estimated standard deviation of the mean. A table of values for $t_{v,P}$ is given on the next page (Table 1). The value for $t_{v,P}$ depends on v , the number of degrees of freedom in the measurement, and P , the confidence limits that have been selected. For cases where we compute an average

value from a series of measurements, $\nu = N - 1$, where N is the number of measurements that have been made. When data are fit to a straight line, $\nu = N - 2$.

TABLE 1 - CRITICAL VALUES FOR t

ν	P=0.90	P=0.95	P=0.99
1	6.31	12.7	63.7
2	2.92	4.30	9.92
3	2.35	3.18	5.84
4	2.13	2.78	4.60
5	2.02	2.57	4.03
6	1.94	2.45	3.71
7	1.89	2.36	3.50
8	1.86	2.31	3.36
9	1.83	2.26	3.25
10	1.81	2.23	3.17
15	1.75	2.13	2.95
20	1.72	2.09	2.85
30	1.70	2.04	2.75
∞	1.64	1.96	2.58

Adapted from D. P. Shoemaker, C. W. Garland, J. W. Nibler, Experiments in Physical Chemistry, Sixth Edition (McGraw-Hill, New York, 1996) Chapter II, Table 3.

We can use the above procedure to assign confidence limits for the mean value obtained from the above data set. If we choose $P = 0.95$ (95% confidence limits), then

$$\Delta = t_{4,95} s_m = (2.78)(0.000196 \text{ g}) = 0.00054 \text{ g} \quad (5)$$

where we have obtained the value for $t_{4,95}$ from Table 1. We interpret this result as meaning that there is a 95% probability that the true value for the mass of the metal block lies within $\pm 0.00054 \text{ g}$ of the average value found from the measurements.

In this class we will always report experimental values at 95% confidence limits. For the above data set, for example, we would summarize the results by saying

$$\text{mass of metal block} = 10.29864 \text{ g} \pm 0.00054 \text{ g (at 95\% confidence limits)} \quad (6)$$

Note that the confidence limits are reported to (at most) two significant figures, and that the number of significant figures in the mean value is chosen to be consistent with the confidence limits.

One use of confidence limits is to decide whether an experimental result agrees or disagrees with a literature value or theoretical result. If the literature value falls within the confidence limits, we say that the experimental result and the literature value agree at the 95% confidence limits (or other limits, if a different value for P is chosen), while if the literature value falls outside the confidence limits we say that the experimental results and literature value disagree (again at the 95% confidence limits). Disagreement indicates that there is something wrong, either with the experimental result or the literature value to which it is being compared. Two common sources leading to disagreement are systematic error in the measurement or a mistake in the calculations carried out to obtain the final results. It is always a good idea to check your calculations, particularly when there is disagreement between your

results and literature results. It is also a good idea to review the procedure used in your measurements and consider at what steps in the procedure systematic errors could occur.

A question often faced in an experiment is whether or not a particular measurement should be discarded. For example, consider the following set of experimental data

<u>Trial</u>	<u>Value</u>
1	6.1815 g
2	6.1819 g
3	6.1015 g
4	6.1809 g
$\mu = 6.16145$ g	$s = 0.03997$ g

There is a large estimated standard deviation in the data due to the value from trial 3 being much different than the value from the other measurements of the mass of the block. Should the value from trial 3 be discarded? There are methods that have been developed for "testing" whether an experimental result should be thrown out (such as the "Q-test"), but in the final analysis the decision to keep or discard data is based on experience. In the above case, for example, the value from trial 3 differs from the results of the other trials by an amount that is large compared to the precision expected for measurements made on an analytical balance, and should therefore be discarded. But what if the value for trial 3 had been 6.1799 g? Would this be different enough from the other three values to be discarded? In this case, it is more difficult to decide whether or not to keep the value from trial 3. The best advice in trying to decide whether or not to discard data is to keep data unless there is a clear discrepancy between the results from one measurement or set of measurements and the remaining experimental data. It is often useful when trying to decide whether to keep or discard data is to make additional measurements when possible to get a better idea of the amount of scatter expected in the measurement.

Data fit to a line. For many experiments we expect a linear relationship between experimental quantities. For example, when the vapor pressure of a liquid is measured as a function of temperature, we expect that a plot of $\ln(P)$ vs. $1/T$ should be linear, based on the Clausius-Clapeyron equation. In such cases a method is needed for finding the best values for the slope and intercept of a line fitting the data and of estimating the error in the slope and intercept.

The usual method for fitting data to a straight line is the method of least squares. A discussion of the theoretical basis for this method is given in Reference 4. For a set of N data points $x_1, y_1; x_2, y_2; \dots; x_N, y_N$ the slope (m) and intercept (b) of the line that best fits the experimental data are given by the expressions

$$m = [N (\sum_{i=1}^N x_i y_i) - (\sum_{i=1}^N x_i) (\sum_{i=1}^N y_i)] / [N (\sum_{i=1}^N x_i^2) - (\sum_{i=1}^N x_i)^2] \quad (7)$$

$$b = (1/N) [(\sum_{i=1}^N y_i) - m (\sum_{i=1}^N x_i)] \quad (8)$$

Many calculators have canned programs for finding m and b by the above equations, and the least squares method of fitting data to a line is a part of most statistical data analysis packages, including EXCEL. There is a program available in the physical chemistry laboratory (POLY) that will carry out a least squares fit of experimental data for any polynomial up to 9th order in x . For a linear fit to data the program will find the best values for the slope and intercept of the line that best fits the experimental data, and also calculate the 95% confidence limits on the values for the slope and intercept. Many versions of EXCEL, as well as a number of other statistical data analysis packages, will also find the 95% confidence limits on the slope and intercept when data are fit to a straight line.

Since we often use the results from experimental measurements in carrying out calculations, it is important to know how error propagates in a calculation. There are two important cases to consider; addition and subtraction, and multiplication and division.

Addition and subtraction. If the value of a quantity z is found by adding or subtracting two numbers x and y , the error in z is given by the expression

$$(\Delta z)^2 = (\Delta x)^2 + (\Delta y)^2 \quad (9)$$

where (Δx) , (Δy) , and (Δz) are the absolute errors in x , y , and z .

Multiplication and division. If the value of a quantity z is found by multiplying or dividing two numbers x and y , the error in z is given by the expression

$$|\Delta z/z|^2 = |\Delta x/x|^2 + |\Delta y/y|^2 \quad (10)$$

where $|\Delta x/x|$, $|\Delta y/y|$, and $|\Delta z/z|$ are the relative errors in x , y , and z .

If a calculation involves both addition/subtraction and multiplication/division, the error in the result of the calculation may be found by successive applications of the above rules for error propagation. If a calculation involves a more difficult mathematical operation, (the logarithm of a number, for example), the best way to estimate the error in the result is to carry out the calculation with the best value, the upper limit, and the lower limit, and to examine the range in the results of the calculation in the three cases (a more rigorous method for finding the error is given in Reference 3). Also, in cases where it is clear that one number in the calculation is the main source of error, the above procedure does not need to be carried out in full.

Finally, it is important to consider the likely sources of error in an experimental measurement, their approximate magnitude, and their expected effect on the experimental results. By doing this, one may decide whether the error limits calculated from the reproducibility in the data are reasonable. Methods for improving the procedure used to make an experimental measurement may also be found more easily once the principal sources of experimental error have been identified.

As an example, consider the determination of the density of a metal block, where the mass of the block is found by weighing it on an analytical balance, and the volume of the block is found by the change in the height of water in a graduated cylinder when the block is placed beneath the surface of the water. A typical set of experimental results might be as follows

mass of the block = 16.4128 g \pm 0.0005 g (at 95% confidence limits)

volume of the block = 2.9 mL \pm 0.2 mL (at 95% confidence limits)

density of the block = 5.6 g/mL \pm 0.4 g/mL (at 95% confidence limits)

where the error limits for the mass and volume of the block are based on the reproducibility of the experimental measurements, and the error limits for the density are calculated from the rules for propagation of error. There are several things we might say based on the above information. First, the error limits given for the mass and volume of the block appear reasonable, given the methods used to measure mass and volume. Second, if an improved value for the density is desired, it would make more sense to improve the procedure used to find the volume of the block than to improve the method used for finding the mass of the block. This is because the main source of error in the calculation of the density of the block comes from the volume determination.

The above discussion of error and error analysis should cover the most common situations that will be encountered in the laboratory. There will always be some cases that are not adequately covered by the above rules. However, reasonable methods for the analysis of error can usually be developed based on the underlying philosophy used to deduce the procedures given above.

Additional reading

Additional information concerning error and error analysis can be found in the following books:

1) D. A. Skoog, D. M. West, F. J. Holler, S. R. Crouch Fundamentals of Analytical Chemistry, Ninth Edition, (Saunders, Philadelphia, 2013).

2) D. G. Peters, J. M. Hayes, G. M. Hieftje, Chemical Separation and Measurement, (Saunders, Philadelphia, 1974), Chapter 2.

3) C. W. Garland, J. N. Nibler, D. P. Shoemaker, Experiments in Physical Chemistry, Eighth Edition, (McGraw-Hill, New York, 2009), Chapter 2.

4) P. R. Bevington, Data Reduction and Error Analysis for the Physical Sciences, Second Edition, (McGraw-Hill, New York, 1992).

Revised 08/2016

Physical Chemistry Lab Reports

The following general format should be used in writing your laboratory reports:

1) Title page - This should include your name, the names of any lab partners, the title of the experiment, the course number, and the date.

2) Abstract - A short summary of the objectives, main results, and conclusions for the experiment.

3) Introduction - A short summary of the objectives of the experiment, including what is being measured and how it is being measured. I am not looking for you to regurgitate the introductory material presented in the lab handout in your introduction to the lab report (you can, in fact, cite the lab manual as a reference).

4) Experimental procedure - An outline of the procedure used to carry out experimental measurements. If the procedure used is as given in the lab handout, then you can refer to the handout and do not have to give a discussion of the experimental procedure in the report. If there are any differences between the procedure in the lab handout and that used by you in the experiment, they should be discussed in detail.

5) Results and discussion - This is the main part of the lab report. In this section you should give the primary experimental data and the details and results of any calculations carried out on the data. Organization is important here. Data and results should be presented in as clear, concise, and meaningful a form as possible (data tables, plots of experimental data, etc.). Error estimates for the results should also be discussed in this section of the report, using the principles outlined in the handout on error analysis. If possible, the major sources of experimental error should be identified, and their effect on the experimental results discussed. Results from the experiment should be compared, if possible, to literature and/or theoretical values. Any questions posed in the lab handout should be answered at the end of this section of the report, along with any suggestions for improving the experiment.

6) References - All outside references used in the report should be indicated by a reference number in the body of the report and listed in this section of the report. The correct procedure for doing this can be seen by examination of any of the experimental lab handouts.

Remember that though you will be doing the experiments with lab partners, the laboratory reports are to be done individually. **Copying from the lab report of another student is considered plagiarism and will be punished accordingly.**

A sample lab report is given below and can be used as a model for your lab reports.

Sample Lab Report

The Temperature Dependence of the Density of Methyl Alcohol

John Doe

Lab Partners:
Karen Bolla
John Fahey

Abstract

A Cassia volumetric flask is used to find the density of methyl alcohol for eight temperatures in the range $t = 0$ to 41 °C. The best fit to the data gives

$$\rho(t) = (0.80551 \pm 0.0015) \text{ g/cm}^3 - (8.07 \pm 0.61) \times 10^{-4} \text{ g/cm}^3 \cdot \text{°C} t$$

where the fitting parameters are given at 95% confidence limits. Based on this data we find that at 20 . °C, $\rho = (0.7894 \pm 0.0019) \text{ g/cm}^3$, and $\alpha = (1.022 \pm 0.077) \times 10^{-3} \text{ °C}^{-1}$, also at 95% confidence limits.

Introduction

Unlike gases, the volume occupied by a given amount of a liquid is, to a first approximation, independent of temperature. However, careful measurements demonstrate that small changes in volume, and therefore density, do occur when the temperature of a liquid is changed. These changes can be important in experiments where the properties of a pure liquid or a solution are studied over a range of temperatures. These changes also provide information about the fundamental properties of liquids, such as α , the coefficient of thermal expansion. [1]

The purpose of the present experiment is to study the temperature dependence of the density of methyl alcohol (CH_3OH). The mass and volume of samples of methyl alcohol will be measured over a range of temperatures roughly between 0 °C and 40 °C. These data will be used to find the density of methyl alcohol at each experimental temperature, using the relationship

$$\rho = m/V \tag{1}$$

where m is the mass of methyl alcohol, V is the volume occupied by the methyl alcohol, and ρ is the density. The data will be fit to an empirical equation of the form

$$\rho(t) = \rho_0 + bt + ct^2 + \dots \tag{2}$$

In the above expression $\rho(t)$ is density of methyl alcohol, expressed as a function of t , the temperature (in °C), ρ_0 is the density of methyl alcohol at 0 °C, and b, c, \dots are fitting parameters. The 95% confidence limits on the fitting parameters will be used to determine the appropriate number of terms to include in the power series expansion in eq. 2.

Once an expression for $\rho(t)$ is found, it will be used to find the corresponding expression for $\alpha(t)$, the coefficient of thermal expansion. α is defined by the relationship

$$\alpha = (1/V) (\partial V/\partial T)_p = (1/V) (\partial V/\partial t)_p \tag{3}$$

Using eq. 1 it can be shown that

$$V = m/\rho \tag{4}$$

Substitution of eq. 4 into eq. 3 leads to the result

$$\alpha(t) = \rho (\partial/\partial t)_p \rho^{-1} \tag{5}$$

$$= \rho (\partial(1/\rho)/\partial \rho)_p (\partial \rho/\partial t)_p \tag{6}$$

$$= - (1/\rho) (\partial\rho/\partial t)_p \quad (7)$$

from which $\alpha(t)$ can be found.

The final results from the experiment will be expressions for $\rho(t)$ and $\alpha(t)$. Values for ρ and α at 20. °C will be calculated from these expressions and compared to literature values. Finally, the major sources of error, their expected magnitude, and the effect of these errors on the results will be discussed.

Experimental Method

The experimental method used is a modification of that used in Experiment 9 of the lab manual ("Partial Molar Volume"). [2] Because there are significant differences between the procedure used in that experiment and the procedure used in the present experiment, a detailed outline of the experimental method is given below.

A 100 mL Cassia volumetric flask is thoroughly dried, and its mass measured twice on an analytical balance. The flask is then filled with slightly more than 100 mL of methyl alcohol. The filled flask is placed inside a water bath and held in place using a clamp and ringstand, with the stopper of the flask placed loosely on the top of the flask. The flask and liquid are given 15 minutes to equilibrate. At this time the stopper is fitted into the top of the flask, after which the temperature of the water bath is measured using a mercury thermometer, and the volume of the liquid in the flask is recorded. The flask is then removed from the water bath, dried on the outside, and allowed to cool. Finally, the mass of the filled flask is measured.

A total of 6-10 measurements of temperature, mass, and volume are made by repeating the above procedure, with the temperature of the water bath changed by ~ 5 °C between measurements. Small amounts of methyl alcohol can be added or removed from the flask to keep the volume of liquid slightly larger than 100 mL. After all of the measurements have been completed the flask is emptied and dried, and two additional measurements of the mass of the dry flask are made.

Results

The data for the mass of the Cassia flask when empty are given in Table 1. The experimental data and calculation of the density of methyl alcohol are given in Table 2. Finally, the data are plotted in Figure 1. Note that the data point at 26.4 °C (shown as an x in the plot) was not used in the analysis of the data, as it is clearly not consistent with the other data obtained in the experiment.

TABLE 1 - Mass of dry flask (m_e)

Trial 1	23.4128 g	Trial 3	23.4127 g
Trial 2	23.4131 g	Trial 4	23.4128 g
Average value:	23.41285 g	s =	0.000173 g
		t _{.95,3}	= 3.18

Final result: $m_e = 23.4128 \pm 0.0003$ g, at 95% confidence limits.

TABLE 2 - Data and calculation of ρ

t ($^{\circ}\text{C}$)	V (cm^3)	m (g)	$m - m_e$ (g)	ρ (g/cm^3)
0.2	100.47	104.2791	80.8663	0.80488
6.5	100.56	103.9836	80.5708	0.80122
11.8	100.85	103.7485	80.3357	0.79659
17.1	100.41	102.7773	79.3645	0.79040
21.5	100.56	102.7041	79.2913	0.78849
26.4	100.70	103.1672	79.7544	0.79200 (not used)
31.2	100.38	101.7208	78.3080	0.78012
35.7	100.65	101.4866	78.0738	0.77570
40.9	100.61	101.2402	77.8274	0.77356

NOTE: $m_e = 23.4128$ g (Table 1). Data at 26.4 $^{\circ}\text{C}$ are not used in the subsequent analysis.

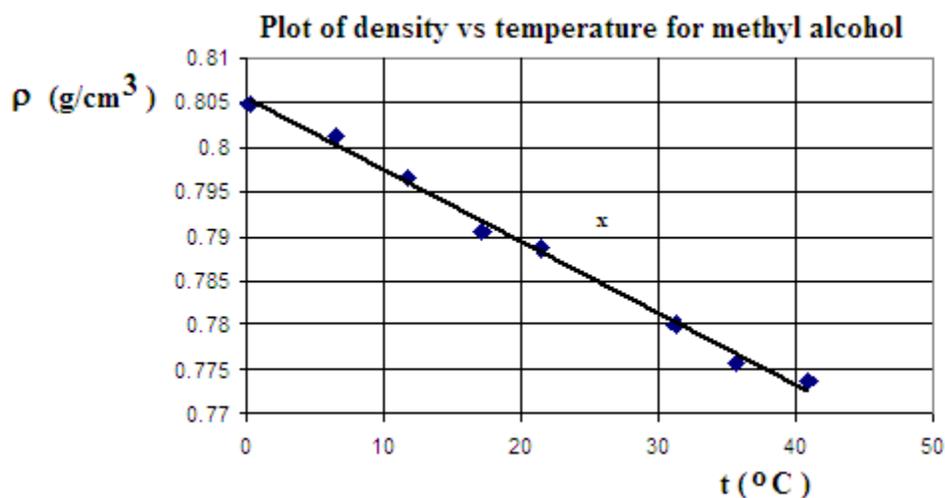


Figure 1.

Data were fit to eq. 2 by a first order polynomial (linear fit) and a second order polynomial (quadratic fit) using the POLY program. The results are given in Table 3.

TABLE 3 - Fit of density vs temperature data to eq. 2

	ρ_0 (g/cm^3)	b ($\text{g}/\text{cm}^3 \cdot ^{\circ}\text{C}$)	c ($\text{g}/\text{cm}^3 \cdot ^{\circ}\text{C}^2$)
linear	0.80551 ± 0.0015	$(- 8.07 \pm 0.61) \times 10^{-4}$	
quadratic	0.80581 ± 0.0023	$(- 8.55 \pm 2.6) \times 10^{-4}$	$(1.16 \pm 6.1) \times 10^{-6}$

Since the second order term (c) in the quadratic fit is not significantly different from zero at 95% confidence limits, a linear fit to the data is used. Therefore, the final expression for the density of methyl alcohol in the range $0 - 40$ $^{\circ}\text{C}$ is

$$\rho(t) = (0.80551 \pm 0.0015) \text{ g}/\text{cm}^3 - (8.07 \pm 0.61) \times 10^{-4} \text{ g}/\text{cm}^3 \cdot ^{\circ}\text{C} t \quad (8)$$

Values for $\alpha(t)$ can be found using eq. 7. Note that $(\partial\rho/\partial t)_p = b$ when a linear fit to the density data is used, and so

$$\alpha(t) = -b/\rho(t) \quad (9)$$

where b is given in Table 3 and $\rho(t)$ is given in eq. 8.

Equations 8 and 9 can be used to find the values for ρ and α at $t = 20.^\circ\text{C}$. The results, with the 95% confidence limits found using the rules for propagation of error in addition/subtraction and for multiplication/division in calculations, are $\rho(20.^\circ\text{C}) = (0.7894 \pm 0.0019) \text{ g/cm}^3$, and $\alpha(20.^\circ\text{C}) = (1.022 \pm 0.077) \times 10^{-3} \text{ }^\circ\text{C}^{-1}$.

Discussion

The major sources of error in this experiment are as follows:

Measurement of mass. The precision of the analytical balance used in the experiment is estimated to be $\pm 0.0003 \text{ g}$. This would lead to an error in m and m_e , and therefore a corresponding error in ρ of $\sim \pm 4 \times 10^{-6} \text{ g/cm}^3$, a negligible error.

Measurement of volume. The volume of liquid in the Cassia volumetric flask can be read to a precision of approximately $\pm 0.03 \text{ mL}$. This would lead to an error in V , and therefore a corresponding error in ρ of $\sim \pm 0.0002 \text{ g/cm}^3$. Since the same flask is used in all of the measurements, there is also the potential of systematic error. The uncertainty in the volume of the Cassia flask (not the reading uncertainty) is $\sim 0.08 \text{ mL}$ [2], leading to a corresponding systematic error in ρ of $\sim \pm 0.0006 \text{ g/cm}^3$.

Measurement of temperature. The reading error for the thermometer used in the experiments is $\sim 0.2 \text{ }^\circ\text{C}$. The systematic error in the thermometer is estimated to be approximately the same magnitude as the reading error. Using the experimental value for b , this would lead to random error in ρ of $\sim |b\Delta t| = 0.0002 \text{ g/cm}^3$, and a systematic error of approximately the same magnitude.

The combination of the above three sources of random error would lead to a combined random error due to the measurement process used in the experiment of $\sim 0.0003 \text{ g/cm}^3$, about six times smaller than the reported error in the value for density at $t = 20.^\circ\text{C}$, $\pm 0.0019 \text{ g/cm}^3$.

There are additional errors expected to be present due to the difficulty in drying the outside of the volumetric flask before weighing and the volatility of methyl alcohol (which increases as t increases). These are the most likely sources of the additional random error observed in the experimental results. Note that the dependence of the volatility of methyl alcohol on temperature might also be a possible source of systematic error.

Literature values for the density and coefficient of thermal expansion for methyl alcohol are given at $t = 20.^\circ\text{C}$ in the CRC Handbook of Chemistry and Physics. [3] The literature value for $\rho(20.^\circ\text{C})$ is 0.7909 g/cm^3 , within the 95% confidence limits of the experimental value. The literature value for $\alpha(20.^\circ\text{C})$ is $1.49 \times 10^{-3} \text{ }^\circ\text{C}^{-1}$, approximately 45% larger than the value found experimentally and well outside the 95% confidence limits. The reason for the difference is not known, though it should be noted that a temperature dependent systematic error, such as might be caused by the increasing volatility of methyl alcohol with temperature, could account for the difference. The experimental value for α is also sensitive to the curvature in the plot of ρ vs t , and so the difference might indicate that the use of a second order polynomial fit for ρ is justified. The values for α reported in ref. [3] also show a stronger dependence on temperature than those found in the present experiment. The reason for this is not known.

In summary, we were able to obtain high precision values for the density of methyl alcohol that were in good agreement with the literature. There was a significant difference (at 95% confidence limits) between the literature value for α and the value found in this experiment, with the reason for the difference not clearly identified.

References

1. Atkins, P. W. and J. de Paula. Physical Chemistry, 10th Edition. W. H. Freeman: New York, 2014. The coefficient of thermal expansion is defined and briefly discussed on page 93.

2. Garland, C. W., J. W. Nibler, and D. P. Shoemaker. Experiments in Physical Chemistry, 8th Edition. McGraw-Hill: New York, 2003, pp. 172-178.

3. CRC Handbook of Chemistry and Physics, 94th Edition, 2013-2014. Retrieved online 1/19/2014. ρ is taken from a data table on p 15-25, and α from a data table from page 6-156.

The heat of combustion of an organic compound

Introduction [1]

Formation and combustion reaction

One of the most basic pieces of information concerning a chemical compound is $\Delta H^\circ_{\text{form}}$, the standard enthalpy of formation of the compound. By definition, the standard enthalpy of formation of a chemical compound is equal to q , the heat evolved or taken up, when one mole of the compound is formed under standard conditions of temperature and pressure from elements in their standard state. Standard temperature and pressure are usually taken to be $T = 25\text{ }^\circ\text{C}$ (298.15 K) and $p = 1.000\text{ bar}$ [2]. For example, the enthalpy of formation for benzoic acid ($\text{C}_6\text{H}_5\text{COOH}(\text{s})$) is equal to q for the constant pressure process



By definition, a reaction where heat is released by the system is an exothermic reaction, while a reaction where heat is absorbed by the system is an endothermic reaction. The sign convention for q is that q is positive for processes where heat is absorbed by the system from the surroundings (endothermic reactions), and is negative for processes where heat is released by the system to the surroundings (exothermic reactions). For constant pressure processes, q and ΔH are equal, and so for these types of processes the definitions and sign conventions for q also apply to ΔH .

The usefulness of the enthalpy of formation in thermodynamic calculations is related to the fact that enthalpy is a state function. As a consequence of this, the change in enthalpy for any process depends only on the initial and final state of the system, and is independent of the path used to get from the initial to final state. For example, for the general chemical reaction



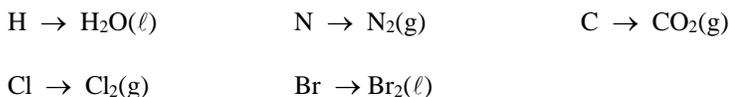
it is easy to show [3]

$$\Delta H_{\text{rxn}} = [c(\Delta H_{\text{form}}(\text{C})) + d(\Delta H_{\text{form}}(\text{D}))] - [a(\Delta H_{\text{form}}(\text{A})) + b(\Delta H_{\text{form}}(\text{B}))] \quad (3)$$

The change in enthalpy for any reaction can therefore be calculated if the enthalpy of formation of each reactant and product involved in the reaction is known. Short tables of formation enthalpies are usually given in physical chemistry texts, and more extensive tables are available in the literature [4].

While the enthalpy of formation of a chemical compound represents a useful means of summarizing large quantities of thermodynamic data, it is usually difficult to determine the enthalpy of formation directly. For example, the stoichiometric reaction given in equation (1) for formation of benzoic acid is not a reaction that can be carried out in the laboratory. Instead, formation enthalpies are almost always calculated indirectly from data from other types of reactions.

One of the most useful types of reactions for obtaining thermodynamic information is the combustion reaction. By definition, $\Delta H^\circ_{\text{comb}}$, the standard enthalpy of combustion for a compound, is equal to q for the reaction of one mole of the compound with oxygen to form combustion products in their standard state. The combustion products for the more common elements are given below [5]



As an example, the combustion reaction for benzoic acid is



Unlike the formation reaction, the combustion reaction represents a process that often can be carried out in the laboratory. Once the enthalpy of combustion for a compound is known, the enthalpy of formation can be calculated. Using benzoic acid as an example, application of equation (3) to the combustion reaction for benzoic acid gives

$$\Delta H^{\circ}_{\text{comb}} = [7 (\Delta H^{\circ}_{\text{form}} (\text{CO}_2(\text{g}))) + 3 (\Delta H^{\circ}_{\text{form}} (\text{H}_2\text{O}(\ell)))] - [(\Delta H^{\circ}_{\text{form}} (\text{C}_6\text{H}_5\text{COOH}(\text{s}))) + (15/2) (\Delta H^{\circ}_{\text{form}} (\text{O}_2(\text{g})))] \quad (5)$$

If it is assumed that the enthalpy changes given above are for standard conditions of temperature and pressure, equation (5) may be rearranged to give

$$\Delta H^{\circ}_{\text{form}}(\text{C}_6\text{H}_5\text{COOH}(\text{s})) = [7 (\Delta H^{\circ}_{\text{form}} (\text{CO}_2(\text{g}))) + 3 (\Delta H^{\circ}_{\text{form}} (\text{H}_2\text{O}(\ell)))] - \Delta H^{\circ}_{\text{comb}} (\text{C}_6\text{H}_5\text{COOH}(\text{s})) \quad (6)$$

where we have made use of the fact that the enthalpy of formation of any element in its standard state is equal to zero. Since the standard enthalpy of formation for $\text{CO}_2(\text{g})$ and $\text{H}_2\text{O}(\ell)$ are known, equation (6) can be used along with the experimental value of the standard enthalpy of combustion for benzoic acid to find the enthalpy of formation of the compound.

Bomb calorimetry

A schematic diagram of a bomb calorimeter is given in Figure 1. The calorimeter consists of a reaction vessel contained in a bucket of water that is itself placed inside of an insulated jacket. A high precision thermometer is used to measure the temperature of the water, which is mixed by a motor driven propeller to remove temperature gradients. Inside of the reaction vessel is a cup for holding the sample to be burned. Combustion is initiated by passing current through a fuse wire. To guarantee complete sample combustion, the reaction vessel is filled with 10-15 atmospheres of oxygen, and the sample compressed into a pellet. The heat evolved from the combustion of the sample causes an increase in the temperature of the water surrounding the reaction vessel, which is measured by the thermometer.

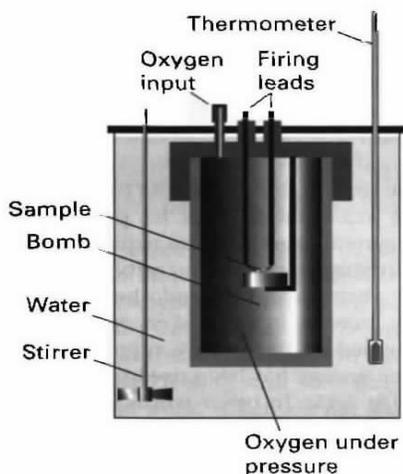


Figure 1. Bomb calorimeter

If C_B , the heat capacity of the calorimeter, is known, then q , the heat evolved from the combustion of the compound, is given by the expression

$$q = - C_B (\Delta T) \quad (7)$$

where $\Delta T = T_f - T_i$ is the change in temperature of the water following combustion. If the mass of the compound burned in the combustion reaction is known, then ΔU_{comb} , the internal energy of combustion, is

$$\Delta U_{\text{comb}} = q/m \quad (8)$$

where ΔU_{comb} has units of energy/mass. The molar internal energy of combustion can also be calculated if the molecular weight of the compound is known

$$\Delta U_{\text{comb}} = q/n \quad (9)$$

where n is the number of moles of compound burned, and ΔU_{comb} has units of energy/mole. Note that it is the internal energy of combustion that is determined in bomb calorimetry, and not the enthalpy of combustion. This is because the combustion reaction is carried out under conditions of constant volume instead of constant pressure. The molar internal energy and molar enthalpy of combustion are related by the expression [6]

$$\Delta H_{\text{comb}} = \Delta U_{\text{comb}} + (\Delta n_g)RT \quad (10)$$

where Δn_g is the change in the number of moles of gas for the combustion reaction. For example, for the combustion of benzoic acid (equation (4)), $\Delta n_g = -1/2$. The difference between the enthalpy and internal energy of combustion is small, but the conversion between ΔU_{comb} and ΔH_{comb} should be made because of the accuracy with which combustion measurements can be carried out.

Treatment of experimental data

The following experimental information is needed to proceed in the analysis of the data from the calorimetric measurements:

Mass of compound burned (m_X) - This is obtained by weighing the sample pellet on an analytical balance as indicated above.

Mass of wire burned (m_W) - There is a small contribution to the heat evolved in combustion from the fuse wire. To correct for this, the mass of fuse wire that is burned must be determined. This is equal to the difference between the initial and final mass of the wire.

Change in temperature (ΔT) - The change in temperature from the combustion is found numerically or by the graphical method indicated in Figure 2 on the next page. Be careful to obtain ΔT as accurately as possible. Note that ΔT is the difference between the final and initial temperature measured at the midpoint of the temperature rise.

The value of q is related to the internal energy of combustion of the compound and the fuse wire by the following equation [7]

$$q = m_X (\Delta U^{\circ}_{\text{comb}} (X)) + m_W (\Delta U^{\circ}_{\text{comb}} (W)) \quad (11)$$

The internal energy of combustion of the wire is $\Delta U^{\circ}_{\text{comb}} (W) = -5850 \text{ J/g}$. There are only two unknowns in equation (11), the value of q and the value of $\Delta U^{\circ}_{\text{comb}} (X)$. If C_B , the heat capacity of the calorimeter, is known, then equation (7) may be used to find q . Equation (11) can then be used to determine $\Delta U^{\circ}_{\text{comb}} (X)$. Alternatively, by burning a compound with a known value of internal energy of combustion, equation (11) may be used to calculate q , and equation (7) then used to find C_B .

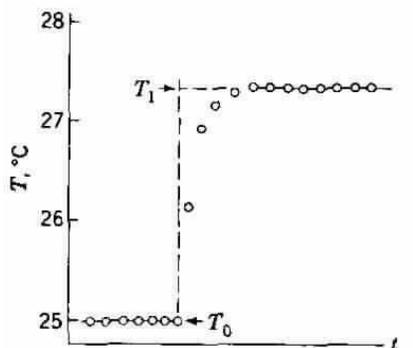


Figure 2. Method for determining ΔT from experimental data.

Experimental

Combustion measurements should be made on two compounds: benzoic acid and a compound assigned by the instructor. At least three measurements should be made for each compound.

The data on benzoic acid will be used to determine C_B , the heat capacity of the calorimeter. Benzoic acid is used because it is a compound that can be obtained in high purity, burns easily and completely to well defined combustion products, and has a known value for the internal energy of combustion, $\Delta U^\circ_{\text{comb}}(\text{C}_6\text{H}_5\text{COOH}(\text{s})) = -26410. \text{ J/g}$. Using this value for the internal energy of combustion, the results from the combustion measurements, and equations (7) and (11), the value of C_B for the calorimeter can be found.

For the assigned compound, the experimental data and the value for C_B found from the data obtained for benzoic acid should be used to determine the internal energy of combustion. The balanced combustion reaction and equation (10) should be used to convert from $\Delta U^\circ_{\text{comb}}$ to $\Delta H^\circ_{\text{comb}}$. The experimental value found for $\Delta H^\circ_{\text{comb}}$ can then be compared with the value reported in the literature [8].

Procedure for calorimeter measurement

The procedure to be used in making a measurement with the bomb calorimeter is as follows:

- (1) Prepare a pellet of the compound to be burned. The mass of the pellet should be approximately 1 g. The exact mass of the pellet should be determined using an analytical balance.
- (2) Cut a piece of fuse wire approximately 3" in length. Find the mass of the wire using an analytical balance.
- (3) Assemble the bomb calorimeter. Do this as follows:
 - a) Thread the fuse wire between the electrodes of the reaction vessel so that the wire rests on the bottom of the sample cup.
 - b) Place the sample pellet in the cup so that it is in contact with the fuse wire.
 - c) Add 1 mL of water to the inside of the reaction vessel. This is done so that the gas inside the bomb is saturated with water vapor, so that any additional water produced by the combustion reaction appears as $\text{H}_2\text{O}(\ell)$.
 - d) Assemble the reaction vessel.
 - e) Carefully fill the reaction vessel with 10-15 atmospheres of oxygen.
 - f) Place the reaction vessel inside the metal bucket, and, using volumetric glassware, fill the bucket with 2.000 liters of water. Use a 1.000 L or 2.000 L flask to do this. The same amount of water must be used in each trial so that the heat capacity of the calorimeter is kept constant.
 - g) Place the bucket with reaction vessel inside the insulated jacket.
 - h) Make the electrical connections between the detonator and the reaction vessel.
 - i) Replace the top of the insulated jacket, and begin stirring the water inside the metal bucket.

NOTE: BECAUSE OF THE DANGER INVOLVED IN THE USE OF COMPRESSED GASES, YOU MUST HAVE YOUR INSTRUCTOR DEMONSTRATE THE ABOVE PROCEDURE TO YOU BEFORE YOUR FIRST MEASUREMENT ON THE BOMB CALORIMETER. ALSO, HAVE YOUR INSTRUCTOR OBSERVE YOU WHEN YOU MAKE YOUR FIRST MEASUREMENTS USING THE CALORIMETER.

(4) Measure the temperature of the water surrounding the reaction vessel at 30 second intervals. Continue these measurements until a stable initial baseline is obtained. Note that it should be possible to measure T to the nearest ± 0.01 °C.

(5) Detonate the bomb by pressing the detonator button. Keep the button pressed down until the red light indicating current flow goes out. This indicates that the fuse wire has burned through. You should see a sharp increase in the temperature of the water within a minute of detonation if the compound has successfully been ignited.

(6) Continue to measure the temperature of the water surrounding the reaction vessel at 30 second intervals until a stable baseline has once again been achieved.

(7) Disassemble the bomb. Remove the reaction vessel from the bucket, and open the pressure relief valve to reduce the pressure inside the reaction vessel to atmospheric pressure. Then remove the top of the reaction vessel. Check to make sure the pellet has completely burned. Collect and weigh any unburned lengths of fuse wire, but be sure not to weigh any of the nodules formed from melted (and oxidized) wire.

Lab Report

Your lab report should include the following:

- 1) The determination of C_B from the experimental data on benzoic acid combustion.
- 2) The determination of $\Delta U^\circ_{\text{comb}}$ for the assigned compound. Values for the internal energy of combustion should be given in both J/g and kJ/mole.
- 3) The balanced combustion reaction and the experimental value of $\Delta H^\circ_{\text{comb}}$ for the assigned compound (in units of kJ/mole), and a comparison of the experimental value for the enthalpy of combustion with that found in the literature. [10]
- 4) A determination of $\Delta H^\circ_{\text{form}}$, the enthalpy of formation for your assigned compound, using your experimental value for $\Delta H^\circ_{\text{comb}}$ for the compound, the balanced combustion reaction, and the values for the enthalpy of formation of $\text{CO}_2(\text{g})$ and $\text{H}_2\text{O}(\ell)$ given in the Appendix of Atkins and de Paula (ref. 1).
- 5) An estimate of the error in your values for C_B , and $\Delta U^\circ_{\text{comb}}$ for the assigned compound.
- 6) A discussion of sources of experimental error, their magnitude, and their effect on C_B and $\Delta U^\circ_{\text{comb}}$.

References

1. A general introduction to thermodynamics as it applies to energies and enthalpies of reaction is given in P. W. Atkins, J. de Paula Elements of Physical Chemistry, Seventh Edition, (Oxford University Press, New York, 2017), Chapter 2.
2. Strictly speaking there is no standard temperature for thermodynamic data, but such data are often reported at $T = 25$. °C. Standard pressure is 1.000 bar. Literature and texts prior to the mid-1980s use 1.000 atm = 1.01325 bar as standard pressure. In practice, except for high precision measurements, use of these slightly different standard pressures has negligible effect on the value of $\Delta H^\circ_{\text{comb}}$.

3. This is an application of Hess's law (Atkins and de Paula, pp. 73-74).

4. The CRC Handbook of Chemistry and Physics has a collection of data on enthalpies of formation and enthalpies of combustion. More extensive tabulations of such data are also available in the literature.

5. Although the combustion products for the elements are defined as indicated in this table, in experimental work these are often not the actual products that are formed. For example, combustion of compounds containing nitrogen will produce a range of nitrogen oxides ($\text{NO}(\text{g})$, $\text{NO}_2(\text{g})$, etc.). In such cases, the amounts of each nitrogen containing compound formed must be determined (by titration, for example), and the experimental results appropriately corrected.

6. This relationship follows from the definition of enthalpy, $H = U + pV$. From this it follows that $\Delta H = \Delta U + \Delta(pV)$. For one mole of reaction, and assuming that the volume occupied by solids and liquids is small compared to that occupied by gases, and that gases behave ideally, it follows that $\Delta(pV) = \Delta n_g RT$, where Δn_g is the change in the number of moles of gas per mole of reaction.

7. Strictly speaking, we are not working under standard conditions, and therefore should use ΔU instead of ΔU° . However, the difference between ΔU and ΔU° for our experimental conditions is extremely small, and is therefore neglected.

8. A table of enthalpies of combustion may be found in The CRC Handbook of Chemistry and Physics.

Acknowledgements: Figure 1 is taken from P. W. Atkins, Elements of Physical Chemistry, Third Edition, (Freeman, New York, 2002). Figure 2 is taken from D. P. Shoemaker, C. W. Garland, J. N. Nibler, Experiments in Physical Chemistry, Sixth Edition, (McGraw-Hill, New York, 1996).

Revised 8/2020

The determination of the enthalpy of vaporization of water

Introduction

The Clausius-Clapeyron equation [1]

A pure chemical substance can exist as a solid, a liquid, or a gas [2]. These different states of matter are called phases. When a compound is converted from one state to another, a phase transition is said to occur.

As a starting point for considering the thermodynamics of a phase transition, consider a pure substance at equilibrium under conditions of temperature and pressure such that two phases are present. If these two phases are labeled a and b, then the condition of thermodynamic equilibrium implies that

$$\mu_a = \mu_b \quad (1)$$

where μ_a and μ_b are the chemical potential (partial molar free energy) for each phase.

Now consider a small change in temperature for the system, with a corresponding small change in pressure, such that the equilibrium between the two phases is maintained. The change in the chemical potential for the two phases is

$$d\mu_a = (\partial\mu_a/\partial p)_T dp + (\partial\mu_a/\partial T)_p dT \quad (2)$$

and

$$d\mu_b = (\partial\mu_b/\partial p)_T dp + (\partial\mu_b/\partial T)_p dT \quad (3)$$

However, for a pure substance, the chemical potential and molar free energy are equal. Therefore, the Maxwell equation for Gibbs free energy

$$dG = V dp - S dT \quad (4)$$

may be used to substitute into equations (2) and (3), to give

$$d\mu_a = V_{a,m} dp - S_{a,m} dT \quad (5)$$

and

$$d\mu_b = V_{b,m} dp - S_{b,m} dT \quad (6)$$

where $V_{i,m} = V_i/n$ is the i^{th} molar volume, and $S_{i,m} = S_i/n$ is the i^{th} molar entropy. Since the two phases remain at equilibrium following the change in temperature and pressure, the chemical potential of the two phases remains equal, so that

$$V_{a,m} dp - S_{a,m} dT = V_{b,m} dp - S_{b,m} dT \quad (7)$$

This equation may be rearranged to give the expression

$$dp/dT = \Delta S_{pt}/\Delta V_{pt} \quad (8)$$

where "pt" indicates phase transition, $\Delta S_{pt} = S_{b,m} - S_{a,m}$, and $\Delta V_{pt} = V_{b,m} - V_{a,m}$. This equation is called the Clapeyron equation, and is true in general for phase transitions. Since for a phase transition $\Delta S_{pt} = \Delta H_{pt}/T_{pt}$, equation (8) may also be written as

$$dp/dT = \frac{\Delta H_{pt}}{T_{pt}(\Delta V_{pt})} \quad (9)$$

For the case of a transition from a solid to a gas (sublimation) or a liquid to a gas (vaporization), equation (9) can be further simplified. Under normal conditions, $V_{g,m}$, the molar volume of a gas, is much larger than $V_{s,m}$ or $V_{l,m}$, the molar volume of the corresponding solid or liquid. Therefore, for a phase transition from a solid or liquid to a gas

$$\Delta V = V_{g,m} - V_{s/l,m} \cong V_{g,m} \quad (10)$$

Further, for the pressure range under which measurements are usually made, $V_{g,m}$ is approximately equal to the value calculated from the ideal gas law. Therefore

$$V_{g,m} = V_g/n = RT/p_{pt} \quad (11)$$

If equations (10) and (11) are used to substitute into equation (9), we get

$$dp/dT = \frac{p_{pt}(\Delta H_{pt})}{R(T_{pt})^2} \quad (12)$$

If we assume that ΔH_{pt} is independent of temperature, and drop the "pt" subscript from other terms in the equation, equation (12) may be rewritten as

$$dp/p = (\Delta H_{pt}/RT^2) dT \quad (13)$$

where ΔH_{pt} is the enthalpy change for the phase transition. But since $dp/p = d(\ln p)$, and $dT/T^2 = -d(1/T)$, this can be rewritten as well, to give

$$d(\ln p)/d(1/T) = -\Delta H_{pt}/R \quad (14)$$

the Clausius-Clapeyron equation in differential form. If the temperature and pressure are measured for a pure substance over a range of conditions for which the liquid and vapor phases are in equilibrium with one another, the enthalpy of vaporization for the substance can be found from the slope of a plot of $\ln(p)$ vs $(1/T)$.

Determination of the vapor pressure

The experimental information needed to use the Clausius-Clapeyron equation and determine the enthalpy of vaporization of a liquid is the vapor pressure of the liquid as a function of temperature. By definition, the vapor pressure is the equilibrium pressure of vapor above a pure liquid. As a consequence of the Gibbs phase rule, the vapor pressure of a liquid is a function of a single variable, the temperature of the system.

An experimental apparatus for the determination of the vapor pressure of a pure liquid is given in Figure 1. Your apparatus is slightly different than the one in the figure, and consists of a three-neck round bottom flask which contains the liquid whose vapor pressure is to be determined. One neck of the flask is fit with a thermometer for temperature measurements. The position of the thermometer is adjusted so that the bulb of the thermometer is slightly above the level of the liquid in the flask, so that it is the temperature of the vapor above the liquid that is measured in the experiment. The central neck of the flask is connected through a condenser to a ballast bulb (to limit the rate at which the pressure of the system can be changed), connected to a manometer (used to measure pressure) and vacuum pump (used to control the pressure inside the system). The condenser is placed between the flask and the manometer to keep liquid from condensing in other parts of the system. The third neck of the flask is stoppered.

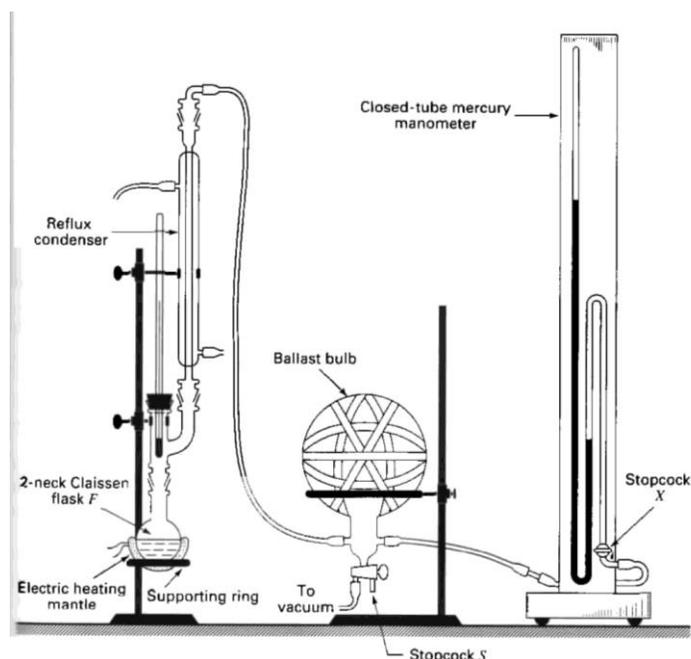


Figure 1. Apparatus for the determination of the vapor pressure of a liquid.

The procedure for determination of the vapor pressure of a liquid is as follows. The 250 mL round bottom flask is first thoroughly cleaned, then filled with approximately 75 mL of the liquid being studied. A few boiling chips should also be added to the flask. The flask is then connected to the condenser, and the thermometer is fitted to one of the side arms. The pressure of the system is reduced to approximately 400 torr. The condenser water supply and the heating mantle are then turned on, and the liquid heated until it begins to boil. Once equilibrium has been reached (two or three minutes of steady boiling of the liquid), the pressure and temperature of the vapor above the liquid should be determined. Because the manometer used in the experiment has one side arm open to the room, the difference in the height of the mercury between the two arms of the manometer (expressed in mm) is equal to the difference (in torr, as 1 torr = 1 mm Hg) between the pressure inside the room and the pressure inside the system. To convert the pressure measurements to absolute pressure, the pressure inside the room, p_{room} , must be measured separately using a mercury barometer. The pressure of the system is then given by the expression

$$p_{\text{system}} = p_{\text{room}} - \Delta p \quad (17)$$

where

$$\Delta p = \Delta h = h_{\text{high}} - h_{\text{low}} \quad (18)$$

where Δh is the difference between in height between the high side and the low side of the manometer, expressed in mm.

After pressure and temperature have been measured, a small amount of air should be allowed to leak into the system to raise the pressure by 30-40 torr. Once equilibrium has been reestablished, a second set of temperature and pressure measurements can be made. This procedure is repeated until approximately ten data points in the pressure range 400-760 torr have been obtained.

The data from the experiment is analyzed by plotting $\ln(p)$ against $1/T$, as suggested by equation (14). The slope of the plot can then be used to find ΔH_{vap} , the enthalpy of vaporization of the liquid.

Experimental

Experimental

Experimental measurements should be carried out on water [3]. At least two sets of experimental data should be taken. Each data set should be analyzed independently using the method presented above. Based on the results of the data analysis a value for the enthalpy of vaporization for the liquid can be found. The experimental value for ΔH_{vap} represents the enthalpy of vaporization at the average temperature of the data set, which can be assumed to be equal to $\Delta H_{\text{vap}}^{\circ}$, the value at the normal boiling point of the liquid [4].

Lab report

Your lab report should include the following:

1) The details of your determination of the enthalpy of vaporization for the liquid studied in the experiment, including a plot of $\ln(p)$ vs. $1/T$ for each data set. Your experimental values for $\Delta H_{\text{vap}}^{\circ}$ should be compared to the value reported in the literature [5].

2) A discussion of error in the experiment. Note that you have several things to consider in your error discussion, including a) error in the experimental value for $\Delta H_{\text{vap}}^{\circ}$ based on your plot of $\ln(p)$ vs $1/T$, b) agreement between your duplicate measurements of $\Delta H_{\text{vap}}^{\circ}$ c) expected error in $\Delta H_{\text{vap}}^{\circ}$, based on how precisely p and T can be measured using the experimental apparatus, d) comparison of your results with the value found in the literature.

References

1. Phase diagrams, phase boundaries, and the Clapeyron and Clausius-Clapeyron equations are discussed in P. W. Atkins, J. de Paula Elements of Physical Chemistry, Seventh Edition, (Oxford University Press, New York, 2017), pp. 124-130.

2. Actually, most substances have several different possible solid phases, distinguished by differences in their crystal structures. Helium can also have more than one liquid phase.

3. If desired, another liquid can be used in place of water. Low molecular weight alcohols are a good choice for alternatives to water in this experiment, as they have normal boiling points near that of water and are not particularly toxic (though they are flammable).

4. For precise work corrections would be made for the temperature dependence of the enthalpy of vaporization and for nonideal gas behavior in the vapor phase. Those corrections are fairly small, and so will not be applied here.

5. Values for $C_{p,m}$ for liquid water and water vapor can be found in the Appendix of most physical chemistry textbooks, or in the CRC Handbook of Chemistry and Physics.

Acknowledgements: Figure 1 is taken from D. P. Shoemaker, C. W. Garland, J. N. Nibler, Experiments in Physical Chemistry, Sixth Edition, (McGraw-Hill, New York, 1996).

Revised 8/2020

The equilibrium constant of an indicator

Introduction

Titration

One of the most basic analytical procedures is titration [1]. In a titration, one reactant, called the titrant, is slowly added to a solution containing the second reactant. By measuring the volume of titrant required for complete reaction to occur and by knowing the stoichiometry of the reaction and the concentration of the titrant the concentration of the reactant being titrated can be found.

As an example, consider the titration of a known volume of sodium hydroxide solution (NaOH) with a solution of hydrochloric acid (HCl). The reaction that takes place is



If we define V_{NaOH} as the initial volume of sodium hydroxide solution, V_{HCl} as the volume of hydrochloric acid solution required to completely react with the sodium hydroxide solution, and $M(\text{HCl})$ as the molarity of the hydrochloric acid solution, then the concentration of the sodium hydroxide solution is given by the expression

$$M(\text{NaOH}) = (V_{\text{HCl}}/V_{\text{NaOH}}) M(\text{HCl}) \quad (2)$$

Since volume can be measured to a high degree of precision we can, by titrating with an HCl solution of known concentration, accurately determine the concentration of a solution of NaOH or other strong base.

To use titration to find the concentration of a solution, there must be some way of experimentally determining the equivalence point of the reaction. For an acid-base titration the equivalence point is the point at which the number of equivalents of acid and base in the solution being titrated are equal. Often an indicator is used to determine the equivalence point. An acid-base indicator is a molecule that exists in two (or more) forms with different colors which depend on pH. If a small amount of indicator is added to the solution being titrated we can use the change in the color of the indicator as a means of identifying the equivalence point for the titration. This method will work only if the end point (the point at which the indicator changes color) coincides with the equivalence point for the titration.

Acid-base properties of indicators

An indicator in an acid-base titration can be represented as a molecule that has two forms, a protonated form HInd that exists at low pH, and a deprotonated form Ind⁻ that exists at high pH. The equilibrium between the protonated and deprotonated forms of the indicator can be represented by the reaction



with equilibrium constant

$$K_{\text{eq}} = (a_{\text{H}^+})(a_{\text{Ind}^-})/(a_{\text{HInd}}) \quad (4)$$

where a_i is the activity of the i^{th} substance in solution. For aqueous solutions at low concentration it is usually a good approximation to set the activity of a substance equal to the molarity of the substance, so that

$$K_{\text{eq}} = [\text{H}^+][\text{Ind}^-]/[\text{HInd}] \quad (5)$$

A fundamental property of an acid-base indicator is the pK of the indicator, defined as

$$pK = -\log_{10}(K_{eq}) = \log_{10}([HInd]/[Ind^-]) - \log_{10}[H^+] \quad (6)$$

Since the pH of a solution is defined as

$$pH = -\log_{10}[H^+] \quad (7)$$

it follows that

$$pK = \log_{10}([HInd]/[Ind^-]) + pH \quad (8)$$

It is clear by examination of equation (8) that when the pH of a solution is equal to the pK of the indicator there are equal concentrations of the protonated and deprotonated forms of the indicator. At this point, then, we are at the midpoint of the color change of the indicator.

Spectrophotometric determination of pK

Now consider the case of a series of solutions with the same total concentration of indicator but different values for pH. If we measure the spectrum of a particular solution, the absorbance that will be observed will be given by the expression

$$A_{obsd} = f A_{HInd} + (1-f) A_{Ind^-} \quad (9)$$

where A_{obsd} is the observed absorbance, A_{HInd} and A_{Ind^-} are the absorbances that would be observed if only the protonated or deprotonated form of the indicator were present, respectively, and f is the fraction of indicator molecules in the protonated form. Since

$$[HInd]/[Ind^-] = f/(1-f) \quad (10)$$

it follows from equation (8) that

$$pK = \log_{10}\{f/(1-f)\} + pH \quad (11)$$

While equation (11) gives a general expression for finding the pK of an indicator, some care must be used in applying the equation to experimental data. Since there will always be some uncertainty in determining A_{obsd} , A_{HInd} , and A_{Ind^-} , equation (11) will not be reliable when $f \cong 0$ or $f \cong 1$. In fact, equation (11) will give the most reliable results for the pK of an indicator when $f \cong 0.5$.

Experimental

Stock solutions

Hydrochloric acid - Dissolve 2.0 mL of concentrated hydrochloric acid (37 % HCl) in water, to a final volume of 250.0 mL, to make a 0.10 M solution of HCl.

Sodium hydroxide - Dissolve 1.0 g of sodium hydroxide (MW = 40.0 g/mole) in water, to a final volume of 250.0 mL, to make a 0.10 M solution of NaOH.

Potassium hydrogen phthalate - Dissolve 10.2 g of potassium hydrogen phthalate (MW = 204.2 g/mole) in water, to a final volume of 500.0 mL, to make a 0.10 M solution of $KHC_8H_4O_4$.

Indicator stock solutions. Prepare one of the following stock solutions of indicator, as chosen by your lab instructor (or obtain a sample of previously prepared indicator stock solution from your instructor).

Bromophenol blue stock solution - Mix 2 mL of stock NaOH solution with water to a final volume of 20 mL. Dissolve 0.02 g of bromophenol blue in this solution, then dilute with water to form a solution with a final volume of 100.0 mL and a bromophenol blue concentration of 0.20 g/L.

Bromocresol green stock solution - Mix 2 mL of stock NaOH solution with water to a final volume of 20 mL. Dissolve 0.01 g of bromocresol green in this solution, then dilute with water to form a solution with a final volume of 100.0 mL and a bromocresol green concentration of 0.10 g/L.

Methyl orange stock solution - Dissolve 0.01 g of methyl orange in 40 mL of ethanol, then dilute with water to form a solution with a final volume of 100.0 mL and a methyl orange concentration of 0.10 g/L.

Methyl red stock solution - Dissolve 0.01 g of methyl red in 40 mL of ethanol, then dilute with water to form a solution with a final volume of 100.0 mL and a methyl red concentration of 0.10 g/L.

Buffer solutions

Prepare 50 mL of each of the seven buffer solutions given in Table 1. Solutions can be prepared by using either a graduated cylinder or measuring pipet to measure the required volume of each stock solution.

Table 1 - Buffer solutions

Solution	Nominal pH	HCl stock (mL)	Phthalate stock (mL)	NaOH stock (mL)
1	2.5	21.9	28.1	-
2	3.0	15.4	34.6	-
3	3.5	7.0	43.0	-
4	4.0	0.9	49.1	-
5	4.5	-	42.6	7.4
6	5.0	-	34.4	15.6
7	5.5	-	28.9	21.1

Determination of approximate pK of the indicator

Clean and dry nine test tubes. Pipette 10.0 mL of either stock HCl solution, stock NaOH solution, or one of the buffer solutions into each test tube. Add 1.0 mL of indicator stock solution to each test tube. By comparing the color of each indicator-buffer solution to the color of the indicator-HCl solution (in which all of the indicator is in the protonated form) and the indicator-NaOH solution (in which all the indicator is in the deprotonated form), find the buffer solution where the color of the indicator is intermediate between that of the protonated and deprotonated forms. The pH of that buffer solution is approximately equal to the pK for the indicator.

Spectroscopic determination of the pK of the indicator

Choose the two buffers in Table 1 with pH closest as to the estimated value for pK of the indicator. Prepare two solutions of indicator in strong acid and strong base by diluting 1.0 mL of indicator stock solution with either the HCl stock solution or the NaOH stock solution, to a final volume of 25.0 mL. Prepare two additional solutions of indicator in the two buffer solutions selected above by diluting 1.0 mL of indicator stock solution with each buffer, to

a final volume of 25.0 mL. **Volumetric glassware (1.0 mL volumetric pipette, 25.0 mL volumetric cylinder) must be used in this step to ensure that the concentration of indicator in each of your solutions is the same.** Measure the absorption spectrum of each the indicator solution in strong acid and strong base in the range 200-800 nm. Based on your spectra, select two wavelengths to determine A_{obsd} , A_{HInd} , and A_{Ind} . Measure the absorbance of these two solutions and the two solutions prepared in the previous section at the two wavelengths selected for study. Using equation (9) and (11) and your experimental results, calculate the value for pK of the indicator for each buffer solution at each experimental wavelength. If possible, measure the pH of the buffer solution with a calibrated pH meter to improve the accuracy of your value for pH, and therefore for your value of pK.

Lab Report

Your lab report should include the following:

- 1) The estimated value of pK, based on the visual examination of the indicator-buffer solutions.
- 2) The absorbance spectrum for the protonated and deprotonated forms of the indicator, the wavelengths selected for determination of pK, and your reason for selecting these wavelengths.
- 3) The average value for pK from your data.
- 4) For your error analysis, you will have four values for pK, determined from your two wavelengths and two buffer solutions. The standard deviation in the average value for pK gives one way of estimating experimental error. You might also consider the error expected from the equipment (spectrophotometer, pH meter, analytical balance) and procedure (pipetting of solutions, use of graduated cylinders) used in carrying out the measurements.

References

1. Acid-base titrations are discussed in P. W. Atkins, J. de Paula Elements of Physical Chemistry, Seventh Edition, (Oxford University Press, New York, 2017), pp. 208-211, as well as in any standard textbook of general chemistry. Many examples of applications of titrations are given in D. A. Skoog, D. M. West, F. J. Holler, Fundamentals of Analytical Chemistry, Sixth Edition, (Saunders, Philadelphia, 1992).

Revised 8/2020

Method of initial rates in the bromination of acetone

Introduction [1]

Method of initial rates

Several methods exist for determining the rate law for a chemical reaction. One of the most powerful methods is the method of initial rates [2]. Consider the following chemical reaction



where A, B, and C are reactants, D, E, and F are products, and a, b, ..., f are the stoichiometric coefficients for the chemical reaction. The rate of the reaction, R, is defined as

$$R = - (1/a) d[A]/dt = - (1/b) d[B]/dt = \dots = (1/f) d[F]/dt \quad (2)$$

Note that the rate of the reaction can be given either in terms of the rate of disappearance of a reactant or the rate of appearance of a product. Note also that the rates of appearance or disappearance are weighted by the stoichiometric coefficients of the reaction.

The rate law for the chemical reaction is an expression that gives the rate of the reaction as a function of the concentrations of reactants and products, and of temperature.

$$R = f(A, B, \dots, F, T) \quad (3)$$

In fact, the rate law may also depend on the concentrations of molecules that appear neither as products nor as reactants (as in the case of a catalyst), on the solvent in which the reaction occurs, and on other parameters as well.

For a large number of chemical reactions, it has been found that the general (and not very useful) relationship given in equation (3) takes the following simple form

$$R = k [A]^p [B]^q [C]^r \quad (4)$$

where k is the rate constant for the reaction, which is a function only of temperature, and [A], [B], ... are concentrations of substances on which the rate of reaction is dependent. The coefficients of these concentrations, p, q, ... are called the order of the reaction with respect to [A], [B], ..., while the sum of the coefficients, p + q + ... is called the overall reaction order. It should be emphasized that equation (4) is based on observation, and that there are many chemical reactions that do not follow such a simple rate law. Also, as noted above, there is no reason why equation (4) might not include a dependence on the concentration of a product molecule or of a catalyst.

Consider the initial rate of reaction for a system that obeys the rate law given in equation (4). If the initial concentrations of A, B, and C are [A]_i, [B]_i, and [C]_i, then the initial rate of the chemical reaction, R_i, is

$$R_i = k [A]_i^p [B]_i^q [C]_i^r \quad (5)$$

As the reaction proceeds and reactants are converted into products, the concentrations of A, B, and C will decrease. However, if the rate of reaction is measured before the reaction has had a chance to proceed very far, the rate of reaction will be given by equation (5). The usefulness of equation (5) lies in the fact that it is often possible to select experimental conditions such that the initial concentrations of reactants are known, which allows the determination of the rate law from experimental measurements, as discussed below.

Consider the initial rate of reaction for two sets of starting conditions, with subscripts 1 and 2, and at the same temperature.

$$R_1 = k [A]_1^p [B]_1^q [C]_1^r \quad (6)$$

$$R_2 = k [A]_2^p [B]_2^q [C]_2^r \quad (7)$$

If we divide equation (7) by equation (6), we get

$$R_2/R_1 = ([A]_2/[A]_1)^p ([B]_2/[B]_1)^q ([C]_2/[C]_1)^r \quad (8)$$

Now assume in selecting the initial concentrations of reactant molecules we choose $[B]_1 = [B]_2$ and $[C]_1 = [C]_2$, that is, only the initial concentration of A is allowed to change. All terms not involving the concentration of A will drop out of equation (8), leaving

$$R_2/R_1 = ([A]_2/[A]_1)^p \quad (9)$$

or, taking the natural logarithm of both sides of the equation and solving for p

$$p = \ln(R_2/R_1)/\ln([A]_2/[A]_1) \quad (10)$$

By comparing the initial rate of reaction under conditions where the initial concentration of A has been varied while the initial concentration of other reactants has been held constant, we have been able to determine the order of the reaction with respect to A. By a similar procedure, we may also determine the reaction order with respect to B and C. Once the reaction orders are known, the value for the rate constant can be found by solving equation (5) for k.

When there is a large amount of experimental data available, a better method for determining the reaction orders can be found. The starting point is once again equation (5). If we take the natural logarithm of both sides of equation (5), we get

$$\ln(R_i) = \ln k + p \ln[A]_i + q \ln[B]_i + r \ln[C]_i \quad (11)$$

Taking the partial derivative of R_i with respect to $[A]_i$ gives

$$p = \partial \ln(R_i) / \partial \ln([A]_i) \quad (12)$$

What equation (12) tells us is that if we plot $\ln(R_i)$ vs $\ln([A]_i)$ for a set of experimental conditions where all other initial concentrations have been held constant, the slope of the resulting best fitting line to the experimental data will be equal to p, the order of the reaction with respect to A. Again, a similar procedure may be used to find the order of the reaction with respect to B, C, and so forth.

Bromination of acetone reaction

The chemical reaction for the bromination of acetone in aqueous solution has the following stoichiometry



The rate law for this reaction may be written as

$$R = k [\text{H}^+]^p [\text{CH}_3\text{COCH}_3]^q [\text{Br}_2]^r \quad (14)$$

where we have taken into account in the rate law the fact that reactions of this type are often acid catalyzed. This particular reaction is known to be zeroth order in Br_2 ($r = 0$), and so the rate law becomes

$$R = k [\text{H}^+]^p [\text{CH}_3\text{COCH}_3]^q \quad (15)$$

In addition, since we are working in this experiment under conditions where the initial concentrations of hydrogen ion and acetone are much larger than the concentration of bromine present, both $[H^+]$ and $[CH_3COCH_3]$ remain approximately constant throughout the course of the bromination reaction. That means that the rate of the reaction for a particular set of initial conditions is also approximately constant, simplifying the determination of the rate of reaction.

The purpose of the present experiment is to determine the order of the bromination reaction with respect to hydrogen ion and acetone, and to then find the value for the rate constant for the reaction.

Experimental

Stock solutions of bromine, hydrogen ion, and acetone are prepared as follows:

Bromine - The 0.02 M Br_2 stock solution is prepared by the chemical reaction of bromate ion (BrO_3^-) with bromide ion (Br^-). To make 250 mL of bromine stock solution, weigh out 0.278 g of $KBrO_3$ and 0.992 g of KBr . Add these compounds together in a 250 mL volumetric flask. Half fill the volumetric flask with water and swirl to dissolve the salts. Add 2 mL of 3 M H_2SO_4 to the volumetric flask, and then fill to the mark with distilled water. The chemical reaction that produces Br_2 takes approximately two hours to go to completion.

Hydrogen ion - To make 250 mL of 1.0 M HCl stock solution carefully dilute 20.0 mL of concentrated HCl to a final volume of 250 mL in a volumetric flask [3].

Acetone - To make 250 mL of 4.0 M acetone stock solution dilute 73.4 mL of reagent grade acetone to a final volume of 250 mL in a volumetric flask.

Absorption measurements will be carried out on either a double beam UV-visible spectrophotometer or a single beam Spec 20 spectrophotometer. The instrument should be allowed to warm up for at least 15 minutes prior to the first experimental measurements. If the cuvette holder of the spectrophotometer is connected to a temperature bath, set the bath temperature to 20. °C. The spectrophotometer should be zeroed at 400 nm by the method appropriate for the instrument used, with deionized water used as a reference or blank. During the kinetic runs the sample cuvette will be filled with a sample of the solution in which the bromination reaction is taking place, while the reference cuvette (if used) will remain in place and filled with deionized water.

The reaction rate will be found for four conditions where all initial concentrations except that of hydrogen ion are held constant, and four conditions where all initial concentrations except that of acetone are held constant (solution 1 can be used in both of the determinations of the reaction order). A table listing the volumes of each stock solution to be used in each trial is given on the next page. All solutions should be made up to a final volume of 50 mL by addition of distilled water. The solutions are prepared by mixing the appropriate amounts of each stock solution as indicated above, in the order HCl stock solution, acetone stock solution, deionized water, and bromine stock solution. **DO NOT ADD THE BROMINE STOCK SOLUTION UNTIL JUST PRIOR TO THE START OF EACH OF YOUR MEASUREMENTS.**

After adding bromine to the solution, mix rapidly, then fill a cuvette with solution. Measure the initial absorbance of the solution (at 400 nm) on a spectrophotometer. This initial absorbance is expected to be $A \cong 0.7$. Continue to make absorption measurements at one minute intervals for a period of 10 minutes, or until the initial absorbance has decreased to below 0.05.

For each experimental condition plot absorbance against time to determine dA/dt , the rate of change of absorbance as a function of time. Since Beer's law states

$$A = \epsilon c \ell \quad (16)$$

(where A = absorbance, ϵ = extinction coefficient, c = concentration of absorbing species, and ℓ = path length of the sample cell), we may show that the rate of change of the concentration of Br_2 with time, $d[\text{Br}_2]/dt = dc/dt$, is given by the expression

$$dc/dt = (1/\epsilon\ell) dA/dt \quad (17)$$

The extinction coefficient (also sometimes called the absorption coefficient) for Br_2 at 400 nm is $\epsilon = 160$. L/mole \cdot cm. None of the other chemical species absorb light at this wavelength. The pathlength for the cuvette or sample tube is $\ell = 1.0$ cm.

Since ϵ and ℓ are known, equation (17) can be used to find the rate of change in bromine concentration with time. Since bromine is a reactant, the rate of the reaction for each trial is

$$\text{Rate} = - d[\text{Br}_2]/dt \quad (18)$$

By analyzing the experimental data as suggested by equation (12), determine the order of the reaction with respect to hydrogen ion and acetone. After the reaction orders have been found, determine the value of the rate constant for the reaction. When determining the value of the rate constant for the bromination reaction, you should first round off the experimental rate orders to the nearest integer values. Note that the above procedure for determining the rate law for the bromination of acetone reaction is valid only because the rate law is zeroth order with respect to Br_2 , and because we have chosen to work under conditions where $[\text{H}^+]$, $[\text{CH}_3\text{COCH}_3] \gg [\text{Br}_2]$. As a consequence of this, a plot of absorbance vs time (which is equivalent to a plot of bromine concentration against time) gives a straight line whose slope is related to the rate of the reaction. You should think about how changing either of the above two conditions would affect your observed experimental results.

TABLE 1. Experimental conditions for kinetic runs.

Solution	1.0 M HCl	4.0 M acetone	dH ₂ O	0.020 M Br ₂
1	10 mL	10 mL	20 mL	10 mL
2	15 mL	10 mL	15 mL	10 mL
3	20 mL	10 mL	10 mL	10 mL
4	25 mL	10 mL	5 mL	10 mL
5	10 mL	15 mL	15 mL	10 mL
6	10 mL	20 mL	10 mL	10 mL
7	10 mL	25 mL	5 mL	10 mL

Lab Report

Your lab report should include the following:

- 1) A table containing your raw data (absorbance vs time for each trial).
- 2) A plot of absorbance vs time for each trial, and an explanation of how the observed rate of reaction was obtained from these plots.

3) The details (including any data plots) for your determination of the order of the reaction with respect to H^+ ion and acetone.

4) The average value and 95% confidence limits for k , the rate constant for the reaction, including correct units, along with an explanation of how these results were obtained.

5) You do not need to compare your experimental results (reaction orders and rate constant) with literature values.

References

1. A general discussion of chemical kinetics is given in P. W. Atkins, J. de Paula Elements of Physical Chemistry, Seventh Edition, (Oxford University Press, New York, 2017), Chapter 6 (pp. 249-314).

2. Atkins and de Paula, pp. 259-260.

3. Remember that in preparing a dilute solution of a strong acid, the concentrated strong acid should be slowly pipetted into a container that is at least half-filled with water

Revised 8/2020

Kinetics of the mutarotation reaction of glucose

Introduction

Optical isomers

Most simple chemical compounds can be superimposed on their mirror image. For example, Figure 1 gives a molecule of 2-propanol and the mirror image of the molecule. The mirror image can be superimposed on the original molecule and is therefore not distinguishable, but is in fact the same molecule.

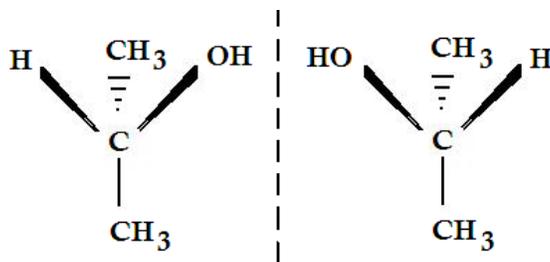


Figure 1. 2-propanol and its mirror image.

There is, however, a class of molecules that cannot be superimposed on their mirror image. A simple example of such a molecule is 2-butanol, shown in Figure 2. The two molecules of 2-butanol in the figure are mirror images of one another, just as was the case in Figure 1. However, unlike the mirror images in Figure 1, the 2-butanol molecule and its mirror image cannot be superimposed on one another, and therefore represent distinct molecules. Molecules that cannot be superimposed on their mirror image are called optically active molecules, for reasons discussed below, with the non-superimposable forms of the molecules called optical isomers.

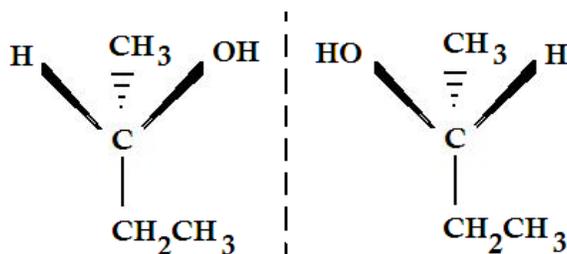


Figure 2. 2-butanol and its mirror image.

Additional information concerning optically active molecules and optical isomers can be found in reference [1] or most other standard organic texts.

Rotation of light

The physical property that distinguishes an optically active molecule from an optically inactive molecule is the way in which the molecule interacts with polarized light. Polarized light is light where the electromagnetic oscillations have been oriented in a particular plane perpendicular to the direction in which the light is moving. Polarized light can be produced by reflection of light from a surface or by passing light through a crystal or oriented polymeric film. When polarized light passes through a solution containing only optically inactive molecules, no change in the plane of polarization of the light is observed. However, if an optically active molecule is present in the solution, the plane of polarization of the light will be rotated either to the right (positive, D, or dextrorotatory) or to

the left (negative, L, or levorotatory). The angle of rotation of the plane of polarization of the light is given the symbol α . Some of the properties of polarized light and its interaction with optically active molecules are discussed in reference [2].

The amount of rotation that a plane polarized beam of light undergoes when passing through a solution containing optically active molecules depends on many factors, including the concentration of optically active molecules in solution, the wavelength of the polarized light, the pathlength, the temperature, and the solvent. Because of this, a reference condition is needed for reporting optical activity. The specific rotation of an optically active compound, given the symbol $[\alpha]_D^T$, is defined as the observed rotation for a 1 g/mL concentration of the pure optically active compound in a 10 cm polarimeter cell, at a fixed temperature T, using polarized light from the D line of a sodium emission lamp (actually a closely spaced doublet line occurring at 589.3 nm, corresponding to the $^2P \rightarrow ^2S$ electronic transition). The relationship between α_{obsd} , the rotation observed for a particular concentration and pathlength, and $[\alpha]_D^T$, the specific rotation of the compound is

$$[\alpha]_D^T = 10(\alpha_{\text{obsd}})/c\ell \quad (1)$$

where c is the concentration of the optically active compound (in g/mL) and ℓ is the pathlength of the polarimeter cell (in cm).

The mutarotation reaction

Glucose is a monosaccharide, a sugar with the chemical formula $C_6H_{12}O_6$. In water, glucose exists in two cyclic forms (which themselves have non-superimposable forms that are their optical isomers), as shown in Figure 3. These two forms of glucose are not mirror images of one another because there is more than one optically active site in the molecule. As it happens, both of these molecules are dextrorotatory.

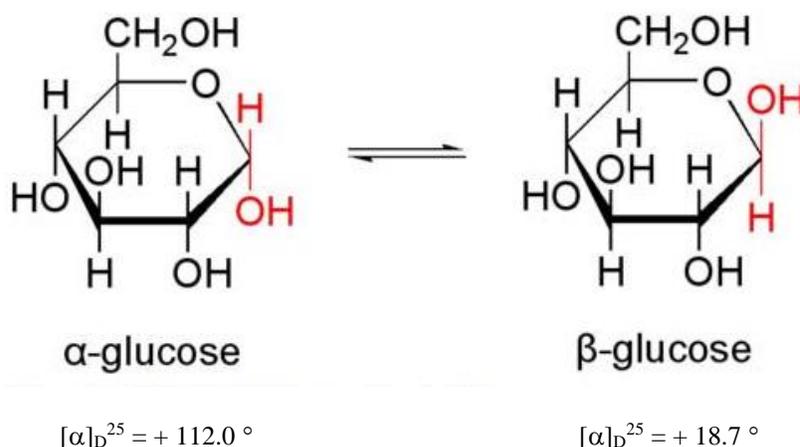


Figure 3. The α and β isomers of D-glucose.

The mutarotation reaction occurs by protonation of the ring oxygen atom followed by formation of the linear, or aldehydic, form of the sugar. When the cyclic form of the sugar is regenerated either the α or the β configuration can occur. Thus one cyclic form of glucose may be converted to the other cyclic form of glucose. Whether we begin with the α or the β form of glucose, the aldehydic intermediate is the same. The mutarotation reaction thus generates an equilibrium concentration of α and β forms from any initial nonequilibrium concentration of starting material.

Kinetics

The mutarotation reaction is a kinetic system with the form



where

A = α -D (+) glucose

B = β -D (+) glucose

k_1 = rate constant for conversion of A into B

k_{-1} = rate constant for conversion of B into A

The rate law in differential form is then

$$d[A]/dt = -k_1 [A] + k_{-1} [B] \quad (3)$$

where $d[A]/dt$ is the rate of change in the concentration of A with time. Note that at equilibrium (with equilibrium quantities labeled eq)

$$(d[A]/dt)_{eq} = 0 = -k_1 [A]_{eq} + k_{-1} [B]_{eq} \quad (4)$$

or

$$[B]_{eq}/[A]_{eq} = K_{eq} = k_1/k_{-1} \quad (5)$$

which gives a simple relationship between the equilibrium constant for the reaction and the rate constants for the reaction.

Returning to equation (3), we may integrate to obtain the time dependence of the concentration of A. The result [3] is

$$([A]_t - [A]_{eq})/([A]_0 - [A]_{eq}) = \exp[-(k_1 + k_{-1})t] \quad (6)$$

or

$$\ln\{([A]_t - [A]_{eq})/([A]_0 - [A]_{eq})\} = -(k_1 + k_{-1})t = -k_{obsd}t \quad (7)$$

where we have defined $[A]_0$ as the concentration of A at some convenient starting time $t = 0$ (which, because the reaction is first order, is arbitrary), $[A]_{eq}$ as the concentration of A at equilibrium, and k_{obsd} , the observed rate constant, as the sum of the forward and reverse rate constants for the reaction (that is, $k_{obsd} = k_1 + k_{-1}$). Note that the rate at which the system approaches equilibrium is determined by the sum of k_1 and k_{-1} .

The difference between the optical rotation of a solution containing α -D (+) glucose and β -D (+) glucose and the rotation observed at equilibrium is directly proportional to the concentration of the α -isomer (relative to the equilibrium concentration) for a fixed path length and total glucose concentration. Equation (7) can therefore be rewritten as

$$\ln\{(\alpha_0 - \alpha_{eq})/(\alpha_t - \alpha_{eq})\} = k_{obsd}t \quad (8)$$

where α_t is the observed rotation of the solution at time t , α_0 is the observed rotation at $t = 0$, and α_{eq} is the rotation observed when the system has reached equilibrium. Notice that we do not need to convert the observed rotation of the solution to a specific rotation, nor do we need to know the constant of proportionality that relates α_t to $[A]_t$.

A plot of the left hand side of equation (8) versus time has a slope equal to k_{obsd} . The equilibrium constant for the mutarotation reaction can be found by measuring the optical rotation of a solution that has achieved equilibrium, given the total concentration of glucose in the polarimeter cell, the path length of the cell, and the specific rotation of each glucose isomer. Based on the values for k_{obsd} and K_{eq} it is possible (using $k_{\text{obsd}} = k_1 + k_{-1}$ and $K_{\text{eq}} = k_1/k_{-1}$) to find individual values for k_1 and k_{-1} for each experimental condition, though this will not be done in the present experiment.

While the mutarotation reaction will take place in neutral ($\text{pH} = 7$) solutions, the reaction is also catalyzed by the presence of hydrogen ion. We therefore expect the observed rate constant for a series of experiments carried out at different hydrogen ion concentrations to fit an equation of the form

$$k_{\text{obsd}} = k_n + k_a [\text{H}^+] \quad (9)$$

where k_n is the rate constant for the neutral (uncatalyzed) reaction, and k_a is the rate constant for the acid catalyzed reaction. By plotting k_{obsd} vs $[\text{H}^+]$ experimental values for both k_n and k_a can be found.

Experimental

A stock solution of hydrochloric acid (HCl) is prepared by carefully diluting 2.0 mL of 37% HCl to a final volume of 100.0 mL with water [4]. This results in a solution that is 0.240 M in HCl. From this stock solution, prepare four additional solutions as follows:

Solution	HCl stock solution (mL)	Water (mL)
1	5.0	45.0
2	10.0	40.0
3	15.0	35.0
4	20.0	30.0

The hydrogen ion concentration should be calculated for each solution. Remember HCl a strong acid, and so $[\text{H}^+] = [\text{HCl}]$.

Optical rotation measurements will be taken using an electronic polarimeter. The instrument should be allowed to warm up for a minimum of 15 minutes prior to the first experimental measurements. The machine is calibrated by adjusting the optical rotation of a sample of deionized water to zero.

The procedure for carrying out a kinetic run is as follows. Place the 50.0 mL buffer solution and a magnetic stir bar to a 100 mL beaker. Add approximately 4.0 g of glucose to the beaker while stirring the solution vigorously. Be sure to record the exact mass of glucose used as you will need this information in calculating the equilibrium constant for the mutarotation reaction. When the glucose has completely dissolved, fill a 10 cm polarimeter cell with solution so that there is at most only a small air bubble inside the cell (you might want to practice filling the polarimeter cell with distilled water before attempting a kinetic run). Place the polarimeter tube inside the polarimeter, and measure the rotation due to the solution. This initial value of rotation is α_0 , and should be approximately + 8.0 °. Continue to measure the rotation of the solution at 1 minute time intervals for 10 to 15 minutes. A final measurement of the observed rotation should be made after sufficient time has elapsed so that equilibrium between the two forms of glucose has occurred (you can leave the excess solution in a labeled beaker and arrange to have the rotation read the following day). The value of the rotation measured at that time is α_{eq} .

You should also record the temperature of the room for the day that data is taken. While the temperature will not be used in your calculations, differences in temperature on different days can affect the rate constant (and, to a lesser extent, the equilibrium constant) for the reaction.

Lab report

Your laboratory report should include the following:

- 1) A table containing your raw data (rotation vs time for each solution, including the values for α_{eq}).
- 2) A plot of $\ln\{(\alpha_0 - \alpha_{eq})/(\alpha_t - \alpha_{eq})\}$ vs t for each solution, and an explanation of how these plots were used to determine the value for k_{obsd} for each solution.
- 3) The experimental values for K_{eq} for each solution. You will have to derive an equation for finding K_{eq} based on the information you have available to you.
- 4) The average value for K_{eq} , and the 95% confidence limits for that value. This can be found by taking an average of the four experimental values for K_{eq} . Doing this assumes that the value for K_{eq} is independent of $[H^+]$. Is that a reasonable assumption? Why or why not?
- 5) A discussion of the effect of hydrogen ion concentration on the value of k_{obsd} , including a determination of experimental values for the neutral (k_n) and acid catalyzed (k_a) rate constants, along with an appropriate plot of the data.

References

1. T. W. G. Solomons, C. B. Fryhle, S. A. Snyder Organic Chemistry, Twelfth Edition, (Wiley, New York, 2016) pp. 193-213.
2. C. W. Garland, J. W. Nibler, D. P. Shoemaker Experiments in Physical Chemistry, Eighth Edition, (McGraw-Hill, Philadelphia, 2009), pp. 611-612.
3. S. W. Benson, Foundations of Chemical Kinetics, (McGraw-Hill, New York, 1960), pp. 27-29.
4. Remember that in preparing a dilute solution of a strong acid, the concentrated strong acid should be slowly pipetted into a container that is at least half-filled with water

Acknowledgements: Figures 1-4 are taken from T. W. G. Solomons, Organic Chemistry, Sixth Edition, (Wiley, New York, 1996).

Revised 8/2020