

PHYSICAL CHEMISTRY

SIC2003

Level II



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INTRODUCTORY NOTE

An experiment in physical chemistry is designed with the aim to illustrate the basic principles in chemistry. Typically, every experiment will be accompanied by its background and underlying theory, detailed experimental procedure and suggestions on methods to analyze the results followed by a brief discussion.

Before the laboratory session, please READ the General Laboratory Instruction (<https://kimia.um.edu.my/LabManual/fizikal/general-laboratory-instruction-2007.pdf>) which provides the basic principles in physical methods. In the General Laboratory Instruction, you will first be introduced to the basic idea of measurements, standards and associated quantitative aspects such as units, dimensionalities, symbols, and uncertainty. This is followed by accuracy, precision, data analysis, error estimation, general equipment and tools, and scientific writing. It intends to give the necessary background discussion which you MUST read before entering the laboratory. It is also important that you continue to practice the advice given here not only during your study but throughout your lifetime as a scientist. Of course, the brief manual is by no means complete. You may refer to a more elaborate introduction on similar subject in most general chemistry textbooks. There are also many sources on the Internet which you can browse through.

The physical chemistry experiments designed here are to accompany the physical chemistry lecture courses. Through these experiments you will experience measuring some of the physical properties of interest with known precision. Moreover, they will allow you to understand the concept behind the measurements and how to relate experimental results to the basic concepts in the lecture courses.

The quantitative measurements you have made produces numerical values which are subject to error due to many reasons such as the nature of the instrument and how the experiment is designed. Thus, it is equally important to repeat the experimental procedure a few times until the result is consistent. Sometimes the experimental procedure may be varied to check for convergence of the values by different methods. In addition to these, a physical chemist must estimate the value of error in his measurement to get improved accuracy of the measured value compared to a standard value.

A good laboratory practice is to process the raw data immediately to get a rough idea of the results of the experiment immediately. By doing so, anything which deviates from expectation may be checked immediately before dismantling the experimental set up. For example, graph should be plotted roughly during the laboratory. Should a linear behavior be expected and some points are found to deviate, then the experiments related to these odd data points may be repeated immediately.

Laboratory report should be processed immediately for two obvious reasons. First, if the processed result is unsatisfactory, the experiment may be repeated immediately. Secondly, since the detail information about the experiment is fresh in memory a better report will be produced.

SAFETY IN THE LABORATORY

Further information in the details of the safety and health practice in the Universiti Malaya can be found at:



Occupational Safety & Health and Environment (OSHE), Universiti Malaya



Universiti Malaya Safety Handbook



Manual Keselamatan dan Kesihatan Pekerjaan, Universiti Malaya

The University has a statutory obligation to comply with the safety requirements and you, as a student, have a duty to abide by the regulations. The following notes are to guide you in good laboratory practice and to familiarize yourself with the safety aspects of your laboratory work.

Emergency Telephone Numbers:

- | | |
|--|------------------------------|
| • National Emergency Number | 999 (Mobile phone, dial 112) |
| • Universiti Malaya Security Office | +603 7967 7070 |
| • Universiti Malaya Medical Centre (UMMC) Emergency Department | +603 7949 2892 |
| • Universiti Malaya Students' Health Clinic | +603 7967 6445 |
| • Occupational Safety & Health and Environment (OSHE) | +603 7967 6597 |
| • Department of Chemistry Office | +603 7967 4204 |
| • Pantai Fire Station (Jalan Pantai Baru) | +603 2282 4444 |
| • Pantai Police Station (Jalan Pantai Baru) | +603 2282 2222 |

(The numbers given above are working telephone numbers, as of 5th October 2022)



****This agreement is applicable for all *PHYSICAL AND POLYMER CHEMISTRY* Laboratory Classes****

In the interest of safety and accident-prevention, there are regulations to be followed by all students in designated Chemistry Laboratories at the Department of Chemistry, Faculty of Science, Universiti Malaya (UM). Faculty and staff members are authorised to deny the use of any laboratory to students who do not adhere to the regulations mentioned below or in instances when the safety of any of the student, staff or faculty member in the laboratory might be jeopardised.

Regulations for all Chemistry Laboratories are as follows:

1. Common safety practice and guidelines **MUST** be obeyed at all times when you are in the laboratory. Please refer to the UM or Chemistry Department Safety Handbook regularly. This handbook is available in every laboratory. When unsure on any matter related to safety, seek help from the lecturer-in-charge.
2. Proper attire must always be worn in all chemical laboratories, including shoes that completely cover the foot (no high-heeled shoes), and a shirt that covers the entire upper torso, including the stomach and the back. Lab coats must be worn in the laboratory at all times. Long hair must be tied back. No loose or baggy clothes and dangling jewellery is allowed.
3. Safety eyewear must always be worn during laboratory sessions.
4. **CONTACT LENSES** should not be worn in the lab as chemicals can get between the eye and the lens
5. Prior to handling any chemical, please make sure you have read its Safety Data Sheet (SDS).
6. Do not dispose mercury into the sink. Mercury is expensive, toxic and poisonous. Used and contaminated mercury must be transferred into the residue bottle which is provided. Any spillage of mercury **MUST** be reported to the lab assistant.
7. **DO NOT** dispose of organic solvent into the sink. Any used organic solvent must be transferred into the appropriately labelled waste bottles. Please consult the lab assistant if you are uncertain.
8. When dealing with compressed gases, high pressure or high voltage equipment, please read and understand the instruction thoroughly before proceeding with the experiment.
9. Be organised. Maintain a clean, open work area free of anything except materials directly required for the exercise. Keep laboratory material/equipment away from edges of work surfaces and electrical cords from hanging below the surface of tables.
10. Equipment and/or chemicals should never be taken out of the lab unless authorised by the instructor or laboratory staff.
11. Be familiar with the location and the use of the following in your laboratory: e.g. broken glass receptacle, first-aid kit, emergency gas shut-off valves, closest fire alarm, fire extinguisher, eye wash, safety shower, and emergency exit and routes.
12. Be prepared. Study the assigned experiment before you come to lab. Be familiar with the lab exercise to prevent confusion and accidents. No unauthorised experiments are to be performed. Students must follow the procedural instructions in the lab handout/manual unless modifications to the procedures have been announced by the

laboratory supervisor, in which case the student must follow the supervisor's procedural instructions.

13. NEVER TOUCH ANY FORM OF BROKEN GLASS. Broken glass should be disposed of only by laboratory staff.
14. Lab experiments have been designed to minimize unnecessary exposure to any hazardous substances; however, it is not advisable for pregnant women or those with certain medical conditions to be exposed to any chemicals. We cannot ensure that a pregnant student will not be exposed to chemicals that might be unhealthy for her or her foetus. In addition, we cannot know the level of exposure, the length of exposure or the number of encounters that might occur with any chemical during a semester. By maintaining the safety rules, we expect that all students, including a pregnant student, should be able to carry out lab procedures safely. However, it is the Department's professional advice that pregnant students should be advised NOT to take a lab course unless she is willing to understand and assume the risks. She should certainly be seeking and following proper medical advice from her physician.
15. If you are pregnant, or you suspect, should become, or plan to become pregnant during the semester, or have any medical condition or concern, including but not limited to the following, immunocompromised system, seizures, epilepsy, severe allergies, it is your, the student's, responsibility to consult with your medical care provider regarding any medical issue associated with taking this lab. Students are encouraged to provide their physician with a list of the chemicals that they might be exposed to while in lab. They should also check the SDS sheets to be aware of the hazards of the chemicals.



SAFETY INFORMATION ACKNOWLEDGEMENT INFORMED CONSENT

This copy is to be signed and kept by student

I acknowledge receipt and that I have read and understand the lab safety regulations stated in the Chemical Laboratory Safety Agreement and in UM or Chemistry Department Safety Handbook, and that I received a briefing on these regulations from my laboratory Instructor/Lecturer. I also acknowledge that I was given the opportunity to ask any relevant questions during the safety briefing. I understand that there may be inherent risks and possible hazardous exposure with laboratory experiments depending on one's medical condition. If I am pregnant, or suspect to be pregnant, should become, or plan to become pregnant during the semester, or have a medical condition that may be affected by my participation in this laboratory session, I understand that it is my responsibility to discuss any and all issues with my medical care provider.

Further, I accept any and all risk associated with the use of the Chemistry laboratory(s) and the equipment contained therein. I also understand that I am responsible for my personal property at all times. By signing this agreement, I fully understand and consider it my responsibility to comply with the safety regulations outlined above. I hereby agree for myself, my family, successors, and assigns to hold harmless the Universiti Malaya, Department of Chemistry of the Universiti Malaya, Faculty of Science of the Universiti Malaya, Lecturers, Laboratory Staff and assigns from any and all claims, causes of action, suits, liabilities, damages, losses, demands, costs, expenses or judgments for damages or injuries to myself or others arising from my participation in the lab, whether or not I consulted a medical provider as delineated above.

Name	:	Course	:
Matric Number	:	Sem / Session	:
IC Number	:	Lecturer	:
Signature	:	Date	:

Provide the name and telephone number of two "Emergency Contacts" that can be reached during lab class times. Please note that your medical or physical condition may be released to the contact person at the time of the emergency call. Indicate the relationship to the person and the telephone location (office, home or cellular).

Emergency contact 1

Name: Relationship: Contact number:

Emergency contact 2

Name: Relationship: Contact number:



SAFETY INFORMATION ACKNOWLEDGEMENT INFORMED CONSENT

This copy is to be signed by student and returned to lecturer/PPS

I acknowledge receipt and that I have read and understand the lab safety regulations stated in the Chemical Laboratory Safety Agreement and in UM or Chemistry Department Safety Handbook, and that I received a briefing on these regulations from my laboratory Instructor/Lecturer. I also acknowledge that I was given the opportunity to ask any relevant questions during the safety briefing. I understand that there may be inherent risks and possible hazardous exposure with laboratory experiments depending on one's medical condition. If I am pregnant, or suspect to be pregnant, should become, or plan to become pregnant during the semester, or have a medical condition that may be affected by my participation in this laboratory session, I understand that it is my responsibility to discuss any and all issues with my medical care provider.

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Name : Course :

Matric Number : Sem / Session :

IC Number : Lecturer :

Signature : Date :

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Emergency contact 1

Name: Relationship: Contact number:

Emergency contact 2

Name: Relationship: Contact number:

SCIENTIFIC WRITING

Log Book

A scientist keeps all information on his/her experiment neatly and orderly. Thus, as part of your training to become a good scientist, you **MUST** have a log book or sometimes it is called a jotter book. Everything you do and measure in the day must be reported in the jotter book. **DO NOT** use loose papers to record your results. You may lose them. Moreover this log book or jotter book must be numbered and dated accordingly. It is also useful to have a carbonized jotter book which allows you to hand a carbonized copy of the result to the lab supervisor which in this case, the lecturer-in-charge. The log book should be readable to you after many years and certainly readable to other people.

Formal Report

Apart from keeping the laboratory log book, you are required to write a short formal report on every experiment assigned to you. Some lecturers may wish to assign you to write an extended report for one of these experiments. You can also use an Electronic Lab Notebook (ELN). Please discuss with your lecture-in-charge for the detailed format.

Two types of report styles which we recommend are: a short scientific report and an extended scientific report.

- 1) A Short Formal Report will have the following format:
 - i. Title Page
 - ii. Results and Discussion (separate section is highly recommended)
 - iii. Conclusion
 - iv. References

- 2) An Extended Formal Report will have the following format
 - i. Title Page
 - ii. Background and Theory
 - iii. Procedure
 - iv. Results and Discussion (separate section is highly recommended)
 - v. Conclusion
 - vi. Future Work (optional)
 - vii. Appendices (optional)
 - viii. References

Title Page

It contains the title of the experiment, when the experiment was conducted (date), your name and your partner's name (if any), your group and lecturer's name.

Background and Theory

In the short formal report, it is unimportant to write the "Background and Theory" unless you are using a different theory than that suggested in the experimental manual. You may simply refer to the manual or obtain from references.

Procedure

Likewise, in the short formal report, it is unimportant to write the "Procedure" since this is already clearly stated in the manual. If however, a different procedure is adopted for some reason (and this may happen), you must report this clearly.

Results and Discussion

All raw and processed results must be recorded neatly and clearly. Repeated values may be tabulated with clear headers. If there is more than one table, please give a clear and legible title to each one of them.

Discussion section aims to analyze the results you obtain. This is done by describing them, explaining the results with respect to the theoretical expectation either by proving the theory or otherwise. When results are in agreement with the theory, (you may feel happy) the discussion may be written in support of the theory which may now be used to predict other possible conditions. However, if result differ from the expected, the discussion may be more interesting. Here is the case when the theory may be weak or wrong or the experimental result is wrong. Discussion may be centered in scrutiny of the theory and all its assumptions or on the other hand, on possible sources of errors in the experimental procedure.

Conclusion

This summarizes the experimental findings and relates them to the objectives of the experiment.

References

These days, no scientist works in isolation. Thus, as a good scientific practice, the reference section must be included to make students aware that the experiment they conducted is related to many other previous works which have been reported in the literature.

Plagiarism Warning!

Some of these experiments are carried out in groups of usually a pair of students. Therefore expectedly, each member of a group followed an identical procedure in the laboratory and has the same set of raw data. Members of a group are allowed to discuss the analysis of data with one another. However, preparation of the report including data analysis, interpretation and discussion must be prepared by the individual student submitting the report.

The Department does not tolerate plagiarized reports!

GUIDELINES AND MARKING SCHEME FOR PRACTICAL REPORT

Section A Lab Performance (Total 20%)

1. Pre-entering lab (5%)

Score	Criteria
0	No preparation of experimental procedure, no proper attire-shoes; goggles; lab coat.
1-2	Summary of procedures too brief, lack of details and confusing.
3-5	Presents easy to follow steps in lab experimental, logical and adequately detailed; safety attire checked.

2. Skill & Techniques (15%)

Score	Criteria
0	No skill is demonstrated.
1-5	Wrong glassware used, wrong technique, spillage and wasting of chemicals.
6-10	Right glassware used, incorrect or lack of lab technique.
10-15	Presents correct lab skill, clean and tidy.

Section B: Assessment of Understanding/Revision on Conducted Experiments (20%)

Score	Criteria
	Unable to answer any questions. Test/Quiz

Late Report -1 marks / day

Section C: Lab report (Total 60%)

	Score	Criteria
Introduction (Including objective)	1	Very little background information provided, or information is incorrect.
	2	Some introductory information, but still missing some major points.
	3	Introduction is nearly complete, missing some minor points.
	4	Introduction complete and well-written; provides all necessary background principles for the experiment.

Experimental Procedure	1	Missing several important experimental details or not written in paragraph format.
	2	Written in paragraph format, still missing some important experimental details.
	3	Written in paragraph format, important experimental details are covered, some minor details missing.
	4	Well-written in paragraph format, all experimental details are covered.
Results (Data, figures, graphs, tables, etc.)	1	Figures, graphs, tables contain errors or are poorly constructed, have missing titles, captions or numbers, units missing or incorrect, etc.
	2	Most figures, graphs, tables OK, some still missing some important or required features.
	3	All figures, graphs, tables are correctly drawn, but some have minor problems or could still be improved.
	4	All figures, graphs, tables are correctly drawn, are numbered and contain titles/captions.
Discussion	1	Very incomplete or incorrect interpretation of trends and comparison of data indicating a lack of understanding of results.
	2	Some of the results have been correctly interpreted and discussed; partial but incomplete understanding of results is still evident.
	3	Almost all of the results have been correctly interpreted and discussed, only minor improvements are needed.
	4	All important trends and data comparisons have been interpreted correctly and discussed; good understanding of results is conveyed.
Conclusions	1	Conclusions missing or missing the important points.
	2	Conclusions regarding major points are drawn, but many are misstated, indicating a lack of understanding.
	3	All important conclusions have been drawn, could be better stated.
	4	All important conclusions have been clearly made, student shows good understanding.
Spelling, Grammar, Sentence Structure	1	Frequent grammar and/or spelling errors, writing style is rough and immature.
	2	Occasional grammar/spelling errors, generally readable with some rough spots in writing style.
	3	Less than 3 grammar/spelling errors, mature, readable style.
	4	All grammar/spelling correct and very well-written.
Appearance and Formatting	1	Sections out of order, too much handwritten copy, sloppy formatting.
	2	Sections in order, contains the minimum allowable amount of handwritten copy, formatting is rough but readable.
	3	All sections in order, formatting generally good but could still be improved.
	4	All sections in order, well-formatted, very readable.

Total section C marks = $(x / 28) * 60\%$

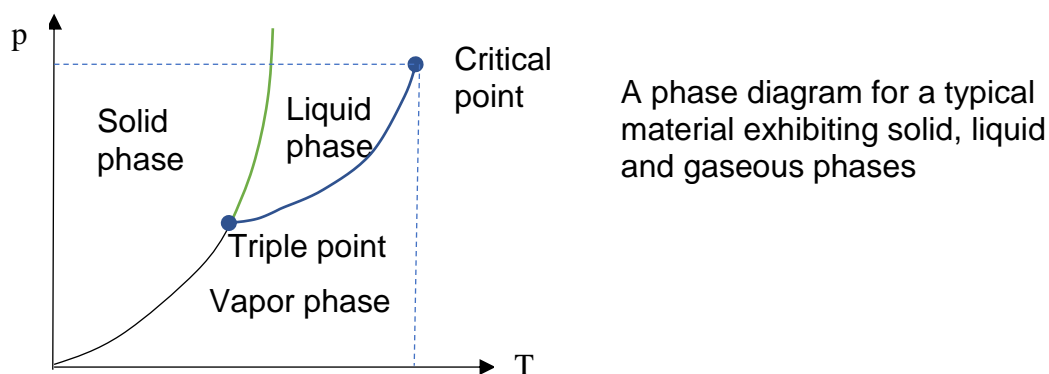
EXPERIMENT 1

THERMODYNAMICAL PROPERTIES OF LIQUID-VAPOUR PHASE EQUILIBRIUM

Background

In physical sciences, a phase is a set of states of a macroscopic physical system that have relatively uniform chemical composition and physical properties (i.e. density, crystal structure, index of refraction and so forth). The most familiar examples of phases are solids, liquids, and gases.

The different phases of a system may be represented using a **phase diagram**. The axes of the diagrams are the relevant thermodynamic variables. For simple mechanical systems, we generally use the pressure and temperature.



The markings on the phase diagram show the points where the free energy is non-analytic. The open spaces, where the free energy is analytic, correspond to the phases. The phases are separated by lines of non-analyticity, where phase transitions occur, which are called **phase boundaries**. Any point along the phase boundaries indicates conditions where two phases can coexist in equilibrium.

In the diagram, the phase boundary between liquid and gas does not continue indefinitely. Instead, it terminates at a point on the phase diagram called the **critical point**. At temperatures and pressures above the critical point, the physical property differences that differentiate the liquid phase from the gas phase become less well-defined. This reflects the fact that, at extremely high temperatures and pressures, the liquid and gaseous phases become indistinguishable. In water, the critical point occurs at around 647 K (374 °C) and 22.064 MPa.

Thermodynamic considerations

The distribution of kinetic energy among molecules is not uniform, and it changes randomly. This means that at, say, the surface of a liquid, there may be an individual molecule with enough kinetic energy to jump into the gas phase. Likewise, individual gas molecules may have low enough kinetic energy to join other molecules in the liquid phase. This phenomenon means that at any given temperature and pressure, multiple phases may co-exist.

Under specific conditions of temperature and pressure, a bowl of liquid X in dry air will evaporate until the partial pressure of X equals the vapor pressure of X. At this point, the rate of molecules leaving and entering the liquid phase becomes the same (this is known as the liquid-gas phase equilibrium).



When phase equilibrium is achieved between the two phases, the chemical potentials of the two phases would equal each other.

$$\mu^l = \mu^g \quad (2)$$

$$d\mu^l = d\mu^g \quad (3)$$

Deriving from the definition of chemical potential,

$$d\mu = V_m dp - S_m dT \quad (4)$$

Substituting equation (4) into equation (3), we can obtain

$$V_m^l dp - S_m^l dT = V_m^g dp - S_m^g dT \quad (5)$$

Rearranging $dp(V_m^g - V_m^l) = dT(S_m^g - S_m^l)$:

$$\frac{dp}{dT} = \frac{\Delta_l^g S_m}{\Delta_l^g V_m} \quad (6)$$

where the change in molar entropy is given by

$$\Delta_l^g S_m = S_m^g - S_m^l$$

and the change in molar volume is given by

$$\Delta_l^g V_m = V_m^g - V_m^l$$

At any specific temperature T,

$$\Delta_l^g \mu = \Delta_l^g H_m - T \Delta_l^g S_m \quad (7)$$

From equation (2), $\mu^l = \mu^g$, therefore

$$\Delta_l^g \mu = \mu^g - \mu^l = 0$$

$$\Delta_l^g S_m = \frac{\Delta_l^g H_m}{T} \quad (8)$$

Substituting (8) into equation (6), we can obtain

$$\frac{dp}{dT} = \frac{\Delta_l^g H_m}{T \Delta_l^g V_m} \quad (9)$$

Equation (9) is also known as the Clapeyron equation. It can be applied to any equilibrium between two phases, such as the process of melting or evaporation.

In the phase equilibrium between liquid and gas, the Clapeyron equation can be modified to a more useful form by making some appropriate assumptions.

At any temperature below the critical temperature of a liquid, the molar volume of the liquid is very much smaller than the molar volume of the gas,

$$V_m^l \ll V_m^g$$

For vaporization, Clausius showed how the Clapeyron equation may be simplified by assuming that the vapor approaches ideal gas behaviour,

$pV_m = RT$, or $V_m = \frac{RT}{p}$. That is,

$$\Delta_l^g V_m = V_m^g - V_m^l = V_m^g = \frac{RT}{p}$$

and equation (9) can be written as (10) as

$$\frac{dp}{dT} = \frac{p\Delta_l^g H_m}{RT^2} \quad (10)$$

ΔH_m can be assumed to remain unchanged within the range of temperatures of this experiment, and equation (10) can then be used to derive the Clausius-Clapeyron equation

$$\frac{d(\ln p)}{d(1/T)} = -\frac{\Delta_l^g H_m}{R} = -\frac{\Delta_{vap} H_m}{R} \quad (11)$$

Alternatively, equation (10) can be rearranged to

$$\frac{dp}{p} = \frac{\Delta_l^g H_m}{RT^2} dT$$

and upon integration gives equation

$$\log p = \frac{-\Delta_l^g H_m}{2.303RT} + \text{integration constant} \quad (12)$$

The enthalpy of vaporization can be determined from the gradient of the plot of $\log p$ versus $1/T$, and subsequently the entropy of vaporization can then be calculated by using equation (8).

Experimental Procedure

The following apparatus can be used to determine the vapor pressure of a liquid at various temperatures.



The liquid sample (*t*-butyl alcohol) is introduced into the distillation flask through side-arm G, and the valve is then closed.

The pressure in the system is slowly reduced by closing tap B, and opening tap A connected to a pump. When the pressure reaches the desired value (start with a lower pressure, around 30-40 mmHg or 40-50 kPa), tap A is closed.

The temperature of the distillation flask is raised by using a heating mantle, until the liquid begins to boil. Regulate the heating so that the liquid boils at suitable rate, and the vapor condenses through the condenser (make sure water is circulating properly through it) and the liquid is returned to the distillation flask. Allow the distillation to run smoothly for a few minutes until the temperature reaches a steady reading. Record the temperature and the equilibrium pressure.

Increase the pressure in the system by 3-5 mmHg (around 6 kPa) by allowing a small amount of air to enter through tap B slowly. As the pressure in the system increases, boiling will stop. It is now necessary to increase the heating to start the boiling again. Record the new boiling point and the corresponding pressure.

Repeat this procedure until a series of temperatures and pressures are obtained (at least 8 – 10 points).

The pressure reading of the manometer p_m is a measure of the difference between the atmospheric pressure p_a and the pressure inside the flask p .

$$p = p_a - p_m$$

The atmospheric pressure is read directly on a Fortin Barometer, and corrected to 273.15 K.

The following quantities are filled into the table.

No.	Temperature, T	Pressure, p	$\log p$	$1/T$

Plot $\log p$ versus $1/T$. Apply the linear least squares method to obtain the gradient and evaluate the uncertainty.

Calculate the enthalpy and entropy of vaporization of t-butyl alcohol. Determine from your graph the normal boiling point of t-butyl alcohol (the temperature at which the vapor pressure is 101.3 kPa).

Discussion

Compare this experiment with another method of determination of enthalpy of evaporation of a liquid. Discuss the application of Trouton's Rule to t-butyl alcohol.

References

1. Barrow, G.M. (1996). Physical Chemistry (6th ed.). McGraw-Hill Companies.
2. Moore, W.J. (1998). Physical Chemistry (5th ed.). Longman Publishing Group.
3. Atkins, P., Paula, J.D. & Keeler, J. (2017). Physical Chemistry (11th ed.). Oxford University Press.

EXPERIMENT 2

HEAT OF NEUTRALISATION

Background

The heat which is evolved when one mole of an acid is neutralised with one mole of a base is called the *molar heat of neutralisation*. The objective of this experiment is to measure the molar heats of neutralisation of several acids with the strong base sodium hydroxide.

The experiment is carried out by neutralising the acid solution with a small volume of concentrated sodium hydroxide solution. The heat evolved, $\Delta_a H$, is made up of the heat of neutralisation, $\Delta_n H$, and the heat of dilution of the sodium hydroxide solution, $\Delta_d H$. The heat of dilution of the sodium hydroxide solution is also to be measured. The heat of neutralisation, then, can be obtained from the equation

$$\Delta_n H = \Delta_a H - \Delta_d H \quad (1)$$

Cooling Corrections

Since no adiabatic calorimeter can be insulated perfectly from its surroundings, there will always be some heat lost from the calorimeter. This loss of heat can be compensated.

Heat is generated in the calorimeter either slowly or rapidly. An example of the former is the heat produced by an electrical heater whereas the heat produced when an acid is neutralised with a base is an example of the latter. The respective temperature profiles are shown in Figure 1 (heat is slowly generated) and Figure 2 (heat is rapidly generated).

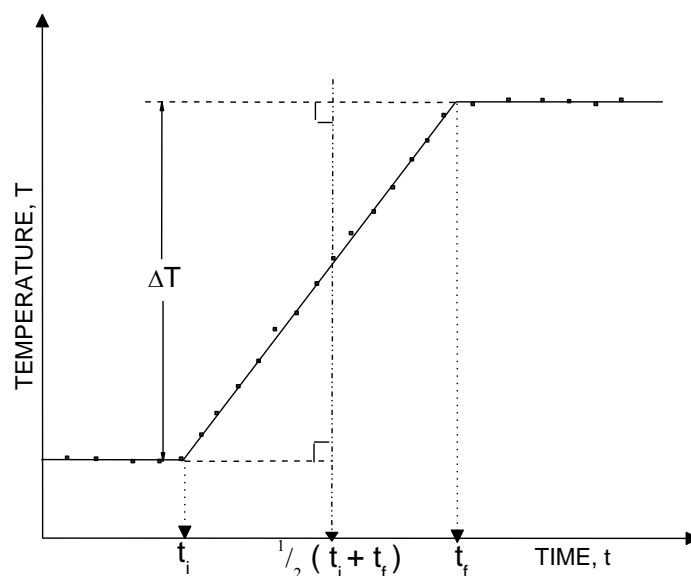


Figure 1

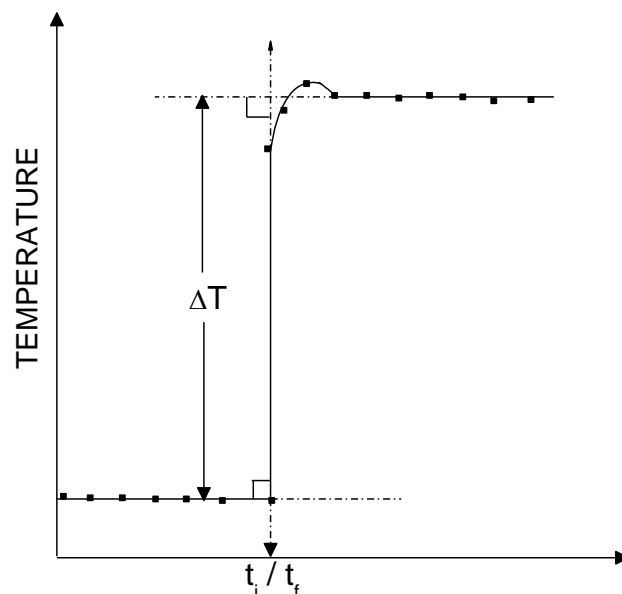


Figure 2

The heat produced is expressed as follow:

$$q = C_p \Delta T \quad (2)$$

t_i and t_f in Figure 1 and Figure 2 refer to times at which the heater is switched on and off.

To compensate for the possible heat lost to the surroundings, ΔT i.e. $T_f - T_i$ should be derived graphically (extrapolation).

Experimental procedure

Calibration of the calorimeter

The calorimeter is calibrated electrically with 120 cm³ of distilled water (measured with a graduated cylinder), using a current of 0.5A. (see Appendix A on page 9).

Neutralisation of an acid

120 cm³ of 0.5 mol dm⁻³ HCl solution (measured with a graduated cylinder) are placed in the calorimeter. After slow stirring, temperature readings are taken at regular intervals. A graph of temperature vs. time is plotted after each reading is taken. When the temperature is changing at a constant rate, 3 cm³ of the concentrated sodium hydroxide solution (100g NaOH in 100g water) is added, and the time of addition is noted. Temperature readings are taken until the values again change at a constant rate.

The experiment is repeated with each of the following in place of the hydrochloric acid: nitric acid, acetic acid and monochloroacetic acid.

Heat of dilution of sodium hydroxide

The above procedure is repeated, with 120 cm³ of distilled water in place of the acid.

Calculations

The molar heats of neutralisation of the various acids are to be calculated.

Discussion

You should account for any similarities and differences in the molar heats of neutralisation of the various acids.

How significant is the loss of heat from the calorimeter to its surroundings?

Reference

(1) Atkins, P., Paula, J.D. & Keeler, J. (2017). Physical Chemistry (11th ed.). Oxford University Press.

APPENDIX A

CALIBRATION OF THE CALORIMETER

In experiments involving heat of neutralisation, substances that absorb heat are water (120 cm^3), various types of ions and the calorimeter. Heat capacity of the system consists of these three parts. Therefore,

$$C_p = C_p(\text{water}) + C_p(\text{ions}) + C_p(\text{calorimeter})$$

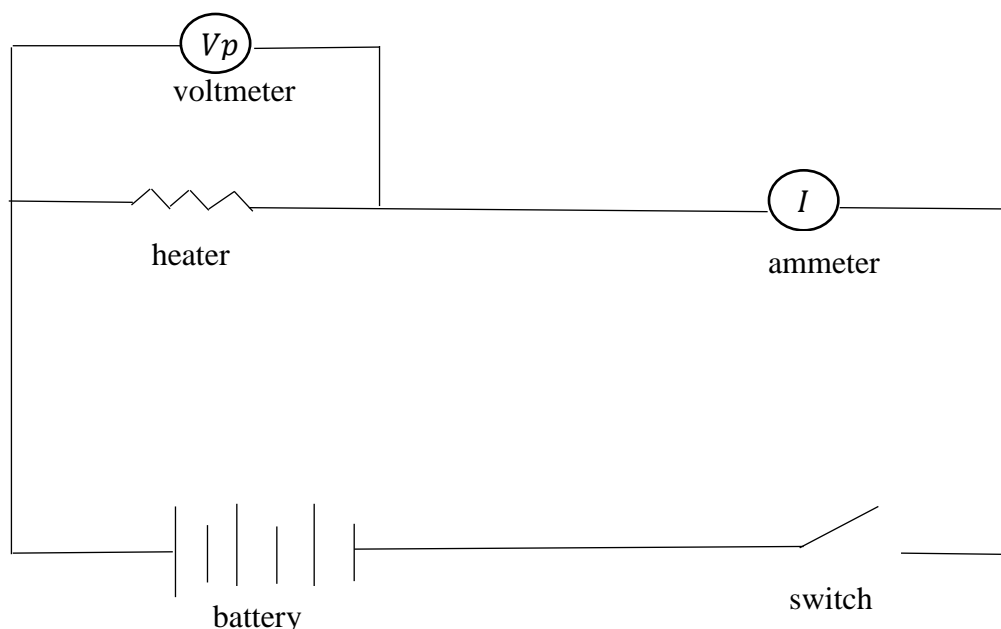
Heat capacity is an extensive property i.e. it depends on the mass. Since the mass of the ions are very small as compared to that of the other substances, the heat capacity due to the ions can be ignored. So,

$$C_p = C_p(\text{water}) + C_p(\text{calorimeter})$$

Therefore, every single system studied is the same in terms of heat capacity and the heat capacity of the system has to be obtained.

An experiment to determine the heat capacity of the calorimeter and its contents is called calorimeter calibration. Calibration is usually carried out electrically. In this method, the heater (a piece of resistance wire) which is immersed in water, is switched on and the temperature of the system rises. From the measurements of temperature rise and the electrical energy used, the heat capacity of the system can be calculated.

The circuit diagram of an appropriate technique to calibrate a calorimeter is as shown below.



Let us say the current is I , the potential difference across the heater, V_p , temperature rise, ΔT and the time the heater is on, t . Therefore,

$$C_p \Delta T = I V_p t$$

and

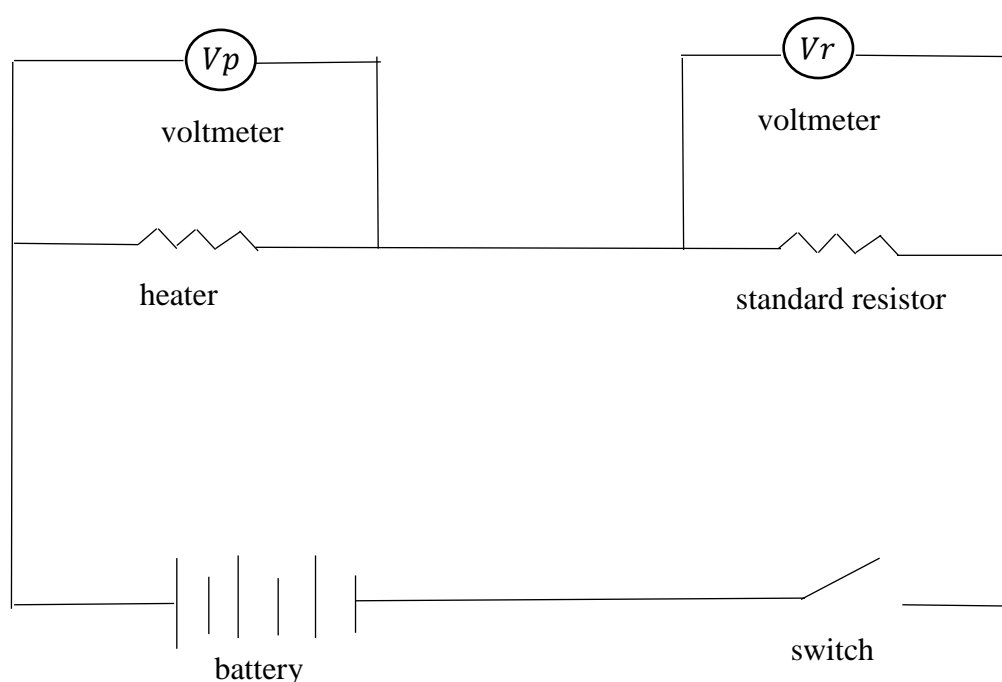
$$C_p = I V_p t / \Delta T$$

If no heat is lost to the surrounding,

$$\Delta T = T_{(\text{heater off})} - T_{(\text{heater on})}.$$

Otherwise, cooling correction has to be used in order to obtain T.

In general, potential difference can be measured more precisely from the current. In order to measure the current with the same precision, the ammeter must be replaced with a piece of standard resistor. If the potential difference across the standard resistor is measured, the current can be calculated by using the Ohm's law. The new circuit diagram is as follows.



Let us say V_r is the potential difference across the standard resistor R. Therefore

$$I = \frac{V_r}{R}$$

Then

$$C_p = \frac{V_r V_p t}{R \Delta T}$$

or,

$$C_p, JK^{-1} = \frac{(V_r, V)(V_p, V)(t, s)}{(R, \Omega)(\Delta T, K)}$$

EXPERIMENT 3

IONIC TRANSPORT NUMBERS

Background

Ions in an electrolyte solution allow the passage of electrical current when there is a potential difference between two electrodes immersed in the solution. Electrical current is carried by cations which move towards the cathode (negative electrode) and anions which move towards the anode (positive electrode). The contribution of the particular ion to the electrical current depends on the speed or velocity of the transport of the ions to the respective electrode. Therefore, the speed or velocity of the ions will depend on the charge, size, electrical field strength and the constituents of the electrolyte solution. In this experiment, the contribution of a particular ion to the electrical current in the aqueous electrolyte solution will be determined from their ionic transport numbers. The moving boundary method may be used for such experiments.

Please note that the data of ionic transport numbers and their dependency on electrolyte concentrations often can be used to obtain information on solvation, ion association, electrolyte diffusion and liquid junction potentials.

Ionic transport number theory

The transport numbers t_i for cation i (or anion) is defined as the amount of cation constituents (or anions) which passes an imaginary plane in the solution towards the cathode (or anode) when 1 Faraday of electrical charge is passed across the plane. The word constituent is used here, because the definition of ionic transport numbers also includes complex ions. As an example, in an aqueous solution of $\text{ZnCl}_2(\text{aq})$, the cation Zn^{2+} moves towards the cathode by its constituents which are Zn^{2+} and ZnCl^+ and towards the anode by its constituents which are ZnCl_3^- and ZnCl_4^{2-} complex ions. But the problem of ionic associations between ions and complex ions does not arise in strong electrolyte solutions. In this experiment, only strong electrolytes will be considered.

In a strong electrolyte solution such as $\text{HCl}(\text{aq})$ where there is complete dissociation to H^+ and Cl^- ions, the ionic transport number t_i is proportional to the ionic mobility μ_i and to $Z_i \cdot C_i$, so

$$t_i \propto |Z_i| C_i \mu_i \quad (1)$$

where μ_i = mobility (velocity when influenced by 1 Volt cm^{-1} potential gradient), C_i = ionic concentration of ion i and Z_i = ionic charge.

Through Faraday's law for univalent electrolytes,

$$\sum_i t_i = t_+ + t_- = 1 \quad (2)$$

and

$$t_+ = \frac{C_+ \mu_+}{C_+ \mu_+ + C_- \mu_-} = \frac{\mu_+}{\mu_+ + \mu_-} = \frac{\lambda_+}{\lambda_+ + \lambda_-} = \frac{\lambda_+}{\Lambda_m} \quad (3)$$

where:

λ_+ = molar conductivity of cation = $\mu_+ F$

λ_- = molar conductivity of anion = $\mu_- F$, and

Λ_m = molar conductivity of electrolyte

F = Faraday constant = $(9.64870 \pm 0.00016) \times 10^4 \text{ C mol}^{-1}$

The equation for t_- is the same as (3). For strong electrolyte, t_+ and t_- are the same as the fractions of electrical current being conducted by the respective cations and anions. This is not true, however, for solutions containing complex ions.

The moving boundary method theory

Consider two strong univalent electrolytes, AX and BX. X is an anion which exists in both electrolytes. If electrolyte BX is poured on top of electrolyte AX in a capillary tube, the boundary will change from sharp and contrasting to become blurred because of ion diffusion. But when an electrical field with suitable strength is applied, the boundary will remain sharp and contrasting. It will also move parallel to the direction of the electrical field. If the ionic mobility of A is greater than the ionic mobility of B, the boundary will move downwards through the tube (see Diagram 1); this is a falling boundary. How can this phenomenon be explained?

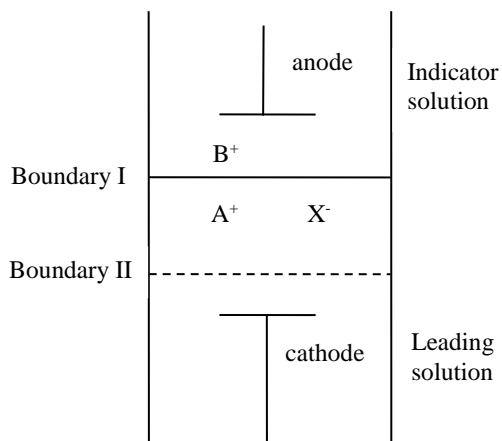


Diagram 1

Say for example, the concentrations of both solutions AX and BX are the same as before. Because of $\mu_A > \mu_B$, the AX solution will have a larger electrical conductivity than the BX solution. In this condition, the AX solution is called the leading solution and BX is the indicator solution. The reason why the same amount of electrical current passes the two solutions is that the potential gradient (E) in the AX solution is less than that in the BX solution (see Diagram 2). An ion A which enters the BX solution

is influenced by a larger electrical field strength and this makes the ion re-enter the leading solution. Also, an ion B which enters the AX solution will be slowed because of the influence of a lower electrical field strength. The moving boundary will move faster than the ion B, and the B ion is absorbed back into the original solution. This 'back and forth' effect (electrical restoring effect) will result in the sharp and contrasting boundary between the two AX and BX solutions, although there occurs diffusion of ions between the two solutions.

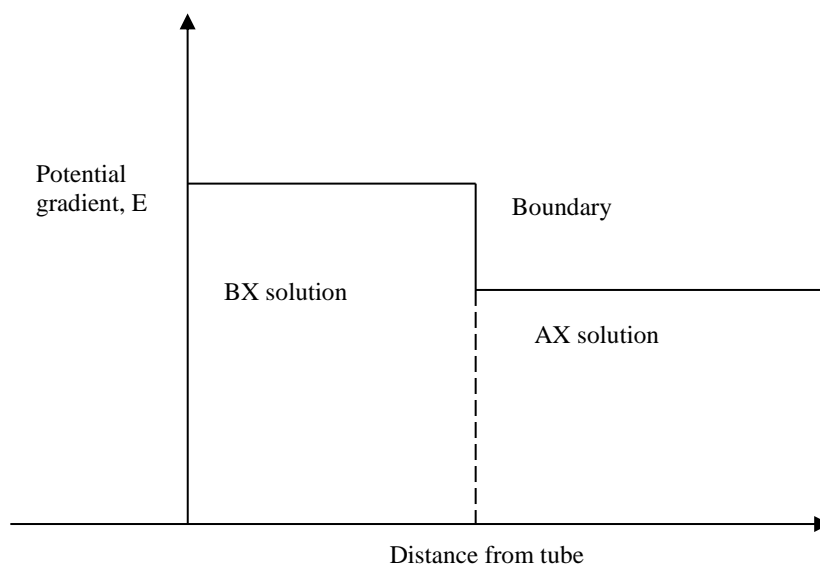


Diagram 2

On the boundary, the speed of ion A is the same as ion B, thus

$$v_{(boundary)} = v_A = \mu_A \cdot E_{AX} = v_B = \mu_B \cdot E_{BX} , \quad (4)$$

where E = potential gradient, v = speed, μ = mobility.

At the beginning of the experiment, the condition which (4) signifies has yet to be attained, but after a short while after the electrical current is switched on, the BX concentration behind the boundary will change a little (to C_{BX}^*) until the condition (4) exists. Let us say the boundary moves from I to II (Diagram 1) through a volume V_F when 1 F electrical charge has passed. So $C_{AX} \cdot V \cdot F$ mol of ions has passed the II plane and $C_{BX}^* \cdot V \cdot F$ mol of B ions has crossed the I plane (Diagram1).

From the definition of ionic transport numbers,

$$t_A^{AX} \text{ (in AX solution)} = \frac{C_{AX} \cdot V_F}{It} \quad (5)$$

$$t_B^{BX} \text{ (in BX solution)} = \frac{C_{BX} \cdot V_F}{It} \quad (6)$$

The C_{BX}^* concentration behind the boundary is named the Kohlrausch concentration of the indicator solution. If an electrical current I passes for a time t , then It Coulombs of charge are passed, and if the boundary moves through a volume V_F in the time t ,

So t_A^{AX} can thus be determined because C_{AX} , V_F , I , t , are known or can be measured.

Experiment

The determination of ionic transport numbers of H^+ in aqueous solution of 0.1 M HCl.

For this experiment, a suitable indicator solution LiCl is used because the ionic mobility of Li^+ is less than the ionic mobility of H^+ . The boundary in this experiment is the falling boundary because the density of LiCl is less than the density of HCl. A little bromophenol blue indicator is added to both solutions so the boundary will be sharp and clear.

Leading solution: Add 0.5 cm^3 methanolic bromophenol blue solution (5 g in 1 dm^3 methanol) to 120 cm^3 0.1 mol dm^3 HCl (Prepared by the laboratory assistant).

Indicator solution: The LiCl solution used has around the same concentration ($\pm 20\%$) as the Kohlrausch concentration. Add 0.5 cm^3 bromophenol blue to 120 cm^3 LiCl solution.

Method: The electrolysis cell which will be used is shown in Diagram 3.

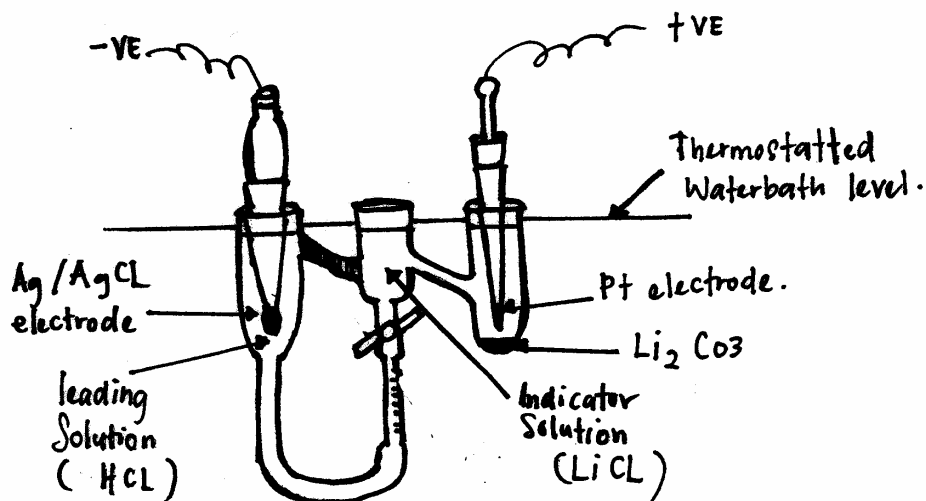


Diagram 3

In the moving boundary method, one of the compartments of the electrolysis cell must be covered. The cathode is the Ag / AgCl electrode, made from molten AgCl. The anode compartment has a platinum electrode which is kept opened to facilitate gas evolution during electrolysis. A little solid Li_2CO_3 is added to the platinum electrode compartment to suppress the formation of H^+ (the electrolytic product) ions.

The electrolysis cell must be cleaned before used. The cleaning can be done with dilute sulphuric acid followed by distilled water. The vacuum grease to smoothen the joints and cell taps should be used only sparingly. Wash the leading solution compartment of the electrolysis cell with HCl twice. Then fill with the solution until the solution level rises up to the cell tap. Close the cell tap. Insert the Ag / AgCl reference electrode carefully so that there will be no gas bubbles trapped in the cell compartment. Throughout the experiment, the cell compartment should not contain any gas bubbles.

Remove any excess HCl from the top of the cell tap using a dropper. Wash the anode cell compartment with the LiCl solution several times. Then fill with the LiCl solution and insert the Platinum electrode. Add a little Li_2CO_3 solid to the cell compartment below the platinum electrode and close the middle cell compartment with a stopper.

Place the cell in the water bath (see Diagram 3). Connect the cell electrodes to the DC power supply. Be sure that the electrodes are well connected before the DC power supply is switched on (Please ask the laboratory demonstrator or laboratory assistant).

Caution

Do not touch any electrical circuits when the power supply is switched on.

Always switch off the main electrical supply in the power plug when you want to touch any electrical circuits.

The DC power supply can deliver a potential of 300 V and can be dangerous.

Open the cell tap before the DC power supply is switched on. First deliver a current of 4-5 mA through the cell until the boundary reaches the first graduated scale in the graduated tube. Then hold the current steady at 3 mA throughout the experiment. Record the time taken for the boundary to reach each graduated scale in the graduated tube.

When the boundary has reached the final scale in the graduated tube, perform these qualitative tests as below:

- (i) Switch off the electrical current a while and observe the boundary. Switch on the electrical supply again.
- (ii) Reverse the wire connection to the electrodes so that the electrical current will flow to the opposite direction. Observe the boundary. Then reconnect the wires to the electrodes as before.

Record all your observations.

Volume correction for the electrolysis cell

1. Fill in the electrolysis cell with distilled water until the water level reach any level of the graduated scale (the marked graduated line).
2. Use a graduated pipette to further fill in distilled water into the electrolysis cell; until additional distilled water added in fill up one part of the graduated scale. Therefore, the exact volume of each graduated part is determined.

Calculations

Draw a graph of volume versus time t . Calculate the ionic transfer numbers t_{H^+} for the H^+ ions in the 0.1 mol dm^{-3} HCl solution.

Discussion

Explain briefly all your observations about the qualitative tests that you have carried out in this experiment.

If the molar conductivity of 0.1 mol dm^{-3} HCl solution is $420 \times 10^{-4} \text{ S m}^2 \text{ mol}^{-1}$ at $30 \text{ }^\circ\text{C}$, what are the values of λ_{H^+} and λ_{Cl^-} for the solution?

Why is there a huge difference between the values of λ_{H^+} and λ_{Cl^-} ?

How can the precision of the experiment be improved?

References

1. Atkins, P., Paula, J.D. & Keeler, J. (2017). Physical Chemistry (11th ed.). Oxford University Press.
2. Levine, I.N. (1995). Physical Chemistry (4th ed.). McGraw Hill.

EXPERIMENT 4

PARTIAL MOLAR PROPERTIES OF SOLUTIONS

Background

Any extensive property X of a solution can be represented by partial molar properties X_A , X_B of the constituent substances A and B, respectively. These molar properties are functions of the temperature, pressure and concentration of that solution. Here we will take A as being the solvent while B is the solute. Concerning the volume of a solution, the total volume, V , is given through the partial molar volume by equation (1)

$$V = n_A V_A + n_B V_B \quad (T, p \text{ constant}) \quad (1)$$

where n_A and n_B are mole fractions.

The partial molar volume can be calculated by measuring the density of the solution.

Apparent molar volume, ϕV_B , is defined by equation (2)

$$\phi V_B = \frac{(V - V_A^*)}{n_B} \quad (T, p \text{ constant}) \quad (2)$$

where V_A^* is the molar volume for pure A.

From equation (2),

$$V = n_B \phi V_B + n_A V_A^* \quad (T, p \text{ constant}) \quad (2a)$$

and therefore

$$\begin{aligned} V_B &= (\partial V / \partial n_B)_{n_A, T, p} \\ &= \phi V_B + n_B (\partial \phi V_B / \partial n_B)_{n_A, T, p} \end{aligned} \quad (3)$$

and, $V_A = (V - n_B V_B) / n_A$

$$= \frac{[n_A V_A^* - n_B^2 (\partial \phi V_B / \partial n_B)_{n_A, T, p}]}{n_A} \quad (4)$$

From the density ρ measured from the experiment and the molar mass of both components M_A , M_B , ϕV_B is given as:

$$\phi V_B = \frac{[(n_A M_A + n_B M_B) / \rho - n_A V_A^*]}{n_B} \quad (5)$$

The molality of the solute is defined by:

$$m_B = \frac{n_B}{n_A M_A} \quad (6)$$

Substituting n_B into equation (5),

$$\phi V_B = \frac{(\rho_A - \rho)}{m_B \rho_A \rho} + \frac{M_B}{\rho} \quad (7)$$

where ρ_A is the density of the pure solvent.

Equation (7) is used to calculate the values of the apparent molar volume from the density measurements.

Therefore, partial molar volumes can be obtained by using equations (3) and (4). You should plot ϕV_B versus n_B , but sometimes it is more useful if you plot ϕV_B versus $m_B^{1/2}$.

$$\left(\frac{\partial \phi V_B}{\partial n_B}\right)_{n_A, T, p} = \left(\frac{\partial \phi V_B}{\partial m_B^{1/2}}\right)_{n_A, T, p} \left(\frac{\partial m_B^{1/2}}{\partial n_B}\right)_{n_A, T, p} \quad (8)$$

By using equation (6), equation (8) becomes,

$$\left(\frac{\partial \phi V_B}{\partial n_B}\right)_{n_A, T, p} = \frac{\left(\frac{\partial \phi V_B}{\partial m_B^{1/2}}\right)_{n_A, T, p}}{\left(2m_B^{1/2} n_A M_A\right)} \quad (9)$$

Therefore

$$V_B = \phi V_B + \left(\frac{1}{2}\right) m_B^{1/2} \left(\frac{\partial \phi V_B}{\partial m_B^{1/2}}\right)_{n_A, T, p} \quad (3a)$$

$$\text{and } V_A = V_A^* - \left(\frac{1}{2}\right) m_B^{3/2} M_A \left(\frac{\partial \phi V_B}{\partial m_B^{1/2}}\right)_{n_A, T, p} \quad (4a)$$

Experimental

Prepare accurately an aqueous solution containing about 2, 4, 8, 12 and 16% (w/w) sodium chloride. For this experiment the total volume required for each solution is 100 cm³. Determine the volume of the pycnometer by using pure water. Ask the demonstrator about how to use the pycnometer. Fill the pycnometer with the prepared solutions and determine their weight. From these measurements, determine the respective densities. For each solution, carry out the density determination three times. **Another additional step is to measure the density of the prepared solutions using a densitometer. You are**

required to compare the density values obtained by calculation and measurement. Ask the demonstrator about how to use the densitometer.

Results and Calculation

All weighings must be corrected for air buoyancy (ask the demonstrator). Calculate the molality of each solution and determine the apparent molar volume ϕV_B for each molality. Plot ϕV_B against $m_B^{1/2}$ and use equations (3a) and (4a) in order to obtain the values of the partial molar volumes.

Questions

1. How can partial molar volumes indicate the types of interaction between the components of each solution?
2. What is the significance when you plot ϕV_B against $m_B^{1/2}$ as compared to the plot of ϕV_B against m_B for the solutions of sodium chloride in water?

Note:

- (i) Prepare all solutions by accurately weighing the amount of salt and water used
- (ii) To make corrections for air buoyancy on all the weights, use the formula below:

$$W_v = W_a + W_a d_u \left(\frac{1}{d_m} - \frac{1}{d_w} \right)$$

W_v = true weight (in vacuum)

W_a = value read from the balance

d_u = density of air (assumed to be 0.0012g cm³)

d_w = 8.0g cm³ (steel density)

d_m = density of the weighted object

References:

1. Atkins, P., Paula, J.D. & Keeler, J. (2017). Physical Chemistry (11th ed.). Oxford University Press.
2. Libretexts. 9.2 Partial Molar Quantities. Retrieved from https://chem.libretexts.org/Bookshelves/Physical_and_Theoretical_Chemistry_Textbook_Maps/DeVoe's_Thermodynamics_and_Chemistry/09:_Mixtures/9.2_Partial_Molar_Quantities

EXPERIMENT 5

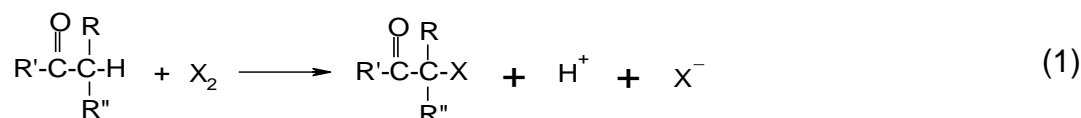
KINETICS OF CHEMICAL REACTION - IODINATION OF CYCLOHEXANONE

Background

Many reactions that follow simple rate laws actually occur through a series of steps. These steps are called elementary reactions because they cannot be broken down further into simpler reactions. The sequence of elementary reactions that add up to give the overall reaction is called the mechanism of the reaction.

A mechanism is a hypothesis about the elementary steps through which chemical change occurs. Sometimes the elementary steps can be studied in isolation, but in most cases, they cannot be easily separated. Sometimes more than one mechanism could be proposed for a particular chemical reaction, and evidence of the correct mechanism is often indirect. A valid mechanism must agree with all the facts about the kinetics and knowledge about the reactants and intermediates involved. It must be able to explain the rate law of the backward as well as the forward reaction.

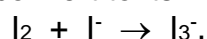
In general, the halogenation of a ketone can be represented as follow:



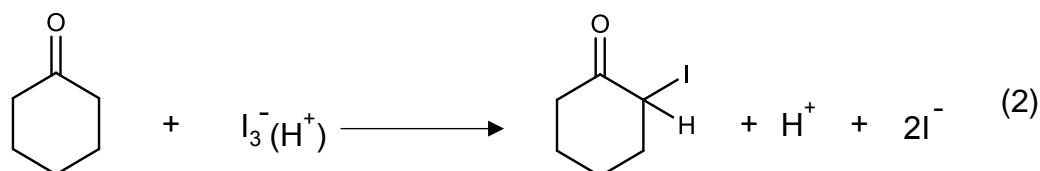
where X = halogen atom. This reaction could be catalyzed by H^+ in acidic solution or by OH^- in alkaline solution.

Iodination of cyclohexanone

In this experiment, the rate of iodination of cyclohexanone in an aqueous medium is being measured. To increase the amount of iodine in the solution, it is necessary to convert to its more soluble complex ion I_3^- by addition of excess of iodide ion:



The overall reaction of iodination of cyclohexanone in an aqueous solution with excess I^- ion can be represented as follows



(S = cyclohexanone)

Following the rate law of chemical kinetics, the differential rate equation for the reaction could be written in the following form

$$-\frac{d[S]}{dt} = -\frac{d[I_3^-]}{dt} = k[S]^a[I_3^-]^b[H^+]^c \quad (3)$$

where k = rate constant; a , b and c are the orders of reaction with respect to S , I_3^- and H^+ , respectively.

This experiment is carried out to determine the value of k , a , b and c , and to suggest a mechanism which agrees with the rate equation that has been obtained.

As the I_3^- ion is the only colored species in the reaction mixture, a spectrophotometer could be employed to measure the change in its concentration, by using the Beer-Lambert Law

$$A(I_3^-) = \varepsilon l[I_3^-] \quad (4)$$

where A = absorbance, ε = molar absorption coefficient, $[I_3^-]$ = concentration and l = optical path length, that is, the distance traveled by the light through the solution. The most suitable wavelength for the measurement of I_3^- ion concentration is 565 nm.

[Subsequently the absorbance A refers to that due to I_3^- , measured at 565 nm].

Deriving from equation (4),

$$[I_3^-] = \varepsilon^{-1}l^{-1}A \quad (5)$$

where $\varepsilon^{-1}l^{-1}$ may be treated as a single constant and is calculated from the absorbance measurement made during spectrophotometer calibration.

The progress of reaction (3) could be monitored by measuring the change in the concentration of I_3^- with reaction time.

However, the rate of change in the values of solution absorbance, $-dA/dt$, can be correlated to the rate of change in the concentration of I_3^- by equation (6).

$$-\frac{d[A]}{dt} = -\varepsilon l \frac{d[I_3^-]}{dt} \quad (6)$$

The general rate equation (3) can therefore be written as

$$-\frac{d[A]}{dt} = k\varepsilon l[S]^a[I_3^-]^b[H^+]^c \quad (7)$$

A direct comparison between rate and concentration can be done approximately by taking as a measure of the derivative dA/dt the corresponding ratio of finite increments $\Delta A/\Delta t$.

Then by making a run at each of two different initial concentrations of any one component, say the cyclohexanone, keeping the other concentrations constant, the data may be used to determine the order of reaction with respect to that component.

Let the two rates and corresponding initial concentration be $(dA/dt)_{II}$, $(dA/dt)_{IV}$, and $[S]_{II}$, $[S]_{IV}$, respectively. Then

$$-\left(\frac{dA}{dt}\right)_{II} = \{k\epsilon l[I_3^-]^b[H^+]^c\}[S]_{II}^a \quad (8)$$

$$-\left(\frac{dA}{dt}\right)_{IV} = \{k\epsilon l[I_3^-]^b[H^+]^c\}[S]_{IV}^a \quad (9)$$

From equations (8) and (9), dividing and taking logarithms, we can obtain

$$a = \frac{\log\left(\frac{(dA/dt)_{II}}{(dA/dt)_{IV}}\right)}{\log\left(\frac{[S]_{II}}{[S]_{IV}}\right)} \quad (10)$$

$$\text{or } a = \frac{\{\log (dA/dt)_{II} - \log (dA/dt)_{IV}\}}{\{\log [S]_{II} - \log [S]_{IV}\}}.$$

An exactly analogous procedure yields the values of b and c .

Experimental Procedure

1. The following solutions are to be prepared from the stock solutions:

	Volume of stock solution used /cm ³			
	I	II	III	IV
Cyclohexanone	20	20	20	14
HCl	10	10	6	10
Distilled Water	14	16	20	22
KI ₃	6	4	4	4

[Cyclohexanone] stock = 0.230 mol dm⁻³

[HCl] stock = 0.500 mol dm⁻³

[KI₃] = 0.0360 mol dm⁻³

2. Mix the acid, ketone and water together in a 100 cm³ conical flask. Label the flask and place in the 303 K constant temperature bath and allow the flask and its content to equilibrate for at least 15 minutes.
3. Thermostat the KI₃ stock solution separately as well.
4. While waiting for the flask and its content to equilibrate, prepare of about 10 cm³ "reference/ blank" solution. It should contain same % of cyclohexanone and HCl

for respective mixture I, II, III and IV. The distilled water can be added up to make it 10 cm³. Use these solutions to calibrate the spectrometer.

5. After thermal equilibrium has been attained, the reaction is started by pipetting the required amount of the KI₃ solution into the flask. You may start with mixture I.
6. As soon as the pipette has drained, the timer is started and the mixture mixed thoroughly. Do not take out the mixture out from the bath.
7. Prior to measurement, prepare spreadsheet in Excel for plot absorbance versus time.
8. Immediately, a sample is transferred from the flask to a spectrophotometer sample cell (using a dropper) and its absorbance measured.
9. The sample cell is then emptied, rinsed with distilled water, and dried.
10. Further samples are taken and measured at intervals of 2 minutes, until sufficient points are obtained for giving a good plot of absorbance A versus time.
11. Carry out the same procedure each of the mixture II, III and IV.
12. Determine the gradient of each plot of absorbance, Abs versus time.

Operation of the Spectrophotometer

The operation manual can be obtained from the lecturer-in-charge or the Laboratory Assistant. Make sure you know how to operate the instrument (you can ask the lecturer/demonstrator/lab assistant for help).

Make sure you measure the absorbance of KI₃ solution of 0.00360 mol dm⁻³ (dilute 10 times from [KI₃] stock solutions) a few times to obtain the best average value for ϵl . Use distilled water to calibrate the spectrometer.

Calculations and Conclusion

The values of dA/dt for each experiment may be obtained readily from the slopes of graphs of absorbance A as a function of time for each experiment. The slopes should be determined by a graphical method, together with the uncertainty analysis.

The uncertainties in the values of $\log dA/dt$ and $\log (\text{concentration})$ are then used to determine the uncertainties in the reaction orders obtained.

Using the value of ϵl which you have determined, the rate constant k can be calculated using equation (7) for each of the four runs (I)-(IV). The average value and its standard deviation are then obtained. The mean value should be compared with the literature value.

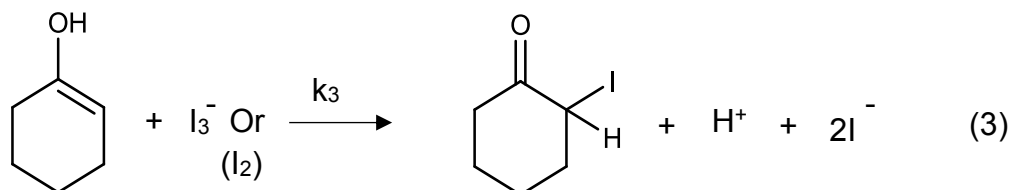
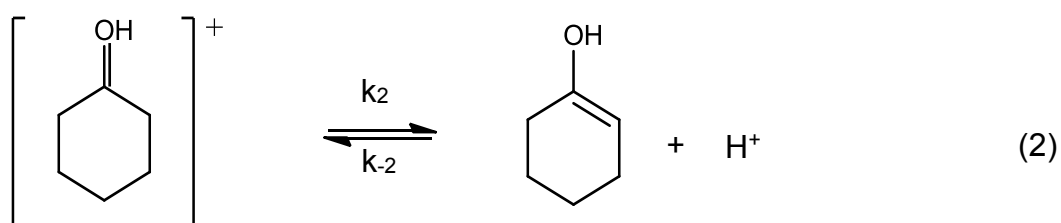
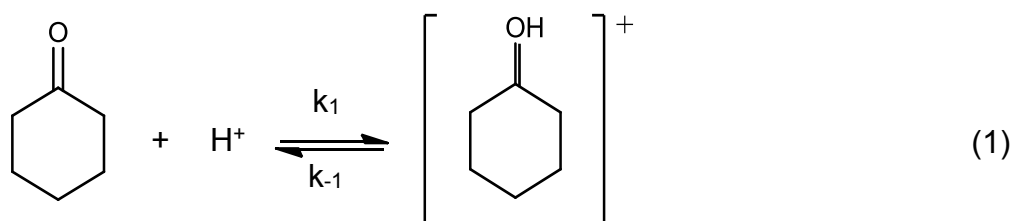
There are three mechanisms of reaction being proposed for the iodination of cyclohexanone (Schemes A, B and C). Show whether the form of the rate equation

which you have determined is consistent with any of these. If so, which step of the chosen mechanism is the rate-determining one?

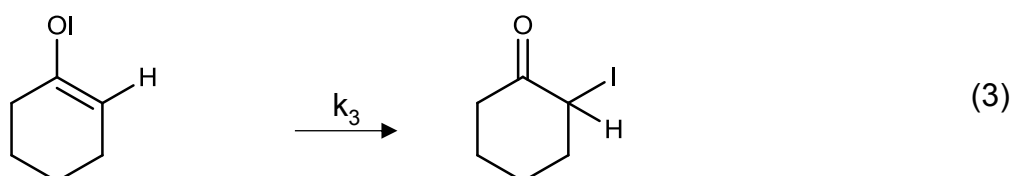
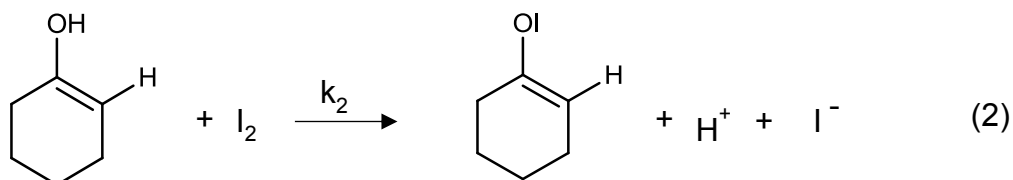
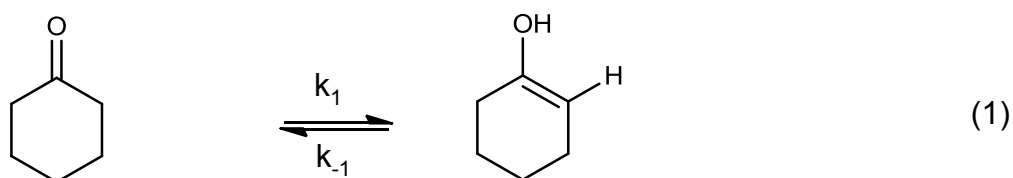
Are your results consistent with the observation that the rate of bromination of ketones is exactly the same as the rate of iodination?

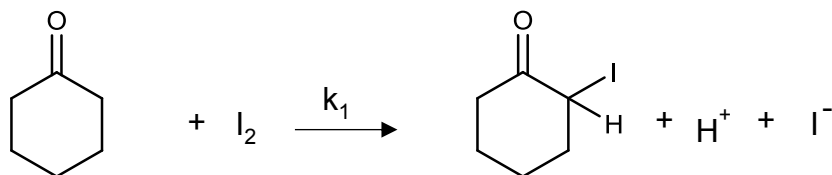
PROPOSED MECHANISMS OF IODINATION OF CYCLOHEXANONE

Scheme A



Scheme B



Scheme C**References:**

1. Barrow, G.W. (1966). Physical Chemistry (2nd ed.). McGraw-Hill.
2. Morrison, R.T. & Boyd, R.N. (1959). Organic Chemistry, Allyn & Bacon.
3. Atkins, P., Paula, J.D. & Keeler, J. (2017). Physical Chemistry, (11th ed.). Oxford University Press.
4. Levine, I.N. (1995). Physical Chemistry (4th ed.). McGraw-Hill.
5. Alberty, R.A. & Silbey, R.J. (1997). Physical Chemistry (2nd ed.). John Wiley.

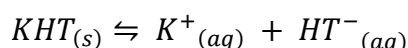
EXPERIMENT 6

DETERMINATION OF MEAN ACTIVITY COEFFICIENT AND SOLUBILITY OF POTASSIUM HYDROGEN TARTRATE (KHT) IN AQUEOUS SOLUTION AT 28 °C

Background

The solubility of potassium hydrogen tartrate (KHT) in distilled water and in aqueous sodium chloride solutions at concentrations 0.05, 0.10, 0.15 and 0.20 mol dm⁻³ are determined at 28 °C by the following method.

For the equilibrium dissociation reaction



it is assumed that the dissociation is complete, meaning that no overall neutral ion pairs ($K^+ \dots HT^-$) nor other reactions are present to reduce the apparent number of ions in solution. The concentrations of the various species present in units of M (mol dm⁻³ of solution) can be written

$$[K^+] = c, [HT^-] = c, [Na^+] = m, [Cl^-] = m$$

where the species within brackets [...] refer to ionic concentrations. It is further assumed that the sodium chloride salt fully dissociates. With these assumptions, the ionic strength I for the single charged species mixture is given by:

$$I = \frac{[K^+] + [HT^-] + [Na^+] + [Cl^-]}{2} = c + m.$$

The solubility constant for KHT, K_s , is given by

$$K_s = a_{K^+} a_{HT^-} = [K^+][HT^-] \gamma_{K^+} \gamma_{HT^-} = [K^+][HT^-] \gamma_{\pm}^2 \quad (1a)$$

which implies

$$K_s = c^2 \gamma_{\pm}^2 \quad (1b)$$

where by convention, $\gamma_{K^+} \gamma_{HT^-} = \gamma_{\pm}^2$; γ_{\pm} is termed the mean activity coefficient and theories provide various expressions to compute this quantity with varying accuracy. For (1a), a_{K^+} , a_{HT^-} refers to the activity of the K^+ and HT^- ions where in general $a_X = [X] \gamma_X$ for species X , where γ_X is the activity coefficient of the said species. It follows from (1a) that

$$\log K_s = 2 \log c + 2 \log \gamma_{\pm} \quad (2)$$

where \log here refers to base 10 logarithms (\log_{10}).

According to the extended Debye-Huckel theory (see reference [1]), γ_{\pm} is determined from

$$\log \gamma_{\pm} = \frac{-AI^{1/2}}{(1+I^{1/2})} + bI \quad (3)$$

where b is a parameter and A is the Debye-Huckel constant with the value $A = 0.5160$ at 28°C . Using (3) in (2) and rearranging leads to

$$\log K'_s = \left\{ 2 \log c - \frac{2AI^{1/2}}{(1+I^{1/2})} \right\} = \log K_s - 2bI \quad (4)$$

The expression in curly brackets in (4) is defined as $\log K'_s$ and it can be computed explicitly, and so (4) can be written as a linear form $\{y = mx + d\}$ with m the gradient and d the intercept, where

$$\log K'_s = \log K_s - 2bI \quad (5)$$

Plotting $\log K'_s$ against I would produce a straight line graph with intercept $\log K_s$ and gradient $-2b$. Once K_s has been determined, γ_{\pm} may be determined for any concentration using (1(b)).

Experimental procedure

The experiment involves two parts:

PART 1: Preparation of various saturated solutions of KHT in differing concentrations of NaCl solution at 28°C .

1. Prepare 250 cm^3 of stock NaCl solution of concentration 0.2000 M using Analar grade NaCl. ('Analar' is an abbreviation for analytical reagent).
2. By appropriate dilution^a, make 100 cm^3 NaCl solutions of concentration 0.1500 , 0.1000 and 0.0500 M from the stock solution.
3. 100 cm^3 NaCl solutions of concentration 0.2000 , 0.1500 , 0.1000 , 0.0500 and 0 M are individually contained in stoppered conical flasks.
4. Equilibrate them in the water bath at 28°C for about 5 minutes.
5. Add excess potassium hydrogen tartrate, KHT salt (meaning add until a residue of undissolved KHT remains) to each of these solutions.
6. Shake them for about 5 minutes and repeat this process of shaking the solution followed by equilibration several times until the total shake time is about 20 minutes.
7. Then, leave the flasks in the water bath without shaking and let the precipitate of excess KHT salt settle down at the bottom of the flask.

^aTo prepare a $Y \text{ M}$ 100 cm^3 solution from the stock solution, dilute $X \text{ cm}^3$ of stock with distilled water to make up to 100 cm^3 where. $Y \times 100 = X \times 0.2000$

PART 2: Determination of the HT^- concentration by titration with a standardized solution of sodium hydroxide

1. Prepare 100 cm³ of sodium hydrogen tartrate, NaHT solution of concentration 0.04 M.
2. Prepare 500 cm³ of standard NaOH solution of concentration approximately 0.04 M^b.
3. Standardize the NaOH solution of approximately 0.04 M using 0.04 M NaHT solution; use phenolphthalein as an indicator.
4. The standard NaOH solution must be used as soon as possible after the standardization procedure because it will react with the carbon dioxide present in the air, changing its concentration in the process. As a preventive measure, a drying tube containing solid pellets of NaOH may be placed at the top end of the burette which contains the standardized NaOH to arrest this reaction process during titrations.
5. Pipette 10 cm³ aliquots of the solutions in the water bath (from Part 1) and titrate with the standardized NaOH solution using phenolphthalein as the indicator. The standardized pipette (calibrated by gravimetric determination of volume from distilled water at 28 °C) must be at the same temperature as the KHT solution. This is achieved by immersing the pipettes in a tube containing distilled water and maintained at 28 °C in a temperature-controlled water bath. There are two options of pipetting the aliquots to prevent introduction of KHT precipitate into the pipette whenever solutions are drawn in.

Option 1:

Filter each of the five solutions gravitationally. The process of filtering is proceeded in water bath. Once filtered, pipette 10 cm³ aliquots of the solutions.

Option 2:

A tube containing a cotton filter is placed at the end of the pipette to prevent solid KHT from being drawn into the pipette. Should the filter fail, your readings would be adversely affected. You should prepare the cotton filters by washing the cotton ball(s) or strands inserted into the tube several times with distilled water by drawing the fluid into the pipette with the tube fitted at the end.

6. For each of the five solutions prepared, a minimum of three titrations should be performed until results consistent to within ± 0.05 cm³ NaOH solution volume are obtained.

^bConfirm that the stoichiometry of the sodium or potassium salt of HT^- in the neutralisation reaction is $HT^- + OH^- \longrightarrow H_2O + T^{2-}$.

Results and Calculations

- (i) Calculate the solubility, c for KHT for each of the four solutions from the titration results.
- (ii) Determine $\log K'_s$ and I for each of the solutions, and plot a graph of $\log K'_s$ vs. I . From the intercept, determine K_s , the solubility constant (also variously known as the solubility product constant, solubility equilibrium constant...etc.).

- (iii) Determine γ_{\pm} , the mean ionic activity coefficient γ_{\pm} for KHT for each of the solutions using Eq. (1).
- (iv) Determine b which features in Eq. (3) and (4). What is the physical significance of this parameter and discuss the magnitude of the b parameter that you obtain by comparing with the associated physical variable from the experimental literature.
- (v) Compute ΔG° at 28 °C for the reaction $KHT(s) \leftrightarrow K^{+} + (aq) + HT^{-} (aq)$
- (vi) Plot γ_{\pm} as determined from the experiment and from the extended Debye-Huckel equation against the ionic strength. Which is the more accurate value for this quantity? Discuss also the relative differences in magnitude for the two methods.

Reminder: For each of the above computations, you must provide error estimates for the required quantities to one significant figure.

Questions:

- (i) How would you determine $\Delta H^{\circ}(T)$ and $\Delta S^{\circ}(T)$ in general and in particular when ΔH° and ΔS° are assumed independent of temperature in the vicinity (± 10 °C) of 28 °C?
- (ii) What assumptions are made regarding the activity of KHT (solid state) in Calculation (5) above to compute ΔG° ?

Reference

1. Atkins, P., Paula, J.D. & Keeler, J. (2017). Physical Chemistry (11th ed.). Oxford University Press