

CHEM 355/PHYSICAL CHEMISTRY LAB

EXPERIMENT PACKET

- 1. THE KINETICS OF AQUATION OF THE TRANS-DICHLOROBIS (ETHYLENEDIAMINE)-COBALT(III) ION**
- 2. pK_A OF METHYL RED**
- 3. BINARY LIQUID-VAPOR PHASE DIAGRAM**
- 4. CALORIMETRY LAB WITH PARR 6755 SOLUTION CALORIMETER**
- 5. THE SOLUTBILITY PRODUCT OF $PbCl_2$ FROM ELECTROCHEMICAL MEASUREMENTS**
- 6. THERMODYNAMICS OF PHASE EQUILIBRIUM AND SOLUTION PROPERTIES**

The Kinetics of Aquation of the *Trans*-dichlorobis (ethylenediamine)-Cobalt(III) ion¹

Purpose: Determine the order, rate constant, activation energy, and pre-exponential factor for the ligand exchange reaction of a water for a chloride ion in *trans*-dichlorobis (ethylenediamine)-cobalt(III) ion.

Introduction

There are two questions of general importance when considering all chemical reactions. The first question concerns the feasibility of carrying out a reaction, that is determining the equilibrium position of a reaction. Chemical thermodynamics deals with the position of equilibrium. The second question concerns how fast the equilibrium position is established. This area is called chemical kinetics. Together the questions are: how far and how fast?

Numerous rules and concepts can aid the prediction of whether a particular reaction will occur (thermodynamic considerations). Some of the following are used in the study of chemistry: activity series, rules of exchange reactions, equilibrium constants, solubility product constants, oxidation-reduction potentials, and free energies of reactions.

However, the prediction of how fast a chemical reaction will occur is much more difficult. The ultimate factor controlling the rate of reaction involves the mechanism of reaction, which involves a detailed time picture of exactly how the molecules and atoms are interacting during the course of the reaction.

The Rate Expression

The rate expression for a chemical reaction is based on data obtained from a kinetic study conducted in the laboratory. From the experimental rate expression, a detailed mechanism for the reaction can be developed. In general, the rate of a chemical reaction



1

will be given by

$$\text{rate} = -\frac{1}{a} \frac{d[A]}{dt} = -\frac{1}{b} \frac{d[B]}{dt} = \frac{1}{p} \frac{d[P]}{dt}$$

2

where the brackets refer to concentrations generally in moles liter⁻¹. The rate expression frequently has the form

$$\text{rate} = k [A]^n [B]^m$$

3

where k is the rate constant, [A] is the concentration of A and [B] is the concentration of B in moles liter⁻¹ and n and m are exponents called the reaction orders. There is no necessary relation between the values of the exponents n and m and the coefficients a and b in equation 1. This situation exists because the chemical equation gives no information about the mechanism of the reaction and the values of n and m depend on the mechanism. For example, the transformation of A + B into products may proceed via more than one step.

In this experiment the rate expression for a chemical reaction will be determined, as well as the temperature dependence of the rate constant.

First-Order Rate Expression

One of the simplest types of rate expression is first-order in one of the reactants:

$$\text{rate} = -\frac{d[A]}{dt} = k[A]$$

For equation 1 this would be the case if $n = 1$ and $m = 0$ or if $[B]^m$ is kept constant and included in k . This could be done experimentally by having B in great excess, in which case, the overall concentration change of B during the course of the reaction would be negligible. The process is then said to be first-order in A. The integrated rate expression is,

$$\ln \frac{[A]}{[A]_0} = -kt \text{ or } \ln [A] = -kt + \ln[A]_0 \quad 5$$

where $[A]_0$ is the initial concentration A at time zero and $[A]$ is the concentration at any time, t . The half-life of a chemical reaction is the time required for one-half of the reactant that was present at the start of a given time period to react. A first-order reaction has a constant half-time, $t_{1/2}$, since:

$$\ln \frac{[A]_{1/2}}{[A]_0} = -\ln 2 = -k t_{1/2} \quad \text{or} \quad t_{1/2} = \frac{0.693}{k} \quad 6$$

Second-Order Rate Expression

If $n=2$ and $m=0$ or $[B]^m$ is held constant in equation 3,

$$\text{rate} = -\frac{d[A]}{dt} = k[A]^2 \quad 7$$

the reaction is second-order in A and integration of equation 7 gives:

$$\frac{1}{[A]} - \frac{1}{[A]_0} = k t \quad 8$$

The half-life for a second-order reaction is found from

$$\frac{1}{([A]_{1/2})} - \frac{1}{[A]_0} = k t_{1/2} \quad \text{or} \quad t_{1/2} = \frac{1}{[A]_0 k} \quad 9$$

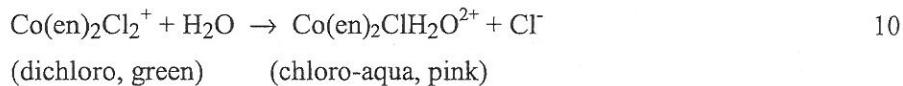
Determining the Reaction Order

To determine the order of a reaction, concentration versus time measurements are collected in the laboratory, and the data are plotted. According to equation 5, for a first-order reaction a plot of $\ln[A]/[A]_0$ versus t should yield a straight line. According to equation 8, for a second-order reaction a plot of $1/[A]$ versus t should yield a straight line.

The Reaction To Be Studied

Trans-dichloro-bis-ethylenediamine cobalt (III) ion, $\text{Co}(\text{en})_2\text{Cl}_2^+$, is a complex ion that forms a green solution when dissolved in water. Ethylenediamine, here symbolized as "en," is $\text{H}_2\text{N}-\text{CH}_2-\text{CH}_2-\text{NH}_2$. Ethylenediamine is a bidentate ligand, which means that the cobalt ion in this complex has a coordination number of six. In solution, a water molecule may replace one of the Cl^- ions in this complex, giving a mixture of *cis*- and *trans*- $\text{Co}(\text{en})_2\text{ClH}_2\text{O}^{2+}$, which forms a

pink solution. The purpose of this experiment is to investigate the kinetics of this aquation reaction:



The forward reaction may be expressed by the rate law

$$-\frac{d[\text{Co(en)}_2\text{Cl}_2^+]}{dt} = k [\text{Co(en)}_2\text{Cl}_2^+]^n \quad 11$$

where k is the rate constant, and n is the apparent order of the reaction. One might expect the concentration of H_2O to enter into the rate expression. Since this experiment is done in dilute aqueous solution, the concentration of water is large (55 M) and very nearly constant, so any dependence on $[\text{H}_2\text{O}]$ is incorporated into the constant k . The reverse reaction can be disregarded under the conditions in this laboratory.

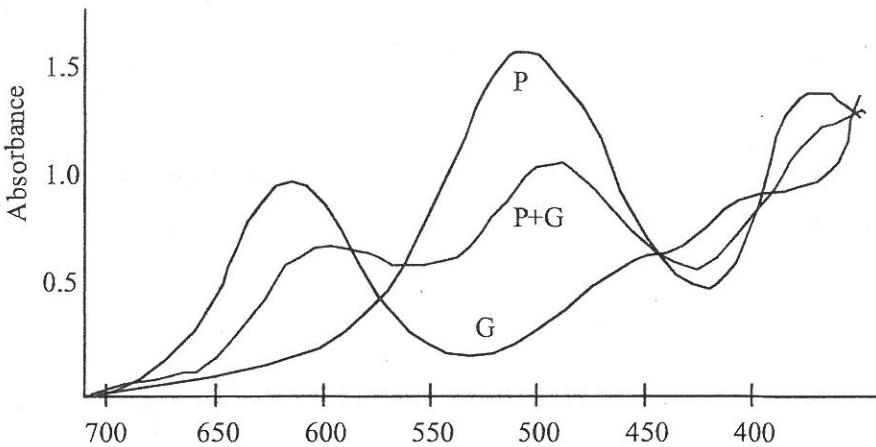


Figure 1.

P: Spectrum of an aqueous solution of $\text{Co}(\text{en})_2(\text{H}_2\text{O})\text{Cl}^{2+}$. This solution is pink because it absorbs strongly in the green region.

G: Spectrum of an aqueous solution of $\text{Co}(\text{en})_2\text{Cl}_2^+$. This solution is green because it absorbs strongly in the red and blue regions.

P+G: Spectrum of an aqueous solution of an aqueous mixture of the two species in equal concentrations.

Absorbance Measurements

The progress of the reaction is observed spectrophotometrically. The absorbance spectra of the dichloro and chloro-aqua complexes and a mixture of the two is shown schematically in Figure 1.

The concentrations of dichloro, $[\text{M-Cl}]$, and chloro-aqua, $[\text{M-H}_2\text{O}]$, forms are related to the absorbance, A , by the Lambert-Beer law. The absorbance of the solution is just the sum of the absorbances of the two species:

$$A = A_{\text{M-Cl}} + A_{\text{M-H}_2\text{O}} \quad 12$$

where the absorbance of each species is:

$$A_{M-Cl} = a_{M-Cl} \ell [M-Cl] \quad \text{and} \quad A_{M-H_2O} = a_{M-H_2O} \ell [M-H_2O]$$

where a is the molar absorption coefficient, ℓ the length of the optical path within the solution, and $[M-Cl]$ and $[M-H_2O]$ are the concentrations. (Please note that $[A]$, in brackets, is the concentration of species A, while A , without brackets, is the absorbance of the solution.) Within the visible region, the spectra of the dichloro and the aqua forms are distinctly different, but there is not a single maximum, free from overlap with other absorptions, that may be used for spectrophotometric analysis. To be able to follow the reaction progress at one wavelength, the following property of the stoichiometry of this reaction is used:

$$[M-H_2O] = [M-Cl]_0 - [M-Cl] \quad 13$$

From equations 12 and 13 the following relation can be derived:

$$\frac{[M-Cl]}{[M-Cl]_0} = \frac{A_t - A_\infty}{A_0 - A_\infty} \quad 14$$

where $[M-Cl]$ is the concentration at time t ; $[M-Cl]_0$ is the concentration at $t=0$; A_t is the absorbance at time t ; A_0 the absorbance at time $t=0$; and A_∞ is the absorbance after the reaction has gone to completion. Absorbances are for the reaction mixture composed of dichloro and chloro-aqua forms in solution.

Equation 14 eliminates the necessity of determining molar absorption coefficients and possible error in the initial concentration of the dichloro compound resulting from initiation of the reaction before the sample completely dissolves. Plots of $\ln[M-Cl]/[M-Cl]_0$ or alternatively $1/([M-Cl]/[M-Cl]_0)$ will verify the reaction order.

Determination of the Activation Energy

The second part of the exercise is the determination of the activation energy of the reaction. The rate constant for a reaction is related to the energy of activation, E_a , by the equation

$$k = A e^{-E_a/RT} \quad 15$$

where A , the pre-exponential factor, is a constant characteristic of the reaction, R is the gas constant, and T is the absolute temperature. By taking the logarithm of both sides, we obtain:

$$\ln k = -\frac{E_a}{R} \frac{1}{T} + \ln A \quad 16$$

Thus if you determine the rate constant for the aquation of $trans$ -Co(en)₂Cl₂⁺ at several different temperatures, you can make a plot of $\ln k$ against $1/T$. A straight line drawn through the points should have a slope of $-E_a/R$, and a determination of the slope permits a calculation of E_a . The intercept is used to calculate the pre-exponential factor.

Because the rate constant can be readily calculated from the half-time, $t_{1/2} = \ln 2/k$, a determination of the half-time is equivalent to a determination of the rate constant. Show that a plot of $\ln t_{1/2}$ versus $1/T$ would have a slope of E_a/R . Also determine the relationship of the pre-exponential factor to the intercept of this plot. The experimental procedure is to determine the half-time for several different temperatures.

Procedure

Part I. Determining the Visible Absorption Spectra of the Reactant and Product

The instructions for using the Ocean Optics Diode Array spectrophotometer are at the end of this manual. The $\text{Co}(\text{en})_2\text{Cl}_2^+$ complex is available as the chloride salt, $[\text{Co}(\text{en})_2\text{Cl}_2]\text{Cl}$. Determine the spectrum of a fresh cold dilute solution of $\text{Co}(\text{en})_2\text{Cl}_2^+$ (make sure the water is cold before mixing with the solid complex to delay hydrolysis). Determine the spectrum of a hydrolyzed solution, which is $\text{Co}(\text{en})_2(\text{H}_2\text{O})\text{Cl}^{2+}$. The concentration is not important to determine the spectra. Choose an appropriate wavelength for the analysis by reference to your spectra and Figure 1.

Part II. Determining the Reaction Order

A time-course kinetic run will be done using a Spectronic 20 set to the wavelength you chose. Since both of the complexes in the reaction absorb throughout the visible region, the absorbance remains rather high during the entire course of the reaction. To yield better accuracy and precision in your measurements, it is best to use the initial solution at time zero to set 100%, rather than a pure water blank. This procedure will expand the scale of the spectrophotometer.

A suitable initial concentration range for the kinetic runs is 0.01–0.015 M. Make sure to do all solution preparation calculations before you come to lab. Measure absorbance versus time data for the hydration at 55°C in a thermostated bath. Use a test tube, clamped in the bath for a reaction vessel. Use a volume of 25 mL. Before adding the complex to the test tube, make sure the water in the test tube is at the bath temperature. Take aliquots from the solution in the water bath and determine the absorbance in the spectrophotometer every 1 to 2 minutes. Return the aliquot to the test tube in the bath, so that you don't run out of solution.

Calculations

Plot the data as discussed above, determine the reaction order and calculate the rate constant. Include both your first-order and second-order plot. Use least-squares curve fitting to determine the slope, rate constant, and the uncertainty in the rate constant.

Part III. Determination of the Activation Energy

The half-time of the reaction may be measured without the use of a spectrophotometer by comparing the color of the reaction to a reference made from a 50:50 mixture of the unhydrolyzed dichloro complex and the hydrolyzed chloro-aqua complex. This color reference is possible since at temperatures close to 0°C, a water solution of $\text{Co en}_2\text{Cl}_2^+$ undergoes no appreciable aquation. A solution of the hydrolyzed chloro-aqua complex can be easily prepared by placing a solution of the dichloro complex in a beaker of hot water for 5 to 10 minutes or by using the final solution from Part II. The design of the experiment is up to you. You are to determine the activation energy and the pre-exponential factor. This determination will probably require about five different temperature measurements. A suitable temperature range for the rate measurements is approximately 50°–85°C. Make sure the concentrations in each run match your color reference fairly accurately ($\pm 3\%$). Do the initial concentrations for each run have to be exactly the same? It is essential that strict temperature control be maintained: place, thusly, a water-filled test tube in a heated water bath, and allow it to reach the temperature of the bath before adding the $[\text{Co}(\text{en})_2\text{Cl}_2]\text{Cl}$.

Calculations

Plot the data as discussed above, determine the activation energy and the pre-exponential factor from the slope and intercept of the straight line. Use least-squares curve fitting to determine the values and the propagated uncertainties.

Report

In the Introduction, describe the experiment and the expected results in a few sentences. For the Theory Section, just reference this write-up, but include the requested derivation that starts with Eq. 16; show that a plot of $\ln t_{1/2}$ versus $1/T$ would have a slope of E_a/R and determine the relationship of the pre-exponential factor to the intercept of the plot. For the Procedure Section, just reference this write-up. For the Results Section, provide the data in a tabular format, including all information necessary to repeat your calculations. Attach all three of your graphs. Report the order of the reaction, the rate constant at 55°C, the activation energy, and pre-exponential factor. Include any slopes and intercepts determined by curve fitting and the uncertainties in the quantities. Remember to use propagation of error rules in presenting the standard deviations in the final results. Discuss the chemical significance of the results. In other words, state why these results are useful and important. Discuss why someone might need to do a study of this type. Are the results for this system unusual or do they fall within the normal range of similar results for other systems? Answer the question in the procedure section of Part III (do the initial concentrations for each run have to be exactly the same?).

References

1. This lab write-up contains excerpts from the following sources:
 - a) W. L. Jolly, *Encounters in Experimental Chemistry*, Harcourt, Brace, and Jovanovich, New York, 1972.
 - b) R. E. Davis, D. S. Page, "The Kinetics of the Hydrolysis of Sodium Borohydride", in *Modular Laboratory Program in Chemistry*, KINE-070, Willard Grant, Boston, 1972.
 - c) The Harvard (summer school) *General Chemistry laboratory manual*, 1979.
 - d) U. A. Hofacker, *Chemical Experimentation*, Freeman, San Francisco, CA., 1972. Exercise 14.

Alternate Work

If the *cis*- complex is available, the kinetics of the *cis-trans* isomerization, in methanol solution, may be studied. Conditions and procedures, mentioned above, may be used for the *cis-trans* isomerization as well.

pK_a of Methyl Red¹⁻³

Purpose By measuring absorbance spectra as a function of pH, the pK_a of methyl red will be determined.

Introduction

Methyl red (4-dimethylaminobenzene-2'-carboxylic acid) is a commonly used indicator for acid-base titrations. We will measure the visible absorption spectra of the acidic and basic forms of this compound. Next we will prepare a series of buffered solutions of methyl red at known pH. By following the change in absorbance as a function of pH we will determine the acid dissociation constant, or pK_a. This technique is not restricted to indicators, and can be used with any substance whose absorption spectrum changes with pH.

The acid form of the indicator, which we will designate as HMR, is zwitter ionic, Figure 1. The basic form is designated as MR⁻.

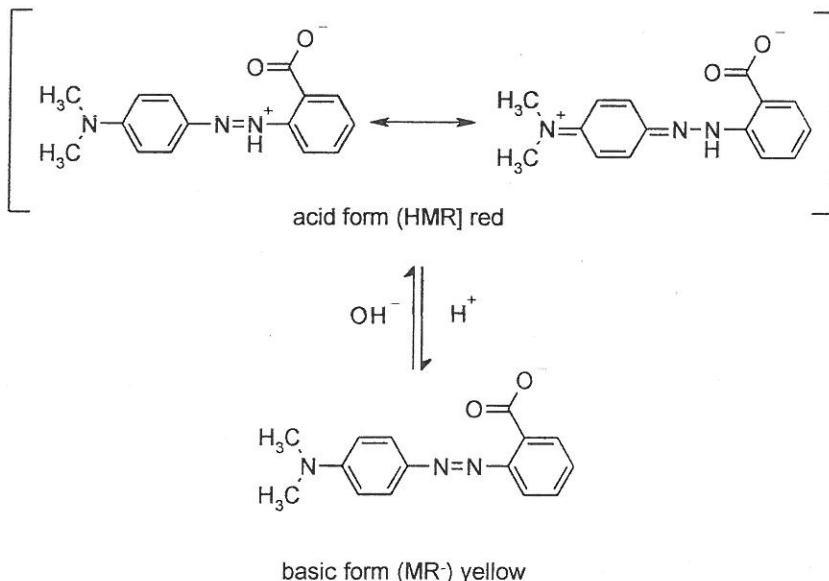


Figure 1. Acid and base forms of methyl red.

The equilibrium of interest is



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The equilibrium constant is the acid dissociation constant:

$$K_a' = \frac{[H_3O^+][MR^-]}{[HMR]} \quad 2$$

The prime indicates that we have used concentrations rather than activities. Activities are necessary in true thermodynamic equilibrium constants. Using concentrations, instead, gives the effective or conditional equilibrium constant. By definition $pH = -\log [H^+]$ and $pK_a = -\log K_a$. Taking the ($-\log$) of both sides of Eq. 2 gives:

$$pK_a' = pH - \log \frac{[MR^-]}{[HMR]} \quad 3$$

In this experiment we will determine this equilibrium constant, pK_a' , by varying the pH and measuring the ratio $[MR^-]/[HMR]$. We will use acetic acid-acetate buffers to control the pH, since the K_a value for acetic acid is in the same range as the K_a' value for methyl red. The pH of these buffers force methyl red to distribute itself somewhat evenly between the two colored forms.

The absorption of light is governed by the Beer-Lambert Law:

$$A = \epsilon \ell [X] \quad 4$$

where A is the absorbance, ϵ is the molar absorption coefficient, ℓ is the path length of the cell in centimeters, and $[X]$ is the concentration of the absorbing species in moles per liter. The absorbance of mixtures is the sum of the separate absorbencies. In mixtures of the acid and base forms of methyl red the total absorbance is

$$A = A_{MR^-} + A_{HMR} \quad 5$$

The absorption spectra of HMR and MR^- are given schematically in Figure 2. For two components in solution, the absorbance must be measured at two different wavelengths. The best wavelengths to choose for the analysis are where one form absorbs strongly and the absorbance of the other form is negligible. Examination of Figure 2 reveals that there are no wavelengths where one form, acid or base, absorbs exclusively. For this case, we need to set up two equations in two unknowns, one equation for each wavelength. Call the two wavelengths λ_1 and λ_2 . The absorbance at λ_1 is A_1 and at λ_2 is A_2 . The two measurements then provide two simultaneous equations with two unknowns:

$$A_1 = \epsilon_{1,MR^-} \ell [MR^-] + \epsilon_{1,HMR} \ell [HMR] \quad 6$$

$$A_2 = \epsilon_{2,MR^-} \ell [MR^-] + \epsilon_{2,HMR} \ell [HMR] \quad 7$$

The molar absorbance coefficients are illustrated in Figure 2. The molar absorbance coefficients are determined from standard solutions that contain one component alone. Eqs. 6 and 7 provide two equations in two unknowns. For an unknown solution, the absorbances at the two wavelengths, A_1 and A_2 , are determined and then Eqs. 6 and 7 are solved for the unknown concentrations $[MR^-]$ and $[HMR]$ at each given pH.

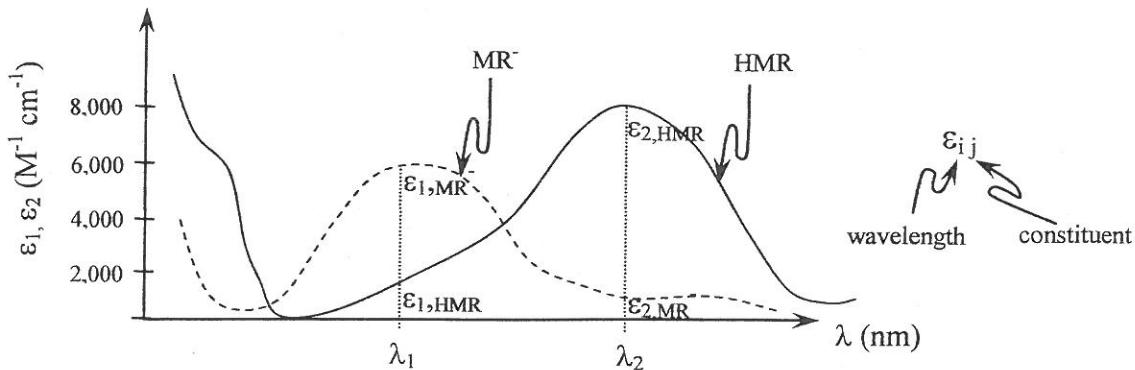


Figure 2: Absorbance of a solution is the sum of the absorbances of the constituents. Measurements at two wavelengths are necessary to determine the composition of a two-constituent solution if the absorbance bands overlap. The first subscript indexes the wavelength and the second subscript indexes the constituent.

An isosbestic point is defined as the wavelength where two species have the same molar absorptivity. At the isosbestic point the total absorbance of a solution of the two ions is independent of their relative concentrations but is dependent only upon the total dye concentration. The appearance of an isosbestic point is evidence that only two species are involved. Figure 2 shows two isosbestic points. You will use your spectra to determine if there are only two absorbing species in this experiment.

Ionic Strength Dependence

Equilibrium constants involving ionic species are especially sensitive to ionic strength. The ionic strength is a measure of the total ion concentration in solution. The activity of all the species in solution are a function of the ionic strength. In this experiment we are neglecting the difference between activity and concentration, so the pK_a' applies to only one specific ionic strength. The ionic strength is defined as

$$I = \frac{1}{2} \sum c_i z_i^2$$

7

where c_i is the concentration of ion i and z_i is the charge on ion i . The sum is taken over all ions in solution. For a 1:1 salt of singly charged ions, such as NaCl, KCl, and sodium acetate, the concentration of the salt is equal to the ionic strength. KCl is added to the solution in this experiment to maintain a constant ionic strength.

Procedure**Equipment and Solutions**

2 x 100-mL volumetric flasks
3 x 10-mL volumetric pipets
1 x 10-mL graduated cylinder
7 x 30-mL beakers
2 x 50-mL burets
2 x plastic buret funnels
1 x stirring rod
2 x Pasteur pipets
1 x box Chem wipes
1 x buret stand
3 x 150 mL beakers
1 x plastic cuvette
pH meter and electrodes, pH 4 and 7 buffers for standardization
0.10 M acetic acid, 0.10 M sodium acetate, and 1.0 M KCl

Stock Solution of Methyl Red

Prepare a 0.05% solution of methyl red by dissolving 0.025 g in 20 mL of 95% ethanol in a 50 mL in a volumetric flask. Add water to within a few mL of the mark. Add ~0.1 M NaOH drop-by-drop until all the solid dissolves and then dilute to the mark. Transfer 20 mL of this solution into 50 mL of 95% ethanol in a 200 mL volumetric flask. Dilute to the mark with water. This solution should be orange colored. (This solution may be made up for you; check with your instructor.) Make sure to record the actual weight of methyl red used to make up this solution.

Basic Solution of Methyl Red

Prepare a basic solution of methyl red by adding to a 100-ml volumetric flask the following: 10.0 ml of 0.100 M sodium acetate, 10.0 ml of the stock methyl red solution, and using a graduated cylinder 9 ml of 1.0 M potassium chloride. Dilute to the mark with distilled water and mix thoroughly.

The ionic strength of all solutions will be kept at 0.1M using KCl.

The molarity of methyl red in this solution is negligible, compared to the KCl concentration.

Acid Solution of Methyl red

Prepare an acidic solution of the indicator by adding to a 100-ml volumetric flask the following: 10.0 ml of 0.100 M acetic acid solution, 10.0 ml of the stock methyl red solution, and 10 ml of the 1.00 M potassium chloride solution. Dilute to the mark with distilled water and mix thoroughly.

This solution requires more potassium chloride solution to maintain an ionic strength of 0.1 M because the acetic acid is not strongly ionized and therefore does not contribute ions to the solution.

Preparation of Buffer Solutions

Fill two burets with the acidic and basic methyl red solutions. Prepare five buffer solutions, by

mixing V ml of the basic solution with (20-V) ml of the acidic solution in small beakers. A range from 10 ml to 18 ml for V will give optimum results.

Measurement of the pH of the Methyl red-Buffer Solutions

Calibrate the pH meter using pH 7 and pH 4 buffers. Measure the pH of each of the five buffer solutions by inserting the measuring electrodes directly into each of the beakers you prepared in the last step. Be sure to rinse and dry off the electrodes (with a stream of air from an empty wash bottle) before inserting them into the next solution, to avoid cross contamination and dilution. Instructions on the use of the pH meter is in the Instrument Instructions section of this lab manual. You can do these measurements after you determine the absorbance spectra, if you are careful in keeping sufficient volume of your solutions to submerge the pH electrode past the reference junction.

Absorbance Measurements

In this experiment you will use an Ocean Optics diode array spectrophotometer. This instrument will allow you to scan the full spectrum of the solution at each pH. You will then be able to verify the existence of an isosbestic point. Instructions for use of the Ocean Optics diode array spectrophotometers are given in the Appendix. You should overlay the spectra to make the isosbestic point easier to see. Scan your spectra from 350-850 nm.

- (a) Calibrate with distilled water.
- (b) Rinse the cuvette with two small portions of the basic methyl red solution, that is in just sodium acetate, then fill the cuvette and measure its absorbance. This spectrum will be used to calculate ϵ_{1,MR^-} and ϵ_{2,MR^-} .
- (c) Rinse the cuvette with two small portions of the acidic methyl red solution, that is in just acetic acid, then fill cuvette and measure its absorbance. This spectrum will be used to calculate $\epsilon_{1,HMR}$ and $\epsilon_{2,HMR}$.
- (d) Use the above spectra to pick the two absorbance wavelengths. Measure the absorbance of each of the prepared buffered solutions: rinse the cuvette twice with small amounts of each new each solution, then fill. Change to a new file between each spectrum to overlay the spectra. Measure the spectrum.

Calculations

Calculate the concentration of methyl red in your solutions. Use the spectrum in just sodium acetate to calculate ϵ_{1,MR^-} and ϵ_{2,MR^-} . Use the spectrum in just acetic acid to calculate $\epsilon_{1,HMR}$ and $\epsilon_{2,HMR}$. Use Excel and Eqs. 6 and 7 to determine the concentrations of $[MR^-]$ and $[HMR]$ at each pH. Plot $\log([MR^-]/[HMR])$ versus pH. Fit a straight line to the plot. The intercept of this line with the x axis (not the y axis as usual) corresponds to equal concentrations of the basic and acidic forms of the indicator. From the pH at the x intercept, determine the pK_a' . Also determine the pK_a' from the y intercept. In your report rearrange Eq. 3 to give straight line form with $y = \log([MR^-]/[HMR])$ and prove that the x intercept is pK_a' and the y intercept is $-pK_a'$.

Report

Include an Introduction, Theory, Procedure, Results, and Discussion. In the Introduction, describe the experiment and the expected result in a few sentences. For the Theory section, just reference the write-up, but also do the requested derivation from the Calculations section. In other words, the Theory section is just a reference (e.g.: please see " **pKa of Methyl Red** " in the CH341 Lab Manual for the theory and procedure) and the short derivation.

For the Procedure section, describe enough of your procedure so that another student could easily repeat your experiments. Tell exactly what you did using explicit volumes, weight, and temperature. Give the manufacturer and model of any major instrumentation (UV-Vis spectrophotometer in this experiment). Use past tense to describe your procedure. Don't copy the procedure from the write-up; state exactly what you did.

For the Results section, provide the data in a tabular format, including all information necessary to repeat your calculations. Please format your tables in a fashion similar to the literature (i.e. don't attach an Excel spreadsheet). Attach your graph. Graphs should be at least one-third page in size with axes labeled and with units. Slopes and intercepts from curve fitting should always be given with uncertainties. Include the uncertainty for the pK_a' values propagated from the curve fit values (see the Error Analysis handout for instructions for representing uncertainties). (You do not need to propagate the uncertainties of the volume measurements through to the final results. Just start with the uncertainties in the fit coefficients).

In the Discussion section, comment on the uncertainty of the final results:

1. What is the predominate random experimental error? Note that correctible student mistakes are not random experimental errors. For example, spills or not following the instructions produce systematic errors, so you should not report them as random errors.
2. Which pK_a' is more accurate, and why?
3. Compare your final results to the literature value.
4. Estimate the expected error in the final result based on the measurement errors. Based on your estimate answer the following question. Is the difference between your equilibrium constant and the literature value larger than the technique is capable of? In other words, is there some unaccountable source of error? To help you answer this question, please note the following helpful hint on error propagation for this experiment.

Did you find an isosbestic point? Discuss the importance of finding an isosbestic point.

Finally in the Discussion section, also discuss the chemical significance of the results. The chemical significance can be addressed in several alternate ways:

- State why these results are useful and important, or
- State how this experiment and technique fit into the larger world of chemistry, or
- Discuss why someone might need to do a study of this type.

Estimating the Expected Error in the Final Result Based on the Measurement Errors: You can estimate an upper bound for the expected error in the result by using just one data point and Eq. 3. Least squares curve fitting will give a smaller error, since the result is based on multiple trials, but doing the calculation with just one data point will give an upper bound for the final error. The uncertainty in absorbance measurements is ± 0.002 at best. Since using the Beer-Lambert Law for calculating concentrations involves multiplication and division, the errors in the concentrations

from the absorbances propagate as relative errors (even though we used some matrix tricks in the process). The uncertainty in pH measurements is ± 0.03 , unless extra care is taken. For answering the question "is the difference between your equilibrium constant and the literature value larger than the technique is capable of?" only a rough estimation of the expected error is necessary. A complete and precise propagation of errors treatment is not necessary. You will need to use propagation of errors rules, but focusing only on the major errors with approximate calculations is sufficient.

Literature Cited

1. S. W. Tobey, *J. Chem. Ed.*, **1958**, 35, 514.
2. F. Daniels, J. W. Williams, P. Bender, R. A. Alberti, C. D. Cornwell, J. E. Harriman, "Acid Dissociation Constant of Methyl Red," in *Experimental Physical Chemistry*, McGraw-Hill, New York, NY, 1970, pp. 113-115.
3. Ramett, R. W., "The Dissociation Quotient of Bromocresol Green," *J. Chem. Ed.*, **1963**, 40, 252.
4. Ramett, R. W., "Equilibrium Constants from Spectrophotometric Data," *J. Chem. Ed.*, **1967**, 44, 647.

BINARY LIQUID-VAPOR PHASE DIAGRAM

METHOD

A boiling-point curve can be constructed from data obtained in actual distillations in an ordinary "one-plate" distilling Apparatus. Small samples of the distillate are taken directly from the condenser, after which small samples of the residue are withdrawn with a pipette. The samples of distillate and residue are analyzed, and their compositions are plotted on a boiling-point diagram against the temperatures at which they were taken. In the case of the distillate the temperature to be plotted should be that recorded at the point where the distillation is stopped to take the sample of residue.

For analysis of the samples, a physical method is often preferable to chemical methods. Chemical analysis usually is appropriate only when a simple titration of each sample is involved, as in the case of the system HCl-H₂O. If a physical property is chosen as the basis for an analytical method, it should be one which changes significantly and sensitively over the entire composition range to be studied. For the system acetone-chloroform, the use of a refractometer is recommended for analyzing the specimens. In Table 1 the refractive index is given at various compositions for this system.

Table 1. Refractive-index vs. Composition for Acetone-Chloroform Mixtures

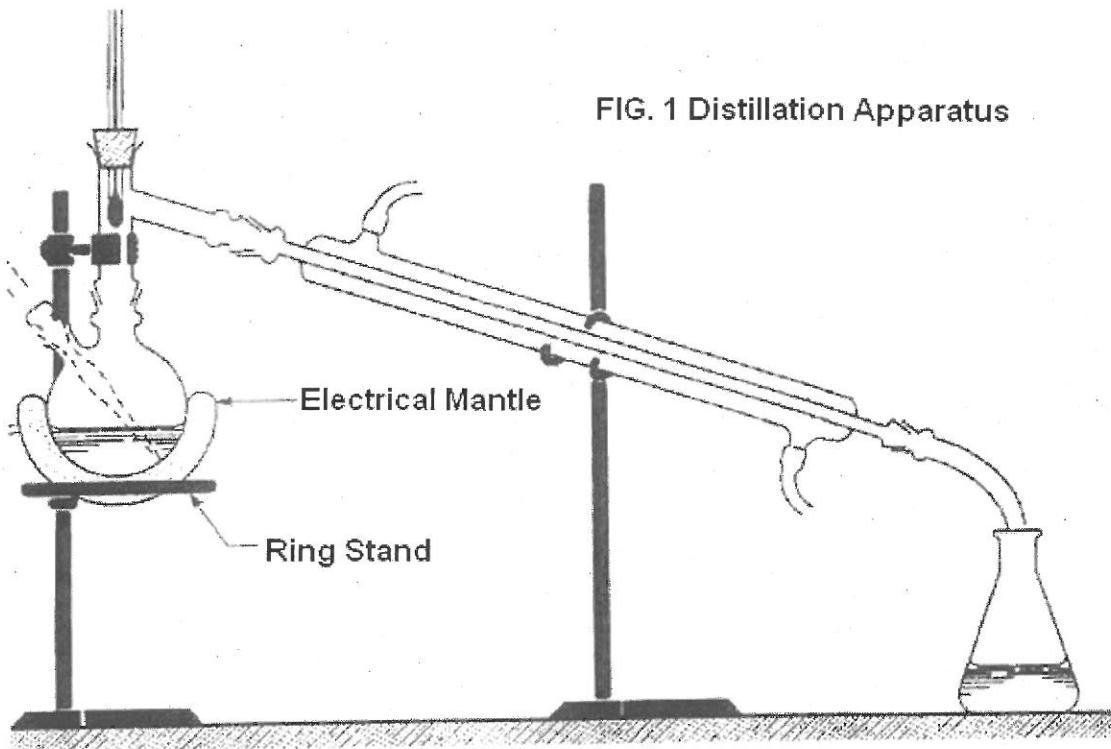
n_D^{25}	M% CHCl ₃						
1.3562	0.00	1.3780	23.50	1.4000	47.55	1.4220	72.85
1.3570	0.75	1.3790	24.60	1.4010	48.70	1.4230	74.10
1.3580	1.75	1.3800	25.65	1.4020	49.80	1.4240	75.30
1.3590	2.75	1.3810	26.70	1.4030	50.90	1.4250	76.50
1.3600	3.80	1.3820	27.80	1.4040	52.00	1.4260	77.70
1.3610	4.85	1.3830	28.85	1.4050	53.10	1.4270	78.95
1.3620	5.90	1.3840	29.95	1.4060	54.20	1.4280	80.20
1.3630	7.00	1.3850	31.00	1.4070	55.30	1.4290	81.40
1.3640	8.10	1.3860	32.05	1.4080	56.45	1.4300	82.65
1.3650	9.20	1.3870	33.15	1.4090	57.60	1.4310	83.90
1.3660	10.30	1.3880	34.25	1.4100	58.75	1.4320	85.15
1.3670	11.40	1.3890	35.30	1.4110	59.90	1.4330	86.40
1.3680	12.50	1.3900	36.40	1.4120	61.05	1.4340	87.70
1.3690	13.60	1.3910	37.50	1.4130	62.25	1.4350	89.00
1.3700	14.70	1.3920	38.60	1.4140	63.40	1.4360	90.35
1.3710	15.80	1.3930	39.75	1.4150	64.55	1.4370	91.65
1.3720	16.90	1.3940	40.85	1.4160	65.75	1.4380	93.00
1.3730	18.00	1.3950	42.00	1.4170	66.90	1.4390	94.35
1.3740	19.10	1.3960	43.10	1.4180	68.10	1.4400	95.75
1.3750	20.20	1.3970	44.25	1.4190	69.30	1.4410	97.20
1.3760	21.30	1.3980	45.35	1.4200	70.50	1.4420	98.55
1.3770	22.40	1.3990	46.45	1.4210	71.70	1.4431	100.00

EXPERIMENTAL

A simple distilling apparatus that can be used for this experiment is shown in Fig. 1. The thermometer bulb should be about level with the side arm to the condenser. Except when samples of distillate are being taken for analysis, an adequate receiving flask should be placed at the lower end of the condenser.

Before beginning the distillations, prepare twenty test tubes for taking samples. Write on the corks the designations 1L, 1V, 2L, ..., 10V (L=liquid residue; V=condensed vapor or distillate). The samples to be taken are about 2ml in size.

FIG. 1 Distillation Apparatus



When the distillation is proceeding at a normal (not excessive) rate at about the desired temperature, quickly replace the receiver with a vial and read the thermometer. After about 2ml has been collected, read the thermometer again, replace the receiver, and cork the vial tightly. Turn off and lower the heating mantle to halt the distillation. At the point where the temperature just begins to fall, record another thermometer reading. After the flask has cooled 10° or 20°, remove the stopper at the top of the flask and insert a 2ml pipette equipped with a rubber bulb. Fill the pipette, discharge it into the appropriate test tube, and cork it.

The following procedure is recommended for economical use of materials in carrying out this experiment. The paragraph numbers correspond to sample numbers. A graduated cylinder is adequate for measuring liquids. The temperatures recommended are those appropriate for 760mm; at ambient pressures differing markedly from this the temperatures should be adjusted accordingly.

1. Pure Acetone. Introduce 180ml of acetone into the flask. Determine the boiling point by distilling to constant temperature. (This temperature should be close to 56.3°C at 760mm) Collect samples (1V and 1L) for analysis if desired.
2. 58°C (acetone-rich side of azeotrope). Cool the distilling flask, and return the distillate of paragraph 1 to the flask. Add 20ml of chloroform. Begin distillation. When the temperature reaches about 58°C, collect about 2ml of distillate (2V) and 2ml of residue (2L).
3. 60°C. Resume the distillation. Take samples (3V, 3L) at about 60°C.
4. 62°C. Resume the distillation and continue to about 61°. Cool the flask somewhat and add 35ml of chloroform and 65ml of acetone. Resume the distillation. Take samples (4V, 4L) at about 62°C.
5. 63.5°C. Resume the distillation and continue to about 63°. Cool the flask somewhat and add 50ml of chloroform and 50ml of acetone. Resume the distillation, saving the distillate for later use. Take samples (5V, 5L) at about 63.5°.
6. Azeotrope. Resume the distillation and continue distilling until the boiling point ceases to change significantly, and take samples (6V, 6L). (If the boiling point does not become sufficiently constant, analyze the remaining residue with the refractometer and make up 100ml of solution to the composition thereby found. Distill this to constant temperature and take samples.)
7. Pure Chloroform. Rinse the flask with a little chloroform. Introduce 80ml of chloroform and determine the boiling point as in paragraph 1.
8. 62.5°C (chloroform-rich side of azeotrope). Cool the flask. Return the distillate of paragraph 7 and add 20ml of combined distillate and residue of paragraphs 5 and 6. Resume the distillation and take samples at about 62.5°.
9. 63.5°C. Cool the flask, return the distillate of paragraph 8, and add about 50ml of the distillate and the residue of 5 and 6. Resume the distillation, and take samples (9V, 9L) at about 63.5°.
10. Azeotrope (to check paragraph 6 from the other side). Resume the distillation, continue to constant boiling point, and take samples (10V, 10L).

At any convenient time after the samples have been taken, their indices of refraction should be measured and recorded. If the experiment is being done by several teams using the same refractometer, it is wise to take samples to the refractometer as soon as six or eight samples are ready, or fewer if the instrument happens to be free. If careful attention is given to the proper technique of using the refractometer, it should be possible to take readings at the rate of one sample per minute.

At the end of the experiment all acetone-chloroform mixtures should be poured into a designated waste vessel.

At some time during the laboratory period, the barometer should be read. The ambient temperature should be recorded for the purpose of making thermometer stem corrections.

CALCULATIONS

By interpolation in Table 1 convert the refractive indices to mole fractions. Plot the temperatures (after making any necessary stem corrections) against the mole fractions. Draw one smooth curve through the distillate points V and another through the residue points L. Label all fields of the diagram to indicate what phases are present. Report the azeotropic composition and temperature, together with the atmospheric pressure (i.e., the properly corrected barometer reading).

APPARATUS

Claissen distilling flask; 0 to 100° or 50 to 100°C thermometer, graduated to 0.1°C; one hole cork stopper for thermometer to fit flask, solid cork stopper; straight-tube condenser with one hole stopper to fit distilling side arm; two lengths of rubber hose for condenser cooling water; distilling adapter with one hole stopper to fit end of condenser; two clamps and clamp holders; two ring stands; one iron ring; electrical heating mantle; 20 small test tubes with corks; 100ml graduated cylinder, two wide mouth 250ml round bottom flasks; 2ml pipette; pipette bulb; two 500ml glass stoppered Erlenmeyer flasks.

Refractometer, thermostated at 25°C, clean cotton-wool, acetone wash bottles, reagent-grade acetone (300ml) and reagent-grade chloroform (200ml).

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Operating Instruction Manual

593M



6755

Solution Calorimeter

Operating Instruction Manual

For models produced after November 2010





QUICK START

Before starting to use the calorimeter for the first time, it is recommended that the user perform a dry run with the calorimeter completely assembled, but with no liquid in the Dewar and no sample in the rotating cell. This will give the user an opportunity to become familiar with the individual parts of the calorimeter and the manner in which they must be handled. The calorimeter must be standardized prior to analyzing a sample.

1. Allow at least 20 minutes for the calorimeter to warm up.
2. Turn on the stirrer motor switch on the 6755 calorimeter.
3. Prepare and weigh the sample to 0.0001g or 1 mL in the PTFE dish.
4. Fill the Dewar volumetrically or by weight.
5. Install the thermistor probe in the cover opening and press the bushing firmly into place to anchor the probe in its proper position.
6. Lower the cover assembly with the cell and thermistor probe into the Dewar and set the cover in place on the air can, then drop the drive belt over the pulleys, start the motor and press the start key.
7. The pre-period will now start. When the reactants come to thermal equilibrium, the thermometer will beep. Initiate the reaction by pressing downward on the push rod to drop the sample out of the rotating cell.
8. During the reaction period, the enthalpy change will occur.
9. The calorimeter will again come to equilibrium during the post period and at the conclusion of the test, the calorimeter will signal the user and produce a report.
10. Stop the calorimeter motor, raise the cover carefully and wipe any excess liquid from the parts that were immersed in the Dewar. Remove the thermistor probe from the cover and remove the sample dish from the end of the push rod; then remove the rod and release the glass cell from the drive shaft.
11. Lift the Dewar out of the air can and empty it. Wash and dry all wetted parts carefully.
12. At the end of the testing period, turn OFF the thermometer at the power switch.



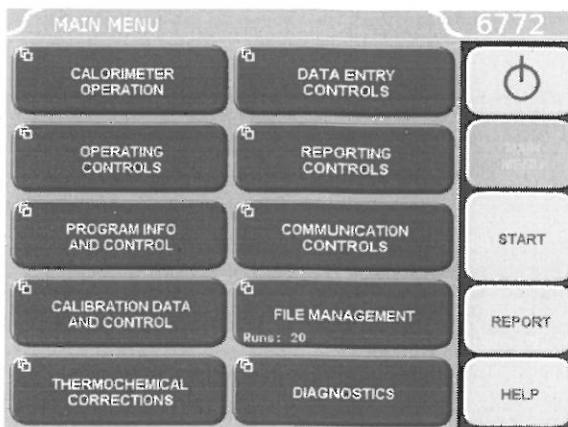
OPERATION

Menu System

All configurations and operations are handled by a menu-driven system operated from the bright touch screen display. The settings and controls are organized into eight main sections as displayed on the MAIN MENU.

Note:

Keys with a "double box" in the upper left hand corner lead to sub-menus.



Menu Keys

The controls that change the data field information in the menus will be one of the following:

- 1. Toggles.** These data fields contain ON/OFF or YES/NO choices. Simply touching the key on the screen toggles the choice to the other option. The current setting is displayed in the lower right corner of the key.
- 2. Option Selection.** These data fields contain a list of options. Touching the key on the screen steps the user through the available choices. The current setting is displayed in the lower right corner of the key.
- 3. Value Entry Fields.** These data fields are used to enter data into the Calorimetric Thermometer. Touching the key on the screen brings up a sub-menu with a key pad or similar screen for entering the required value. Some keys lead to multiple choices. Always clear the current value before entering a new value. Once entered the screen will return to the previous menu and the new value will be displayed in the lower right corner of the key.
- 4. Data Displays.** Most of these keys display values that have been calculated by the Calorimetric Thermometer and are informational only. Certain ones can be overridden by the user entering a desired value through a sub-menu. The value is displayed in the lower right corner of the key.

Note:

Some keys will respond with an opportunity for the user to confirm the specified action to minimize accidental disruptions to the program and/or stored data.

Control Keys

There are five control keys which always appear in the right column of the primary displays. These keys are unavailable when they are gray instead of white.

- 1. Escape.** This key is used to go up one level in the menu structure.
- 2. Main Menu.** This key is used to return to the main menu touch screen from anywhere in the menu structure.
- 3. Start.** This key is used to start a Calorimetric Thermometer test.



4. **Report.** This key is used to access the test results stored in the Calorimetric Thermometer, to enter thermochemical corrections, and to initiate a report on the display, printer or attached computer.
5. **Help.** This key is used to access help screens related to the menu currently displayed on the touch screen.
6. This key appears in the Escape key location when the main menu is displayed. This key is used to shut down the calorimeter program before turning off the power.

Programming

The program in the 6772 Calorimetric Thermometer can be extensively modified to tailor the unit to a wide variety of operating conditions, reporting units, laboratory techniques, available accessories and communication modes. In addition, the calculations, thermochemical corrections and reporting modes can be modified to conform to a number of standard test methods and procedures. Numerous provisions are included to permit the use of other reagent concentrations, techniques, combustion aids and short cuts appropriate for the user's work.

Note:

Changes to the program are made by use of the menu structure. Any of these items can be individually entered at any time to revise the operating program.

Default Settings

The 6772 Calorimetric Thermometer is preprogrammed with default settings for use with the 1341 Plain Jacket Calorimeter. On the operating controls page of the 6772 Thermometer is the Method of Operation key. This key toggles the thermometer between solution and combustion calorimetry. **Make sure that the calorimeter is set to solution calorimetry.** This will force the calorimeter to restart and bring up the appropriate set of menus and eliminate all of the keys dedicated to combustion calorimetry.

The default values of the 6772 are designed to operate with the 1341 Plain Jacket calorimeter. Therefore, **the following parameters must be changed in the Calorimetry Parameters menu found in the Diagnostics Menu.**

Correction (K) Parameters:

K1	0.5
K2	0.00080
K3	1.0
K4	0.0
K5	0.0

Blackout (B) Parameters:

Misfire Blackout (B2)	72
Derivative Blackout (B3)	0.5
Dynamic Blackout (B4)	6
Equilibrium Blackout (B5)	18
Dynamic Derivative Blackout (B6)	0.02
Dynamic Time Blackout (B7)	20

**Note:**

To perform an exothermic run, set the Tolerance Parameter (L2) to -1.

See Table 1 for a listing of the factory default settings. A more in-depth explanation of these parameters is found on the corresponding parameter group help pages. These default settings remain in effect until changed by the user. Should the user ever wish to return to the factory default settings, go to the Program Info and Control Menu, User/Factory Settings, touch Reload Factory Default Settings and YES. Non-volatile memory is provided to retain any and all operator initiated program changes; even if power is interrupted or the unit is turned off. If the unit experiences an intentional or unintentional "Cold Restart", the controller will return to the last known settings.

The default parameters of the 6772 Calorimetric Thermometer can be changed to guarantee that the thermometer, when cold restarted, will always be in the desired configuration before beginning a series of tests. Users who wish to permanently revise their default settings may do so using the following procedure:

- Establish the operating parameters to be stored as the user default settings.
- Go to the Program Info and Control Menu, User/ Factory Settings, User Setup ID, and enter the desired User Setup ID.
- Select Save User Default Settings

To re-load the user default setting, go to the Program Info and Control Page, User/Factory Settings, Re-load User Default Settings, and YES.

Performing an analysis

Tests can be run in a strictly manual fashion or automatically where the thermometer sequences the calorimeter through the pre and post periods. The manual sequencing approach is useful for applications where raw data is logged and subsequently analyzed, off-line. In the automatic mode, the thermometer fully sequences the test and applies real time corrections to the calorimeter temperature rise in order to correct for all systemic heat leak effects. In either case, the operator must determine the appropriate temperature source for the jacket.

- Probe – This method uses a thermistor probe attached to the jacket wall to measure the actual temperature of the surroundings (at the chosen point) and the heat leak correction are based upon the actual differences between the bucket and this external jacket temperature.
- Calculated – During the initial equilibrium period this method analyzes the actual heat leak rate and calculates the apparent temperature of the surroundings which would generate this rate and applies this calculated jacket temperature for the determination.
- Fixed – In this method the operator determines what his jacket temperature will be and enters it into the thermometer. All heat leak corrections are then based upon this fixed jacket temperature.

For most applications the calculated method is recommended.



Sample size

The rotating sample cell will hold up to 20 ml of liquid sample or a solid sample weighing up to one gram. More than one gram of solid may be used in some cases, but smaller samples are preferred so that the heat capacity and ionic strength of the system will not change significantly when the reactants are mixed. The Dewar must be filled with not less than 90 ml and not more than 120 ml of liquid to properly cover the rotating cell.

Filling the Dewar

It is best to lift the Dewar out of the air can during the filling operation. The liquid to be placed in it can be measured volumetrically, or the Dewar can be placed on a solution or trip balance and filled by weight. After filling the Dewar, set it in the air can and gently push the spacer ring down as far as it will go.

Loading a solid sample

Solid samples should be suitably ground so that they will dissolve quickly or mix uniformly with the liquid in the Dewar. Place the 126C PTFE Dish on an analytical balance and weigh the sample directly into the dish. Be careful not to drop any of the sample into the push rod socket. After the final weighing, set the dish on a flat surface and carefully press the glass bell over the dish to assemble the cell. Do not grasp or press the thin-walled glass stem during this operation; it is fragile and will break easily. Instead, grasp the bell and press it firmly onto the dish. Then lift the cover from the calorimeter and attach the cell to the stirring shaft by sliding the plastic coupling onto the shaft as far as it will go and turning the thumbscrew finger tight. If the thumbscrew is not tight against the shaft, the contents will not be released. If necessary, use a 9/64 Allen wrench to tighten further. Hold the cover in a horizontal position and lower it carefully until the bottom of the rotating cell rests on a firm, flat surface; then insert the push rod through the pulley hub and press the end of the rod into the socket in the 126C Sample Dish.

Loading a liquid sample

Liquid samples can be measured into the rotating cell either by volume or by weight. Best precision is obtained by weighing, but filling from a volumetric pipette may be adequate in some cases. Set the 126C PTFE Dish on a flat surface and press the glass bell over the dish, handling the glass carefully as described above. If the sample is to be weighed, tare the empty cell on a laboratory balance; insert a pipette through the glass stem and add the liquid, then reweigh the cell. Attach the cell to the stirring shaft and insert the push rod.

Installing the loaded cover assembly

Install the thermistor probe in the cover opening and press the bushing firmly into place to anchor the probe in its proper position. Lower the cover assembly with the cell and thermistor probe into the Dewar and set the cover in place on the air can, then drop the drive belt over the pulleys and start the motor as required.



Combining the reactants

Each test in a solution calorimeter can be divided into three distinct time periods:

1. A pre-period during which the reactants are allowed to come to an initial thermal equilibrium. The thermometer will beep to inform the operator that it has established the initial equilibrium and that it is now time to initiate the reaction.
2. A reaction period during which the reactants are combined and an enthalpy change occurs in the system.
3. A post-period during which the calorimeter again comes to equilibrium. The thermometer will produce a report when the final equilibrium has been achieved and that the test is complete.

At the end of the pre-period, start the reaction by pressing the push rod downward to drop the sample out of the rotating cell. This should be done quickly without interrupting the rotation of the rod without undue friction from the finger. Push the rod down as far as it will go; after which it should continue to rotate the pulley. Let the stirrer continue to run during the reaction and the calorimeter reports its results.

Emptying the calorimeter

Stop the calorimeter motor, raise the cover carefully and wipe any excess liquid from the parts that were immersed in the Dewar. Remove the thermistor probe from the cover and remove the sample dish from the end of the push rod; then remove the rod and release the glass cell from the drive shaft. Lift the Dewar out of the air can and empty it; then wash and dry all wetted parts carefully.

The two operating modes, (manual or automatic) are outlined below:

Manual Test Sequencing

Some users may wish to construct their own thermo gram and apply the classic graphical corrections developed by Dickenson and others. In this case, the actual temperatures can be logged to the memory of the thermometer and then analyzed at the end of the test. These logged temperatures can be recalled to display on the thermometer, printed on an attached printer or transferred to a computer using either the Ethernet Connection or a Compact Flash Card. The Ethernet Connection can also be used to transfer temperatures to a computer for plotting.

First, select the appropriate jacket temperature source as described previously. Then fill the Dewar. Next, prepare and load the reaction. After the calorimeter is fully assembled, turn on the motor, and then turn on the stirrer by pressing the stirrer key on the calorimeter operation menu screen. Turn on the data logger (accessed via the Diagnostics page) in order to periodically record the bucket or calorimeter temperature. The bucket temperature is updated every 12 seconds. Turn on the calorimetric pre-period. The pre-period should last for 6-7 minutes. After the 6-7 minute pre-period test phase, start the reaction by pressing the push rod downward to drop the sample out of the rotating cell. This begins the reaction and subsequent post-period. The calorimeter



temperature should begin to significantly change at this point, indicating sample reaction. The calorimetric post-period should last for an additional 6-7 minutes from sample introduction. At the conclusion of the post-period, turn the stirrer off by pressing the stirrer key once again. The motor switch may be left in the "on" position for subsequent tests. Empty and clean the calorimeter.

If the data log destination is a log file, the log file is located at /flash/datalog.csv and may be retrieved via FTP. The log file is easily imported into a spreadsheet program where the calorimeter temperature can be plotted in order to realize a thermal curve. Instructions for working with or analyzing thermal curves are found in the calculations section.

Automatic Test Sequencing

The solution calorimeter will perform all calculations for the user. To do this, first select the appropriate jacket temperature source. For most applications, the calculated jacket approach works well. First, select the appropriate jacket temperature source as described previously. Then fill the Dewar. Next, prepare and load the reaction. After the calorimeter is fully assembled, turn on the motor, and then press the START key located on the right hand side of the screen. This will activate the stirrer that gently circulates the water that surrounds the glass cell. The thermometer will prompt for the sample ID number and the mass of the sample in grams. This begins the calorimetric pre-period. After the thermometer determines that adequate temperature equilibrium is realized, the thermometer will prompt the user to start the reaction by pressing the push rod downward to drop the sample out of the rotating cell. This starts the calorimetric post-period. The calorimeter temperature should begin to significantly rise at this point, indicating sample combustion. The calorimetric post-period will last for an additional 6-7 minutes until the calorimeter temperature drift rate sufficiently stabilizes. At the end of the post-period the calorimeter will signal the end of the test and generate a report.

Stop the calorimeter motor, raise the cover carefully and wipe any excess liquid from the parts that were immersed in the Dewar. Remove the thermistor probe from the cover and remove the sample dish from the end of the push rod; then remove the rod and release the glass cell from the drive shaft. Lift the Dewar out of the air can and empty it; then wash and dry all wetted parts carefully.



CALCULATIONS

Standardization

A sample of tris (hydroxymethyl) aminomethane, commonly called TRIS, is furnished with the 6755 Calorimeter to provide a reliable standardizing reagent. TRIS is furnished as a dry powder which can be used directly from the bottle as supplied without further preparation, but undue exposure to air and moisture should be avoided in order to preserve the integrity of the standard.

For standardizing the 6755 Solution Calorimeter, solid TRIS can be dissolved in dilute hydrochloric acid in a controlled reaction for which the amount of heat evolved is well established. In the recommended standardization procedure described below, 0.5 gram of TRIS is dissolved in 100 ml of 0.1 N HCl to evolve 58.738 calories per gram of TRIS AT 25 °C.

1. Tare the Dewar on a solution or trip balance and add exactly 100.00 + .05 grams of 0.100 N HCl.
2. Weigh 0.50 +.01 gram of TRIS into the 126C Teflon Dish on an analytical balance to an accuracy of +.0001 g.
3. Assemble the rotating cell; place it in the calorimeter and start the motor.
4. Let the calorimeter come to equilibrium; then initiate the reaction by depressing the push rod.
5. Analyze the thermogram to determine the net corrected temperature rise, ΔT_c . At the conclusion of the test the instrument will report a net corrected temperature rise, ΔT_c .
6. Calculate the known energy input by substituting in the equation:

$$QE = m[58.738 + 0.3433(25 - T(0.63R))]$$

where:

QE = the energy input in calories

m = weight of TRIS in grams

T(0.63R) = temperature at point 0.63R on the thermogram

Note:

The term, $0.3433(25 - T(0.63R))$, adjusts the heat of reaction to any temperature above or below the 25 °C reference temperature.



Calculate the energy equivalent of the calorimeter and its contents by substituting in the equation:

$$e = \frac{QE}{\Delta T_C}$$

where:

e is expressed in calories per °C.

Determine the energy equivalent of the empty calorimeter by subtracting the heat capacity of the 100 g of 0.1N HCl from e , as follows:

$$e' = e - (100.00)(0.99894)$$

where:

e' = energy equivalent of the empty calorimeter in calories per °C.

100.00 = mass of 0.100N HCl in grams

0.99894 = specific heat of 0.1N HCl at 25 °C

Example:

A standardization reaction involving 0.5017 grams of TRIS, and 100.00 grams of 0.100N HCl producing a net corrected temperature rise of $\Delta T_C = 0.244$ °C with 0.63 rise, $T(0.63R)$, at 24.301 °C.

In this reaction the known energy input is:

$$\begin{aligned} QE &= 0.5017 [58.738 + 0.3433 (25 - 24.301)] \\ &= 29.589 \text{ calories} \end{aligned}$$

The energy equivalent, e , of the calorimeter and its contents is then computed:

$$\begin{aligned} e &= \frac{29.589}{0.244} \\ &= 121.27 \frac{\text{cal}}{\text{°C}} \end{aligned}$$

The energy equivalent, e' , of the empty calorimeter is then computed:

$$\begin{aligned} e' &= 121.27 - (100)(0.99894) \\ &= 21.38 \frac{\text{cal}}{\text{°C}} \end{aligned}$$

Calculating the Energy Change

The energy change, Q , measured in this calorimeter is calculated by multiplying the net corrected temperature change, ΔT_C , by the energy equivalent, e , of the calorimeter and its contents.

$$Q = (\Delta T_C)(e)$$

If ΔT_C is measured in °C and e is expressed in calories per °C, Q will be reported in calories. (The energy equivalent, e , is determined by a standardization procedure).

The change in enthalpy, ΔH , at the mean reaction temperature is equal to $-Q$ divided by the amount of sample used in the experiment, expressed either in moles or grams.

$$\Delta H_T = \frac{-Q}{m}$$

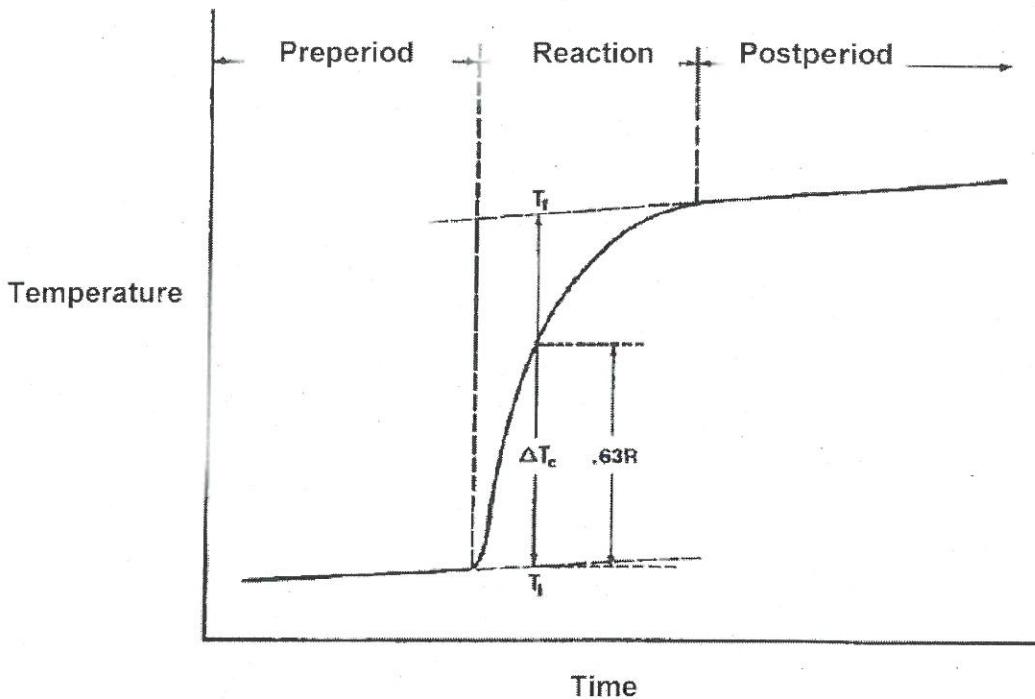
where T is the temperature at the 0.63R point on the thermogram.

Enthalpy values are usually expressed in kilocalories per mole.

Procedures for converting enthalpy changes, ΔH , to thermodynamic standard conditions and for using ΔH in other computations can be obtained from thermodynamics or thermochemistry textbooks, or from literature references.

Reading the Thermogram

Figure 2
Thermogram



In order to determine the net temperature change produced by the reaction, it is necessary to interpolate a point on the thermogram at which the temperature reached 63 percent of its total rise. This can be done easily by following Figure 2, although other variations of this method can be used as well.

1. Place a straight edge over the preperiod drift line and extend this line well past the point at which the reaction was initiated.
2. Move the straight edge to the postperiod drift line and extrapolate this line backward to the firing time. If there are fluctuations in the drift lines due to noise or other variations in the signal, use the best average when drawing these extrapolations.



6755 Solution Calorimeter Instruction Manual

3. Using a centimeter scale, measure the vertical distance, R , between the two extrapolated lines at a point near the middle of the reaction period.
4. Multiply the distance, R , by 0.63.
5. Set the zero end of the centimeter scale on the extrapolated preperiod drift line and move the scale along this line to locate a vertical intercept with the thermogram which is exactly 0.63 R above the preperiod drift line. Draw a vertical line through this point to intercept both drift lines.
6. Read the initial temperature, and the final temperature, at the points of intersection with the drift lines and subtract to determine the corrected temperature rise, ΔT (see Figure 2)

$$\Delta T_c = T_f - T_i$$



REPORTS

The 6772 Calorimetric Thermometer can transmit its stored test data in either of two ways. The Auto Report Destination key on the Reporting Controls Menu toggles the report destination between the display and an optional printer connected to the RS232 printer port of the Calorimetric Thermometer. Test results are stored as files using the sample ID number as the file name. A listing of the stored results is accessed by pressing the REPORT command key. The REPORT command key brings up a sub-menu on which the operator specifies.

Select From List This key displays the stored results specified with the following two keys.

Run Data Status This key enables the operator to display five report options:

- only preliminary and final reports
- only final reports
- only preliminary reports
- only pre-weighed sample reports
- all stored reports.

The displayed files can be sorted by filename (sample ID number), by type, by status or by date of test by simply touching the appropriate column. Individual files can be chosen by highlighting them using the up and down arrow keys to move the cursor. Press the SELECT key to actually enter the selection. Once selected the highlight will turn from dark blue to light blue. A series of tests can be selected by scrolling through the list and selecting individual files. The double up and down keys will jump the cursor to the top or bottom of the current display. If a range of tests is to be selected, select the first test in the series, scroll the selection bar to the last test in the series and press EXTEND SEL to select the series.

The DESEL ALL key is used to cancel the current selection of files.

To bring the selected report or series of report to the display, press the DISPLAY key. To send the reports to the printer press the PRINT key.



MEMORY MANAGEMENT

The 6772 Calorimetric Thermometer will hold data for 1000 tests in its memory. These tests may be pre weights, preliminary or final reports for either calibration or determination runs. Once the memory of the controller is filled, the controller will not start a new analysis until the user clears some of the memory.

The FILE MANAGEMENT key on the main menu leads to the file management sub-menu. The RUN DATA FILE MANAGER key leads to a listing of the files. Single files can be deleted by highlighting the file and pressing the DELETE key. The controller will then ask the user to confirm that this file is to be deleted. A series of files can be deleted by selecting the first file in the series and then the last file in the series using the EXTEND SEL key and then pressing the DELETE key.

RUN DATA FILE MANAGER			
FILENAME	TYPE	STATUS	DATE
TEST9	DET	FINAL	12/04/04
TEST8	DET	FINAL	12/04/04
TEST7	DET	FINAL	12/04/04
TEST6	DET	FINAL	12/04/04
TEST5	DET	FINAL	12/04/04
TEST4	DET	FINAL	12/04/04
TEST3	DET	FINAL	12/04/04
TEST20	DET	FINAL	12/04/04

Below the table are several control buttons:

- SELECT
- EXTEND SEL.
- ▲ (Up arrow)
- ▼ (Down arrow)
- RENAME
- DELETE
- ESCAPE
- DESEL. ALL
- ▼ (Down arrow)
- HELP

The controller of the 6772 Calorimetric Thermometer can accept SD memory cards. These cards can be used to:

- Copy test file data for transfer to a computer
- Copy user settings for back up
- Reload user settings to the controller to restore or update the controller's operating system.
- Copy the data log file for transfer to a computer.

SD memory cards are inserted into the slot on the back of the control section of the Calorimetric Thermometer. Keys are provided on the FILE MANAGEMENT sub-menu to initiate some of these functions. The data log is transferred from the User Defined Functions Menu on the Diagnostics Menu.



TROUBLESHOOTING

Error List

The calorimeter will run a number of diagnostic checks upon itself and will advise the operator if it detects any error conditions. Most of these errors and reports will be self-explanatory. The following list contains errors that are not necessarily self-evident and suggestions for correcting the error condition.

A Misfire Condition Has Been Detected. This error will be generated in the event the total temperature change fails to exceed 0.5 °C after the first minute of the post-period. Note that if your reaction is endothermic that you may have to change the L2 parameter to -1. This is found in the Main Menu -> Diagnostics -> Calorimetry Parameter -> Tolerance (L) Parameters.

A Preperiod Timeout Has Occurred. The calorimeter has failed to establish an acceptable initial temperature within the time allowed. Possible causes for this error are listed below:

- A cell leak.
- Poor bucket stirring.
- Lid not tight.
- Initial Dewar temperature outside the acceptable range.

The Current Run Has Aborted Due To Timeout. The calorimeter has failed to establish an acceptable final temperature within the time allowed. Possible causes for this error are listed below:

- A cell leak.
- Poor bucket stirring.

There Is A Problem With The Bucket Thermistor. Possible electrical open or short. This error will result if the temperature probe response is not within the expected range. Probe substitution can be useful in determining the cause of the problem (probe or electronics). The valid working range of the probe resistance is 1000 to 5000 ohms.

- Check connection.
- Replace probe.

There Is A Problem With The Jacket Thermistor. Possible electrical open or short. This error will result if the temperature probe response is not within the expected range. Probe substitution can be useful in determining the cause of the problem (probe or electronics). The valid working range of the probe resistance is 1000 to 5000 ohms.

- Check connection.
- Replace probe.

You Have Exceeded The Run Data File Limit (1000 Files). The memory set aside for test runs has been filled. Use the memory management techniques to clear out non-current tests.

CALORIMETRY LAB

1. Determine the change in enthalpy for solid sodium sulfate, Na_2SO_4 , when dissolved in a 5 gram/liter aqueous solution of barium chloride, $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$.
2. Determine the heat of solution of solid potassium nitrate, KNO_3 , when dissolved in water.

The Solubility Product of PbCl_2 from Electrochemical Measurements

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Electrochemical cell measurements have been used to determine the thermodynamic properties of chemical reactions (1, 2). The experiment presented in this article is not found in physical chemistry laboratory textbooks; however, it reinforces material often discussed in lectures. The experiment illustrates how thermodynamic properties such as the change in the standard Gibbs energy, ΔG° , and the equilibrium constant of a reaction are related to the emf, at different temperatures, of electrochemical cells in which the reaction takes place. The experiment is an application of a metal-insoluble salt electrode to determine the solubility of a sparingly soluble salt, PbCl_2 .



$$K_{\text{sp}} = [\text{Pb}^{2+}][\text{Cl}^-]^2$$

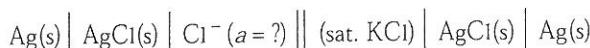
It is suited for a second- or third-year physical chemistry laboratory. The students learn to use equipment for temperature control and to freshly prepare a $\text{Ag}|\text{AgCl}$ electrode.

Experiment

The following items are needed for the experiment.

- Two standard (sat. KCl)| $\text{AgCl}(\text{s})|\text{Ag}(\text{s})$ electrodes (Corning Glass)
- A high impedance voltmeter (Hewlett-Packard 34420 Nano Volt/Micro Ohm Meter)
- Magnetic stirrers
- Two potassium nitrate salt bridges
- An RCS Lauda Temperature Controller/Circulating System
- Specially designed beakers with jackets for circulation of thermostated water to control the temperatures of the solutions in the half-cells (Figure 1)
- Silver electrode
- Platinum electrode
- 1.5-V battery

Two cells were used in the emf measurements at identical temperatures and with identical 1 M KNO_3 salt bridges. These cells, numbered 1 and 2 respectively are:



The right side electrode is common to both cells. The left side electrode in cell 2 is a standard reference $\text{Ag}|\text{AgCl}(\text{s})$

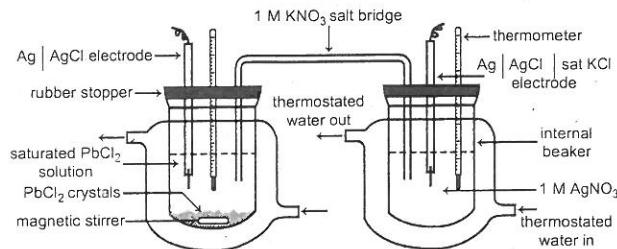


Figure 1. Diagram of the cell 1. Cell 2 is very similar to cell 1; the only difference is that the saturated PbCl_2 is replaced by 1 M KCl.

electrode dipped in 1 M KCl. The left side electrode of cell 1 is a $\text{Ag}|\text{AgCl}(\text{s})$ electrode dipped in a saturated PbCl_2 solution. The diagram of cell 1 is shown in Figure 1.

The difference between the emf values of these cells measured at the same temperature T permits the calculation of K_{sp} at T :

Derive the equation to determine a in cell 1.

The metal-insoluble salt electrode is a second-order indicator electrode since it is used to measure the Cl^- activity, which is not directly involved in the electron-transfer process (3).

Hazards

Powdered PbCl_2 is harmful if swallowed; avoid breathing the PbCl_2 dust. It is toxic if absorbed through the skin. Concentrated nitric acid is toxic and may be fatal if swallowed or inhaled. It is extremely corrosive. Contact with skin or eyes may cause severe burns and permanent damage. Hydrochloric acid (1M) is corrosive. Inhalation of vapor is harmful and ingestion may be fatal. Liquid can cause severe damage to skin and eyes. Potassium nitrate is harmful if swallowed and may cause reproductive disorders.

CALCULATIONS

Determine the temperature dependence of K_{sp} .

Use these values to determine $\Delta S, \Delta H$ and ΔG .

Experiment 2. The salt bridge solution should be prepared in advance by dissolving some strands of dried agar in boiling 1M KNO_3 solution in a ratio of 0.1 g to 10 mL. This solution is then poured into the inverted salt bridge glass tube and allowed to cool until it gels. Two such salt bridges are prepared. The bridges are stored with both ends dipping into a 1M KNO_3 solution in stoppered Erlenmeyer flasks and should be good for several weeks.

Experiment 3. The saturated PbCl_2 solution is prepared by adding about 5 g of finely powdered PbCl_2 (F.W. 278.10, Fisher Scientific Company, Catalog No. L-46 75308) to 200 mL of distilled water in a 250 mL beaker. Place a Teflon-coated bar magnet in the beaker and set it on a heater-stirrer. Turn on the stirrer and heat the solution to about 70 °C. Transfer this solution and the magnetic stirrer to the half-cell beaker in which a few grams of PbCl_2 crystals are already placed. Allow the solution to cool to 20 °C.

Experiment 4. Cell 1, kept constant to ± 0.1 K, is set up as shown in Figure 1.

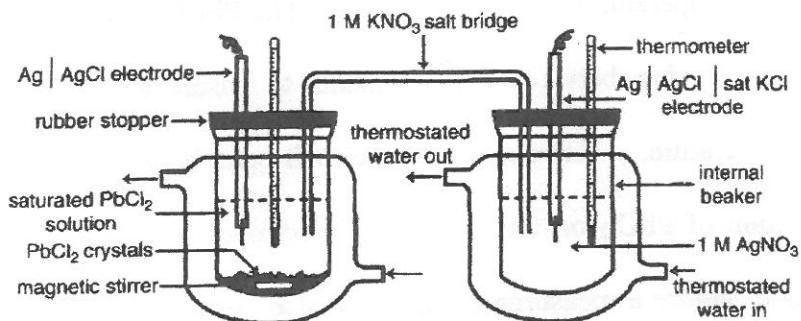


Figure 1. Diagram of cell 1. Cell 2 is very similar to cell 1; the only difference is that the saturated PbCl_2 is replaced by 1M KCl.

The reference $\text{Ag} | \text{AgCl(s)} | \text{sat. KCl}$ electrode, manufactured by Corning Glass (Cat. No. 476416) is common to cells 1 and 2. Cell 2, not shown in the figure, is

constructed by connecting the reference $\text{Ag} | \text{AgCl}(\text{s}) | \text{sat. KCl}$ electrode via a KNO_3 salt bridge to a similarly thermostated half cell constructed from an $\text{Ag} | \text{AgCl}(\text{s})$ electrode dipping in a 1 m KCl solution. Using circulating water from an RCS Lauda temperature controller the three half cells are brought to the temperature at which the *emf* measurements are made. The temperatures are controlled to better than ± 0.05 K and measured to ± 0.1 K. The cells' circuits are kept open except when a voltage measurement is made. A Hewlett-Packard 34420A Nano Volt / Micro Ohm Meter which gives a stable reading with a sensitivity of ± 0.01 mV is used. The meter's input resistance is greater than $10 \text{ G}\Omega$ for the 1 mV to 10 V range used. All half cells are constantly stirred with a magnetic stirrer to minimize the effect of concentration polarization during *emf* measurements.

While stirring the PbCl_2 saturated solution and the solution in the other two half cells are brought to a constant temperature in the vicinity of 20 °C. The magnetic stirrers in all the half cells are kept on during the *emf* measurement to minimize the effect of concentration polarization. This measurement is repeated seven or eight times at reasonably spaced temperatures up to about 60 °C. The PbCl_2 saturated solution is heated slowly while stirring between measurements to ensure that equilibrium is attained at each temperature. Keeping the cell circuit open between measurements prevents accumulation of PbCl_2 on the $\text{AgCl} | \text{Ag}$ electrode. Gentle tapping of the $\text{AgCl} | \text{Ag}$ electrode before a measurement is made also ensures the removal of any accumulated PbCl_2 on it.

Thermodynamics of Phase Equilibrium and Solution Properties

5

EXPERIMENT 10

Mutual Solubilities of Liquids in a Binary Two-Phase System

Objective

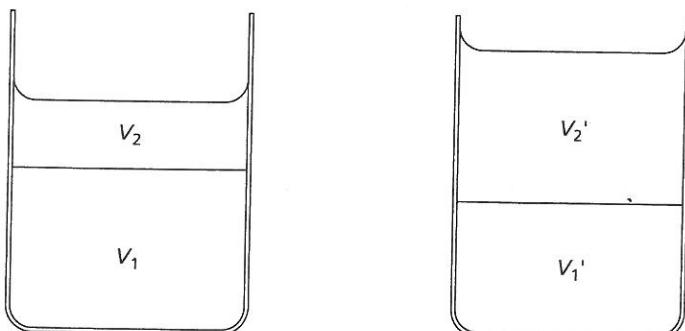
To construct the mutual solubility curve of a binary two-phase liquid system (for example, 1-butanol/water or methanol/cyclohexane).

Introduction

It is sometimes necessary to know the mutual solubilities of liquids in a two-phase system: for example, how much water is dissolved in an organic liquid with which it is in contact, and also the amount of the organic compound that is in the aqueous phase. Although a number of analytical techniques can be used to obtain this information, a procedure that is both conceptually and operationally simple and *does not require the removal of liquid samples for analysis* (which might change the equilibrium compositions) was described by A. E. Hill in 1923.¹ This elegant approach (which Hill called a “thermostatic method”) is based on a volumetric technique and requires knowledge only of the *bulk* composition of the system, that is, the total mass of each component in the mixture. We assume that the two liquids are in equilibrium in a two-phase system. Thus the phase rule applies.

If you were to combine two pure liquids *A* and *B*, you might find that a two-phase system is formed at a given temperature and pressure. Consider two samples of this binary system that have different bulk quantities of *A* and *B*. Assume that each of the two samples, at the same temperature and pressure, is at equilibrium. See Figure 1.

Figure 1. Two samples of a two-phase, two-component system containing arbitrary amounts of each component. Both solutions are at the same temperature and pressure.



If m_A and m_B are, respectively, the *bulk masses* of components *A* and *B* in one sample, and m_A' and m_B' are the bulk masses in the other sample, then it follows that

$$\begin{aligned} m_A &= d_{A1}V_1 + d_{A2}V_2 & \text{and} & \quad m_A' = d_{A1}V_1' + d_{A2}V_2', \\ m_B &= d_{B1}V_1 + d_{B2}V_2 & \text{and} & \quad m_B' = d_{B1}V_1' + d_{B2}V_2', \end{aligned} \quad (1)$$

where V_1 and V_2 are the volumes of the lower phase (higher density) and upper phase (lower density) of one sample, and V_1' and V_2' refer to the volumes of the respective phases in the other sample. We represent d_{A1} and d_{A2} as the equilibrium densities (or mass concentrations) of component A in phases 1 and 2, respectively. Likewise, d_{B1} and d_{B2} are the densities of B in phases 1 and 2. Since the samples are at the same temperature and pressure, the phase rule requires that the equilibrium compositions be the same for both samples (that is, $d_{A1} = d_{A1}'$, $d_{A2} = d_{A2}'$, etc.). These equalities are valid assuming that, in the mixed sample, A and B can each be treated as a single, chemically independent, component.

This system can also be described by the phase diagram in Figure 2 in which we plot the density against temperature. The locus of points on the curve represents phase equilibrium conditions. Points inside the curve characterize two phases in coexistence while those outside the curve indicate the presence of one phase. The diagram shows that as T increases, the density of the lower phase increases while that of the upper phase decreases. At some particular temperature, called the critical temperature (T_c), these densities become equal and the two phases coalesce into one.

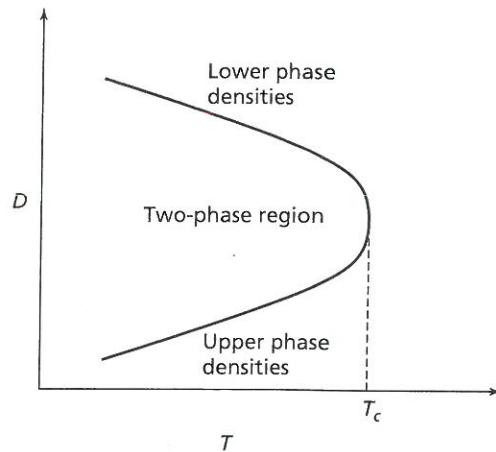


Figure 2. Schematic phase diagram of two immiscible liquids. Density is plotted against temperature. The upper and lower portions of the curve represent the densities of the lower and upper phases, respectively.

Equations (1) represent *material balances* that express the equilibrium compositions of the A–B system as two equations in two unknowns.² Because the bulk masses (m_A , m_A' , and so on) and the equilibrium volumes (V_1 , V_1' , and so on) are *measurable* quantities, the simultaneous solution of equations (1) allows the four equilibrium concentrations d_{A1} , d_{A2} , d_{B1} , and d_{B2} to be determined. From the top two expressions in equation (1) for m_A and m_A' , we can represent d_{A1} explicitly using determinants:

$$d_{A1} = \frac{\begin{vmatrix} m_A & V_2 \\ m_A' & V_2' \end{vmatrix}}{\begin{vmatrix} V_1 & V_2 \\ V_1' & V_2' \end{vmatrix}} = \frac{m_A V_2' - m_A' V_2}{V_1 V_2' - V_1' V_2}. \quad (2)$$

We can substitute this value of d_{A1} into either of the top expressions in equation (1) to find the equilibrium density of component A in phase 2; using the left-hand one, we get

$$d_{A2} = \frac{m_A - d_{A1} V_1}{V_2}. \quad (3)$$

The identical treatment of the bottom two expressions in equation (1) yields the analogous results for d_{B1} and d_{B2} . More intuitively, we can just replace the A in equations (2) and (3) by B .

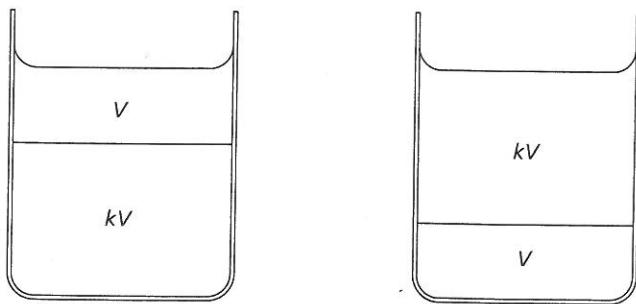
If we were to study more than two equilibrium samples of A and B , each exhibiting two phases at the same temperature and pressure, we could determine the densities d_{A1} , d_{A2} , d_{B1} , and d_{B2} more precisely using a statistical treatment. This approach is described in the Appendix.

The simplicity of the method is very appealing. However, it should be clear (and it is mathematically demonstrable) that the approach begins to break down as the mass ratio m_A/m_B in one sample is similar to or approaches the mass ratio in the other sample, m_A'/m_B' . In the extreme case where two *identical* samples are considered, no unique information about the system composition can be obtained. Moreover, as the ratio of m_A'/m_A becomes very small (or large), the quality of the information deteriorates because the determined concentrations are sensitive to the error associated with reading the positions of the meniscuses. Thus there exists an *optimal* mass ratio that provides maximum precision in the determination of the equilibrium compositions using this methodology (for a given volumetric error). Hill was aware of this situation, and in a paper with W. M. Malisoff (1926) presented the analysis of this system optimization.² We will show just the result here, but if you are curious to see how to obtain the result, see the Appendix.

Consider again two samples of a two-phase liquid system consisting of components A and B at the same temperature and pressure. These samples are designed so that the volumes are *exactly reversed* for each of the two phases. See Figure 3. The ratio of the two phases is denoted by k ($k > 1$). It turns out that the system can be designed to yield the most precise determination of the equilibrium densities of component A in the two phases (d_{A1} and d_{A2}) if k has the value

$$k_{\text{opt},A} = \frac{d_{A2}}{d_{A1}}. \quad (4)$$

Figure 3. A set of complementary solutions of a two-phase, two-component system at the same temperature and pressure. The volumes of the two phases in the samples are exactly reversed.



This ratio of densities (or solubilities, since the two liquids are in equilibrium) is called the *distribution ratio* (or distribution coefficient) of component A in the two phases and is a thermodynamic quantity because its value depends on equilibrium solubilities. Note that k is presumed to be > 1 . If in reality, however, $d_{A2} < d_{A1}$, then the denotation of the phases must simply be reversed—the upper phase in Figure 2 is 1 and the lower one is 2. An analogous result is found for the optimal volume ratio in the complementary solutions for determining the solubility of component B :

$$k_{\text{opt},B} = \frac{d_{B1}}{d_{B2}}. \quad (5)$$

In general, these optimal conditions are not the same for the two components because the mutual solubilities of A and B are different. Nevertheless, $k_{\text{opt},A}$ and $k_{\text{opt},B}$ are often close enough that a satisfactory (although not absolute) optimization of the experiment can simultaneously accommodate both components. Since the distribution ratio is not known before the experiment is performed (finding d_{A1} and d_{A2} is, after all, the objective of the experiment), a preliminary experiment can be performed to obtain approximate values of the equilibrium compositions. From a practical point of view, it is desirable to choose a complementary system in which k is not too large because in this case relative volumetric errors would become important.

In this experiment, you will not attempt to seek optimal conditions. Rather, you will prepare samples that will provide reasonably accurate results. These samples will have complementary volumes (after mixing) that are in a ratio of approximately 3:1. This means that if the volume ratio of the upper phase to the lower phase in one sample is 3:1, that ratio for the other sample is 1:3.

Safety Precautions

- ◆ Safety glasses or goggles must be worn in the laboratory.
- ◆ Be particularly careful in removing and manipulating the hot sample cylinders.
- ◆ Small amounts of 1-butanol (or other organic) vapors will be released. Work in an open, ventilated laboratory. If the fumes are objectionable, assemble the apparatus in a fume hood.
- ◆ Do not allow the cylinders to build up pressure as they are heated; vent periodically by briefly removing the stoppers.

Procedure

Several different binary liquid systems can be studied using the Hill-Malisoff method. The choice depends on such factors as convenience, expense, and ventilation considerations. If mutual solubilities are determined at different temperatures, the miscibility diagram of the system can be constructed. In this case, it is desirable to study a system that has an upper consolute temperature that is in an experimentally convenient range (that is, less than 100°C). The *upper consolute temperature* is the point above which the two liquids are miscible in all proportions; see Figure 2.

Unfortunately, many of the systems that manifest easily accessible upper consolute temperatures contain a noxious component and must therefore be handled in a fume hood. For example, the cyclohexane/aniline system has an upper consolute temperature of $\sim 60^\circ\text{C}$; that of phenol/water is $\sim 66^\circ\text{C}$. Other possible systems are methanol/cyclohexane and 1-butanol/water (or other butanol isomers and water).

In this experiment, you will study the 1-butanol/water system or the methanol/cyclohexane system between 0 and $\sim 70^\circ\text{C}$. Because the upper consolute temperature of the former is $\sim 125^\circ\text{C}$, only a portion of its miscibility curve can be constructed. The upper consolute temperature of the latter system, however, is more accessible.

Prepare two 1-butanol/water (or methanol/cyclohexane) samples that manifest two phases at room temperature. The volumes of the two phases need not be complementary but should be distinctly unequal, in a roughly 3:1 ratio. You will determine the densities of the phases for this unoptimized system from equations (2) and (3). See Figure 1.

1. Weigh directly into a tared 10-mL graduated cylinder (graduations of 0.1 mL) appropriate amounts (\pm 10 mg) of 1-butanol and distilled water (or methanol and cyclohexane) to make a two-phase system with a roughly 3:1 volume ratio for a total volume of about 6–7 mL. Use a Pasteur pipet to transfer the liquids. Likewise, add the amounts of these components to the other graduated cylinder to make up an approximately complementary two-phase mixture. Label or otherwise identify each cylinder and its stopper. Stopper the cylinders and *gently* invert each several times, venting the cylinder periodically.
2. Remove the stoppers and place each of the cylinders in the bath at the lowest temperature (this temperature will be different for the two systems). After a minute, firmly replace each stopper on its respective cylinder. After another minute or so, remove the cylinders one at a time using a test tube holder (or other appropriate device) and carefully invert several times. Replace the cylinder in the bath as quickly as possible. If possible, invert the cylinders directly in the bath. If at this point or in subsequent stages the two phases do not separate cleanly, remove the cylinder and *very gently* tap it on a firm surface. *It is important that the two phases are mixed thoroughly to ensure that phase equilibrium is reached.*
3. Repeat the inversions after 1 to 2 min. Wait for a few minutes until the meniscus positions of each sample have become established. Record these positions to the nearest 0.03 mL.
4. Remove the cylinders and place them in the next higher temperature bath (or use an immersion heater to raise the temperature by 5 to 10°C). Following the procedure in steps 2 and 3, invert the cylinders and read the meniscus positions after equilibrium is reached. Be sure to vent the cylinder cap briefly to relieve the pressure buildup. *Be careful of escaping vapor.*
5. Continue this procedure until you reach about 60°C.
6. For the methanol/cyclohexane system, the upper consolute temperature (or critical solution temperature), T_c , can be determined approximately. Fill a clean cylinder with a mixture (total mass \sim 6–8 g) that is about 77% cyclohexane by mass. Mix thoroughly and place in a 2-L beaker that contains sufficient hot water (\sim 55–60°C) to completely cover the liquid in the cylinder. Invert the cylinder several times; vent periodically to release vapor. The liquid should appear as a homogeneous, one-phase system. Add sufficient quantities of crushed ice to the bath water so that the temperature drops 1 to 2°C per minute. Record the temperature at the first sign of a pale blue, hazy appearance to the cooling methanol/cyclohexane mixture. This phenomenon, called *critical opalescence*, appears just above T_c . It is caused by the strong light scattering that accompanies large fluctuations in the density within the sample as the two phases begin to separate. (See Experiment 12 for a discussion of critical opalescence.) If you overshoot T_c , the system will appear distinctly milky or cloudy. Slowly reheat the system by a few degrees until it homogenizes and then repeat the cooling process.

The detection of the onset of critical opalescence is best done by having a light source—a bright window, lightbulb, or, better yet, a low-power helium-neon laser—illuminate the sample at *right angles* to the viewing axis (*avoid looking into the laser beam!*).

Data Analysis

1. Tabulate the equilibrium volumes of the two phases in each cylinder at the different temperatures studied.
2. Using these data, along with the bulk masses of the two components, determine the equilibrium densities d_{A1} , d_{B1} , d_{A2} , and d_{B2} . From this information, obtain the mole fractions of the two components in the two phases at each temperature studied.
3. Construct the $T-x_A$ phase diagram for the system. It should resemble Figure 4. For specific guidance consult your physical chemistry text or your instructor.

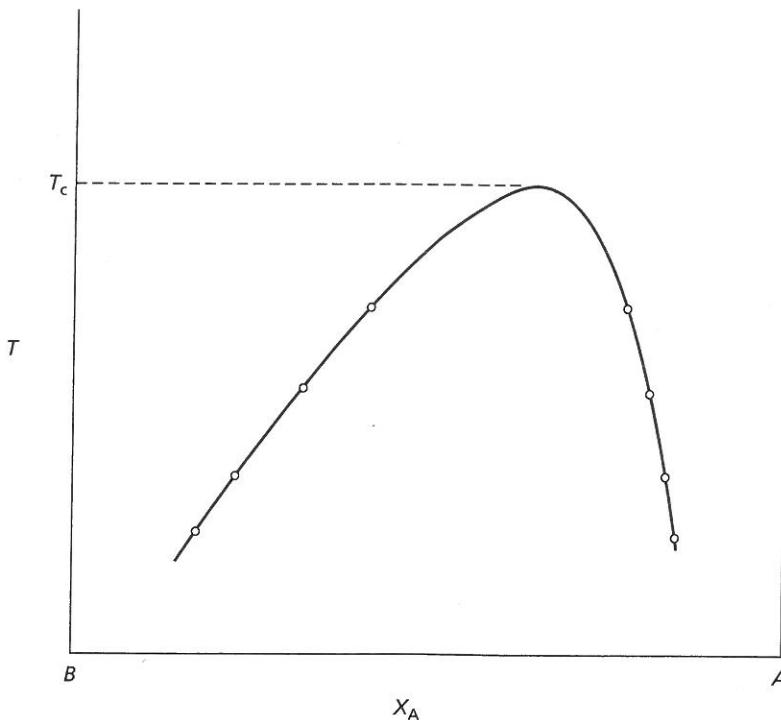


Figure 4. Schematic $T-x_A$ diagram. T_c is the upper consolute temperature. Each of the four pairs of horizontal circles represents the equilibrium mole fractions of A in the two phases at the particular temperatures.

4. Determine the mutual solubilities of the two components, as well as the distribution (or partition) coefficients at the various temperatures and compare your results with literature values where possible.

Questions and Further Thoughts

1. Suppose the distribution coefficient of component A in a binary system is 20. According to the Hill-Malisoff method, the mass ratio m_A/m_B for optimal solubility precision is 20:1. If a 10-mL graduated cylinder is used in the experiment, the smaller volume contained in each tube is less than 0.5 mL. Does this correspond to maximal volumetric precision? How do you decide how to achieve the maximal *overall* experimental accuracy in an experiment such as this?
2. What other types of analytical methods can be used to determine the compositions of a two-phase liquid system? Discuss approaches that can be used (a) without removing samples and (b) by withdrawing small aliquots.

- What is the advantage of applying the Hill-Malisoff method to a binary system contained in a series of N samples ($N > 2$)?
- Can the methodology be extended to a ternary two-phase system? Set up the initial equations analogous to (1) and (2). Ternary liquid equilibrium is conveniently studied by “titrating” a homogeneous binary phase consisting of components A and B with the other component—for example, pure liquid A —until the mixed ternary system manifests a two-phase appearance. This condition is easily detected as an emulsion.

Notes

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- A. E. Hill and W. M. Malisoff, *J. Am. Chem. Soc.*, 48:918 (1926).

Further Readings

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Appendix

Multiple Samples

Suppose we have three samples, denoted as 1, 2, and 3. As before, we represent the components as A and B , but now we denote the two phases as upper u and lower l . The total mass of A in each of the three samples is

$$m_{A1} = d_{Au}V_{u1} + d_{Al}V_{l1}$$

$$m_{A2} = d_{Au}V_{u2} + d_{Al}V_{l2}$$

$$m_{A3} = d_{Au}V_{u3} + d_{Al}V_{l3}.$$

In general, for the i th sample,

$$m_{Ai} = d_{Au}V_{ui} + d_{Al}V_{li} = d_{Au}(V_{tot} - V_{li}) + d_{Al}V_{li},$$

or

$$\frac{m_{Ai}}{V_{tot}} = d_{Au}\left(1 - \frac{V_{li}}{V_{tot}}\right) + d_{Al}\frac{V_{li}}{V_{tot}}.$$

This equation can be rearranged to give

$$\frac{m_{Ai}}{V_{tot}} = (d_{Al} - d_{Au})\left(\frac{V_{li}}{V_{tot}}\right) + d_{Au}.$$

A plot of m_{Ai}/V_{tot} versus V_{li}/V_{tot} , where, in this instance, $i = 1, 2$, and 3, should be linear, and you can obtain the equilibrium mass densities of A in the two phases from the slope and intercept. A similar approach is used with respect to component B .

Optimizing the System

Refer to Figure 3, which shows a set of complementary solutions of A and B at the same temperature and pressure.

Thus, if $V'_1 = V$ and $V'_2 = kV$, then $V_1 = kV$ and $V_2 = V$. k is the equilibrium volume ratio in the complementary samples and is greater than 1 in the example illustrated in Figure 3. Moreover, the subscripts 1 and 2 denote, respectively, the lower and upper phases. The material balance for component A in *each* sample is

$$\begin{aligned} m_A &= d_{A1}kV + d_{A2}V, \\ m'_A &= d_{A1}V + d_{A2}kV. \end{aligned} \quad (A1)$$

A similar set of equations can be written for component B . The composition of A in phase 1 can be conveniently expressed using determinants:

$$d_{A1} = \frac{\begin{vmatrix} m_A & V \\ m'_A & kV \end{vmatrix}}{\begin{vmatrix} kV & V \\ V & kV \end{vmatrix}} = \frac{km_A - m'_A}{(k^2 - 1)V}. \quad (A2)$$

Equation (A2) gives the equilibrium mass-based concentration d_{A1} as a function of the experimental measurables m_A , m'_A , and V and the methodological variable k . Using the propagation of errors expression, the uncertainty in d_{A1} can be written

$$u(d_{A1}) = \left[\left(\frac{\partial d_{A1}}{\partial k} \right)_{m_A, m'_A, V}^2 u^2(k) + \left(\frac{\partial d_{A1}}{\partial m_A} \right)_{m'_A, V, k}^2 u^2(m_A) + \dots \right]^{1/2} \quad (A3)$$

where the remaining terms deal with the standard uncertainties associated with m'_A and V . In equation (A3), all terms but the first arise from intrinsic *experimental* uncertainties beyond our control. Since the first term involves k , the arbitrarily chosen volume ratio, its impact on $u(d_{A1})$ can be modified (minimized) by careful experimental design.

The value of k will be optimal when it yields the *minimum* error in d_{A1} . Thus its optimal value may be determined by setting the coefficient $(\partial d_{A1}/\partial k)$ equal to zero and solving the resulting equation. In this way, the value of k for which the measured d_{A1} is *least* sensitive (k_{opt}) is obtained; it corresponds to a minimization of the reading error in the meniscuses. Differentiating equation (A3) with respect to k and equating to zero gives, after simplification,

$$k^2 - 2k \frac{m_A'}{m_A} + 1 = 0. \quad (A4)$$

The solution of equation (A4) is

$$k_{\text{opt}} = \frac{m_A'}{m_A} \pm \left[\left(\frac{m_A'}{m_A} \right)^2 - 1 \right]^{1/2} \quad (A5)$$

or, rearranging equation (A5),

$$\left(\frac{m_A'}{m_A} \right)_{\text{opt}} = \frac{k^2 + 1}{2k}. \quad (A6)$$

Equation (A6) provides a value of the optimal *volume* ratio k in terms of the mass ratio of one component, A , in the two complementary samples. [Note that according to the initial premise, $k > 1$ and thus equation (A6) requires that $m'_A > m_A$; moreover, the positive root in that equation must be used. If in reality, however, $m'_A < m_A$, equations (A5) and (A6) are physically meaningless. In this case, the optimization relates instead to d_{A2} .]

The result in (A6) would clearly be more useful if we could express $(m'_A/m_A)_{\text{opt}}$ in more specific terms. To obtain such information, we divide the second equation in (A1) by the first; after dividing by V , we get

$$\frac{m'_A}{m_A} = \frac{d_{A1} + kd_{A2}}{kd_{A1} + d_{A2}}. \quad (A7)$$

Now, equating the expressions for m'_A/m_A in (A6) and (A7), after clearing terms we have the cubic equation

$$d_{A1}k^3 - d_{A2}k^2 + d_{A1}k + d_{A2} = 0. \quad (\text{A8})$$

This can be simplified by dividing by d_{A2} and defining r as d_{A1}/d_{A2} :

$$rk^3 - k^2 - rk + 1 = 0. \quad (\text{A9})$$

The solution of equation (A9) yields one real and two conjugate complex roots. The physically meaningful result from (A9) is

$$k_{\text{opt}} = \frac{1}{r} = \frac{d_{A2}}{d_{A1}}, \quad (\text{A10})$$

where r (or $1/r$) is called the *distribution ratio* (or distribution coefficient) of component A in the two phases and is a thermodynamic quantity because its value depends on equilibrium solubilities. The optimal mass ratio in the two samples is [from equation (A6)]

$$\left(\frac{m'_A}{m_A}\right)_{\text{opt}} = \frac{r^2 + 1}{2r}. \quad (\text{A11})$$

Consider this result. It is reasonable to expect the optimal volume ratio k (or mass ratio) to be equal to some *characteristic* property of the system, and this turns out to be its distribution ratio, r . (Note that k is assumed to be > 1 ; thus $1/r = d_{A2}/d_{A1}$ is also presumed to be > 1 . If in reality, however, $d_{A2} < d_{A1}$, then the denotation of phases must be reversed; that is, the upper phase in Figure 3 is 1, and the lower one is 2.)

An analogous result can be obtained for the optimal volume and mass ratios for component B . In general, these optimal conditions are not the same for the two components because the mutual solubilities of A and B are different; thus, if the optimization condition derived is $k_A = d_{A2}/d_{A1}$, the constraint pertinent to component B , k_B , is

$$k_B = \frac{d_{B1}}{d_{B2}}. \quad (\text{A12})$$